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PAPER

Levels and chemical composition of PM in a city near a large Cu-smelter in Spain

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A long-term series (2001–2008) of chemical analysis of atmospheric particulate matter (PM_{10} and $PM_{2.5}$) collected in the city of Huelva (SW Spain) is considered in this study. The impact of emission plumes from one of the largest Cu-smelters in the world on air quality in the city of Huelva is evidenced by the high daily and hourly levels of As, other potentially toxic elements (*e.g.* Cu, Zn, Cd, Se, Bi, and Pb) in particulate matter, as well as the high levels of some gaseous pollutants (NO_2 and SO_2). Mean arsenic levels in the PM10 fraction were higher than the target value set by European Directive 2004/107/EC (6 ngAs m^{-3}) for 1st January 2013. Hourly peak concentrations of As and other metals and elements (Zn, Cu, P and Se) analyzed by PIXE can reach maximum hourly levels as high as 326 ngAs m^{-3}, 506 ngZn m^{-3}, 345 ngCu m^{-3}, 778 ngP m^{-3} and 12 ngSe m^{-3}. The contribution of Cu-smelter emissions to ambient PM is quantified on an annual basis in 2.0–6.7 μg m^{-3} and 1.8–4.2 μg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. High resolution outputs of the HYSPLIT dispersion model show the geographical distribution of the As ambient levels into the emission plume, suggesting that the working regime of the Cu-smelter factory and the sea breeze circulation are the main factors controlling the impact of the Cu-smelter on the air quality of the city. The results of this work improve our understanding of the behaviour of industrial emission plumes and their impact on air quality of a city, where the population might be exposed to very high ambient concentrations of toxic metals during a few hours.

1. Introduction

In the last decades, there has been a growing interest in the study of arsenic pollution in several Geochemical Systems, mainly due to its adverse effects on human health.[1,2] High concentrations of arsenic and other potentially toxic elements of environmental interest may be present in the atmospheric aerosol, both of natural (*e.g.* terrestrial crustal, volcanoes and groundwater) and anthropogenic (*e.g.* Cu-smelters, burning coal, pesticides and some glass raw materials) origin.[3,4]

Exposure to high concentrations of arsenic may produce an acute toxic effect in humans, which is quickly diagnosed.[5,6] However, low doses of arsenic do not result in an acute toxic

Environmental impact

The results of this work improve our understanding of the behaviour of industrial emission plumes and their impact on air quality of a city, where the population might be exposed to very high ambient concentrations of toxic metals during a few hours. This is one of the first studies on the levels and composition of atmospheric particulate matter in order to estimate the contribution of the copper smelter emissions on air quality of the population during eight years (2001–2008). The geochemical signature of copper smelter emissions has been recognized in respirable particles (PM10 and PM2.5). Hourly peak concentrations of arsenic and other metals (Zn, Cu, P and Se) can reach maximum hourly levels.

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effect, but may give rise to cancer after prolonged exposure.[5,6] This metalloid has been classified as a human carcinogen.[4] Several toxicological studies have demonstrated that the toxicity of arsenic is dependent on the chemical form, oxidation state, physical state (gas or solution), rate of absorption into cells, rate of elimination, and the nature of chemical constituents in the toxic compound.[7,8]

Since 1960, several industrial estates have been established in the Ria of Huelva (south-western Spain, Fig. 1), making this area one of the major industrial areas in Spain. The main factories are involved in Cu-smelting from complex sulfides, production of phosphoric acid from phosphorite, petroleum and paper manufacturing.[9]

Epidemiological studies[10] and cancer maps of Spain[11] have defined this region as one of the areas with the greatest risk of certain types of cancer in Spain, which may be related to industrial activities.[12]

Cu-smeltering is recognized as one of the main anthropogenic sources of arsenic in atmospheric particulate matter, and is considered as the main origin of arsenic pollution episodes in the world. The Cu-smelter located in Huelva is considered the second largest in Europe and seventh in the world in terms of production with 3.2×10^6 Tonnes Cu per year.[13]

Atmospheric emission plumes from industrial states close to the city of Huelva impact on areas of high ecological interest, such as Doñana National Park (NP).[14] Other pollution events in Doñana NP have been linked to the rupture of the raft of toxic sludge at Aznalcollar Mine in 1998.[15]

Under specific meteorological conditions, atmospheric emissions, especially emission plumes from the Cu-smelter, may impact on urban areas, either Huelva capital[16,17] and rural sites in the metropolitan area.[18] An increase in the ambient air metal levels (*e.g.* Cu, Zn, As, Pb, Se, Bi, Ni and V, among others) in PM in this area, at levels well above the concentrations described in highly polluted urban areas in Europe, has been referenced by Querol *et al.*, 2004;[19] 2008[20] and Putaud *et al.*, 2004.[21]

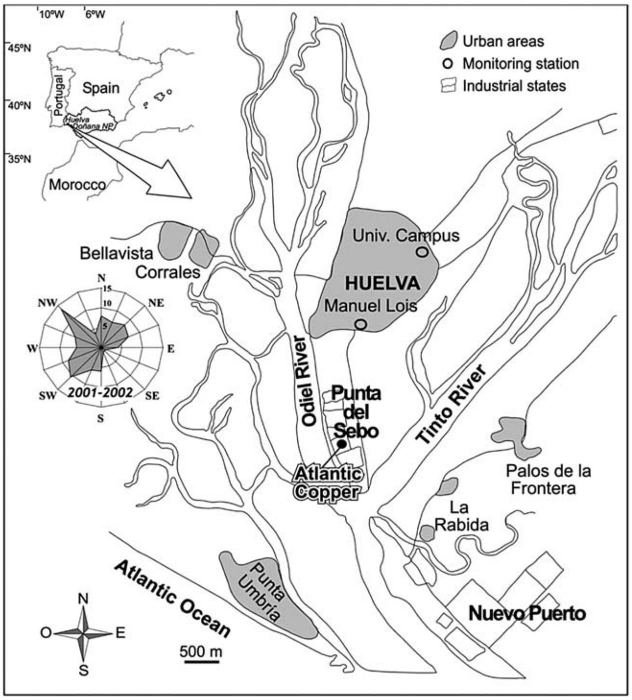


Fig. 1 Map of the study area showing monitoring stations and industrial estates. Wind rose diagram for the period 2001–2002 recorded at the Spanish National Meteorological Service's Huelva station.

From an epidemiological point of view, a annual target mean value for As in PM_{10} of 6 ng m^{-3} was established by the European Directive 2004/107/CE[22] starting 1st January 2013. Recent studies of the As species in total suspended particles,[23] PM_{10}[24] and $PM_{2.5}$[25] in the area of Huelva have shown that the presence of the more toxic As(III) is related to an anthropogenic origin and fine grain size. The results of these studies can be considered of significant interest for further evaluation of the European Directive.

In this work, the variability of daily levels of PM_{10} and $PM_{2.5}$ and major and trace components in the period 2001–2008 was investigated to evaluate the impact of Cu-smelter emission plumes on ambient air PM levels of the city of Huelva (SW Spain). The study is also supported by data obtained from hourly $PM_{2.5}$ and $PM_{2.5-10}$ analysis by PIXE (Particle Induced X ray Energies), and the study of high-resolution atmospheric dispersion output using the HYSPLIT model.

2. Materials and methods

Study site

The study area is situated in the south-western end of the autonomous region of Andalusia (southern Spain) and near a 'World Reserve of the Biosphere' (Doñana National Park) located north of the Guadalquivir Estuary (Fig. 1).

Andalusia is the most populous region in Spain (8 M inhabitants, accounting for 18% of the Spanish population), and the second most extensive region (87 268 km^2, 17% of Spain). Its population density is 92 inhabitants per km^2. This region serves as a transitional zone between the African and European continents from a climatic perspective, with very dry summers (35 mm of rainfall as a mean for the June–September period) and a mean annual rainfall of 520 mm yr^{-1}.

The city of Huelva (around 140 000 inhabitants) is located in the south-west of the Iberian Peninsula, in the confluence of the Odiel and Tinto rivers. Both rivers flow into the Atlantic Ocean and form a common estuary (Ria of Huelva, Fig. 1).

The main industrial emissions, next to the southern part of the city, are derived from a Cu-smelter and phosphate factories (Punta del Sebo), which under specific meteorological conditions may significantly influence air quality in urban areas. The predominant wind directions are SW, NW and NE (see rose diagram in Fig. 1 inset), which are heavily influenced by synoptical conditions and sea breeze circulation.

Ambient air PM_{10} and $PM_{2.5}$ were measured and sampled in an urban air quality monitoring station (Manuel Lois) located at the core-centre of Huelva from January 2001 to April 2003. From March 2003 to December 2008 an urban monitoring station was set up in the University Campus (1.5 km from Manuel Lois in a NE director). These monitoring stations belong to the Department of the Environment of the Autonomous Government of Andalusia, and can be considered as representative of urban background monitoring stations in the city of Huelva.

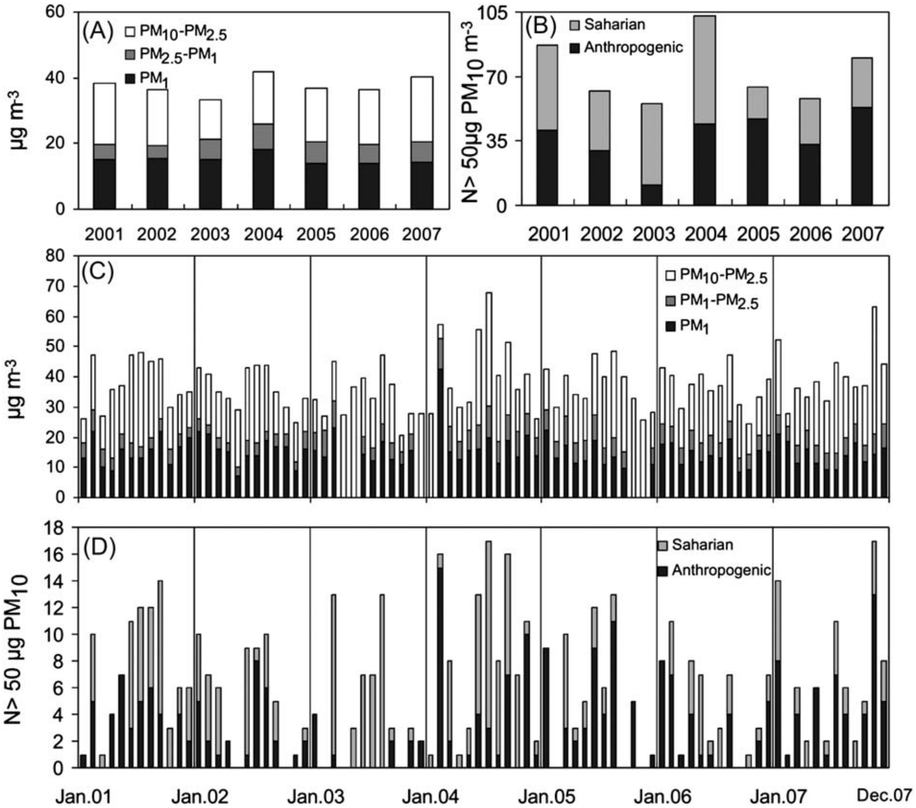


Fig. 2 (A) Annual and (C) monthly mean levels of PM10–2.5, PM2.5–1 and PM1, and exceedances of 50 µg PM10 m^{-3} from 2001 to 2008 at the Manuel Lois station (January 2001 to April 2003) and the University Campus station (May 2003 to December 2008) with indications of the cause of the exceedance (anthropogenic and Saharan) ((B) annual; (D) monthly).

Sampling and monitoring strategies for PM and gaseous pollutants

Daily mean PM_{10} and $PM_{2.5}$ levels from 2001 to 2008 were considered in this study. A high-volume PM_{10} Grasseby-Andersen (68 m^3 h^{-1}) and a high-volume sampler (MCV-CAVF-PM1025 model, 30 m^3 h^{-1}) equipped with $PM_{2.5}$ inlets were used in the M. Lois (January 2001 to March 2003) and University Campus monitoring stations (May 2003 to December 2008).

Schleicher and Schuell QF20S and Munktell quartz filters were used for PM sampling. At the two monitoring sites, one daily sample was collected every four and eight days during the study periods from 2001 to 2003, and from 2004 to 2008, respectively. After sampling, PM filters were placed in a desiccator for 24 h at 20 °C and 50% relative humidity. Subsequently, filters were weighted using a Sartorius LA130 S-F balance (0.1 mg sensitivity).

A total of 821 filters were sampled during the eight-year period, for which 269 were collected at Manuel Lois (165 and 104 of PM_{10} and $PM_{2.5}$, respectively) and 552 at the University Campus (279 and 273 of PM_{10} and $PM_{2.5}$, respectively).

Additionally, levels of PM_{10}, $PM_{2.5}$ and PM_1 were recorded in real time at both monitoring stations by means of a GRIMM 1107 Optical counter. Real time PM10 monitoring was also carried out and with a Beta Attenuation instrument (THERMO). Levels of gaseous pollutants, such as SO_2, NO_x and O_3, were also measured using standard methods.

A two-stage streaker sampler (manufactured by P.I.X.E. International Corporation) was employed for the collection of

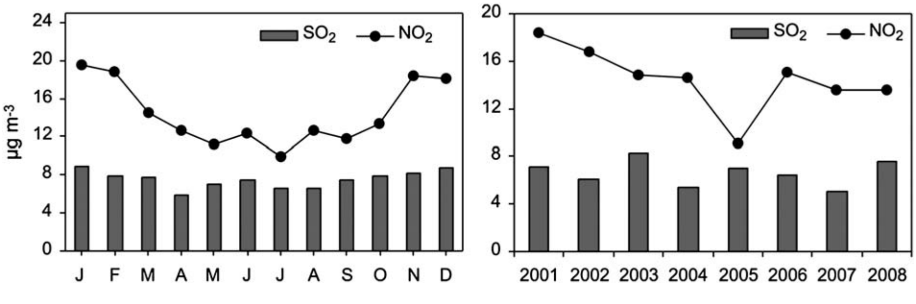


Fig. 3 Monthly and annual concentrations of gases (NO_2 and SO_2) in Huelva from 2001 to 2008.

Table 1 Daily mean, median levels and maximum of PM_{10} and $PM_{2.5}$, and major and trace components concentration in PM_{10} and $PM_{2.5}$ obtained from 2001 to 2008; in the Manuel Lois station (January 2001 to April 2003) and University Campus El Carmen station (May 2003 to December 2008)

	PM_{10}			$PM_{2.5}$		
Fraction PM	Mean	Median	Max.	Mean	Median	Max.
PM/μg m^{-3}	37	34	171	20	18	104
C total	5.98	5.18	29.4	4.16	3.79	16.4
C org	5.47	4.67	28.7	4.03	3.66	15.1
Cnm	6.55	5.61	34.5	4.83	4.40	18.1
CO_3^-	2.66	2.23	20.7	0.67	0.49	16.1
SiO_2	5.40	4.29	81.1	1.15	0.86	29.0
Al_2O_3	1.80	1.43	27.0	0.40	0.29	9.68
Ca	1.29	1.04	7.75	0.31	0.22	8.96
K	0.46	0.38	3.64	0.20	0.15	1.84
Na	1.12	0.89	14.3	0.32	0.24	8.07
Mg	0.29	0.25	3.66	0.09	0.07	1.10
Fe	0.72	0.60	8.13	0.16	0.13	2.97
PO_4^{3-}	0.34	0.16	3.89	0.10	0.05	0.88
nss SO_4^{2-}	4.14	3.01	35.9	3.38	2.44	23.8
ss SO_4^{2-}	0.28	0.23	3.57	0.09	0.06	4.22
NO_3^-	2.61	2.06	33.4	1.11	0.67	11.1
Cl	1.06	0.61	15.1	0.27	0.18	2.87
NH_4^+	1.27	0.91	12.6	1.30	0.88	10.7
Undeterminated	6.94	5.95	44.4	5.46	4.20	48.3
Anthropogenic	13.9	12.3	81.9	10.5	9.11	33.0
Crustal	12.9	10.6	152	3.04	2.32	53.9
Marine	2.36	1.70	33.0	0.66	0.51	13.0
Secondary	7.64	5.98	81.9	5.65	4.17	32.6
C non mineral/ng m^{-3}	6.27	5.51	34.5	4.83	4.40	18.1
Li	0.61	0.48	9.44	0.12	0.09	3.43
Be	0.04	0.02	0.59	0.03	0.01	0.47
Sc	0.30	0.12	5.74	0.15	0.01	9.99
Ti	64.8	42.7	1305	19.8	11.3	571
V	6.09	4.73	98.0	3.77	2.49	20.3
Cr	2.44	1.83	40.0	0.92	0.25	34.3
Mn	13.6	9.33	350	3.31	2.74	52.8
Co	0.35	0.26	6.79	0.20	0.10	8.55
Ni	3.71	2.59	100	2.43	1.61	40.8
Cu	64.3	37.9	858	30.8	22.4	341
Zn	40.6	30.1	221	37.6	22.0	1327
Ga	0.83	0.34	23.2	0.50	0.11	14.4
Ge	1.04	0.06	316	0.07	0.01	1.69
As	6.30	1.96	62.1	5.23	0.97	60.3
Se	1.74	0.74	26.6	1.15	0.43	16.9
Rb	1.52	1.28	14.7	0.46	0.35	7.28
Sr	5.09	3.49	362	1.13	0.89	15.7
Y	0.41	0.28	31.4	0.14	0.10	2.46
Zr	1.91	0.59	17.1	1.14	0.10	9.45
Nb	0.19	0.12	3.57	0.11	0.01	6.01
Mo	5.45	0.01	895	0.77	0.01	33.6
Cd	0.73	0.32	14.1	0.62	0.22	12.7
Sn	2.18	1.71	13.5	1.31	0.91	11.0
Sb	2.04	1.53	78.9	0.72	0.56	6.29
Cs	0.09	0.06	2.65	0.08	0.01	6.01
Ba	20.7	10.9	233	11.5	2.35	292
La	0.54	0.42	11.5	0.17	0.13	2.87
Ce	0.95	0.78	18.1	0.28	0.21	5.61
Pr	0.10	0.08	2.10	0.03	0.01	0.62
Nd	0.43	0.33	8.45	0.12	0.09	2.57
Sm	0.08	0.06	1.49	0.03	0.01	0.48
Eu	0.02	0.01	0.27	0.01	0.01	0.25
Gd	0.09	0.06	0.82	0.05	0.03	0.49
Tb	0.01	0.01	0.12	0.07	0.00	6.01
Dy	0.08	0.05	3.53	0.04	0.02	0.64
Ho	0.01	0.01	0.14	0.07	0.00	6.01
Er	0.04	0.03	0.31	0.03	0.01	0.30
Tm	0.01	0.01	0.68	0.01	0.00	0.20
Yb	0.04	0.02	0.57	0.03	0.01	0.49
Lu	0.01	0.00	0.40	0.01	0.00	0.20
Hf	0.13	0.01	10.3	0.10	0.03	1.95
Ta	0.06	0.01	1.16	0.05	0.01	1.44
W	0.07	0.02	1.48	0.10	0.01	4.36
Tl	0.11	0.06	1.27	0.08	0.01	2.08
Pb	21.0	12.7	231	15.8	8.23	164
Bi	1.02	0.28	15.7	0.83	0.12	16.3
Th	0.21	0.15	2.52	0.10	0.03	2.85
U	0.20	0.12	1.32	0.12	0.03	1.95

the fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions of PM with a hourly resolution. The sampler was located in the University Campus monitoring station from 16th to 22nd of October 2007. The fine fraction was collected on a 0.4 mm pore-size Nuclepore® filter and the coarse on paraffin-coated 7.5 mm thick Kapton® foil. The filter speed during sampling, the pumping orifice width and the beam size we used for the subsequent analysis were such that an overall resolution of about one hour was obtained on the elemental composition of $PM_{2.5}$ and $PM_{2.5-10}$. Simultaneously to PIXE sampling, measurements of PM_{10} were performed with a high-volume captor (MCV-CAVF-PM1025 model, 30 m^3 h^{-1}) every 12–24 h, to contrast the results obtained with the two sampling methods.

In order to characterize the PM chemical composition and the grain-size distributions of emission plumes from the Cu-smelter, PM_{10} and $PM_{2.5}$ were sampled simultaneously with a high-volume captor (MCV CAVF-PM1025 model) at a flow rate of 30 m^3 h^{-1}, on a sandy track, in the vicinity of the factory during plume fumigation surface episodes.

Chemical analysis

Major and trace components. After gravimetry determination of PM levels, a half of each filter was digested in an acid medium (2.5 ml HNO_3 : 5 ml HF : 2.5 ml $HClO_4$) following the method by Querol *et al.*[26] All acids used were of Suprapur quality. Determinations of the content of major and trace elements in the resulting digestions were performed by means of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-AES). The mean precision and the accuracy fall below typical analytical error (in the range of 3–5% and <10%, respectively), and were controlled by repeated analysis of a ¼ of filter loaded with 5 mg of SRM 1633b (coal fly ash) reference material (NIST, Gaithersburg, MD, USA). The detection limits obtained were 0.1 ng m^{-3} for most trace elements analyzed. Blank filters were analyzed simultaneously from the batches of their respective filter samples and the corresponding blank concentrations were subtracted for each sample.

The soluble fraction of a 75 cm^2 portion of each filter was extracted with MilliQ-grade deionised water at 60 °C, and the content of major anions (SO_4^{2-}, NO_3^-, and Cl^-) and NH_4^+ in the leachates was determined by means of Ion Chromatography.

The silica and carbonate content was indirectly determined by stoichiometry from the Ca, Mg and Al content, on the basis

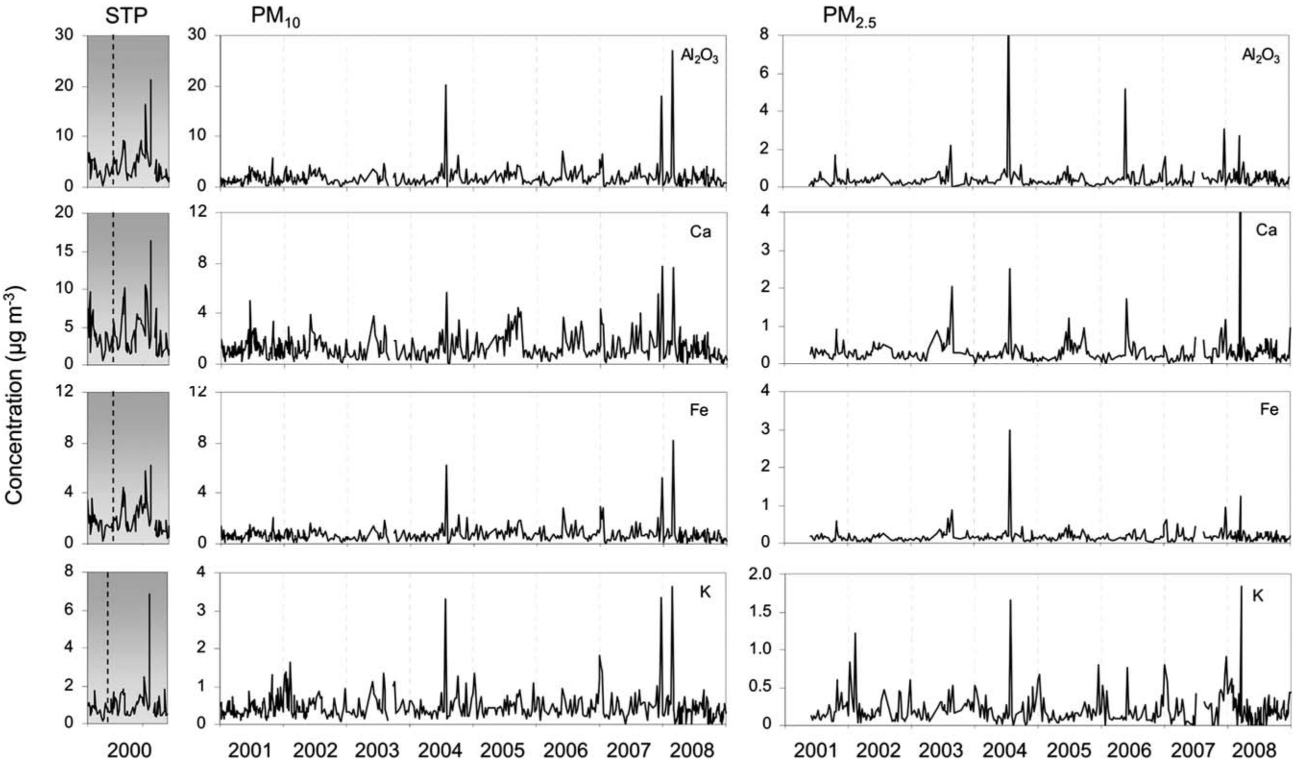


Fig. 4 Seasonal evolution of crustal component element concentrations in PST,16 and PM10 and PM2.5 from January 2001 to December 2008 in the city of Huelva.

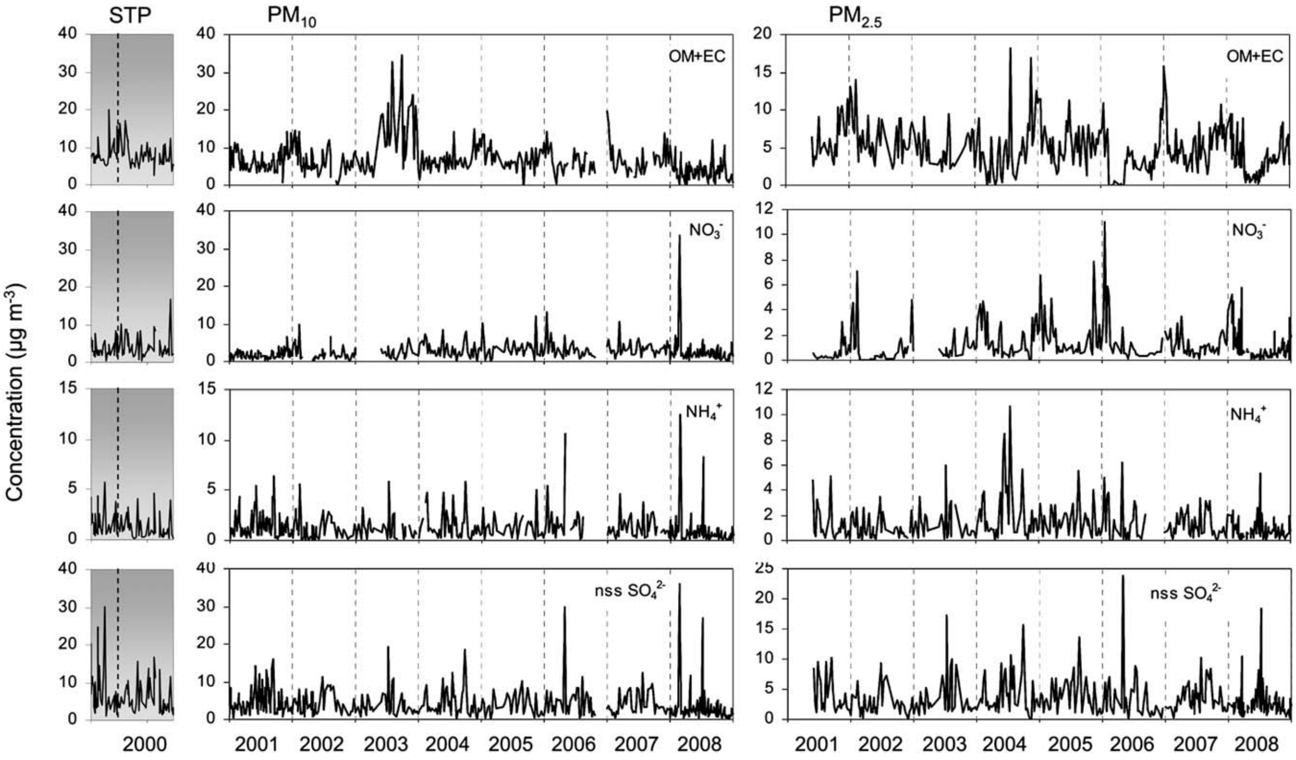


Fig. 5 Seasonal evolution of the OM + EC and secondary inorganic components (SICs) concentrations in PST,16 and PM10 and PM2.5 from January 2001 to December 2008 in the city of Huelva.

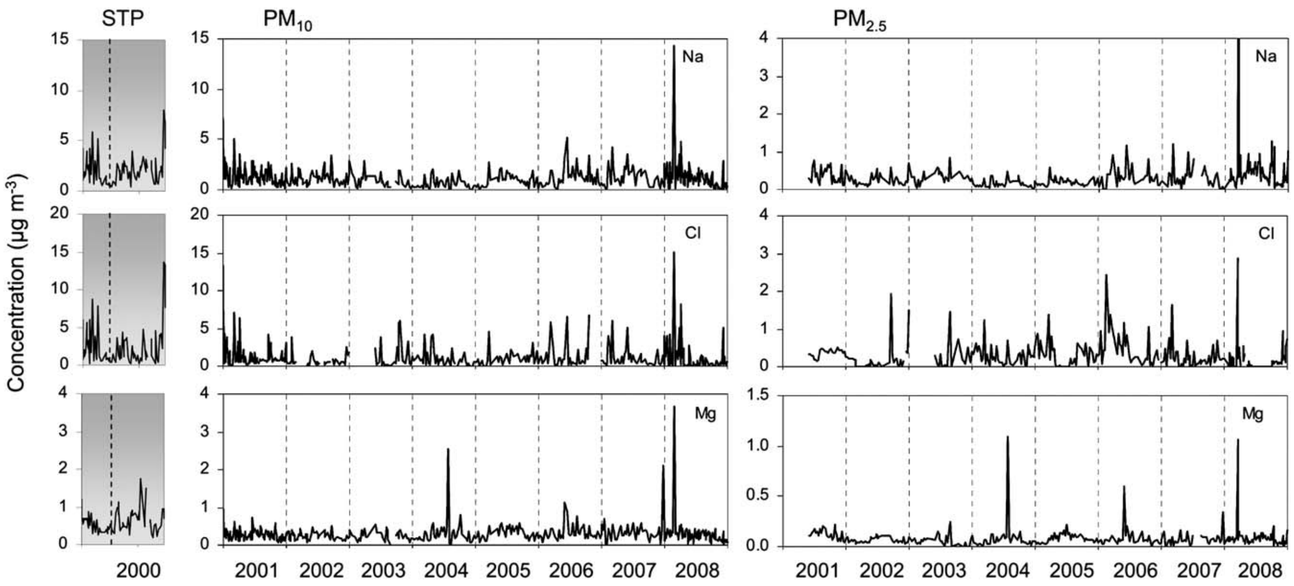


Fig. 6 Seasonal evolution of marine aerosol component element concentrations in PST,16 and PM10 and PM2.5 from January 2001 to December 2008 in the city of Huelva.

of previous experimental equations by Querol *et al.*[26] The marine sulfate was also indirectly determined by stoichiometry from the concentrations of Na and Cl in marine water (8.33 Na eq/Cl eq).[27]

PIXE analysis. Hourly concentrations of trace elements (As, Zn, Cu, P and Se) were analysed by PIXE (Particle Induced X-ray Emission) using the 3 MV Tandetron accelerator at the LABEC laboratory in Florence, Italy. This technique has previously been applied to aerosols from industrial[28] and urban[29] environments.

Almost 300 hourly samples, corresponding to one week's sampling of fine and coarse PM, were analysed. The 3 MeV proton beam (20–30 nA) scanned the streak in steps corresponding to 1 h of aerosol sampling; each spot was irradiated for about 200 s. PIXE spectra were fitted using the GUPIX software package and elemental concentrations were obtained *via* a calibration curve from a set of thin standards of known areal density. Concentration uncertainties were usually around 5% due mainly to uncertainties regarding the thickness of standard foils.[28] Mean Detection Limits (MDLs) were about 10 ng m^{-3} for low-Z elements and approximately 1 ng m^{-3} for medium–high Z elements.

Statistical analysis

In order to identify different source contributions to ambient PM_{10} and $PM_{2.5}$ levels at the sampling site, Principal Component Analysis (PCA) was performed using the complete chemical data series of concentrations of PM_{10} and $PM_{2.5}$ as independent variables. The contribution of the main sources to PM in the monitoring station was quantified by receptor modelling techniques (Multilinear regression approach).[30] Since the sum of the analysed components is close to 75% in weight of the total levels of PM_{10} and $PM_{2.5}$, the results of the multicomponent study allow the origin of most of the mass in the sampled aerosol to be known.

Long range atmospheric transport

The large scale air mass origin was daily interpreted using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT4) model (http://www.arl.noaa.gov/ready/open/hysplit4.html),[31] with vertically modelled transport back-trajectories being calculated for 5 days at 750, 1500 and 2500 m a.s.l.

These interpretations were coupled with information obtained from TOMS-NASA aerosol index maps (http://toms.gsfc.nasa.gov/),[32] SKIRON aerosol maps (http://forecast.uoa.gr/),[33] NAAP aerosol maps (Naval Research Laboratory, http://www.nrlmry.navy.mil/aerosol/), the Dust Regional Atmospheric Modeling (DREAM) system (http://www.bsc.es/projects/earthscience/DREAM)[34] and satellite images provided by NASA's SeaWIFS[35] (http://oceancolor.gsfc.nasa.gov/SeaWiFS/) to discover African dust outbreaks.

Arsenic dispersion model

Arsenic concentrations were modelled using the HYSPLIT model.[36] Emissions include several major industrial sources in the area of Huelva, Spain, composed of 5 main stacks located at 37.23 N, 6.95 W with an average height of 40 m. For this application, the HYSPLIT model was configured to release 5000 three-dimensional lagrangian particles per hour to represent the dispersion and transport of As. The meteorological data used by the model were based on output from the Mesoscale Meteorological model version 5 (MM5) using four nested grids with the highest horizontal resolution of 2 km. In order to compare the model output with the measurements we extracted the simulated concentrations from the grid cell in which the measurement station resides.

3. Results and discussion

Time series of levels of PM and gaseous pollutants

The mean 2001–2008 levels of PM_{10}, $PM_{2.5}$ and PM_1 were 38, 21 and 15 μg m^{-3}, respectively (Fig. 2). High concentrations were

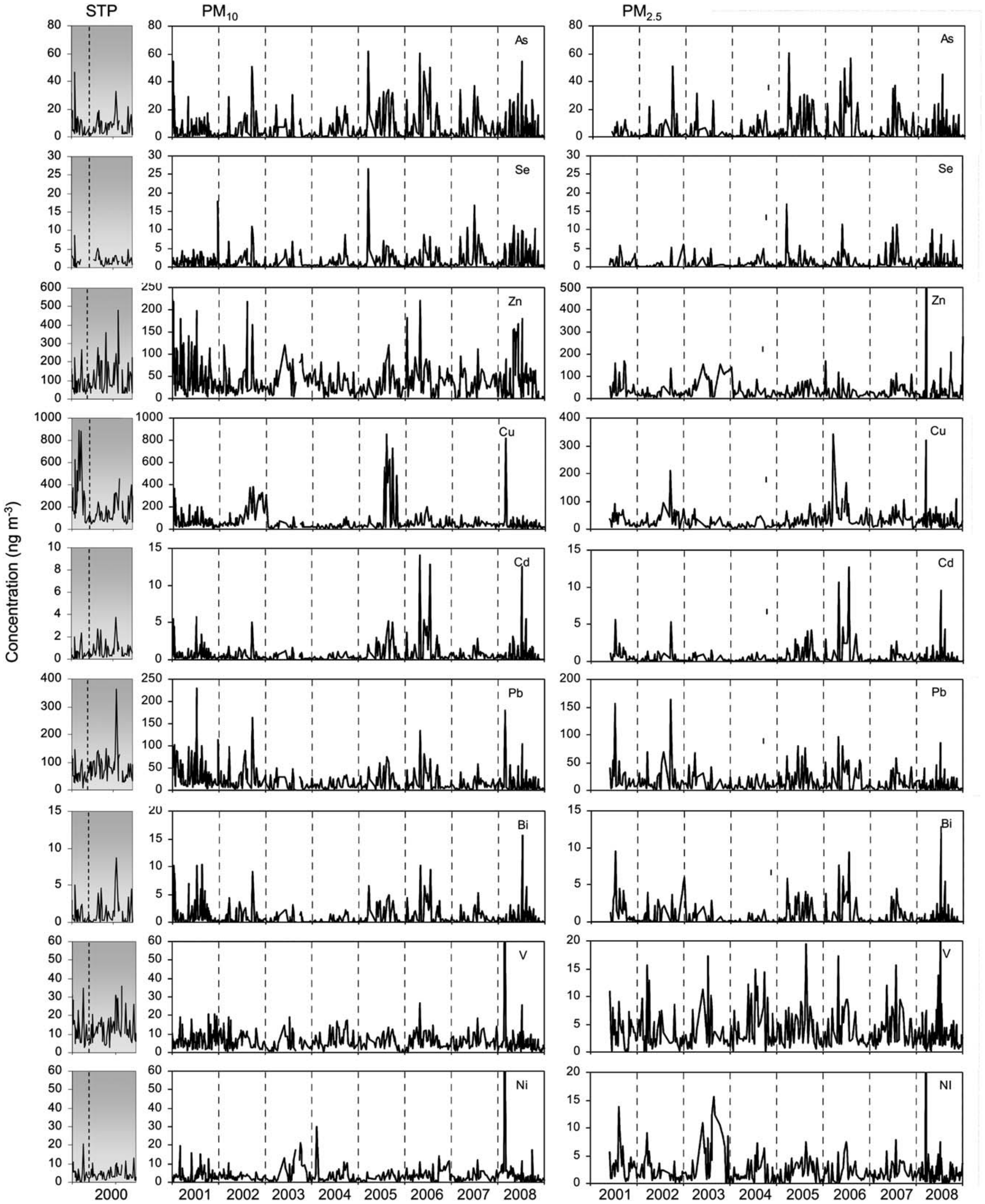


Fig. 7 Seasonal evolution of trace element concentrations in PST,16 and PM10 and PM2.5 from January 2001 to December 2008 in the city of Huelva.

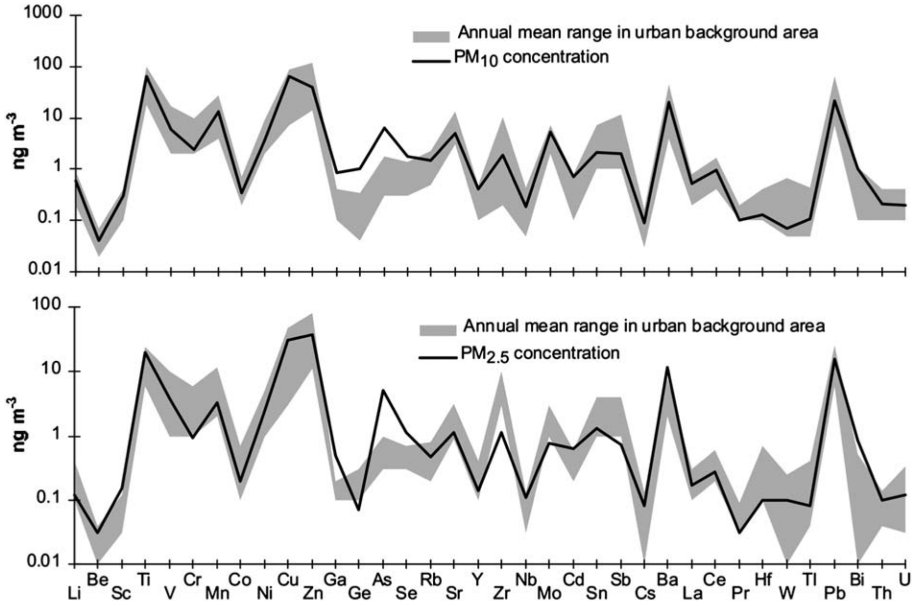


Fig. 8 Annual concentration of trace elements in PM10 and PM2.5 in Huelva, and concentration ranges of annual trace element levels in PM10 measured in urban background monitoring stations in Spain.38.

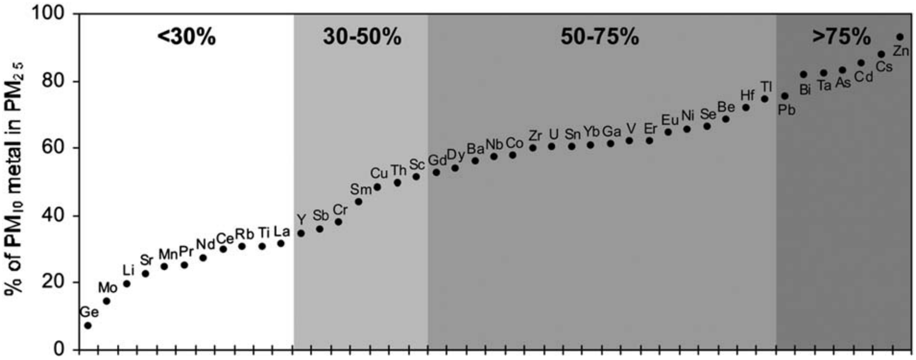


Fig. 9 Percentages of amounts of trace metals in the coarse PM10 fraction compared with the fine PM2.5 fraction.

measured in 2004 (42 µg PM_{10} m^{-3}, 26 µg $PM_{2.5}$ m^{-3}, 18 µg PM_1 m^{-3}) and 2007 (40 µg PM_{10} m^{-3}, 20 µg $PM_{2.5}$ m^{-3}, 14 µg PM_1 m^{-3}). On the basis of the daily and monthly averages of $PM_{10-2.5}$, $PM_{2.5-1}$ and PM_1, the highest levels were reached during the summer months and in February to March (Fig. 2C). The high PM_{10} levels in the summer of 2004 are consistent with the high frequency and intensity of North-African air mass outbreaks (Fig. 2B). Furthermore, the highest levels of PM_1 were registered in February 2004 during intensive anthropogenic pollutant episodes (Fig. 2C).

The number of annual exceedances of the EU daily limit of 50 µg PM_{10} m^{-3} (2008/50/CE)[37] were the highest (103 cases) in 2004, of which 59 were coincident with North-African dust outbreaks. The number of non-natural exceedance (44) was higher, than the limit of 35 days per year (2008/50/CE European Directive)[37] (Fig. 2B). Anthropogenic exceedance days mainly occurred in winter months, and occasionally in spring and June–September and November–December (Fig. 2D).

The number of exceedance of the EU daily limit coinciding with North-African dust outbreaks decreased during 2002, 2005, 2006 and 2007, and increased in 2001, 2003 and 2004. These exceedances occurred mostly in February to March and the summer months (Fig. 2D).

Levels of SO_2 did not exceed the hourly (>350 µg SO_2 m^{-3}) and daily limit (>125 µg SO_2 m^{-3}), set as mandatory since 2005[37] at the stations in the study. The mean annual levels of NO_2 were also well below the annual value fixed for 2010 limit (40 µg m^{-3}, 2008/50/CE).[37] The annual means were similar in the period of the study (ranging from 10 to 20 µg NO_2 m^{-3}).

NO_2 and SO_2 exhibited different monthly variations, as shown by Fig. 3. The levels of NO_2 increased from summer to winter (10 to 20 µg m^{-3}), while those SO_2 are almost constant for all months of the study period (2001–2008), with sporadic hourly peaks. These peak concentrations corresponded to the impact of industrial emission plumes. In the case of the city of Huelva, the main source of arsenic and other metals (*e.g.* Cu, Zn, Pb, Se, Bi, Ni and V) is a Cu-smelter located in the Punta del Sebo industrial state.[16,17] The impact of these emissions on Huelva's air quality occurs during south-westerly wind and breeze regimes.

Table 2 Levels of trace elements (PM_{10} and $PM_{2.5}$) in emission plumes sampled on 25th August 2005 in the proximity of the Cu-smelter factory

Fraction PM	PM_{10}	$PM_{2.5}$
Date	25/08/2005	25/08/2005
PM/μg m^{-3}	47	49
ng m^{-3}		
Li	0.47	0.15
Be	<0.01	<0.01
Sc	<0.01	<0.01
Ti	87.4	9.6
V	2.90	1.39
Cr	<0.01	<0.01
Mn	40.4	11.5
Co	1.31	0.35
Ni	5.50	<0.01
Cu	1357	151
Zn	798	449
Ga	3.87	<0.01
Ge	<0.01	<0.01
As	239	46.5
Se	12.6	7.67
Rb	1.56	0.67
Sr	2.38	<0.01
Y	0.31	0.19
Zr	<0.01	<0.01
Nb	<0.01	<0.01
Mo	<0.01	<0.01
Cd	6.71	2.98
Cs	0.04	<0.01
Ba	83.2	3.97
Sum REE	1.86	1.48
Ta	<0.01	<0.01
W	<0.01	<0.01
Tl	1.35	0.86
Pb	458	302
Bi	10.3	4.32
Th	<0.01	<0.01
U	<0.01	<0.01

Chemical composition of PM

Table 1 shows the mean and maximum levels for the aerosol components in Huelva. The time series of major aerosol component concentrations at the monitoring stations are shown in Fig. 4–6. In addition, we have plotted the time series described in Querol *et al.*[16] for the fraction TSP.

The mean concentrations for the whole study period were 37 μg PM_{10} m^{-3} and 20 μg $PM_{2.5}$ m^{-3}, respectively. The concentration of PM_{10} obtained is very similar to the mean value measured using the beta-attenuation monitor at the Huelva stations (38 μg PM_{10} m^{-3}), once corrected by an annual factor ranging between 0.84 and 1.16, using the filter sampling of the high-volume captors. For this reason, it is interpreted that the sampling using high-volume captors is representative of the study period.

Major components. The major components of PM_{10} are crustal (12.9 μg m^{-3}), Secondary Inorganic Components (SICs, 7.6 μg m^{-3}), organic matter plus elemental carbon (OM + EC, 6.3 μg m^{-3}), and marine aerosol (2.4 μg m^{-3}). The main crustal components are SiO_2 (5.4 μg m^{-3}), CO_3^{2-} (2.7 μg m^{-3}), Al_2O_3 (1.8 μg m^{-3}), Ca (1.3 μg m^{-3}), K (0.5 μg m^{-3}), and Mg (0.3 μg m^{-3}). The concentration of SICs (sum of ammonium, sulfate and nitrate) is high but is within the range of the urban-industrial background monitoring station in Spain (6–13 μg PM_{10} m^{-3}).[20] The main anthropogenic SICs are sulfate (4.2 μg m^{-3}) and nitrate (2.6 μg m^{-3}). The marine components are low compared with the other components.

SIC and OM + EC aerosols are dominant in $PM_{2.5}$ (SIC, 5.7 μg m^{-3}; OM + EC, 4.8 μg m^{-3}), and are in the range described in the other urban background monitoring stations in Spain (3.0–7.4 μg $PM_{2.5}$ m^{-3} and 4.7–11.4 μg $PM_{2.5}$ m^{-3}, respectively).[38] The crustal component is enriched in $PM_{2.5-10}$ compared with $PM_{2.5}$, being nearly four times higher in the coarse than the fine fraction.

Crustal components display a seasonal pattern, with higher summer and lower in winter levels, with overlapped sporadic peaks, mainly in February–March and summer (Fig. 4). The peak levels occurred during North-African dust outbreaks. The time evolution of Fe and K may also be influenced by traffic emissions and wood combustion, respectively.

OM + EC and NO_3^- levels were lower in summer than winter. However, NH_4^+ and nss SO_4^{2} display a converse pattern (Fig. 5). This fact was a consequence of the high summer SO_2 oxidative conditions and the low thermal stability of NH_4NO_3 in this period.[39]

Levels of typical marine components, such as Na^+, Cl^- and Mg, showed a clear seasonal variability, with Na^+ levels reaching their maximum in summer due to the higher intensity of sea breezes (Fig. 6). Cl^- levels decrease during summer months as a consequence of volatilization as HCl during the formation of $NaNO_3$ from gaseous HNO_3 and marine NaCl.[40–42]

Trace elements in PM. High mean levels of trace elements in PM_{10} have been reported for Huelva; Ti (64.8 ng m^{-3}), Cu (64.3 ng m^{-3}), Zn (40.6 ng m^{-3}), Pb (21.0 ng m^{-3}), Mn (13.6 ng m^{-3}), As (6.3 ng m^{-3}), V (6.1 ng m^{-3}), Mo (5.5 ng m^{-3}), Ni (3.7 ng m^{-3}) and Cr (2.4 ng m^{-3}). The annual mean concentrations of Ni, Cd and Pb in PM_{10} are lower than the target or limit values in European Directives 2004/107/EC (20 ng Ni m^{-3} and 5 ng Cd m^{-3})[22] and 2008/50/EC (500 ng Pb m^{-3}).[37] However, the concentration of As during the time study reached the target value established by the European Directive 2004/107/EC (6 ng As m^{-3})[22] for 31st December 2012.

Arsenic and other elements with similar geochemical behaviour (*e.g.* Cu, Zn, Se and Bi) show also high concentrations in $PM_{2.5}$ (5.2 ng As m^{-3}; 30.8 ng Cu m^{-3}; 37.6 ng Zn m^{-3}; 1.2 ng Se m^{-3} and 0.8 ng Bi m^{-3}). Fig. 7 shows the time evolution of PM_{10} levels of elements related with Cu-smelter emission plumes (*e.g.* As, Se, Cu, Zn, Bi). The plots show that elements display a zig-zag time evolution with more frequent peak levels in summer than winter.

Fig. 8 shows a comparison of mean concentrations for trace elements at Huelva monitoring station, and the concentration ranges for annual trace element levels measured at urban background monitoring stations.[20] PM in Huelva is enriched in As, Se, Bi, Cd, Cu, Pb, Zn, Ti, Ga, Ge and Mo.

Percentages of amounts of trace metals in the coarse PM_{10} fraction compared to the fine $PM_{2.5}$ fraction are summarised in Fig. 9. Crustal-related trace elements are enriched in the $PM_{2.5}$ fraction compared to PM_{10} with less than 30% (Ge, Mo, Li, Sr, Mn, Pr, Nd, Ce, Rb, Ti and La) and 30–50% (Y, Sb, Cr, Sm, Cu, Th and Sc). Typical anthropogenic elements were concentrated

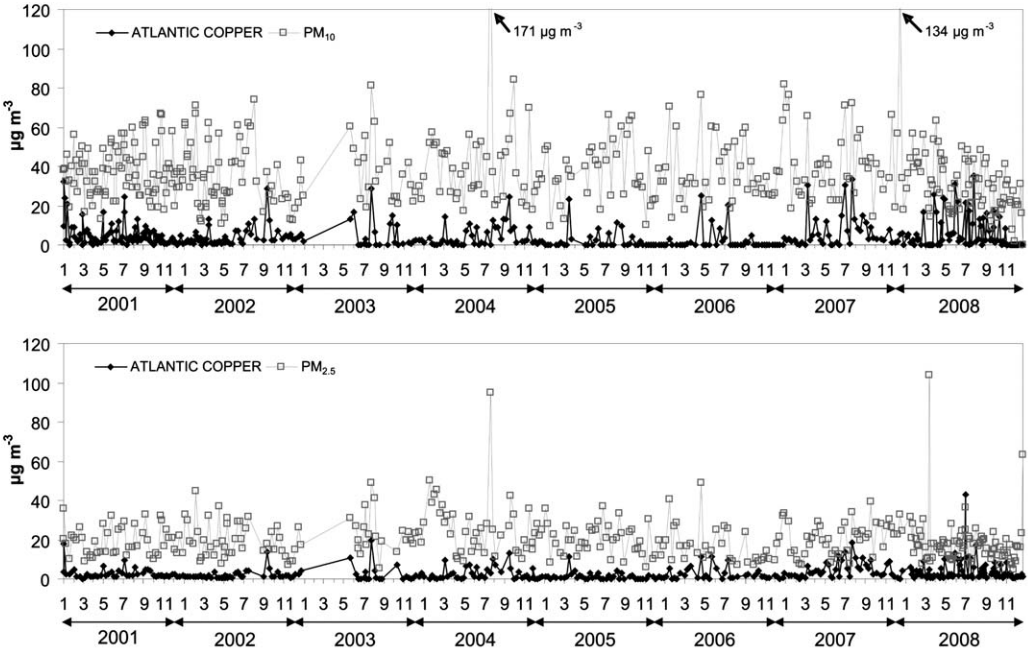


Fig. 10 Daily source contribution of copper smelter factory (in µg m^{-3}) to levels of PM10 and PM2.5 in Huelva during the period 2001–2008.

in the fine fraction: 50–75% (Th, Sc, Gd, Dy, Ba, Nb, Co, Zr, U, Sn, Yb, Ga, V, Er, Eu, Ni, Se, Be, Hf and Tl), and higher than 75% (Pb, Bi, Ta, As, Cd, Cs and Zn).

Table 2 summarizes the trace elements chemical composition of the emission plumes sampled during their impact in the proximity of the Cu-smelter factory (25th August 2005, 16:30–18:30 h GMT). The sampling date and the mean PM$_{10}$ and PM$_{2.5}$ concentrations during sampling are indicated. High concentrations of As, Ti, Mn, Cu, Zn, Se, Cd, Ba, Pb and Bi were obtained.

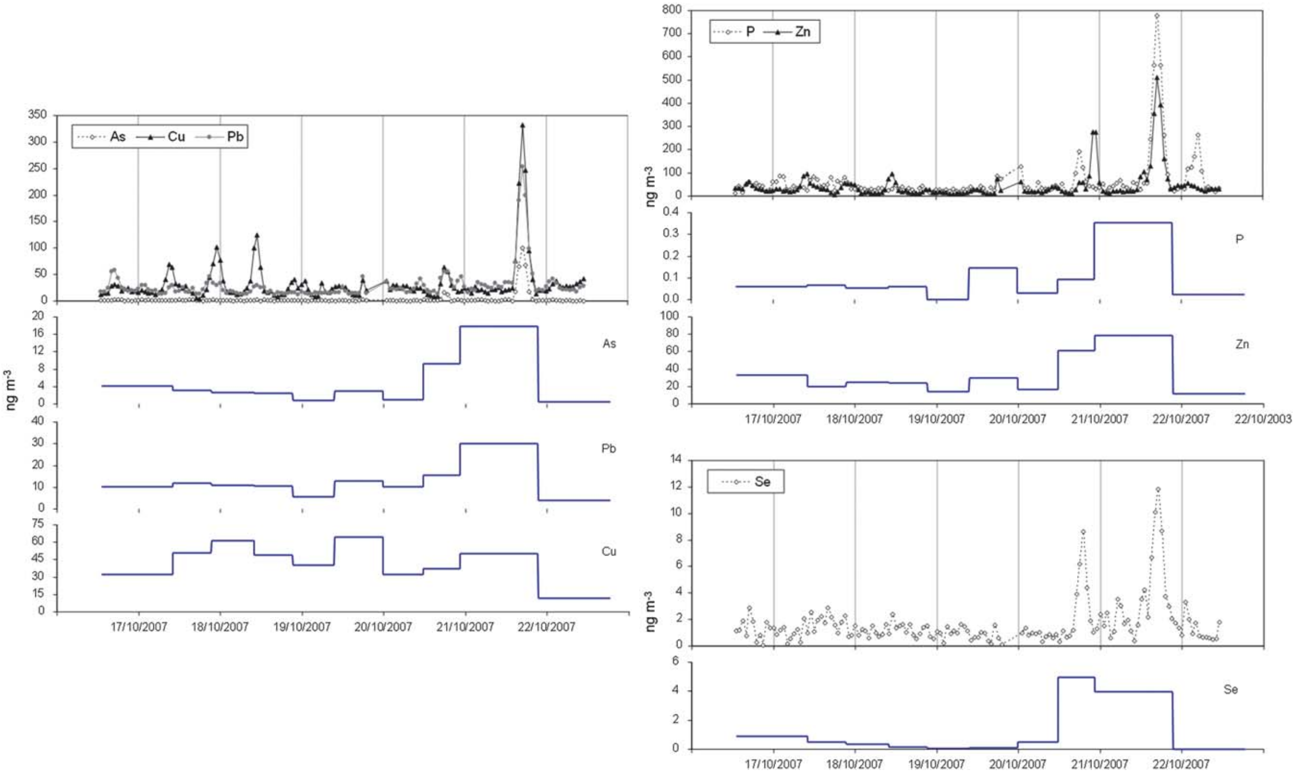


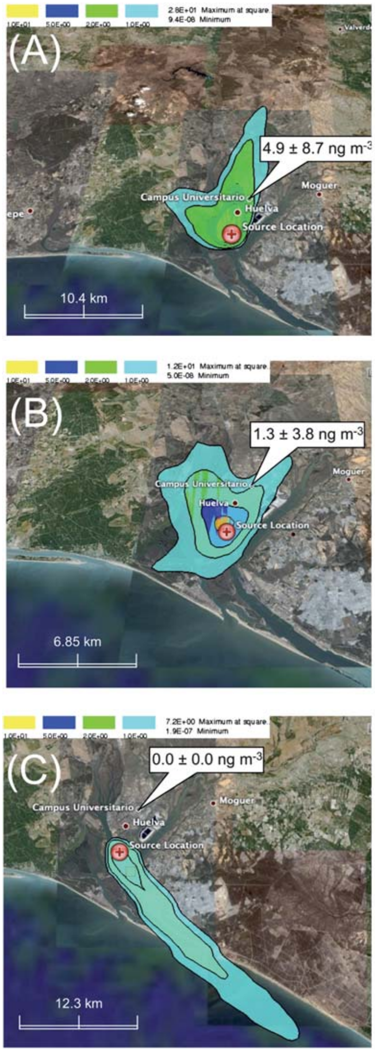
Fig. 11 Hourly concentrations of trace elements (As, Cu, Pb, P, Zn and Se) obtained by PIXE, and mean 12 and 24 hour concentrations of the same elements obtained by ICP-MS using a high volume captor.

The calculations of Principal Component Analysis and source contributions show as Cu-smelter emissions contribute between 4.4 μg m^{-3} in PM_{10} and 2.8 μg m^{-3} in $PM_{2.5}$ as annual average, ranging between 2.0 and 6.7 μg m^{-3} and 1.8–4.2 μg m^{-3}, in PM_{10} and $PM_{2.5}$, respectively (Fig. 10). The greatest contribution of this source was recorded in 2007 and 2008.

Hourly trace metal chemical composition. Hourly concentrations of trace elements (As, Zn, Cu, P and Se) were obtained by PIXE for the $PM_{2.5}$ and PM_{10} fractions. Almost all the $PM_{2.5-10}$ hourly samples had As concentrations below the MDL, about 1 ng m^{-3}, on average.

Peak As levels coincided with Cu, Zn, Pb, P and Se, which reached maximum concentration values of 326 ng m^{-3}, 506 ng m^{-3}, 245 ng m^{-3}, 778 ng m^{-3} and 12 ng m^{-3}, respectively, during the 21st October 2007 (Fig. 11).

In the $PM_{2.5}$, As concentration proved to be well above 2 ng m^{-3}, on average, for only 6% of the cases, during two impact episodes, as can be seen in Fig. 11. In these cases, hourly concentrations ranged from 3 to 100 ng m^{-3}.



Star date	10/08/2003
End date	11/08/2003
$\mu g\ m^{-3}$	
PM	63
nss SO_4^{2-}	10.9
NO_3^-	3.37
NH_4^+	2.67
$ng\ m^{-3}$	
Ti	93.8
V	10.3
Cu	42.1
Zn	32.2
As	7.44
Se	1.65
Pb	21.4
Bi	0.95

Star date	14/06/2004
End date	15/06/2004
$\mu g\ m^{-3}$	
PM	51
nss SO_4^{2-}	8.87
NO_3^-	4.64
NH_4^+	2.31
$ng\ m^{-3}$	
Ti	109
V	13.9
Cu	31.7
Zn	36.3
As	10.1
Se	2.70
Pb	25.1
Bi	1.29

Star date	15/08/2003
End date	16/08/2003
$\mu g\ m^{-3}$	
PM	32
nss SO_4^{2-}	1.63
NO_3^-	1.16
NH_4^+	0.23
$ng\ m^{-3}$	
Ti	58.6
V	2.60
Cu	20.9
Zn	4.98
As	0.80
Se	0.14
Pb	2.49
Bi	<0.01

Fig. 12 HYSPLIT model outputs for three different days (August 10 and 15, 2003, and June 14th, 2004), and major and trace element concentrations obtained at the University Campus monitoring station.

Comparison of hourly and daily concentrations showed good agreement for As, Cu, Zn, Pb, P and Se in PM (Fig. 11). These results identify short time intervals in which the impact of arsenic and other heavy metal concentrations in emission plumes occurred at the monitoring station.

High resolution modelling of arsenic episodes

HYSPLIT was run and compared with field measurements for three different summer days, namely August 10th and 15th, 2003, and June 14th, 2004. Fig. 12 shows the geographical distribution of the concentration of Arsenic (ng m^{-3}) as calculated by the model. On August 10th 2003 and June 14th 2004, the typical summertime sea breeze transported the pollutant inland, increasing the concentrations in the city of Huelva. Conversely, on August 15th 2003 during the passage of a frontal zone the pollutant plume was directed toward the south-east preventing the build-up of As in the area of Huelva. Similar behaviour to that described for As was found in other metals with high concentrations (*e.g.* Cu, Zn, Pb, Se, Bi, V, and Ti) identified from the chemical analysis of PM_{10} in the University Campus urban background monitoring station.

A comparison of the model outputs and the measurements for the University Campus site is displayed in Fig. 12. The model is able to predict whether the source impacts on the measurement site; however, it underpredicts As concentrations. This underprediction could be due, among other factors, to the uncertainty in the emission rates from the Cu-smelter factory and the wind speed and direction in the meteorological model driving the transport and dispersion. Future work will include the investigation on how these factors affect the geographical distribution of As in the area of Huelva.[43]

4. Conclusions

A long-term time series (eight years) of chemical analysis of whole PM obtained in a city deeply affected by the As-rich emission plumes of a nearby Cu-smelter factory was studied. Peaks of $PM_{2.5}$ are correlated with simultaneous increases of levels of gaseous pollutant (NO_2 and SO_2), essentially derived from the industrial sites and during sea-breeze episodes.

PM in Huelva is enriched in As, Se, Bi, Cd, Cu, Pb, Zn, Ti, Ga, Ge and Mo. High annual mean arsenic concentration was determined in PM (6.3 ng PM_{10} m^{-3} and 5.2 ng $PM_{2.5}$ m^{-3}), reaching the 6 ng m^{-3} mean annual target value for PM_{10} proposed by the European Commission for 2013.

Daily peak concentrations of arsenic and other major compounds (SO_4^{2-} and NH_4^+) and trace elements (*e.g.* Cu, Zn, Pb, Se and Bi) in PM, sampled using a high-volume captors, occurred under synoptic conditions in which the winds had S and SW components, transporting the pollutants from a nearby Cu-smelter to the city. These elements display a zig-zag pattern time evolution with more frequent peak levels in summer than winter.

The mass contribution of Cu-Smelter emissions to ambient PM is reached 2.0–6.7 μg m^{-3} and 1.8–4.2 μg m^{-3}, in PM_{10} and $PM_{2.5}$, respectively. Furthermore important contributions to ambient levels of toxic elements, such as As, Se, Bi, Pb, Cd, PO_4^{3-} and Cu, are also relevant.

Hourly peak concentrations of As, Zn, Cu, P and Se were identified using Streaker measurement and PIXE analysis. A comparison of hourly and daily concentrations showed good agreement between As, Cu, Zn, Pb, P and Se in PM.

The geographical distribution of the As concentration was modeled with HYSPLIT software, an application which allows us to distinguish days when the impact of Cu-smelter dispersion plumes is registered at the monitoring station for a few hours.

This study determines the distribution of airborne arsenic particulate at urban background stations in the city of Huelva. This plays a critical role, and affects the population. A Cu-smelter factory, located 3 km to the south-west of the city, is the main source of atmospheric particulates containing arsenic and other trace elements (*e.g.* Cu, Pb, Zn, Se, Bi and Cd). Our final conclusion is that simultaneously using the results from daily chemical analysis of PM and techniques such as high resolution sampling and modelling, of arsenic and other metals, can help to identify short time intervals in which the impact of emission plumes with high metal concentrations on air quality occurred in Huelva.

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