

Levels of 25 trace elements in high-volume air filter samples from Seville (2001–2002): Sources, enrichment factors and temporal variations

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A B S T R A C T

The measurement of trace element concentration in aerosols is of interest for environmental studies and for human health assessment. The temporal variability of total suspended particles (TSP) and its elemental composition in Seville, in SW Spain, is of particular complexity since Atlantic air masses and Saharan Dust Intrusions (SDI) overlap to local natural and anthropogenic sources. This paper is aimed to study the temporal evolution (in a monthly basis) of the concentrations of 25 trace elements, determined by ICP-MS, in high-volume air filter samples from Seville, covering a two-year period: 2001–2002. The mean TSP value for this period was $79.7 \mu\text{g m}^{-3}$ and showed peak values in August 2001 and June 2002, likely related to SDI. Enrichment factors (EF) for Se, Sb and Zn and Pb were above 100, which revealed their anthropogenic sources. The comparison among EF from Seville and Huelva, a highly industrialized city nearby Seville, showed higher levels of anthropogenic elements there than in Seville. Simulations of the transport/dispersion of pollutants starting in Huelva confirm that air pollutants can reach Seville in the course of around 6 hours although they do not contribute significantly to the levels found in this city. A significant temporal correlation was found between elements which have a common source, being crustal (Al, Ti, Be, Co, Cs, Fe, Cr, Mn, U, Sr and Th) or anthropogenic sources (Zn, Pb, Cd). The temporal variations of those crustal elements are similar and related with the TSP levels for both years, with the clearly visible peaks probably related with the Saharan dust intrusion.

Keywords:

Aerosol
Trace metals
ICP-MS
Enrichment factors

1. Introduction

One of the main sources of atmospheric contamination in large cities comes from atmospheric particulate matter and gases derived from anthropogenic activities such as traffic and industry (Finlayson-Pitts and Pitts, 2000; Baldasano et al., 2003; Artiñano et al., 2003), which can impact on rural and

ecological interest areas modifying the regional background concentrations.

The measurement of trace element concentrations in aerosols is of great interest for the assessment of human population exposure and for a wide set of environmental studies. It has been well established the correlation between concentration of fine aerosol particles and human mortality (Swietlicki et al., 1996; WHO, 2006). Particle size governs the degree of penetration of aerosols in the respiratory system. Aerosol particles exhibit a large variability in shape and chemistry with an also variable concentration of highly toxic elements such as cadmium (Moreno et al., 2006). Some of these hazardous elements are of anthropogenic origin

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(e.g. from metallurgical industries and combustion of fossil fuels). Consequently, the World Health Organization has established air quality guidelines (WHO, 2005, 2006). In the same line, the European Union has set an annual limit value for aerosol particles below 10 μm in diameter (PM_{10}) of $40 \mu\text{g m}^{-3}$ (Air Quality Directive, 2008/50/EC).

Concentrations of some trace elements in aerosols have been reported for a large variety of locations all over the world. These studies have been favored by the recent spreading of ICP-MS technique, allowing for the simultaneous and multi-elemental determination of a wide set of target analytes at trace and ultra-trace concentrations (Buzika et al., 2006; Chandra Mouli et al., 2006; Moreno et al., 2006).

There are many studies of trace elements in air filter samples based on open digestion procedures with different reagents such as aqua regia (Castilho et al., 2012), $\text{HF} + \text{HNO}_3$ (Gerboles et al., 2011) and $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ (Birnbaum et al., 2006), but the most satisfactory results are obtained using microwave-digestion procedures (Sandroni et al., 2002; Sastre et al., 2002). For all elements with fractions associated with silicates, many studies propose reagents mixtures with HF. The use of HF in the filter digestions requires the use of H_3BO_3 to redissolve fluoride precipitates (Gerboles et al., 2011; Kulkarni et al., 2007) with the operational problems that this entails. For this reason, many other studies use digestion procedures based on the US-EPA 3051 methodology using only HNO_3 (Birnbaum et al., 2006; Shaltout et al., 2014).

Aerosols play an important role in atmospheric processes such as cloud formation, radiative balance, and the kinetic reactive transport of pollutants (Jacobson, 2001; Pay et al., 2012). Their relationships with ecosystems are also of relevance; e.g. it has been shown that Saharan dust represents a potential source of nutrients (P, Fe) for the Mediterranean waters (Guieu et al., 2002). Although powerful numerical models have been developed to simulate aerosol dynamics in the atmosphere (Karyampudi et al., 1999; Balk et al., 2010; Pay et al., 2012), a gap still persists between simulated and observed concentrations, which require improving the current level of understanding of the physical and chemical processes involved and a better characterization of emissions.

Aerosol dynamics in SW Spain is of particular complexity since local contributions of natural and anthropogenic origin are interfered by air masses coming from the Atlantic Ocean and by external contributions from Saharan dust (which is one of the most important dust sources on the Planet as reported by Prospero et al. (2002)). This last is responsible of some sporadic excesses of the PM_{10} limit values in the Iberian Peninsula (Dueñas et al., 2002; Escudero et al., 2007). Particularly, Pay et al. (2012) reported contributions of desert dust loads to daily PM_{10} values exceeding $100 \mu\text{g m}^{-3}$ in several locations from southern Spain. Saharan aerosols are dominated by mineral dust, mainly composed by silicates (Kandler et al., 2007). It also has been shown that Saharan Dust Intrusion (SDI) provoked maximum concentrations of some anthropogenic radionuclides such as ^{239}Pu and ^{137}Cs in Seville city, in SW Spain (Chamizo et al., 2010). Recently, Gómez-Guzmán et al. (2012) found that anthropogenic ^{129}I concentrations in rainwater from Seville were affected by airborne releases from Sellafield and La Hague facilities. Numerical models to study spatial and temporal variability of aerosol concentrations across Spain have been developed, among others, by Pay et al. (2012).

Other studies in the city of Seville have been conducted previously, for example, by Fernández Espinosa et al. (2001, 2004) and Usero et al. (1988) who applied, respectively, ICP-AES technique to measure concentrations of a set of 11 target elements in urban aerosols and AAS to measure a set of 13 elements in particulate samples. This paper is aimed to study the temporal evolution (on a monthly basis) of the concentrations of 25 trace elements, determined by ICP-MS, in high-volume air filter samples from Seville, covering a two-year period: 2001–2002. The study focuses on the detailed chemical characterization of total suspended particles (TSP) in the city of Seville in order to identify the major emission sources having a significant influence on the levels and composition of TSP.

2. Materials and methods

2.1. Sampling conditions

Seville is the largest city in the Southern Spain. It has a metropolitan population of around 750,000 inhabitants and on workdays this increases to about 2 million due to incoming traffic from the nearby towns. The annual mean traffic density in 2002 was of 1.2×10^6 vehicles a day. Seville is located at 37.39°N and 5.98°W in a valley at an altitude of 8 m above the sea level and has a subtropical Mediterranean climate, with a drier summer and wet winter. The annual average temperature is 25°C during the day and 13°C at night. The wind direction in this region is dominated by two directional components (SW and NE) and it is located around 90 km away from Huelva, a highly industrialized city (see Fig. 1). The red dot in the central map of Fig. 1 represents Seville city and numbers represent the most important nearby industries emitting atmospheric heavy metals (As, Ni, Zn, Cd and Pb, in decreasing order) as extracted from the database E-PRTR (The European Pollutant Release and Transfer Register, <http://prtr.ec.europa.eu>).

Seville harbor has an important truck shipping traffic devoted mainly to the transport of agricultural goods and foodstuffs and secondarily of scrap iron and cement. Transport of persons and goods contributed in 1998 to the emission to the atmosphere of 32 and 97 tons of Pb in the provinces of Huelva and Seville, respectively; most of them in the urban area (Caro-Gómez et al., 1998). After these authors, the total atmospheric emission of particulate material from all sources (industry, metal extraction, transport and domestic) in this year was 31720 and 18693 tons in Huelva and Seville provinces, respectively.

The sampling station was installed in 1999 at 30 m above the ground, on the roof of the building of the Faculty of Physics of the University of Seville, beside the harbor area and close to high traffic roads (Fig. 1). The sampling system is a continuous high-volume air sampler ASS-500 (Innovation Technik Physik, Erlangen, Germany) which generates a mean flow rate of $950 \text{ m}^3 \text{ h}^{-1}$. Airborne dust samples were collected weekly in a polypropylene filter, type G3, size $440 \times 440 \text{ mm}^2$ and with a collection efficiency of 93% at the flow rate previously mentioned. The effective cut-off diameter was obtained from the manufacturer specification.

For this work, filter samples from years 2001 and 2002 were used. From the 10th of August to the 17th of September 2001, the filters corresponded to 4 days of sampling. For the rest of the studied years (2001 and 2002), the filters corresponded to

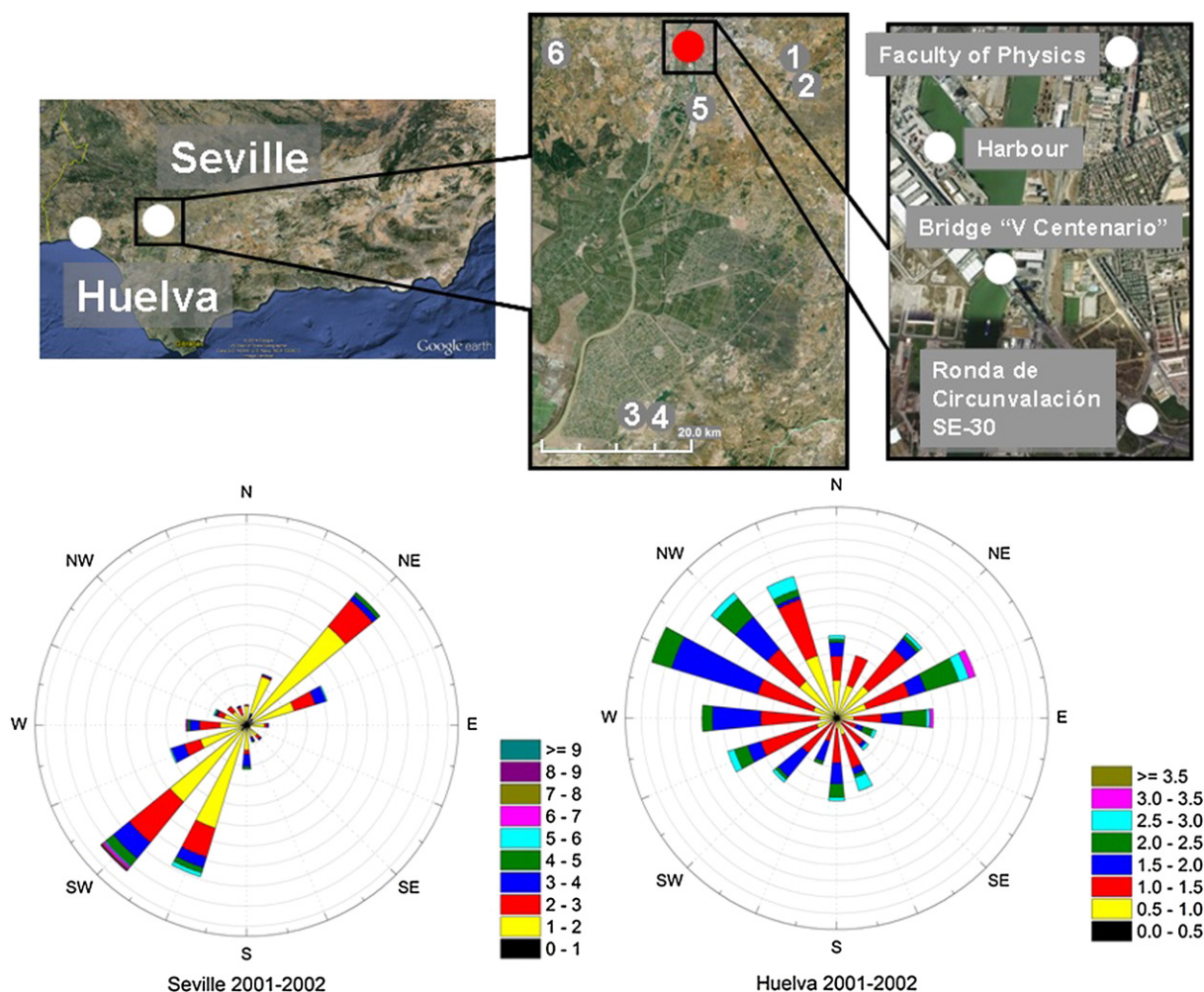


Fig. 1. Map of the studied area showing both Seville and Huelva cities in Southern Spain. Wind rose diagrams for the period 2001–2002 recorded at two stations of the Meteorology National Institute of Spain (INM). The red dot in the central map represents Seville city and numbers represent the most important nearby industries emitting atmospheric heavy metals (As, Ni, Zn, Cd and Pb, in decreasing order) as extracted from the database <http://prtr.ec.europa.eu> (1: production of pig iron or steel including continuous casting, 2: manufacture of glass, including glass fiber, 3: manufacture of ceramic products including tiles, bricks, stoneware or porcelain, 4: vegetable raw materials, 5: surface treatment of metals and plastics using electrolytic or chemical processes, and 6: cement clinker in rotary kilns).

7 days of sampling. For every month, 4 weekly filters were available (each one corresponding to 7 days of non-stop sampling). We took similar aliquots of each weekly filter and grouped them in months, in order to obtain monthly data. The observed variability in the metal concentration is therefore characteristic of each studied month. To obtain monthly averages, 1% aliquots of individual weekly filters (each one with a mass of around 300 mg) were cut, grouped with such temporal resolution, and processed. All polypropylene blank filters were treated under the same conditions to determine the blank level for all elements studied in this work. The total mass of aerosol in the filter was determined by a gravimetric method: the clean polypropylene filter was weighted before its incorporation in the sampler. The sampler contains a couple of electric resistances to get the filter dry during the whole sampling period. Finally, when the sampling period finished, the filter was weighted again and the total mass of aerosol incorporated in the filter was calculated by subtracting the mass of the clean filter from the mass of the filter after the sampling period.

2.2. Sample preparation

In this work filter samples were chemically prepared using the microwave digestion method described in [Chamizo et al. \(2010\)](#) and [Enamorado-Báez et al. \(2013\)](#) and briefly summarized here. Approximately 1.2–1.5 g of filter sample (accounting both filter and aerosol masses) was mixed with 8 mL HNO₃ 65% suprapure and 4 mL 18 MΩ deionized water, introduced in fluoropolymer liner vessels and covered with ceramic jackets. After the homogenization, the vessels were closed and introduced in a microwave digestion system Anton Paar MX-3000, equipped with a 16-positions rotor and two temperature probes. This selected sample mass is the maximum allowed in the vessels to avoid overpressure and/or temperature peaks during the digestion procedure. The digestion process consisted of two steps: i) the temperature was raised from room temperature (25 °C) to 120 °C in 30 minutes and maintained for 20 minutes; ii) the temperature was increased to 180 °C in 20 minutes and maintained for 40 minutes. Subsequently, the samples were

cooled down to room temperature, the aliquots were filtered with 20–25 μm diameter pore 110 mm diameter size Whatman® filters, transferred to Teflon beakers and heated to dryness on a hot plate at a temperature below 95 °C. Finally, the dry and solid samples were dissolved in 20 mL of 2% HNO_3 suprapure and diluted with 18 M Ω deionized water to a final volume of 100 mL. It is worth noting that prior to the acid digestion the samples were not converted into ashes in a muffle furnace to avoid losses of volatile elements.

The used digestion method has been tested against a set of certified samples with different matrices: organic materials and soil samples (Enamorado, 2013; Enamorado et al., 2014). The average recovery was (92 \pm 17)% in organic matrices and (89 \pm 19)% in soils (when excluding in these latest Al, Ti, Ba, and Sb with values below 50%). Due to the smaller particle sizes, the digestion yield for the mineral aerosol components is expected to be higher than that for soils.

2.3. Trace elements analyses

The samples were analyzed with ICP-MS technique in the Agriculture Research Centre of the University of Seville. More details are given in (Enamorado et al., 2013, 2014), so only a brief description will be made. The instrument used in this study was a Thermo Elemental X7 (Thermo Fisher, Cambridge, U.K.) with quadrupole mass analyzer and multichannel detector (for pulse counting and analog methods). It is equipped with an auto-sampler ASX-500 (CETAC, Omaha, NE, USA) and a concentric (Meinhard) quartz nebulizer for ultra-trace analysis. Different data quality tests were carried out during each instrumental running using the recommendations provided by US EPA 200.8 methodology, such as replicate samples, matrix matching, spike, fortified blanks, recovery and memory tests, and inclusion in the series of some certified samples (Creed et al., 1994).

The trace element components of the studied TSP have been quantitatively analyzed. Replicated measurements of the blank filters served to determine the method detection limit (MDL), as described in Enamorado et al. (2014, 2013) by using the US-EPA 200.8 and US-EPA 3051 definitions. Each blank was prepared using a clean filter, the same amount and mixture of reagents, and the same experimental procedure than the unknown samples.

For all elements, MDL ranged from 0.0058 $\mu\text{g L}^{-1}$ for Be to 15.1 $\mu\text{g L}^{-1}$ for Fe, being, at the highest value, lower than 7% of all concentration values in year 2001 and 5% of the concentration values in year 2002. The MDL levels reported in this study are shown in Table 2 (Supplementary Electronic Material). They are comparable to those reported by Chandra Mouli et al. (2006), also using ICP-MS, and they result significantly lower than those reported by other studies applying ICP-AES (López et al., 2005).

3. Results and discussion

3.1. Total suspended particulate (TSP)

TSP instead of PM_{10} sampling was preferred in the current study, carried out from January 2001 to December 2002, to characterize all the PM size ranges. The monthly mean of TSP levels measured in Seville in 2001 and 2002 are shown in Fig. 2.

Mean values for both years are quite similar (83.4 and 76.0 $\mu\text{g m}^{-3}$) for 2001 and 2002 respectively, comparable to those of 79 $\mu\text{g m}^{-3}$ previously reported for Seville by Fernández Espinosa et al. (2001) in spring 1996 and lower than those of 210 $\mu\text{g m}^{-3}$ reported by Usero et al. (1988) between November 1984 and November 1985.

Querol et al. (2002) reported mean TSP levels of 91.3 g m^{-3} in the city of Huelva (approximately 90 km SW away from Seville) for the period from July 1999 to December 2000. These authors reported TSP peak events in spring-summer and autumn, associated to Sahara dust outbreaks in this period.

To study the effects of the weather patterns on TSP levels, monthly rainfall levels have also been included in Fig. 2, where it can be seen that maximum TSP levels are achieved during months with almost absence of rainfall (August in 2001 and June in 2002). It is worth to note that during those 2 months there was a prevalence of winds blowing South-west over Seville, most likely carrying Saharan dust intrusion which provoked maximum concentrations of TSP (Fernández Espinosa et al., 2001). The same SDI had been already identified by other authors in different parts of Spain, with also maximum crustal dust (and so TSP) content in August 2001 and June 2002 (Querol et al., 2008; Salvador et al., 2007), in agreement with the results shown in this work, with peak values in August 2001 (117 $\mu\text{g m}^{-3}$) and June 2002 (92 $\mu\text{g m}^{-3}$) of SDI-attributable origin.

A number of studies (e.g. Querol et al., 2004, 2008; Escudero et al., 2007; Artiñano et al., 2001; Rodríguez et al., 2002, among others) show that the Iberian Peninsula exceeds some of the thresholds of air quality established in the legislation. Exceedances in $\text{PM}_{2.5}$, PM_{10} and TSP levels are not only caused by anthropogenic emission but also the long-range transport of atmospheric mineral dust sources from deserts. Those exceedances are more often in summer and are usually associated with different causes, such as: higher frequency of African dust outbreaks over the Iberian Peninsula, lower precipitation, higher resuspension due to soil dryness, increased formation of secondary aerosols and recirculation of air masses that prevent air renovation (Pay et al., 2012).

3.2. Trace elements concentrations

The annual mean, minima and maxima concentrations for the 25 elements (Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl, Pb, Th and U) measured in this study are shown in Table 1. These values have been corrected by blank levels.

Fig. 3 depicts the temporal variation in the concentrations for both years 2001 and 2002. In all cases concentrations have been normalized using the mean concentration of every element, i.e., for each element, the result shown in Fig. 3 is obtained by dividing the real concentration by the arithmetic mean concentration of this element in both years. The higher annual mean concentrations were obtained for Fe (2012 and 1112 ng m^{-3}), Al (1097 and 595 ng m^{-3}), Zn (142 and 63 ng m^{-3}), Mn (34 and 19 ng m^{-3}), Ba (34 and 20 ng m^{-3}), Ti (33 and 20 ng m^{-3}) and Pb (32 and 23 ng m^{-3}) (the two values given in brackets for each element correspond to years 2001 and 2002, respectively). The annual mean values of trace element

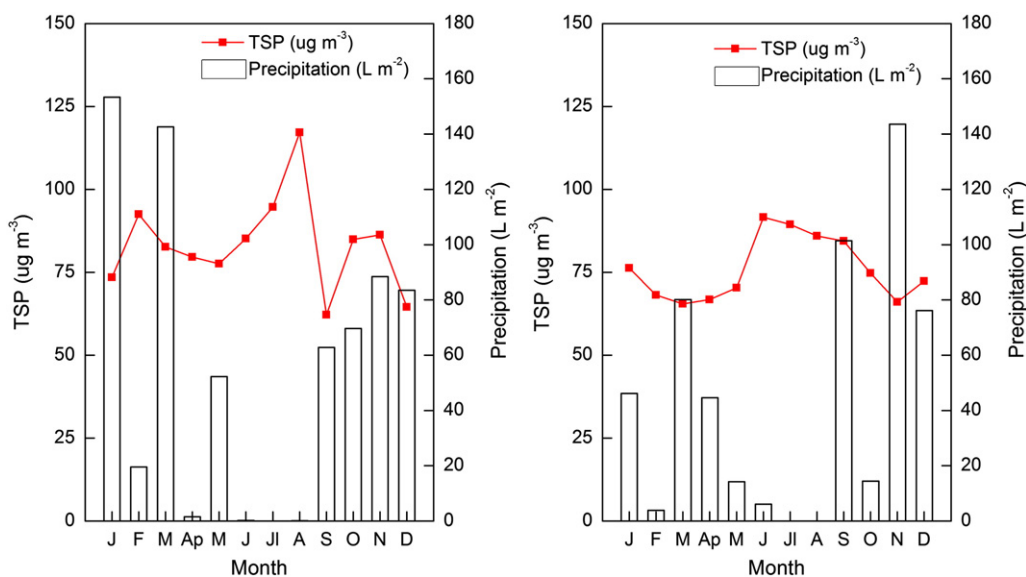


Fig. 2. TSP concentration (red line) and precipitation (black bar) for years 2001 (left) and 2002 (right) in Seville.

concentrations (in ng m^{-3}) analyzed in this work followed the order: Fe

Some of the most interesting elements to study due to their toxic character with industrial and traffic origin are Ni, As, Cd, Mn, V, Zn and Pb (Fernández et al., 2000; Fernández Espinosa et al., 2001, 2004), although none of their concentrations exceed the air quality guidelines values in force at that time (Air Quality Directive, 2004/107; Air Quality Directive, 2008/50; WHO, 2005) during both sampling periods. Pb has been

historically considered as a marker of the vehicle traffic until the early introduction of legislation about the use of unleaded fuel in the European countries from 1 January 2000 (EC, 1998). Since then, Pb emissions from traffic have been dramatically reduced. As a reference, industrial sources of Pb in the areas of Seville and Huelva accounted during 2007 for the emission to the atmosphere of 1.7 and 6.0 tons, respectively (from E-PRTR database). Contributions from the sector of transport have been commented above. Both annual mean and maximum Pb concentrations for years 2001 (31.6 and 54.8 ng m^{-3}) and 2002 (23.3 and 40.4 ng m^{-3}) were below the annual EC limit (500 ng m^{-3}) and the range of $0.01\text{--}2 \mu\text{g m}^{-3}$ WHO guideline value (WHO, 2005). Some studies as Querol et al. (2002) and Sánchez de la Campa et al. (2007) reported higher levels in the city of Huelva (83 and 698 ng m^{-3} , and 20 and 76 ng m^{-3} as mean and maximum values, respectively) in studies conducted between July 1999 and June 2002.

Table 1

Mean \pm 1 STD (standard deviation) concentrations of trace elements (ng m^{-3}) and TSP ($\mu\text{g m}^{-3}$) collected in Seville during years 2001 and 2002.

	2001		2002	
	Range	Mean \pm 1 STD	Range	Mean \pm 1 STD
Be	0.02–0.2	0.06 ± 0.04	0.02–0.06	0.03 ± 0.01
B	0.3–3.5	1.6 ± 1.0	1.7–4.0	3.0 ± 0.7
Al	535–3157	1097 ± 752	257–1069	595 ± 267
Ti	18–87	33 ± 20	11–33	20 ± 8
V	0.7–49	10 ± 13	0.5–13	6 ± 3
Cr	4–18	10 ± 4	1.3–11	5 ± 3
Mn	20–79	34 ± 17	10–28	19 ± 6
Fe	1043–4740	2012 ± 1068	571–1877	1112 ± 400
Co	0.4–1.6	0.7 ± 0.4	0.2–0.7	0.4 ± 0.1
Ni	1.6–6.8	3.8 ± 1.7	2.5–5.0	4.0 ± 1.0
Cu	15–46	26 ± 9	6–26	17 ± 7
Zn	57–483	142 ± 118	20–106	63 ± 25
As	0.03–3.8	1.5 ± 0.9	0.5–1.7	1.0 ± 0.4
Se	0.2–2.5	1.0 ± 0.7	0.3–0.8	0.6 ± 0.2
Sr	7–29	12 ± 6	4–10	8 ± 2
Mo	0.7–2.4	1.4 ± 0.5	0.3–1.2	0.8 ± 0.3
Ag	0.06–0.7	0.3 ± 0.2	0.06–0.5	0.2 ± 0.1
Cd	0.05–1.1	0.6 ± 0.3	0.07–0.5	0.3 ± 0.1
Sb	1.0–6.0	3 ± 2	0.4–5.0	2.0 ± 1.4
Cs	0.07–0.5	0.2 ± 0.1	0.04–0.2	0.1 ± 0.04
Ba	17–58	34 ± 12	6–34	20 ± 9
Tl	0.05–0.2	0.1 ± 0.04	0.02–0.1	0.1 ± 0.03
Pb	19–55	32 ± 12	8–40	23 ± 10
Th	0.2–1.3	0.5 ± 0.3	0.07–0.2	0.1 ± 0.06
U	0.005–0.3	0.1 ± 0.07	0.04–0.5	0.1 ± 0.1
m	62–117	83 ± 15	66–92	76 ± 10

Prior to this legislation, Usero and Gracia (1987) detected the highest Pb concentrations (ranging $200\text{--}350 \text{ ng m}^{-3}$) of their study in sampling stations located in zones with high vehicular traffic in the “Campo de Gibraltar” area. Moreno-Grau et al. (2000) have reported mean annual Pb values in different areas around Cartagena (Spain) representing an industrial zone (1010 ng m^{-3}), an urban zone with heavy road traffic (690 ng m^{-3}) and an urban zone with scarce road traffic (250 ng m^{-3}). Other authors have also previously reported average Pb levels in Seville: Fernández Espinosa et al. (2001) of 64 ng m^{-3} in spring 1996, Fernández et al. (2000) of 44 ng m^{-3} in 1993 and Usero et al. (1988) of 680 ng m^{-3} in 1984–1985, being this last high level associated to the use of leaded fuel to feed vehicles.

Zinc is released to atmosphere in the area of Seville by the production of pig iron and glass manufacture (see Fig. 1), with 8.0 and 2.15 tons in year 2007 (from E-PRTR database; the closest data to our sampling conditions). Also, it could be released from tires due to the friction and heating and it is also used as pesticide component (Ramadan et al., 2000). Thurston and Spengler (1985) have also indicated that refuse incineration

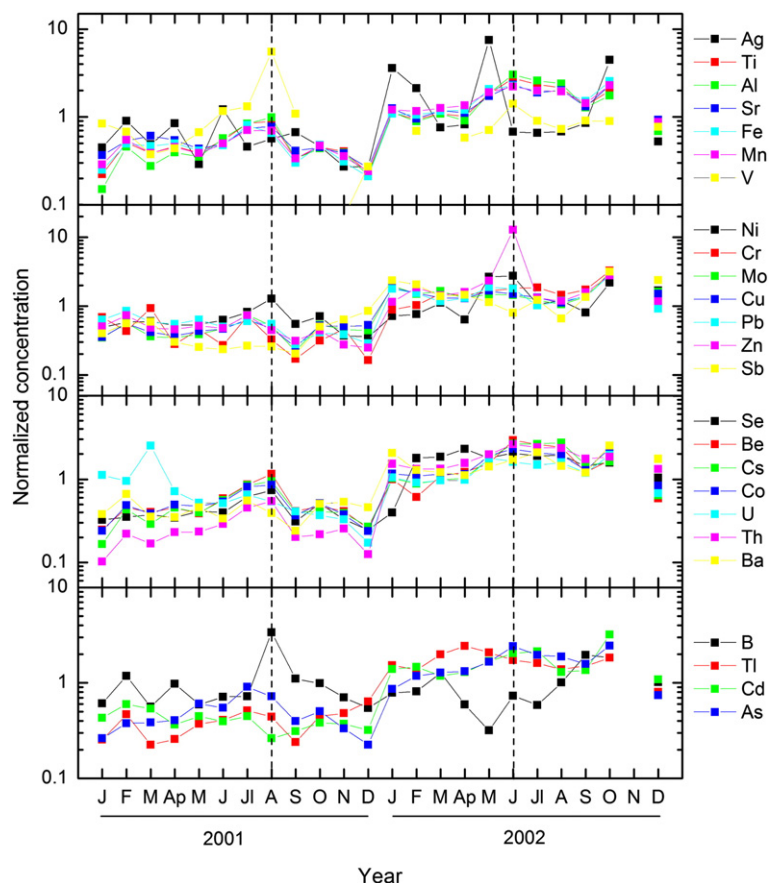


Fig. 3. Normalized monthly concentrations (depicted from volumetric concentrations) for 25 elements in TSP for years 2001 and 2002. Values for each element have been normalized to its arithmetic mean over the two year period (in ng m^{-3} basis).

constitutes another source for this element. All those possible sources made the Zn annual mean values reach 142 and 63 ng m^{-3} for 2001 and 2002, respectively. Similar levels have been reported in Cartagena and Zaragoza (Spain) (López et al., 2005; Moreno-Grau et al., 2000), Huelva (Querol et al., 2002), Santa Cruz de Tenerife (Alastuey et al., 2005) and in Seville in earlier times (53 ng m^{-3} in 1993 and 340 ng m^{-3} in 1984–1985) (Fernández et al., 2000; Usero et al., 1988).

Cadmium is emitted by both natural and anthropogenic sources. Airborne Cd originates mainly from anthropogenic processes such as non-ferrous metal production, mining and refining zinc and lead ores, combustion of fossil fuels, and operation of waste incinerators and power plants (Mutlu et al., 2012). Industrial sources of Cd in the area of Seville accounted for the emission to the atmosphere of 69 kg of Cd during 2007, and 279 kg in Huelva (from E-PRTR database). The main natural sources of airborne Cd are terrestrial dust, wildfires, and volcanic activity (Hieu and Lee, 2010). Annual mean and maximum Cd levels measured in Seville (0.56 and 1.11 ng m^{-3} for 2001 and 0.33 and 0.51 ng m^{-3} for 2002, respectively) were within the range of 0.1–20 ng m^{-3} given by WHO (2005). Those levels are lower than 5.45 ng m^{-3} reported by Moreno-Grau et al. (2000) in Cartagena (Spain) in an urban area with low road traffic, agrees with results given by Fernández Espinosa et al. (2001) in Seville for samples collected in spring 1996 and are lower than reported by Usero et al. (1988) and Fernández

et al. (2000) also in Seville (3.3 ng m^{-3} in 1984–1985 and 2 ng m^{-3} in 1993, respectively). Mean and maximum values in Huelva were also reported by Querol et al. (2002) and Sánchez de la Campa et al. (2007), being 1 and 4 ng m^{-3} for years 1999–2001 and 0.3 and 0.6 ng m^{-3} for years 2001–2002, below the EU standard target value of 5 ng m^{-3} (Air Quality Directive, 2004/107).

Vanadium is mainly related with oil combustion, and from E-PRTR database there are not atmospheric releases linked to industrial activities neither in the area of Seville nor in Huelva. It showed mean annual values of 10 and 5.7 ng m^{-3} for years 2001 and 2002, respectively, below the range of 50–200 ng m^{-3} given by WHO (2005), in agreement with levels reported by Querol et al. (2002) and Sánchez de la Campa et al. (2007) in the city of Huelva (15 ng m^{-3} in 1999–2001 and 7 ng m^{-3} in 2001–2002) and by Fernández et al. (2000) in Seville (5.9 ng m^{-3} in 1996), and lower than reported by Usero et al. (1988) in Seville in 1984–1985 (38 ng m^{-3}). Manganese can be considered as a trace crustal component (Querol et al., 2002), although it is also related to industrial processes and brake-drum abrasion (Harrison et al., 1996), although not reported in E-PRTR database for this area. It was detected at annual mean values of 34 and 19 ng m^{-3} for 2001 and 2002, respectively. Mean values for both elements are in agreement with values reported by Usero et al. (1988), Fernández et al. (2000) and Fernández Espinosa et al. (2001) also in Seville (20 ng m^{-3} in

1984–1985, 8.2 ng m⁻³ in 1993 and 16.5 ng m⁻³ in 1996, respectively), with levels reported by Querol et al. (2002) and Sánchez de la Campa et al. (2007) in Huelva in the period 1999–2002, and were within the range of 10–70 ng m⁻³ given by WHO (2005).

Concerning Ni, this element is mainly associated with fossil fuel use, oil burning and emissions from industrial sources (Quiterio et al., 2004). Industrial sources of Ni in the area of Seville emitted to the atmosphere 297 kg of Cd during 2007, and 4.0 tons in Huelva (from E-PRTR database). It can also be released from vehicle exhaust as it is used as an additive in fuels, though it was at low concentrations (3.8 and 3.5 ng m⁻³ for 2001 and 2002, respectively) in the atmosphere of Seville, well below the target value of 20 ng m⁻³ given by Air Quality Directive, 2004/107 and in agreement with levels in Huelva (5 ng m⁻³ in 1999–2001 and 4 ng m⁻³ in 2001–2002) reported by Querol et al. (2002) and Sánchez de la Campa et al. (2007). Previous levels in Seville were also reported by Usero et al. (1988), Fernández et al. (2000) and Fernández-Espinosa et al. (2001) (26 ng m⁻³, 35 ng m⁻³ and 3.3 ng m⁻³ in 1984–1985, 1993 and 1996 respectively). Copper is usually associated with industrial areas, diesel engines and wearing of brake vehicles (Swietlicki et al., 1996). From E-PRTR database there are not atmospheric releases linked to industrial activities in the area of Seville, although they are quite noticeable in Huelva, with more than 13 tons released during 2007. This trace element, one of the heavy metals characterized by its toxicity, showed annual mean values of 26.3 and 16.5 ng m⁻³ for 2001 and 2002, respectively, below the mean levels determined in Huelva (210 ng m⁻³ and 50 ng m⁻³) by Querol et al. (2002) and Sánchez de la Campa et al. (2007) and associated to the major industrial emissions in the Ria of Huelva. Previous levels in Seville were 21.5 ng m⁻³ (Fernández et al., 2000) and 26.7 ng m⁻³ (Fernández-Espinosa et al., 2001).

Arsenic is a toxic element for human health and is considered a carcinogen. It is released to the atmosphere from the smelting of metals, the combustion of fuels and the use of pesticides (Sánchez-Rodas et al., 2007). Industrial sources of As in the area of Seville accounted for the emission to the atmosphere of 29.5 kg during 2007, and 1.86 tons in Huelva (from E-PRTR database). Its annual mean and maxima concentrations for both years (1.5 and 3.7 ng m⁻³ in 2001 and 0.9 and 1.7 ng m⁻³ in 2002) were within the range of 1–30 ng m⁻³ given by WHO (2005) and by other EC standard, such as 6 ng m⁻³ for heavy metals (Air Quality Directive, 2004/107). The As levels measured can be considered high when compared with the levels referenced by Air Quality Directive, 2004/107 in Europe, which usually do not exceed the 1.5 ng m⁻³. However, these levels meet the requirements of Directive 2004/107/CE concerning the annual As target value of 6 ng m⁻³, which had to be met in January 2013.

Regarding Ba, it has also been proposed as tracer of unleaded fuel and diesel oil-powered motor vehicle emissions (Monaci et al., 2000), and it was detected at an annual mean concentrations of 33.5 and 19.7 ng m⁻³ for 2001 and 2002, respectively, in agreement with values reported in Huelva in 1999–2001 (35 ng m⁻³, Querol et al., 2002) and in 2001–2002 (23 ng m⁻³, Sánchez de la Campa et al., 2007).

A summarized comparison of concentrations for selected elements measured in this work and in previous studies in Seville (Fernández et al., 2000; Fernández Espinosa et al., 2001) and Huelva (Querol et al., 2002; Sánchez de la Campa et al., 2007) is given in Table 3 (Supplementary Electronic Material).

Atmospheric releases of heavy metals (As, Ni, Zn, Cd and Pb) from the industries nearby Seville for year 2007 are given in Table 5 (also as Supplementary Electronic Material), as extracted from E-PRTR database.

3.3. Enrichment factors

The contribution of anthropogenic emissions to atmospheric elemental levels was calculated using the enrichment factor (EF). This calculation helps to determine whether a certain element has additional or anthropogenic sources other than its major natural sources (López et al., 2005). The advantage of this method is the reduced uncertainty in the interpretation of absolute concentrations (affected by factors such as wind speed and direction, rainfall, distance from the source, etc.) (Usero and Gracia, 1987). Despite the fact that there is no rule for the choice of the reference material, Si, Al (Chatterjee et al., 2007) and Fe (Yaroshevsky, 2006; Lee and Hieu, 2011) are the most common elements used for this purpose. In this work Fe has been used as reference for each element, assuming minor contributions of pollutant Fe and the upper continental crustal composition given by Taylor and McLennan (1985). The EF of an element X in an aerosol sample is defined as:

$$EF_{\text{crust}} \equiv (X/R)_{\text{air}} / (X/R)_{\text{crust}} \quad (1)$$

where R is the reference element (Fe). If the EF is < 1, the element is depleted in the environment and crustal sources are predominant. If enrichment factor is > 1, the element is relatively enriched in the environment. In general EF > 5 indicates that a large fraction of the element can be attributed to non-crustal or anthropogenic sources (Wu et al., 2007).

Annual mean results obtained for years 2001 and 2002 are depicted in Fig. 4, where gray colored areas are delimited by monthly maxima and minima EF's of every element and the lines contained inside of those areas represent the annual average EF. The sequence of EF in Seville was: Se

As it can be seen the EF of almost all elements are very similar for both years, excepting for B and U, being their EF values for 2002 three and two times higher than for 2001 respectively, and Th, being its EF value in 2002 two times lower than in 2001. When monthly EFs for year 2001 (25 elements times 11 months, excluding November) were plotted versus the same EFs for year 2002, a high correlation between them was found (Fig. 5), which suggests that there is no annual or monthly variability in their origins.

Selenium, Sb, Cd, Zn and Pb, being all elements with a toxic character showed the highest EF, with values for Se, Sb and Cd in the range of 100–1000 and for Zn and Pb close to 100. For example, despite the already non-utilization of Pb in gasoline, EF of Pb still remained high. Other high EF values for Pb and Zn were previously reported in the Mediterranean coast of Israel (Herut et al., 2001), Thessalonica (Greece) (Manoli et al., 2002), Zaragoza (Spain) (López et al., 2005) and the “Campo de Gibraltar” area, also in Spain (Usero and Gracia, 1987). Copper, associated with metal emissions in industry and with road traffic in urban areas, was also one of the enriched elements.

Arsenic and Mo showed values in the range of 10–100, suggesting that those elements also seemed to be enriched with noncrustal sources but to a lesser extend. Lower EF values (in the range of 1–10) were obtained for B, V, Cr, Mn, Co, Ni, Sr, Cs, Ba, Tl,

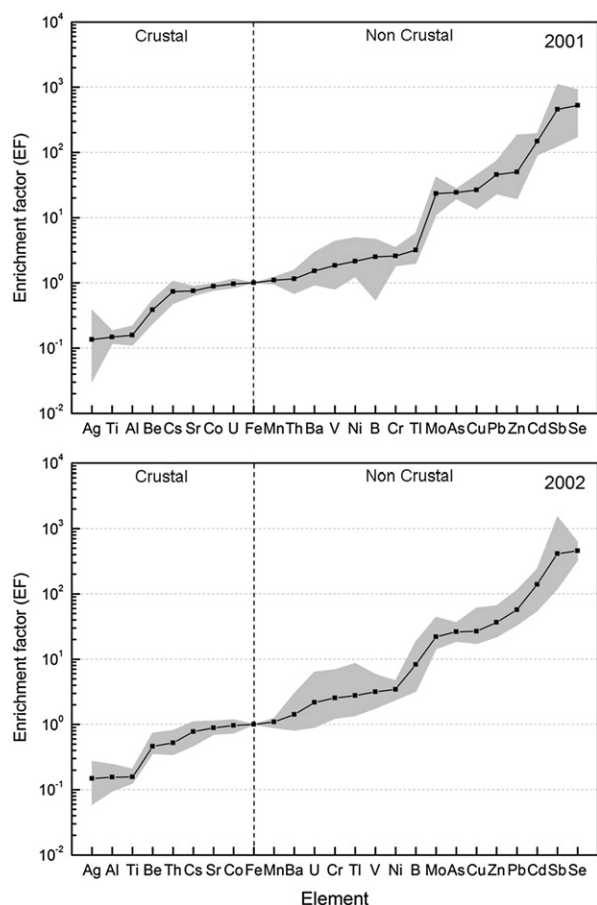


Fig. 4. Enrichment factor values using the element's concentrations in Seville for years 2001 (up) and 2002 (down) and Fe as reference element.

Th and U, showing that those elements are mainly originated from crustal source. Similar EF values for Ba, Ni, Mn, Sr, Ca and Co were reported by López et al. (2005) in Zaragoza (Spain) and for Mn and Cr by Herut et al. (2001) in European coastal sites.

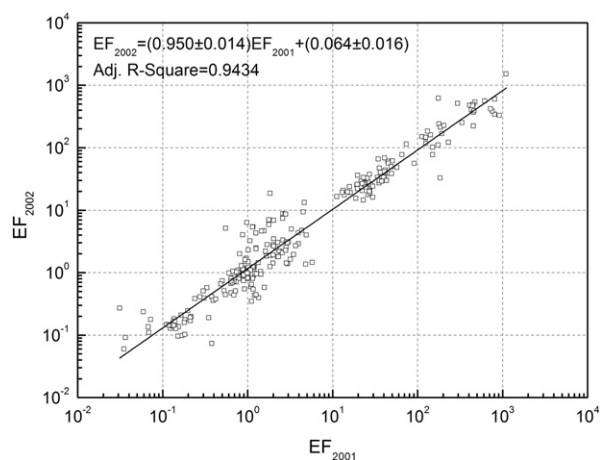


Fig. 5. Correlation between monthly EF for the different elements in 2001 and 2002 in Seville.

Other elements with negligible contribution of anthropogenic sources were Be, Al, Ti and Ag, suggesting that crustal soil, resuspended soil and marine aerosols are the dominant sources for those elements. Similar deductions were obtained by Wu et al. (1994) for the Al concentrations over the Chesapeake Bay (USA) and López et al. (2005) for Al concentration over Zaragoza (Spain).

It should be noted that the elements of anthropogenic origin such as Zn, Pb, Cd, etc., also present high correlation coefficients, since they originate from similar sources (e.g. industrial activities and traffic origin). They also agree well with the group of elements with very high EF, which indicates different grades of enrichment due to anthropogenic sources. These findings are consistent with the previously indicated about the different anthropogenic sources of these elements (vehicles, incinerators, etc.). As an example, the positive correlation found between Pb, Cd and Zn for both years 2001 and 2002 is depicted in Fig. 6, which can be attributed to an association between heavy metals for an urban area far from a direct industrial contribution (Moreno-Grau et al., 2000). Table 4 (given as Supplementary Electronic Material) shows a Pearson correlation coefficient matrix for all elements in the air filter samples (depicted from volumetric concentrations) combining both years 2001 and 2002 with TSP, and excluding the data from November 2001 because almost all of them were below the MDL.

As summary, some of the elements with high EF values are associated with known industrial emissions (E-PRTR database) or they have been associated elsewhere with other non-industrial anthropogenic activities. A comparative analysis against similar data from the nearby industrial city of Huelva (next subsection) will be helpful to improve our insight about their respective origin.

3.4. An intercomparison study with the nearby industrialized city of Huelva

As mentioned above, Seville is around 90 km away from the city of Huelva, a highly industrialized city located in the south western end of the Andalusia autonomous region (shown in Fig. 1). This area suffered an extensive industrialisation process in the 1960s, when large chemical and petrochemical industries were set up. At the moment of the sampling campaign the major industrial settlements surrounded the city of Huelva

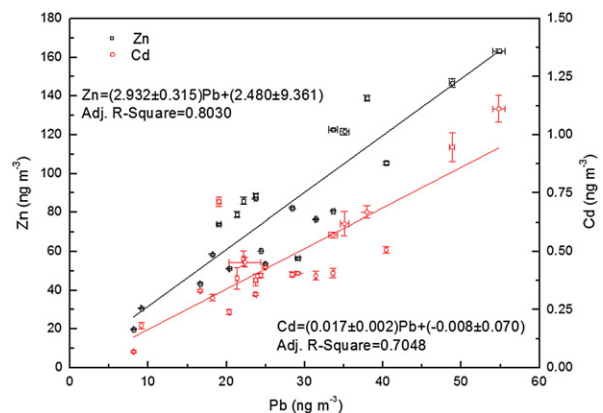


Fig. 6. Zinc and Cd concentrations versus Pb concentration, as determined by ICP-MS, in the air of Seville for the two studied years.

were (Querol et al., 2002): phosphoric acid based industry, metallurgical and petrochemical activities, production of TiO₂ pigments, production of chlorine and sodium hydroxide and cellulose paste from wood.

The wind direction in this region is dominated by three directional components (NE–ENE, NW–NNW and SSW–W). The air masses may then transport the pollutants emitted in the area of Huelva towards the NE, direction where Seville is located, which renders this area vulnerable to possible impacts of emission plumes. To test this hypothesis, dispersion and deposition analyses were performed using the National Oceanic and Atmosphere Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) atmospheric transport/dispersion model, together with meteorological data spanning the relevant sampling periods. The model has been designed to support a wide range of simulations related to the atmospheric transport and dispersion of pollutants and hazardous materials to the Earth's surface, and it is used to track and forecast the releases of various substances to the atmosphere including radioactive materials, volcanic ash and wildfire smoke (Draxler and Rolph, 2014; Rolph, 2014). The HYSPPLIT atmospheric transport/dispersion model shows an aerial view of the distribution of pollutants starting at a particular sampling point and date.

The dispersion of a pollutant is calculated by assuming particle dispersion: a fixed number of particles are advected about the model domain by the mean wind field and spread by a turbulent component. The model's default configuration assumes a 3-dimensional particle distribution (horizontal and vertical). We have reconstructed the transport/dispersion of pollutants starting in Huelva in days with SW wind blowing and the modeling results confirm that for those cases air pollutants can reach Seville in the course of around 6 hours. One of those simulations starting in Huelva at August 2nd, 2001 is shown in Fig. 7. It is worth to note that this date extends with a Saharan

dust outbreak over the study area. From this figure it is clear that any local atmospheric emission from Huelva reaching Seville would cause in the latter concentrations a factor ten lower than those in the origin due to atmospheric dilution.

We have calculated the mean concentration (ng m⁻³) of all elements studied in this work between July 2001 and June 2002 and compared with those data from Sánchez de la Campa et al. (2007) corresponding to Huelva city in the same period of time. When excluding those of crustal origin we found a linear correlation among them ($r^2 = 0.8423$) as shown in Fig. 8. The slope of this linear correlation (i.e. the ratio $C_{Seville}/C_{Huelva}$) is around 1 and not 0.1 as expected if concentrations at Huelva were representative of the near-field conditions.

Any atmospheric dispersion model has to include the effect of diffusion, which dilutes the concentration of the elements in air volumes larger every time. We would expect, in the case of continuous emissions in Huelva, that the mean concentrations measured there and in its surrounding were at least one or two orders of magnitude higher than those measured in Seville, as expected from Fig. 7. Nevertheless, concentrations are similar (as shown from the slope in Fig. 8).

Atmospheric dispersion is intrinsically a 3-D process. Taking into account the relative emplacement of the sampling stations and the main emission sources shown in Sánchez de la Campa et al. (2007), the station at Huelva is upstream of the dominant W–E winds, while the more distant stations at Paterna and Trigueros can receive plumes transported by winds blowing from SW (secondary peak in the wind rose). Thus, in the case of Cu, emitted to the atmosphere by several tons per year in the nearby Atlantic Cooper factory, in Huelva city, mean annual concentrations in aerosols measured at Huelva were only 30% higher than in Paterna stations, while this last registered the highest peak value.

Fig. 9 shows the comparison between EF in Seville and Huelva for the period July 2001–June 2002. For all elements

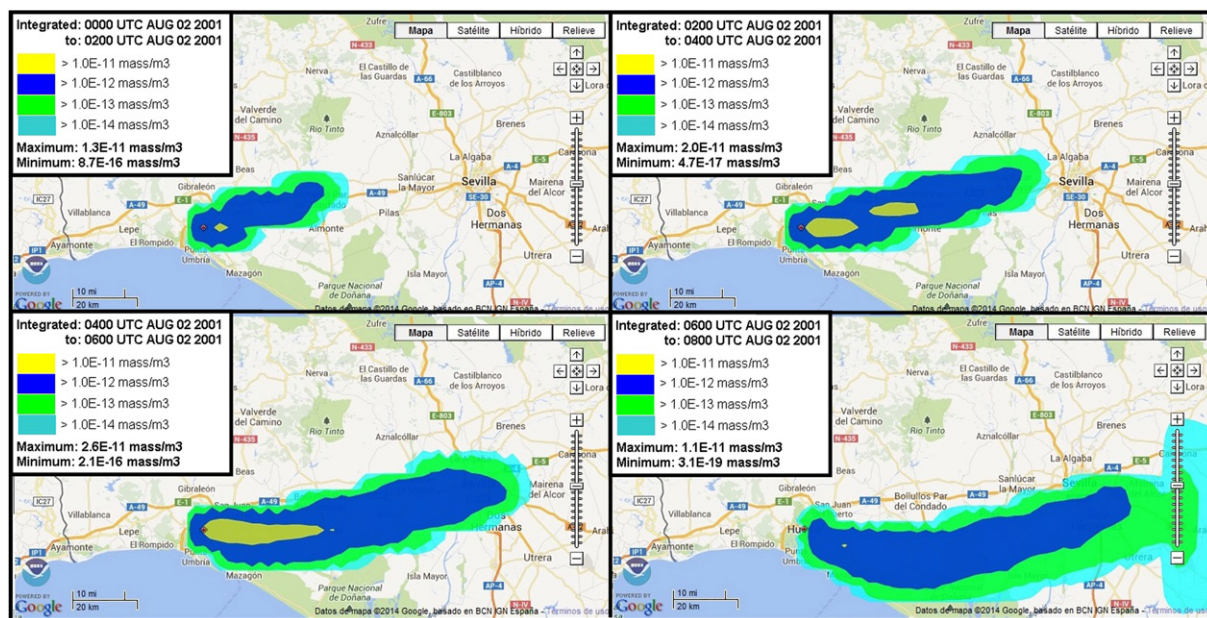


Fig. 7. NOAA HYSPLIT examples of transport/dispersion of pollutants originating at Huelva in August, 2nd 2001. Note that the model is computed at 2-h intervals spanning a 8-h period starting at 00:00 UTC on the date given.

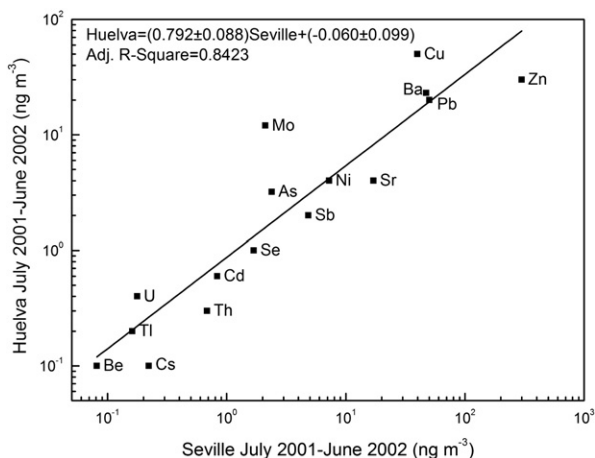


Fig. 8. Correlation among concentrations (ng m^{-3}) of anthropogenic elements in Huelva and Seville in the period July 2001–June 2002. Data from Huelva extracted from Sánchez de la Campa et al. (2007).

except Zn those values are higher in Huelva than in Seville. Anyway, interpretation of Fig. 9 is a complex task. For a set of elements, namely Cu, As and Ni, the local atmospheric emissions in Huelva (from E-PRTR database) are more than one order of magnitude higher than those from Seville, and by a factor 4 for Cd and Pb. To our opinion, the emplacement of the sampling station at Huelva, upstream of the main winds, makes this not to be a representative of the maximum concentrations in the near-field. If we also take into account the dilution by atmospheric dispersion and the local sources at Seville, the concentrations measured at both sites are of the same order.

Thus, values of both EF in Seville and Huelva also follow the same trend with some exceptions. Uranium is an interesting case: although this is assumed to be a crustal element (Sánchez de la Campa et al., 2010), its EF in Huelva is around 10. Large industrial units based on the production of phosphoric acid and various phosphate products are located in the vicinity of Huelva, carried out by Fertiberia Huelva, FMC Foret, Rodhia Iberia S.A., using for this purpose phosphate rocks. Those rocks have relatively high ^{238}U concentrations (in the order of 1500 Bq kg^{-1})

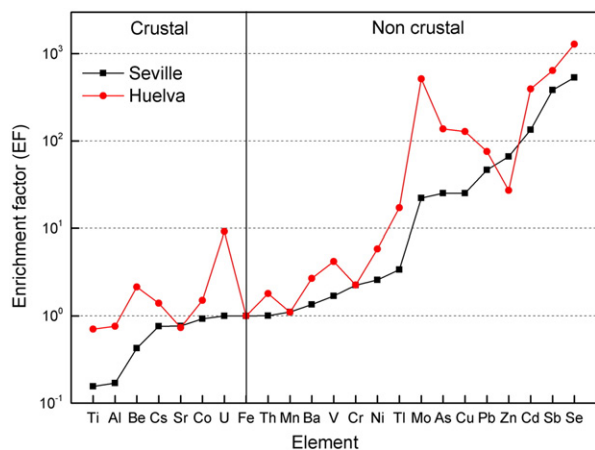


Fig. 9. Comparison between EFs in Huelva and Seville for the period July 2001–June 2002 using Fe as reference element. Data from Huelva extracted from Sánchez de la Campa et al. (2007).

and, during the industrial process, are crushed and chemically attacked with sulphuric acid, so it is reasonable to think that part of the dust produced during the crushing could be emitted to the atmosphere and increase the EF of this element.

Another interesting case is Mo, a sub-product in the copper production, with EF of 513 in Huelva and 22 in Seville. In Huelva, the very active metallurgical activities from the 1970s are nowadays reduced to copper production from imported sulphites by Atlantic Copper. This industrial activity would explain the EF found in Huelva for this element, although this element does not appear in the E-PRTR database.

Finally, Zinc is also another interesting case as is the only element measured in this study with EF higher in Seville (66) than in Huelva (22), which would mean that there is a strong local source of this element in Seville. We already referred to the local sources of cement and glass manufacture, although they are not well aligned with the main winds; and its concentrations can also be enhanced by road traffic (from tires due to the friction), about three times more intense in Seville than in Huelva. It is worth to note that our sampling station (on the roof of the building of the Faculty of Physics of the University of Seville) is located in an area with industrial and traffic influence (Fernández-Espinosa et al., 2004). Also worth to note the nearby “Ronda de Circunvalación SE-30” which permits to surround the city of Seville and the bridge “V Centenario,” the least with a mean traffic density in 2002 of around 87500 vehicles a day, so 7% of the total traffic density of Seville.

3.5. Temporal variations

The time series of the crustal elements (Al, Ti, Mn and Fe) show a pattern that follows the TSP evolution, with two clearly peaks in August 2001 and June 2002, related with Sahara dust intrusion events (figure not shown). As mentioned in previous sections, Seville suffered Saharan dust intrusions during August 2001 and June 2002, which would explain the high TSP levels obtained for those two months (Chamizo et al., 2010). Thus, the three previous months (May to July) of 2001 provide a baseline of $86 \pm 5 \mu\text{g m}^{-3}$, respectively (mean and standard deviation of mean). As the recorded monthly mean TSP value in August 2001 was $117 \mu\text{g m}^{-3}$, the estimated SDI-attributable contribution to TSP was $\sim 31 \mu\text{g m}^{-3}$. Pay et al. (2012) reported mean values of desert dust loads in southern Spain in summer between 9 and $15 \mu\text{g m}^{-3}$, although with few daily values over $100 \mu\text{g m}^{-3}$, which is consistent in magnitude with the present estimate. In June 2002, the measured TSP exceeded in $\sim 24 \mu\text{g m}^{-3}$ the baseline value from the three previous months ($68 \pm 1 \mu\text{g m}^{-3}$) of the same year, and this relative increment persisted during most of the summer period.

The SDI over the studied area occur when air masses over the Sahara desert move northward over the Iberian Peninsula. This results in an increase of TSP levels due to the high mineral load of the Saharan air masses (Alastuey et al., 2005). The low concentrations of mineral elements and TSP before the Saharan event are caused by the arrival of Atlantic air masses preceding the northward high particulate flow (Rodríguez et al., 2001). The sharp and rapid increases in particulate and mineral element levels are due to plume-like behavior of the Saharan intrusion. Furthermore, the rapid decrease in particulate and related elements levels recorded at the end of the events is frequently due to rainfall scavenging following most of the

events produced (Ávila et al., 1998). This pattern of high rainfall after the intrusion is clearly seen in 2001, with around 60 L m⁻² precipitation after the event.

Fig. 3 (depicted from volumetric concentrations) allows for a gross-view of the elemental fingerprint of Saharan dust by identifying those elements whose normalized concentrations noticeably deviate from the trend line in August 2001, when the most pronounced SDI took place. Although V has also a traffic origin, this is the element most clearly related to SDI in August 2001, and it is possible to distinguish a second peak associated to the SDI in June 2002. Pérez et al. (2008) also reported an increase in V concentrations in PM_{2.5} associated to SDI. When Fig. 3 is redrawn from specific concentrations (i.e. in µg g⁻¹; not shown) it is easier to identify a set of elements with a pronounced peak in August 2001. The ones with normalized concentrations greater than 2.0 were (in decreasing order): V, Cs, Th, Al and Ti.

4. Conclusions

The measurement (in a monthly basis) of TSP and the concentrations of 25 trace elements in high-volume air filter samples from Seville over a two-year period: (2001–2002) allowed for the following conclusions: (i) the mean TSP value for this period was 79.7 µg m⁻³ and showed a clear peak value in August 2001 of 117 µg m⁻³, with a SDI-attributable contribution of ~31 µg m⁻³; (ii) trace element concentrations were comparable to the values previously reported for Seville and below their respective maximum allowed levels (WHO and EU regulations); (iii) enrichment factors (EF) for Se, Sb, Zn and Pb were above 100, what revealed their anthropogenic sources; (iv) measured EF in Huelva for the same sampling period showed overall higher values than in Seville; (v) the temporal variations of crustal elements were similar and related with the TSP levels for both years; and finally (vi) temporal variability in specific concentrations (i.e. in µg g⁻¹) allowed to identify a set of elements with noticeable peak values in August 2001, and thus conforming the fingerprint of this SDI event: Al, Ti, Mn and Fe.

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References

Alastuey, A., Querol, X., Castillo, S., Escudero, M., Ávila, A., Cuevas, E., Torres, C., Romero, P.M., Expósito, F., García, O., Díaz, J.P., Van Dingenen, R., Putaud, J.P., 2005. Characterization of TSP and PM_{2.5} levels at Izaña and Sta. Cruz de Tenerife (Canary Island, Spain) during Saharan Dust Episode. *Atmos. Environ.* 39, 4715–4728.

Artiñano, B., Querol, X., Salvador, P., Rodríguez, S., Alonso, D.G., Alastuey, A., 2001. Assessment of airborne particulate levels in Spain in relation to the new EU directive. *Atmos. Environ.* 35, S43–S53.

Artiñano, B., Salvador, P., Alonso, D.G., Querol, X., Alastuey, A., 2003. Anthropogenic and natural influence on the PM₁₀ and PM_{2.5} aerosol in Madrid (Spain). *Analysis of high concentration episodes. Environ. Pollut.* 125, 456–465.

Ávila, A., Alarcón, M., Queralt, I., 1998. The chemical composition of dust transported in red rains—its contributions to the biochemical cycle of a holm oak forest in Catalonia (Spain). *Atmos. Environ.* 32, 179–191.

Baldasano, J.M., Valera, E., Jiménez, P., 2003. Air quality data from large cities. *Sci. Total Environ.* 307, 141–165.

Balk, T., Kukkonen, J., Karatzas, K., Bassoukos, T., Epitropou, V., 2010. A European open access chemical weather forecasting portal. *Atmos. Environ.* 45, 6917–6922.

Birnbaum, E.R., Trout, A.T., Boland, K.S., Sauer, N.N., 2006. Nitric acid dissolution of large mixed cellulose ester filters for beryllium determination. *Inorg. Chim. Acta* 361, 3069–3074.

Buzika, D., Gerboles, M., Borowiak, A., Tricherini, P., Passarella, R., Pedroni, V., 2006. Comparison of voltammetry and inductively coupled plasma-mass spectrometry for the determination of heavy metals in PM₁₀ airborne particulate matter. *Atmos. Environ.* 40, 4703–4710.

Caro-Gómez, E., Contreras-González, J., Jiménez-Beltrán, S., Nacharro-Ortega, P., 1998. Inventario de emisiones a la atmósfera de la Comunidad Autónoma Andaluza. In: Andalucía, Junta (Ed.), *Consejería de Medio Ambiente*. ISBN: 84-89650-62-4.

Castilho, I.N.B., Welz, B., Vale, M.G.R., de Andrade, J.D., Smichowski, P., Shaltout, A.A., Colares, L., Carasek, E., 2012. Comparison of three different sample preparation procedures for the determination of traffic-related elements in airborne particulate matter collected on glass fiber filters. *Talanta* 88, 689–695.

Chamizo, E., García-León, M., Enamorado, S.M., Jiménez-Ramos, M.C., Wacker, L., 2010. Measurement of plutonium isotopes, ²³⁹Pu and ²⁴⁰Pu, in air-filter samples from Seville (2001–2002). *Atmos. Environ.* 44, 1851–1858.

Chandra Mouli, P., Venkata Mohan, S., Balaran, V., Praveen Kumar, M., Jayarama Reddy, S., 2006. A study on trace elemental composition of atmospheric aerosols at a semi-arid urban site using ICP-MS technique. *Atmos. Environ.* 40, 136–146.

Chatterjee, M., Silva Filho, E.V., Sarkar, S.K., Sella, S.M., Bhattacharya, A., Satpathy, K.K., Prasad, M.V., Chakraborty, S., Bhattacharya, B.D., 2007. Distribution and possible source of trace elements in the sediment cores of a tropical macrotidal estuary and their ecotoxicological significance. *Environ. Int.* 33, 346–356.

Method 200. 8. Determination of trace elements in waters and wastes by inductively coupled plasma mass spectrometry. In: Creed, J.T., Brockhoff, C.A., Martin, T.D. (Eds.), *Revision 5.4, Environmental Monitoring Systems Laboratory, Office of Research and Development, U. S. Environmental Protection Agency*.

Draxler, R.R., Rolph, G.D., 2014. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://ready.arl.noaa.gov/HYSPLIT.php>). NOAA Air Resources Laboratory, Silver Spring, MD.

Dueñas, C., Fernández, M.C., Cañete, S., Carretero, J., Liger, E., 2002. Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean coast. *Sci. Total Environ.* 299, 97–113.

Enamorado, S., 2013. Aplicación de la Espectrometría de Masas con fuente de plasma (ICP-MS) al estudio de la transferencia a planta de radionúclidos y metales pesados. Resultados de ensayos efectuados en cultivos con suelos sódicos y enmiendas cálcicas de fosfatos. University of Seville (Tesis Doctoral).

Enamorado, S., Abril, J.M., Delgado, A., Más, J.L., Polvillo, O., Quintero, J.M., 2014. Implications for food safety of the uptake by tomato of 25 trace-elements from a phosphogypsum amended soil from SW Spain. *J. Hazard. Mater.* 266, 122–131.

Enamorado-Báez, S.M., Abril, J.M., Gómez-Guzmán, J.M., 2013. Determination of 25 trace element concentrations in biological reference materials by ICP-MS following different microwave-assisted acid digestion methods based on scaling masses of digested samples. *ISRN Anal. Chem.* 2013 (Article ID 851713).

Escudero, M., Querol, X., Ávila, A., Cuevas, E., 2007. Origin of the exceedances of the European daily PM limit value in regional background areas in Spain. *Atmos. Environ.* 41, 730–744.

European Commission, 1998. Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EC.

Fernández Espinosa, A.J., Ternero Rodríguez, M., Barragán de la Rosa, F.J., Jiménez Sánchez, J.C., 2001. Size distribution of metals in urban aerosols in Seville (Spain). *Atmos. Environ.* 35, 2595–2601.

Fernández Espinosa, A.J., Ternero Rodríguez, M., Fernández Álvarez, F., 2004. Source characterization of fine urban particles by multivariate analysis of trace metals speciation. *Atmos. Environ.* 38, 873–886.

Fernández, A.J., Ternero, M., Barragán, F.J., Jiménez, J.C., 2000. An approach to characterization of sources of urban airborne particles through heavy metal speciation. *Chemosphere Global Change Sci.* 2, 123–136.

- Finlayson-Pitts, B.J., Pitts, J.N., 2000. *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*. Academic Press, London (969 pp.).
- Gerboles, M., Buzuca, D., Brown, R.J.C., Yardley, R.E., Hanus-Illyar, A., Salfinger, M., Vallant, B., Adriaenssens, E., Claeys, N., Roekens, E., Segal, K., Jurasovic, J., Rychlik, S., Rabinak, E., Tanet, G., Passarella, R., Pedroni, V., Karlsson, V., Alleman, L., Pfeffer, U., Gladtko, D., Olschewski, A., O'Leary, B., O'Dwyer, M., Pockeviciute, D., Biel-Cwikowska, J., Tursic, J., 2011. Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM₁₀ in Europe. *Atmos. Environ.* 45, 3488–3499.
- Gómez-Guzmán, J.M., Enamorado-Báez, S.M., Pinto-Gómez, A.R., Abril-Hernández, J.M., López-Gutiérrez, J.M., García-León, M., 2012. Anthropogenic ¹²⁹I concentration and ¹²⁹I/¹²⁷I ratio in rainwater from Seville (Spain) in the period 2005–2008 as affected by airborne releases from Sellafeld and La Hague facilities. *Atmos. Environ.* 56, 26–32.
- Guieu, C., Loye-Pilot, M.-D., Ridame, C., Thomas, C., 2002. Chemical characterization of the Saharan dust end-member: some biogeochemical implications for the western Mediterranean Sea. *J. Geophys. Res.* 107, 2002. <http://dx.doi.org/10.1029/2001JD000582>.
- Harrison, R., Smith, D., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environ. Sci. Technol.* 30, 825–832.
- Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M.D., 2001. Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. *Atmos. Environ.* 35, 803–813.
- Hieu, N.T., Lee, B.K., 2010. Characteristics of particulate matter and metals in the ambient air from a residential area in the largest industrial city in Korea. *Atmos. Res.* 98, 526–537.
- Jacobson, M.Z., 2001. Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols. *J. Geophys. Res.* 106, 1551–1568.
- Kandler, K., Benker, N., Bunde, U., Cuevas, E., Ebert, M., Knippertz, P., Rodríguez, S., Schütz, L., Weinbruch, S., 2007. Chemical composition and complex refractive index of Saharan Mineral Dust at Izaña, Tenerife (Spain) derived by electron microscopy. *Atmos. Environ.* 41, 8058–8074.
- Karyampudi, V.M., Palm, S.P., Reagen, J.A., Fang, H., Grant, W.B., Hoff, R.M., Moulin, C., Pierce, H.F., Torres, O., Browell, E.V., Melfi, S.H., 1999. Validation of the Saharan dust plume conceptual model using lidar, Meteoros, and ECMWF data. *Bull. Am. Meteorol. Soc.* 80, 1045–1075.
- Kulkarni, P., Chellam, S., Flanagan, J.B., Jayanti, R.K.M., 2007. Microwave digestion ICP-MS for elemental analysis in ambient airborne fine particulate matter: rare earth elements and validation using a filter borne fine particle certified reference material. *Anal. Chim. Acta* 599, 170–176.
- Lee, B.K., Hieu, N.T., 2011. Seasonal variation and source of heavy elements in atmospheric aerosols in a residential area of Ulsan, Korea. *Aerosol Air Qual. Res.* 11, 679–688.
- López, J.M., Callén, M.S., Murillo, R., García, T., Navarro, M.V., de la Cruz, M.T., Mastral, A.M., 2005. Levels of selected metals in ambient air PM₁₀ in an urban site of Zaragoza (Spain). *Environ. Res.* 99, 58–67.
- Manoli, E., Voutsas, D., Samara, C., 2002. Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmos. Environ.* 36, 949–961.
- Monaci, F., Moni, F., Lanciotti, E., Grechi, D., Bargagli, R., 2000. Biomonitoring of airborne metals in urban environments: new tracers of vehicle emissions, in place of lead. *Environ. Pollut.* 107, 321–327.
- Moreno, T., Querol, X., Alastuey, A., Viana, M., Salvador, P., Sánchez de la Campa, A., Artiñano, B., de la Rosa, J., Gibbons, W., 2006. Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail. *Atmos. Environ.* 40, 6791–6803.
- Moreno-Grau, S., Pérez-Tornell, A., Bayo, J., Moreno, J., Angosto, J.M., Moreno-Clavel, J., 2000. Particulate matter and heavy elements in the atmospheric aerosol from Cartagena, Spain. *Atmos. Environ.* 34, 5161–5167.
- Mutlu, A., Lee, B.-K., Park, G.-H., Yu, B.-G., Lee, C.-H., 2012. Long-term concentrations of airborne cadmium in metropolitan cities in Korea and potential health risks. *Atmos. Environ.* 47, 164–173.
- Pay, M.T., Jiménez-Guerrero, P., Jorba, O., Basart, S., Querol, X., Pandolfi, M., Baldasano, J.M., 2012. Spatio-temporal variability of concentrations and speciation of particulate matter across Spain in the CALIOPE modelling system. *Atmos. Environ.* 46, 376–396.
- Pérez, L., Tobias, A., Querol, X., Künzli, N., Pey, J., Alastuey, A., Viana, M., Valero, N., González-Cabré, M., Sunyer, J., 2008. Coarse particles from Saharan dust and daily mortality. *Epidemiology* 19, 800–807.
- Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S.E., Gill, T.E., 2002. Environmental characterization of global sources of atmospheric soil dust identified with the nimbus 7 total ozone mapping spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.* 40. <http://dx.doi.org/10.1029/2000RF000095>.
- Air Quality Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to limit values for arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. *Off. J. Eur. Communities* N° L23 (26.01), 10 (Brussels).
- Air Quality Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 relating to ambient air quality and a cleaner atmosphere in Europe. *Off. J. Eur. Communities* N° L152 (11.06), 16 (Brussels).
- Querol, X., Alastuey, A., de la Rosa, J., Sánchez de la Campa, A., Plana, F., Ruiz, C., 2002. Source apportionment analysis of atmospheric particulates in an industrialized urban site in southwestern Spain. *Atmos. Environ.* 36, 3113–3125.
- Querol, X., Alastuey, A., Rodríguez, S., Viana, M.M., Artiñano, B., Salvador, P., Mantilla, E., García do Santos, S., Fernández Patier, R., de la Rosa, J., Sánchez de la Campa, A., Menéndez, M., Gil, J.J., 2004. Levels of particulate matter in rural, urban and industrial sites in Spain. *Science of Total Environment* 334, 359–376.
- Querol, X., Alastuey, A., Moreno, T., Viana, M.M., Castillo, S., Pey, J., Rodríguez, S., Artiñano, B., Salvador, P., Sánchez, M., García Dos Santos, S., Hércz Guerraleta, M.D., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Sanz, M.J., Palomo-Marín, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., Sánchez de la Campa, A., 2008. Spatial and temporal variations in airborne particulate matter (PM₁₀ and PM_{2.5}) across Spain 1999–2005. *Atmos. Environ.* 42, 3964–3979.
- Ramadan, Z., Song, X.-H., Hopke, P.K., 2000. Identification of sources of phoenix aerosol by positive matrix factorization. *J. Air Waste Manag. Assoc.* 50, 1308–1320.
- Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM₁₀ and TSP levels in Southern and Eastern Spain. *Atmos. Environ.* 35, 2433–2447.
- Rodríguez, S., Querol, X., Alastuey, A., Mantilla, E., 2002. Origin of high summer PM₁₀ and TSP concentrations at rural sites in Eastern Spain. *Atmos. Environ.* 36, 3101–3112.
- Rolph, G.D., 2014. Real-time Environmental Applications and Display sYstem (READY) Website (<http://ready.arl.noaa.gov>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Salvador, P., Artiñano, B., Querol, X., Alastuey, A., Costoya, M., 2007. Characterisation of local and external contributions of atmospheric particulate matter at a background coastal site. *Atmos. Environ.* 41, 1–17.
- Sánchez de la Campa, A.N., de la Rosa, J., Querol, X., Alastuey, A., Mantilla, E., 2007. Geochemistry and origin of PM10 in the Huelva region, southwestern Spain. *Environ. Res.* 103, 305–316.
- Sánchez-Rodas, D., Sánchez de la Campa, A.M., de la Rosa, J.D., Oliveira, V., Gómez-Ariza, J.L., Querol, X., Alastuey, A., 2007. Arsenic speciation of atmospheric particulate matter (PM₁₀) in an industrialised urban site in southwestern Spain. *Chemosphere* 66, 1485–1493.
- Sastre, J., Sahuquillo, A., Vidal, M., Rauret, G., 2002. Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Anal. Chim. Acta.* 462, 59–72.
- Shaltout, A.A., Bornan, J., Welz, B., Castilho, I.N.B., Al Ashkar, E.A., Gaita, S.M., 2014. Method development for the determination of Cd, Cu, Ni and Pb in PM_{2.5} particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Microchem. J.* 113, 4–9.
- Swietlicki, E., Puri, S., Hansson, H.-C., 1996. Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques. *Atmos. Environ.* 30, 2795–2809.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell, Oxford, U.K.
- Thurston, G.D., Spengler, J.D., 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmos. Environ.* 19, 9–25.
- Usero, J., Gracia, I., 1987. Atmospheric concentration of heavy metals and total suspended particulates in the “Campo de Gibraltar” region, Spain. *Int. J. Environ. Anal. Chem.* 30, 69–82.
- Usero, J., Rosa, F., Ternero, M., Gracia, I., 1988. A determination of the sources in the Seville urban aerosol. *Int. J. Environ. Anal. Chem.* 33, 233–244.
- WHO, 2005. *Air Quality Guidelines for Europe, Global Update 2005, Particulate matter, ozone, nitrogen dioxide and sulphur dioxide*. WHO Regional Office for Europe.
- WHO, 2006. *Europe Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide, Global Update 2005*. World Health Organization. Available at: http://www.euro.who.int/_data/assets/pdf_file/0005/78638/E90038.pdf.
- Wu, Z.Y., Han, M., Lin, Z.C., Ondov, J.M., 1994. Chesapeake Bay atmospheric deposition study, year 1: sources and dry deposition of selected elements in aerosol particles. *Atmos. Environ.* 28, 1471–1486.
- Wu, Y.S., Fang, G.C., Lee, W.J., Lee, J.F., Chang, C.C., Lee, C.Z., 2007. A review of atmospheric fine particulate matter and its associated trace metal pollutants in Asian countries during the period 1995–2005. *J. Hazard. Mater.* 143, 511–515.
- Yaroshevsky, A., 2006. Abundances of chemical elements in the Earth's crust. *Geochem. Int.* 44, 48–55.