



Temporary Variations and Sources of Trace Metal and Radionuclides in Atmospheric Aerosols of Málaga (Spain)

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Abstract The present study focuses on the simultaneous analysis of metallic species and radionuclide data from January 2009 to December 2011 in the dust deposited on filters in Málaga (Spain). Some metallic elements (Ca, Fe, K, Mg, Na, Zn, Pb, Cu, Ni) and radionuclides (^7Be and ^{210}Pb) have been determined by inductively coupled plasma-mass spectroscopy and gamma spectrometry, respectively. For this analysis, daily variation of PM_{10} mass concentration was additionally recorded at the nearest station belonging to the regional atmospheric pollution monitoring network. The comparison between ^{210}Pb , elemental lead, and PM_{10} mass concentration

reveals a different time variation for raining months, and an increase in the $^{210}\text{Pb}/\text{Pb}$ ratio indicates local sources of the particulate mass. Principal components analysis (PCA) applied to the datasets and calculation of enrichment factors relative to soil and seawater reveal that the atmospheric aerosol chemistry in this area of the Mediterranean is mostly influenced by crustal and marine sources rather than anthropogenic ones.

Keywords PM_{10} · Metals · Radionuclides · Aerosols · ICP-MS · Pollution

Highlights

- Time series of ^7Be , ^{210}Pb , and metals recorded at Malaga are analyzed over a 3-year period.
- Correlation analysis for this period shows poor interactions between radionuclides and metals
- African dust and marine origin could be the principal source of aerosol particles
- Anthropogenic emissions could be the third source of aerosols

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1 Introduction

Air pollution episodes happen in many places around the world and could result in severe health issues for humans. The chemical analysis of aerosols is fundamental to understand the relation between air quality and its health effects. Atmospheric particulate matter (PM) may be considered as a complex pollutant with dissimilar chemical composition, sources of origin, and formation mechanisms and, thereupon, with different impacts on human health and the environment (Richards 1997; Adamson et al. 2000).

The Directive 2008/50/EC established limit values for suspended particulate matter with an aerodynamic diameter less than $10\ \mu\text{m}$ (PM_{10}), being $40\ \mu\text{g m}^{-3}$ (PM_{10}) the annual daily value, and $50\ \mu\text{g m}^{-3}$ the daily value not to be exceeded for more than 35 days per year⁻¹.

Environmental contamination due to anthropogenic lead emissions has been a serious problem globally. The use of leaded gasoline, as well as industrial emissions and household waste incineration, has caused huge lead emissions to the atmosphere in the past.

Very limited studies have been conducted jointly to assess the seasonal cycle and long-term variability of radionuclides and metals in aerosols despite their relevance. Systematic measures of air quality are necessary in order to explore the relationships between different mix of pollutants and their principal sources. In this research, we investigate the occurrence and characteristics of

airborne metals and radionuclide concentrations in aerosols, and study their temporary variations, together with PM_{10} , in one of the main coastal Mediterranean cities of Spain which, apart from local emissions, may be influenced by advected aerosol from continental Europe and the Sahara Desert. This work could be used as an incentive to perform other studies in order to develop strategies that would control and diminish air pollution problems, and it would help to develop future oversight and more coordinated strategies amongst neighboring countries. The main aim of the research done is to identify emission sources for metals in atmospheric aerosols and to better understand their transport and deposition. The paper starts by briefly introducing the region of study and it is followed by a description of the different datasets. The results present an analysis of the annual cycle, inter-annual variability, and trends of metallic species, radionuclides, and PM_{10} . Based on this study, identification of possible sources of metals associated with atmospheric aerosols was carried out using principal component analysis (PCA) and enrichment factors.

2 Materials and Methods

2.1 The Study Area

Figure 1 shows the map of the area where the study was conducted from January 2009 to December 2011 and

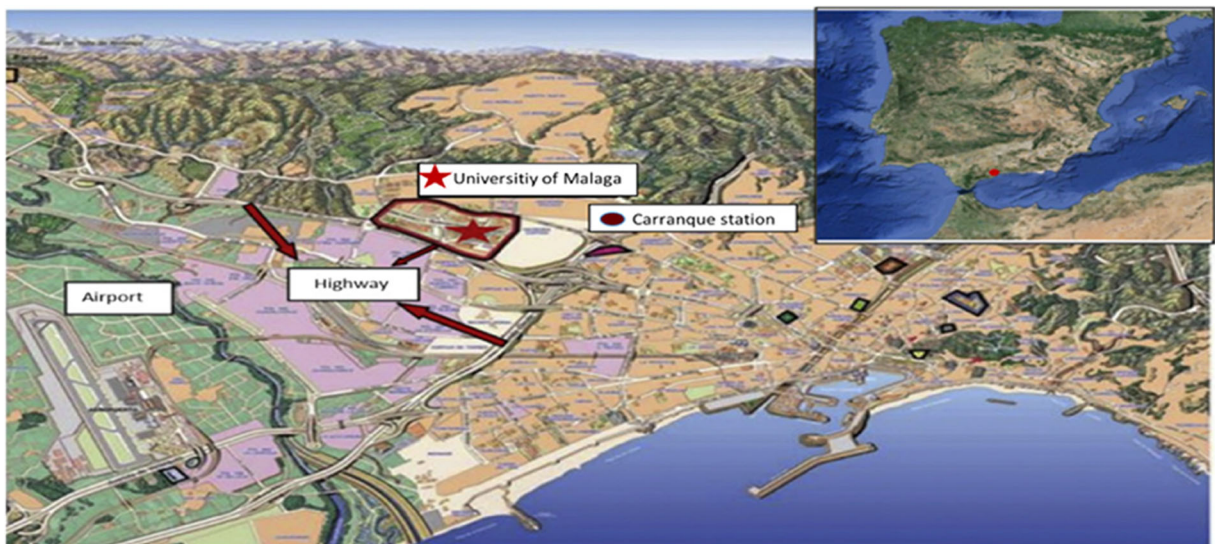


Fig. 1 Map with the location of the two sampling stations in the city of Málaga (SE Spain): the Laboratory of Environmental Radioactivity (University of Málaga) and the station belonging to the regional atmospheric pollution monitoring network

the location of the two sampling points in the city of Málaga (SE Spain). One of such points is based in the Laboratory of Environmental Radioactivity (University of Málaga) whereas the other sampling point is a nearby monitoring station (Carranque station) which belongs to the network of surveillance and control for atmospheric pollution of Andalusia. Málaga is located in the southern part of the Iberian Peninsula and is the major coastal city of the Andalusian Region, with a population of approximately 600,000 in its metropolitan area. This coastal city on the shores of the Western Mediterranean Sea is bordered to the north by a high mountain range and delimited to the south by Northern Africa. The climate in Málaga is moderate, with temperate to warm temperatures and a distinctly marked seasonal variation of precipitation.

2.2 Sampling and Analysis

Airborne particulate samples were weekly collected at the sampling station in the Campus of the University of Málaga, in the north-western outskirts of Málaga (36° 43' 40" N; 4° 28' 8" W). This sampling point is located approximately at 5 km from the coastline, near the airport, and surrounded by roads with traffic exhaust. On the flat roof of the Central Research Facilities (SCAI) building (University of Málaga), airborne particulate samples were collected at a height of 10 m above the ground onto G3 40 × 40 cm polypropylene filters using a high-volume sampler (ASS-500 station) with an air-flow rate of approximately 700 m³ h⁻¹. The deposited mass was determined by a gravimetric method; i.e., the aerosol particles' mass was calculated by subtracting the mass filter from the total mass after sampling and being desiccated to a constant weight.

Afterwards, each filter was folded and pressed to obtain a surface area of about 8 × 8 cm² (with the same geometry as the standard and blank filter) and stored 4 days before being counted. Gamma spectrometry measurements were performed to determine the ⁷Be and ²¹⁰Pb activity concentration of the samples using a coaxial-type germanium detector (Canberra Nuclear: Genie 2000). Gamma lines of 477.7 keV and 46.5 keV were used, respectively. Details of the low-background gamma-ray detection system used and the calibration of the resulting samples for gamma spectrometry have been previously described (Dueñas et al. 1999; Gordo et al. 2015a). The counting intervals ranged from

172,800 to 216,000 s. The concentrations were corrected for decay to the mid-collection period.

Filters were analyzed by ICP-MS in the SCAI of the University of Málaga. The analysis is quantitative multi-elemental (72 items) with detection limits in the order of magnitude of ng kg⁻¹. In order to ensure quality of the analytical results, background contamination of metals was accounted for by subtracting field blank values (unexposed filters blank) from the concentrations. Whenever a trial took place, the equipment was calibrated using standards which follow an identical procedure as samples do. Concentrations of chemical elements Ca, Fe, K, Mg, Na, Zn, Cu, Pb, and Ni in mg kg⁻¹ were measured. They were selected due to their diverse origin in the atmosphere (crustal, anthropogenic, marine...). Additional information on sample preparation, ICP-MS measurement, and an ANOVA test carried out to ensure the representativeness of the sample is given in Online Resource 1.

For the purposes of analysis and interpretation of our results, daily PM₁₀ levels were additionally recorded during the same study period from the nearest air quality station in Málaga belonging to the network of surveillance and control of the atmospheric pollution of Andalusia (Carranque station; 36° 43' 40" N; 4° 28' 8" W). This site is part of the Department for Environment of the Andalusian Government, and further details on the instrumentation and sampling procedures are available in De la Rosa et al. (2010). The concentrations of PM₁₀ were measured every 10 min through the use of two samplers working simultaneously: beta attenuation and gravimetric.

In order to identify the number of African outbreaks, we have applied a procedure based on (1) PM₁₀ levels compared with the limit values established by the EU directive (Directive 2008/50/EC) to determine the number of exceedances, and (2) air parcel backward trajectories computed for the event of exceedances in PM₁₀ levels to verify the origin of air masses.

2.3 Enrichment Factors and Source Assessment

Samples of soil and seawater were taken near our sampling points so as to calculate enrichment factors. Additional information on sampling, sample preparation, and ICP-MS measurement of seawater and soil samples can be found in Online Resource 2.

Enrichment factors (EF) have been used to identify the origin of the elements. To calculate these, we

compared the ratio of the element collected in the atmosphere or in precipitation with a reference material showing similar ratio, as it follows in Eqs. (1) and (2).

$$EF_{\text{seawater}} = [X/\text{Na}]_{\text{aerosol}}/[X/\text{Na}]_{\text{seawater}} \quad (1)$$

$$EF_{\text{soil}} = [X/\text{Ca}]_{\text{aerosol}}/[X/\text{Ca}]_{\text{soil}} \quad (2)$$

where X is to the concentration of the element of interest, $[X/\text{Na}]_{\text{seawater}}$ refers to the ratio from seawater composition, and $[X/\text{Ca}]_{\text{soil}}$ to the ratio from crustal composition (see Table 3).

In order to estimate the marine and crustal contributions to different species in aerosol, their respective sea salt fraction (SSF), crustal fraction (CF), and anthropogenic fraction (AF) were calculated using Eqs. (3) and (4), as described in Zhang et al. (2007).

$$\text{SSF} = 100 \cdot [X/\text{Na}]_{\text{seawater}}/[X/\text{Na}]_{\text{aerosol}} \quad (3)$$

$$\text{CF} = 100 \cdot [X/\text{Ca}]_{\text{soil}}/[X/\text{Ca}]_{\text{aerosol}} \quad (4)$$

3 Results and Discussion

3.1 Radionuclides

A total of 157 weekly collected polypropylene (PP) filters were analyzed in the period 2009–2011. ^7Be

and ^{210}Pb were detected in 100% and 96% of the filters, respectively. The results from individual measurements of these radionuclides were examined to derive the statistical estimates characterizing the distributions.

Figure 2 shows the box and whisker diagrams by season of the ^7Be and ^{210}Pb recorded activities, in addition to other statistics. January–March corresponds to winter, April–June to spring, July–September to summer, and October–December to autumn. The maximum values of ^7Be are principally registered in the spring months due to the contraction of the tropopause that takes place in mid-latitudes, thus producing an exchange of air between the troposphere and the stratosphere (Ioannidou et al. 2012; Gordo et al. 2015a). The ^{210}Pb concentrations show a seasonal variability, the highest ones occurring in summer. High temperatures in summer months favor a greater exhalation of radon due to the maximum emanation coefficient, which has a positive linear correlation with heating rate and specific surface (Zhang et al. 2019), while in winter, along with a lower amount of sun's heat, soils are frequently wet and, consequently, the emanation of radon decreases. In summer, this fact causes the accumulation of ^{210}Pb in the upper troposphere and lower stratosphere. During the humid months, the accumulated ^{210}Pb descends from the washing layers of the troposphere and is deposited through precipitation, which implies an increase in ^{210}Pb levels on rainwater, although sometimes this rule may not be applied (Daish et al. 2005). Finally, ^{210}Pb from aerosols is deposited

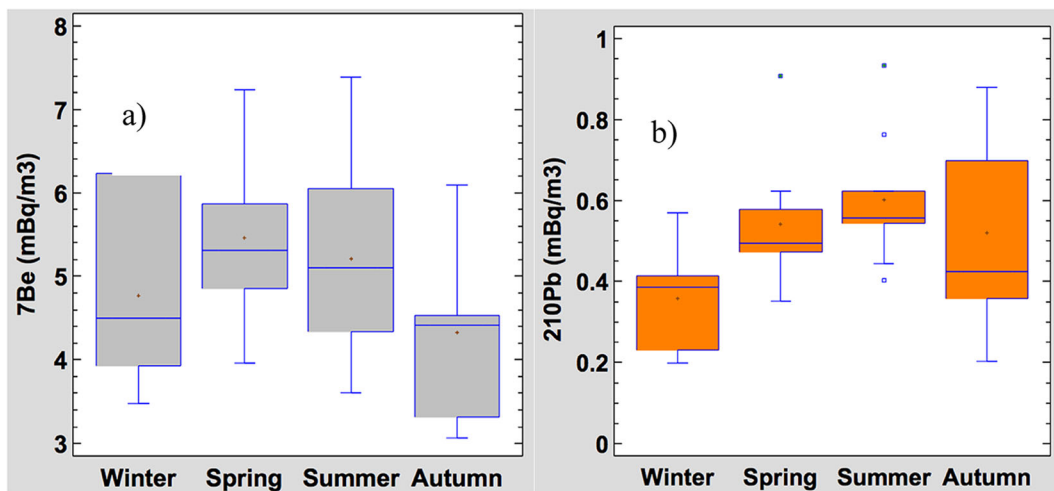


Fig. 2 Seasonal distribution of (a) ^7Be and (b) ^{210}Pb during 2009–2011. The vertical box shows the middle 50%, the median (horizontal line), and mean (cross). Outliers more than three

interquartile ranges below the lower quartile or above the upper quartile are shown as individual data points

in the earth's crust through the phenomena of either dry or wet precipitation.

3.2 PM₁₀

A total of 157,680 data records of PM₁₀ concentrations have been processed (1 record every 10 min) during 2009–2011. Additional data are given in Online Resource 3.

Dust is the most important natural aerosol over Europe. Episodes of Saharan dust transport are responsible for the highest PM₁₀ levels in Mediterranean cities (Fuzzi et al. 2015; Querol et al. 2009).

Daily concentration levels of PM₁₀ have been compared with the limit value (50 $\mu\text{g m}^{-3}$) in order to identify the exceedances of PM₁₀ in the time series of the air quality network. The seasons of the year presenting fewer episodes were autumn and winter, with 43 and 49 episodes, respectively, and that represented 14% and 16% of the total number of exceedances occurred during the years 2009 to 2011. The months of June, July, and August exhibited the highest number of days exceeding PM₁₀ limits with a total of 144 episodes during the 3 years of study. Exceedances of the daily maximum values in summer months represented a 47% of the total number of episodes. In spring, a total of 23% of the exceedances occurred during the study period.

The ratio $^{210}\text{Pb}/\text{PM}_{10}$ can be used to estimate sources of PM₁₀ (Brattich et al. 2016). It varies from less than 0.007 (February 2009) up to 0.02 mBq ^{210}Pb per μg of PM₁₀ during the month of September 2009. The $^{210}\text{Pb}/\text{PM}_{10}$ ratio reported in Brattich et al. (2016) is characterized by winter maximum and summer minimum, and it ranges from less than 0.005 to more than 0.040 mBq

^{210}Pb per μg of PM₁₀. In contrast, a seasonal behavior was not appreciated in our study, although the ratio $^{210}\text{Pb}/\text{PM}_{10}$ presented a high correlation with the amount of rainfall ($r = -0.51$). Figure 3 shows the monthly evolution of both parameters (rainfall and $^{210}\text{Pb}/\text{PM}_{10}$ ratio). In the raining months, an opposite behavior is observed between both variables ($r = -0.67$). This indicates that rain has a drag effect on atmospheric ^{210}Pb , although not to the same extent on PM₁₀. Dueñas et al. (2012) found a strong correlation between ^{210}Pb measured in rainwater and the amount of monthly collected rain ($r = 0.87$). Besides, the radionuclide ^{210}Pb is long-range transported. Thus, the decrease in the $^{210}\text{Pb}/\text{PM}_{10}$ ratio indicates the local sources of a particulate mass (Paatero et al. 2017). Additionally, the $^{210}\text{Pb}/\text{Pb}$ ratio could also offer potential knowledge to track Pb sources and transportation, as researched in by Yang and Appleby (2016).

3.3 Metals

The main statistics of the results obtained for the different metals analyzed over the 3 years of study are shown in Table 1. Determination of the elemental composition of the collected samples was successfully achieved by using ICP-MS. Related uncertainties were low, ranging from 2.6 for K up to 10% for Zn.

The data reveal the following order according to average concentrations: $\text{Ca} > \text{Na} > \text{Mg} > \text{Fe} > \text{K} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Pb}$. High standard deviations of averages are due to the variance of the measurements every week and the amount of data ($n = 157$), but the corresponding maximum and minimum values are lower. Shah et al.

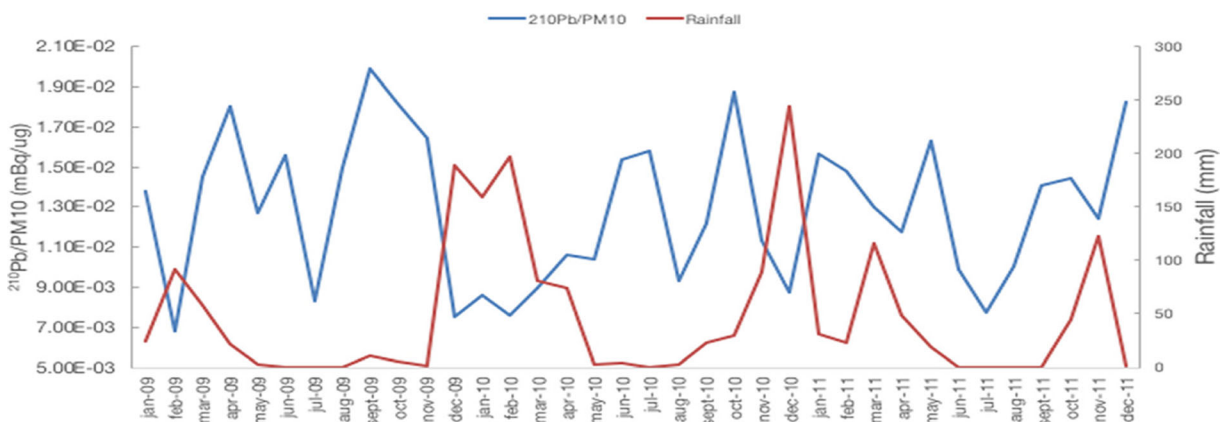


Fig. 3 Monthly evolution of rainfall and $^{210}\text{Pb}/\text{PM}_{10}$ ratio

Table 1 Main statistics of the chemical elements analyzed

	Maximum (mg kg ⁻¹)	Minimum (mg kg ⁻¹)	Average (mg kg ⁻¹)	Median (mg kg ⁻¹)	Standard deviation (mg kg ⁻¹)	Relative uncertainty (%)
Ca	21 ± 4	2.9 ± 0.8	10	10	3	3
Fe	7.2 ± 1.3	1.06 ± 0.01	3.0	2.7	1.2	2.9
K	3.0 ± 1.2	0.41 ± 0.06	1.6	1.5	0.5	2.6
Mg	6.8 ± 1.3	0.88 ± 0.06	3.1	2.8	1.2	3
Na	20 ± 5	0.11 ± 0.02	5	4	4	6
Zn	2.4 ± 0.3	(2.3 ± 0.7) · 10 ⁻²	0.2	0.1	0.3	10
Pb	(4.3 ± 0.1) · 10 ⁻²	(3 ± 1) · 10 ⁻³	0.02	0.01	0.03	3.2
Cu	0.4 ± 0.2	(1.2 ± 0.3) · 10 ⁻²	0.05	0.05	0.04	6.6
Ni	0.167 ± 0.003	(4.4 ± 1.3) · 10 ⁻³	0.03	0.02	0.02	7

(2012) and Fang et al. (2014) carried out a comparison of atmospheric metallic elements of total suspended concentrations at various sampling sites. The order of the elements recorded in our samples is similar to that reported therein. Figure 4 a shows the seasonal variation of the elements that appear in levels of traces (Zn, Pb, Cu, and Ni) and b for the major elements analyzed (Ca, Fe, K, Mg, and Na). All of them registered their minimum values in winter, perhaps due to the fact that the atmosphere is cleaner during this season. The maximum values were registered in summer for the major elements and also for Ni. In contrast, Cu and Zn showed their highest concentration in spring whereas the concentrations of Pb were constant during the year.

In order to explain the behavior of the determined elements, a principal component analysis (PCA), as well as an enrichment factor and source assessment methods, has been carried out to better elucidate factors governing the chemical composition of atmospheric aerosols. The results are presented in the following section.

3.4 Principal Component Analysis

Principal component analysis (PCA) was applied to the datasets in order to determine possible associations amongst the variables tested. The matrix of correlations can be seen in Table 2. PM₁₀ is significantly correlated with Fe ($r = 0.58$), K ($r = 0.57$), Ca ($r = 0.51$), Mg ($r = 0.43$), and Na ($r = 0.35$). The moderate correlation coefficients for the rest of the metals, amongst themselves as well as with other ones, indicate an anthropogenic mixed origin, as explained below.

During the present study, poor correlation was observed amongst the radionuclides considered and the major and trace elements analyzed, which indicates a dissimilar behavior. In fact, low values of the correlation coefficients are not necessarily due to the lack of correlation but may suggest different mechanisms promoting different covariance in the atmosphere. Positive correlations however exist between most of the elemental pairs in aerosol samples, suggesting an identical source or co-contamination.

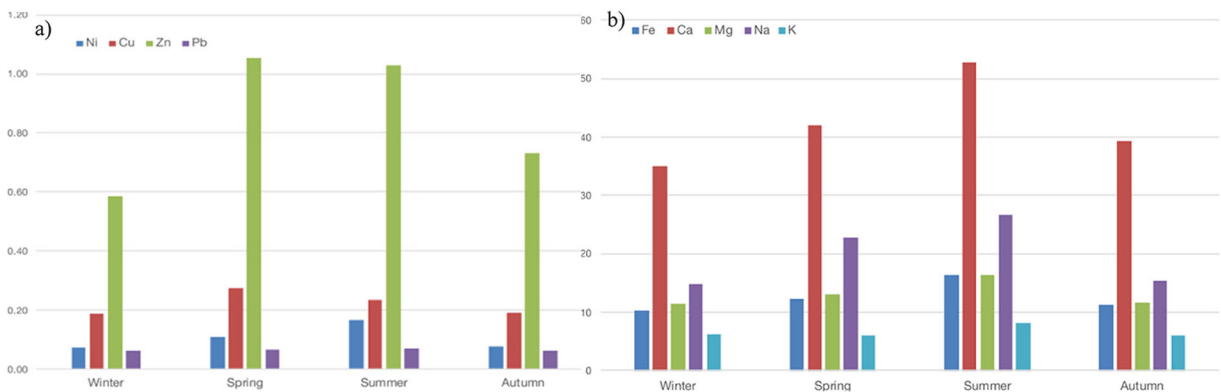
**Fig. 4** Seasonal variations of the concentrations (in mg kg⁻¹) of (a) trace metals and (b) major elements studied in the period of 2009 to 2011

Table 2 Matrix of correlations of the different variables

	⁷ Be	²¹⁰ Pb	PM ₁₀	Ni	Cu	Zn	Fe	Pb	Ca	Mg	Na	K	Intru
⁷ Be	1.0												
²¹⁰ Pb	0.20	1.0											
PM ₁₀	0.30	0.54	1.0										
Ni	0.11	0.01	0.17	1.0									
Cu	0.08	0.05	0.19	0.21	1.0								
Zn	0.04	-0.04	0.04	0.38	0.39	1.0							
Fe	0.34	0.36	0.58	0.31	0.14	0.09	1.0						
Pb	0.07	0.19	0.27	0.15	0.37	0.28	0.30	1.0					
Ca	0.27	0.33	0.51	0.28	0.10	0.07	0.90	0.26	1.0				
Mg	0.34	0.22	0.43	0.25	0.09	0.09	0.83	0.28	0.90	1.0			
Na	0.27	0.04	0.35	0.25	0.16	0.17	0.41	0.28	0.44	0.60	1.0		
K	0.27	0.33	0.57	0.27	0.11	0.04	0.84	0.23	0.80	0.75	0.46	1.0	
Intrus.	0.27	0.34	0.65	0.13	0.19	0.07	0.56	0.29	0.42	0.42	0.46	0.52	1.0

Varimax (variance maximizing) rotation has been applied to the datasets (the results are given in Online Resource 4) and shows the rotated component matrix that has allowed us to distinguish 3 factors or sources (PCs) that together explain 64% of the total variance of the sample.

- PC1 factor: Components identified in this factor are Ca, Fe, Mg, K, and Na with loading values higher than 0.64, and it represents the 41% of the total variance. Ca, Fe, Mg, and K are predominantly crustal elements, showing good correlations

amongst them. Sodium in turn has a different source, being of marine origin

Figure 5 simultaneously shows the monthly temporal evolution of elements with crustal and marine origin over the 3 years of study. Monthly temporal evolution of Fe, Mg, K, and Ca is similar, registering the highest levels in the months of July and August and the minimum in November and December. Likewise, maximum values of Na were obtained in the months of July and August, and minimum ones in January and November.

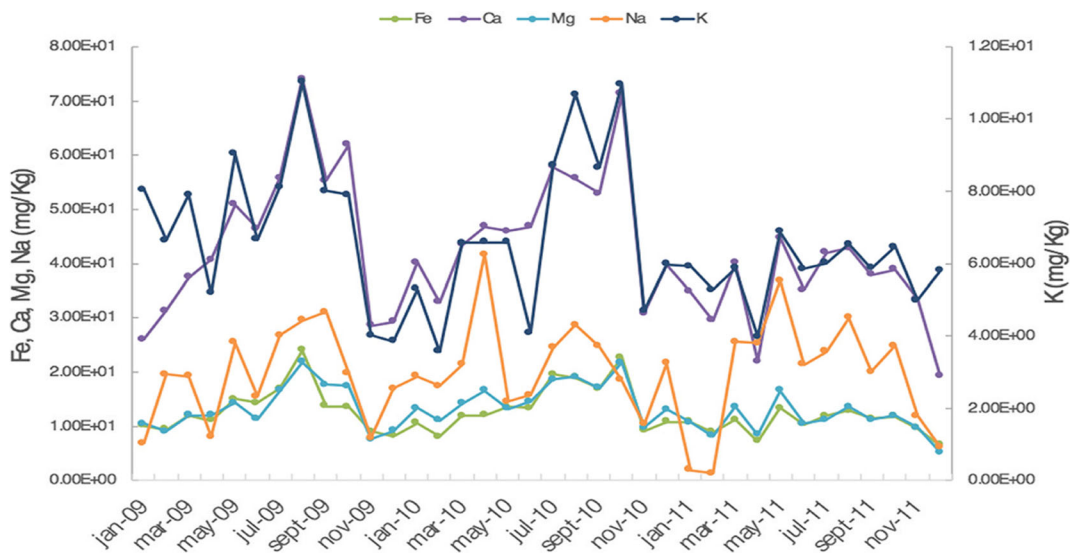


Fig. 5 Temporal evolution of metals with crustal and marine origin

This component is therefore related to the prevailing breeze regime in Malaga with winds that go from sea to land and from land to sea. Hence, both the marine and the crustal components are within the same factor.

- PC2 factor: 13% of the total variance of the variables studied is explained by this component. This factor mainly encompassed ^{210}Pb along with PM_{10} levels and a number of African intrusions with high coefficients; ^7Be presents its higher value in this component; thus, it contributes as well—but slightly—to this factor. These radionuclides (^7Be and ^{210}Pb) can be considered good radiotracers of air masses with a continental origin, and their concentrations increase when intrusion of dust from Africa is recorded, also raising PM_{10} levels. At heights below 3000 m a.g.l., ^{210}Pb is a good radiotracer, but as described in Gordo et al. (2015b), ^7Be is also closely linked to levels of PM_{10} due to the masses of African origin traveling at heights exceeding 3000 m a.g.l. Therefore, African events that reach our site traveling at heights exceeding 3000 m a.g.l are loaded with elements of natural origin, both crustal (desert sand) and marine (they have to cross the Mediterranean Sea to reach the sampling point). On the other hand, events that occur at medium or low altitude are sedimentating these elements before reaching the sampling point, collecting only the radioactive isotopes, thus certifying the good behavior of both radionuclides (^7Be and ^{210}Pb) as tracers of African intrusions.

Gordo et al. (2015b) showed that during the 3 years studied, July registered 59 exceedances in PM_{10} levels in Málaga, and the origin of the air mass for these days was 56% from Africa. A similar situation occurred in August when 58% of the frequency of the air masses had an African origin. The minimum values were recorded at the end of autumn or winter, coinciding with low levels of PM_{10} .

- PC3 factor: It represents 10% of the total variance and it can be identified with local emissions of urban character (especially traffic). This factor is associated with some of the minority components, such as Pb, Zn, and Cu, mainly linked to traffic emissions (Sternbeck et al. 2002). In general, these metals have an anthropogenic origin. There are good correlations amongst themselves and also

with other components, as it may be seen on Table 2 correlation values. The highest correlation was found in Zn vs Cu ($r=0.39$) and Pb vs Cu ($r=0.37$).

The inventory of emissions due to road traffic for the years 2009, 2010, and 2011, issued by the Junta de Andalucía (see Online Resource 4), shows that major heavy metals derived from this source. The first place is occupied by Cu with a 60% in 2009 and 47% in 2010 and 2011, followed by Zn with a 28% in 2009 and 39% in 2010 and 2011 and Pb with an 8% in 2009 and 11% in 2010 and 2011. Cu, Zn, and Pb constitute up to 97% of the emissions of heavy metals caused by traffic in this Mediterranean coastal city during the 3 years of the study.

Ni could also be included in this group due to 0.46 as its higher loading value; it reflects an (industrial) anthropogenic contribution. It reveals, therefore, a contribution of strictly local character. This element is consistent with the heavy metals emitted in great concentrations by the cement and food industries in Málaga, and it shows a good correlation factor with the second most abundant element: Zn ($r=0.38$). Besides, Ni was also enriched in residual oil which was commonly used for ships (Corbin et al. 2018); thus, it is possible that the Ni content in Málaga was also originated from ship emissions since Málaga has got the second largest port in Spain.

The inventory of emissions due to the production of cement and the food industry in Andalusia (Junta de Andalucía 2009, 2015) shows that Ni represented a 37% in 2009 and a 34% in 2010 and 2011 of the total emissions from the cement industry in Málaga, while Zn represented the 17% in 2009 and 2010 and 21% in 2011. That explains between 51 and 56% of the total emissions. In the case of the food industry, Ni represented a 50, 57, and 61% in 2009, 2010, and 2011, respectively, for the total emissions due to the food industry in Málaga, while Zn accounted for the 11%, 14%, and 11% during those years. This explains 71 to 76% of the total emissions.

3.5 Enrichment Factors and Source Assessment

Table 3 shows the results of the determination of the elemental composition of collected samples of soil and seawater taken close to our sampling point, using ICP-MS. The result of this analysis is similar to that obtained by other researchers (Taylor 1964; Keene et al. 1986).

Table 3 Soil and seawater concentrations in g kg^{-1}

Element	Soil concentration	Seawater concentration
Na	3.7 ± 0.1	10.8 ± 0.2
Mg	15.94 ± 0.13	1.26 ± 0.01
K	20.0 ± 0.5	0.489 ± 0.002
Ca	54.6 ± 0.2	0.457 ± 0.009
Fe	36.4 ± 0.8	$(1.82 \pm 0.15) \cdot 10^{-4}$
Ni	$(4.6 \pm 0.2) \cdot 10^{-2}$	$(4.2 \pm 3.4) \cdot 10^{-6}$
Cu	$(3.6 \pm 0.2) \cdot 10^{-2}$	$(4.2 \pm 3.9) \cdot 10^{-4}$
Pb	$(2.3 \pm 0.1) \cdot 10^{-2}$	$(1.8 \pm 1.2) \cdot 10^{-6}$
Zn	0.126 ± 0.011	$(1.7 \pm 0.9) \cdot 10^{-5}$

The major elements identified in our samples were Ca in soil and Na in seawater (see Table 3); therefore, these elements were taken as references; Na has been taken as the reference element for seawater (Safai et al. 2004) and Ca as the reference element for continental crust (Zhang et al. 2007).

Table 4 gives the EF values for soil and seawater components. High EF of seawater was found for Fe, Ni, Pb, Cu, and Zn which indicates that large amounts of these ions were mainly originated from a non-marine source.

According to Zhang and Liu (2002), EF_{soil} values between 0.5 and 1.5 indicate that the metal comes entirely from natural weathering processes, while $EF > 1.5$ suggests that the sources are more likely to be of anthropogenic origins. The results of the present study show that EF_{soil} values of K, Mg, Ca, and Fe < 1.5 , which indicates none or minimal enrichment (Table 4).

All potentially hazardous elements considered in the study, Cu, Zn, Ni, and Pb, present $EF > 1.5$, revealing an anthropogenic source. Applied statistical analysis showed that Mg, K, Ca, and Fe are mainly of crustal origin from soil and dust whereas Na has a marine origin (85%). These results are similar to those given in other studies such as Tecer et al. (2012) and Omoniyi et al. (2013). The element Ni has both crustal (33%) and anthropogenic (67%) origin.

4 Summary

Atmospheric aerosol science arises several open questions that require basic and fundamental studies capable of explaining the observed phenomena, providing the fieldwork with new directions and enabling more effective model predictions for future conditions and scenarios. In order to identify emission sources for metals in atmospheric aerosols and to better understand their transport and deposition, it is necessary to characterize metal emissions from specific local sources and long-range transported metals. The present study examined their temporary variation over 3 years at an urban background site. Regarding the analysis of the concentration of metals in the weekly collected filters, observed major elements (Ca, Fe, K, Mg, and Na) and trace elements that appear in concentrations of 10 to 100 times lower (i.e., Zn, Pb, Cu, and Ni) data reveal the following order in accordance with their average concentrations: $\text{Ca} > \text{Na} > \text{Mg} > \text{Fe} > \text{K} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Pb}$.

The correlation analysis shows poor interactions between radionuclides and elemental concentrations.

Table 4 Enrichment factors for different constituents in atmospheric aerosols relative to soil and seawater, and source contributions

Element	Aerosol soil ratio	Soil ratio	EF_{soil}	Aerosol marine ratio	Marine ratio	EF_{marine}	SSF (%)	CF (%)	AF (%)
Na	0.5	0.07	7	1	1	1	85	15	0
Mg	0.3	0.3	1	0.7	0.1	6	17	83	0
K	0.2	0.4	0.4	0.3	0.05	7	13	87	0
Ca	1	1	1	2	0.04	51	2	98	0
Fe	0.3	0.7	0.4	0.6	$2 \cdot 10^{-5}$	$4 \cdot 10^4$	0	100	0
Ni	$3 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	3	$5 \cdot 10^{-3}$	$4 \cdot 10^{-7}$	$1 \cdot 10^4$	0	33	67
Cu	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	8	0.01	$4 \cdot 10^{-5}$	$3 \cdot 10^3$	0	12	87
Pb	$2 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	4	$4 \cdot 10^{-3}$	$2 \cdot 10^{-7}$	$2 \cdot 10^4$	0	23	77
Zn	0.02	$2 \cdot 10^{-3}$	9	0.04	$2 \cdot 10^{-6}$	$3 \cdot 10^4$	0	12	88

Strong positive correlations were observed amongst most elemental pairs suggesting the same origin and similar geochemical behavior.

In the statistical analysis performed VARIMAX, the total number of variables are grouped into three factors that together explained 63% of the variance of the samples, and, in addition, an enrichment factor and source assessment methods had been carried out, the following conclusions being inferred from both methods:

- First factor: Its components are the natural elements detected in highest concentration in atmospheric aerosol: Ca, Fe, Mg, K, and Na. The first four elements are predominantly from crustal origin, although it also reflects a contribution of marine component (Na). Ni contributed largely to this group as well. The analysis of source contributions shows that Ni has different sources: crustal and anthropogenic. Therefore, Ni contributed both to the first and to the third factor. PM_{10} and 7Be are also categorized into this group: 7Be is a good radiotracer of air mass with African origin and high levels of PM_{10} and 7Be , and low ^{210}Pb indicates intrusion from altitudes higher than 3000 m a.g.l. That would explain the high levels of natural elements with diverse origins, crustal, and marine.
- Second factor: It is associated with the studied radionuclides 7Be and ^{210}Pb with PM_{10} levels. It is identified with air masses with African origin.
- Third factor: elements grouped in this factor (Pb, Zn, Ni, Fe, Cu, and ^{210}Pb) are identified with urban emissions, particularly traffic.

In general, traffic emissions and industrial aerosol events did not cause exceedances of the daily European limit value for PM_{10} . Instead, Saharan dust events were in most cases responsible for the exceedance of the limit value at our sampling station.

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