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Monitoring of heavy metals in topsoils, atmospheric particles and plant leaves to identify possible contamination sources

S. Rossini Oliva [a,1], A.J. Fernández Espinosa [b,*]

[a] Department of Plant Biology and Ecology, University of Seville, Av. Reina Mercedes s/n, Apdo. 1095, E-41080 Seville, Spain
[b] Department of Analytical Chemistry, University of Seville, C. Profesor García González s/n, E-41012, Seville, Spain

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Abstract

The research reveals results of metal pollution on urban topsoil in relation to the metal content in leaves of two plant species and atmospheric particles. The content of pollutants (Ba, Cd, Cu, Fe, Mn, Ni, Pb, V and Ti) was determined by ICP-OES. Twenty-two samples of soil were collected over a six-month period from two different urban sites and one from a rural zone. Regarding the pollution level, the studied soils were found to be low. Results for enrichment (EF) and concentration (CF) factors showed that soils were enriched in Pb, Ba, Cu and Ni. However, both species of plants showed a common behavior for all elements acting as excluders. ANOVA and different multivariate statistical analyses confirmed that the main pollution source of soil was traffic and fertilizers. Cd, Fe, Mn, Ti and V elements were attributed to natural sources. Also, it was suggested that *N. oleander* leaf is useful as a bio-monitors of soil pollution by Cu. Similarly, a direct relationship was found between the content of Cu in soils with the Cu level in PM_{10} atmospheric particles. The origin was attributed to dry and wet atmospheric deposition processes.

Keywords: Soil; Leaf; Atmospheric pollutants; Metals; PM_{10}

1. Introduction

Nowadays it is well known that cities suffer from considerable air pollution due to the release of different pollutants into the atmosphere whose levels can be toxic. Vehicular traffic is widely recognized to be a significant and increasing source of atmospheric and soil pollution in urban environments [1–3]. Traffic is particularly different to other sources of air pollution because vehicular emissions are readily inhaled by humans due to their close proximity before the atmospheric dilution can affect public health. Besides, important parameters such as the number and type of vehicles, slow moving traffic, etc., affect air pollution levels in urban areas.

The relationship between emissions and pollution levels varies depending on the city. Infrastructure and town planning determine the emission pattern while meteorology and topography determine dispersion and transformation [4]. With regard to anthropogenic emissions in Seville, the main source is vehicular traffic, since the industrial influence is quite low [5,6]. Because of air pollution, urban soils can be contaminated by metals from different anthropogenic sources and from natural processes [7]. These pollutants can also bio-accumulate in plants. Atmospheric pollution is one of the major sources of heavy metal contamination in soils and roadside dusts in urban areas [8]. The contribution of metals from anthropogenic sources in soils is higher than the contribution from natural sources [9]. Soils in an urban environment may have a direct influence on human health via direct contact or suspended dust [10]. In addition, high levels of metals in urban soils have been recognized as important sources of metal intake for children, thereby elevating metal levels in children's blood. In addition, soil ingestion constitutes an exposure route of contaminants to children as water or food ingestion [11].

It is important to assess the possible sources of pollutants in urban soils. The literature reported that urban soils often contain

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* Corresponding author. Tel.: +34 954554368; fax: +34 954557168.
E-mail addresses: sabina@us.es (S.R. Oliva), anjose@us.es (A.J.F. Espinosa).
[1] Tel.: +34 954557056; fax: +34 954557059.

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enriched levels of heavy metals [10,12–17]. This suggests that the contribution of each one of them is often difficult to determine since urban soils are periodically disturbed by irrigation, construction activities and partial or total replacement [13]. The distribution of several heavy metals in some soils of Seville was studied in 2002 [10], but concentrations of some toxic metals (e.g. Ba, Cd, V, etc.) remain poorly documented and require more investigation.

On the other hand, it is well known that plants accumulate trace elements from the atmosphere and have been used in several bio-monitoring studies [18–22], offering low-cost information about environmental quality with the advantage of easy sampling. A close connection of the soil "O-horizon" with plant chemistry and atmospheric inputs was demonstrated in Northern Europe [23]. In our previous study [24], where more than twenty samples of plant leaves (*Nerium oleander* L. and *Lantana camara* L.) and airborne particles (PM_{10}) were analyzed, it was reported that the only correlation between metal concentrations in PM_{10} particles with either *N. oleander* or *Lantana camara* leaves was found for Fe and Cu for oleander with respect to PM_{10}. Regarding these results, it would be interesting to investigate if elements in atmospheric particles are also related with soil contents. At the same time, the assessment of metal enrichment and composition of urban soils is essential to establish if topsoils are polluted in the sampling sites. Therefore, the objectives of the present study were: firstly, to assess the grade of soil contamination in representative sites of the city of Seville; secondly, to compare metal levels of PM_{10} particles and leaves of *N. oleander* L. and *L. camara* L. [24] with levels of the soil where the plants grow; thirdly, to know the behavior of elements in both species of plants, also investigating the metals in which soils are enriched.

Therefore, the relationships between metal contents in topsoils, atmospheric particles and plant leaves studied in the present work would offer interesting and essential results that contribute to the knowledge of the bio-monitoring process.

2. Experimental

2.1. Sampling sites and characteristics of soils

Seville is the administrative center of Andalusia. It represents the most densely populated city of Southern Spain with around 700,000 inhabitants and a population density of 5000 inhabitants per km^2. It is situated 10 m above sea level on an extensive plain crossed by the Guadalquivir River and has a Mediterranean climate with an average annual temperature of 19 °C and rainfall of 580 mm. Traffic of cars and trucks represents the most important pollution source because industries are rather scarce. Important crustal particle contributions in Seville and Southern Spain are well documented by the local scientific community and both regional and national governments. These particles come from the lands surrounding the city and from the North Africa deserts.

According to local and regional authority information, the sampling sites that represent the area of Seville most affected by the highest vehicular emissions is Torneo (TRN); another site with a low traffic density was Porvenir (POR). During the sampling period, the traffic densities in Torneo and Porvenir were 23,067 and 6908 vehicles per day (VPD) respectively; the annual average daily traffic (AADT) in Seville was 16,838 vehicles per day (VPD). A third sampling site was chosen in Castilblanco as the control site (BLK) in a rural area at 40 km

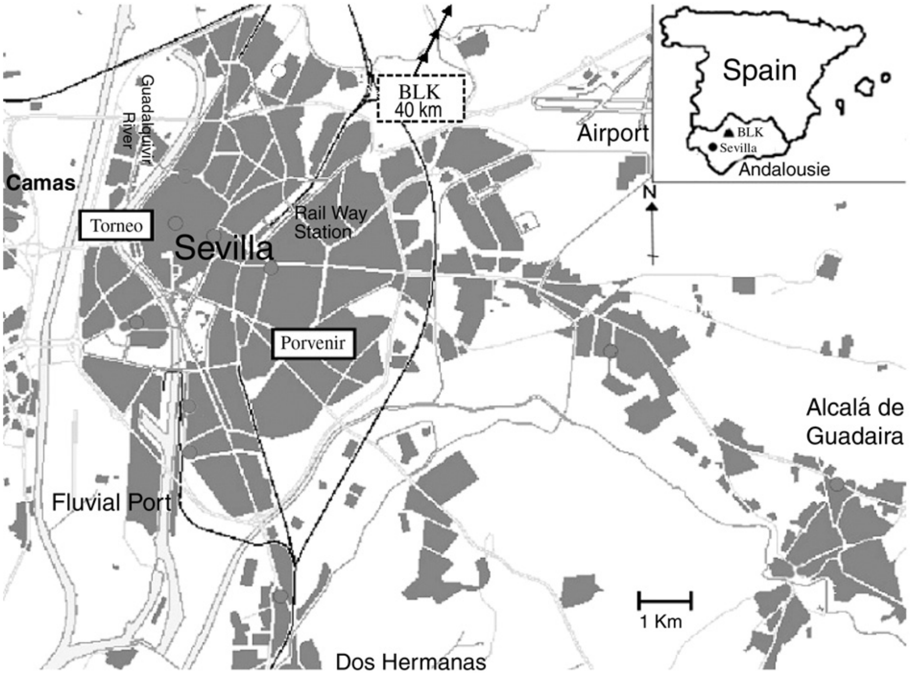

Fig. 1. Location of the three sampling sites in the area of Seville.

toward the Northern Seville, away from any traffic emissions but with similar weather characteristics.

Soils where both species of plants grew were at different locations in each sampling site but in close proximity. TRN was located near a cross street in Torneo Street. Samples were collected from ornamental soils located in the border of the street. Both plant species grew only at 11 m of distance. POR was located into a residential area (Porvenir's District). Soil samples were collected from the garden of a residential building. Both plant species was planted only at 14 m of distance. Finally, BLK site was located in the Sierra Norte Mountains, in the Sierra Morena mountain range, near a little dam of the Cala Reservoir, at 350 m above sea level. Both plant species had grown only at 3 m of distance in BLK.

The soil characteristics surrounding the three sampling sites were different. Therefore, sampling sites were classified in the following manner: BLK was characterized only by natural and unaltered soil. TRN and POR soils were characterized by natural soil and asphalt. Besides, TRN and POR soils were usually disturbed by different processes, such as irrigation or construction activities. These processes contaminate and modify its composition and structure. This never occurred in BLK soil. Soils nomenclature was differentiated according to the plant where they grew, "oleander soils" and "lantana soils".

2.2. Sampling of airborne particles, leaves of plants and soils

In a previous work [24], 22 samples of PM_{10} particles, samples of *N. oleander* and *L. camara* leaves and samples of soils were collected simultaneously in 3 sampling sites (Fig. 1) during November 2003 to March 2004. 8–9 samples were collected at POR and TRN, two per month, and 5 samples at BLK, one per month. Therefore, a total of 22 samples of PM_{10}, 22 of oleander leaves, 22 of lantana leaves, 22 of oleander soils and 22 of lantana soils were collected.

Atmospheric particles were collected with a standard high-volume sampler MCV, model CAV-A/HF equipped with a PM_{10} inlet MCV, model PM10/CAV. The PM_{10} inlet was used to collect all particles of less than 10 μm (aed). Fiberglass filters of 8×10 in (24.5×20.3 cm) were used as collection media. Samples of airborne particles were collected in different days of the week, therefore, representing the different meteorological and environmental conditions of the city. Sampling periods were from 0:00 a.m. to 23:59 p.m. For sampling of leaves in both species of plant, several branches from three healthy-looking plants were cut off from the sides of the canopy. The effect of rain events on sampling conditions was delimited collecting plants and airborne particle samples a week after the last rain event of importance, according to the recommendations of Markert [18] and Bargagli [20]. Once in the laboratory, about 300 mg of fresh mature leaves (including the petioles) were mixed to provide a unique sample. Samples were dried overnight at 70 °C and then ground to a fine powder.

Regarding to the soil samples, twenty-two samples of topsoil were collected from the three sites (POR, TRN and BLK) for the two different species of plants (*N. oleander* and *L. camara*). They were collected from near-surface soil (5–10 cm depth) at the same time as plant and PM_{10} samples. They were collected where plants grew, using a standard spade and put in black bags. All soil samples were dried at room temperature until a constant weight was achieved and sieved through a 2 mm mesh screen; one aliquot was ground in an agate ball mill (Retsch Model PM400) to obtain a more homogenous grain distribution at a size <50 μm.

2.3. Analytical procedure

Filters loaded with PM_{10} particles and plant samples were treated according to the previous work [24]. Aliquots of 500 mg of soil samples were mineralized with an acid mixture adding 8 ml of HNO_3 and HCl (1:3) to the vessels of a microwave assisted digestion system. A Milestone-model Ethos 900 microwave oven equipped with six Teflon® vessels was used to digest the samples. The specific digestion program used consisted in three steps: 1, heating at 300 Watts during 10 min; 2, waiting at 0 Watts during 1 min; 3, heating at 600 W during 5 min. After digestion and cooling, digested soil solutions were

Table 1
Results on metal levels of reference materials

Element	Certified value	Experimental value	Recovery (%)	AOAC [a] criteria (%)
GBW 07604 (Poplar Leaves)				
Fe	274±10	283±11	103.1	90–107
Ti	20.4±1.7	17.3±2.2	85.0	80–110
Pb	1.5±0.2	1.3±0.3	84.7	80–110
Ni	1.9±0.2	1.6±0.2	83.9	80–110
Cd	0.32±0.04	0.22±0.02	68.8	60–115
Mn	45±2	42.4±2.6	94.3	80–110
Cu	9.3±0.5	8.5±0.8	91.5	80–110
V [b]	(0.64)	0.5±0.1	(72.0)	60–115
Ba	26±2	21.8±2.5	83.7	80–110
NIST-SRM 1648 (Urban Particulate Matter)				
Fe (%)	3.91±0.20	3.99±0.08	102.2	97–103
Ti [b]	(4000)	3613±95	(90.3)	95–105
Pb	6550±162	6242±170	95.3	95–105
Ni	82±6	70±3	86.0	80–110
Cd	75±7	62±8	82.7	80–110
Mn	786±34	777±18	98.9	90–107
Cu	609±55	561±8	92.1	90–107
V	127±14	122±3	96.1	90–107
Ba [b]	(737)	713±23	(96.7)	90–107
NIST-SRM 2711 (Montana II Soil)				
Fe (%)	2.89±0.06	2.81±0.06	97.2	97–103
Ti (%)	0.306±0.023	0.296±0.009	96.7	95–105
Pb	1162±31	1109±36	95.4	95–105
Ni	20.6±1.1	14.8±0.5	71.9	80–110
Cd	41.70±0.25	36.55±0.27	87.6	80–110
Mn	638±28	607±5	95.1	90–107
Cu	114±2	111±5	97.6	90–107
V	81.6±2.9	70.2±0.8	86.0	80–110
Ba	726±36	689±27	94.9	90–107

Recoveries were compared with the American Organization of Analytical Chemists (AOAC) criteria.

[a] AOAC, 1993.

[b] Value not certified. Values of metal concentrations are in μg g^{-1} or in percentages (%).

washed and transferred diluting to 15 ml sterile conical centrifugal tubes before the instrumental analysis.

Because of the second objective of the work was to compare metals levels in PM_{10}, leaves and topsoils, the acid mixture applied to soils and the metals measured were the same than in PM_{10} and leaves [24]. The aim was to find the relationships between metal concentrations in soils and metal concentrations in leaves and PM_{10}. Therefore, although in soil analysis, HF is frequently used to put in solution metals attached to silicates, in order to still extract the same type of metals that on PM_{10}, which have also important amounts of silicates, and due to the difficulty of applying HF to the fiberglass material of filters, HF was not used in the acid mixture applied to soils. The undestroyed silicates constituted a minimum residue.

On the other hand, the elements measured were the same with that in plant and particles. The concentrations of Ba, Cd, Cu, Fe, Mn, Ni, Pb, V and Ti were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Fisons-ARL 3410 sequential multi-element instrument. The standard operation conditions of this instrument are summarized as follows: the carrier gas, plasma gas, and coolant gas used was argon; the carrier gas and plasma gas flow rates were 0.8 l $\mathrm{min}^{\mathrm{i©1}}$ (40 and 23 psi), the coolant gas flow rate was 7.5 l $\mathrm{min}^{\mathrm{i©1}}$ (28 psi) and the integration time is 1 s. One axial mini-torch (power of 650 W) consumes argon gas at a radio frequency of 27.12 MHz. Consequently, it is capable of consuming a few ml of sample at a flow rate of 2.3 ml min^{-1} using a Meinhard nebulizer. In order to avoid errors due to the effect produced by the different viscosity and density of the acid matrix of samples on the ICP nebulization, calibration graphs have been made from results obtained from the same acid matrix.

The accuracy of the determinations was previously checked by analysis of two NIST reference materials, SRM 1648 Urban Particulate Matter, SRM 2711 Montana II Soil and one GBW reference material from the Chinese National Research Centre for Certified Reference Materials, GBW 07604 Poplar Leaves. The recoveries range was according to the AOAC criteria, which proved the validity of the optimized methodology (Table 1).

A gold solution was used as the internal standard to spike samples, blanks and reference materials in order to check the correct extraction of the elements. Previously, a study concluded that gold was not present in urban air [25] or plants [18] and its presence within the Teflon vessel had no influence on analytical determinations of the other metals.

All ultra-pure reagents and standards were supplied by Merck. Distilled water was of Milli-Q grade obtained from a Waters-Millipore apparatus, model Plus. Since individual blanks were not available for each filter used for sampling of particles, a set of unexposed filters was analyzed as blanks, using the same procedure used for samples. The mean unexposed filter values in µg kg^{-1} were: 9214 for Ba, 0 for Cd, 0.4 for Cu, 75 for Fe, 2.1 for Mn, 0,4 for Ni, 1691 for Pb, 0 for V and 1.2 for Ti. They were determined and subtracted from each sample to obtain the best estimate of each element in PM_{10} particles.

2.4. Data treatment and statistical analysis

Two parameters were calculated in order to characterize the origin and transfer of elements: 1. The concentration factor (CF), expresses the ratio of metal concentration (M) between plants and soils: $CF=(M_{plant}/M_{soil})$. The ratio was calculated for both species of plants revealing the behavior about the pollutants studied. 2. The enrichment factor of soil (EF_{soil}), is the relative abundance, with regards to Iron, of one element (M) in a soil compared to its relative abundance (M/Fe) in the local control site: $EF_{soil}=(M/Fe)_{soil}/(M/Fe)_{control}$. The enrichment factor was used to establish which elements of soils had been relatively enriched, allowing the evaluation of the anthropogenic impact.

Statistical analysis was carried out using the CSS: STATISTICA (StatSoft, Inc.) software package. Basic statistics were used to calculate the mean values and standard deviations for $n=8$, 9 and 5 samples collected in POR, TRN and BLK. The following statistical tools used $n=22$ total samples collected. ANOVA was used to detect significant differences between

Table 2
Metal concentrations, in mg kg^{-1}, and standard deviations, ±SD(RSD%); Mean of n soil samples collected in the different sites

Sampling site	Ba	Cd	Cu	Fe (%)	Mn	Ni	Pb	V	Ti
N, POR ($n=8$)	266±28 (10%)[a]	6.50±0.44 (7%)[a]	72.1±9.8 (14%)[a]	2.25±0.16 (7%)[a]	554±23(4%)	23.7±1.2 (5%)[a]	174±16 (9%)[a]	44.5±5.3 (12%)[a]	1162±315 (27%)[a]
N, TRN ($n=9$)	339±60 (18%)[a]	6.33±0.82 (13%)[a]	71±17 (24%)[a]	2.24±0.29 (13%)[a]	612±73 (12%)	23.7±2.3 (10%)[a]	142±29 (20%)[a]	43.9±5.6 (13%)[a]	1690±234 (14%)[a]
N, BLK ($n=5$)	94.3±8.1 (8%)	10.30±0.92 (9%)	30.3±5.4 (18%)	3.67±0.40 (11%)	612±89 (14%)	13.2±3.4 (26%)	22.4±4.2 (19%)	102±14 (14%)	6232±1639 (26%)
L, POR ($n=8$)	294±36 (12%)[a]	7.8±1.1 (14%)[a]	80±21(26%)	2.71±0.54 (20%)[a]	583±74 (13%)[a]	29.3±7.1 (24%)[a]	123±20 (16%)[a]	57.9±7.6 (13%)[a]	1687±449 (27%)[a]
L, TRN ($n=9$)	189±74 (39%)[a]	6.58±0.89 (14%)[a]	77±49(64%)	2.28±0.33 (14%)[a]	470±50 (11%)[a]	18.9±3.7 (20%)[a]	92±57 (62%)[a]	48±12(25%)[a]	1776±562 (32%)[a]
L, BLK ($n=5$)	86.0±3.7 (4%)	10.60±0.80 (8%)	25.7±1.8 (7%)	3.87±0.16 (4%)	649±56(9%)	10.60±0.50 (5%)	20±12(60%)	110.0±5.6 (5%)	8353±1490 (18%)
Madrid et al. [10]	n.a.	n.a.	68±64	2.01±0.32	471±103	22±6	137±160	n.a	n.a.
De Miguel et al. [13]	369±64	n.a.	72±37	2.31±0.35	437±118	14±4	161±82	30±3	2135±319

n.a., Not available.; (RSD%, relative standard deviation in percentage).

N: soil of *Nerium oleander*; L: soil of *Lantana camara*.

[a] Indicate significant (Scheffé Test, $p<0.05$) statistical differences with respect to the BLK.

sampling sites ($p < 0.05$). The Scheffé's multiple mean comparison test was also used in the ANOVA. The relationship between metal concentration in atmospheric particles and plants and soils was tested by the Pearson correlation coefficients (r). Cluster analysis (CA) and Principal Component Analysis (PCA) were used as classification tools. The components of the PCA were rotated using a Varimax rotation. Cluster analysis was performed using the Ward method as the amalgamation rule and Euclidean distance as metric.

3. Results and discussion

3.1. Metal concentrations in soil samples

Descriptive statistics of metal concentrations of soils in the different sites are reported in Table 2. The dispersion of data was small for Cd, Fe, V and Mn in oleander soils and lantana soils. The standard deviations were high for Cu, Ba and Pb, mainly in lantana soils. This difference indicates that soil composition was homogeneous in the case of the first group of metals in both types of soils, whilst Pb, Cu and Ba had different levels in lantana soils, possibly due to its anthropogenic origin [6]. Large element variability rather than a high concentration provides an indication of an unusual element source [6,17].

In Table 2 the average content of elements is compared to those reported in Seville in 2002 [10] and in urban soils of Madrid in 1998 [13]. There were some similarities between the present data and those of Seville in 2002 [10], whilst the comparison also suggests that the soils studied had higher contents in Ni and V than in Madrid. With regards to traffic sources, it is well known that Pb originates from leaded fuel used in the past [6] and that the principal source of Cu, together Mo and Sb, is break linings in motor vehicles, respectively [26,27]. According to the Quebec Ministry of Environment (QME), the Pb and Cu contents in soils of both sampling sites were considered as Level B, which is the acceptable limit for residential, recreational and institutional sites. Levels of Pb and Cu observed in the background site (BLK) were lower than those usually considered as control values ($Cu = 40\ mg\ kg^{-1}$, $Pb = 50\ mg\ kg^{-1}$) and they are lower than values reported in Seville in 2002 for the Alamillo Park, a site considered as background by this study [10]. However, Ti and again V contents in BLK were higher than background values reported in Madrid in 1998 [13].

3.2. Oleander soils

Results of the Scheffé Test show that element concentrations in oleander soil differed significantly ($p < 0.05$) among the sampling sites, except for Mn. The Pb concentration was significantly lower in BLK with respect to the other two sampling sites and differences in Pb concentrations between them were not found. However, both Pb mean values in POR y TRN were much higher than those reported for soils sampled around an industrial area of Huelva (Spain) [17] and for an urban soil of Siena (Italy) [19]. Lead is linked to the deposition of atmospheric particles on soils generated primarily from traffic and from other anthropogenic activities [13]. Differences between soils suggest that Pb content on the soil surface was the result of accumulation process from traffic sources during the past years. Traffic in Seville was concentrated around the historical center before the new roads and avenues constructed for the Exposition Universal of 1992 (Expo92). This high traffic density in the past could have affected TRN and POR and is probably the reason for high Pb levels in soils.

Regarding Cu and Ni concentrations, they were significantly lower in BLK than in POR and TRN, but differences between both urban sites were not observed. Both elements are considered as anthropogenic. Apart from traffic, contamination of soils by Cu could be derived from the use of fertilizers, sprays, bactericides, fungicides and agricultural or municipal wastes as well as from industrial emissions [28,29].

Similarly, Ba and Ni concentrations were also found to be lower in BLK than in the other sites, while concentrations in TRN were significantly higher than in POR. Barium is another element associated with traffic [19,24]. However, Cd, Fe, Ti and V concentrations were significantly higher in BLK than in the urban sites, whilst no differences were observed between TRN and POR. In addition, the Mn concentration in BLK was significantly higher than in TRN, but lower than in POR. This constitutes a contrary pattern than the previous elements commented on above, i.e. Cu, Ni, Ba and Pb.

3.3. Lantana soils

In the case of the lantana soils, results of the Scheffé Test showed that, as in oleander soils, the Cd, Fe, V and Ti concentrations were significantly higher in BLK than in the urban sites. Besides, values of Ti concentrations in BLK were

Table 3
Correlation matrix of the total element concentrations in *N. oleander* and *L. camara* soils

	Ba	Cd	Cu	Fe	Mn	Ni	Pb	V	Ti
N. oleander									
Ba	1.00								
Cd	**−0.71**	1.00							
Cu	**0.88**	**−0.64**	1.00						
Fe	**−0.70**	**0.99**	**−0.66**	1.00					
Mn	0.15	0.37	0.00	0.41	1.00				
Ni	**0.87**	**−0.76**	**0.81**	**−0.75**	0.17	1.00			
Pb	**0.81**	**−0.78**	**0.88**	**−0.81**	−0.21	**0.86**	1.00		
V	**−0.78**	**0.97**	**−0.74**	**0.98**	0.30	**−0.85**	**−0.87**	1.00	
Ti	**−0.75**	**0.92**	**−0.75**	**0.93**	0.22	**−0.90**	**−0.88**	**0.97**	1.00
L. camara									
Ba	1.00								
Cd	−0.03	1.00							
Cu	0.75	−0.47	1.00						
Fe	−0.26	0.97	−0.45	1.00					
Mn	0.10	**0.76**	−0.35	0.84	1.00				
Ni	0.76	−0.13	0.44	−0.17	0.15	1.00			
Pb	**0.87**	**−0.62**	**0.87**	**−0.67**	−0.38	0.51	1.00		
V	−0.50	**0.95**	**−0.62**	**0.95**	**0.73**	−0.42	−0.76	1.00	
Ti	**−0.62**	0.52	−0.46	**0.72**	0.58	−0.47	**−0.63**	**0.87**	1.00

Correlations significant at $p < 0.05$ are in bold.

higher than in the urban soils of other work [20]. Fe, Ti and V are normally present in soils [24,30]. Therefore, results of the Scheffé Test on oleander soils and lantana soils confirm a contrary behavior between the two groups of elements, indicating that Fe, Ti, V and Cd were associated to crustal elements and that elements Pb, Cu, Ni and Ba were associated to vehicular traffic. Along with these two groups, conclusions on Manganese suggested a different behavior.

3.4. Comparison with plant and particle contents

Inter-element relationships provide interesting information on heavy metal sources and pathways. Correlation analysis (Table 3) shows that Pb, Ba, Cu and Ni were negatively correlated with Cd, Fe, V and Ti suggesting that these elements came from different sources. These correlations corroborated the results of Section 3.1. Additionally, Ba, Cu, Ni and Pb were inter-correlated in oleander and lantana soils, suggesting that they have a common origin associated with traffic. Correlation coefficients were higher in oleander soils than in lantana soils (Ba–Cu $r=0.88/0.75$, Ba–Ni $r=0.87/0.76$, Ba–Pb $r=0.87/0.81$, Cu–Pb $r=0.88/0.87$, Cu–Ni $r=0.81/0.44$, Pb–Ni $r=0.86/0.51$). Similarly, Fe, Ti, V and Cd were also inter-correlated between them with correlation coefficients similar in both soils (Fe–V $r=0.98/0.95$, Fe–Ti $r=0.93/0.72$, Fe–Cd $r=0.99/0.97$, Cd–V $r=0.97/0.95$, Cd–Ti $r=0.92/0.52$, Ti–V $r=0.97/0.87$). Therefore, the highest coefficients were found in oleander soils for anthropogenic elements while similar coefficients were obtained in both types of soils for earth crustal elements. It should be noted that cadmium, usually from anthropogenic sources, appeared together with typical crustal elements in the present work. It was the only unusual result hard to explain. However, low dispersion values for its level in soil (Table 2), even for the less abundant element, confirm the association with these metals.

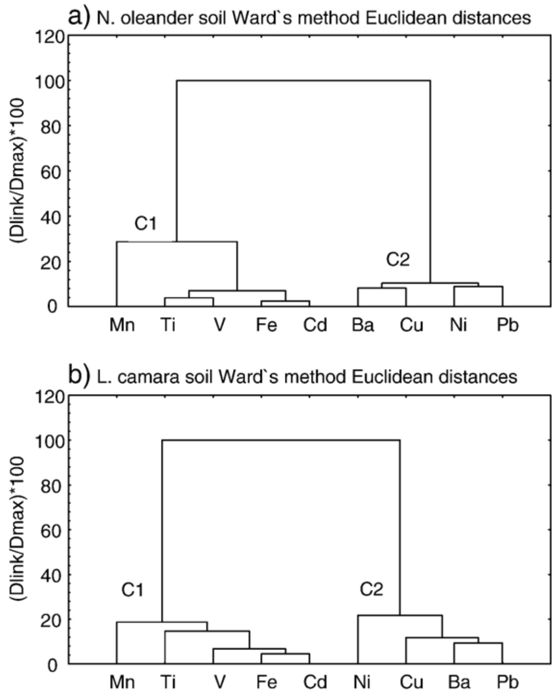

Fig. 2. Hierarchical clustering results (dendrogram) of heavy metal concentrations in oleander (a) and lantana (b) soil samples.

Table 4
Factor loadings for the metal contents in oleander and lantana soil samples

Variable	PC1	PC2
Oleander soil		
Ba	**0.92**	0.21
Cd	**−0.86**	0.44
Cu	**0.89**	0.12
Fe	**−0.86**	0.47
Mn	−0.01	**0.96**
Ni	**0.96**	0.16
Pb	**0.92**	−0.15
V	**−0.93**	0.34
Ti	**−0.94**	0.25
Eigenvalue	6.8	1.4
% Var	76.1	15.7
Lantana soil		
Ba	−0.19	**−0.97**
Cd	**0.93**	0.21
Cu	−0.38	**−0.76**
Fe	**0.97**	0.19
Mn	**0.90**	−0.14
Ni	0.13	**−0.87**
Pb	−0.49	**−0.78**
V	**0.87**	0.45
Ti	**0.71**	0.58
Eigenvalue	5.8	2.1
% Var	64.0	21.1

% Var, percentage of explained variance.
Marked loadings are >0.7.

Spatial and seasonal variations in element concentrations of plant leaves and PM_{10} were found to be independent to those of surface soil. Regarding the plant leaves, no clear correlations between soil and plant leaves were found (table of correlations is not presented) indicating that concentrations of elements in plant leaves arise mainly via the atmosphere. In the present study, the soil contamination didn't influence the chemical composition of either species. Some authors studying plant species were unable to find a direct relationship with the soil contamination of local geogenic dust [31]. Thus, the relationships are applicable to species growing near the ground level and plant chemistry is considerably influenced by local soil dust. According to these authors, the "O-horizon" of soil receives atmospheric deposition just like plants. Therefore, the present results suggest that neither *N. oleander* nor *L. camara* are good bio-monitors of soil pollution with regard to the studied element. The exception is constituted by a very clear correlation found between the content of Cu in oleander leaf and in oleander soil ($r=0.90$). In a previous study made in an industrial area of Southern Spain, no correlations were found between the oleander soil and the oleander leaf for Cu, Pb and Zn [32]. Other studies reached the same conclusion [33]. Therefore, results indicate that the total metal content in plant tissues is not only a function of the total metal content of the soil, but also depend on other factors such as climatic and

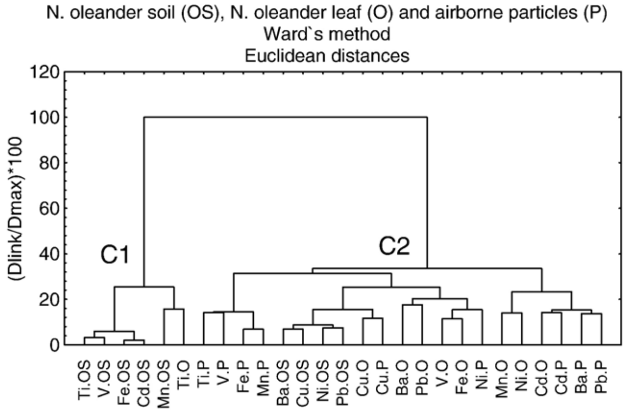

Fig. 3. Hierarchical clustering results (dendrogram) of heavy metal concentrations in topsoil, PM_{10} and oleander leaf samples. OS, oleander soil, P, PM_{10}, O, oleander leaves.

environmental influences. Considering that Seville soils are calcareous with pH of 7.3–8.0 [10] and that it is well known that acids pH favor the solubility of elements, it can be suggested that oleander leaves are suitable only as bio-monitors for Cu soil pollution. This conclusion has to be used as a preliminary affirmation. Recently it was pointed out [34] that the use of correlation analysis to study plant species as bio-monitors for soils is insufficient.

Regarding atmospheric particles, general results suggest that surface soil pollution was not directly influenced by the inputs of PM_{10} particles. Only in oleander soils, a high relationship with PM_{10} concentrations was found, again, for Cu ($r=0.88$). Considering that the previous work [24] found a relationship between contents of Cu and Fe in oleander leaf and PM_{10}, we were expecting that a similar relationship between PM_{10} and soil contents would suggest, as a first approach, that part of the elements absorbed into leaf plants could be transferred to the plant soil by rain. However, Cu is usually accumulated in the top horizons [28,29] and the washing process does not remove all Cu deposited on the leaf surface [35]. Therefore, an alternative explanation might be that Cu inputs to soils come directly from atmospheric deposition. Furthermore, the most important statement on Cu contamination is the great affinity of surface soils to accumulate Copper, whilst Iron level is highly variable in soil horizons due to different soil processes [28]. The lack of relationship between the composition of surface soil and PM_{10} composition for the other elements can be explained by the elements in the soil profile following different patterns. The total soil composition is the result of a long contamination and deposition process originating from the past due to different pollution sources, whilst the PM_{10} composition varies on a daily basis.

Table 5
Mean CF value for all elements in oleander soil and lantana soil

Sampling site	Ba	Cu	Fe	Mn	Ni	Pb	V	Ti
N, POR	0.086	0.067	0.005	0.076	0.007	0.004	0.016	0.008
N,TRN	0.097	0.099	0.005	0.030	0.004	0.006	0.014	0.005
N,BLK	0.243	0.086	0.002	0.039	0.000	0.012	0.005	0.002
L, POR	0.036	0.149	0.008	0.030	0.004	0.010	0.022	0.009
L, TRN	0.031	0.078	0.003	0.050	0.008	0.005	0.009	0.003
L, BLK	0.043	0.303	0.003	0.052	0.004	0.038	0.008	0.003

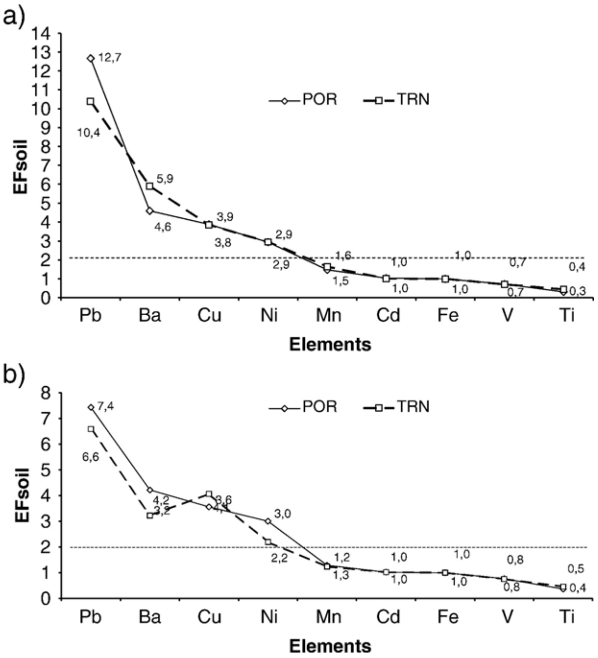

Fig. 4. Mean EF value for all elements. a), *N. oleander* soil; b), *L. camara* soil. The horizontal line indicates the EF threshold=2.

3.5. Principal component and hierarchical clustering analysis

In order to interpret the results better, Principal Component Analysis (PCA) and Cluster Analysis (CA) were employed. PCA was applied separately to the oleander soil and lantana soil data. In summary, the differentiation between anthropogenic and lithogenic elements was revealed again by PCA and CA.

In the case of oleander soils, two Principal Components (PCs) were extracted explaining a total variance of 92% (Table 4). The first PC (PC1, variance of 76%) included all elements except Mn. Nickel, Pb, Ba and Cu concentrations had high positive loadings (>0.9), negatively correlated with Ti, V, Cd and Fe with high negative loadings (>0.9). Based on earlier discussions, results suggest that the distribution of Ni, Pb, Ba and Cu was mainly controlled by anthropogenic sources and that Ti, V, Cd and Fe could be inferred to as lithogenic. The second PC (PC2, variance of 16%) was formed only by Mn, which again confirms that it had a different origin. Results of the Scheffé Test (Table 2) demonstrated that geochemical and geographical distribution was different from the previous groups.

The same distribution was obtained by the study of clusters from CA (Fig. 2-a). Results reveal two clusters of elements: the first one (C1) included elements that had previously been interpreted as crustal elements (Cd, Fe, Ti and V, together Mn) and the second cluster (C2) discriminated the anthropogenic elements Ca, Cu, Ni and Pb. Therefore, C1 contained two sub-clusters where Mn was classified as an independent variable.

For lantana soils, the PCA distribution was different to that for oleander soils (Table 4), however the same groups were extracted. The two PCs explained 85% of the total variance but PC1 and PC2 were contrarily distributed. PC1 was formed by Fe, Cd, Mn, V and Ti and the second PC contained Ba, Ni, Pb and Cu. Thus, in lantana soils, anthropogenic sources had less significance (PC2, variance of 21%) than crustal elements (PC1, 64%).

Cluster analysis (Fig. 2-b) gave a similar result enabling the identification of two main groups of elements, C1 formed by Ti, V, Fe, Mn and Cd and C2 formed by Ni, Cu, Ba and Pb.

Therefore, results of multivariate analysis confirmed again that elements studied come from two different sources in both types of soils, while oleander soils have a higher accumulation grade of anthropogenic elements.

On the other hand, a different cluster analysis was performed using all data concerning oleander soil, PM_{10} particles and oleander leaf contents (Fig. 3). Two main clusters were obtained; one of those (C2) included a sub-cluster formed by the Cu content in PM_{10} particles (Cu · P), Cu in oleander leaves (Cu · O) and Cu in oleander soils (Cu · OS). This result supports the idea that there exists a relationship between Cu content in leaves, soils and PM_{10} particles.

3.6. Concentration factors and enrichment factors

3.6.1. Concentration factor

The ratio between plant and soil concentrations of elements (CF) is an index of soil–plant transfer that favors the understanding of plant uptake characteristics [36] and it is widely used in bio-monitoring studies [17]. Ratios > 1 indicate that plants are enriched in elements (accumulator), ratios around 1 indicates that plants are not influenced by elements (indicator), and ratios < 1 shows that plants exclude the elements from uptake (excluder) [37].

Results of CF (Table 5) display that both species exhibited the same behavior. Values were < 1 for all elements indicating a low translocation from soil to plant leaves in all sampling sites. Therefore, both species act as excluders for all studied elements. In a study around industrial areas, the same behavior was found for oleander leaves, except for Cu [17,33].

3.7. Enrichment factors

In order to evaluate if metal content in soil derives from natural or anthropogenic sources, the enrichment factor was calculated. Different contamination categories were recognized based on the EF parameter [16]. In the current study, enrichment factor values >2 were considered indicatives of some enrichment corresponding mainly to anthropogenic inputs. Thus, both types of soils were clearly enriched by Pb, Ba, Cu and Ni in POR and TRN compared to the local background levels (Fig. 4a and b), confirming that they are derived from anthropogenic activities.

The EF_{soil} for Pb was the highest value, indicating that urban soils were highly enriched by this element. This confirms the cause suggested above; it could be the consequence of a long deposition process during the past when leaded gasoline was used. Similarly, Ba enrichment could be due to vehicle emissions [6,19].

Some studies on enrichment of Cu in soils due to the input of airborne pollutants were reported [29]. Apart from traffic, Cu enrichment of soils was attributed to the frequent use of copper fertilizers, as copper sulfate, in numerous soils of Seville.

Nickel also showed high EF_{soil} values and it is strongly suggested that sewage sludge applied to urban soils is one of the possible reason for the enrichment. This also accounts for the Cu accumulations.

4. Conclusions

Regarding to the first objective of the present work, the levels of all elements studied were under the maximum acceptable limit for residential, recreational and institutional areas. The study supports the conclusion that the studied soils of Seville are not significantly contaminated by metals, even if there are higher levels of Pb, Ba, Cu and Ni than in the control site. The two species tested by the EF behaved as excluders of all the studied elements.

Regarding the second objective, the main source of pollutants such as Ba, Cu, Ni and Pb is the vehicular traffic, sludge application and the use of fertilizer. Soil pollution was not directly related to inputs of fine airborne particulate matter (PM_{10}) by direct deposition except for copper. For copper, dry deposition (sedimentable particles) or wet deposition (rain water) were the two suggested causes of direct deposition. For the other elements, a long deposition process over the time was the most probable cause. In addition, *N. oleander* and *L. camara* are not useful as bio-monitors of soil pollution for the studied elements. The only exception to the previous finding was *N. oleander* leaf, which was suggested as a candidate for the monitoring of Cu soil pollution, although more investigation is needed to confirm it. Therefore, copper is found to be the only element interrelated between the three systems, soils, plants and atmospheric particles.

Regarding the third objective, results on CF and EF_{soil} parameters suggested that there was a low metal translocation from soil to both plants in all sampling sites of Seville, indicating that the accumulation in soils of anthropogenic elements was caused by atmospheric dry and wet deposition process.

Interesting conclusions on Fe and Cu accumulations on *N. oleander* leaves from PM_{10} particles have already been published in a previous study [24]. Conclusions on Pb, Ba, Ni and Cu accumulation processes on both types of soils from PM_{10} particles were demonstrated in the present study. Consequently, interesting studies on dry and wet deposition of urban atmospheric samples will be developed as an issue of another study.

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