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

[1]S. Rossini Oliva and [2]A.J. Fernández Espinosa*

[1]*Department of Plant Biology and Ecology, University of Seville, Av. Reina Mercedes s/n, Apdo. 1095,E-41080 Seville, Spain, Tel.: +34954557056; Fax: +34954557059*
E-mail: sabina@us.es
[2] *Department of Analytical Chemistry, University of Seville, C. Profesor García González s/n, E-41012, Seville, Spain, Tel.: +34954554368; Fax: +34954557168*
E-mail: anjose@us.es

*Corresponding author

Abstract

The research reports results on metal pollution of urban topsoils 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, Ti and V) was determined by ICP-OES. Twenty-two samples of soil were collected during six months from two different sites of an urban area and from one 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 is 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., affects air pollution levels in urban areas.

The relationship between emissions and pollution levels varies depending on cities. 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 by direct contact or suspended dust [10]. In addition, high levels of metals in urban soils have been recognized as important sources of metal intake in children, elevating metal levels in children's blood. Also, 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 enriched levels of heavy metals relative to natural and anthropogenic background levels [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 elements (e.g. Ba, Cd, V, etc.) remain poorly documented and need 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 found between metal concentrations in PM_{10} particles with either *Nerium oleander* or *Lantana camara* leaves were significant 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, the assessment of the grade of soil contamination in representative sites of the city of Seville. Secondly, the comparison study of trace element levels in PM_{10} particles, leaves of *Nerium oleander* L. and *Lantana camara* L. [24] in relation to those in the soil where the plants have grown. Thirdly, knowledge of the different behaviors of elements in both studied species of plants, investigating also the metals in which soils are enriched.

The relationship between metal contents in plants and particles with soils might be useful to establish a pattern of behavior for bio-monitoring species, providing information of great interest for environmental authorities.

2. Experimental

2.1. Sampling sites

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 5,000 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.

2.2. Sampling and analytical procedure

Twenty-two samples of particles smaller than 10 μm (PM_{10}) and samples of *N. oleander* and *L. camara* adult leaves were collected during autumn 2003 to spring 2004 from different sites [24] (Figure 1). According to local and regional authority information, one of the sampling sites, which represent the area of Seville most affected by the highest vehicular exhausts, is Torneo (TRN); another site with a low traffic density is Porvenir (POR). During the sampling period, the traffic densities in Torneo and Porvenir were 23,067 and 6,908 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 toward the Northern Seville.

Twenty-two soil samples were collected from three sites (POR, TRN and BLK) for two different species of plants (*N. oleander* and *L. camara*). Soils where both plants grow were at different locations in each sampling site, but in close proximity. Soil samples were collected (5-10 cm depth) at the same time as plant and PM_{10} samples. 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.

The soil characteristics surrounding the three sampling sites were different. Therefore, sampling sites can be classified in the following manner: BLK is characterized only by natural and unaltered soil. TRN and POR substrates had been heavily disturbed and were characterized by natural soil and asphalt. Soils were differentiated according to the plant where they grew, oleander soil and lantana soil.

Filter and plant samples were treated according to a previous work [24]. Soil samples were mineralized with 8 ml of a mixture of HNO_3 and HCl (1:3) in a microwave digestion system. This method is widely used in environmental geochemistry studies and recommended by the National Government regulation. After digestion and cooling, sample solutions were transferred to 15 mL sterile tubes. The concentrations of Ba, Cd, Cu, Fe, Pb, Mn, Ni, Ti and V were determined simultaneously by inductively coupled plasma atomic emission spectrometry (ICP-OES), using a Fisons-ARL 3410 sequential multi-element instrument.

The accuracy of the determinations was previously checked by analysis of a NIST reference material (SRM 2711). The recovery range was from 71.9 to 97.6 %, which proved the validity of the methodology used.

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.

2.3. Data 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 analyses were carried out using the CSS: STATISTICA (StatSoft) software package. Basic statistic was used to calculate the mean values and standard deviations while ANOVA was used to detect significant differences between 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.

3. Results and discussion

3.1. Element concentrations in soil samples

Descriptive statistics of metal concentrations of soils in the different sites are reported in Table 1. The dispersion of data is small for elements in oleander soils and lantana soils except for Cu, Ba, Ni and, mainly Pb in lantana soils; this indicates that soil compositions are homogeneous for the other elements, being Pb, Cu, Ba and Ni elements of variable composition possibly originated from anthropogenic sources [6]. Large element variability rather than a high concentration provides an indication of an unusual element source [6,17].

In Table 1 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 are some similarities between the present data and those of Seville in 2002 [10], whilst the comparison also suggests that the soils studied have higher contents in Ni and V than in Madrid. This can correspond to some degree of pollution by these metals in Seville probably due to frequent emissions during the past from nearby big industries actually disappearing [25]. With regards to traffic sources, it is well known that Pb and Cu come from leaded fuel and brake linings in motor vehicles, respectively [6]. According to Quebec Ministry of Environment (QME), the Pb and Cu contents in soils of both sampling sites can be considering 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) are 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].

Oleander soils

Results of the Scheffé Test show that element concentrations in oleander soil differ significantly ($p < 0.05$) among the sampling sites, except for Mn. The Pb concentration was significantly low 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 are 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 is the result of accumulation process from atmospheric sources during the past years, mainly traffic. Traffic in Seville was concentrated surrounding the historical center before the new roads and avenues made due to the Exposition Universal of 1992 (Expo92). This high traffic density in the past affecting TRN and POR 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 were not observed. Both elements were considered as anthropogenic, which explains the lower values found in BLK. Apart from traffic, contamination of soils by Cu is probably derived from use of fertilizers, sprays, bactericides, fungicides and agricultural or municipal wastes as well as from industrial emissions [26,27]. Ni emissions normally come from combustion of fossil fuels. Furthermore, atmospheric pollution by Ni is high in Seville due to industrial sources [24].

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.

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 higher than in the urban soils of other work [20]. Fe and V can be considered elements from soils [28] and Ti is a lithophilic element [24]. 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 the elements Pb, Cu, Ni and Ba were associated to vehicular traffic. Besides these two groups, conclusions on Manganese suggest a different behavior.

3.2. Comparison with plant and particle contents

Inter-element relationships provide interesting information on heavy metal sources and pathways. Correlation analysis (Table 2) shows that Pb, Ba, Cu and Ni were negatively correlated with Cd, Fe, V and Ti suggesting that these elements come from different sources. These correlations corroborate 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, appears together with typical crustal elements. It is the only unusual result hard to explain. However, low dispersion values for its level in soil (Table 1), even for the less abundant element, confirm the association with these metals.

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 are not presented) indicating that concentrations of elements in plant leaves arise mainly via the atmosphere. In the present study, the soil contamination has not influenced 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 [29]. 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 [30]. Other studies reached the same conclusion [31]. 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 depends on other factors such as climatic and 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 [32] 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 is 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 [26,27] and the washing process does not remove all Cu deposited on the leaf surface [33]. 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 [26]. 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 past due to the different pollution sources, whilst the PM_{10} composition varies on a daily basis.

3.3. 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 3). 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 is mainly controlled by anthropogenic sources and that Ti, V, Cd and Fe can be inferred to as lithogenic. The second PC (PC2, variance of 16%) is formed only by Mn, which again confirms that it has a different origin. Results of the Scheffé Test (Table 1) demonstrated that geochemical and geographical distribution was different from the previous groups.

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

For lantana soils, the PCA distribution is different to that for oleander soils (Table 3), however the same groups were extracted. The two PCs explain 85% of the total variance but PC1 and PC2 were contrarily distributed. PC1 is formed by Fe, Cd, Mn, V and Ti and the second PC contains Ba, Ni, Pb and Cu. Thus, in lantana soils, anthropogenic sources have less significance (PC2, variance of 21%) than crustal elements (PC1, 64%).

Cluster analysis (Figure 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 confirm again that elements studied come from two different sources in both types of soils, which 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 (Figure 3). Two main clusters were obtained; one of those (C2) includes 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.

3.4. Concentration factors and enrichment factors

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 [34] 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 non-influenced by elements (indicator), and ratios <1 shows that plants exclude the elements from uptake (excluder) [35].

Results of CF (Table 4) display that both species exhibit 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 of all studied elements. In a study around industrial areas, the same behavior was found for oleander leaves, except for Cu [17,31].

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 are 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 are clearly enriched by Pb, Ba, Cu and Ni in POR and TRN compared to the local background levels (Figure 4, a and b), confirming that they are derived from anthropogenic activities.

The EF_{soil} for Pb was the highest value, indicating that urban soils are 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 [27]. Apart from traffic, Cu enrichment of soils is 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, apart from industrial combustions, sewage sludge applied to urban soils is one of the possible reason for the enrichment. This also accounts for the Cu accumulations.

4. Conclusions

The levels of all elements studied are 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. 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 is 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 candicate 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.

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

Interesting conclusions on Fe and Cu accumulation on *N. oleander* leaves from PM_{10} particles have already published in a previous study [24]. Conclusions on Pb, Ba, Ni and Cu accumulation process 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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Table 1. Mean element concentrations (mg kg^{-1} ± SD) in soil samples collected in different sites. N: soil of *Nerium oleander*; L: soil of *Lantana camara.*

Sampling site	Ba	Cd	Cu	Fe (%)	Mn	Ni	Pb	V	Ti
N, POR	266±28*	6.50±0.44*	72.1±9.8*	2.25±0.16*	554±23	23.7±1.2*	174±16*	44.5±5.3*	1162±315*
N,TRN	339±60*	6.33±0.82*	71±17*	2.24±0.29*	612±73	23.7±2.3*	142±29*	43.9±5.6*	1690±234*
N,BLK	94.3±8.1	10.30±0.92	30.3±5.4	3.67±0.40	612±89	13.2±3.4	22.4±4.2	102±14	6232±1639
L, POR	294±36*	7.8±1.1*	80±21	2.71±0.54*	583±74*	29.3±7.1*	123±20*	57.9±7.6*	1687±449*
L, TRN	189±74*	6.58±0.89*	77±49	2.28±0.33*	470±50*	18.9±3.7*	92±57*	48±12*	1776±562*
L, BLK	86.0±3.7	10.60±0.80	25.7±1.8	3.87±0.16	649±56	10.60±0.50	20±12	110.0±5.6	8353±1490
Madrid et al. (2002)	n.a.	n.a.	68±64	2.01±0.32	471±103	22±6	137±160	n.a	n.a.
De Miguel et al. (1998)	369±64	n.a.	72±37	2.31±0.35	437±118	14±4	161±82	30±3	2135±319

*Indicate significant (Scheffé test, $p<0.05$) statistical differences with respect to the BLK.
n.a., not available.

Table 2. Correlation matrix of the total element concentrations in *N. oleander* and *L. camara* soils

N. oleander	Ba	Cd	Cu	Fe	Mn	Ni	Pb	V	Ti
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	Cd	Cu	Fe	Mn	Ni	Pb	V	Ti
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

Table 3. Factor loadings for the metal contents in oleander and lantana soil samples. Marked loadings are >0.7.

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.

Table 4. 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

FIGURE CAPTIONS

Figure 1. Location of sampling sites in the studied area of Seville

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

Figure 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.

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

Figure 1

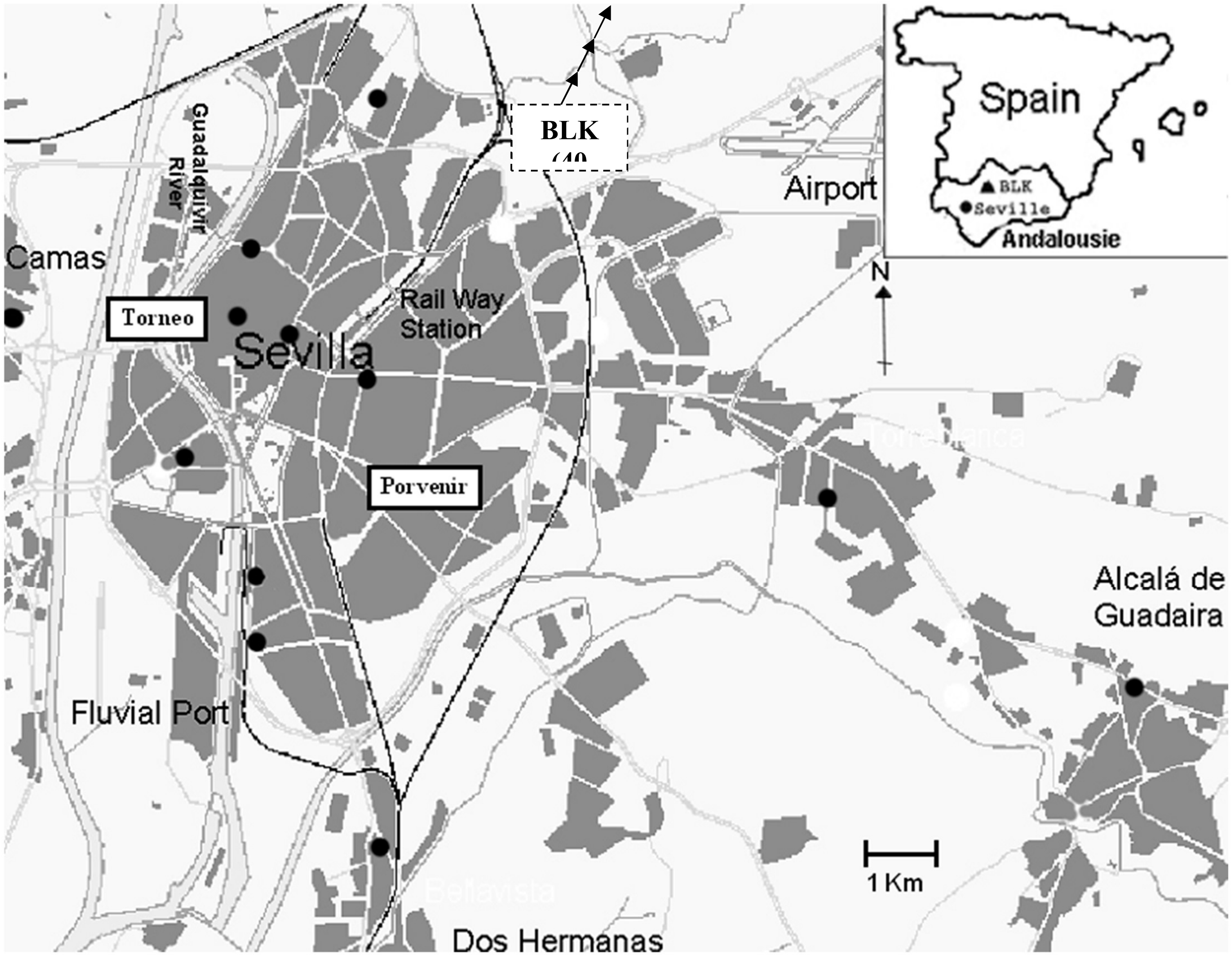
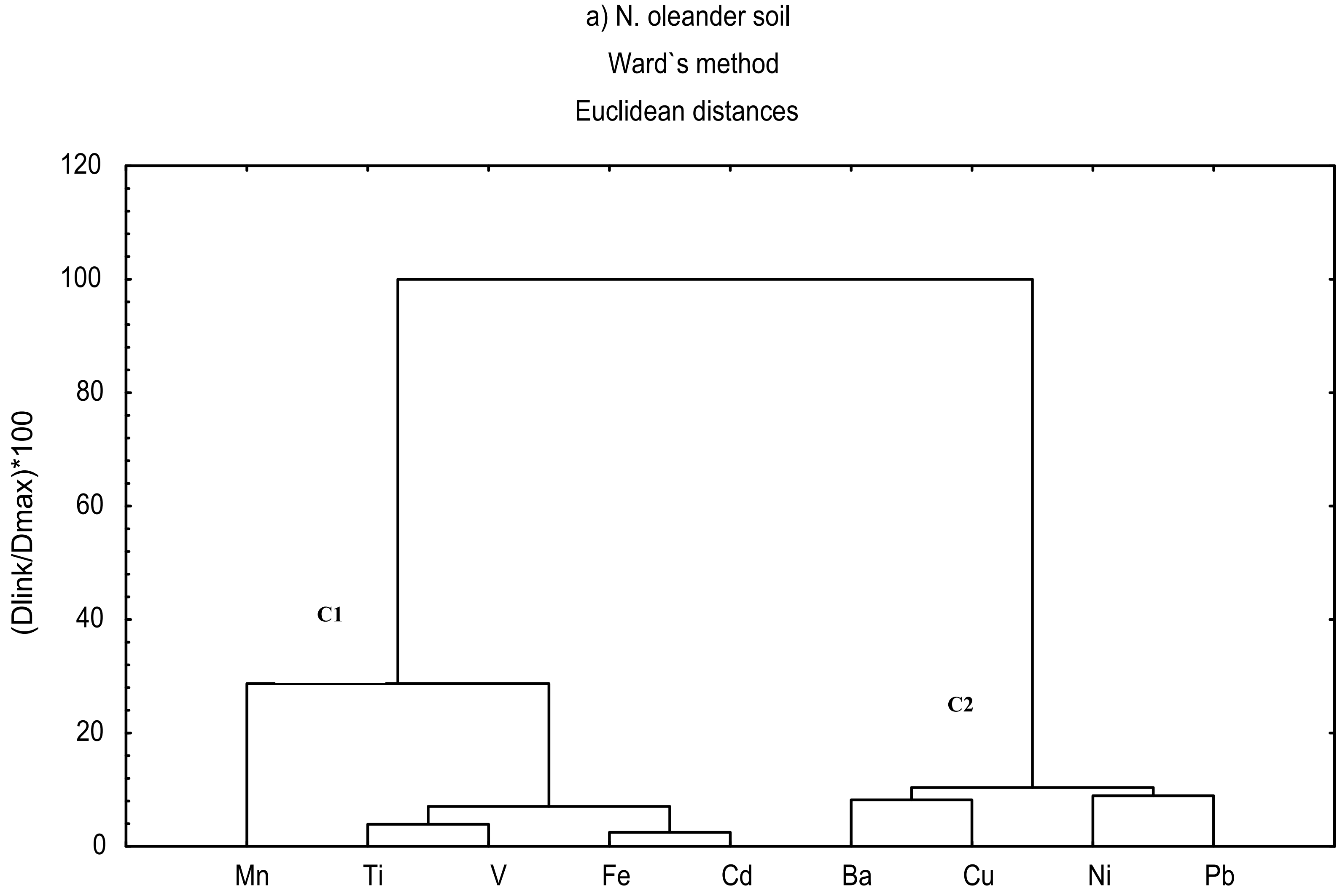

BLK
(40
Airport
Spain
▲BLK
●Seville
Andalousie
Guadalquivir River
Camas
Torneo
Rail Way Station
Sevilla
N
Porvenir
Torreblanca
Alcalá de Guadaira
Fluvial Port
1 Km
Bellavista
Dos Hermanas

Figure 2-a


a) N. oleander soil

Ward`s method

Euclidean distances

Figure 2-b

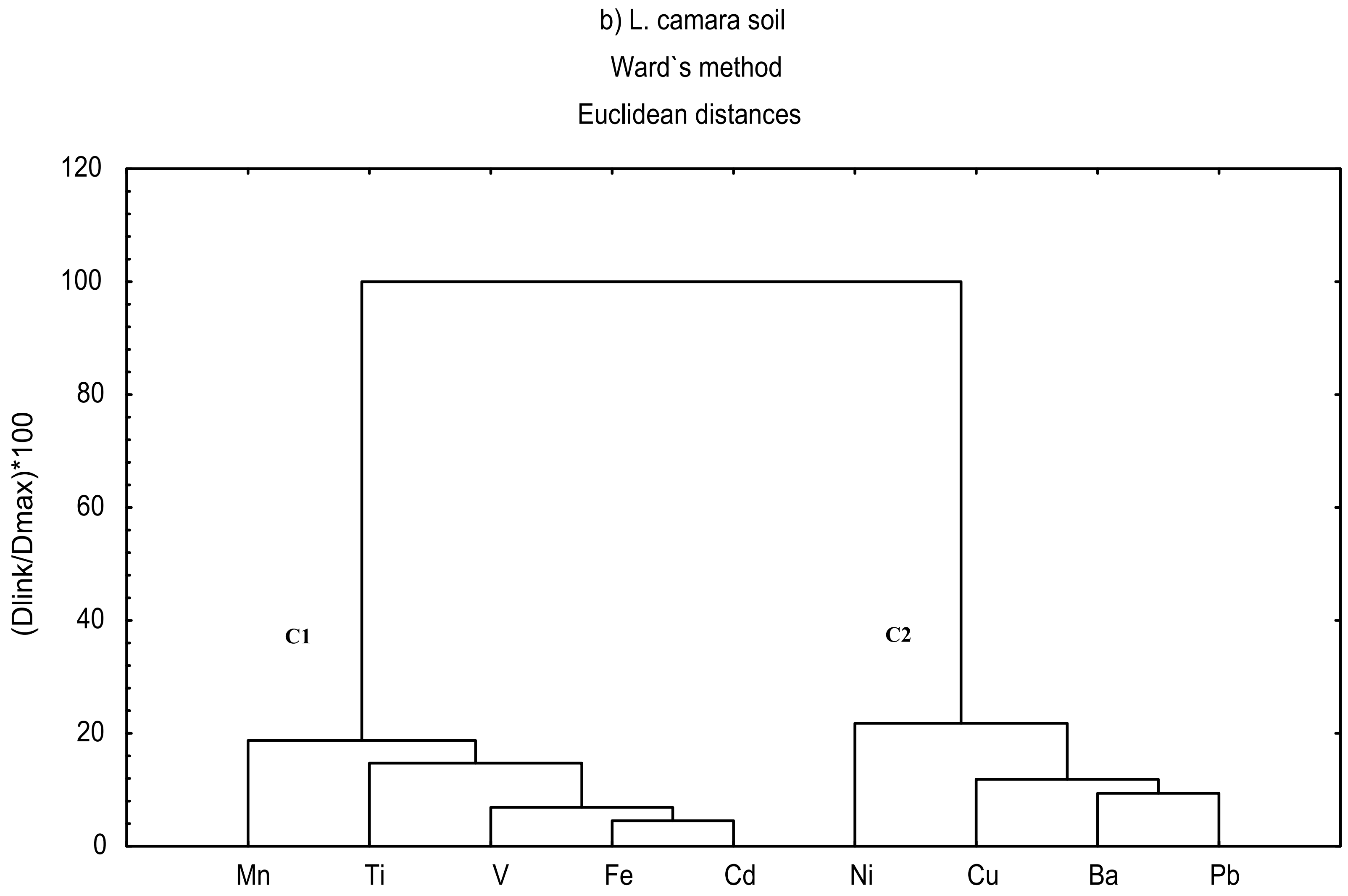

b) L. camara soil
Ward`s method
Euclidean distances
(Dlink/Dmax)*100
120
100
80
60
40
20
0
C1
C2
Mn
Ti
V
Fe
Cd
Ni
Cu
Ba
Pb

Figure 3

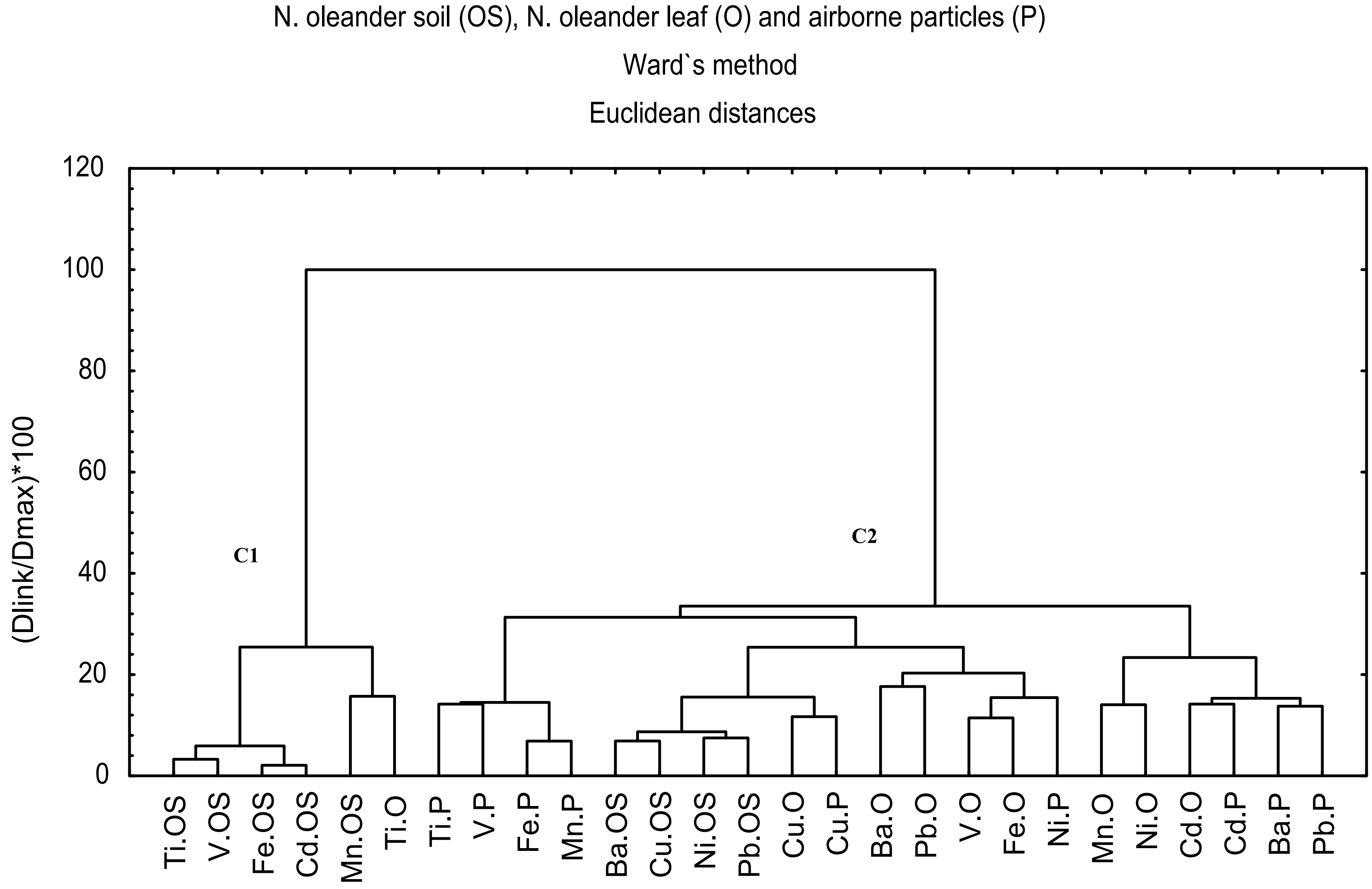

N. oleander soil (OS), N. oleander leaf (O) and airborne particles (P)
Ward`s method
Euclidean distances
(Dlink/Dmax)*100
120
100
80
60
40
20
0
C1
C2
Ti.OS
V.OS
Fe.OS
Cd.OS
Mn.OS
Ti.O
Ti.P
V.P
Fe.P
Mn.P
Ba.OS
Cu.OS
Ni.OS
Pb.OS
Cu.O
Cu.P
Ba.O
Pb.O
V.O
Fe.O
Ni.P
Mn.O
Ni.O
Cd.O
Cd.P
Ba.P
Pb.P

Figure 4-a

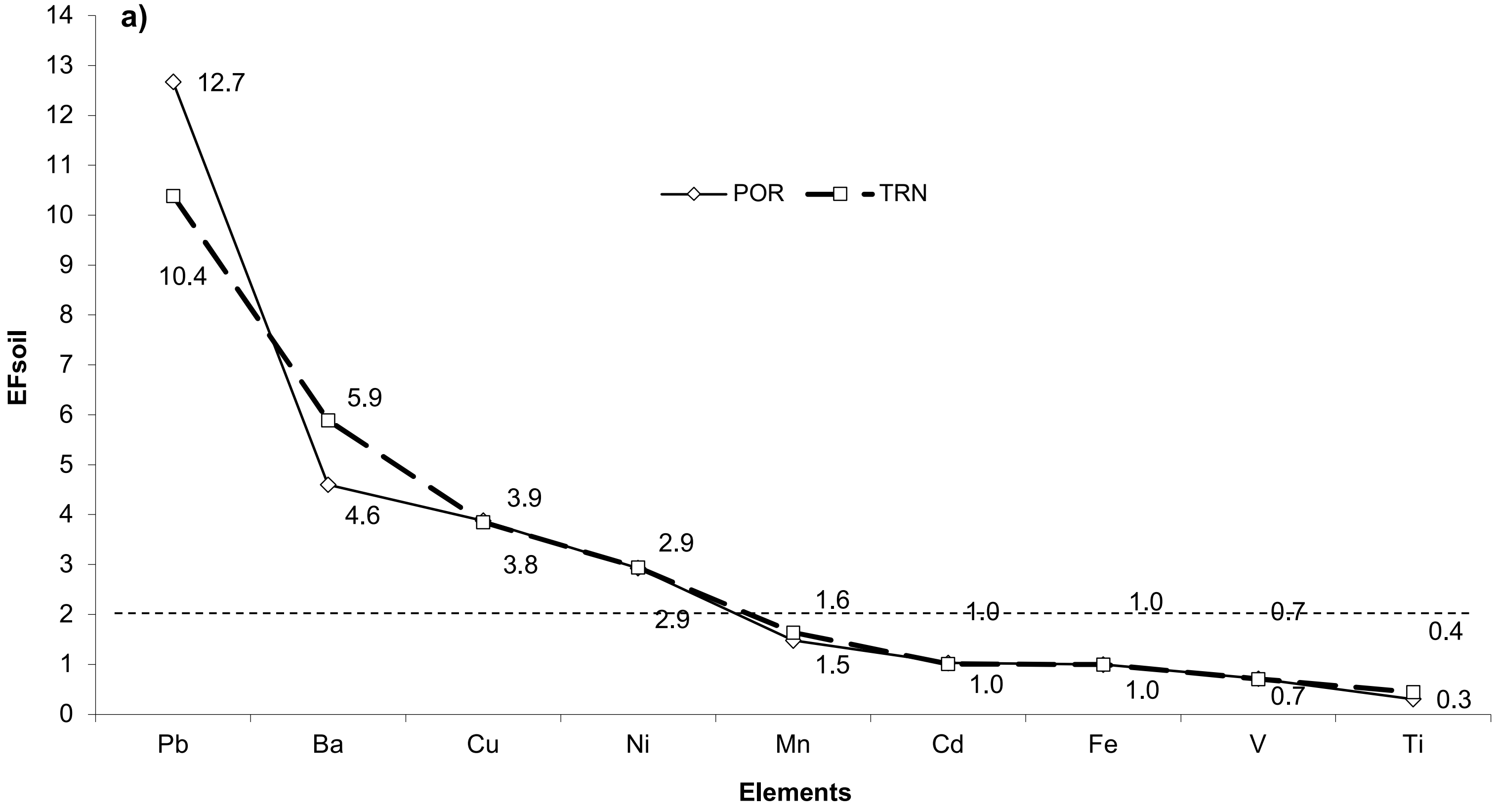
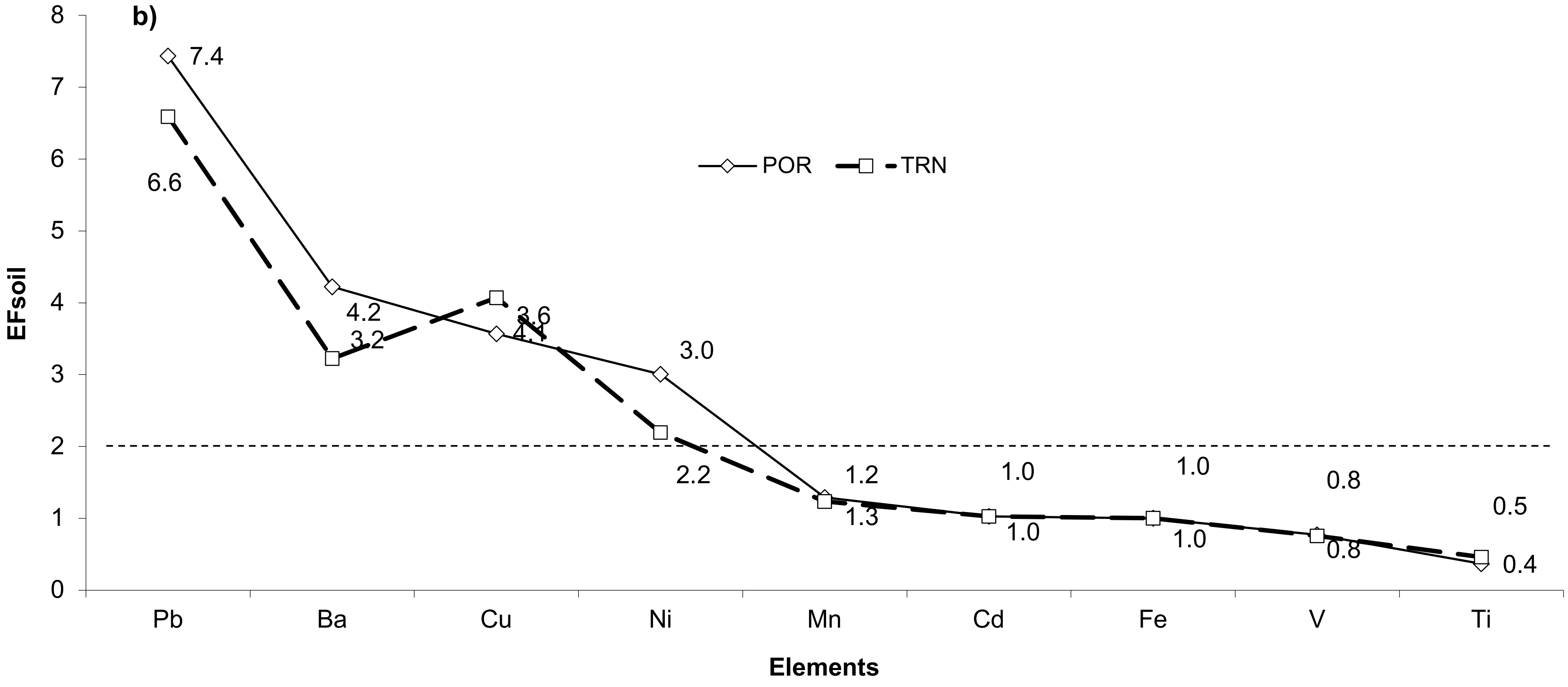

a)
EFsoil
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
POR
TRN
12.7
10.4
5.9
4.6
3.9
3.8
2.9
2.9
1.6
1.5
1.0
1.0
1.0
1.0
0.7
0.7
0.4
0.3
Pb
Ba
Cu
Ni
Mn
Cd
Fe
V
Ti
Elements

Figure 4-b


b)
EFsoil
8
7
6
5
4
3
2
1
0
POR
TRN
7.4
6.6
4.2
3.2
3.6
4.1
3.0
2.2
1.2
1.3
1.0
1.0
1.0
1.0
0.8
0.8
0.5
0.4
Pb
Ba
Cu
Ni
Mn
Cd
Fe
V
Ti
Elements