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# Elevated heavy metal concentrations in top soils of an Aegean island town (Greece): total and available forms, origin and distribution

**I. Massas · C. Ehaliotis · S. Gerontidis · E. Sarris**

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**Abstract** Elevated heavy metal concentrations in urban top soils are principal indicators of environmental pollution; however, relative data on the heavy metal status in soils of Greek island towns, that are regional administrative centers and popular tourist destinations, are missing. A survey was conducted to examine heavy metal concentrations in the urban soils of Ermoupolis, the capital of Syros island and of the prefecture of Cyclades complex in the Aegean Sea. Total (aqua-regia extracted) and available (DTPA extracted) concentrations of Cu, Pb, Zn, Ni, Cr, Sn and Fe were determined in top soil samples collected from green areas and open spaces of the town and in surface samples from inland reference soils of the island. Mean values for the aqua-regia extracted fraction of Cu, Pb and Zn were 117, 155 and 440 mg kg$^{-1}$ respectively, up to four times higher than the respective mean values of the reference soils. Enrichment factors (EFs) for these metals indicated high accumulation in the urban top soils and the available to total concentration ratio of Cu, Pb, Zn and Fe was higher for the urban compared to the reference soils, suggesting differences in metal sequestration, resulting in higher metal availability in the urban soils. GIS analysis was used to visualize the spatial distribution of EFs of the studied heavy metals. Factor Analysis and Cluster Analysis, applied to aqua-regia and DTPA data sets, adequately elucidated the origin of metals grouped under each factor or cluster.

**Keywords** Aqua regia · Cluster analysis · DTPA · Enrichment factor · Factor analysis · Heavy metals · Island soils · Urban soils

## Introduction

Since top soils are main “receptors” of elements emitted to urban environments from various sources as motor exhaust pipes, industrial activities, waste disposal and incineration, heavy metal concentrations in top soils are considered as tracers of environmental pollution and “health indicators” for the urban environment (Onianwa 2001; Imperato et al. 2003; Turkoglu et al. 2003; Yilmaz et al. 2003; Moller et al. 2005; Bretzel and Calderisi 2006; Crnkovic et al. 2006; Ljung et al. 2006; Hjortenkrans et al. 2006; Wang and Qin 2006; Wang et al. 2006). Contamination of urban soils with heavy metals can also cause groundwater contamination because metals in the polluted soils tend to be more mobile than those of unpolluted ones due to speciation (Wilcke et al. 1998, Manta et al. 2002).

I. Massas (✉) · C. Ehaliotis · S. Gerontidis · E. Sarris
Soil Science Laboratory, Agricultural University of Athens,
Iera odos 75,
118 55 Athens, Greece
e-mail: massas@aua.gr

Heavy metals are always present in soils due to natural weathering of parent rock material and pedogenesis processes. However, their accumulation into soils has been the subject of much attention since they do not decay with time and they may become toxic to microbial and plant biota when exceeding threshold values. Heavy metals are generally present in soils in cationic forms and therefore they may show low availability even at high total concentrations, since they interact with the soil matrix. However, they can become mobile as a result of changing environmental conditions or by saturation exceeding the buffering capacity of a soil, a situation referred to as "chemical time bomb" (Facchinelli et al. 2001).

Urban soils differ from agricultural and natural soils, mainly because they are characterized by the absence of soil structure leading to compaction, modified soil reaction, restricted aeration and water drainage, high content of anthropogenic materials, and modified community structure and activity of soil organisms (Bretzel and Calderisi 2006).

To determine whether or not urban soils are contaminated by certain elements, background levels of these elements are needed. Background measurements represent natural elemental concentrations in the soils without human interference. However, due to long-range transport of contaminants, truly pristine ecosystems may no longer exist, making the establishment of background concentrations a difficult task (Chen et al. 1999).

The status of a range of heavy metals, usually arising from various pollution sources, is typically examined within in situ pollution studies. Therefore, factor and principal component analyses (FA and PCA) have been widely used to reveal variable redundancy, and combine variables into single factors (Wilcke et al. 1998; Chen et al. 1999; Kumru and Bakac 2003; Navas and Machin 2002; Bretzel and Calderisi 2006). Cluster analysis (CA) is often coupled to FA and PCA to provide groupings of individual variables according to distances or similarity indices (Facchinelli et al. 2001; Granero and Domingo 2002; Manta et al. 2002; Wang et al. 2005; Han et al. 2006). The interpretation of the above data processing aids to identify pollution sources and apportion natural vs. anthropic contribution. GIS processing software is increasingly used in environmental studies because of its ability to expose non point source contaminants (Sultan 2007; Wang et al. 2006) and as a visual aid in interpreting heavy metals spatial distribution.

Data for heavy metals concentrations in the soils of major Greek cities are scarce and mainly reported for the city of Athens (Yassoglou et al. 1987; Chronopoulos et al. 1997; Chronopoulou-Sereli et al. 1999; Michopoulos et al. 2005; Riga-Karandinos et al. 2006), whereas data for small towns and isolated island soils are completely missing.

Ermoupolis is the capital of Syros, a typical semi-arid Mediterranean island, and of the prefecture of the Cyclades islands complex in the Aegean Sea, latitude 35°16′0 N and longitude 26°16′60 E (Fig. 1). The town has approximately 25,000 inhabitants, but the population increases considerably during July and

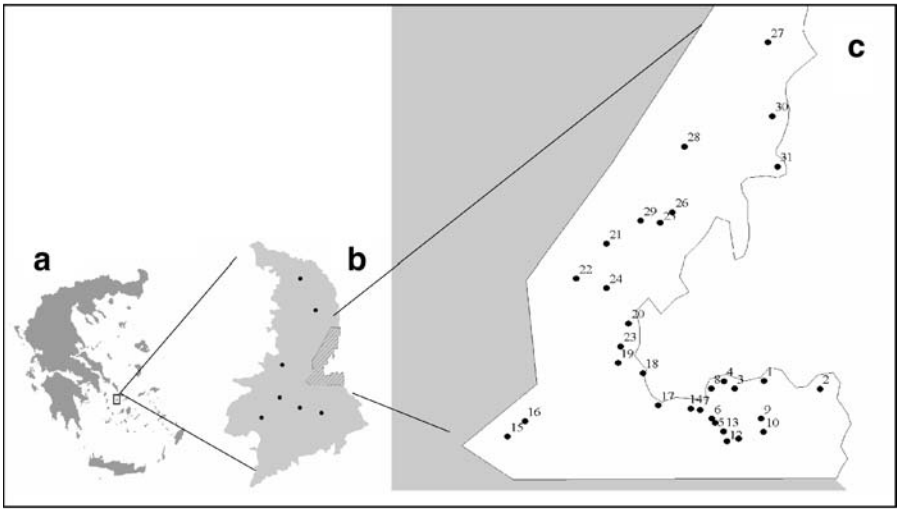


**Fig. 1** Study area and sampling sites: **a** Greece-Syros island, **b** Syros island – inland reference soils sampling sites, **c** Ermoupolis – urban soils sampling sites

August each year, and the proximity of Syros island to Athens makes it an attractive tourist destination during weekends. Ermoupolis is characterized by a dense building layout with narrow streets, covering an area of approximately 600 ha. Its location at the foot of two hills, protects the town from the northern and western winds but does not aid the dispersion of the pollutants produced by the traffic load (peaking during the summer period), the local power station, the shipyard facilities and other minor manufacturing plants, present within the administrative limits of the town or in its precincts.

The aims of this survey were: (1) to measure total and bio-available concentrations of Zn, Cu, Fe, Pb, Ni, Cr and Sn in the top soils of Ermopoulis (Syros island-Greece) (2) to check for possible enrichment of the urban soils with the above heavy metals, and (3) to detect spatial distribution and different sources of metals accumulation in the urban soils.

## Materials and methods

### Soil sampling

A total of 38 top soil samples (0–10 cm depth) were sampled from the island of Syros. Thirty one of them were obtained from green areas and open spaces within the urban network of Ermoupolis. The rest were from inland sites arbitrarily selected to represent the natural soils of the island (Fig. 1). Since these seven samples served for estimating the reference metal concentrations in the soils of Syros, sampling from agricultural soils and soils close to point pollution sources (roads, industrial activities, waste disposal sites) was excluded. At each sampling site three sub-samples, each from a 40×40 cm surface area, were obtained and mixed to make a bulk sample.

### Analytical methods

The soil samples were air-dried for approximately 48 h and sieved through a 2-mm sieve. The samples were analyzed for cation exchange capacity (CEC) by the Na-acetate method (Bower et al. 1952), organic matter by the Walkley–Black procedure (Nelson and Sommers 1982), mechanical composition by the Bouyoucos hydrometer method (Bouyoucos 1951), pH by glass/calomel electrodes in 1:1 soil–water ratio, exchangeable cations were obtained by the $NH_4$-acetate method (Page 1982) and carbonates, expressed as equivalent $CaCO_3$, by measuring the evolved $CO_2$ following HCl dissolution.

"Pseudo-total" metal concentrations were obtained by digesting soil samples with aqua regia (Gasparatos and Haidouti 2001). This method is widely used in soil pollution studies and the term "pseudo-total" accounts for that aqua regia digestion not completely destroying silicates. The bio-available fraction of the studied metals was extracted with DTPA, as described by Lindsay and Norvell (1978). For simplicity, the terms *total* and *available* are used in the text for the aqua-regia and DTPA extracted metal fractions respectively.

All metal concentrations were determined by atomic absorption spectrophotometry, using a Varian-spectra A300. The calibration standards were prepared in the same matrix used for the soil samples. At all stages of sample preparation and analysis stringent precautions were taken to minimize contamination from air, glassware and analytical grade reagents were used. A control sample was analyzed for every 10 samples and reproducibility was tested by reanalyzing 30% of the samples. The analytical precision, measured as relative standard deviation, was less than 3%.

### Enrichment factors (EFS)

There is no unique determination of the term enrichment factor in soil pollution studies. Usually, the ratio of metal concentration in the studied soils divided by the respective mean value for the world unpolluted soils or for the background soils of the region is used (Manta et al. 2002; Cemek and Kizikkaya 2006; Wang et al. 2006). Another common way to express an EF of topsoils, presented as TEF (top enrichment factor) by Facchinelli et al. (2001), is to divide the metal concentration in the surface soil by the respective concentration in the subsurface sample(s).

In this study EFs of all the studied metals were calculated for every sampling site in the town as the total concentration of the metal in the sampling site divided by the mean total metal concentration of the inland reference soils. EFs greater than unity indicate that the respective metals are more abundant in the urban soils relative to inland reference soils. However, small enrichments should not be considered as significant, though they are indicators of metal accumulation, because they arise form differences in the composition of urban and reference soil material used in EF calculation. Therefore a threshold value of EF>1.5 was used in this study.

Spatial distribution of enrichment factors (EF) in the urban soils of Ermoupolis is visualized on maps produced by ARC-VIEW GIS V9.0 software. The SPATIAL ANALYST extension was used for spatial analysis, while for every EF data set a grid archive was created to interpolate EF values between the sampling sites and grids with a 9 m cell size created by the inverse distance weighted method.

### Statistics

In this study two multivariate techniques were applied to the data sets, cluster analysis (CA) and factor analysis (FA). The statistical analysis, descriptive statistics, correlation, FA and CA were performed using Statistica 6 software for Windows.

## Results and discussion

### Soil physicochemical characteristics

The physico-chemical properties of the urban soils of Ermoupolis and the inland reference soils of the island of Syros are presented in Table 1. No clear pattern of differences between the urban and inland soils is observed except that the mean organic matter content and the mean exchangeable sodium, potassium and magnesium concentrations were higher in the urban soils. The higher organic matter content is probably due to vegetation differences. In many green areas of the town the presence of higher plants leads to top soil enrichment with organic materials while in the inland sampling sites soils were bare or covered with sparse low height vegetation resulting to lower organic matter input. Differences in exchangeable sodium, potassium and magnesium values are mainly attributed to salts of these elements present in the sea spray that moistens most of the urban soils, and in some cases also increases the EC of top soils close to the coastal line (data of EC not presented). Overall, the soils of the island are characterized by low to medium clay and organic matter content and neutral to alkaline pH related to the presence of carbonate salts.

### Total metal concentrations

Descriptive statistics for the aqua regia extracted fraction of Zn, Ni, Cr, Pb, Cu, Sn and Fe for both the urban and inland soils are listed in Table 2. Urban soils showed higher total concentrations for Zn, Pb and Cu compared to inland soils. They also showed large and skewed data distributions resulting in higher mean compared to median values, which was not observed in inland soils and points to urban influences (site specific pollution). Urban soils also appear to be enriched with Zn, Pb and Cu compared to reference values for world unpolluted soils. Accord-

**Table 1** Descriptive statistics of physicochemical properties of the studied soils ($N$=31 and $N$=7 for urban and inland reference soils respectively)

| | Clay (%) | Silt (%) | Sand (%) | O.M.[a] (%) | pH (1:1) | $CaCO_3$ (%) | C.E.C.[b] | $K^+$ | $Na^+$ meq/100g | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Urban soils | | | | | | | | | | | |
| Mean | 12.4 | 31.1 | 56.5 | 2.56 | 7.8 | 16.3 | 11.83 | 0.53 | 1.16 | 12.22 | 2.46 |
| Median | 10.8 | 29.7 | 57.5 | 1.94 | 7.8 | 16.4 | 10.84 | 0.46 | 1.06 | 13.25 | 2.41 |
| S.D. | 6.2 | 5.6 | 8.6 | 2.03 | 0.7 | 14.9 | 4.86 | 0.30 | 0.98 | 5.09 | 1.15 |
| C.V.% | 50 | 18 | 15 | 79 | 9 | 91 | 41 | 57 | 84 | 42 | 47 |
| Inland soils | | | | | | | | | | | |
| Mean | 13.3 | 32.2 | 54.5 | 1.72 | 7.9 | 19.6 | 12.64 | 0.31 | 0.53 | 16.24 | 1.38 |
| Median | 10.8 | 31.6 | 54.9 | 1.74 | 7.9 | 16.6 | 12.04 | 0.25 | 0.51 | 17.35 | 1.41 |
| S.D. | 4.1 | 5.6 | 6.8 | 0.90 | 0.1 | 12.3 | 2.55 | 0.16 | 0.29 | 5.14 | 0.42 |
| C.V.% | 31 | 17 | 12 | 52 | 1 | 63 | 20 | 52 | 55 | 32 | 30 |

[a] Organic matter

[b] Cation exchange capacity

**Table 2** Descriptive statistics for total (aqua regia extracted fraction) and available (DTPA extracted fraction) metal concentrations in the urban soils of Ermoupolis and the inland reference soils of Syros island

| | Total metal concentrations | | | | | | | Available metal concentrations | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fe[a] | Zn | Ni | Cr (mg kg$^{-1}$) | Pb | Cu | Sn | Fe | Zn | Ni | Cr (mg kg$^{-1}$) | Pb | Cu |
| Urban soils | | | | | | | | | | | | | |
| Mean | 3.7 | 440.4 | 47.5 | 66.6 | 155.1 | 116.5 | 5.4 | 12.4 | 9.0 | 0.6 | 0.3 | 21.5 | 9.8 |
| Median | 3.8 | 216.9 | 24.4 | 56.6 | 109.5 | 68.6 | 4.9 | 12.7 | 6.6 | 0.6 | 0.3 | 11.7 | 5.9 |
| SD | 1.2 | 644.1 | 54.6 | 44.3 | 89.7 | 218.7 | 3.7 | 6.9 | 6.6 | 0.2 | 0.0 | 25.3 | 10.6 |
| Min. | 0.7 | 57.5 | 10.2 | 14.3 | 40.3 | 16.7 | 2.6 | 2.2 | 1.5 | 0.3 | 0.2 | 1.7 | 2.0 |
| Max. | 6.0 | 3062.0 | 252.3 | 241.2 | 383.0 | 1277.0 | 22.8 | 32.4 | 26.3 | 1.2 | 0.4 | 99.0 | 41.3 |
| CV% | 32 | 146 | 115 | 66 | 58 | 188 | 68 | 56 | 73 | 35 | 15 | 116 | 108 |
| *N* | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 |
| Inland soils | | | | | | | | | | | | | |
| Mean | 4.6 | 124.7 | 48.8 | 64.0 | 76.2 | 41.7 | 4.7 | 5.9 | 0.9 | 0.6 | 0.3 | 3.3 | 1.4 |
| Median | 4.4 | 111.9 | 45.5 | 65.6 | 73.0 | 42.2 | 4.2 | 6.4 | 0.7 | 0.5 | 0.3 | 3.3 | 1.2 |
| SD | 0.7 | 48.6 | 20.9 | 14.8 | 13.5 | 6.7 | 0.8 | 2.0 | 0.6 | 0.4 | 0.0 | 1.5 | 0.6 |
| Min. | 4.0 | 76.3 | 24.6 | 41.1 | 63.0 | 33.6 | 4.0 | 3.0 | 0.2 | 0.4 | 0.2 | 1.5 | 0.7 |
| Max. | 5.9 | 226.9 | 79.0 | 85.7 | 103.3 | 54.1 | 6.0 | 8.5 | 1.9 | 1.6 | 0.3 | 5.9 | 2.3 |
| CV% | 15 | 39 | 43 | 23 | 18 | 16 | 16 | 34 | 66 | 70 | 8 | 47 | 41 |
| *N* | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |

[a] Values for aqua regia extracted Fe expressed as %

ing to Kabata-Pendias and Pendias (1992) mean Zn, Pb and Cu concentrations in world unpolluted top soils were 100, 44 and 24 mg kg$^{-1}$, respectively, while the respective values for the urban soils of Ermoupolis were 440, 155 and 117 mg kg$^{-1}$. This is up to four times higher than Zn, Pb and Cu mean concentration values for the inland reference soils and two fold higher than the respective median concentration values. In contrary, no considerable differences for Cr, Ni, Sn and Fe concentrations between urban and inland soils were traced. In a recent study for Athens top soils, Riga-Karandinos et al (2006) reported that mean Zn, Pb and Cu concentrations were 449, 578 and 233 mg kg$^{-1}$ respectively. A similar mean value for Zn concentration was obtained by this study, while for Pb and Cu the average concentrations in Ermoupolis top soils were four and two times lower. As it can be seen in Table 3, where average total heavy metal concentrations from various cities and urban areas are presented, the accumulation of Pb in Ermoupolis top soils is generally among the lowest, while those of Cu and Zn are among the highest. Though Ermoupolis is much smaller in size and population than the cities presented in Table 3, the high Zn and Cu concentrations may partially be explained by the architectural structure of the town

**Table 3** Average heavy metal concentrations in urban top soils (mg kg$^{-1}$)

| City/area | Pb | Zn | Cu | Cr | Ni | Sn |
|---|---|---|---|---|---|---|
| Bangkok[a] | 47.8 | 118 | 41.7 | | | |
| Palermo[b] | 202[i] | 138[i] | 63[i] | 34[i] | 17.8[i] | |
| Naples[c] | 262 | 251 | 74 | 11 | | |
| Athens[d] | 577.7 | 449 | 233 | | | |
| Xuzhou[e] | 43.3 | 144.1 | 38.2 | 78.4 | 34.3 | 5.1 |
| Coastal Tuscany[f] | 218.6 | 127.7 | 85 | | 59 | |
| Mexico City (low traffic)[g] | 354.1 | 336 | 61.7 | | | |
| Mexico City (high traffic)[g] | 1,189 | 742 | 98.2 | | | |
| Ermoupolis[h] | 155.1 | 440.4 | 116.5 | 66.6 | 47.5 | 5.4 |

[a] Wilcke et al. (1998)

[b] Manta et al. (2002)

[c] Imperato et al. (2003)

[d] Riga-Karandinos et al. (2006)

[e] Wang et al. (2005)

[f] Bretzel and Calderisi (2006)

[g] Morton-Bermea et al. (2002)

[h] This study

[i] Median values

that does not aid the dispersion of pollutants and the fact that most of the few open and green spaces are close to streets, parking places or manufacturing activities, thus directly affected by the emitted pollutants. Additionally, a high percentage of cars are still operating on leaded gasoline, and may not be properly maintained, since the periodical technical vehicle control applied in the country is not mandatory in Syros island. Following the guide values and quality standards used in the Netherlands for assessing soil contamination (Alloway 1995), mean concentrations of the three metals in the urban soils were up to three times higher than the reference A values (140, 85 and 36 mg kg$^{-1}$, for Zn, Pb and Cu respectively) and in a few sampling sites Zn concentration exceeded the intervention C value (indicating that such soils must be cleaned-up). Considering the test B values (now discontinued), in many sites Zn, Cu and Pb concentrations were measured above the proposed limit, pointing to further investigation and monitoring of these metals in the soils of Ermoupolis. Cr, Ni, and Sn mean total concentrations in Ermoupolis soils are not considerably different from those reported in the literature for urban top soils (Table 3) and do not exceed the reference A guide values.

### Available metal concentrations

DTPA metal concentrations of the top soil samples are presented in Table 2. They may be considered as the available fraction of the metal for microbial assimilation and plant uptake (Qian et al. 1996; Wilcke et al. 1998, Muniz et al. 2001) that may readily enter the food chain. Mean available Pb and Cu concentrations in Ermopoulis top soils were well above the permissible limits for the bio-available concentrations of heavy metals in soils, determined by DTPA extraction, (Kaur and Rani 2006), while mean available Zn concentration was close to the threshold value, pointing to serious soil contamination and to increased possibilities for Pb, Cu and Zn to accumulate into the microbial and plant biota. The higher mean compared to the median values for these metals also indicate site specific pollution and is in line with the total concentration values (Table 2). Cr, Ni and Fe available fractions were within the proposed limits. The very low Sn availability in the studied soils resulted from poor analytical precision; thereby Sn DTPA concentration values are not included. To compare metals availability between urban and inland soils the available to total concentration ratio, expressed as % was calculated for each metal and sampling site. The mean % values of this ratio for all metals are presented in Fig. 2. With the exception of Cr, the availability of the studied metals was significantly higher in urban soils compared to the inland soils (from two times for Ni to five times for Zn), which is in line with findings indicating greater partitioning of heavy metals in the available fraction in contaminated, compared to uncontaminated top soils (Wilcke et al. 1998).

### Enrichment factors and their spatial distribution

EF values up to 30 and 24 for Cu and Zn were found for the urban soils, indicating serious soil contamination due to site specific pollution sources. EF values> 1.5 were observed for all the studied heavy metals, but it was for Zn, Pb and Cu that EFs>1.5 were produced for more than half of the urban sampling sites. Distribution patterns of the enrichment factors of the main pollutant metals (Zn, Cu and Pb) and Sn (for comparison reasons) in the whole urban area of Ermoupolis are presented in Figs. 3 and 4. Similar EF distribution patterns are observed for the pairs Zn and Cu and Pb and Sn. EF values for Zn and Cu exhibit their maximum along the southern part of the town, coinciding with manufacturing and industrial activities, though increased values are also calculated for almost all the urban surface soils. EF values for Pb are maximized in the center of the city but high values are also found for most of the town area, and their distribution is overlapping with the respective Zn and Cu distributions, indicating to an extent a common origin of these metals, mainly vehicle emissions. The

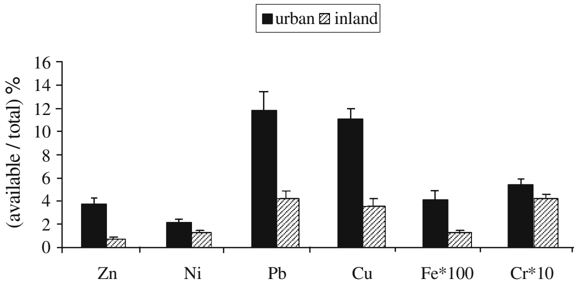


**Fig. 2** Mean available/total concentration ratio (%) of the studied metals for urban and inland soils

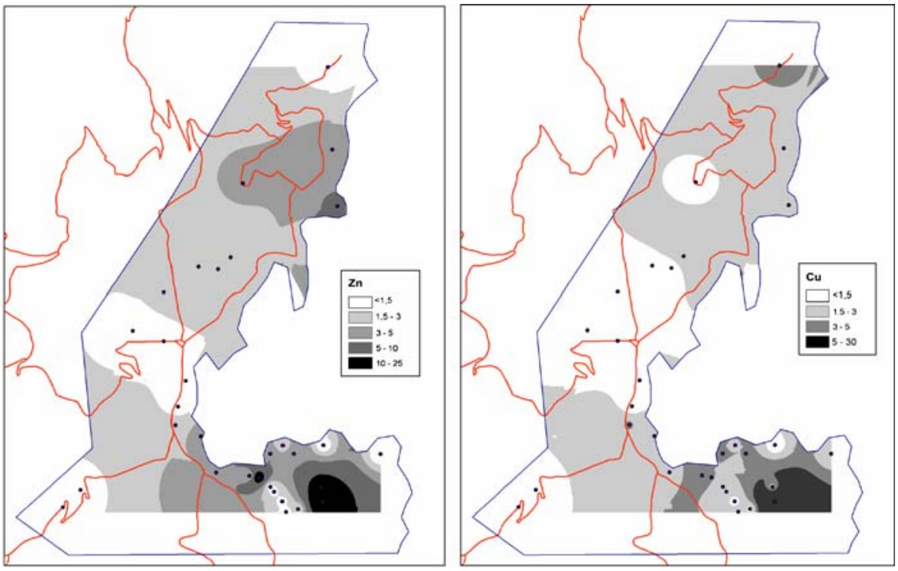


**Fig. 3** Spatial distribution of enrichment factors for Zn and Cu in Ermoupolis top soils

EF values for Sn presented in Fig. 4 are generally low with the exception of a "hot spot" around sampling site 3 in the Southern part of the city probably related to the presence of the nearby shipyard facilities (Jartum et al. 2003). Otherwise the distribution pattern of EF values for Sn is almost identical to the respective distribution for Pb, indicating that the small enrichment of soils with Sn in some urban sampling sites is due to emissions produced by vehicles circulation.

## Factor analysis (FA)

To reduce the high dimensionality of sample/variable space, a factor analysis was applied on standardized urban soil data values for all variables (aqua regia and DTPA data sets). Moreover, FA may delineate the principal processes and sources of the distribution of heavy metal pollution (Korre 1999). The obtained factors were rotated using a varimax normalized algorithm and the factor extraction was done with a

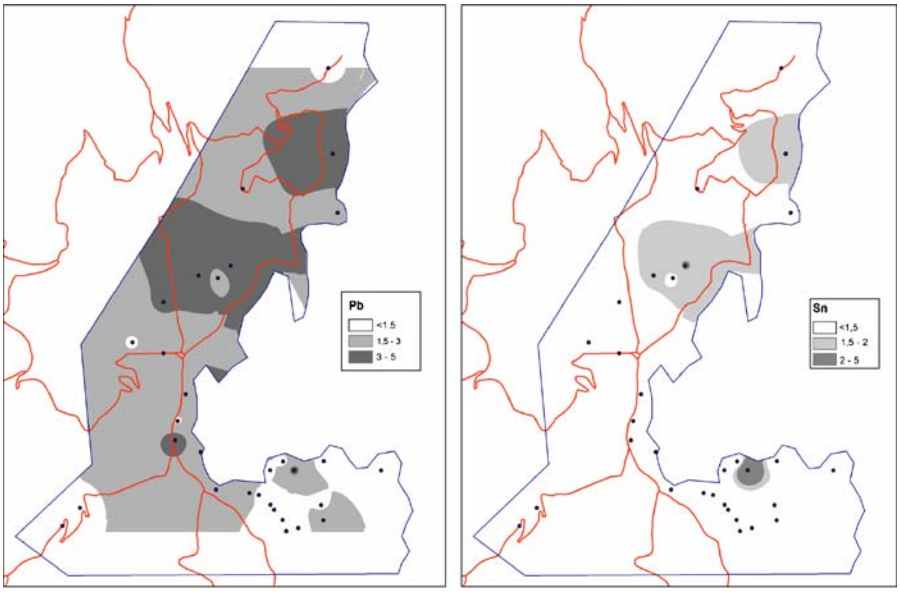


**Fig. 4** Spatial distribution of enrichment factors for Pb and Sn in Ermoupolis top soils

minimum eigenvalue greater then 1 (Manly 1994). FA enabled the extraction of three factors for total and two factors for available metal concentrations explaining 85 and 75% of the total variance respectively (Tables 4 and 5). The communalities shown by the variables are fairly high in both data sets, therefore all the elements are well represented by the extracted factors (Tables 4 and 5).

### *Total metal concentrations data set*

Factor 1 exhibits high loadings for Zn, Cu and Ni and more than 36% of the variance is explained through that factor. Factor 2, describing 25% of the variance, has high factor loadings for Fe and Cr. Factor 3 includes the metals Pb and Sn, explaining 23% of the total variance. The factor scores of all urban sampling sites were calculated and illustrated in Fig. 5. The first factor (factor 1, Fig. 5a), loaded for Zn (0.939), Cu (0.915) and Ni (0.876) shows the highest scores at sampling sites 7, 9 and 10. These sites are located in the Southern part of the city which shows high EF values for Zn and Cu (Fig. 3). The elements grouped under this factor have been linked to the abrasion and corrosion of brake linings, metals and alloys in vehicles and machinery (de Miguel et al. 1997; Jiries et al. 2001; Hjortenkrans et al. 2006). Zn may also derive from tire wear and lubricants (Wang et al. 2005) whereas Cu and Ni may also derive from exhaust fumes to a lesser extent (Hjortenkrans et al. 2006). Apart from automobile traffic, north and west winds may transfer and deposit air particulates on the soils of this area, from the nearby shipyard facilities, the local power station, minor industries and the fossil fuel tank site. Thus, factor 1 is considered as a tracer of pollution sources associated both with traffic and industrial activities (anthropogenic factor). The inclusion of Ni in this factor is not clearly interpreted. Though Ni is an element considered as a pollutant from both industrial and vehicular emissions, the low enrichment factors (EFs) of this metal in the urban surface soils lead to the assumption that Ni originated partly from the parent material, since spots of ultramafic rocks are present in the island giving genesis to soils rich in Ni and Cr. The available fraction of Ni is increased in the urban surface soils however (Fig. 2), indicating a degree of enrichment probably due to polluting sources, not demonstrated by EFs since they were calculated for the total metal concentrations. The second factor (factor 2, Fig. 5b), loaded for Cr (0.902) and Fe (0.879) shows its highest scores at sampling sites distributed in the whole town. This factor may be called the natural origin factor, based on the low total metal concentrations, the low enrichment factors (close to 1) for both metals and the relatively low coefficient of variation of the Fe and Cr total concentrations (Table 2). The third factor (factor 3, Fig. 5c), which consists of Pb (0.890) and Sn (0.887), is significant along the center of the town, with the highest traffic burden, narrow roads and dense building structure that do not facilitate the dispersion of pollutants, and also close to the major town's parking areas. So, this factor appears to be related to the traffic of vehicles (traffic factor).

**Table 4** Values of the extracted factor loadings for the total concentrations of the studied heavy metals

| Factor | Factor 1 | Factor 2 | Factor 3 | Communality |
|---|---|---|---|---|
| Fe | −0.022 | 0.879 | 0.011 | 0.773 |
| Zn | 0.939 | 0.028 | 0.023 | 0.884 |
| Ni | 0.876 | 0.365 | –0.105 | 0.911 |
| Cr | 0.182 | 0.902 | 0.006 | 0.846 |
| Pb | 0.134 | −0.157 | 0.890 | 0.835 |
| Cu | 0.915 | −0.071 | 0.051 | 0.846 |
| Sn | −0.138 | 0.174 | 0.887 | 0.836 |
| Eigenvalue | 2.713 | 1.625 | 1.593 | |
| % Var. expl. | 36.54 | 25.42 | 22.77 | |
| Cum. % var. | 36.54 | 61.96 | 84.73 | |

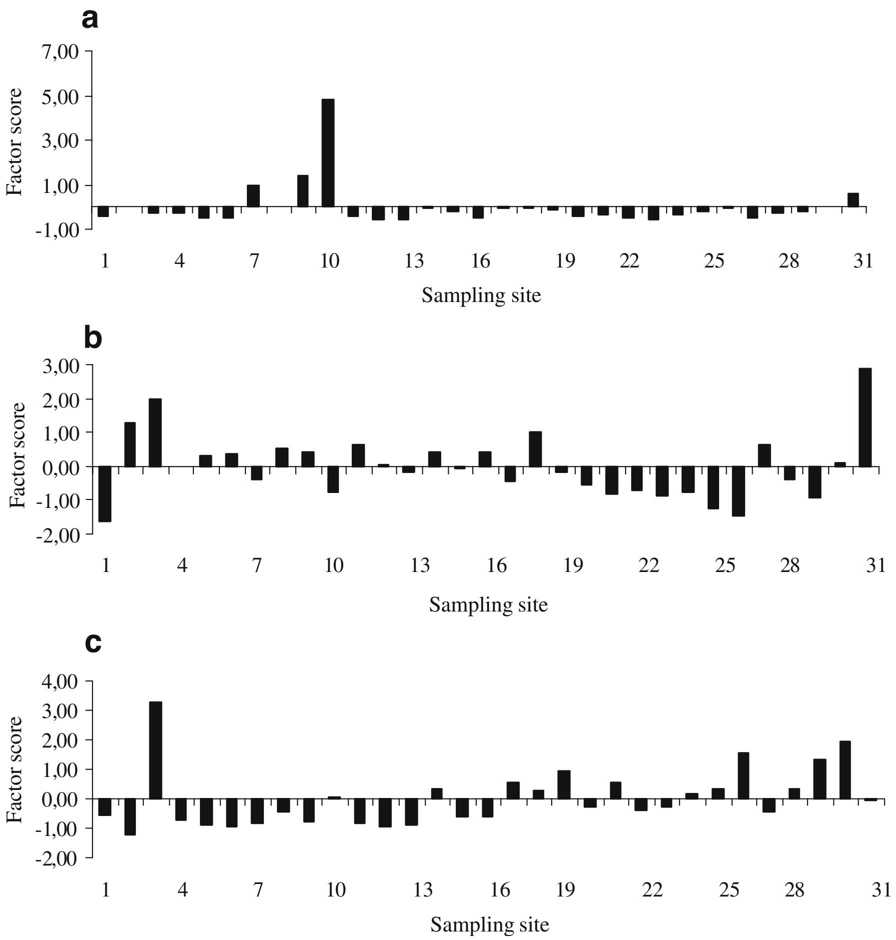
**Table 5** Values of the extracted factor loadings for the available concentrations of the studied heavy metals

| Factor | Factor 1 | Factor 2 | Communality |
|---|---|---|---|
| Fe | −0.030 | 0.887 | 0.787 |
| Zn | 0.827 | 0.375 | 0.825 |
| Ni | 0.100 | 0.883 | 0.790 |
| Cr | 0.801 | −0.354 | 0.766 |
| Pb | 0.743 | −0.090 | 0.560 |
| Cu | 0.815 | 0.369 | 0.801 |
| Eigenvalue | 2.698 | 1.831 | |
| % Var. expl. | 42.55 | 32.93 | |
| Cum. % var. | 42.55 | 75.48 | |

### *Available metal concentrations data set*

Two variable groupings were highlighted by the FA, factors 1 and 2. The variance explained through these

**Fig. 5** Factor scores for total metal concentrations: **a** Factor-1 score, **b** Factor-2 score, **c** Factor-3 score



two factors is 43 and 33% respectively, resulting in a cumulative variance explained of 75%. Factor 1 has high factor loadings for Zn (0.827), Cu (0.815), Cr (0.801) and Pb (0.743) and exhibits high scores along the whole town pointing to increased metal availability due to both vehicular and industrial emissions spread throughout the top soils of Ermoupolis (Fig. 6a). These elements were recently shown to be significantly positively correlated and to derive from both traffic and industrial activities in urban dusts (Yongming et al. 2006). Apparently, in urban areas located in semi-arid zones, the upper few millimeters of poorly structured light soils may serve both as producers and receptors of urban dusts leading to cross-contamination and this explains the above similarity. Factor 2 is loaded for Fe (0,.887) and Ni (0.883) and shows the highest scores for the southern part of the town (sampling sites up to 14), not a purely residential area neighboring to the shipyard facilities (Fig. 6b).

## Hierarchical clustering analysis

In a parallel approach aiming to identify distinct groups of heavy metals, that may reflect common origin affecting their distribution, an explorative cluster analysis was performed on both aqua regia and DTPA data sets of the urban soils (standardized values), using the weighted-pair group average based on correlation coefficients – Pearson coefficient (Fig. 7, b; Manly 1994).

For the total metal concentrations, the obtained results allowed for the discrimination of two main groups of elements clustered at a level of similarity (0.99). The first group consisted of Pb and Sn and the second group of Fe, Cr, Zn, Ni and Cu, further

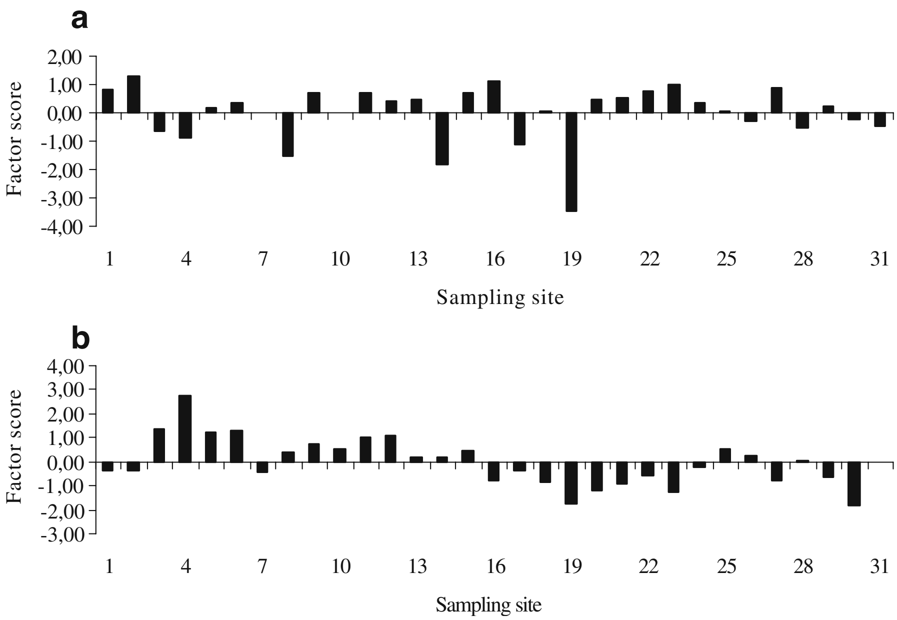


**Fig. 6** Factor scores for available metal concentrations: **a** Factor-1 score, **b** Factor-2 score

divided into two well defined subgroups (Fe, Cr/Zn, Ni and Cu) clustered at a level of similarity 0,88. For the available metal concentrations, CA resulted in the discrimination of two groups of elements – Cu–Zn–Cr–Pb/Ni–Fe (Fig. 7b). For both total and available metal data sets, the elements included in each group identified by the CA analysis are the same that produce the high loadings for each factor in the FA (Tables 4 and 5). This denotes the robustness of the specific metal groupings in terms of variability allocation and pollution source identification.

## Conclusions

Following different paths of data interpretation, it is evident that the surface soils of the town of Ermoupolis are mainly enriched in Zn, Cu and Pb,

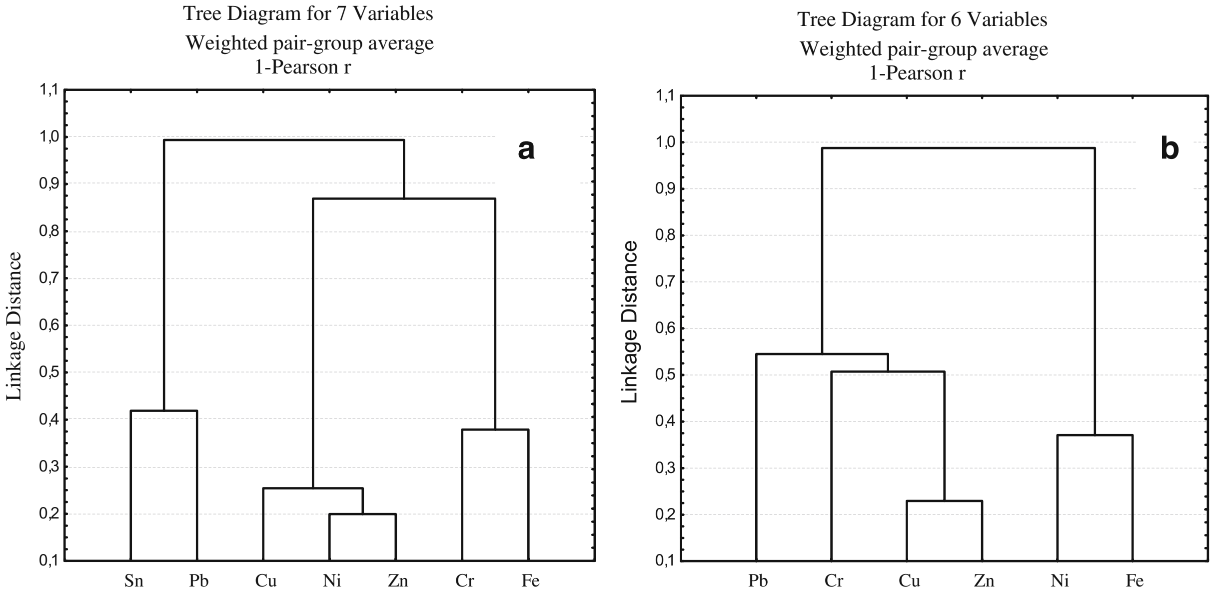


**Fig. 7** Hierarchical clustering results (dendrogram) of the heavy metals concentrations in top soil samples of Ermoupolis town: **a** total fraction, **b** available fraction

heavy metals associated to both traffic and industrial activities. The multivariate statistical techniques used for this study, factor and cluster analyses, adequately grouped the studied heavy metals and delineated their origin. The spatial distribution of urban soil enrichment factors for the total metal concentrations revealed that most of the top soils within the urban net of Ermoupolis present elevated contents of (1) Pb, attributed mainly to vehicular emissions and (2) Zn and Cu, that are similarly distributed and attributed to mixed industrial and vehicular inputs. Higher metal availability was observed in urban compared to reference soils indicating that the partitioning of the metals into the available fraction increases as the soil gets enriched due to anthropogenic inputs. Based on the results of this exploratory study and considering that soil contamination is a strong indicator of environmental pollution, a re-arrangement of the traffic flow, especially during summer time, should be a near future plan, maintenance control of the vehicles registered at Syros island must be implemented and measures should be taken to avoid further contamination of the southern part of the town, which is rapidly evolving into a residential area.

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