ASSESSMENT OF LEAD AND CADMIUM CONTAMINATION IN ROADSIDE SOILS AND PLANTS FROM CHANIA CITY (GREECE).

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EXTENDED ABSTRACT

Heavy metals, such us Pb and Cd are common pollutants in urban environments mainly due to traffic emissions. This study investigated the pollution of Pb and Cd in urban soils and plants of Chania city. The soil samples were collected from the roadside of the major squares, parks and traffic islands at three depths (0-5cm, 5-15cm and 15-30cm).The leaves of *Nerium oleander* L. (Oleander) were used as biomonitors of heavy metal contamination and they were collected next to the soil sampling sites. The total and bioavailable forms of Pb and Cd in soils were extracted with boiling Aqua Regia and DTPA respectively. The total concentrations of Pb and Cd in unwashed leaves of *Nerium oleander* L. were extracted with concentrated nitric acid. The content of the pollutants in soils and leaves was determined by using flame Atomic Absorption Spectrometry.

Total soil concentration data in the three depths, according to Dutch classification scheme (environmental guideline for metal pollution in soils) indicated that the studied soils can be considered medium polluted of Pb and Cd. In all sampling sites, the total contents of Pb and Cd decreased with depth suggesting undisturbed conditions and airborne deposition from vehicle exhausts. The highest total concentrations of Pb and Cd were found in the centre of the city (Agora square) mainly due to heavy traffic load. The bioavailable concentrations of the studied metals were low maybe due to basic soil pH and to high content of free calcium carbonate and decreased slightly with soil depth. The available concentrations and the bioavailability decreased slightly with soil depth for both metals maybe due to the reduction of the organic matter content and the increase of free calcium carbonate and pH values. The highest available concentrations of Pb and Cd in the surface (0-5 cm) and subsurface (5-15 cm) soils were found in the centre of the city (Agora square). Although Pb seemed to be more available in soils, for plant uptake, the *Nerium oleander* plants in Chania city can be considered unpolluted of Pb and contaminated of Cd, according to literature criteria. The main cause of the relative high concentrations of Cd in *Nerium oleander* plants was that the determination of the studied metals was carried out in unwashed leaves and therefore, there was aerial deposition of Cd due to tire abrasion. The major sources of Pb in urban environments are mainly the leaded fuel used in the past and the paints, so the airborne deposition of Pb is lower than the past decades. Also, Pb is accumulated in the roots, in great concentrations and the translocation of Pb from the roots to tops is limited.

Key words: Heavy metals, urban soil, bioavailability, traffic emissions

1. INTRODUCTION

Vehicular traffic is a significant and increasing source of atmospheric and soil pollution in urban environments. Because of air pollution, urban soils can be contaminated by metals from different anthropogenic sources and from natural processes. These pollutants can also bio-accumulate in plants. Atmospheric pollution is one of the major sources of heavy metal contamination in soils and plants in urban areas (Rossini Oliva and Fernández Espinosa, 2007). Many higher plant leaves are used as biomonitors of heavy metal pollution in urban environment (Aksoy and Ozturk, 1997).

Lead and cadmium are common pollutants in urban soils. The main sources of Pb and Cd are the leaded fuel used in the past and the leaded building- paints (Fernández Espinosa and Ternero Rodríguez, 2004; Kelly *et al*., 1996) and the tyre wear respectively (Chronopoulos *et al*., 1997; Moller *et al*., 2005). Lead and cadmium have no essential biological function and are highly toxic to plants, animals and humans. Lead impairs the renal hemopoietic and nervous systems (Lin *et al*., 1998). The major hazard to human health from cadmium is its chronic accumulation in the kidneys, where it can cause dysfunction (Chronopoulos *et al*., 1997). The objectives of this study were to evaluate the Pb and Cd soil pollution according to soil depth, their bioavailability to plants and the plant contamination.

2. MATERIALS AND METHODS

2.1. Plant selection

Nerium oleander was selected as a possible biomonitor of heavy metal pollution for several reasons: it occurs widely in both urban and rural areas; it has a wide geographical range and ecological distribution throughout the world; and sampling, identification and cultivation is easy and inexpensive.

Nerium oleander is an evergreen sclerophyllous shrub forming clumps up to 6 m tall and usually occurs with a spread of 2.5-4.5 m. In the wild, it grows on well drained soils, open areas, along dry water courses and ravines on both coastal and inland areas from sea level to 800 m. As an introduced species, it is grown in gardens and is also popular as an urban ornamental plant (Aksoy and Ozturk, 1997).

2.2. Study area

Chania is a coastal city and it's located in the north part of Chania Prefecture, on the island of Crete, Greece (Figure 1). The city area occupies a surface of 1,265 ha, and has approximately 53,400 inhabitants. The area has a typical Mediterranean climate with mild winters and dry summers. The annual average temperature and rainfall are 18.5°C and 622 mm, respectively. The city of Chania is a typical small Greek city without heavy industry and composes an important centre for tourism. Pollution due to industry is negligible, but maybe there is considerable pollution especially from heavy metals due to heavy traffic load.

2.3. Sampling and Analytical Methods

Samples were collected during the summer of 2007, from soil and the plant *Nerium oleander* L. (Oleander) from the roadside of the major squares, parks and traffic islands of Chania city. The sampling was carried out from seven different sites, representative of the study area (Figure 1).

Soil samples were collected at three depths (0-5cm, 5-15cm and 15-30cm). From each sampling site, four soil subsamples (at the three depths), were selected in a square area of 1m^2, using a stainless steel sampling tube. The subsamples from each sampling site and depth were mixed and homogenized. All soil samples were kept in plastic bags. The soil samples were air-dried at room temperature, disaggregated in a ceramic pestle and mortar, and sieved through a 2 mm sieve to remove stones and pebbles. The <2 mm fraction of the soil was used for all soil analyses. Particle size distribution was determined by the Bouyoucos hydrometer method (Bouyoucos, 1951) and pH was determined by glass and calomel electrodes in 1:1 soil–water ratio (Page, 1982). Calcium carbonate was measured by a volumetric method (Muller and Gatsner, 1971). Organic matter was determined by the Walkley–Black procedure (Nelson and Sommers, 1982). The total heavy metal content was estimated by refluxing 1g of soil in 15 ml hot aqua regia for 16 hours (Gasparatos and Haidouti. 2001). The available metal contents were determined by extraction of the soils with 0.005M DTPA (pH=7.3). 20 ml of DTPA solution were added to the 10 g of soil sample placed in polypropylene bottles. The bottles were shaken on a rotating shaker for 2 h and then were centrifuged for 10 min in 3000 rpm (Lindsay and Norvell 1978).

Plant samples were collected from the same sites with soil samples. About 100g of mature leaves of *Nerium oleander* were collected from one plant at different heights. All plant samples were oven-dried, unwashed, at 60 -70°C for 3 days, milled in a micro-hammer cutter and passed through a 1.5-mm sieve. 0,5g samples of dried and ground plant material were ashed at 550°C for 3 h. The weighed ash was digested in 5 ml concentrated HNO_3. Then the samples were diluted with deionised water to the final volume for Pb and Cd determination. (Jones and Case, 1990).

The concentrations of Pb and Cd were measured in soil and plant samples by flame Atomic Absorption Spectrometry (Perkin Elmer, AAnalyst 700). All samples were treated in duplicate. In all cases, standards (stock standard solution of 1000 mg/l concentration) and blank were treated in the same way as the real samples to minimize matrix interferences during analysis.

Figure1. Study area with sampling sites.

3. RESULTS AND DISCUSSION

3.1. Soils

The texture of the studied soils of Chania city was mainly sandy loam and sandy clay loam. The soil pH was basic and the free calcium carbonate was high at the most of the collected soil samples. The organic matter content in all sampling sites, was higher in the surface layer (0-5 cm) than in the lower layers, suggesting relatively undisturbed conditions. In Table 1 are presented the certain soil properties of the studied soils at the three depths.

Table 1. Soil properties of the studied soils of Chania city.

Soil depth (cm)	pH		$CaCO_3$ (%)		Organic matter (%)	
	Range	Median	Range	Median	Range	Median
0-5	7.6 - 8.2	7.98	8.5 - 37.0	27.68	3.4 - 5.9	5.50
5-15	7.9 - 8.5	8.35	15.2 - 43.8	27.82	1.9 - 4.3	2.22
15-30	8.0 - 8.6	8.36	18.7 - 48.5	33.97	1.2 - 3.5	2.05

3.1.1. Total heavy metal concentrations

Total soil Pb content in the surface soils ranged between 46.3 and 223.3 mg/kg, with a median value of 139.5 mg/kg. A large number of soils (about 71%) were between the critical soil total concentration range for Pb, which is 100-400 mg/kg.
Total soil Cd content in the surface soils ranged between 2.6 and 3.5 mg/kg, with a median value of 2.8 mg/kg. About 43% of the surface studied soils were found between the critical soil total concentration range for Cd, which is 3-8 mg/kg. The critical soil total concentration is defined as the range of values above which toxicity is considered to be possible (Maiz *et al.,*1997).
In all the soil samples collected at 0-5 cm, 5-15cm and 15-30cm depths from the sampling sites, the total content of Pb and Cd decrease with the depth (Figure 2). The trend was larger and more uniform for Pb than Cd. The decrease of organic matter according to the soil depth indicated undisturbed conditions in soils (Yassoglou *et al.,*1987). Assuming that the studied soils were undisturbed, in the surface layer (0-5cm) the concentrations of Pb and Cd were higher due to anthropogenic sources, mainly by atmospheric deposition from automobile exhausts. Lead in urban soils originates from leaded fuel used in the past (Rossini Oliva and Fernández Espinosa, 2007) and the main source of Cd is tyre abrasion (Moller *et al.,* 2005). Despite the sharp increase of unleaded fuel utilization, followed by a rapid decline of Pb levels in the atmosphere, the content of Pb in urban soil still remains high with a consequent associated risk for children via the soil–hand–mouth pathway. The most contaminated soils are in the proximity of the motorway and streets with high traffic flows (Imperato *et al.,* 2003). The highest total concentrations of Pb and Cd (at the three depths) were found in the centre of the city (Agora square) mainly due to heavy traffic load.

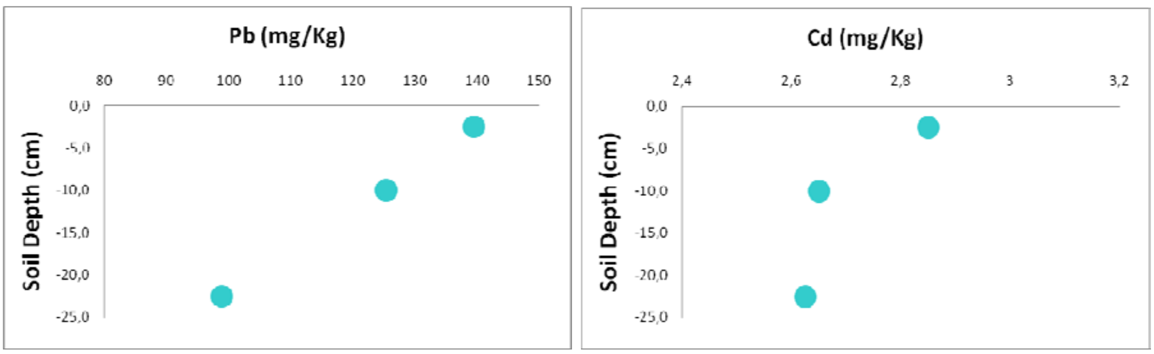

Figure 2. Vertical distribution of total (median values) contents of Pb and Cd in soils of Chania city

There is no international agreement on metal concentrations in soil that constitute significant contamination. In order to evaluate the level of total metal contamination in soils have been developed several environmental - soil remediation guidelines. This study has used the three level ("A, B and C") Dutch classification scheme. According to this scheme, soils which have metal concentrations below the "A" level are considered to be uncontaminated or background values. Soils with metal concentrations exceeding the "B" level require further investigation and soils which have metal concentrations which exceed the "C" level require remediation (Verner *et al.*, 1996). The results of this study showed that the median soil concentrations of Pb and Cd, at the three depths, exceeding the "A" level (but were below the "B" level) indicated that the studied soils can be considered medium polluted of Pb and Cd (Figure 3).

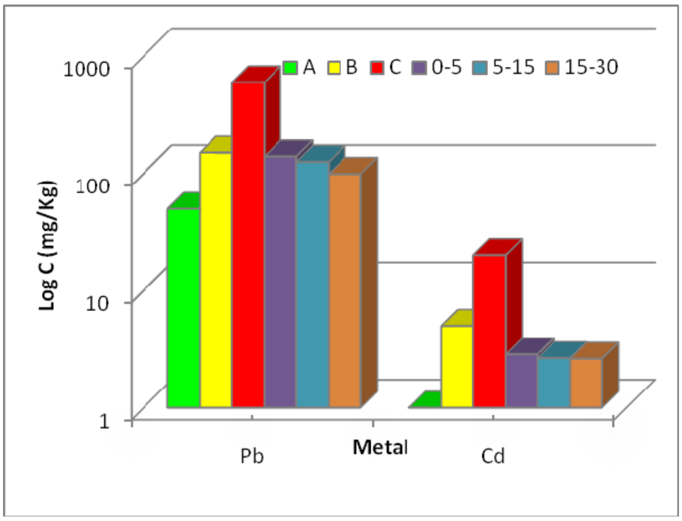

Figure 3. Median soil concentrations of Pb and Cd at three depths in comparison to the Dutch classification scheme levels (Verner *et al*., 1996).

3.1.2. Bioavailable heavy metal concentrations

The determination of total heavy metal concentrations in soils might be useful to predict the potential environmental risk posed by these metals, but do not always provide a good indicator of metals' labile fraction available for plant uptake (Gasparatos *et al*., 2001). The severity of pollution depends not only on total heavy metal content of the soil, but also on the proportion of their mobile and bioavailable forms, which are generally controlled by the texture and other physicochemical properties of soils (Imperato et al., 2003). Consequently, element availability is very important when assessing the effect of soil contamination on plant metal uptake and related phytotoxic effects (Mench *et al*., 1994; Papafilippaki *et al*., 2008).

Bioavailable concentrations of Pb in the surface layer (0-5cm) ranged between 2.3 and 25.1mg/kg with a median value of 15.9 mg/kg. The available concentrations of Pb in the subsurface layer (5-15cm) ranged from 1.8 to 19.6 mg/kg with median 11.5 mg/kg. At depth 15-30cm the bioavailable Pb concentrations were found between 1.4 and 18.1 mg/kg with a median value of 11.1 mg/kg.

The available Cd content in the surface studied soils ranged from 0.048 to 0.113 mg/kg with median 0.06 mg/kg. In the subsurface layer, the available Cd ranged from 0.035 to 0.11 mg/kg with median 0.055 mg/kg. At depth 15-30cm the range was from 0.033 to 0.095 mg/kg and the median value was 0.041 mg/kg.

The relative bioavailability expresses the ratio of metal concentration (M) between bioavailable and total forms: $RB=(M_{DTPA}/M_{TOTAL})$. The percentages of the total metals extracted with DTPA (bioavailable concentrations) could be a good indicator of the quantity of metal available for plants and could reflect their comparative mobility (He and Singh, 1993). According to Ulrich et al., (1999), the metals are potential available for plant uptake, if the bioavailability percentage is above to 10%. The relative bioavailability for the studied metals is presented in Table 2.

Table 2. % Bioavailability of Pb and Cd in the studied soils.

Soil depth (cm)	% Bioavailability Pb		% Bioavailability Cd	
	Range	Median	Range	Median
0-5	4,99-16,11	10,54	1,67-3,68	2,00
5-15	4,22-14,19	9,42	1,22-3,82	1,80
15-30	3,41-11,57	8,49	1,12-3,45	1.61

About 71% of the studied surface soils had relative bioavailability above 10% and Pb can be considered potential available for plant uptake. The bioavailability of Pb was found more than 5 times higher than Cd. In general the bioavailability of the studied metals was low. The low availability of these metals may caused from the high retention capacity of the studied soils, due to their calcareous nature and to high presence of free calcium carbonate (Pichering, 1982; Gasparatos et al., 2001). Also, the basic soil pH, due to the presence of free calcium carbonate, affects the bioavailability of the heavy metals, because high pH values increase the adsorptive capacity of soils (Papadopoulos & Rowell, 1988). In addition the reduction of soil pH values increases the bioavailability and the mobility of the metals (Adriano, 1986; Papafilippaki et al., 2008). The available concentrations and the bioavailability for both metals decreased slightly with the soil depth. The decrease of the available forms according to the soil depth may caused due to the reduction of the organic matter content and the increase of free calcium carbonate and pH values. The highest available concentrations of Pb and Cd in the surface (0-5 cm) and subsurface (5-15 cm) soils were found in the centre of the city (Agora square) maybe due to the higher total metal concentrations which associated to heavy traffic load and to higher content of organic matter.

3.2. Plants

The concentrations of Pb in the studied plants of *Nerium oleander* ranged between 6.9 and 10.15 mg/kg, with a median value of 9.3 mg/kg. Also, the content of Cd in the studied plants was found between 1.02 and 1.23 mg/kg, with a median value of 1.11 mg/kg.
According to literature criteria the concentrations of Pb and Cd in contaminated plants range from 30 to 300 mg/kg and 0.03 to 3.8 mg/kg, respectively (Aksoy and Ozturk, 1997). Also Nakos (1982), reports that the concentrations of Pb and Cd in the leaves of plants for normal plant growth range from 0.05 to 20 mg/kg and 0.01 to 0.1 mg/kg, respectively, and Chronopoulos et al. (1997) determined the concentrations of Pb and Cd in plants of *Pittosporum sinensis* and *Nerium oleander* from uncontaminated areas and found a range of 8-10 mg/kg for Pb and 0.1-0.2 mg/kg for Cd. Consequently, the plants of *Nerium oleander* in Chania city can be considered unpolluted of Pb and contaminated of Cd.
In order to characterize the origin and transfer of the studied metals, the concentration factor was calculated. The concentration factor (*CF*), expresses the ratio of metal concentration (*M*) between plants and soils: $CF=(M_{plant}/M_{soil})$ and reveals the behavior about the pollutants in plants (Rossini Oliva and Fernández Espinosa 2007).
The concentration factor (*CF*) in the studied sampling sites, was calculated for Pb with a range between 0.044 to 0.151, and a median value 0.067 and for Cd was 0.31-0.47 with median value of 0.39.
The ratio between plant and soil concentrations of elements (*CF*) is an index of soil–plant transfer that favours the understanding of plant uptake characteristics and it is widely used in biomonitoring studies. 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) (Rossini Oliva and Fernández Espinosa 2007).

The concentration factor (*CF*) values were found <1 for the studied metals indicating a low translocation from soil to plant leaves in all sampling sites, in agreement with the findings of low bioavailability of these metals in the studied soils of Chania city.

Although the relative bioavailability of Pb was about 5 times higher than Cd in the studied soils the concentration factor (*CF*) values of Pb were sufficiently lower than Cd, indicating lower translocation of Pb from soil to plant leaves and the plants are characterised as unpolluted of Pb. The main cause is that Pb is accumulated in the roots, in great concentrations and the translocation of Pb from the roots to tops is limited (Kabata-Pendias, 2001). Also, the determination of the studied metals was carried out in unwashed leaves and therefore, the airborne deposition of Pb is lower than the past decades due to the use of unleaded fuels.In opposition, the high concentrations of Cd in plants of *Nerium oleander* maybe originate from aerial deposition due to tire abrasion.

4. CONCLUSIONS

This study investigated the pollution of Pb and Cd in soils and plants of Chania city. The total concentrations of the studied metals (according to Dutch classification scheme) indicated that the soils can be considered medium polluted of Pb and Cd. The total concentrations of Pb and Cd decrease with the depth suggesting undisturbed conditions in soils and airborne deposition from vehicle exhausts. The highest total concentrations of Pb and Cd were found in the centre of the city (Agora square) mainly due to heavy traffic load. The bioavailable concentrations of the studied metals were low maybe due to basic soil pH and to high content of free calcium carbonate. The available concentrations and the bioavailability decreased slightly with soil depth for both metals maybe due to the reduction of the organic matter content and the increase of free calcium carbonate and pH values. The plants of *Nerium oleander* in Chania city can be considered unpolluted of Pb and contaminated of Cd. According to the concentration factor (*CF*) values the translocation of Pb and Cd from soil to plant leaves in all sampling sites was low in agreement with the low bioavailability of metals in soils. The high concentrations of Cd in plants of *Nerium oleander* maybe due to aerial deposition since the leaves were measured unwashed.

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