SPATIAL DISTRIBUTION OF Pb AND Cd IN URBAN SOILS OF CHANIA CITY, CRETE (GREECE).

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SUMMARY: Heavy metals, such us Pb and Cd are common pollutants in urban soils mainly due to traffic emissions. In order to investigate the spatial distribution of Pb and Cd in urban soils 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 total and bioavailable forms of Pb and Cd were determined by using flame Atomic Absorption Spectrometry, after their extraction with boiling Aqua Regia and DTPA respectively.
Total concentration data in the three depths, according to Polish contamination standards (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. 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 relative availability of Pb was about four times higher than Cd. The highest total and bioavailable concentrations of Pb and Cd were found in the centre of the city (Agora square) mainly due to heavy traffic load. Also GIS analysis was used to visualise the spatial distribution of the total concentrations of Pb and Cd in the surface soils (0-5cm) in Chania city.

1. INTRODUCTION

Heavy metals in urban soils may come from various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion. These activities send heavy metals into the air and the metals subsequently are deposited into urban soil as the metal containing dust falls. (Chen *et al.,* 2005). Heavy metals may be transported through soils to reach groundwaters and cause groundwater contamination or may be taken up by plants (Manta *et al.,* 2002; Boularbah *et al.* 2006). Also heavy metals are harmful to humans, animals and tend to bio-accumulate in the food chain (Golia *et al.,* 2008; Papafilippaki *et al.*,2008).
Vehicular traffic is a significant and increasing source of atmospheric and soil pollution in urban environments (Rossini Oliva & Fernández Espinosa 2007). Lead and cadmium are common pollutants in urban soils. The main sources of Pb and Cd are the leaded fuel used in the past (Fernández Espinosa & Ternero Rodríguez, 2004) 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 purpose of this study was to investigate the pollution and the spatial distribution of lead and cadmium in urban soils of Chania city.

2. MATERIALS AND METHODS

2.1 Study Area

Chania is a coastal city and its 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.

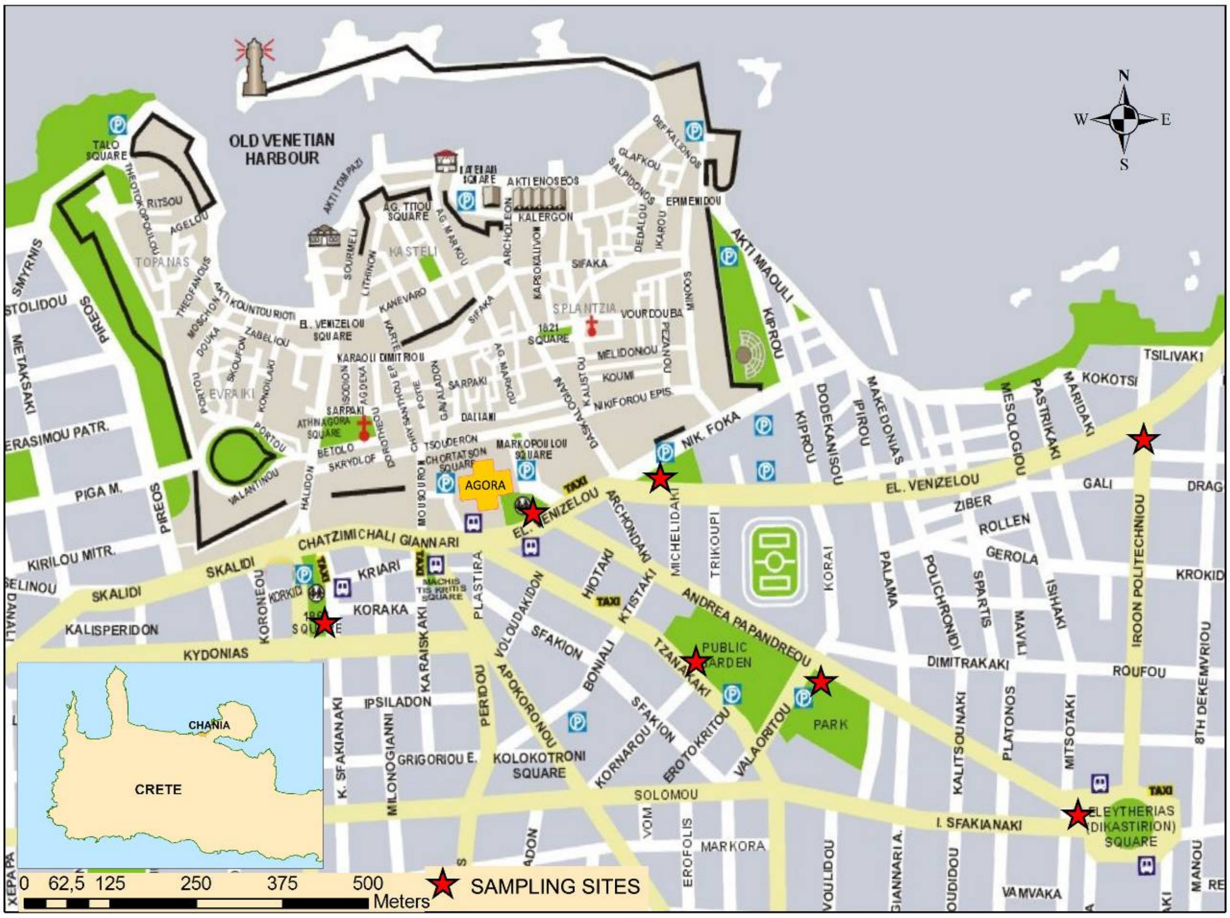

Figure1. Study area with sampling sites.

2.2 Soil sampling

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) from seven different sites, representative of the study area (Figure 1). 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.

2.3 Analytical Methods

The collected 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 & Gatsner 1971). Organic matter was determined by the Walkley–Black procedure (Page, 1982).

The total heavy metal content was estimated by refluxing 1 g of soil in 15 ml hot aqua regia for 16 hours (Gasparatos & 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 10g 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 & Norvell,1978). The concentrations of total and bioavailable metals in the supernatant liquid were measured with a flame Atomic Absorption Spectrometry (Perkin Elmer, AAnalyst 700). All soil 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.

Spatial distribution of the total concentrations of Pb and Cd in the surface soils (0-5cm) in Chania city is visualised on maps produced by ARC GIS V9.2 software.

3. RESULTS AND DISCUSSION

3.1. Soil properties

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	Mean	Median	Range	Mean	Median	Range	Mean	Median
0-5	7.6 - 8.2	7.98	7.98	8.5 - 37.0	27.02	27.68	3.4 - 5.9	5.21	5.50
5-15	7.9 - 8.5	8.26	8.35	15.2 - 43.8	29.43	27.82	1.9 - 4.3	2.76	2.22
15-30	8.0 - 8.6	8.36	8.36	18.7 - 48.5	33.14	33.97	1.2 - 3.5	2.21	2.05

3.2. Total heavy metal content

The total metal concentrations of the studied soils at the three depths of Chania city are presented in Table 2.

In order to evaluate the level of total metal contamination in soils have been developed several environmental - soil contamination guidelines. This study has used the Polish soil classification scheme which developed by Kabata-Pendias *et al.*, (1993). According to this scheme, the mean soil concentrations of Pb and Cd fell into the classification of "medium heavy metal pollution" (Table 3).

TABLE 2. Total metals concentrations (mg/Kg) in soils of Chania city according to the soil depth.

Soil depth (cm)	Total Pb			Total Cd		
	Range	Mean	Median	Range	Mean	Median
0-5	46.3 – 223.3	133.6	139.5	2.6 – 3,5	2.9	2.8
5-15	42.4 – 208.3	116.3	125.3	2.3 – 3.3	2.7	2.6
15-30	41.0 – 184.6	100.8	98.9	2.3 – 2.9	2.6	2.6

TABLE 3. Heavy metals contamination levels (mg/Kg) according to Polish soil classification scheme (Kabata-Pendias *et al.*, 1993)

Metal	O	I	II	III	IV	V
Pb	0 - 30	30 - 70	70 - 100	100 - 500	500 - 2500	> 2500
Cd	0 - 0.3	0.3 - 1	1 - 2	2 - 3	3 - 5	> 5

O = natural (background content), I = slightly elevated content, II = weak pollution, III = medium heavy pollution, V = heavy pollution, V = very heavy pollution (and should be remediated) .

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. For Pb the mean reduction percentage between the surface layer (0-5 cm) and the subsurface layer (5-15cm) was 12.9% and between the 5-15cm layer and the 15-30cm was 10.1%. For Cd the mean reduction percentages between the three depths were 7.8% and 3.3% respectively. 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 & Fernández Espinosa 2007) and the main source of Cd is tyre abrasion (Moller *et al.*, 2005).

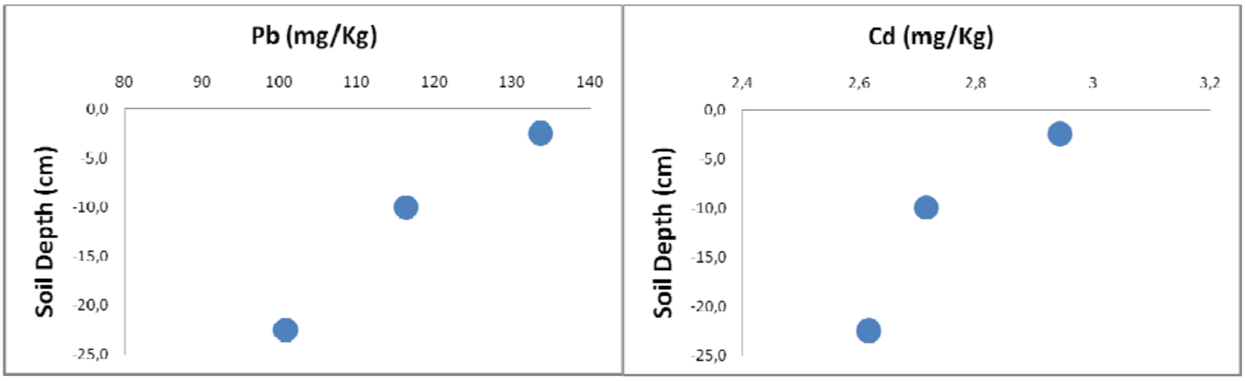

Figure 2. Vertical distribution of total contents of Pb and Cd in soils of Chania city

The spatial distributions of Pb and Cd in the surface soils (0-5 cm) are shown in the maps (Figure. 3a, b respectively). 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 were found in the centre of the city (Agora square) mainly due to heavy traffic load. The lowest concentrations of the studied metals were found in the roadside soil of a park in Elefterios Venizelos street, although this road is a major road of the city, maybe due to the recent construction of the park. 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 (Imperato *et al.*, 2003).

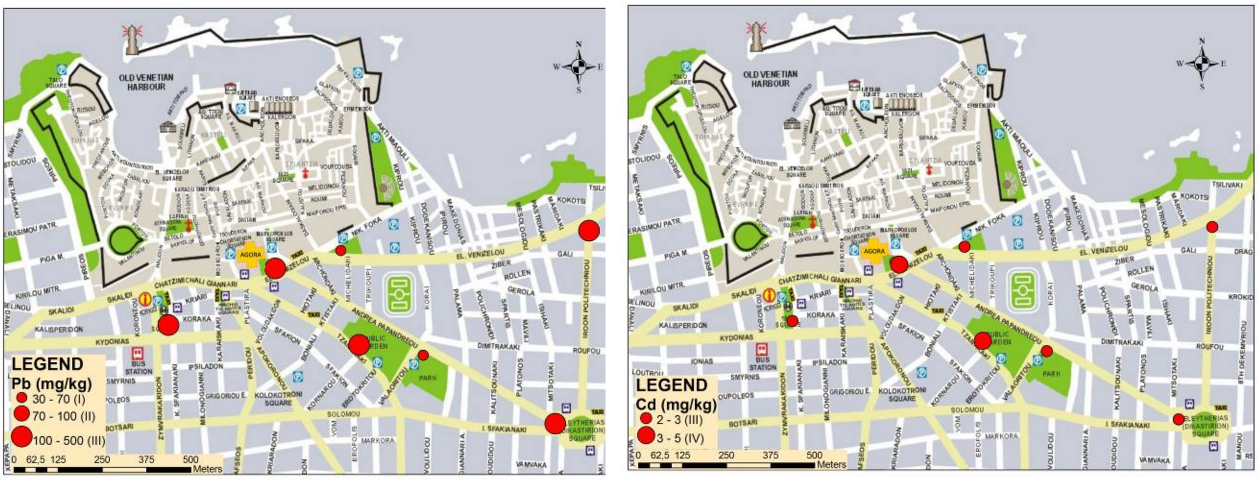

Figure 3. Spatial distribution of the total concetrations of Pb and Cd in the surface soils (0-5cm) of Chania

3.3. Available heavy metal content

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)
The available concentrations of Pb and Cd in the studied soils of Chania city are presented in Table 4.

TABLE 4. Available heavy metals concentrations (mg/Kg) in the studied soils according to the soil depth.

Soil depth (cm)	DTPA Pb			DTPA Cd		
	Range	Mean	Median	Range	Mean	Median
0-5	2.3 – 25.1	14.8	15.9	0.048 – 0.113	0.07	0.06
5-15	1.8 – 19.6	11.5	10.8	0.035 – 0.11	0.06	0.055
15-30	1.4 – 18.9	9.5	11.1	0.033 – 0.095	0.055	0.041

According to Ulrich et al., (1999), the metals are potential available for plant uptake, if the bioavailability percentage is above to 10%. The bioavailable content as a percentage of the total metal content was low, indicating a low availability of the metals. 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, affect 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 availability percentage according to the soil depth for Pb and Cd is presented in Figure 4. The availability of Pb was about four times higher than Cd and decreased slightly with soil depth for both metals. 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.

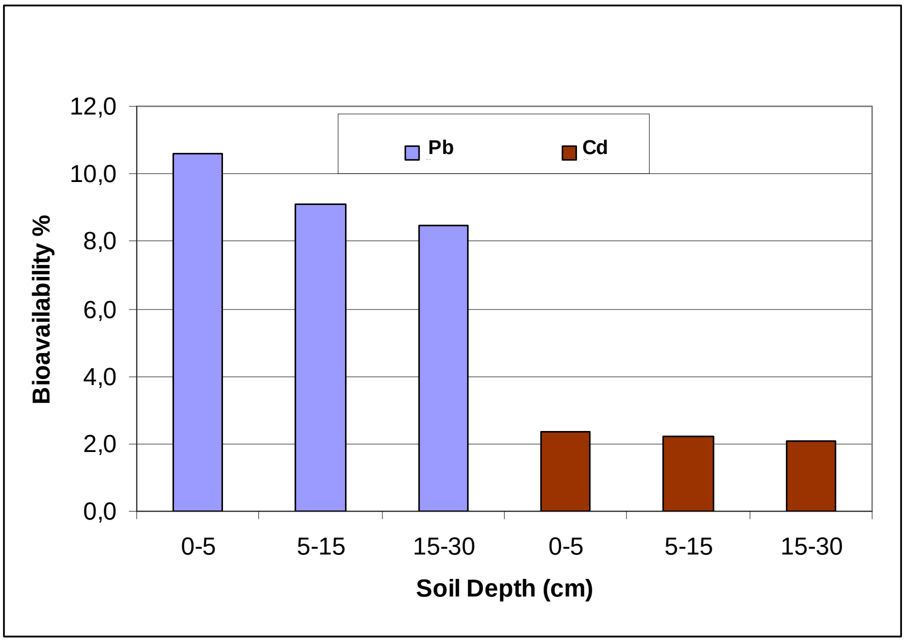

Figure 4. Relative bioavailability (Extractable -DTPA/Total ratio in %) in urban soils of Chania in the three depths.

4. CONCLUSIONS

This study investigated the pollution of Pb and Cd and the spatial distribution in soils of Chania city. The total concentrations of the studied metals (according to Polish 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 bioavailability of Pb was about four times higher than the availability of Cd. 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).

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