LEVELS OF HEAVY METALS AND BIOAVAILABILITY IN SOILS FROM THE INDUSTRIAL AREA OF HERAKLION- CRETE, GREECE.

Papafilippaki A., Velegraki D., Vlachaki C. and Stavroulakis G.

Laboratory of Water & Soil Resources Quality Control, Technological Educational Institute of Crete, 73133 Chania, Greece.
E-mail: npapafilippaki @chania.teicrete.gr; gstav @chania.teicrete.gr

ABSTRACT
This study investigated the hevy metal contamination in topsoils from the industrial area of Heraklion-Crete, Greece. The total and bioavailable forms of Cu, Zn, Pb, Cd and Ni were determined after their extraction with boiling Aqua Regia and DTPA respectively. Total concentration data according to Dutch classification scheme (environmental guideline for metal pollution in soils) indicated that the soils can be considered uncontaminated of Cu, Zn and Pb, and medium polluted of Cd and Ni. The bioavailable concentrations of the studied metals were low maybe due to basic soil pH and to high content of free calcium carbonate. The relative bioavailability followed the order of Cu>Zn≈Pb>Cd>Ni.

1. INTRODUCTION

Heavy metals are among the most common environmental pollutants and their occurrence in soils indicates the presence of natural or anthropogenic sources. The main natural sources of metals in soils are weathering of parent material and soil erosion [1]. The anthropogenic sources are associated mainly with industrial activities such as metal finishing, paint pigment and battery manufacturing, leather tanning, mining activities, foundries and smelters, diffuse sources e.g., piping, constituents of products, combustion by-products, traffic emissions and other human activities like urban composts and municipal waste water sludges depositions and use of pesticides and phosphate fertilizers [2, 3].

Metals are non-biodegradable and therefore persist in soils for long periods. They may be transported through soils to reach ground waters or may be taken up by plants [3]. Also heavy metals are harmful to humans, animals and tend to bio-accumulate in the food chain [4]. Industrial soils, especially those found in or near the metalliferous sites and metal smelters, are highly contaminated with heavy metals, including cadmium (Cd), chromium(Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc(Zn) [3]. The purpose of this study was to investigate the heavy metal pollution in surface soils from the industrial area of Heraklion in comparison to other industrial areas in Greece.

2. MATERIALS AND METHODS

2.1 Study Area

The industrial area of Heraklion is located in the north part of Heraklion Prefecture, on island of Crete, Greece and it is at 4 kilometers distance from the center of Heraklion city (Fig.1). It covers a total area of 210 ha and it's the biggest industrial area in Crete. The whole area is named Alikarnassos and it's a residential area, near to the international airport. The industrial area of Heraklion consists of about 150 enterprises (46 industrial units, 57 small factories and about 40 companies). The main enterprises are industries of plastics, food industries, smelters, factories of building materials and various agencies. In the area around the factories exists the national highway which connects Heraklion to Lasithi.

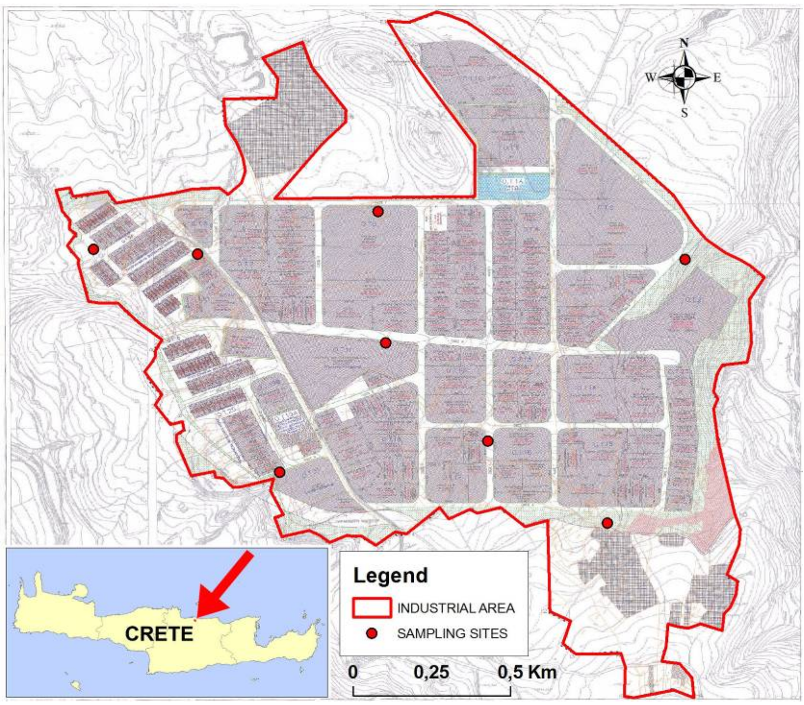

Figure 1. Map of Industrial area of Heraklion with sampling sites.

2.2 Soil sampling

Soil samples were collected in August 2006 from eight different sites, representative of the study area (Fig.1). From each sampling site, four surface soil subsamples (0-5 cm) were selected in a square area of $1m^2$, using a stainless steel sampling tube. The subsamples from each sampling site 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 [5] and pH was determined by glass and calomel electrodes in 1:1 soil–water ratio [6]. Calcium carbonate was measured by a volumetric method [7]. Organic matter was determined by the Walkley–Black procedure [8].

The total heavy metal content was estimated by refluxing 1 g of soil in 15 ml hot aqua regia for 16 hours [9]. 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 [10]. 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.

3. RESULTS AND DISCUSSION

3.1. Soil properties

The texture of the surface soils in the industrial area of Heraklion was loam, sandy loam and clay loam. The soil pH was alkaline, ranged from 7.70– 8.10. The free calcium carbonate was high, due to the soil calcareous nature and the organic mater ranged from 1.03 – 5.25 % (Table 1).

TABLE 1. Certain properties of surface soil samples from the industrial area of Heraklion.

Property	Range	Mean	Median
pH	7.70 – 8.10	7.90	7.90
$CaCO_3$ (%)	14.35 – 84.0	57.86	59.55
Organic matter (%)	1.03 – 5.25	3.23	3.47

3.2. Total heavy metal concentrations

The total metal concentrations of the surface soils of the industrial area of Heraklion are presented in Table 2.

TABLE 2. Total metals concentrations (mg/Kg) in surface soils (0-5cm) of the industrial area of Heraklion.

Element	Range	Mean	Median
Cu	22.55 – 41.80	31.88	30.78
Zn	52.45 – 417.0	118.86	80.80
Pb	33.05 – 136.7	59.15	45.5
Cd	1,65– 3.0	2.54	2.58
Ni	39.55 – 109.9	73.82	76.98

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 [11]. The results of this study showed that the median soil concentrations of Cu, Pb and Zn were below the "A" level indicating that the soils of the studied area can be considered uncontaminated of these metals. The median soil concentrations of Cd and Ni exceeding the "A" level (but were below the "B" level) indicated that the studied soils can be considered medium polluted of Cd and Ni (Figure 2).

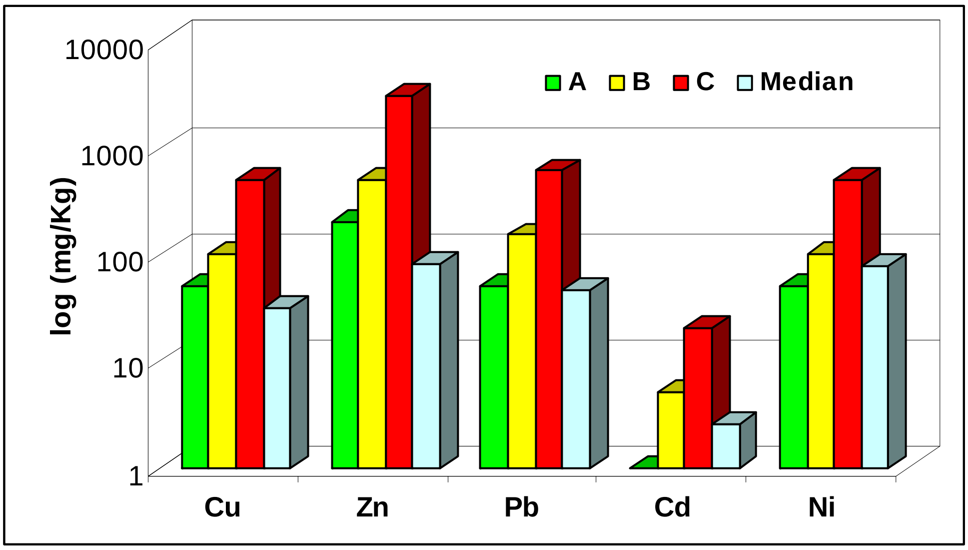

FIGURE 2. Median soil concentrations of Cu, Zn, Pd, Cd and Ni in comparison to the Dutch classification scheme levels [11].

Table 3 shows the total metal concentrations in surface soils from other industrial areas of Greece. In the same table reported data for uncontaminated- rural Greek soils. The total concentrations of the studied metals were elevated in comparison to the reported literature data for uncontaminated Greek soils. The total heavy metal concentrations of the studied area were found lower than that reported for the industrial areas of Athens (Eleonas) and Thriasian plain and similar to the total metal concentrations of the industrial area of Thessaloniki, with the exception of cadmium and lead, which had significantly higher values maybe due to contamination by atmospheric deposition. Also the total concentrations of Cu and Pb in the studied area were found similar to the total metal concentrations of the industrial area of Thessaly, but the total concentrations of Zn and Ni were two times higher and Cd was about 3 times lower than the mean values of the industrial area of Thessaly [4, 12, 13, 14].

TABLE 3. Total metal concentrations (mg/Kg) in various industrial and rural areas of Greece.

		Cu	Zn	Pb	Cd	Ni
Thessaly[a]	Range	29.6 – 66.7	35.6 – 41.7	36.5 – 101.2	4.4 – 20.3	19.6 – 100.3
	Mean	34.5	40.7	49.8	6.9	33.4
Eleonas Athens [b]	Range	23.9 – 213.9	170 – 620	54 – 279		
	Mean	84.87	342.30	112.11	–	–
	Median	82	335	90.40		
Triasian Plain[c]	Range	–	52 – 594	14 – 595	3 – 30	52 – 321
	Mean		138	89	11	129
Thessaloniki[d]	Range	19.7 – 39.5	36 – 124	15.5 – 37	0.16 – 0.26	–
	Median	26.8	68.3	24.2	0.22	
Unconta-minated[d]	Range	3.23 – 14.5	5.4 – 15.8	4.0 – 19.2	0.2 – 0.5	–

a: [4], b: [12], c: [13], d: [14]

3.3. 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 [15]. 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 [16]. Consequently, element availability is very important when assessing the effect of soil contamination on plant metal uptake and related phytotoxic effects [17].
The bioavailable concentrations of the studied heavy metals in soils of the industrial area of Heraklion are presented in Table 4.

TABLE 4. Bioavailable heavy metals concentrations (mg/Kg) in the studied soils.

Element	Range	Mean	Median
Cu	0.71 – 3.19	1.81	1.88
Zn	0.75 – 32.8	6.93	3.39
Pb	0.76 – 6.47	2.82	2.09
Cd	0.053 – 0.13	0.088	0.091
Ni	0.45 – 0.97	0.72	0.73

The percentages of the total metals extracted with DTPA could be a good indicator of the quantity of metal available for plants and could reflect their comparative mobility [18] (Table 5)

TABLE 5. Bioavailable content as a percentage of the total metal content (Extractable -DTPA/Total ratio in %) in the industrial soils of Heraklion (%).

Element	**Range**	**Mean**	**Median**
Cu	3.15 – 7.64	5.65	5.68
Zn	0.98 – 8.00	4.52	4.30
Pb	1.81 – 7.08	4.47	4.55
Cd	2.03 – 5.64	3.50	3.50
Ni	0.64 – 1.68	1.04	1.03

According to Ulrich et al., [19], 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 surface soils, due to their strongly calcareous nature and to high presence of free calcium carbonate [15, 20]. 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 [21]. In addition the reduction of soil pH values increases the bioavailability and the mobility of the metals [22].

The relative availability and consequently the comparative mobility of the studied metals in the surface soils of the industrial area of Heraklion followed the order of Cu>Zn≈Pb>Cd>Ni. Organic matter plays a significant role in the availability and mobility of the heavy metals in soils. The humified organic matter is involved in the formation of soluble complexes especially with Cu, which during organic mineralization, become more available for the plants [23]. This can explain the higher availability of Cu in the studied soils, in relation to the other metals. On the other hand Ni is a strongly retained element to the soil [24] in according with the results of this study.

Table 6 shows the bioavailable metal concentrations and the bioavailability percentage in surface soils in various industrial areas of Greece. The available concentrations of the studied metals were found lower than the reported values for the industrial areas of Eleonas (Athens) and Thessaly, with the exception of zinc which was found higher in the studied area than in the industrial area of Thessaly. Also the bioavailability percentage of the studied metals was found lower in comparison to the other industrial areas (Eleonas, Thriassian Plain and Thessaloniki). In the industrial area of

Eleonas copper seemed to be more available than the other metals and in the industrial area of Thriassian Plain nickel was less available, in agreement with findings of this study [4, 12, 13, 14].

TABLE 6 . Bioavailable metal concentrations and % Bioavailability (Extractable -DTPA/Total ratio in %) in various industrial areas of Greece.

		Cu	Zn	Pb	Cd	Ni
Thessaly[a]	Range	2.8 – 6.1	3.1 – 4.9	3.5 – 7.9	1.1 – 2.6	4.5 – 6.8
	Mean	4.9	3.4	6.9	1.68	5.5
Eleonas Athens [b]	Range	0.38 – 33	0.38 – 42.2	0.74 – 23.9	-	-
	Mean	10.67	14.38	8.31		
	Median	9.76	9.7	6.82		
	% Bioav	11.10	3.65	7		
Triasian plain[c]	% Bioav	-	13	17	10	3
Thessaloniki[d]	% Bioav	13	9	16	59	-

a: [4], b: [12], c: [13], d: [14]

4. CONCLUSIONS

This study investigated the pollution of Cu, Zn, Pb, Cd and Ni in surface soils of the industrial area of Heraklion. The total concentrations (according to Dutch classification scheme) indicated that the soils can be considered uncontaminated of Cu, Zn and Pb, and medium polluted of Cd and Ni. The bioavailable concentrations of the studied metals were low maybe due to basic soil pH and to high content of free calcium carbonate. The relative bioavailability and comparative mobility followed the order of Cu>Zn≈Pb>Cd>Ni. In general the total and bioavailable concentrations of the studied metals were found lower in comparison to other industrial areas of Greece.

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