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Levels of Heavy Metals Pollution in Different Types of Soil of Central Greece

E. E. Golia · A. Dimirkou · I. K. Mitsios

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Abstract This investigation was performed in order to clarify the degree of heavy metals pollution in forest, agricultural and industrial surface soil samples in relation to pre-anthropogenic soils of Almyros region, in Central Greece. In 2004 and 2005 soil samples were collected and analysed for available (DTPA method) and total (Aqua Regia method) Cd, Cr, Cu, Pb, Zn and Ni concentrations. For each metal the enrichment factor with respect to the levels in pre-anthropogenic soils was calculated. All the types of soils appeared to be less polluted than in other investigations. In agricultural and industrial soils the available Cd concentration was higher than the other metals studied. The enrichment factor of Cu in relation to total concentration has the maximum value of the metals studied.

Keywords Heavy metals · Enrichment factor · Forest-agricultural-industrial soils

Heavy metals have been well documented as they are amongst the most hazardous materials threatening the environment worldwide. The environmental pollution of soils directly influences human health since they have excellent ecological transference potential (Kabata-Pendias and Pendias 1992). They are harmful to humans, animals and tend to bio-accumulate in the food chain. Heavy metals in soils can be associated with several reactive materials and may exist in various forms that reflect their solubility and availability to plants. Contamination of soils with heavy metals is widespread in the world and poses a long term risk to ecosystem's health (Alloway 1990).

The levels of heavy metals in soils may be affected by soil materials as well as anthropogenic sources (Golia et al.). The natural concentration of heavy metals in arable soil depends primarily on the geological parent material composition (Morton-Bermea et al. 2002). Native concentrations of heavy metals are relatively high in shales and clays, and usually lower in sands and limestones. Natural heavy metal concentrations in soils are due to erosion and weathering of parent rocks (Yoon et al. 2007).

Although these metals occur naturally in the earth's crust, they tend to accumulate in agricultural soils because of application of commercial fertilizers, insecticides, manure and sewage sludge that contain heavy metals (Peris et al. 2007; Wong et al. 2002). The phosphate fertilizers contain high concentrations of heavy metals and particular Cd, because of the high Cd content on the phosphate rock that are used as a row material for the fertilizers production (Golia et al. 2007).

In industrial areas the automobile exhausts, the uncontrolled factory emissions and activities such as mining and smelting of metal ores have all contributed to elevate levels of heavy in the environment. The high urbanisation and industrial growth rate worldwide has resulted an increase in the levels of pollution of air, soil, as well as in water supplies. The degree of anthropogenic impact in the agricultural and industrial environment can be evaluated in terms of metal contamination of soils (Martin et al. 2006).

The aim of the present study was the monitoring of the degree of anthropogenic influence on the heavy metal pollution in soil samples from both an agricultural and

Professor Mitsios is deceased.

E. E. Golia (✉) · A. Dimirkou · I. K. Mitsios
Department of Agriculture, Crop Production and Rural Environment, Laboratory of Soil Science, University of Thessaly, Fytokou Road, 36 446 N Ionia Magnisias, Greece
e-mail: egol@uth.gr

industrial area of Central Greece and nearby forested areas in order to give a possible clarification of the source of the pollution in the area studied.

Materials and Methods

A 2 years survey (2004–2005) was conducted in Thessaly-Almyros region in Central Greece in order to determine heavy metal concentration in soil. A set of 25 agricultural, as well as, 25 industrial surface (0–30 cm) soil samples, for each year, were collected from the southwest and the east area of Almyros region, respectively. The area is cultivated mostly with vegetables and tobacco, while a relatively new industry for metals reprocessing has been developed in the region studied.

Twenty forest (from Othrys Mountain) surface soil samples, apparently with no anthropogenic input, were also collected. Background levels were calculated on 10 samples of each pre-anthropogenic soil in order to calculate the enrichment factors of the metals studied. Othrys mountain is situated in the highlands at 960–1,100 m above sea level. The area has a Mediterranean climate, with temperature that ranges from 14 to 24°C and annual rainfall of 200–300 mm. Many streams and small rivers traverse the whole area of the study. At the east the region studied rebounds to Pagasitic Gulf (Aegean Sea).

All soil samples were collected randomly from the sampling area. Soil properties were measured (Page et al. 1982) such as clay content (%), organic matter (Walkley-Black method), pH (1:1) and electrical conductivity (1:1). Plant available fractions of metals were determined by using diethylene-triamine-pentacetic acid (DTPA) buffered at pH 7.3 (Lindsay and Norvell 1978). Total concentration of metals was determined using the Aqua Regia ($HCl–HNO_3$, 3:1) extraction method (ISO/DIS 11466 1994) after digestion at 180°C for 2 h. All reagents were of analytical grade (Merck, Germany). The stock solutions of metals (1,000 mg/mL) were prepared from "titrisol" Merck.

The concentration of the metals studied were determined by atomic absorption spectrophotometry (AAS) using flame (F) or the Graphite Furnace (GF) AAS technique (Lajunen 1992). Deuterium background corrections were used in the analysis of metals with the GF-AAS followed the standard Methods of JAOAC (1984). Certified Reference Material (CRM) (No 141R, calcareous loam soil) by BCR (Community Bureau of Reference) was also analyzed for the verification of the accuracy of trace element determination in soils. Recovery values were calculated as the ratio of the BCR results to those of the Aqua Regia digestion and ranged from 95 to 101%. The detection limits based on three times the standard deviation of the blank (n = 10), were found between 0.08 μg L^{-1} (Cd – GFAAS) and 0.3 mg L^{-1} (Cu – FAAS).

The comparison of heavy metal contents between the four types of soil (background, forest, agricultural and industrial) was carried out using the *t*-test. Results from two replicates were averaged prior to statistical analyses, which they obtained using SPSS® (Statistic Program for Social Sciences) for Windows.

Results and Discussion

The soils in the region studied were sandy clay loam (33%), silty loam (28%), clay loam (22%) and clay (17%). The soils according to Soil Taxonomy, they belong to different soil orders such as: Alfisols (31%), Inceptisols (27%), Entisols (22%) and Vertisols (20%) (Soil Survey Staff 1999). The soil samples collected from the forest at Othrys mountain belonged to Alfisols and Inceptisols. Alfisols have an argillic horizon and they appear to have low pH values (<5.4). Inceptisols were occurred both in the soil samples collected from the forest, as well as from the samples were tobacco plants are cultivated (agricultural soils). They had mean pH value of 5.6. The soil samples collected from the industrial part of the area studied

Table 1 Chemical and physical properties of each soil type

	pH (1:1)	Electrical conductivity (μS cm^{-1})	Organic matter (%)	Clay (%)
Background soils, n = 10				
Minimum value	4.2	236.0	1.1	13
Maximum value	6.6	1,900	2.3	39
Mean value	5.3	1,440	1.4	30
CV %	18.8	48.0	31.8	22.7
Forest soils, n = 20				
Minimum value	3.9	244.6	1.5	17
Maximum value	6.2	2,100	5.4	44
Mean value	5.5	1,560	3.9	29
CV %	16.7	54.0	54.5	34.6
Agricultural soils, n = 25				
Minimum value	3.8	104.0	1.0	11
Maximum value	7.4	1,200	2.9	63
Mean value	5.9	556.7	1.6	32
CV %	45.7	34.7	35.1	25.3
Industrial soils, n = 25				
Minimum value	7.3	624.8	1.1	10
Maximum value	8.1	4,443	2.4	59
Mean value	7.7	2,477.9	1.3	31
CV %	15.6	60.6	31.8	28.1

belonged to Endisols and Vertisols. They had mean pH values 7.3 and 8.1, respectively.

Table 1 shows the mean values (of the 2 years of study) of chemical and physical properties of the soil samples.

Soil electrical conductivity ranged between 104.0 and 4,443 μS cm^{-1}, with a high value appeared in industrial soil samples. In forest soils the highest amount of organic matter content was appeared. In soil samples collected from the industrial part of the region studied high values of electrical conductivity were observed. This is probably due to the fact that this region is nearby the coastal zone of the Pagasitic Gulf. The type of nitrogen fertilizers should be carefully chosen and applied, in order to avoid acidification of cultivated soils (Mitsios et al. 2003). The mean values of clay content (%) did not differ among the different types of soils, even though they were classified in different soil orders.

The mean (of the 2 years of the study) concentration of DTPA extractable heavy metals in soils from the different soil types are presented in Table 2.

A comparison of the heavy metals content with background levels shows that both the agricultural and the industrial soils are contaminated. Available Cd had the highest values in agricultural soils. This is probably due to the high amounts of fertilizers that farmers in Thessaly use for the cultivations.

The levels of available concentration of heavy metals were similar with those found in previous research at agricultural areas of Central Greece (Mitsios et al. 2003, 2005; Golia et al. 2007, 2008). All the other metals studied (Cr, Cu, Pb, Zn, Ni) appeared to have higher available concentrations in industrial than in agricultural soil samples.

Table 3 shows the mean (of the 2 years of the study) heavy metal concentrations extracted by Aqua Regia in soils from the different soil types.

The mean total concentration of Zn in the forest soil samples was lower than in other studies (Wong et al. 2002; Micó et al. 2007; Yoon et al. 2007). The maximum total concentrations of Cd, Cu and Zn were observed in agricultural soils of the area studied. The concentrations were lower than in other reports of agricultural areas (Martin et al. 2006; Peris et al. 2007).

The maximum total concentrations of Cr, Pb and Ni were obtained in the industrial soil samples. High amounts of Pb are also, related to the traffic conditions (Morton-Bermea et al. 2002). In the area around the factories a national highway, which connects Athens to Thessaloniki, exists and therefore the high Pb concentration in soils is attributed principally to decades of using gasoline containing Pb additives.

In Figs. 1 and 2 the mean (2004 and 2005) available and total metal concentrations from each soil type, are respectively presented. The soil samples were grouping in four categories for each metal studied.

Table 2 Available (DTPA method) heavy metals concentrations from different soil types

	Cd (mg/kg dry soil)	Cr (mg/kg dry soil)	Cu (mg/kg dry soil)	Pb (mg/kg dry soil)	Zn (mg/kg dry soil)	Ni (mg/kg dry soil)
Background soils, n = 10						
Minimum value	0.009	0.1	0.2	0.9	0.2	0.3
Maximum value	0.1	1.1	1.4	1.9	0.6	1.4
Mean value	0.08	0.7	0.7	1.1	0.4	0.9
CV %	24.5	22.5	23.5	22.5	26.7	22.9
Forest soils, n = 20						
Minimum value	0.01	0.9	0.58	1.5	0.9	1.1
Maximum value	0.9	1.9	2.1	3.6	2.1	2.6
Mean value	0.1	1.1	1.7	2.2	1.1	1.5
CV %	34.9	13.5	13.5	22.6	21.5	20.5
Agricultural soils, n = 25						
Minimum value	0.8	1.5	2.4	2.5	2.9	2.2
Maximum value	2.25	2.9	4.69	4.8	5.6	4.8
Mean value	1.77	2.45	3.2	3.3	4.4	3.5
CV %	16.5	15.4	16.3	17.8	16.5	14.5
Industrial soils, n = 25						
Minimum value	1.1	2.6	2.8	3.5	3.1	4.5
Maximum value	2.6	5.8	6.1	7.9	4.9	6.8
Mean value	1.68	4.56	4.9	6.9	3.4	5.5
CV %	16.8	22.5	29.8	35.9	18.8	22.4

Table 3 Total (Aqua Regia method) heavy metals concentrations from different soil types

	Cd (mg/kg dry soil)	Cr (mg/kg dry soil)	Cu (mg/kg dry soil)	Pb (mg/kg dry soil)	Zn (mg/kg dry soil)	Ni (mg/kg dry soil)
Background soils, n = 10						
Minimum value	0.1	0.2	0.1	0.5	0.5	0.5
Maximum value	0.6	1.1	0.9	1.9	0.9	1.5
Mean value	0.2	0.6	0.3	0.8	0.6	0.7
CV %	23.8	19.8	17.7	22.6	12.5	16.8
Forest soils, n = 20						
Minimum value	1.8	2.5	1.9	2.5	2.1	1.6
Maximum value	3.6	4.9	3.8	4.6	3.6	4.3
Mean value	2.3	3.3	2.9	3.3	2.5	2.7
CV %	15.6	16.5	16.5	19.6	18.4	25.5
Agricultural soils, n = 25						
Minimum value	5.5	4.9	16.8	14.5	14.9	16.5
Maximum value	22.9	8.9	70.5	33.5	45.6	29.5
Mean value	7.8	6.5	23.6	17.8	20.6	19.8
CV %	42.1	19.8	56.6	28.9	22.6	22.9
Industrial soils, n = 25						
Minimum value	4.4	20.3	29.6	36.5	35.6	19.6
Maximum value	20.3	88.9	66.7	101.2	41.7	100.3
Mean value	6.9	29.9	34.5	49.8	40.7	33.4
CV %	39.8	54.7	43.5	28.8	24.5	52.3

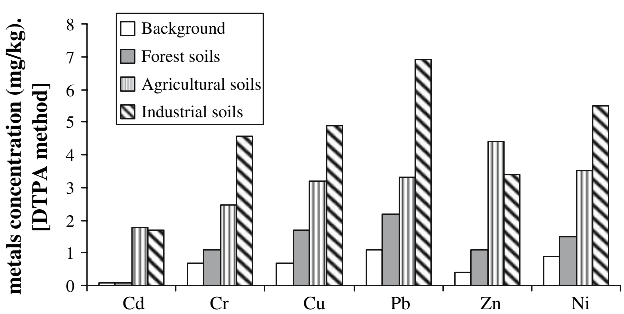

Fig. 1 Mean (2004 and 2005) available metal concentrations (mg/kg dry soil) from each soil type

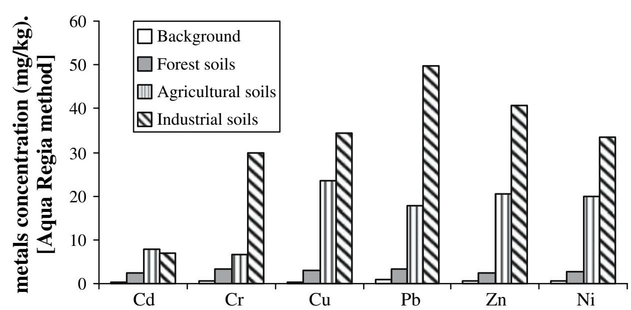

Fig. 2 Mean (2004 and 2005) total metal concentrations (mg/kg dry soil) from each soil type

In forest soils the mean available concentrations of the metals follow the order: Pb > Cu > Ni > Cr = Zn > Cd. The Pb concentration in forest soils was probably caused by the transport of lead from urban and industrial areas nearby Othrys Mountain.

Both Cd and Zn available concentrations followed the order: agricultural > industrial > forest soils, while mean total Zn concentration was higher in industrial soil samples. The low soil pH value in agricultural soils may have caused the increased availability of Zn (Kabata-Pendias and Pendias 1992).

In forest soil samples mean total concentrations (Fig. 2) appeared to have no statistical differences among the metals studied. Total Pb concentrations both in agricultural and industrial soils were lower than those reported in other studies (Morton-Bermea et al. 2002).

In Fig. 3 the heavy metals pollution is illustrated by using the enrichment factor (E.F.) of each metal. The enrichment factors were concluded with respect to the levels in pre-anthropogenic soils and they are presented both for the available and total concentrations of the metals studied. The enrichment factor is calculated as follows: $\text{metal}_{\text{DTPA (forest or agricultural or industrial soils)}}/\text{metal}_{\text{DTPA (background soils)}}$ and in the same way concerning total (Aqua Regia method) metal concentrations.

Although the absolute available as well as total concentrations of the metals can lead to conclusions regarding soil pollution it is better to illustrate the possible

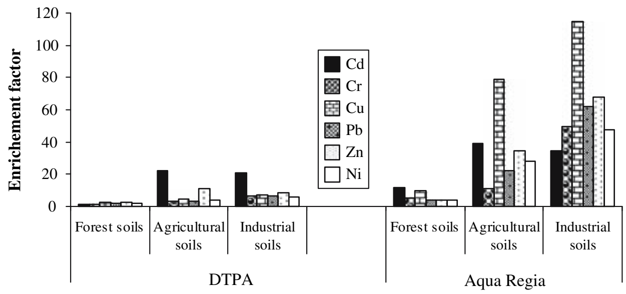

Fig. 3 Enrichment factors of metals from each soil type

environment risk if the E.F. of the metals in each type of soil is taken under consideration.

In forest soil samples the E.F. regarding available mean concentrations (Fig. 3) ranged from 1.3 (Cd) to 2.8 (Zn). In agricultural soils Cd shows enrichment factor up to 22.1 times in relation to available Cd concentration in background levels. In agricultural as well as in industrial soil samples the higher E.F. values were recorded in the case of Cd, indicated the high availability of that metal. The E.F. regarding total mean concentrations ranged from 3.9 (Ni in forest soils samples) to 115 (Cu in industrial soils). The higher E.F. values were observed for Cu in agricultural as well as in industrial soil samples, while Cd appeared to have the lowest E.F. value of the other metal studied in the industrial soil samples.

Concluding, the concentrations of metals in the region studied were lower than in other investigations, in forest, agricultural and industrial soil samples. In forest soil samples (Othrys Mountain) Zn concentrations were more than 100 times lower than in other reports (Morton-Bermea et al. 2002; Wong et al. 2002). In agricultural soils from the areas of central Greece studied the available and total concentrations of Cd in most cases were lower than the critical limits (Alloway 1990; Kabata-Pendias and Pendias 1992). In industrial soil samples the concentrations of all the metals studied were lower than in other studies. Pb total concentration was lower than the values mentioned by other investigators despite the fact that the soil sampling was performed in sites with high traffic conditions (Morton-Bermea et al. 2002).

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