Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, 2010
Πρακτικά 12ου Διεθνούς Συνεδρίου
Πάτρα, Μάιος 2010

Bulletin of the Geological Society of Greece, 2010
Proceedings of the 12th International Congress
Patras, May, 2010

# ANTHROPOGENIC AND GEOGENIC CONTAMINATION DUE TO HEAVY METALS IN THE VAST AREA OF VARI, ATTICA

**Serelis K.G.[1], Kafkala I.G.[1], Parpodis K.[1] and Lazaris S.[2]**

[1] *Laboratory of Mineralogy-Geology, Agricultural University of Athens, 75, Iera Odos, 118 55 Athens, serelis@aua.gr, kafkala@aua.gr, kparpodis@yahoo.gr*

[2] *Agroland S. A. spyroslaz@yahoo.com*

## Abstract

*The purpose of this work was to investigate the soil heavy metal contamination of the area between Koropi and Vari, in Attica, Greece and to determine their anthropogenic or/and geogenic-lithogenic origin. Soil samples were taken from two different depths of 23 uncultivated sampling sites. Determined heavy-metal concentrations ranged widely; mean values in several sites were elevated and much higher than the soil grand mean worldwide. The higher Co and Ni contamination was found in the lower soil depth (10-25cm), while for Cd, Zn, and Pb in the upper depth (0-10cm). These results, in connection with the performed Hierarchical Cluster Analysis and Principal Component Analysis, indicate that there are two contamination sources. The first, concerning Co-Ni, is a geogenic-lithogenic source and the second, concerning Zn-Cd and Pb, is considered as an anthropogenic source. Since in the study area there is no evidence of an existing anthropogenic source (e.g. an industry) and the parent material does not confirm and give reason for the elevated Zn, Cd and Pb contents, it could be concluded that this contamination was due to ancient metallurgical activities in the area.*

***Key words:*** *soil contamination, heavy metals, anthropogenic factors, geogenic- lithogenic factors, HCA, PCA, Vari, Attica.*

## 1. Introduction

Heavy metal soil contamination is a serious environmental problem, mainly due to its impact on human health (Fytianos et al., 2001, Imperato et al., 2003; Selinus et al., 2005; Girard et al., 2005; Shakeri et al., 2009; Zhuang et al., 2009; Singh et al., 2010). Heavy metals are found in the crust in less than 0.01% (Kabata-Pendias and Pendias, 2001). The existence of heavy metals in soils is attributed to both anthropogenic and geogenic (particularly lithogenic) factors. The main human activities resulted in environmental contamination are: mining and smelting, industrial activities, agricultural practices, fossil fuel combustion, waste disposal, transportation etc. and they have been discussed in numerous reports and publications (e.g. Alloway, 1995; Dudka and Adriano, 1997; Kabata-Pendias and Pendias, 2001; Wong et al., 2002; Girard et al., 2005; Selinus et al., 2005; Kribek et al., 2010).

The presence and distribution of heavy metals in soils is influenced mainly by the parent material, the chemical and physical soil properties, the metal speciation, and the climatic conditions. The mineral content of the parent material is one of the most important factors for the amount of trace elements in soils, irrespective of classification or the amount of weathering (Burt et al., 2003).

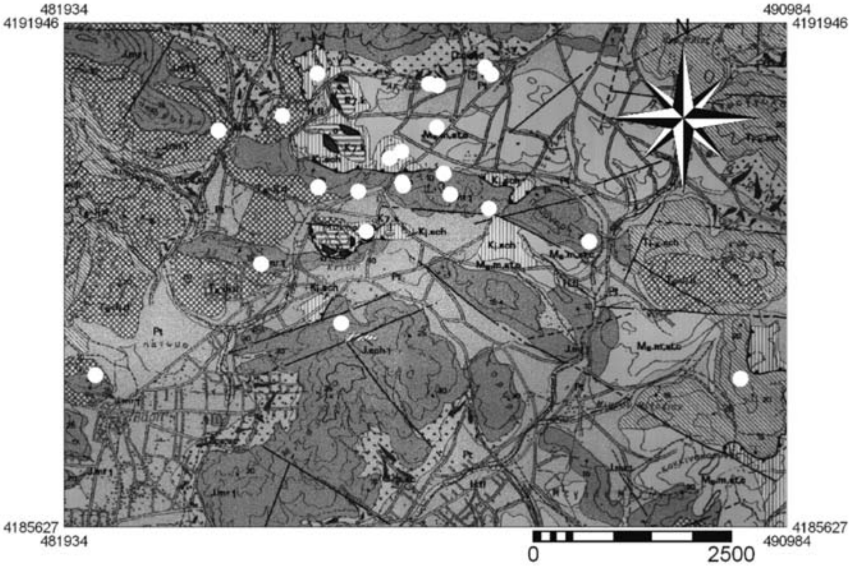

**Fig. 1:** Map showing the locations of the soil sampling sites. a) Ts-J1d, Pirnari dolomites, b) J.mr1, J.sch1: Lower marble, schists intercalations respectively, c) K1.sch, K1.K: schists, recrystallized limestones respectively, d) K7.k: limestones, e) O: ofiolites, f) Ms.m, st, c: marls, loams, sandstones, conglometates, g) Pt: Pleistocene deposits, h) Q.cs, sc: Quaternary undivided old and new talus cones and scree (I.G.M.E. KOROPI-VARI sheet 2004 Geological map, 1:50.000).

Soil contamination can be distinguished according to the intensity, the number, and the distance of pollution sources. ***"Diffuse" contamination*** is the contamination due to 1) a numerous sources, which are poorly identified, 2) sources that are in long distances (dozens of kilometres and sometimes hundreds), 3) mobile sources (vehicles, airplanes etc.). Contamination of this kind is usually moderate. ***"Punctual" contamination*** is due to an identified source, often close to the contaminated soil. This kind of contamination could be due to industrial activities or a heavy vehicle circulation in highways. Referring to a small region, the displacement of a punctual contamination to a diffusive one is given by the following example: the atmospheric emissions by a Pb smelter are a punctual contamination for surrounding soils but they contribute to a diffusive contamination as they move away. In this case, we have a pollution zone "diffuse of proximity" around the source and in many kilometres (Robert, 1996 in Girard et al. 2005).

Our previous studies (Lazaris, 2008) showed that in the forest (uncultivated) area of Vari, Attica (Fig. 1) multiple contaminants co-exist; namely Pb, Cd, Ni, Co, and Zn were determined in the soil horizons. The purpose of this work is to determine the concentrations of the heavy metals Cd, Zn, Pb, Co, and Ni in the soil of the study area and to investigate whether the possible elevated concentrations found are due to anthropogenic or geogenic sources.

## 2. Materials and Methods

### 2.1 Study area and Sampling

The study area belongs to the Attic-Cycladic geotectonic zone of Greece. It is localized by a rectangular with X,Y coordinates of upper left corner [481934, 4191946] and lower right corner [490984, 4185627]. The lithologic formations of the study area are dolomites, marble, schists, limestones, ofiolites (mafic rocks), marls, loams, sandstones, and quaternary deposits (Fig. 1). For centuries, the non-forest area was used for agricultural purposes, which through the years has been transformed to a light industrial one. The last few years though, there is an important urbanisation, legal and illegal. Soil sampling was conducted during October 2008. Twenty three sample sites were chosen (Fig.1) in uncultivated areas and soil was collected from two different depths in each sample site: i) 0-10cm (A depth) and ii) 10-25cm (B depth), making the number of samples forty six. The samples have been transported to the laboratory the same day and have been air-dried at room temperature for several days and passed through a 2mm stainless-steel sieve. Sub-samples were taken for further analysis.

## 2.2 Analytical Methods

Soil characteristics were determined following standard procedures. Measurement of soil pH in 1:1 (w/v) soil to deionised water agitated for 1 hour. Organic matter concentration was determined by the Wakley-Black method which is based on $K_2Cr_2O_7$-$H_2SO_4$ oxidation (Nelson and Sommers, 1982). The determination of total carbonate was performed as equivalent $CaCO_3$ percentage using a Bernard calcimeter (Allison and Moodie, 1965). Particle size distribution was determined by Hydrometer method (Bouyoukos, 1951). Heavy-metal concentrations were determined by extraction with $Na_2$EDTA (ethylenediamine tetraacetic acid) which extracts the exchangeable, carbonate-bound, Fe and Mn oxide-bounds, and a significant quantity of organic-bounds (Clayton and Tiller, 1979). The method involves shaking 10g of soil with 80cm$^3$ of 0.005M EDTA (pH=6.0) in polypropylene tubes for 15 hours at 20$^o$C. EDTA extraction procedure was chosen because it is widely accepted as a successful extractant and it is traditionally proposed for calcareous soils (Quevauviller et al. 1996; Quevauviller et al. 1998). The samples for the extraction procedure ($Na_2$EDTA) were centrifuged for 20min at 3000rpm (≈1500g) to compact most of the soil at the bottom of the tubes. The supernatant was filtered through a Whatman No 42 filter paper. The filtrates were analyzed for heavy metals using flame atomic absorption spectrometry (FAAS).

## 2.3 Statistical Processing

Descriptive statistics and multivariate statistical processing were performed. The data were classified into two groups according to their sample soil depth. Hierarchical Cluster Analysis (HCA) and Factor Analysis (FA) and namely the Principal Component Analysis (PCA) were applied with the use of SPSS 11.0.0 in order to obtain a visual interpretation of data and to detect similarities or differences among them. HCA is used to identify relatively homogeneous groups. The dendrograms were extracted using the Ward method and squared Euclidean distance and there has been a z standardization of the data. PCA analysis, a central tool in chemometrics, was performed using varimax rotation in order to make interpretable components. The component number was selected by using the Kaiser criterion (eigenvalue higher than 1).

## 3. Results- Discussion

Most soils of the study area are Alfisols and in particular suborder Xeralfs. Their mean organic matter content is 0.05 (A depth) and 0.04 (B depth), while mean pH value in both depths is 8.0. The soils are characterised as silty loamy, with clay mean values of 0.13 (A depth) and 0.18 (B depth) and corresponding silt values of 0.41 and 0.55 respectively (Table 1).

Heavy metal -EDTA extracted- concentrations ranged widely among sample sites (data not shown);

**Table 1.** Descriptive statistics of soil properties and heavy-metal concentrations (mg kg$^{-1}$) for A, B depths.

| A | OM$_A$ | pH$_A$ | CaCO$_{3A}$ | CLAY$_A$ | SILT$_A$ | Pb$_A$ | Cd$_A$ | Co$_A$ | Ni$_A$ | Zn$_A$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Min. | 0.01 | 7.70 | 0.10 | 0.04 | 0.24 | 9.65 | 0.00 | 0.50 | 0.00 | 1.29 |
| Max. | 0.08 | 8.30 | 0.50 | 0.23 | 0.68 | 1779.12 | 1.78 | 15.98 | 18.58 | 23.22 |
| Mean | 0.05 | 8.01 | 0.11 | 0.13 | 0.41 | 169.35 | 0.60 | 7.19 | 6.98 | 6.21 |
| Std. Dev. | 0.02 | 0.13 | 0.12 | 0.06 | 0.13 | 381.37 | 0.47 | 4.54 | 4.57 | 4.88 |
| **B** | **OM$_B$** | **pH$_B$** | **CaCO$_{3B}$** | **CLAY$_B$** | **SILT$_B$** | **Pb$_B$** | **Cd$_B$** | **Co$_B$** | **Ni$_B$** | **Zn$_B$** |
| Min. | 0.01 | 7.7 | 0.01 | 0.08 | 0.34 | 10.66 | 0.00 | 0.14 | 0.00 | 0.40 |
| Max. | 0.07 | 8.4 | 0.38 | 0.32 | 0.70 | 1649.88 | 1.45 | 18.44 | 25.77 | 13.65 |
| Mean | 0.04 | 8.00 | 0.09 | 0.18 | 0.55 | 161.36 | 0.53 | 8.30 | 9.43 | 3.52 |
| Std. Dev. | 0.01 | 0.15 | 0.93 | 0.08 | 0.08 | 349.31 | 0.39 | 5.66 | 6.36 | 3.12 |
| Grand mean* | | | | | | 25* | 0.175** | 7.90* | 22* | 64* |

Geometric mean**
OM=Organic Matter

determined mean values of the measured heavy metals in several sites were elevated and much higher than the soil grand mean worldwide (Table 1), as they were reported by Kabada-Pendias and Pendias (2001). Maximum, minimum, and mean values of the examined elements of the entire study area are presented in Table 1. Significant differences and elevated standard deviations were observed.

The higher Co and Ni contamination is found in the lower depth (10-25cm) indicating that they are derived from the parent material, while for Cd, Zn, and Pb in the upper depth (0-10cm) probably due to anthropogenic sources.

It is well known that cobalt and nickel are concentrated in soil horizons rich in organic matter and clays (Van Hullebusch et al., 2006; Lin et al., 2008). They are immobile in alkaline conditions since their oxides, hydroxides, and carbonate forms are very insoluble, while in acid conditions dissolution and leaching are more likely to occur (Alloway, 1995). The study area is not an acidic one and therefore Co and Ni are in a rather immobile form indicating that leaching is difficult to occur. Therefore, it could be suggested that the higher contents in the B depth originate from the parent material; this suggestion is amplified by the presence of relicts of ofiolites, meta-mafic veins, and carbonate rocks (I.G.M.E. Geological map, issue Koropi, 1:50.000) in the area, which inherit the highest amounts of Co and Ni in soils in accordance with Alloway (1995) and Kabata-Pendias and Pendias (2001).

Zn and Cd are very mobile and bioavailable metals, and their higher contents in A depth suggest their anthropogenic origin. Specifically for lead, measured values were extremely high and in some sites were 80 folds higher than the worldwide grand mean, i.e. 1779.12 and 1649.88 mg kg$^{-1}$ compared to the grand mean of 25 mg kg$^{-1}$. This result indicates that in the case of lead the source of contamination is a punctual source. Since in these specific sample sites there is no evidence of an existing anthropogenic source (e.g. an industry) and the parent material does not confirm and give reason for

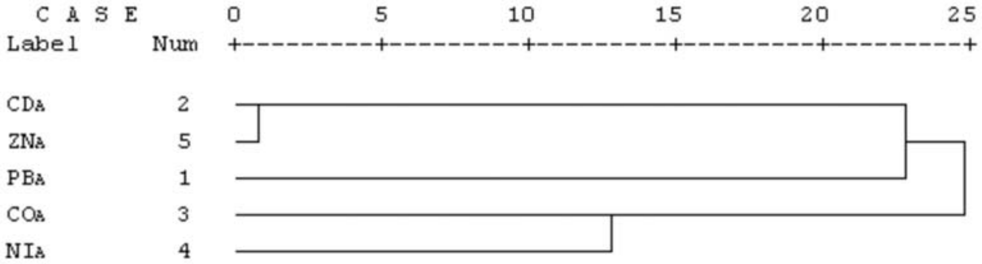

**Fig. 2**: Dendrogram for the descriptors using Ward Method (A depth).

the elevated Zn, Cd, and Pb contents, it could be concluded that probably in this sites there were ancient metallurgical activities. These are in accordance with the findings of Kakavoyianni (2003) which indicate that in the antiquity, the area has been used as an illegal workshop of metallurgy. An archaeological excavation in Lambrika area in 2003 revealed the existence of many litharge fragments (a product resulting from smelting of Pb). Archaeologists interpreted it as a small workshop of Early Helladic I period (3200-2800 BC) (Kakavoyianni, 2003). The existence of Pb could be interpreted only as a relict of smoke (chimney dust) in soil, since smoke liberates a significant portion of Pb and less Zn and Cd (Mousoulos 1976, Godin et al. 1985). Moreover, since half-lives for these metals are: 70-510 years for Zn, 13-1100 years for Cd, and 740-5900 years for Pb (Kabata-Pendias and Pendias, 2001), it could be concluded that their concentrations were much higher in the past.

Further analysis of the measured heavy-metal concentrations was conducted in order to ensure and reinforce the above mentioned suggestions. Hierarchical Cluster Analysis and Principal Component Analysis were performed in order to define their lithogenic or anthropogenic origin and to identify the possible sources of the contamination, although Burt et al. (2003) reported that the separation of natural from anthropogenic sources of trace elements is difficult in soils

## Hierarchical Cluster analysis

### A DEPTH

Dendrogram for the descriptors (Fig.2) shows that two main clusters are extracted: the Co-Ni and the Cd-Zn and Pb cluster, indicating that these metals originated from two different sources. A significant subdivision of the Cd-Zn and Pb cluster into two was observed, showing that Cd-Zn is highly associated to each other, while Pb stands alone. Co and Ni are moderately associated to each other. All three clusters are either slightly correlated to each other or not at all.

### B DEPTH

The dendrogram for B depth (Fig. 3) is similar to that of A depth indicating the same sources of origin. The group of Co-Ni is totally isolated from both Cd-Zn and Pb clusters. Again Pb is almost uncorrelated to the group of Cd-Zn; the metals of the latter group are strongly associated to each other. Nevertheless, Co and Ni are much more correlated to each other in B than in A depth. This is the only difference between the clusters of the dendrograms for the two depths.

## Factor analysis

Four factors are excluded, which account for 87.39% of the total variance in A depth (Table 2) The first component explains the 36.26% of the total variance and is positively and strongly related to

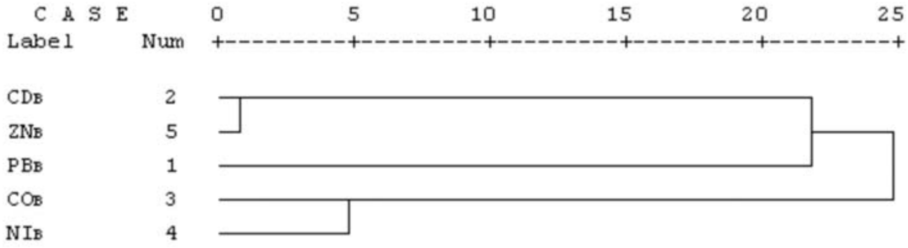

**Fig. 3:** Dendrogram for the descriptors using Ward Method (B depth).

**Table 2.** Principal Component Analysis (Varimax Rotation Method with Kaiser Normalization) for A depth.

| | Component | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| OM$_A$ | 0.11 | 0.10 | **0.93** | -0.07 |
| pH$_A$ | 0.10 | -0.62 | -0.52 | -0.47 |
| CLAY$_A$ | **0.81** | 0.39 | -0.22 | 0.11 |
| SILT$_A$ | **0.95** | 0.09 | 0.06 | 0.09 |
| Pb$_A$ | 0.20 | -0.07 | -0.03 | **0.90** |
| Cd$_A$ | **0.92** | 0.14 | 0.06 | 0.24 |
| Co$_A$ | 0.39 | **0.60** | -0.21 | 0.47 |
| Ni$_A$ | 0.16 | **0.90** | 0.15 | -0.20 |
| ZnA | **0.80** | -0.12 | 0.48 | 0.01 |
| %Variance | 36.26 | 19.43 | 16.43 | 15.27 |
| Cumulative % | 36.26 | 55.69 | 72.12 | 87.39 |

**Table 3.** Principal Component Analysis (Varimax Rotation Method with Kaiser Normalization) for B depth.

| | Component | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| OM$_B$ | **0.82** | -0.09 | 0.14 | 0.04 |
| pH$_B$ | 0.30 | -0.88 | 0.07 | 0.02 |
| CLAY$_B$ | 0.39 | 0.18 | **0.76** | 0.31 |
| SILT$_B$ | 0.24 | 0.04 | -0.92 | -0.01 |
| Pb$_B$ | 0.15 | 0.06 | 0.10 | **0.96** |
| Cd$_B$ | **0.92** | 0.26 | 0.12 | 0.11 |
| Co$_B$ | 0.37 | **0.79** | 0.15 | 0.30 |
| Ni$_B$ | 0.30 | **0.65** | 0.56 | -0.28 |
| Zn$_B$ | **0.84** | -0.03 | -0.20 | 0.14 |
| % of Variance | 30.69 | 21.40 | 20.65 | 13.49 |
| Cumulative % | 30.69 | 52.09 | 72.74 | 86.23 |

clay, silt, Cd, and Zn. The second component, which explains the 19.43% of the total variance, shows high correlation to Ni and a moderate one to Co. The third component with a 16.43% of the total variance has a high factor loading for organic matter. The fourth component, accounting for the 15.27% of the total variance, has a very high factor loading for Pb.

Table 3 represents the four factors that are retained in the analysis and account for the 86.23% of the total variance in B depth. The first component accounts for the 30.69% of the total variance and is composed of very high factor loadings for Cd, Zn, and organic matter. The second component, explaining the 21.40% of the total variance, has a high factor loading for Co and a less high one for Ni. The third component with the 20.65% of the total variance has a high factor loading for clay. The fourth component explaining the 13.49% of the total variance has a very high positive factor loading for Pb.

The results of Hierarchical Cluster Analysis are in accordance with the results of Factor Analysis showing that there are two different contamination sources in the study area: the first source is connected to Cd, Zn, and Pb and is considered as the anthropogenic source, while Co and Ni originate from the second lithogenic source and are more correlated in depth B than in depth A, showing their probable lithogenic origin.

## 4. Conclusions

Measured EDTA extractable concentrations of Cd, Zn, Pb, Co and Ni ranged widely among sample sites and substantial differences were observed. The results of HCA and FA analysis of soil properties and heavy-metal concentrations satisfactorily describe the presence of the five heavy metals in the soil of the study area. The factors and the clusters excluded are in agreement with each other showing two sources of pollution. Firstly the lithogenic source, which provides the heavy metals Co and Ni, with higher concentrations in B depth (lower depth), and secondly the anthropogenic source, which provides the heavy metals Cd, Zn, and Pb, with higher concentrations in A depth. Determined lead concentrations were extremely high and in connection with its long lasting half-life in soils (740-5900y) this metal can threaten the health of animals and humans upon entering in food chain. Since there are not any minerals containing Pb in the lithologic formations of the area or any industries that would produce such concentrations, it could be concluded that probably in this sites there were ancient metallurgical activities. Indeed, this is in agreement with the findings of archaeological excavations which indicate that in the antiquity the area has been used as a workshop of metallurgy.

## 5. References

Allison, L. E. and Moodie, C. D., 1965. Carbonate. In: CA Black (ed.) Methods of Soil Analysis, part 2. Agronomy 9: 1379–1400. Am Soc of Agron, Madison, Wisconsin, USA.

Alloway B. J., 1995. Heavy metals in soils, 2nd Edition, Springer 1995, pp. 384.

Bouyoukos, G.J., 1951. A recalibration of the hydrometer method of making mechanical analysis of soils. Agron. J. 43: 434-437.

Burt, R., Wilson, M., Mays, M.D., Lee, C.W., 2003. Major and trace elements of selected pedons in the USA. *J. Environ. Qual.* 32:2109-2121 (2003).

Clayton, P.M. and Tiller, K.G., 1979. A Chemical Method for the Determination of the Heavy Metal Content of Soils in Environmental Studies. In: *Paper No. 41*, CSIRO Australia, Melbourne Div. Soils Tech. (1979), pp. 1–17.

Dudka, S., Adriano, D.C., 1997. Environmental impacts of metal ore mining and processing: a review. *Journal of Environmental Quality* 26: 590-602.

Fytianos, K., Katsianis, G., Triantafyllou, P., Zachariadis, G., 2001. Accumulation of heavy metals in vegetables grown in an industrial area in relation to soil. *Bull. Environ. Contanim. Toxicol.* 67: 423-430.

Girard, M-C., Walter, C., Rémy, J-C., Berthelin, J., Morel, J-L., 2005. Sols et environnement, Éditions Dunod, Paris, 2005.

Godin, P.M., Feinberg, M. H., Ducauze, C. J., 1985. Modelling of soil contamination by airborne lead and cadmium around several emission sources. *Environmental Pollution Series B, Chemical and Physical*, 10:2 (1985), pp. 97-114.

I.G.M.E. KOROPI-VARI sheet 2004 Geological map 1:50.000. Department of geological maps of IGME, Athens, Greece.

Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D., Violante, P., 2003. Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental Pollution* 124 (2003) 247–256.

Kabata-Pendias, A, and Pendias, H., 2001.Trace elements in soils and plants, 3rd Edition, CRC Press LLC, pp. 413.

Kakavoyianni, O., 2003. A EH I Metallurgy Workshop of Silver in Lambrika, Attica (Koropi). *Archaeology & Arts* 94, 45-48 (in Greek with abstract in English).

Kribek, B., Majer, V., Veselovsky, F., Nyambe, I., 2010. Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: A topsoil vs. subsurface soil concept. doi: 10.1016/j.gexplo.2009.12.005.

Lazaris, Sp., 2008. Determination of heavy-metal contamination sources in soils of Koropi-Vari area, Attica. Master thesis, Agricultural University of Athens (in greek).

Lin, C., Negev, I., Eshel, G., Banin, A., 2008. In situ accumulation of copper, chromium, nickel, and zinc in soils used for long-term waste water reclamation. *Journal of Environmental Quality* 37: 1477-1487.

Mousoulos, P., 1976. Metallurgy of Pb. National Engineering School, Athens 1976 (in greek), pp. 125.

Nelson, D.W. and Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter, pp. 539-579. IN: A. L. Page, R. H. Miller, and D. R. Keeney (eds.) Methods of Soil Analysis Part 2, Chemical and Microbiological Properties Soil Science Society of American, Inc., Madison, WI.

Quevauviller, Ph., Lachica, M., Barahona E., Rauret G., Ure, A., Gomez, A., Muntau, H., 1996. Interlaboratory comparison of EDTA and DTPA procedures prior to certification of extractable trace elements in calcareous soil. *The Science of the Total Environment* 178 (1996) 127-132.

Quevauviller, Ph., Lachica, M., Barahona, E., Gomez, A., Rauret, G., Ure, A., Muntau. H.,1998. Certified reference material for the quality control of EDTA- and DTPA-extractable trace metal contents in calcareous soil (CRM 600). *Fresenius J Anal Chem* (1998) 360 : 505–511.

Selinus, O., Alloway, B., Centeno, J. A., Finkelman, R. B., Fuge, R., Lindh, R., Smedley, P., 2005. Medical Geology, Elsevier Academic Press, 2005, pp. 812.

Shakeri, A., Moore, F. and Modabberi, S., 2009. Heavy Metal Contamination and Distribution in the Shiraz Industrial Complex Zone Soil, South Shiraz, Iran. *World Applied Sciences Journal* 6 (3): 413-425.

Singh, A., Sharma, R.K., Agrawal, M., Marshall, F.M., 2010. Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. *Food and Chemical Toxicology* 48: 611-619.

Van Hullebusch, E.D., Gieteling, J., Zhang, M., Zandvoort, M.H., Van Daele, W., Defrancq, J., Lens, P.N.L., 2006. Cobalt sorption onto anaerobic granular sludge: Isotherm and spatial localization analysis. *Journal of Biotechnology* 121: 227-240.

Wong, S.C., Li, X.D., Zhang, G., Qi, S.H., Min, Y.S., 2002. Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environmental Pollution* 119: 33-44.

Zhuang, P., McBride, M.B., Xia, H., Li, N., Li, Z., 2009. Health risk from heavy metals via consumption of food crops in the visinity of Dabaoshan mine, South China. *The Science of the Total Environment* 404: 1551-1561.