EVALUATION OF HEAVY METALS LEVELS IN SOILS OF TIRANA AREA (ALBANIA)

(VLERËSIMI I NIVELEVE TË METALEVE TË RENDA NË TOKAT E ZONËS SË TIRANËS)

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Abstract

This study was performed on the major soils of Tirana area with the aim to evaluate the contamination and pollution levels of these soils by heavy metals. Samples collected from six representative pedons/soil types of the study area were analysed for the important physicochemical properties using the standard methods and for the total contents of heavy metals Cd, Cr, Ni, Pb, Zn and Cu using atomic absorption spectrometry. Correlation coefficients were determined by SPSS 16.0, the spatial distribution maps of metals were compiled using Geostatistical Analyst and Spatial Analyst, and the reference values are calculated using the formulae of the Dutch system. The results obtained showed that the total contents of Cd, Cr, Ni, Pb, Zn and Cu in soil surface horizons varied widely with the respective mean values of 0.3, 174.2, 305.9, 19.7, 95.5 and 42.7 mg kg^{-1}. The reference values were 0.7, 113.7, 41.9, 85.5, 151 and 36.3 mg kg^{-1}, respectively. These values were similar to the reference values (values A) of the Dutch system. The values of contamination/pollution index (c/p) showed that the studied soils were low polluted with Cr and Cu and high polluted with Ni. Results suggested that the water resources in the study area are potentially threatened by pollution from metals Ni, Cr and Cu.

Keywords: contamination, pollution index, heavy metal, reference value, surface horizons, Albania.

Përmbledhje

Ky studim është realizuar në tokat kryesore të rajonit të Tiranës me qëllim për të vlerësuar nivelet e ndotjes së këtyre tokave nga metalet e rënda. Mostrat e mbledhura nga gjashtë pedone përfaqësuese/tipe tokash të rajonit të studimit janë analizuar për cilësitë e rëndësishme fizikokimike të tokës me metoda standarde dhe për përmbajtjet totale të metaleve të rënda duke përdorur spektrometrinë e absorbimit atomik. Koeficientet e korrelacionit janë përcaktuar me SPSS 16.0, hartat e shpërndarjes hapësinore të metaleve janë përpiluar duke përdorur Geostatistical Analyst and Spatial Analyst, dhe vlerat e referimit janë llogaritur duke zbatuar formulat e sistemit hollandez. Rezultatet e përftuara treguan që përmbajtjet totale të Cd, Cr, Ni, Pb, Zn dhe Cu në horizontet sipërfaqësore të tokave luhateshin së tepërmi me vlera mesatare respektive prej 0.3, 174.2, 305.9, 19.7, 95.5 dhe 42.7 mg kg^{-1}. Vlerat e referimit ishin 0.7, 113.7, 41.9, 85.5, 151.0 dhe 36.3 mg kg^{-1}, respektivisht. Këto vlera ishin të ngjas-

hme me vlerat e referimit (vlerat A) të sistemit hollandez. Vlerat e indeksit kontaminim/ndotje (c/p) treguan që tokat e studiuara ishin pak të ndotura me Cr dhe Cu dhe shumë të ndotura me Ni. Rezultatet sugjeruan që burimet ujore në zonën e studimit janë potencialisht të kërcënuara nga ndotja prej metaleve Ni, Cr dhe Cu.

Introduction

Heavy metals are present in soils in trace amounts. The high metal contents in soil derived from weathering of minerals or from human activity [4, 1]. The study area was not subjected to point pollution sources, while the rural soils have not received agricultural inputs at high application rates. However, the intensive agricultural land use in the area is possible (above 1000 mm annual precipitation). Former investigations have shown that the total contents of Ni and Cr in the surface horizons of these soils were higher than the maximum allowable concentration [3,5], which can have harmful effects on organisms and ecosystems. The high contents of heavy metals in the study area could be especially related to geological structure. The information on affecting degree by heavy metals of soils from this area is limited. Therefore, this study aimed to evaluate the contamination and pollution levels of these soils by heavy metals using the contamination/pollution index (C/p) and to assess the potential risk of contamination of water resources in the study area. Calculation of the contamination/pollution index is an effective method for interpreting the level of soil heavy metals [6].

Materials and methods

The study area is located in the district of Tirana (Central Albania) with a total area of 1238 km^2. It is characterized by a Mediterranean climate and variety of soils, which are very important for the agricultural production in Albania. Six soil types viz, meadow gray cinnamon (eutric cambisol), alluvial (calcaric fluvisol), grey cinnamon (haplic cambisol), mountain meadow (humic leptosol), dark mountain forest (dystric luvisol) and cinnamon mountain soil (chromic cambisol) were used in this study. The sampled profiles are located like in Figure 1 and Table 1. The profiles are sampled according to genetic horizons. Twentyfour surface samples were used for this study. Processed soil samples (< 2 mm) were analyzed for the important physicochemical properties by standards methods and for the total contents of heavy metals Cd, Cr, Ni, Pb, Zn and Cu. Soil pH was measured in 2.5:1 soil 0.01 M $CaCl_2$ suspension by pH-meter, carbonats were determined by calcimeter, texture was determined by Pipette; total carbon was measured by auto-analyser (HERAEUS CHN–RAPID), and total concentrations of Cd, Cr, Ni, Pb, Zn and Cu were measured at aqua-regia extract (AR) by atomic absorption spectrophotometry (AAS).

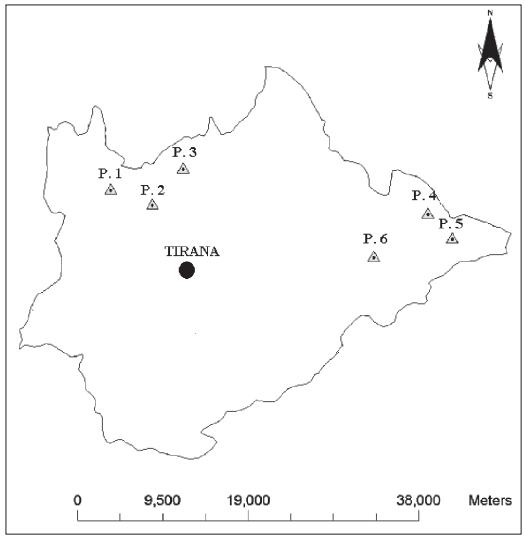

Figure 1. The study area

Profile	Location	Physiography	East	North
P.1	Preze	Alluvial flat	20^{0}15''66'	41^{0}34''21'
P.2	Laknas	Alluvial flat	20^{0}12''32'	41^{0}36''79'
P.3	Tapize	Hills	20^{0}05''38'	41^{0}32''50'
P.4	Bize	Mountains	19^{0}75''63'	41^{0}37''30'
P.5	Bize	Mountains	19^{0}70''15'	41^{0}38''84'
P.6	Qafmolle	Hills	19^{0}60''72'	41^{0}27''01'

Table 1. Coordinates of soil profiles

Soil properties	Range	Mean
pH	4.4-7.5	6.2
$CaCO_3$ (%)	0.0-10.9	3.4
Clay (%)	10.7-58.2	29.9
Organic carbon (%)	0.2-3.8	1.4
CEC (cmolc kg^{-1})	15.3-39.8	25.0

Table 2. The range and the mean values of soil properties

Correlation coefficients were calculated using SPSS 16.0. The spatial distribution maps of metals in soils were compiled using the Geostatistical Analyst/Spatial analyst (krigging interpolation) [2]. The reference values are calculated using the formulae of the Dutch system.

RESULTS AND DISCUSSION

The soils are having wide variations in their physicochemical properties (Table 2), viz., pH (4.4-7.5), $CaCO_3$ (0.0-10.9%), clay (10.7-58.2%), organic carbon (0.2-3.8%), and CEC (15.3-39.8 cmolc kg^{-1}). Correlation analysis revealed the soil factors that influenced the contents of heavy metals. Thus, the soil pH influences the contents of Zn (r=-0.739**), Cu (r=-0.588**), Pb ((r=-0.573*) and Cd (r=-0.499*). $CaCO_3$ influences the contents of Cu (r=-0.725**), Zn (r=-0.608**) and Pb (r=-0.464*), organic carbon influences the contents of Zn (r=0.551*), Cu (r=0.538*) and Pb (r=0.498), and clay influences the contents of Cd (r=0.689**), Zn (r=0.625**), Pb (r=0.574*), and Cu (r=0.545*).

Table 3 shows the range and mean values of the total metal contents, and Figure 2 and 3 show the spatial distribution of the Cr and Ni contents in surface soils from the study area. Thus, the total Cd varied from 0.1 to 2.3 with a mean values of 0.3 mg kg^{-1}, Pb from 7.8 to 57.2 mg kg^{-1} with a mean values of 19.7 mg kg^{-1}, Zn from 68.2 to 178.4 mg kg^{-1} with a mean values of 95.5 mg kg^{-1}, Cu from 34.7 to 56.8 mg kg^{-1} with a mean values of 42.7 mg kg^{-1}, Cr from 101.4 to 323.2 mg kg^{-1} with a mean values of 174.2 mg kg^{-1} and Ni from 156.0 to 559.2 mg kg^{-1} with a mean values of 305.9 mg kg^{-1}. It seems that the total metal contents in the studied soils were in the permissible limits [7], except Ni in all investigated soils and Cr in grey cinnamon soil (haplic cambisol).

Soil properties	Range	Mean	EU Limits
Cd	0.1-2.3	0.3	3
Pb	7.8-57.2	19.7	300
Zn	68.2-178.4	95.5	300
Cu	34.7-56.8	42.7	140
Cr	101.4-323.2	174.2	200
Ni	156.0-559.2	305.9	75

Table 3. The range and the mean values of heavy metals

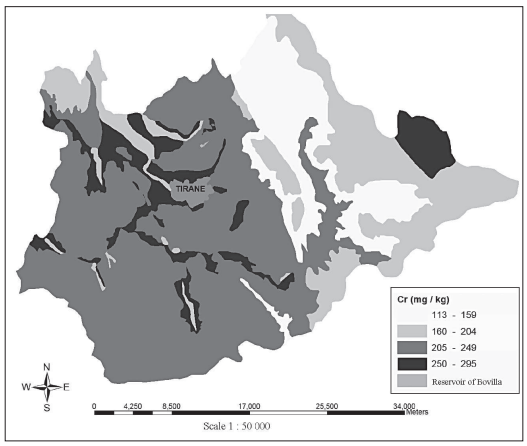

Figure 2. Spatial distribution of the total Cr content in surface soils of Tirana area

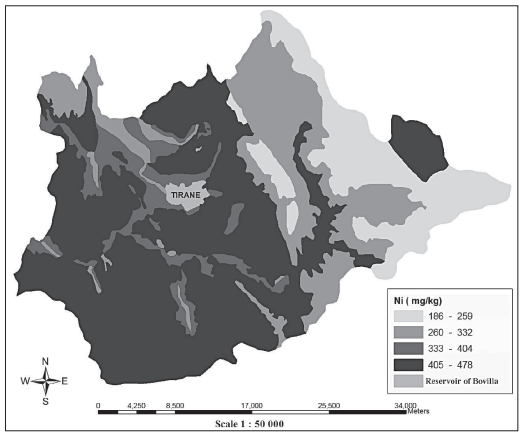

Figure 3. Spatial distribution of the total Cr content in surface soils of Tirana area

In order to interpret the levels of soil heavy metals, the reference values are calculated (Table 4 and Figure 4). These values were for Cd 0.7, Cr 113.7, Ni 41.9, Pb 85.5, Zn 151.0 and for Cu 36.3 mg kg^{-1}. These values were similar to the reference values (values A) of the Dutch system. From comparison of analytically determined values of heavy metals with reference values results that the

Metal	Measured value	Reference value	C/p	Significance
Cd	0.3	0.7	0.4	Medium contamination
Cr	174.2	113.7	1.5	Low pollution
Ni	305.9	41.9	7.3	High pollution
Pb	19.7	85.5	0.2	Low contamination
Zn	95.5	151	0.6	High contamination
Cu	42.7	36.3	1.2	Low pollution

Table 4. Contamination/pollution index (C/p)

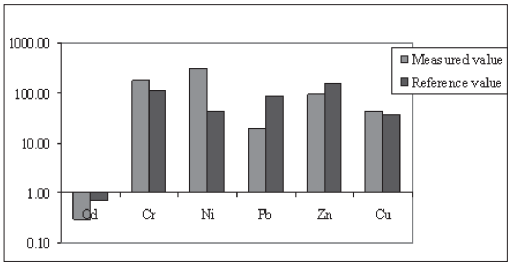

Figure 4. Measure and reference values of heavy metal content at logaritmic scale (mg/kg) in soil

soils studied were low polluted with Cr and Cu and high polluted with Ni. For that reason, a high potential risk of water pollution exists in the study area. Therefore, further work is needed to predict this potential risk of water pollution from metals.

CONCLUSIONS

From the above results it could be concluded that (i) the metal variability in soils of Tirana area can be explained by soil properties as pH, and clay, $CaCO_3$ and humus contents; (ii) the soils of Tirana area are low polluted with Cr and Cu and high polluted with Ni; and (iii) the low clay and humus contents and the acid soil reaction influence on metal mobility in the soil profile, and therefore the water resources in the this area are potencially threatened by contamination with these elements; and (iv) further work is needed to predict the risk of groundwater pollution from metals in the study area.

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