Background and Reference Values of Heavy Metals for Agricultural Soils of the Tirana Region, Albania

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Abstract

Soils of Tirana region are very important for the agricultural production in Albania. These soils are under the different environmental conditions and production systems and are classified according to FAO, 1998 (FAO, 2001) as eutric cambisol, calcaric fluvisol, haplic cambisol, humic leptosol, dystric luvisol and chromic cambisol. Thirty-eight soil samples from six soil sites representative of different parent materials of Tirana region were sampled and analysed for basic characteristics and also for the total form of heavy metals after extraction with aqua-regia. The aim of this research was to establish the background and reference values of heavy metals for agricultural soils of this region. The data on heavy metal contents were submitted to statistical analyses. Results showed that the total Cd, Cr, Ni, Pb, Zn and Cu contents of the study soils varied widely with respective mean values of 0.31, 168.6, 291.89, 17.6, 93.5, 42.3 mg kg⁻¹. The background values of total metal contents based on the 90th percentile criterion were (mg kg⁻¹): Cd (0.8); Cr (227.6); Ni (455.6); Pb (19.9); Zn (113.3) and Cu (51.9). While the reference values were (mg kg⁻¹): Cd (0.7); Cr (113.7); Ni (41.9); Pb (85.5); Zn (151) and Cu (36.3). The reference values for all the analyzed metals (except Cd) are higher than those of Dutch system (Cr - 100; Ni - 35; Cu - 36; Pb - 85 and Zn - 140 mg kg⁻¹).

Key words: total heavy metals, background concentrations, metal distribution, permissible limits, soil pollution

Introduction

Quantities of heavy metals that enter soil as the result of human activity can be assessed on the basis of background values of these elements in soil. Soil background values indicate the naturally occurring geogenic basic contents as well as the generally applicable anthropogenic additional contamination of the soils, and can be used to calculate reference values. These values depend on the soil type and on the soil variables as soil pH, organic matter, soil texture as well as from nature of parent materials and land use class (Labo, 1995).

Up to the year 1990, the study of heavy metals in soils of Albania was focused especially on relationship of Zn, Cu and Mn to the problems of soil fertility and plant nutrition (Gjoka, F. 1999). Other heavy metals like Cd, Cr, Ni, Pb and Hg have been widely ignored, although these elements are known for their toxicity. While, the studies of the last decade were focused on potential toxicity of heavy metals as a result of industrial and agricultural activities and waste disposal on land (Saraci et al., 1995; Gjoka et al., 2002). At present, to interpret the level of soil heavy metals in Albania, the EU maximum allowable limits are used. Information on heavy metal contents in the soils of Albania can be found in three main sources: scientific journals, study reports and dissertation theses. On the other hand, no information exists on the background values of heavy metals in the soils. Therefore, in this study were determined the total Cd, Cr, Ni, Pb, Zn, Cu and some relevant properties of agricultural soils from Tirana region, Albania. The aim was to obtain the background and reference values for the assessment of soil pollution by these metals.
Materials and methods

Study region. Region of Tirana is located in the central part of Albania and has a total surface of 1238.5 km², of which 314.5 km² is arable land. Region’s climate is Mediterranean, where mean annual rainfall are 1015.6 mm, temperature 15.7 °C and potential evaporation 916 mm. This region has a dissected topography and contains a variety of landforms like high mountains, hills, valleys and plains. Soil parent materials are generally composed of Mesozoic limestone in the mountain zone, Tortonian molassic formations, Palaeogene flysch and Cretaceous limestone in the hilly zone, and the Quaternary deposits in the plain zone of study region. Actual vegetation was maize (Zea Mays), wheat (Triticum aestivum), alfalfa (Medicago Sativa), various vegetables and fruit trees at cultivated lands, and beech (Fagus silvatica), oak (Quercus Cerris, Quercus Pubescens, Quercus Ilex), juniper (Juniperus oxycedrus, Juniperus communis), ash (Fraxinus ornus), hornbeam (Carpinus orientalis), hazel-nut (Corylus avellana), and Teridium aquilinum at uncultivated lands. Study region is covered by various soils. The major soil types were meadow gray cinnamon (eutric cambisol), alluvial soil (calcaric fluvisol), grey cinnamon (haplic cambisol), mountain meadow soil (humic leptosol), dark mountain forest soil (dystric luvisol), cinnamon mountain soil (chromic cambisol).

Soil sampling and analyses. Thirty-eight soil samples were collected from the main soils of Tirana region and analysed for the basic soil characteristics and for total Cd, Cr, Ni, Pb, Zn and Cu concentrations. Soil pH were measured in a 2.5:1 v/w 0.01 M CaCl₂ solution:soil ratio by pH-meter; carbonate contents were determined by the gasometrical procedure; texture were determined by the hydrometer method; CEC pot was determined by the Mehlich method; available P and exchangeable K were determined by the CAL-method (P and K were extracted using a 1:20 w/v soil CAL-solution ratio and their concentrations were measured by the spectro- and flame-photometer, respectively); poorly crystalline and free Fe oxides were determined by NH₄-oxalate and Na-dithionite extraction, respectively, and iron was measured by atomic absorption spectrophotometer; total carbon and nitrogen contents were determined by the auto-analyser. The background values for the surface horizons are given as 90th percentile. The reference values are calculated using the formulae of the Dutch system.

Results and discussion

Soil properties. Soils studied are having wide variations in their physicochemical properties. Soil reaction varied from extremely acid to slightly alkaline. The pH values varied from 4.38 to 7.49. The higher pH values were mainly related to content of carbonates in the soils, which varied from 8.14 to 10.16%. In soils with pH values <7.0 the carbonate contents were <0.5%. Correlation coefficient between these two soil variables was high (r=0.78***). The texture varied from loam to silty-clay. Clay content varied from 18.20 to 44.04% with irregular distribution pattern with depth. Soils showed different contents of organic carbon and total nitrogen due to different soil management. The respective values varied from 0.28 to 3.77% and from 0.06 to 0.34% and decreased consistently with depth. Organic carbon was highly correlated with total nitrogen (r=0.99***). C/N ratio varied from 4.7 to 12.3 and is lower for subsoils except fluvisol. Cation exchange capacity (CEC) was medium. Its values varied from 16.65 to 39.76 cmolc kg⁻¹. CEC values were highest in the surface horizons except etric cambisol and calcaric fluvisol. CEC was highly correlated with organic carbon (r=0.74***), and clay fraction (r=0.68**), which indicated that soil humus must be a more dominant influence on soil cation exchange capacity (CEC) than the soil clay fraction. Levels of poorly crystalline and free Fe oxides varied from 1953 to 6630 mg kg⁻¹ and from 6472 to 26265 mg kg⁻¹ respectively. Available P was medium to high, ranging from 11.7 to 34.2 mg kg⁻¹ and generally decreased with depth. Available K was also generally medium to high, its values varied from 39 to 200.2 mg kg⁻¹ and decreased consistently with depth. Available P was negatively and non-significant correlated with poorly crystalline (r=0.55) and free Fe oxides (r=-0.33). Decrease in P with the increase of free Fe is perhaps due to their adsorption from the Fe oxides. Significant negative correlation of available P with soil humus (r=-0.58**) and non-significant correlation with clay (r=-0.35) were also obtained. It appears that the humus controls P availability in these soils. Available K showed non-significant relationship with humus (r=0.15) and clay (r=-0.18).

Total metal (HCl+HNO₃) contents by soil parent material. Total Pb, Zn, Cu, Cr, Cd and Ni content of the study soils (Table 1) varied from 11.04 to 43.39, 70.05 to 142.65, 37.30 to 55.36, 100.1 to 295.1, 0.05 to 1.37 and 156 to 478.4 mg kg⁻¹, respectively. These values were higher than those found by (Celo et al., 1996) in soils from other agricultural regions of Albania. However, contents of metals were in the permissible limits.
Background and Reference Values of Heavy Metals for Agricultural Soils of the Tirana Region, Albania

(Alloway, 1995), except Ni in all investigated soils and Cr in haplic cambisol, and generally had this order: Ni > Cr > Zn > Cu > Pb > Cd. Highest metal contents in the surface horizons were found: Cd in dystric luvisol and humic leptosol over limestone (1.37 and 0.3 mg kg$^{-1}$ respectively); Cr in humic leptosol over limestone (295.1 mg kg$^{-1}$) and eutric cambisol over alluvial deposits (186.65 mg kg$^{-1}$); Ni in humic leptosol over limestone (478.4 mg kg$^{-1}$) and haplic cambisol over clays (468.87 mg kg$^{-1}$); Pb in dystric luvisol over limestone (43.39 mg kg$^{-1}$) and chromic cambisol over clays (19.28 mg kg$^{-1}$); Zn in dystric luvisol over limestone (142.65 mg kg$^{-1}$) and chromic cambisol over clays (103.82 mg kg$^{-1}$); and Cu in humic leptosol and dystric luvisol over limestone (55.36 and 44.39 mg kg$^{-1}$ respectively). These soils showed higher metal contents in the surface horizons compared to calcaric fluvisol developed over recent fluvial deposits. These data confirm the relations between the soil metal content and its parent material, as reported by (Alloway, 1995, Kabata-Pendias, 2001).

Total metal distribution with depth. Distribution of heavy metals in soils is influenced by several factors as parent material, mineralogy, organic matter content, particle-size distribution, soil horizonation, soil age, drainage, vegetation and aerosol inputs (Esser et al., 1991). Results showed three different patterns of metal distribution with respect to soil depth: decreasing metal content with depth; increasing content with depth; and irregular distribution. Decreasing metal content with depth was found for Cr and Cu in profiles 1 (old alluvial deposits) and 4 (limestone), for Cd in profiles 1 (old alluvial deposits) and 5 (limestone); for Ni in profile 4 (limestone); for Pb and Zn in profile 1 (old alluvial deposits). The higher metal contents in the surface horizons are as a result of cycling through vegetation, atmospheric deposition and adsorption by the soil organic matter (Alloway, 1995). However, correlation studies showed non-significant relationship between all analyzed metals and total carbon, and significant relationship between Cd, Pb and Zn and clay. Increasing metal content with depth was observed for Cd, Pb and Zn in profile 4 (limestone); and for Ni and Cu in profile 6 (clays), and seems to be a result of migration of these elements and non-significant contamination. Irregular distribution was noted for Cr, Ni, Pb, Zn, Cu in profile 2 (recent fluvial deposits), Cd in profiles 3 (clays) and 6 (clays), Cr in profiles 2, 3, 5, and 6; Ni in profiles 1, 2, 3, and 5; Pb in profiles 2, 3, 5 and 6; Zn in profiles 2, 3, 5 and 6; Cu in profiles 2, 3 and 5. Generally, this distribution pattern is related to mobility of these elements in soil profile, which determines their concentrations and their position in soil profile (Fergusson, 1990). According to soil pH, the relative mobility of analysed metals might be considered medium. Thus, the findings suggest a tendency for Pb accumulation in the surface and Zn in the deep of soils.

Background values of heavy metals. The data on background values are given as 50th (median) and 90th percentile. Indication of a 90th percentile means that statistically nine of ten soils exhibit low or the same substance contents (Labo, 1995). To determine the reference values of heavy metals, in this study are used the formulae of the Dutch system (Lacatusu, R. 1995). According to Table 2, the background values of total metal contents based on the 90th percentile criterion were as follows (mg kg$^{-1}$): Cd (0.8); Cr (227.6); Ni (455.6); Pb (19.9); Zn (113.3) and Cu (51.9). While the reference values were (mg kg$^{-1}$): Cd (0.7); Cr (113.7); Ni (41.9); Pb (85.5); Zn (151) and Cu (36.3). The reference values for all the analyzed metals (except Cd) are higher than those of Dutch system (Cr -100; Ni - 35; Cu - 36; Pb - 85 and Zn - 140 mg kg$^{-1}$).

![Table 1. Total metal contents of soils (mg kg$^{-1}$) at two sampling depths](image-url)
**Tabela 2. Background values of total metal contents (mg kg\(^{-1}\))**

<table>
<thead>
<tr>
<th>Toka</th>
<th>Cd</th>
<th>Cr</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.31</td>
<td>168.6</td>
<td>291.89</td>
<td>17.6</td>
<td>93.5</td>
<td>42.3</td>
</tr>
<tr>
<td>Background values 50(^{th}) percentile</td>
<td>0.1</td>
<td>162.7</td>
<td>278.4</td>
<td>15.4</td>
<td>89.2</td>
<td>40.5</td>
</tr>
<tr>
<td>Background values 90(^{th}) percentile</td>
<td>0.8</td>
<td>227.6</td>
<td>455.6</td>
<td>19.9</td>
<td>113.3</td>
<td>51.9</td>
</tr>
<tr>
<td>Reference values</td>
<td>0.7</td>
<td>113.7</td>
<td>41.9</td>
<td>85.5</td>
<td>151</td>
<td>36.3</td>
</tr>
</tbody>
</table>

**Conclusions**

The total metal content of soils is dependent on the parent material and pedogenic processes. Content of metals in soils by parent material generally follows the sequence: limestone > clays > old alluvial deposits > recent fluvial deposits.

The distribution of heavy metals in soils is related to soil texture, pH, CaCO\(_3\) and free and poorly crystalline Fe oxides contents. In the soil profile, Pb tended to accumulate in the surface and Zn in the deep of soils.

The correlation studies suggest that the Zn and Pb are more subject to retention in soils with lower pH; Cu is mainly adsorbed at the surface of CaCO\(_3\) particles; Cd, Pb and Zn are associated with the clay fraction; Cu and Cr exist mainly as exchangeable ions absorbed on the surface of soil colloids; and the main compartments for Cd, Pb, Cu and Zn are secondary Fe oxides.

The proposed background and reference values for these soils are: (i) the background values (mg kg\(^{-1}\)): Cd (0.8); Cr (227.6); Ni (455.6); Pb (19.9); Zn (113.3) and Cu (51.9); (ii) the reference values (mg kg\(^{-1}\)): Cd (0.7); Cr (113.7); Ni (41.9); Pb (85.5); Zn (151) and Cu (36.3).

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**References**

- Labo, 1995. Soil Background and Reference Values in Germany.