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PhD THESIS
RESEARCH ON THE HEAVY METAL REGIME IN POLLUTED SOILS OF THE ZLATNA AREA

PhD THESIS ABSTRACT

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I. INTRODUCTION

The introductory chapter addresses theoretical, general environmental problems towards concept of setting a full agreement between multiple economic activities and requirements for conservation and protection of all environmental components.

Therefore, the necessary measures to control malnutrition and undernourishment by employing efficiency factors in increasing food production which involves the enhancement of the soil’s productive capacity.

II. STAGE OF RESEARCH REGARDING HEAVY METALS IN THE SPOIL-PLAT SYSTEM AND THEIR POLLUTING EFFECTS

This chapter relies on multiple bibliographic sources, while it also involves the main theoretical definitions of heavy metals and the conditions under which they become significant polluting sources

2.1. DEFINITION HEAVY METALS (Pb, Cd, Cu, Zn) – CHEMICAL TRAITS AND POLLUTING POTENTIAL

The category of "heavy metals" includes several elements Cd, Cu, Cr, Co, Fe, Hg, Mn, Mo, Ni, Pb, Zn, to be defined by their metallic properties (conductivity, ductility and stability as cations), atomic number greater than 20 and density greater than 5.6 kg/dm³ (Barbu, 2004; Canarache et al., 2006; Lal, 2002).

Their name suggests their inclusion in this category by their specific weight higher than 5mg/cm³ and a potentially toxic character upon high concentrations and they can be classified in trace elements category, as in low concentrations they are quality nutrients for plants. Naturally, they show low concentrations in soils, but can occur in high and potentially toxic concentrations as a result of human activities, especially of the uncontrolled type. In this alternative, their excess can cause disturbances in the soil, plants and water and subsequently in the food chain upper links.

The chemical characteristics of heavy metals - Pb, Cd, Cu, Zn- are tackled and their crustal representation (total representaton), and in soils and plants, as well as their dependence on the presence and activity of some soil indicators - pH, humus, CaCO₃, clay etc. and the influence of human activities that determine the way that these metals can become pollutants of the environment (Black, 1993; Barbu, 2004; Rusu, 2005).
2.2. SOURCES OF HEAVY METALS IN SOILS AND ECOSYSTEMS

According to several bibliographical sources, this chapter assesses the categories of sources of soil contamination with heavy metals, which are both primary sources: fertilizers, irrigation water, organic fertilizers and composts, pesticides, biosolid sludge, amendments (lime and gypsum), and secondary sources: automobile exhaust, thermal coal combustion with effluents, non-ferrous metals industry, spray paint, tire wear, waste combustion.

In connection with the classification, the contribution of these sources of heavy metals is mentioned for such contents that present a high risk for soil, plants, soil microorganisms and obviously their polluting effect for humans and animals.

In connection with these effects, these elements are phyto-toxic. The bibliographical data in mind, "problem" areas in terms of air and soil pollution with heavy metals in Romania are also assessed (PSC Minor, Baia Mare, Zlatna) (Laughlin, 2002; Rusu, 2005).

2.3. HEAVY METAL ACCUMULATION IN SOILS, VEGETATION AND WATERS

2.3.1. Heavy metal accumulation in soils

Existing data about the accumulation of heavy metals in soils are presented, which are representative of the Zlatna area as a result of the non-ferrous metals and mining industry (with reference to concentrations measured in soils and some soil properties altered by the effect of heavy metal pollutant effect) (Barbu, 2004).

2.3.2. Heavy metal accumulation in the vegetation

This subchapter assesses and classifies these metals in terms of bioavailability and vegetation degradation.

The pollutant effect and vegetation degradation is estimated according to the translocation coefficient values (transfer) of such elements in plant, with levels decreasing in the following order Pb > Cd > With > Zn (Șchiopu et al., 2002; Alloway, 1990; Ross, 1994).
2.3.3. Heavy metal accumulation in waters

Reference is made to the complexity of water pollution, linked to contamination due to industrial wastewater, groundwater and river network of the surface. Finally, heavy metals accumulate in the water (regardless of origin), while the groundwater level or essential central affluent determine a phenomenon of pollution over large areas, even at considerable distances from the source of pollution (Proorocu, 2008, Bejan et al., 2007).

2.4. SYNTHESIS OF RESULTS OBTAINED IN THE RESEARCH OF HEAVY-METAL POLLUTION (Pb, Cd, Cu, Zn)

Summarizing the results arising from previous research in the area, the first theoretical principles and concepts that lay the foundations and set directions of research carried out, involve:

- evaluation capacity of pollutants contaminating action in delineating the extent of pollution in the area;
- establish the level of contamination for components in residential areas and forest agri-ecosystems;
- research on the action of pollutants in the food chain to the consumers of products and services;
- effect of agrochemicals measures based on ligands and amendments (mineral and organic) for recovering the circuit of these polluting elements.

Regarding the objectives held by previous research, some results are presented in relation to the assessment of soil contamination with Pb, Cd, Cu, Zn and also the limits of interpretation of pollution according to the Pb content (as total forms).

Simultaneously, differentiated levels of heavy metal contamination are outlined in relation to some key agrochemical indicators of soil pH, humus, clay content, etc.. and in terms of use and occupancy of the land.

The chapter summarizes the effects of ameliorative measures that could control the level of heavy metal contamination, proving the positive effect of the application of amendments (based on zeolite tuff and limestone CaCO₃) and organic and mineral resources (garbage fermented manure, bentonite) either by favorable changes in pH or by
adsorption-fixation processes, which can reduce the level of activity and the polluting action of heavy metals. (resulting from the research of ICPA, 1977-2000; ICPA, 1998; Rusu et al., 1994, 1995)

III. PURPOSE AND OBJECTIVES OF RESEARCH RULES ON THE HEAVY METAL REGIME (Pb, Cd, Cu, Zn) IN POLLUTED SOILS OF THE ZLATNA AREA

3.1. DESCRIPTION OF THE NATURAL SURROUNDINGS OF ZLATNA
The geographical, relief, climate, water network and specific vegetation are presented for the area under research.

3.1.1. Short history of polluting sources with heavy metals in the Zlatna area
Given that the area under study, such activities took place that generated pollutants for centuries (the first "foundry" was inaugurated in 1747), the stages of industrial development of the town are presented, with improvement occurring over technological processes, until cessation of this activity (2004). Furthermore, the approach attempts at finding the ways leading to such an obviously useful an activity to become "aggressive" towards the environment, with the stark landscapes and inhabitants who, paradoxically, have lived on welfare benefits brought by the industrialization of the area (Environmental Newsletter, 2003 cited by Paulette Laura, 2004).

3.2. RESEARCH AND DOCTORAL THESIS OBJECTIVES
The paper submitted as a doctoral thesis works to achieve the overall goal, by pursuing the following objectives for research and study:

- primarily to study the representative soils of the area affected by heavy metal pollution and in dependence on their basic characteristics, to appreciate not only the pollution level characteristics but especially their vulnerability to pollutants that can be measured and the effect of reconstruction activities;
- research by previously evaluating the level of pollution, accumulation and soil contamination with heavy metals (Pb, Cd, Cu, Zn);
study the level of accumulation and concentration of heavy metals in total conventional forms (soluble in HNO₃ + HClO₄ + H₂SO₄) in soil after 10-12 years from the termination of industrial pollutants;

- accumulation and concentration level research in mobile conventional forms (soluble DTPA) in soils after 10-12 years from termination of pollutants;

- soil classification according to classes of heavy metal representation (Pb, Cd, Cu, Zn) according to agrochemical limits established for the case study and according to MAPPM Order no. 756/1997 issued to approve regulations to assess environmental pollution;

- study opportunities to issue forecasts while reducing the concentrations of heavy metals in the soil-plant system following the termination of the pollutants;

- proposing primarily an agrochemical monitoring system of the soil-plant system and to issue recommendations for ecological restoration.

The objectives fit a multidisciplinary area-chemistry, pedology, agrochemistry, ecology and environment and can tackle the theme and purpose in completing the thesis.

3.3. CHARACTERISATION OF HEAVY-METAL EMISSIONS IN ZLATNA DURING 1990-2000 AND 2002-2011

3.3.1. Characterisation of heavy-metal emissions during 1990-2000
It is presented in accordance with the reports conducted during the reference period and mentioned in the Soil Quality Monitoring (I.C.P.A., 1998).

3.3.2. Characterisation of heavy-metal emissions during 2002-2011
It is presented in compliance with the environmental status report of Alba (2011) the evolution of heavy metal emissions into the atmosphere during 2002-2011.
Table 13

The evolution of heavy metal emissions during 2002 - 2011 in the atmosphere in Alba County

<table>
<thead>
<tr>
<th>Year</th>
<th>Annual emission Hg (t/year)</th>
<th>Annual emission Cd (t/year)</th>
<th>Annual emission Pb t/year</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>0.0032</td>
<td>0.0316</td>
<td>4.093</td>
<td>4.127</td>
</tr>
<tr>
<td>2003</td>
<td>0.001</td>
<td>1.300</td>
<td>8.934</td>
<td>10.235</td>
</tr>
<tr>
<td>2004</td>
<td>0.0010</td>
<td>0.0024</td>
<td>0.270</td>
<td>0.273</td>
</tr>
<tr>
<td>2005</td>
<td>0.0010</td>
<td>0.0028</td>
<td>0.280</td>
<td>0.283</td>
</tr>
<tr>
<td>2006</td>
<td>0.0010</td>
<td>0.0046</td>
<td>0.833</td>
<td>0.838</td>
</tr>
<tr>
<td>2007</td>
<td>0.0010</td>
<td>0.0058</td>
<td>0.365</td>
<td>0.371</td>
</tr>
<tr>
<td>2008</td>
<td>0.0010</td>
<td>0.0037</td>
<td>0.284</td>
<td>0.288</td>
</tr>
<tr>
<td>2009</td>
<td>0.0040</td>
<td>0.0140</td>
<td>0.355</td>
<td>0.373</td>
</tr>
<tr>
<td>2010</td>
<td>0.0036</td>
<td>0.0107</td>
<td>0.228</td>
<td>0.242</td>
</tr>
<tr>
<td>2011</td>
<td>0.0054</td>
<td>0.0147</td>
<td>0.293</td>
<td>0.361</td>
</tr>
</tbody>
</table>

Source: Report on the environmental status of Alba county, 2011

The data presented show that pollutants released into the atmosphere during 2002-2011 show quantitative reductions compared to the situation above (1977-1998).

3.4. PEDOLOGIC, AGROCHEMICAL TRAITS AND SOIL VULNERABILITY TO POLLUTION IN THE ZLATNA AREA (Moderately Eroded Eutric Cambosol, Eutric Aluvisol)

Zlatna representative soils investigated are presented and characterized morphologically, physico-chemically and granulometrically with an emphasis on the moderately eroded eutric cambosol (3.4.1), albic stagnic luvisol (3.4.2) and eutric aluvisol (3.4.3.), as well as the conditions and factors that could cause vulnerability under the action of pollutants (advanced acidifying, medium and low content of humifiable organic matter humificabilă, coarse granulometric fraction, etc.).

3.5. ANALYTICAL LABORATORY METHODS EMPLOYED

For the analytical protocol used in soil analyses, the chemical analysis methods recommended and promoted soil monitoring system were employed (ICPA 2011) (Dumitru and Alexandrina Manea, 2011):
– pH suspension in an aqueous solution, with a potentiometric determination;
– organic-C and humus content estimation by means of the Walkley-Black Doughnut modification;
– P-mobile-spectrophotometric determination after solubilizing in a solution of ammonium acetate-lactate (AL solution);
– K-mobile-dosed by the flame photometric extraction solution;
– content of heavy metals (Pb, Cd, Cu, Zn) in total forms by dosage through atomic absorption spectrophotometry after previous solubilization in a mixture of mineral acids (HNO₃ + HClO₄ + H₂SO₄);
– content of heavy metals (Pb, Cd, Cu, Zn) in mobile forms, involving dosage by atomic absorption spectrophotometry after solubilization with a buffered DTPA solution (0.005M);
– granulometric analysis was performed according to the sedimentation velocity of component fractions with a Kubiena pipette.

IV. RESULTS OBTAINED IN THE RESEARCH OF THE HEAVY METAL REGIME (PB, Cd, Cu, Zn) FOR POLLUTED ZLATNA SOIL

The results show an increase in soil acidity, an advanced dealkalinization and contamination of soils degraded by excessively high concentrations of Pb, Cd, Cu, Zn.

4.1. EVOLUTION OF PHYSICO-CHEMICAL AND PHYSICAL TRAITS OF THE SOILS, UNDER THE IMPACT OF HEAVY METAL POLLUTION

The analyses show significant changes in soil units of stationaries under study: acidification, low and medium humus content and particle size (physically) a preponderance of their coarse fraction conditions that can foster mobility and accumulated heavy metals activity.
4.2. HEAVY METAL ACCUMULATION (TOTAL-SOLUBLE FORMS IN NITRIC ACID-PERCHLORIC ACID-SULPHURIC ACID) IN THE SOILS UNDER RESEARCH. INTERPRETATION OF THE FORM CONTENT.

Interpretation of analytical results was achieved by heavy metal reference values in accordance with the Order MAAPPM 756/1997 issued approving rules on assessing environmental pollution (for sensitive land-use). (Fig. 4)

![Fig. 4 Graphic interpretation of the reference values of heavy metals as Law Order M.A.P.P.M. 756/1997 for sensitive land use](image)

In accordance with the values of the specified limits, the content of heavy metals (Pb, Cd, Cu, Zn) in total forms proves their high accumulation in soils and yet, in the years 2011-2012, a great persistence.

Table 23

<table>
<thead>
<tr>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
<td>mg/kg</td>
</tr>
<tr>
<td>313</td>
<td>3,28</td>
<td>365</td>
<td>509</td>
</tr>
<tr>
<td>282,5</td>
<td>0,945</td>
<td>156,5</td>
<td>84</td>
</tr>
<tr>
<td>353</td>
<td>2,12</td>
<td>190,5</td>
<td>203,5</td>
</tr>
<tr>
<td>160,5</td>
<td>1,045</td>
<td>111</td>
<td>116</td>
</tr>
<tr>
<td>563</td>
<td>3,02</td>
<td>446,5</td>
<td>576,5</td>
</tr>
</tbody>
</table>

Domains of variables

<table>
<thead>
<tr>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>160,5-563</td>
<td>0,94-3,28</td>
<td>111-446,5</td>
<td>84-576,5</td>
</tr>
</tbody>
</table>
**Lead (Pb)** – its total forms show high and excessive levels of pollution in surface horizons (0-10 cm and 10-20 cm) with values exceeding systematic intervention threshold values. (Fig. 5)

![Graphic interpretation Pb's comparative values](image)

Fig. 5 Graphic interpretation Pb’s comparative values obtained with the total forms provided by Law Order M.A.P.P.M. 756/1997

The high level of soil contamination with lead is excessively represented element is represented, and these high quantities are still persistent, as such it is the metal of reference in the present and future monitoring of these soils.

**Cadmium (Cd),** the concentrations of total forms mainly located between the normal (1 mg / kg soil) and of the threshold values (3 mg / kg soil). (Fig. 6)

![Comparative graphic interpretation of the form Cd values](image)

Fig. 6 Comparative graphic interpretation of the form Cd values obtained with the total set provided by Law Order M.A.P.P.M. 756/1997
**Copper (Cu)** - holds in almost all concentration values at subhorizontal surface (0-10 cm) above the threshold of intervention (Fig. 7)

![Copper Concentration Diagram](image)

Fig. 7 Graphic interpretation's comparative values obtained with the total forms provided by Law Order M.A.P.P.M. 756/1997

**Zinc (Zn)** - the absolute values of total forms have the highest concentrations benchmarks, but in one stationary (0-10 cm) the zinc content is close to the intervention threshold. (Fig. 8)

![Zinc Concentration Diagram](image)

Fig. 8 Comparative graphic interpretation of the form Zn-values obtained with the total set by Law Order M.A.P.P.M. 756/1997

The analysis of load-contamination level with heavy metals (Pb, Cd, Cu, Zn) in total forms show 10 years after the cessation of the polluter’s activity that the high states of contamination with these elements are still present in the order Pb > With > Cd > Zn.

The highest concentrations of these elements are found in the aluvialsoil of the Ampoiului valley, with a coarse texture and very low clay content. (Fig. 9)
The major effect of pollution is caused by the accumulation of lead in high quantities, but also due to the chemical stability of balance products of the soil.

4.3. HEAVY METAL ACCUMULATION (MOBILE SOLUBLE FORMS IN DTPA) FOR THE SOILS UNDER RESEARCH; INTERPRETATION OF THE MOBILE FORM CONTENT; POSSIBLE PROGNOSES FOR GRADUAL REDUCTION OF THE HEAVY METAL CONTENT IN THE SOILS

Research on the regime of mobile forms resulted from total forms of heavy metals, proves that the pollution of these soils, after the closure of polluting factor is still active phenomenon. (Table 25)

Table 25

<table>
<thead>
<tr>
<th>Pb mg/kg</th>
<th>Cd mg/kg</th>
<th>Cu mg/kg</th>
<th>Zn mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>89,5</td>
<td>1,35</td>
<td>118</td>
<td>95,5</td>
</tr>
<tr>
<td>175,5</td>
<td>0,09</td>
<td>53</td>
<td>2,85</td>
</tr>
<tr>
<td>230</td>
<td>0,88</td>
<td>69</td>
<td>40,5</td>
</tr>
<tr>
<td>142</td>
<td>0,37</td>
<td>47</td>
<td>23</td>
</tr>
<tr>
<td>142,2</td>
<td>1,28</td>
<td>121</td>
<td>89</td>
</tr>
</tbody>
</table>

Domains of variables

| 89,5-230  | 0,09-1,35 | 47-121 | 2,85-95,5 |
**Lead (Pb)** - fits, considering the content of mobile forms (from the superficial horizon), the reference values exceeding the intervention threshold (over 100 mg / kg soil). Excessive lead pollution in mobile form is clearly found at a 0-20cm depth, coinciding with the edaphic volume explored by roots. (Fig. 10)

![Fig. 10 Comparative graphic interpretation of the obtained Pb values in soluble forms with values provided by M.A.P.P.M. 756/1997 Law Order](image)

**Cadmium (Cd)** – shows concentrations of mobile forms fitting normal and threshold values (1-3 mg / kg soil) and others at a normal level. (Fig. 11)

![Fig. 11 Comparative graphic interpretation of the obtained Cd values in soluble forms with values provided by M.A.P.P.M. 756/1997 Law Order](image)

**Copper (Cu)** - exhibits a representation of partially distributed mobile content values between the warning and intervention threshold (100-200 mg / kg soil) and between the normal and the threshold values (20-100 mg / kg soil). (Fig. 12)
Fig. 12 Comparative graphic interpretation of the obtained Cu values in soluble forms with values provided by M.A.P.P.M. 756/1997 Law Order

Zinc (Zn) – shows the lowest representation of mobile forms, close to normal values (Fig. 13)

Fig. 13 Comparative graphic interpretation of the obtained Zn values in soluble forms with values provided by M.A.P.P.M. 756/1997 Law Order

The mutual reporting of total and mobile forms (as percentage representation) shows a reduction of the mobile out of total forms of Pb to Cd and Cu and the lowest values for the Zn element which allows for a forecast that the gradual reduction of active and mobile forms and (reduction) will be more difficult and will take longer for Pb, with average efficiency for Cd, Cu and faster for Zn.
V. VALIDATION OF CHEMICAL ANALYSIS PROCEDURES FOR HEAVY METALS IN THE SOIL

Validation of the determination methods for heavy metals in total forms (soluble in nitric acid, perchloric acid, sulfuric acid) and in mobile forms (soluble in DTPA 0.005M) pursue the conditions of linearity, reproducibility and repeatability to ensure the full and complete applicability of research methods employed in the research of soils contaminated with these elements.

5.1. VALIDATION OF METHODS FOR THE DETERMINATION OF LEAD (Pb) AND CADMIUM (Cd) IN THE SOIL

Method validation was performed for Pb and Cd through the common method for determining the total form (as acid extraction), the mobile form (as extraction with a buffer solution of 0.005M DTPA) and spectrophotometric dosage for priority promotion in the current and dynamic evaluation of pollution with heavy metals. The deviation of accuracy parameters and those of repeatability and reproducibility proved, once meaning classification criteria and standard deviation values were fitted below the standard deviations, that methods are applicable and adaptable to monitor the content of heavy metals in polluted soils.

5.2. APPLICABILITY OF METHODS FOR THE DETERMINATION OF THE HEAVY-METAL CONTENT (Pb, Cd, Cu, Zn) – TOTAL AND MOBILE FORMS IN POLLUTED SOILS

The application of criteria and principles for the validation of the method for determining heavy metals in total and mobile forms has proven versatility and accuracy on the occasion of the current measurements part of the analyses in this thesis. The level of integrity was shown by the significant dependence of the mobile forms on the total forms for the elements determined (Pb, Cd, Cu, Zn).

In the case of lead (Pb) the dependence of the mobile on the total forms can be described by means of a parabolic equation type $y = a + bx + CX2$ (Fig. 19)
The specificity of this dependence shows that the total form feeds on the mobile form, but the level of solubilization was significantly limited for the DTPA solution (0.005 M) for representative representations of soil total forms.

For other heavy metals, models describe the dependence of the mobile on total forms as either parabolic (for CD) or linear (for Cu and Zn) (Fig. 22, Fig. 25 and Fig. 28)

Fig. 19 Dependence of Pb mobile form compared to content of Pb total form (depth 0-20 cm)

Fig. 22 Dependence of Cd mobile form compared to content of Cd total form (depth 0-20 cm)
Dependence of these forms, meaning and high level of confidence support the applicability and scientific value of heavy metal determinations by the two methods that allow parallel interpretations.
5.3. STUDY OF OTHER RELEVANT INDICATORS FOR THE RESEARCH OF HEAVY METAL REGIE IN POLLUTED SOILS

Representation of heavy metals (Pb, Cd, Cu, Zn) in water sources: data obtained show an improvement in river water quality for Ampoi river and an improved water state for the intake groundwater (wells).

![Graph showing heavy metals content in water sources from Zlatna](image)

Fig. 30 Heavy metals content in water sources from Zlatna

Setting the coefficients of translocation (transfer) of heavy metals from soils in plants: the values of these indicators (based on ratios metal-plant/metal-soil (in mg / kg soil)) show levels differentiated by category of the determining element. These values are within the limits in other determinations, while exhibiting higher values (than the previous ones) for Zn and Pb. Lead is a metal that holds translocation coefficients outside the previously established domain (Kloke et al. 1994).

VI. CONCLUSIONS AND RECOMMENDATIONS (SELECTIVE)

The analytical results obtained in the stationaries under research and under analysis reveal several relevant conclusions for the field.

1. Soil analyzes, presents a great variability of physico-chemical characteristics, partially dependent on the pedological soil type and are still significantly altered by prolonged action of pollutants present in the area for over 100 years;

2. The soil reaction (pH) reveals the acidifying and dealkalinizing effects mostly on acidic soils due to emissions from previous years and becomes variable only when the soil has been treated to neutralize the activity by applying
amendments. There was a lasting effect especially on luvisols used as hayfields and untilled, where amendment solubilisation was more difficult and located in the surface subhorizon (0-10 cm) due to compact organic formations in the spontaneous vegetation. For the same type of soil used as arable land, the effect of the amendment was more rapid due to the incorporation applied to the soil.

3. **Lead (Pb)** has proven high and persistent elevated avalues for surface horizons (0-10 cm and 10-20 cm) exceeding all reference benchmarks and intervention thresholds for all stationaries (in total forms).

**Cadmium (Cd)** has concentrations of total forms in between the normal and the threshold values (1-3 mg/kg soil).

**Copper (Cu)** concentrations for total forms are primarily over the alert threshold levels (> 100 mg/kg soil) in the surface horizon (0-10 cm), with one exception.

**Zinc (Zn)** has high values in total forms and a distribution between the normal and the level of the alert threshold (100-300 mg/kg soil) between the threshold values and the intervention ones (576.5 mg/kg soil).

4. **Lead (Pb)** shows the maximum concentration values in mobile forms along the superficial subhorizon (0-10 cm) and with one exception (located at 10-20 cm depth) as absolute values, these concentrations fall above the reference values of the intervention threshold (> 100 mg/kg soil).

**Cadmium (Cd)** has the maximum concentrations mobile forms, with two exceptions, in the superficial subhorizon (0-10 cm), but in terms of size, has a below-normal distribution between them and those of the threshold (<1 mg and between 1-3 mg/kg soil).

The **Copper (Cu)** content of mobile forms located and distributed between the normal and the threshold values (20-100 mg/kg soil) and between the latter and reference values of the intervention threshold (100-200 mg/kg soil).

**Zinc (Zn)** content of mobile forms holds a lower level than the other elements and located close to normal.
4. The reciprocal ratio of the total forms, as well as the assessment of only the mobile content allows for an assessment of the differential persistence and mobility of heavy metals under study (Pb, Cd, Cu, Zn) for each individual element.

The analysis of the representation is presented to show a reduction in the total mobile forms of Cd, Cu and Pb at the lower values in the case of Zn. Likewise, the level of contamination of heavy metals loading (pollution) and the level of persistence can also be reduced.

5. The analyses show a reduction in the total mobile forms of Cd, Cu and Pb, as well as lower values in the case of Zn. Likewise, the level of contamination of heavy metals loading (pollution) and the level of persistence can be reduced.