# THE CONTENT OF HEAVY METALS IN THE SOILS OF THE STATE PROTECTED NATURAL AREAS IN THE SOUTH-EASTERN AREA OF THE REPUBLIC OF MOLDOVA

## CONȚINUTUL METALELOR GRELE ÎN SOLURILE ARIILOR NATURALE PROTEJATE DE STAT DIN REGIUNEA DE SUD-EST A REPUBLICII MOLDOVA

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***Abstract.*** *Heavy metal (HM) content has been assessed in soils within 10 state protected natural areas (SPNA). The soil samples were collected from the soil layer 0-20 which is in direct relation to all biotic (edaphic and bio-indicatory plant organisms, soil microorganisms) and abiotic (atmospheric and wind deposits, physical-chemical processes, etc.) components responsible for the HM circuit within the ecosystems.*
*Evaluated on the basis of the grading scale of soils of the Republic of Moldova, (Кирилюк, 2006), the content of HM (Zn, Cu, Ni, Co) analysed, for the soil layer studied, was included in the categories of very low - high levels. In the evaluated soil layer, no cases of studied HM pollution were recorded. In some cases, however, there are trends in the accumulation of Zn and Cu, but their contents do not exceed the alert threshold (AT) values (tab. 1).*
*Both for APNA and for other terrestrial ecosystems, increased Cu and sometimes Zn content in environmental components are characteristic, as a result of the intensive processing of surrounding agricultural land and forests with phytosanitary products containing Cu and Zn.*
*After Adriano (1986), copper and zinc fall into the category of microelements with a biologically important role for forest ecosystems, deficiencies (<10 mg/kg) or exceed the AT (>100 mg/kg), can cause reduction of root and shoot growth, inhibition of enzymes, risks that in the case of ecosystems investigated are not attested.*
*In the case of the intervention threshold (IT), the studied HM values do not reach these values after Kloke (1980), which excludes the risk of toxicity, in the studied ecosystems, for plants and soil organisms.*
**Keywords:** heavy metals (HM), soil, ecosystems, toxicity.

***Rezumat.*** *Conținutul de metale grele (MG) a fost evaluat în solurile din cadrul a 10 arii naturale protejate de stat (ANPS). Probele de sol au fost prelevate din stratul de sol 0-20 cm, strat care este în relație directă cu toate componentele biotice (organisme vegetale edafice și bioindicatorii, microorganisme din sol) și abiotice (depozite atmosferice și eoliene, procese fizico-chimice etc.)*

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*responsabile de circuitul MG din cadrul ecosistemelor. Evaluat pe baza scalei de clasificare a solurilor din Republica Moldova, (Кирилюк, 2006), conținutul de MG (Zn, Cu, Ni, Co) analizat, pentru stratul de sol studiat, a fost inclus în categoriile de niveluri foarte scăzut - ridicate. În stratul de sol evaluat, nu au fost înregistrate cazuri de poluare cu MG studiate. Cu toate acestea, în unele cazuri, există tendințe în acumularea de Zn și Cu, dar conținutul lor nu depășește valorile pragului de alertă (PA) (tab. 1).*

*Atât pentru ANPS, cât și pentru alte ecosisteme terestre din Republica Moldova, conținutul crescut de Cu și uneori Zn în componentele de mediu este caracteristic, ca urmare a prelucrării intensive a terenurilor agricole și pădurilor din zona de ecoton al acestora cu produse fitosanitare care conțin Cu și Zn.*

*După Adriano (1986), cuprul și zincul se încadrează în categoria microelementelor cu rol biologic important pentru ecosistemele forestiere, deficiențele (<10 mg/kg) sau care depășesc (>100 mg/kg), pot determina substanțial reducerea creșterii rădăcinilor și a lăstarilor, inhibarea enzimelor, riscuri care în cazul ecosistemelor investigate nu sunt atestate.*

*În cazul pragului de intervenție (PI), valorile MG studiate nu ating aceste valori după Kloke (1980), ceea ce exclude riscul de toxicitate, în ecosistemele studiate, pentru plante și pedobionți.*

**Cuvinte cheie:** Metale grele (MG), sol, ecosisteme, toxicitate.

## INTRODUCTION

Today, without any reservations, the ecological status of the components of the environment is deplorable in most of the natural and anthropogenic ecosystems. Environmental pollution is a major danger to everything that means life today: man himself, air, water, soil, flora, fauna, etc.

The danger lies not only in the local harmful effect of the various pollutants, but also in the imbalance, which began to occur on a national, regional, respectively and on a planet-wide scale.

The National Environmental Strategy (NES), 2013-2023, provides that the protection and improvement of the quality of the environment in the Republic of Moldova will become a national priority, and the area of the state natural areas fund to be extended up to 8%.

The Action Plan on the implementation of the NES includes concrete activities for the optimization of the management in the State Protected Natural Areas (SPNA), the Core-areas of the National Ecological Network and of the Wetlands of international importance.

The relatively low share of SPNA in the country and the deplorable state of many of them require the periodic reassessment of the state of their components (air, soil, waters, biota), as well as the conduct of scientific research in other representative ecosystems in order to estimate their natural potential for the extension of the SPNA fund.

This article includes the complex assessment of the state of environmental factors, in particular the condition of the soil at the heavy metal content compartment (GM) in the state-protected natural areas in the south-eastern part of the Republic of Moldova.

The contents of heavy metals were evaluated in the soils of 10 natural areas protected by the state: 6 Natural Monuments (Geological and Paleontological); 3 Nature Reserves (2 forestry and 1 mixed); 1 Monument of landscape architecture.

The soil samples were collected from the soil layer 0-20 cm, which is in direct relation to all biotic (edaphic and bio-indicatory plant organisms, soil microorganisms) and abiotic (atmospheric and wind deposits, physical-chemical processes, etc.) components responsible for the heavy metal (HM) circuit within the ecosystems.

Pollution, in general, is a process of introducing any contaminants into an environment causing effects of instability, disorder, injury or discomfort on physical systems or living organisms. Pollutant is any foreign substance resulting from human activity or from a harmful or undesirable natural source entering the air, soil or water.

Lately, environmental pollution with HM has attracted attention because of the particularly complex problem raised by this phenomenon because most of them are not found in a water-soluble form or, if indeed they exist, the respective chemical species are complexed with organic or non-organic ligands, which radically influences their toxicity.

Some HM like Zn, Fe, Cu, Co or Cr are essential nutrients of plants manifesting toxic character only in high concentrations. Pb, Cd and Hg are toxic metals, without having any functional role in metabolism (Mingorance *et al.*, 2007). It is known that forest ecosystems have a high capacity to filter contaminants, including HM either airborne or polluted soil.

Once in the environment, HM undergoes an absorption process between different living environments (air, water, soil), but also between organisms in the respective ecosystems.

From contaminated soil, for example, plants, on the one hand, assimilate dissolved metals and, on the other hand, pollution by infiltration of groundwater occurs, from which, subsequently, the transfer to surface and drinking water takes place.

Environmental pollution with Cu and Zn, HM that refers to class 2 of toxicity are in fact dangerous for the “soil-plant” system.

That is why different heavy-duty HM exhibits different chemical characteristics and as a result will also differ in terms of behaviour in ecosystems, bioaccumulation and eco-toxicity (Bergmann, 1992).

Each metal can be characterized by an anthropogenic perturbation factor (FPA), defined as the ratio of annual global natural inputs to inputs due to human activities. Pb, Cd, Cu and Zn have the highest-rise FPAs (Bonneau, 1988).

SPNA, like other ecosystems in the Republic of Moldova, have been exposed (currently less) to pollution for a long period of time.

HM contamination is long-lasting because soil metals tend to accumulate in organic-rich horizons and remain in the soil without being transported to other living environments.

The source (Mingorance *et al.*, 2007) indicates such behaviour, primarily of Pb, Zn and Cd, which in the soils of forest ecosystems constitutes 65.0-99.3% of the total content of MG in the ecosystem.

Also, the same source finds a miserable accumulation of the mobile forms of lead in particular and, partially, of copper in the soil layer 0-20 cm, rich in organic matter.

## MATERIAL AND METHOD

*Physical-geographical characterization of the region under study.*

According to the pedo-geographical region of the Republic of Moldova, the South-Eastern part of the country (the research area) is part of the Steppe District of Southern Bessarabia, the pedogeographic subraion of the Lower Dniester Valley.

The territory is characterized by a flat relief with the predominance of slopes with an inclination of 0-$2^0$; altitudes between 20-120 m (average about 50 m), length of slopes of about 300 m.

The terraces are made up of loessoid clay, in the Dniester meadow being deposited recent alluvial layers. In the composition of the soil shell, typical weakly humiferous chernozems predominate (4.3%); carbonate chernozems - on terraces (12.7%); eroded soils – on slopes (30.7%).

In the Dniester meadow were formed alluvial soils, presented by all subtypes, often salinized, including solonceaques.

Soil samples were collected according to the “satellite” method. The mean sample was obtained by mixing nine separate samples of the same volume.

According to the methodological recommendations of the ICP Forests (2012) program, samples were collected for the soil layer 0-20 cm deep, for every 10 cm. Laboratory analysis were performed in the laboratory of Natural and Anthropogenic Ecosystems of the Institute of Ecology and Geography.

After collection the soil samples were dried at room temperature, separating the fraction of particles larger than 2 mm.

Soil samples was used in the analyses carried out.

In order to establish the amplitude of concentrations and to assess the degree of chemical pollution of the soil with HM, the total concentration of Zn, Cu, Ni and Co was determined.

The extraction was carried out with royal water, with the help of which it was possible to determine the fraction of HM that can potentially be released as a result of the action of environmental factors.

It should be noted that the extraction with royal water has superiority in terms of the high degree of standardization compared to other methods.

The total content of HM was determined using flameless and flameless spectrometry (F-AAS, GF-AASA), atomic emission spectrometry and fluorescent Roentgen spectrometry.

## RESULTS AND DISCUSSIONS

In the studied area (fig. 1) significant sources of industrial pollution are missing, except for those in the surrounding area - the power plant in Dnestrovsc city, with an impact twice as large on the republic compared to emissions (t/year) from stationary sources of pollution.

Evaluated on the basis of the soils gradation scale of the RM, (Кирилюк, 2006), the content of HM (Zn, Cu, Ni, Co) analysed, for the studied soil layer, was included in the categories of very low - high levels (tab. 1).

In the evaluated soil layer, no cases of studied HM pollution were recorded. In some cases, however, there are trends in the accumulation of Zn and Cu, but their contents do not exceed the alert threshold (AT) values (tab. 1).

Both for SPNA and for other terrestrial ecosystems from the Republic, increased Cu and sometimes Zn content in environmental components are characteristic, as a result of the intensive processing of surrounding agricultural land and forests with plant protection products containing Cu and Zn.

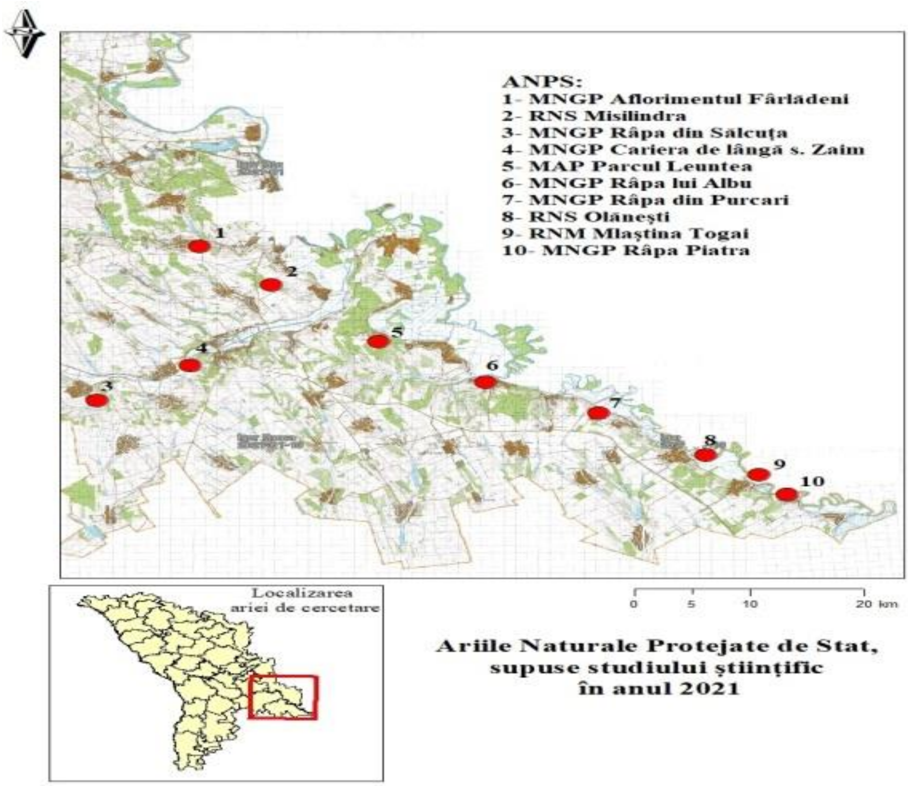


**Fig. 1** Scheme-map of investigated SPNA

*Table 1*

**HM content in the soil of the studied SPNA, mg/kg d.m**

| SPNA studied | Soil layer, (cm) | Zn | Cu | Ni | Co |
|---|---|---|---|---|---|
| **MNGP – Râpa Piatra** | *0-10* | 158 | 76 | 36 | 7 |
| | *10-20* | 120 | 62 | 22 | 5 |
| **MNGP – Râpa lui Albu** | *0-10* | 123 | 60 | 27 | 3 |
| | *10-20* | 105 | 40 | 21 | 3 |
| **MNGP – Râpa din Purcari** | *0-10* | 150 | 73 | 52 | 6 |
| | *10-20* | 135 | 58 | 41 | 3 |
| **RNS – Misilindra** | *0-10* | 110 | 56 | 23 | 5 |
| | *10-20* | 118 | 59 | 27 | 17 |
| **RNS – Olănești** | *0-10* | 146 | 72 | 15 | 4 |
| | *10-20* | 125 | 59 | 12 | 3 |
| **MAP – “Leuntea” Park** | *0-10* | 158 | 76 | 31 | 6 |
| | *10-20* | 171 | 82 | 45 | 6 |
| Alert threshold **(AT)** (Kloke, 1980) | | **300** | **100** | **75** | **30** |
| Intervention threshold **(IT)** (Kloke, 1980) | | **600** | **200** | **150** | **50** |
| Diapason in soils from RM (Кирилюк, 2006) | | **10-166** | **2-400** | **5-75** | **4-18** |
| Mean in soils from RM (Кирилюк, 2006) | | **71** | **32** | **39** | **13** |
| Klark (Lăcătușu, 2008) | | **66** | **22.4** | **23** | **9.6** |

**The levels of heavy metals content in soils from RM, pH – 6-8.5 (Кирилюк, 2006)**

| Content level | Zn | Cu | Ni | Co |
|---|---|---|---|---|
| **Very low** | < 20 | < 10 | < 15 | <5 |
| **Low** | 21-50 | 11-25 | 16-30 | 5,1-10 |
| **Average** | 51-100 | 26-50 | 31-50 | 11-20 |
| **Increased** | 101-150 | 51-75 | 51-70 | 21-30 |
| **High** | 151-200 | 76-100 | 71-100 | 31-40 |
| **Very high** | 201-250 | 101-150 | 101-150 | 41-50 |
| **Pollution level** | | | | |
| **Low pollution** | 251-500 | 151-250 | 151-250 | 51-100 |
| **Moderate pollution** | 501-1000 | 251-350 | 251-350 | 101-150 |
| **High pollution** | 1001-2000 | 351-500 | 351-500 | 151-250 |
| **Critical pollution** | >2000 | >500 | >500 | >250 |

After Adriano (1986), copper and zinc fall into the category of microelements with a biologically important role for forest ecosystems, deficiencies (<10 mg/kg) or exceed the AT (>100 mg/kg), can cause reduction of root and shoot growth, inhibition of enzymes, risks that in the case of ecosystems investigated are not attested.

In the case of the intervention threshold (IT), the studied HM values do not reach these values after Kloke (Kloke, 1978), which excludes the risk of toxicity, in the studied ecosystems, for plants and soil organisms.

However, it should be borne in mind that, although today the concentrations of the total forms of the analysed HM do not far exceed the background content, it should not be forgotten that in the process of genesis the chemical composition of the soil works and irreversible changes may occur.

Therefore, it is insufficient only to establish the presence and content of metal in the soil, which appears as a consequence of the implementation of intensive agricultural technologies, but it is necessary to deeply investigate the limit of the capacity of self-purification of the edaphic environment.

The HM circuit in the soil meets various biological barriers, as a result of which a selective bioaccumulation takes place, which protects living organisms from their excess.

The degradation of the normal functioning of biological barriers is primarily due to the presence of xenobiotic substances, including excess HM in the soil, although the buffering and adsorption capacity of our soils is high.

But the activity of these barriers is limited and often HM still accumulates in the soil and there is a risk of increasing their concentration to toxicity, which causes disturbance of the balance of biological, chemical and physical processes in the soil (Tărîţă and Andriuca, 2006).

## CONCLUSIONS

1. By evaluating the content of heavy metals in soil of the SPNA from the South-East part of the Republic of Moldova was established their concentration, dispersion degree and geochemical evolution, as a consequence of the past and present anthropogenic activity;

2. The presence of the analysed HM (Zn, Cu, Ni, Co) for the studied soil layer was included in the categories of *very low - high* levels. HM concentrations in soil vary within the following limits: Zn–105-171 mg/kg; Cu – 40-82 mg/kg; Ni – 12-52 mg/kg; Co – 3-17 mg/kg;

3. In the evaluated soil layer, no cases of studied HM pollution were recorded. In some cases, however, there are trends in the accumulation of Zn and Cu, but their contents do not exceed the alert threshold (AT) values.

For both SPNA and other terrestrial ecosystems from the Republic of Moldova, increased Cu and sometimes Zn content in environmental components is characteristic, as a result of intensive processing of surrounding agricultural cenozes and forests with plant protection products containing Cu and Zn.

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