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Assessment of heavy metals space-temporal evolution in protected areas from Romania. Case studies

BOGDAN ADRIAN STANESCU*, ADRIANA CUCIUREANU, ILEANA CRINA NICOLESCU, MARIAN GASNAC, GEORGIANA CERNICA

National Research and Development Institute for Industrial Ecology – ECOIND, 57-73 Drumul Podu Dambovitei street, district 6, 060652, Bucharest, Romania
**Corresponding author: stanescubogdan2@gmail.com*

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Abstract
Good knowledge of the concentrations of chemical elements in soil in some geographical regions is fundamental to understanding the pre-existing natural background, on top of which the anthropogenic input is added, especially through pollution. There are many areas left without a geochemical assessment. In these cases knowing the areas where the contribution of the anthropic factor is non-existent or minimal is particularly important from the point of view mentioned previously. This article aims to highlight the spatial and temporal variation of 5 heavy metals identified in soil and water (surface water and underground water) within 5 protected geographical areas in Romania, chosen as case studies. In these areas, the manifestation of natural factors, namely geomorphological, lithological, edaphic, climatic, and, last but not least, the anthropogenic factor that cannot be neglected, gives the possibility of an objective, quantifiable evaluation of the areas under study. The comparisons made highlighted the zonal variability underlying the influencing factors, as well as the way in which the normal values are or are not exceeded.

Keywords: *assessment, heavy metals, soil, pollution*

INTRODUCTION

Soil is a basic component of the biosphere [1]. The important thing is that it offers support for the development of life on the planet [2]. Anthropogenic activities expose it to pollution, with heavy metals being widespread [3]. That is why the study of soil pollution and the creation of databases regarding its quality are of major importance in the evaluation of environmental factors and the analysis of anthropogenic input [4-10].

A good knowing of the concentrations of heavy metals in the soil, respectively the concentrations of natural background, ensures the objective evaluation of anthropogenic sources that manifest themselves in the most different ways [11]. Can be mention from poor agricultural practices that cause the loss of soil fertility, from the improper and excessive use of chemical fertilizers that cause soil acidification, to activities with a major impact on terrestrial ecosystems [12]. This includes mining activities, the storage of industrial and municipal waste, the discharge of partially purified water, improper irrigation and many others [13]. Industrial emissions, respectively pollution by means of particulate matters containing heavy metals determine the spread of pollutants over large geographical areas and the long-term damage to terrestrial ecosystems [14].

Also, maintaining a balance regarding the content of heavy metals in the soil is particularly important for maintaining the health of the soil, a damage to the soil can cause adverse effects on

the soil water of the microbiota with greater implications on the health of the vegetation and animals [15-18]. The Earth's crust naturally has a natural content of heavy metals, and anthropogenic activities do nothing but change the distribution of these concentrations or increase the intake of heavy metals in areas polluted by anthropogenic activities [19]. That's why monitoring and distinguishing between the anthropogenic and natural factors is especially important in understanding the processes and in maintaining the soil and other environmental factors at acceptable quality conditions [20].
The degree of contamination of the soil can be quantified by the large-scale use of different concentration reporting procedures by using pollution indices or environmental risk quantification formulas. Each country tries to evaluate the quality of the soils on large geographical areas and establish, based on the results obtained, geo-atlases that contain databases related to natural background concentrations, precisely in order to detect the natural contribution from the anthropogenic one. Certain premises are created so that in future industrial developments those areas that already have a contribution of pollution are avoided, being able to achieve through an adequate territorial management, a balance in the distribution of resources and a sustainable development, without affecting the quality of the environmental factors [21].
The following presents results from the evaluation of the heavy metal content of soils in protected areas in Romania, respectively in 5 areas chosen as case studies for the evaluation of natural background concentrations.

MATERIALS AND METHODS

Localization

Localization of the study areas can be found in figure 1.

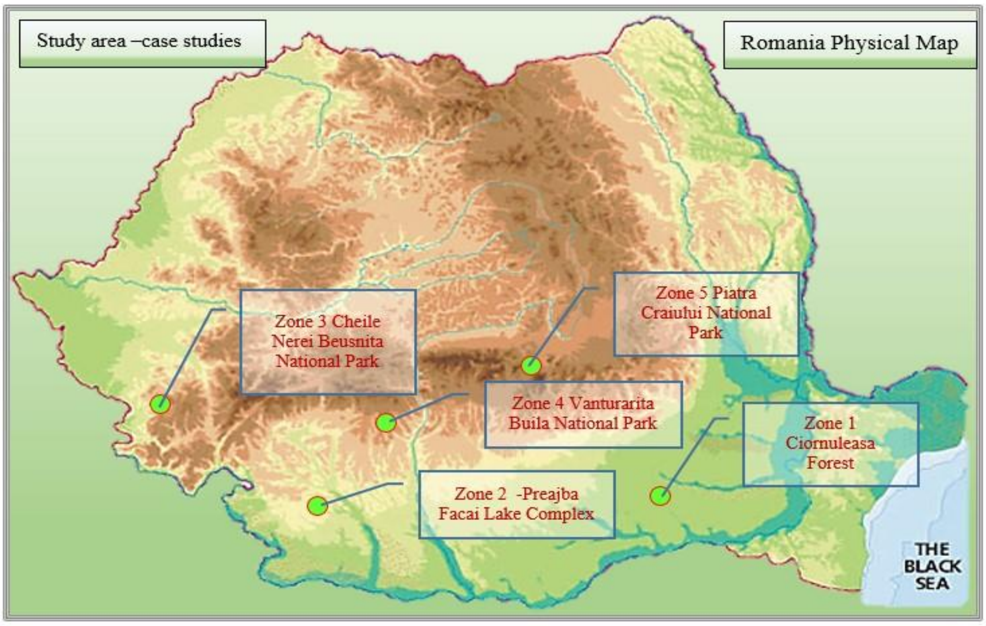

Fig. 1. Localization of the 5 protected areas from Romania- Case studies on Physical Map

For each zone, the most suitable sampling areas were studied in the field, following safe access roads, in relation to local conditions, their relevance in close connection with the objectives of the assessment.

Conceptual Model

The conceptual model can be found schematically in figure 2.
Investigation of the quality of soil and water environmental factors in different geographical areas requires various environmental conditions, relief, geology, hydrogeology, waters, soils, vegetation

to which is added the manifestation of anthropogenic factors directly or indirectly towards these protected areas.

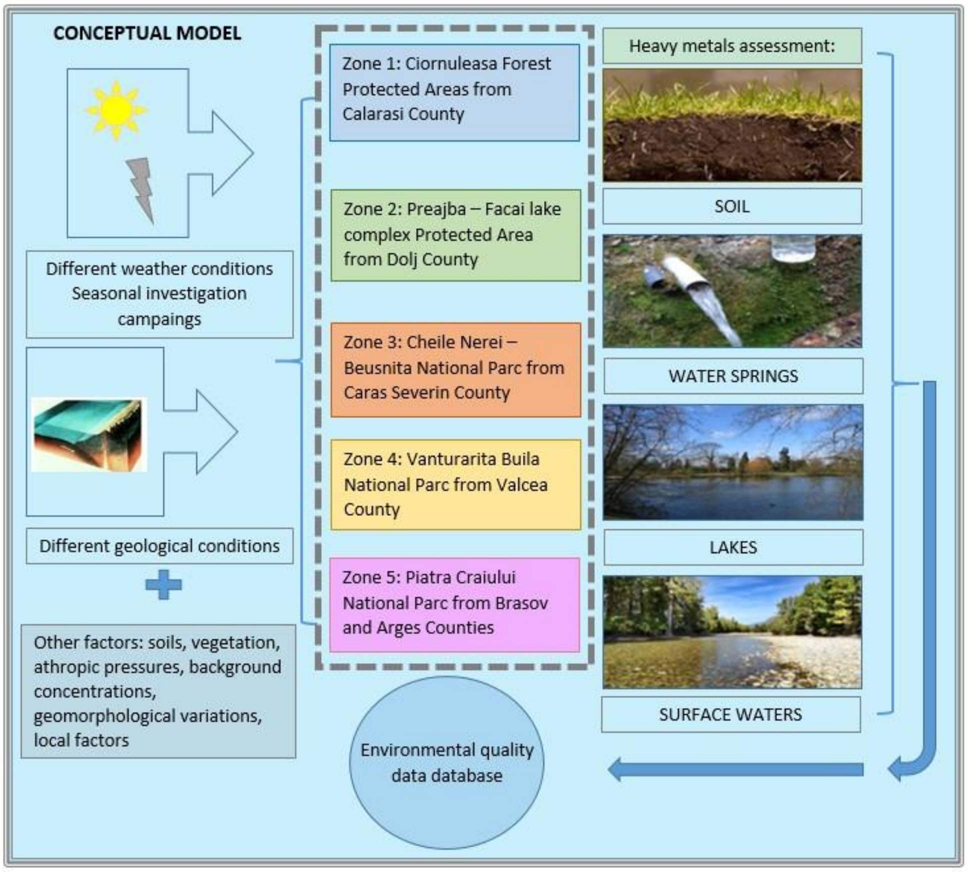

Fig. 2. Conceptual Model assessment of the 5 protected areas from Romania- case studies.

The flow of data describing the quality of the environmental factors from these areas, obtained after several seasonal campaigns, determines the creation and consolidation of a particularly important environmental database.

Data collecting and processing

For each area of interest that was included in the process of evaluating the quality of soil and water environmental factors, respectively the determination of heavy metals, an experimental field was established from which samples were periodically taken, and these were analyzed in specialized laboratories from National Research and Development Institute for Industrial Ecology –ECOIND (NRDI ECOIND).

The number of soil samples for each area is presented as a matrix in table 1.

Table 1. Soil sampling experimental matrix

Number of samples/ sample type	1	2	3	4	5	6	7	8	9	10	Zone
Soil											**1**
Soil											**2**
Soil											**3**
Soil											**4**
Soil											**5**

A constant concern of the scientific community is to know, as well as possible, the natural background concentrations of some chemical elements in soil in order to be able to highlight the evolutionary contribution of the pollution of the anthropogenic factor added to this natural background.
Among the heavy metals, the following presents a relevant selection of results for the content of Arsenic, Cadmium, Copper, Lead and Zinc in soils, in the period 2021-2022.
Sampling was carried out with adequate equipments, the Edelman type pedological kit. An GPS receiver, Montana 610 model from Garmin, was used to locate the samples. Labeling and preservation of the samples was carried out properly, and the time of transport of the samples from sampling point to the laboratory was reduced to a minimum. The testing laboratory applied standardized test methods, and a high-performance analysis equipment was used to determine the concentrations of heavy metals, namely an inductively coupled plasma mass spectrometer, Agilent 7900 series.The equipment is used for the determination of metal content in liquid and solid samples. The equipment has high performance parameters, with very low detection limits, of the order ppt.
In order to be able to appreciate the results obtained, an index corresponding to each concentration of heavy metals in the soil was calculated by referring to the normal values from the specific legislation in Romania. The evaluation criteria by applying these indexes is presented in table 2.

Table 2. Soil assessment by Pollution Index

Parameter	Normal values	Pollution index (p.i.)	Assessment criteria
Toxic Metal (Arsenic, Cadmium, Copper, Lead and Zinc)	Normal value of Heavy Metal	$\frac{Concentration\ of\ heavy\ metal}{Normal\ Value\ for\ Heavy\ Metal}$	P.I. < 1 very good 1 < P.I.< 2 good 2 < P.I.< 3 weak 3 < P.I.< 5 poor

RESULTS AND DISCUSSION

The analytical results obtained for the soil samples analyzed from each protected area allowed the calculation of P.I., using the average value of the concentrations obtained for each analyzed parameter. Table 3 shows the calculation of **P.I.** for Zone 1 – Ciornuleasa Forest Protected Area.

Table 3. Pollution Index calculating for Ciornuleasa Forest (Zone 1), period 2021-2022

Parameter	Normal values (mg/kg d.m.)	Average Conc. 2021	Average Conc. 2022	Pollution index 2021 (P.I.)	Pollution index 2022 (P.I.)
Arsenic	5	6.26	4.35	1.25	0.87
Cadmium	1	0.20	0.32	0.20	0.32
Copper	20	23.92	30.61	1.20	1.53
Lead	20	15.71	13.50	0.79	0.68
Zinc	100	66.59	73.71	0.67	0.74
Average	-	-	-	0.82	0.83

It can be observed that values reported to the normal values determine a very good quality of the soils in this investigated area. Also, the pollution index values situated between 1 and 2 are recorded in the case of Arsenic and Copper, but the values determine a good quality of the soils.
Table 4 shows the calculation of **P.I.** for Zone 2 – Preajba-Facai Lake complex Protected Area.
Reported to the normal values it can be observed that values present a very good quality of the soils in this investigated area. All **P.I.** calculated are situated below value 1.

Table 4. Pollution Index calculating for Preajba-Facai Lake complex (Zone 2), 2021-2022

Parameter	Normal values (mg/kg d.m.)	Average Conc. 2021	Average Conc. 2022	Pollution index 2021 (P.I.)	Pollution index 2022 (P.I.)
Arsenic	5	0.14	0.14	0.03	0.03
Cadmium	1	0.12	0.14	0.12	0.14
Copper	20	6.2	7.6	0.31	0.38
Lead	20	9.4	11.2	0.47	0.56
Zinc	100	17.5	20.6	0.18	0.21
Average	-	-	-	0.22	0.26

Table 5 shows the calculation of **P.I.** for Zone 3 – Cheile Nerei – Beusnita National Park.

Table 5. Pollution Index calculating for Cheile Nerei – Beusnita National Park (Zone 3), 2021-2022

Parameter	Normal values (mg/kg d.m.)	Average Conc. 2021	Average Conc. 2022	Pollution index 2021 (P.I.)	Pollution index 2022 (P.I.)
Arsenic	5	2.14	3.26	0.43	0.65
Cadmium	1	0.45	1.10	0.45	1.10
Copper	20	19.61	16.27	0.98	0.81
Lead	20	15.71	17.25	0.79	0.86
Zinc	100	88.77	89.82	0.89	0.90
Average	-	-	-	0.71	0.86

Most **P.I.** values reveals a very good quality of the soils in terms of the content of heavy metals. Punctually, the value of 1 is exceeded in the case of Cadmium, in 2022.
Table 6 shows the calculation of **P.I.** for Zone 4 – Vanturarita-Buila National Park

Table 6. Pollution Index calculating for Vanturarita-Buila National Park (Zone 4), 2021-2022

Parameter	Normal values (mg/kg d.m.)	Average Conc. 2021	Average Conc. 2022	Pollution index 2021 (P.I.)	Pollution index 2022 (P.I.)
Arsenic	5	0.14	0.14	0.03	0.03
Cadmium	1	0.02	0.02	0.02	0.02
Copper	20	7.40	8.41	0.37	0.42
Lead	20	12.6	23.1	0.63	1.16
Zinc	100	65.4	52.3	0.65	0.52
Average	-	-	-	0.34	0.43

Most **P.I.** values reveals a very good quality of the soils in terms of the content of heavy metals. Punctually, the value of 1 is exceeded in the case of Lead in 2022.
Table 7 shows the calculation of **P.I.** for Zone 5 – Piatra Craiului National Park

Table 7. Pollution Index calculating for Piatra Craiului National Park (Zone 5), 2021-2022

Parameter	Normal values (mg/kg d.m.)	Average Conc. 2021	Average Conc. 2022	Pollution index 2021 (P.I.)	Pollution index 2022 (P.I.)
Arsenic	5	2.43	3.23	0.49	0.65
Cadmium	1	0.38	0.29	0.38	0.29
Copper	20	23.85	22.71	1.19	1.14
Lead	20	18.69	19.19	0.93	0.96
Zinc	100	73.54	88.98	0.74	0.89
Average	-	-	-	0.75	0.79

P.I. values reveals a very good quality of the soils in terms of the content of heavy metals. Punctually, the value of 1 is exceeded in the case of Copper in 2021 and 2022.
Figure 3 shows the distribution of the average **P.I.** values for each analyzed area in order to be able to observe in a quantifiable way the differences from one area to another, depending on the specifics of each one.

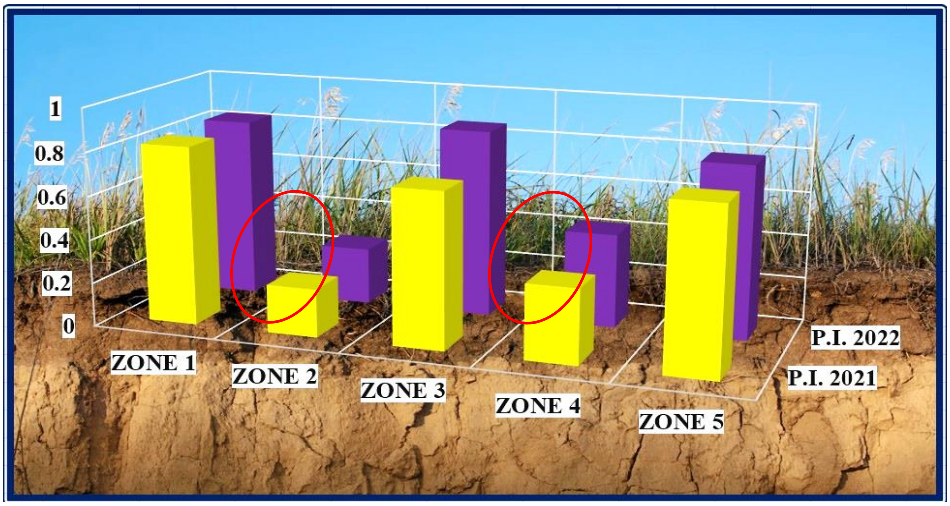

Fig. 3. Distribution of Pollution Index in each studied zone in period 2021-2022

It is noted that **P.I.** with the lowest values correspond to areas 2 and 4 where the measured concentrations of heavy metals showed lower values. By averaging the obtained results, it is found that the final values highlight a very good quality of the soils in these areas, which indicates that anthropogenic pressures, manifested mainly through pollution, did not cause the pollution of these areas.

CONCLUSIONS

The protected areas are distinguished by their local particularities which are induced by the manifestation of several categories of factors: geomorphological, geological, climatic, the diversity of soil formation conditions and their typology, time as the duration of the manifestation of processes, as well as the influence of different degrees of anthropic pressure.
The evaluation of the quality of the environmental factors in the protected areas is capable of bringing essential information regarding their degree of protection and the way in which the anthropic factor is present in these areas, mainly through pollution. The application of the evaluation method by using the pollution indices calculated for each measured parameter can identify both aspects related to pollution, as well as a quick analysis of the pollution potential in these protected areas.
Furthermore, the use of pollution evaluation indices allow a quick evaluation on objective bases, in the sense that they are dimensionless values that can be quickly interpreted through the legend. Protected areas remain benchmarks that can ensure the evaluation of anthropogenically polluted areas by comparison with them. The natural background must be conserved and protected so that anthropogenic pressures remain localized exclusively in urbanized areas and those already anthropogenically modified.
The analysis carried out in this study highlighted the fact that the soils present a very good and good quality, which is a positive aspect of the degree of protection of the soil resources in these areas.

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