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SOIL AND SPRING WATER POLLUTION IN TWO PROTECTED NATURAL AREAS IN MARAMUREŞ DISTRICT

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ABSTRACT. This paper presents recent data on soil contamination with Pb, Cd, Cu and Zn at 5 and respectively 30 cm in depth and the pollution of surface waters in two protected areas in Maramureş County. The measured values are presented in comparison with the limits defined by the Romanian legislation. In the case of Creasta Cocoşului reservation, lead pollution reaches the intervention limit at 5 cm in depth and it exceeds the alert threshold at 30 cm. Lead contamination in Chiuzbaia reservation is also high at the 30 cm in depth, the Cd content exceeds the alert limit, while the values for Cu, Zn and Mn are over the normal admitted values. The high level of contamination with heavy metals of these areas is mainly related to local mining activities and non-ferrous metals concentrates processing.

Keywords: *soil pollution, heavy metals, natural protected areas*

INTRODUCTION

Maramureş County has a surface of 6304 km^2, including natural heritage areas of special value: 36 protected natural areas, of which one national park, Rodna Mountains Natural Park – Biosphere reservation, and one natural park, Maramureş Mountains Natural Park. These areas place Maramureş County on the 7th place in Romania as far as the number of protected areas is concerned (Fig.1).

The presence of several pollution sources in the area (former mining activity and metallurgic processing) involves a strict monitoring of the types

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of soils and the physical-chemical features (heavy metals content, pH, humus amount) in relationship with vegetation (types, ecological preferences) but also of the quality of spring waters, especially in the protected areas.

The two reservations under study are presented on the map (Fig. 1); they are located north-east from Baia Mare municipality, where non-ferrous metal concentrates rich in Pb, Cd, Cu and Zn have been processed for the last fifty years in the local metallurgical plants. Some toxic gases and heavy metals powders (particulate emissions) have been, but in small amounts still are released in the air, transported by air currents and finally settled on the surface of the soil in various areas.

In spite of the fact that the activity of these plants have lately take place using more environmental-friendly technologies (according to European legislation) and less-polluting raw materials (including wastes) were used, soil and water pollution are still clearly visible, negatively affecting flora and fauna of the region and consequently, human health. By taking into account the long-term effects of pollution, but also by considering the need for preservation of some areas of high touristic potential, continuous investigation and monitoring activities take place. The two metallurgic plants include installations for pollution prevention and integrated control, IPPC, of which one (related to secondary copper processing) already works in agreement with the UE regulations, while the second one (related to primary lead processing) is currently submitted to specific transformations in the frame of a detailed programme to end in 2010, when the environmental requirements of the EU will have to be fulfilled.

The territory of Maramureş County and especially the areas in the vicinity of Baia Mare represent “environmental hot spots” proper due to the long period of mining activity and non-ferrous metallurgy; for this reason, such areas have been intensely investigated especially concerning heavy metals pollution [1].

The aim of the present work is the quantification of the pollution degree, concerning heavy metals (Pb, Cd, Cu, Zn and Mn), of soil and spring waters in two geological reservations: Creasta Cocoşului and fossiliferous reservation Chiuzbaia. Samples were collected from 5 and respectively 30 cm in depth and the measured and determined values were compared with the limits allowed by the Romanian legislation. Samples collected in the first step of the study were used to evaluate the pollution degree of the areas considered, as a preliminary stage of a more complex research concerning that region.

The obtained data are necessary for soil type mapping and correlation of their physical-chemical features with type and abundance of flora and fauna in the protected areas of Maramureş County, for the evaluation of soil quality and interpretations concerning the influence of pollutants on both vegetation and tourists in these areas.

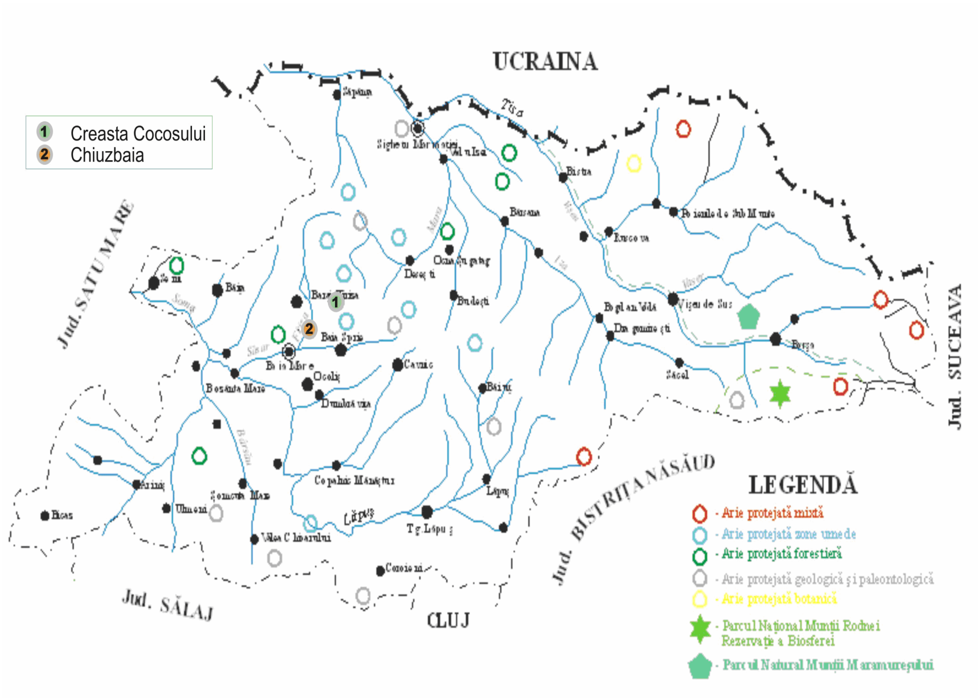

Figure 1. Schematic map of the protected areas in Maramureş County

RESULTS AND DISCUSSIONS

CREASTA COCOŞULUI protected area

The protected natural area Creasta Cocoşului was created in order to protect and conserve some natural elements of special ecological, scientific and landscape value and significance. The most prominent feature within the area is the Creasta Cocoşului itself, a steep and wavy ridge, about 200 m in length, located at an average altitude of 1200 m, with an almost vertical spatial display [2]. The results of the soil investigation in this area are presented in Table 1.

The data on soil samples collected at 5 cm in depth evidenced a high content of lead, about three times more than the intervention threshold in the samples collected from the uppermost part of the Creasta Cocoşului ridge and near the alert threshold for those collected near the spring below the ridge. The lower content in the second group of samples may be correlated to the local pattern of the air currents leading to a better protection of the area. The lead pollution degree is relatively higher (above the alert limit) also in the case of soil samples collected at 30 cm in depth, pointing to a long term “pollution history” in the area.

The experimental data for copper, zinc and manganese fall within the normal limits for this type of soils, however towards the upper limit in the case of copper and zinc. It is worth to mention that cadmium is missing from the investigated soil samples.

Concerning the organic matter content, the soil samples collected in the vicinity of the spring below the ridge are slightly polluted (organic C < 3 %), those collected near the top of the ridge at both 5 and 30 cm depth are medium polluted (< 4 % organic C) while those from the area near Masa Pintii are strongly polluted (> 4 % organic C).

Table 1. Results obtained on soil samples collected from Creasta Cocoşului reserve

Soil sample (Creasta Cocoşului reserve)	pH	Pb mg/kg	Cd mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Humus %	Org. C %
The top of the ridge (5 cm depth)	4.1	311.65	0.0	21.40	90.06	323.18	6.63	3.84
(30 cm depth)	4.3	67.34	0.0	13.91	67.23	190.98	6.03	3.50
Near the spring below the ridge (5 cm depth)	4.5	57.26	0.0	13.15	79.63	366.02	2.72	1.58
Near “Masa Pintii” (5 cm depth)	4.5	294.18	0.0	18.90	92.22	176.61	7.95	4.61
Near *Masa Pintii* (30 cm depth)	4.4	86.026	0.0	15.463	103.99	205.15	7.21	4.18
Normal values [1,2]		20	1	20	100	900		
Alert threshold [1,2]		50	3	100	300	1500		
Intervention threshold [1,2]		100	5	200	600	2500		

[1]in the case of soils for sensitive usage, in mg/kg; [2]according to OMAPM 756/1997 approving Regulations on the evaluation of environmental pollution

Soil acidity showed relatively high (pH about 4) but relatively constant values with depth and horizontal distances in the sampled areas.

CHIUZBAIA protected area

The Chiuzbaia fossiliferous reservation is located at the base of Igniş Peak, between the Plopilor Valley and the “Biserica lui Spiridon” cliff; it is well-known and protected for its diatomite deposits interlayered with volcanic ash containing abundant rests of plant impressions. These geological deposits were formed in a lake surrounded by a dense forest. The leaf impressions point to the following plant species such as, oak (*Quercus*), alder (*Alnus*), beech (*Fagus*), maple (*Acer)*, chestnut (*Castanea)*, besides which birch tree

(*Betula*), hornbeam (*Carpinus*), *Giyptostrobus*, *Liriodendron*, *Magnolia*, *Finus*, elm etc, were present, pointing to a forest growing in a temperate, relatively warmer climate as compared to the present day one. The fossil flora from Chiuzbaia represents one of the richest and best preserved floras of Pliocene age from Romania: over 120 species of which 32 for the first time in Romania, 6 for the first time worldwide, and 3 new varieties have been identified [3].

Table 2. Results obtained on soil samples collected from the Chiuzbaia fossiliferous reserve

Soil sample (Chiuzbaia reserve)	pH	Pb mg/kg	Cd mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Humus %	Org. C %
5 cm depth	4.7	376.04	3.88	26.61	145.18	1217.17	5.95	3.45
30 cm depth	4.7	236.98	3.25	17.62	136.21	1298.12	4.64	2.69
Normal values [1, 2]		20	1	20	100	900		
Alert threshold [1, 2]		50	3	100	300	1500		
Intervention threshold [1,2]		100	5	200	600	2500		

[1]in the case of soils for sensitive usage, in mg/kg; [2]according to OMAPM 756/1997 approving Regulations on the evaluation of environmental pollution

The experimental data on the soil samples from Chiuzbaia fossiliferous reservation collected at 5 and respectively 30 cm in depth are presented in Table 2.

These data point to a relatively higher pollution degree both at surface and in depth by comparison to the first protected area under study, which can be due to the closer proximity from the polluting source, *i.e.* Baia Mare town. A high Pb content, exceeding the intervention limit both at the surface and at depth can be mentioned; high amounts were registered also in the case of the other metals, Cu, Zn and Mn exceeding the normally admitted values. More than that, Cd – a very toxic metal, was also evidenced, in concentrations exceeding even the alert threshold.

Based on the carbon contents, the soils in this area may be classified as slightly (at 30 cm in depth) and medium (at 5 cm in depth) polluted with acidity values close to those recorded in Creasta Cocoşului reserve.

Spring waters

The evaluation of the pollution degree of spring waters in the monitored reserves was performed by investigating water samples from two springs along the tourist path starting from the Şuior mine perimeter, located in the upper part of the climb towards Creasta Cocoşului ridge, while for Chiuzbaia fossiliferous reserve the water sample was collected from the spring located close to the forest road that crosses the reserve.

Table 3 presents the main physical-chemical characteristics of the tested water samples compared with reference values for surface and drinking waters.

The values in Table 3 obtained for this study show that lead and cadmium exceed the admitted limits in the waters in the case of Chiuzbaia Valley and the spring from the base of the Creasta Cocoşului ridge, supporting the data obtained for the soil samples in the same areas.

The acidity of these waters is higher than that of reference surface water and decreases from the top to the bottom of the ridge, probably as a consequence of the pH variation for the corresponding soils.

By comparing the data from Tables 2 and 3, it can be noticed that lead concentrations in soil represent special issues, all the investigated samples showing values higher than the alert threshold or in some cases even values exceeding the intervention limit.

CONCLUSIONS

In the two investigated protected areas, the soil is contaminated with heavy metals (Pb, Cd, Cu, Zn and Mn) in variable amounts depending on the location of the sampling site and depth. High pollution with Pb exceeding the alert threshold was evidenced in the top area of Creasta Cocoşului reserve and exceeding the intervention limit near the spring below the ridge at 5 and 30 cm in depth, as well as in all the investigated sites from Chiuzbaia reserve. The degree of pollution with organic matter varies from slightly polluted soils (at the spring below the Creasta Cocoşului ridge) to strongly polluted soils in the Masa Pintii area from Creasta Cocoşului reserve.

The allowable limits for heavy metals Pb and Cd are exceeded in the water samples collected from Chiuzbaia Valley and in the spring at the base of Creasta Cocoşului ridge as a result of soil pollution in these protected areas. The pH values for the spring waters are lower than those allowed for surface waters and they increase from the top to the base according to the variation of the pH values for the soils.

The high Pb values in some soil samples both at the surface and deeper into the soil suggest the possible influence of the Pb-containing particulate emissions from the dispersion furnace of the company that processes Pb ores in Baia Mare, taking into account that the two reservations are located NE from the metallurgical plant at a distance of only 4.5 km (Chiuzbaia reserve) and respectively 17.5 km (Creasta Cocoşului reserve). The lead content is higher in the samples collected from Chiuzbaia reserve, located closer to the metallurgical plant as compared to Creasta Cocoşului reserve.

Table 3. Physical-chemical features of spring waters

No.	Feature	Chiuzbaia Valley	Creasta Cocoşului – spring at the base of the ridge	Creasta Cocoşului-spring near the top of the ridge	Reference value (surface waters)[3]	CMA value (drinking water)[4]
1	pH	6.196	5.483	4.967	6.5-8.5	6.5-9.5
2	Conductivity, μS/cm	68.5	24.4	41.5		2500
3	CCOMn, mgO_2/l	1.84	2.4	2.72	5.0	
4	Chlorides, mg/l	7.09	7.09	6.38	25	250
5	Sulphates, mg/l	5.10	0.0	1.70	60	250
6	Calcium, mg/l	8.55	3.89	5.44	50	
7	Magnesium, mg/l	3.26	0.47	0.93	12	
8	Total hardness, Ge degrees	1.96	0.652	0.978		5
9	Nitrites, mg/l	0.0	0.0	0.0	0.01 mgN/l	0.5
10	Nitrates, mg/l	22.8	0.10	0.0	1.0 mgN/l	50
11	Ammonium, mg/l	0.025	0.0	0.0	0.4 mgN/l	0.5
12	Pb, mg/l	0.025	0.002	0.0	0.005	0.010
13	Cd, mg/l	0.001	0.002	0.0	0.0005	0.005
14	Cu, mg/l	0.0	0.0	0.0	0.02	0.1
15	Zn, mg/l	0.021	0.018	0.012	0.1	5.0
16	Fe, mg/l	0.087	0.023	0.045	0.3	0.2
17	Mn, mg/l	0.004	0.003	0.006	0.05	0.05

[3]according to the MMGA Order 161/2006 approving the Classification Norms for surface waters quality in the view of establishing the ecological status of the water bodies; [4]according to Law 458/2002 on the quality of drinking water

These preliminary data suggest that soil pollution has an anthropic source related to industrial air pollution by soil deposition of particulate emissions containing heavy metals, especially Pb. If the natural substrate in the area of the reservation would have been rich in heavy metals, these cations should have been present in higher concentrations also in the investigated spring waters.

EXPERIMENTAL SECTION

Soil sampling

Soil samples were collected according to the procedures defined for environmental pollution evaluation and the Romanian standard on soil sampling for pedological and agrochemical studies [4, 5].

Soil sampling at 5 cm in depth is significant for the evaluation of the bioasimilation processes of heavy metals by plants in the upper part of the soil, and thus the potential risks on the trophic chain. Metal distribution patterns in deeper soil layers (30 cm in depth) may evidence the history of pollution or accidental infiltrations.

In the case of Creasta Cocoşului reservation, samples of both soil and water were collected, due to the local morphological-structural complexity of the landscape and of the co-existence of various altitudes.

The tested soils were collected in the upper part of Creasta Cocoşului area at 5 and respectively 30 cm in depth, from the vicinity of the spring at the bottom of the cliff at 5 cm in depth, and from Masa Pintii area at 5, and respectively 30 cm in depth. In the Chiuzbaia reservation, soil samples were collected at 5 cm and 30 cm in depth from a single sampling point.

Water sampling

Water samples were collected and investigated in agreement with the procedures defined by Romanian legislation (surface waters quality types and quality of drinking water, for spring waters) [6, 7].

Water samples were collected from the existing springs in the two reservations. In the case of Creasta Cocoşului area the springs are more abundant, thus two of the springs within the reservation were sampled. In the case of the Chiuzbaia fossiliferous reservation a single spring was tested.

Analytical procedures

The soil samples collected from the pre-established locations were packed in plastic bags and transported to the laboratory. There they have been air dried at room temperatures, then powdered and sieved on a 2 mm mesh. One gram from each dried soil sample was subsequently submitted to acid treatment for releasing the heavy metals into solution. After cooling, the solutions were filtered and diluted with bi-distilled water up to 25 ml volume. The heavy metal content (Pb, Cd, Cu and Zn) in these final solutiuons was determined using atomic absorption spectrometry.

The pH values and the humus content were measured in aqueous mixtures obtained from fresh samples (solid matter: liquid = 1:5), the latter by determining the content of organic carbon (warm oxidation with K dichromate in the presence of sulphuric acid and titration of the excess dichromate with Mohr salt solution).

The pollution degree of the studied soil samples was estimated based on the scale proposed by Parrakova [8], according to the organic carbon content C, as follows:

- unpolluted soil 0-1 %
- slightly polluted soil 1-3 %
- medium polluted soil 3-4 %
- heavily polluted soil 4-6 %

The water samples were collected in 500 ml plastic bottles that were prior to this carefully rinsed and dried in the laboratory; the samples were investigated right after they were brought to the laboratory from the field.

Conductivity and pH were measured by potentiometric methods using a laboratory conductometer and pH meter; the anions were determined by UV-VIS molecular absorption spectrometry while the metallic cations by atomic absorption spectrometry.

Equipment

The investigations on the soil and water samples were performed at the Laboratory for physical-chemical testing of the Agency for Environmental Protection Maramureş, Baia Mare, Romania, using a Varian SpectrAA-250 Plus atomic absorption spectrophotometer, an UV/VIS spectrophotometer with molecular absorption Cecil 8000 series, a WTW InoLab Level2 conductometer, and a WTW InoLab Level2 pH meter.

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