

THE METAL CONTENT OF SOILS IN THE MURES COUNTY AND PHYTOREMEDIATION PROSPECTS USE AS A REMEDIATION METHOD

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ABSTRACT

The soil quality results from complex interactions between its components and may be related to interventions in soil caused by the insertion of compounds more or less toxic, accumulation of toxic products from industrial and urban activities. Currently it tends more towards the adoption of biological methods of soil remediation, and one of these is phytoremediation, innovative and less expensive. So, to see what is the heavy metals' content of soils, soil samples were taken at different distances from the source of pollution (SC Azomureș SA). The soil samples were analyzed to determine the heavy metals' content (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn). There were found exceedings of the normal values provided in the legislation (except for As, Cd, Pb), especially in samples taken near the source of pollution (150m and 250m). It must be noted that recorded exceedings are not alert thresholds.

Keywords: soil pollution, heavy metals content, remediation methods, phytotoxicity, Phytoremediation.

Introduction

Currently in Romania, water quality and ensuring soil conditions became a major issue in the context of our country alignment standards and global requirements in terms of environment and natural resources.

The soil pollution is a growing environmental problem with which Romania is facing in recent years; is the consequence of human activity carried out without the protection of the environmental factor – the soil. Soil pollution is made through the transport of pollutants from the atmosphere, but there are irresponsible actions through which are buried or put in / on soil various high toxic chemical waste.

OMS data shows that at least 50% of the raw materials used in industry contribute to the formation of industrial waste, of which 15% are toxic or harmful to human body. The harmful emissions, as the result of many industrial processes, and not only, are seriously affecting the soil.

In industrial areas, various waste deposited in the soil can contain significant concentrations of metals, but also significant quantities of synthetic organic products. The attention is directed especially

towards the presence of heavy metals, such as: cadmium, copper, magnesium, nickel, lead, zinc, etc., because of their toxicity at low concentrations.

Clearly, both in Romania and abroad, in each year are reported a multitude of accidental or intentional discharges or toxic deposits in soil or water, which cause economic, social and environmental problems.

Ensuring the protection of soil quality as a means to enhance soil resources but also for environmental protection, provides the use of processes and remediation technologies designed to neutralize or block the flow of pollutants and to ensure the desired efficiency and the soil quality[1].

The soil is considered an important ecological factor because [1]:

- is closely correlated with the climate of a region in configuration, nature and structure;
- the formation and protection of groundwater and surface water sources depend on its quality;
- determines vegetation growth and development, thereby indirectly affecting human nutrition;

- has a crucial role in the pattern settlements, provides optimum conditions for the construction of housing, and for social and economic development of human settlements.

The solid waste occupies large areas of land to install the dumps, leading to a sordid mass accumulation, air and groundwater pollution, land-use prevention. Heaps of ashes and slag from nonferrous metals contain traces of toxic heavy metals (Cu, Zn, Cd, Pb, SO₂ and As). Powder and dust cover through wind deposits the vegetation in the surrounding region [3].

Thus, in the legislation is reflected the decree nr. 756/1997 of the Ministry of Water, Forests and Environmental Protection. Regarding the regulations for assessing environmental pollution, as amended by Decree 532/2002 and Decree 1144/2002, which also contains the normal rates, and intervention on the soil for metals and metalloids pollution (Sb, Ag, As, Be, Bi, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Sn, TI, V, Zn) [4].

In order to protect the quality of the fields, are performed soil conservation works and for this, research and design specialists prepare, upon request, studies and projects in conjunction with the planning. The presentation of the main methodological issues related to diagnose the state of pollution of soils and aquifers, respectively of the main technical aspects of remediation technologies, have highlighted the complexity of determining the decisions to choose the most appropriate solutions.

The optimization work in this area involves compromises between the results obtained from the application of remediation technologies and financial, material and human efforts from which these results were obtained.

The comparative analysis between the advantages and disadvantages of each type of remediation technologies should be made in relation with a list of priority targets set according to actual conditions specific to each case. The results of such analysis should guide the final solution to the variant that corresponds in most points of view, to a certain context.

There are several proceedings of remediating contaminated soil, but we mention here phytoremediation, which is an innovative and inexpensive technique which exploits plants that possess properties that allow them to concentrate, to degrade or transform pollutants [2].

Plants that are used for this form of treatment *in vivo* degrade pollutants within the rhizosphere. Pollutants may accumulate in the roots or in the leaves of the plants. This technique can be used to treat large areas where contamination is low and shallow. In these circumstances, the remedial process

is specialized in plant cultivation and through harvesting the pollutants are eliminated. You can still treat the harvested plants to recover destroyed (e.g. by incineration) or concentrated pollutants.

This procedure has the great advantage that it allows *in situ* soil remediation without disrupting the environment too much. On the other hand, the soil thus treated retains its natural physical, chemical and biological properties [2].

It can be used for crops such as maize (*Zea mays*), rape (*Brassica napus ssp oleifera*), wheat (*Triticum aestivum*), cucumber (*Cucumis sativum*), etc., which are able to reduce the ecotoxicity in some soil metals [3].

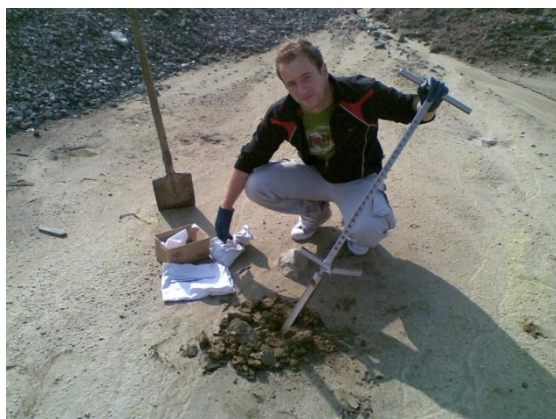
The Mures County includes a number of areas with systematic breaches of environmental quality indicators to standardized rules that affect air, surface water, groundwater and soil. The most critical area, in terms of surface water pollution (with influences on the subsoil) is in downstream Târnaveni, where water quality has fallen outside the category of quality, because of the high concentrations of hexavalent chromium. Another section of the river, affected from the physical, chemical and especially bacteriological point of view, is the downstream from the city of Targu Mures, due to pollution from SC Azomures SA and RA Aquaserv (Cristești wastewater treatment plant) and a third section is located in Odorheiu Secuiesc, Cristuru Secuiesc and Sighisoara, because the discharge of sewage, fecaloid waste, insufficiently treated.

The experimental procedure

In October 2010 soil samples were collected (Figure 1.a, b, c and Figure 2) from five different points located at distances between 150m and 1100m from SC Azomureș SA (lands and rural areas), considered as main source of pollution. Depth of soil sampling is 0-10cm, 10-20cm, 20-30cm.



a)



b)



c)

Fig. 1.a), b), c). Soil Sampling

The researches have been performed on samples obtained from individual samples collected from a changed settlement.

Average samples, properly labeled were transported to the Wessling Romania SRL laboratory,



a)

where they were prepared for the determination of the metal content.

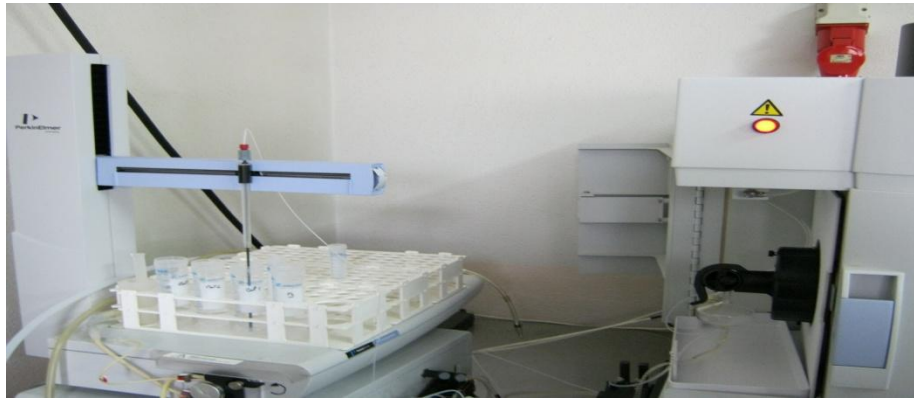
Mineralized soil samples were analyzed by the method of ICP - OES for the determination of metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead, zinc). For mineralization, the soil samples were heated with the mineralizing reagent-royal water under controlled pressure and temperature for dissolution of metals in the samples.



Fig. 2. Soil sample device

The principle of the ICP – OES method

The sample, suitably prepared, is sprayed and placed in a flow of argon inductively coupled plasma, where the components evaporate, atomize and the free ions resulted are excited and they emit photons resulting characteristic frequency of the item. The light emission of the plasma is decomposing and determines the intensity of the spectral lines specific elements which have to be determined. The used device is shown in Figure 3.a), b).



b)

Fig. 3.a), b) spray and lit plasma ICP Wessling

Results and discussions

The distribution and the heavy metals content on the depth sampling of soil (0-30 cm) varies, depending on the soil formation processes, anthropic pollution, etc. (Table 1), and the average of the heavy metal content for the considered points is portrayed in Figure 3. Normal values for metals in soil, according to Appendix 1 of the Decree 756 of 3 November

1997, for the approval of the legislation regarding the environmental pollution assessment are: arsenic-5 mg / kg substrate, cadmium 1 mg / kg substrate, chromium-30 mg / kg substrate, copper 20 mg / kg substrate, mercury-0, 1 mg / kg substrate, nickel 20 mg / kg substrate, lead-20 mg / kg substrate, zinc 100 mg / kg substrate.

Table 1
Metal content of analyzed soil samples (mg / kg substrate)

Sample nr.	Harvest depth(cm)	Arsenic	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
1	0-10	<4	<1	30,7	45,3	<0,3	23,6	16,1	112
2	10-20	<4	<1	32,2	33,6	<0,3	26,7	14,4	87,7
3	20-30	<4	<1	33,0	39,2	<0,3	24,0	16,2	98,6
Average (PA*)	0-30	<4	<1	31,96	39,36	<0,3	24,76	15,56	99,43
4	0-10	<4	<1	30,9	34,0	<0,3	19,9	19,1	93,8
5	10-20	<4	<1	23,1	32,2	<0,3	16,8	19,4	86,2
6	20-30	<4	<1	24,0	29,9	<0,3	19,4	13,1	70,3
Average (PB*)	0-30	<4	<1	26,00	32,03	<0,3	18,70	17,20	83,43
7	0-10	<4	<1	15,2	22,2	<0,3	14,3	7,05	<50
8	10-20	<4	<1	18,2	27,6	<0,3	15,0	14,8	69,6
9	20-30	<4	<1	18,6	20,7	<0,3	18,5	8,44	<50
Average (PC*)	0-30	<4	<1	17,33	23,50	<0,3	15,93	10,09	<56,53
10	0-10	<4	<1	20,3	25,8	<0,3	15,2	15,8	56,8
11	10-20	<4	<1	28,2	25,1	<0,3	20,6	11,9	50,0
12	20-30	<4	<1	22,4	25,3	<0,3	17,9	14,6	53,4
Average (PD*)	0-30	<4	<1	23,63	25,40	<0,3	18,56	14,10	53,40
13	0-10	<4	<1	24,4	24,7	<0,3	17,3	12,5	55,9
14	10-20	<4	<1	27,1	25,1	<0,3	19,7	13,2	57,9
15	20-30	<4	<1	23,7	24,7	<0,3	20,5	12,2	56,0
Average (PE*)	0-30	<4	<1	25,06	24,83	<0,3	19,16	12,63	56,60

(PA*) – 150m distance from the source of pollution, cultivated land
 (PB*) – 250m distance from the source of pollution, cultivated land
 (PC*) – 1100m distance from the source of pollution, cultivated land
 (PD*) – 900m distance from the source of pollution, ruderales land
 (PE*) – 900m distance from the source of pollution, cultivated land

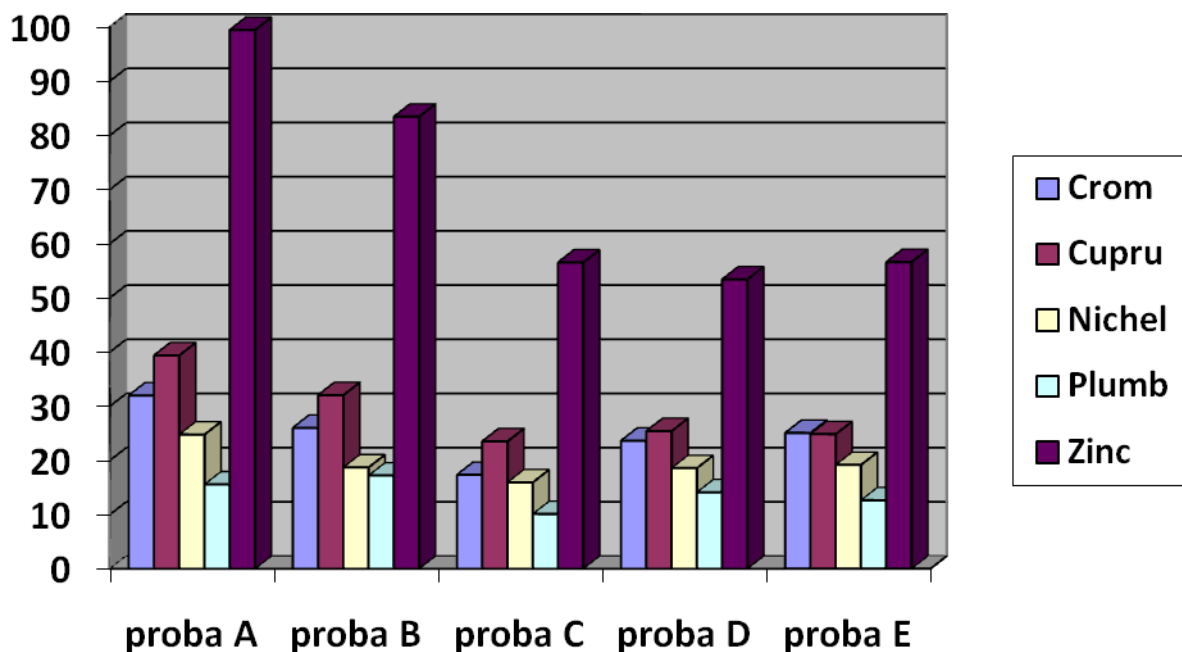


Fig. 4. Average heavy metal content

Comparing the data from Table 1 with the values for heavy metals in the soil provided in the law we see the following:

- for arsenic, cadmium and lead there were not recorded, in the samples, values in excess of normal values;

- chromium exceeds the normal value 30 mg / kg in samples 1-3, samples which were collected from a vegetable garden located at 150 m SC Azomureş SA, as well as sample 4, representing soil taken from about a distance of 250m Azomureş SA. In other samples chromium content is below the normal value;

- All soil samples were subjected to determinations had a copper content which exceeded the limit of 20 mg / kg soil, the highest value (45.3 mg / kg) was recorded in sample 1 and the lowest copper content (20.7) was reported in sample 9, taken from a depth of 20-30 cm;

- the mercury recorded values lower than 0.3 mg / kg in all samples analyzed, regardless of location and depth of harvest;

- only the first three samples exceed the normal range, in terms of nickel content, with 3.6 to 6.7 mg / kg soil;

- the insignificance of the exceeding of zinc content is in a single sample (sample 1) of the total samples analyzed.

Analyzing the environmental content of heavy metals of 30cm depth in five locations (Figure 4) from which soil samples were collected, it is found in the case of copper, exceeding the normal value of 4.83 to 19.36 mg / kg, the highest values being collected in soil samples near the source of pollution. This is due to the intense traffic in the area. Also in the PA were recorded exceeding the content of chromium and nickel, with an average of 1.96 mg / kg, respectively, 4.76 mg / kg.

Conclusions

According to the observations made I highlight the followings:

- Copper expressed its presence in all soil samples analyzed, the highest values being in soil samples collected near the source of pollution. This is

probably due to road and rail traffic and, more intensely, in that area;

- chromium exceeded the normal limit, on the depth of 0-30 cm in soil samples collected from 150m distance from the pollution source;

- in soil samples analyzed the surpassing recorded did not reach the alert regarding soil pollution with heavy metals from the nearby SC Azomureş SA

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