STUDIES AND RESEARCHES CONCERNING THE POLUTTED SOILS DECONTAMINATION BY BIOSYSTEMS

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Abstract. *During the metallurgic technological process results gases, waste water and pollutants which can constitute sources of in both situation of a normal or abnormal functioning of equipment. The spreading of pollutants is influenced by the Aeolian regime of the region and the level of soil pollution can be established with the help of the spreading diagram. Biotechnologies represent an efficient and ecological method of cleaning the soils infested by the metallurgical technologies, based on minimal investment and environmental risk. Based on the measurements made in the nearby areas of metallurgical units from Dâmboviţa County, it might be said that the mycoremediation is the most efficient and fastest between all the cleaning biotechnologies.*

Keywords: metallurgic impact, biotechnologies, soil, bioremediation

1. Introduction

By his actions, the human interfere with the environment, mining the soil and the underground ores which are more enlarge and multiplied at once with the technological development and humans' necessities. According as the technological processes are increased, the emission of the elements with negative impact on the environment factors is increased too.

To establish the natural equilibrium is necessary to find new viable strategies of the relationship between humans and the environment and of rationale use of ores. The equation of using the nature, in which the environment is a way to satisfy the humans' necessity, is the base of the human-nature rapport.

The deteriorated natural environment by the industrial impact has an active influence on life quality by its contribution in stress and illness cases (fig. 1). The environment pollution directly affects the health and individual work capacity, as well as the economical process.

The environment protection actions have two directions: natural and economical environment remediation, by increasing the life and work quality level.

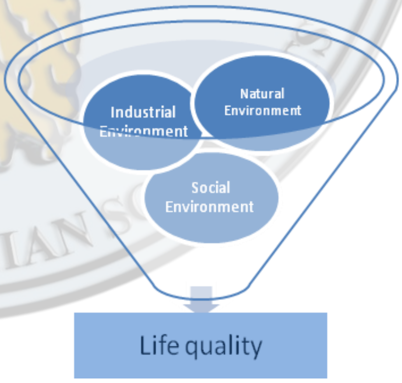

Figure 1 ***Life quality and environment intercommunication***

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2. Method and material

The image of products processing impact is showed by the flux diagram from figure 2. The technological process is represented by a batch of stages interlink through the material and energetically flux. In the flux diagram are included elements from nearby the ecosphere like ores mining and wastes accumulation.

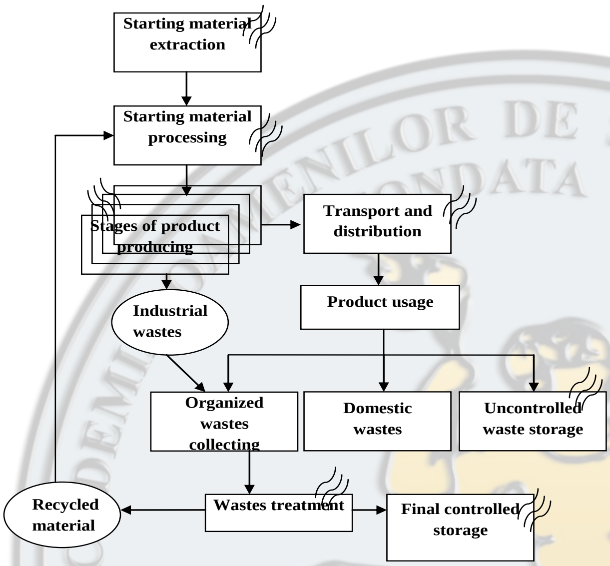


Figure 2 ***Flux diagram of a technological process***

For each stage of the technological flux are represented the emissions in the environment like atmospheric emissions from controlled and diffuse sources, wastes from ground and surface waters, wastes uncontrolled accumulation which can cause the soil pollution.

In the extraction phase of starting material the most affected is the soil, hard destroyed by the mining. Also, is important to consider the dust that is sent out and then deposed on the close vegetable elements.

During the starting material processing and during the production stages, the technological process use high quantities of energy, like power fuels and electricity. This human activity has a great impact on the environment by the gases emission, waste waters and industrial discard.

The materials' recycling represents a first strategy in sustainable development because the natural resources of our country are poor and insufficient and the import of complementary materials is limited by the economical situation. By recycling, we also reduce the pollution and the mining refuse.

2.1. The impact of technological system on the environment

During the technological metallurgic process result gases, waste waters and waste product with a high content of pollutants which can cause a risk in normal function of the equipments or a higher risk in the condition of a disorder or malfunction. The principal pollutants are: CO_2, CO, NO, SO, COV (for example BaP, HPA, dioxins), dusts with heavy metals (Pb, Cu, Zn, As, Cr), cyanide, carbolic and sometimes toxically organic compounds in the waste products [1].

The annual mean concentration excel the maximum admitted values in many places (Baia Mare, Copşa Mică, Mediaş, Targovişte, Arad, Deva, etc.) as for suspension powders as for sedimentable dusts, both tips resulted from the metallurgic industry [17].
The metallurgic industry removes huge quantities of pollutants (powders, smoke, smut, gas) in a wide variety and high noxiousness, like tons and hundreds of tons daily. These are airborne to distance, contaminating huge air volumes and auctioning in a negative way on the people healthiness and on the natural environment.

2.2. The sampling and analyze methods done in the industrial areas of Târgovişte

To establish the most efficient methods using biosystems in the cleaning of metallurgic infested soil we have to take into account more aspects. In the first range, we have to analyze, based on the pollutants spreading diagram, the areas with the higher risk of soil pollution by the metallurgic dusts. According this, we choose as sampling point the areas placed in the west and south-west of the highest metallurgic activities zone, up to 100-500 meters distance.
The soil sample were taken from many points inside the industrial zone of Târgovişte, on the premises of metallurgic units S.C.Mechel S.A., Erdemir Romania and S.C. Oţelinox S.A. from each zone we select aleatory three sampling points and we made a mean sample on the soil profile, down to 20 cm depth. From the same points we sampled the wild growing biosystems (plants, mosses and macro fungus).
The sample proceeding was made in the laboratory, by drying the material in the oven at 60°C, for some hours until the perfect drying. To establish the soil reaction and the pH, the sample were put into solution by mixing the soil with 5 – 10 g of material with 50 ml KCl 0,1N, F 1,000, Tt – 0,0056g/ml.
For settlement the soil and biosystems metal concentration we use the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), Varian Liberty 110[1]. This method is an analytical one use in so many scientific domains because of its high specificity, multi-element analyzes and low limits of detection. A plasma source is use to dissociate the sample in constitutive atoms or ions, stirring them on a superior energetic level. They will revert to the original form by the emission of a characteristic energy photon. This emission is recorded in an optic spectrometer; the radiation intensity is proportional with each element concentration in the sample and is intern calculated by a couple of calibration curves to obtain directly the measured concentration.

[1] The device is in the endowment of National Institute of Research-Development for Chemistry and Petrochemistry - ICECHIM Bucureşti

Before the analyzes with ICP-AES, the biological samples were mineralized in a microwave digestor, with 10 ml concentrated nitric acid, 65% and 2 ml hydrogen peroxide, and for the soil samples were done hot extractions with nitric acid 1:1.

3. Results and discussions

Emission spreading is the most influenced by the wind direction, intensity and frequency, which can be establish by some meteorological measurements (wind rose). According that we can draw up the "pollution rose", which is like 180° rotated image of the wind rose and express the frequency of pollutants spreading on each direction.

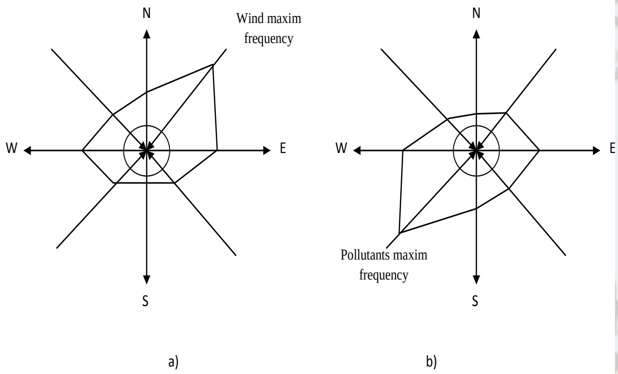


Figure 3 ***Wind rose (a); Pollution rose (b)***

Because of the geographical position and North to South relief steps succession, Dâmboviţa County is under the influence of winds of different tips: continental wind from North and East and Mediterranean wind South-West. For the plain, the Aeolian regime is characterized by the frequency of NE winds (21.6 %) and E winds (19.7 %) with annual mean speed of 2-2.5 m/s, and maximum in the winter up to 125 km/hour, followed by the West wind as intensity and speed [17].

According of this data we realize the "pollution rose" (fig. 3), which indicate the areas with bigger intensity of metallurgic pollution in Dâmboviţa county. From figure 4 we observe that the three metallurgic units of Dâmboviţa County are placed in the South of Târgovişte, so that the city has the lower impact of metallurgic emission, but the fields, locality (Dumbrava and Colanu) and the river Ilfov, placed in South-West of the industrial zone are high affected. The soil is the most influenced by the industrial impact losing its characteristics.

The characteristic soil for this region of Dâmboviţa County is reddish preluvosoil, soil with a carroty color, enough evident in the superior layer and much more evident in the middle layer. Layer A, of humus accumulation, is 30-40 cm depth and brown or reddish-brown color. The structure is with angular clods of 0.5-1.0 cm in very superior layer, and bigger in the depth. The clay complex is not enough saturated and, because of that, the most fine clay migrate on the profile, together with colloidal particles of iron hydroxide. [3]. In the superior part of the profile (down to 15-20 cm) the soil reaction is slightly alkaline, with pH value between 7.00 and 7.80. This is because of the high content in mineral substances and soluble salts (alkaline and alkaline-earth carbonates and bicarbonates, chlorides, sulfates) which is accumulated in different quantities along the profile, after the water evaporation.

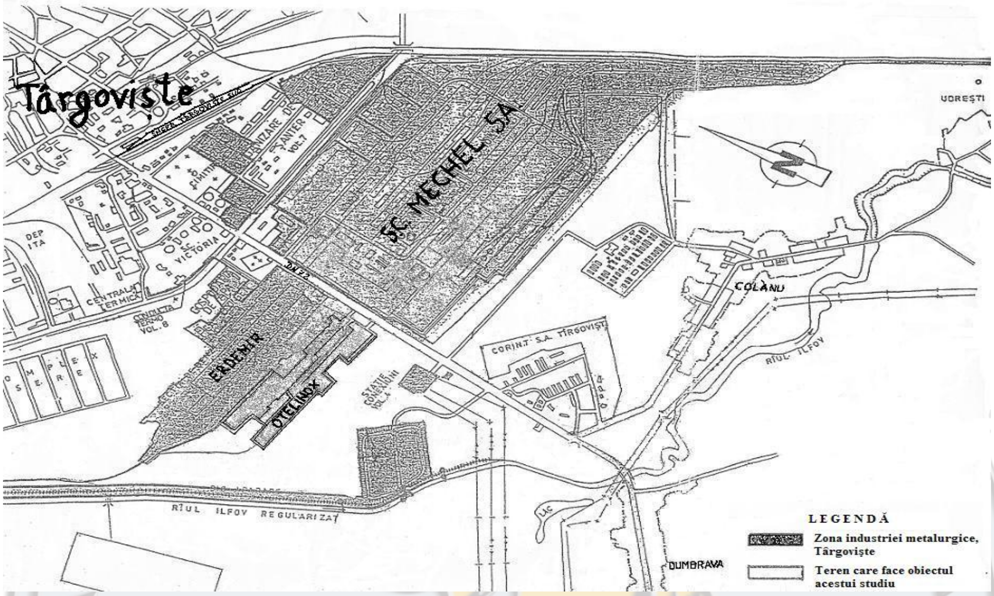


Figure 4 ***The placement of metallurgic units S.C. Mechel S.A, Erdemir Romania and S.C. Otelinox S.A***

The carbonates and bicarbonates (salts which has an alkaline hydrogenation) dissociate in the soil solution, disintegrate in carbonic acid and strong bases (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}), which still dissociate resulting an excess of OH^{-} ions [3].
To distinguish this phenomenon, the diagrams from figure 5 make a comparison between the elemental content of the soil from the polluted areas with some soils, the same tip, from less polluted areas. The samples represent the mean result for many measurements.
As regards of the soil content from the industrial area in other metals, especially the heavy one, the levels are showed in figure 6. Analyzes are done on samples from 6 points inside the industrial zone. In these diagrams are represented the maximum admitted level of metal concentration. We observe that in many sample, the heavy metals level excel the maximum admitted level, and that make the soil to lose them qualities.
To reduce the metal soil concentration until a level which will enable the crop development, on this soil we have to apply some steps to decrease the contamination. Next to the methods concerning the prevention and decreasing the dusts emission, there are some methods of decontamination, based on the soil dislocation and replacement. But, in the last decades, according the sustainable

development, the researchers are looking for ecological methods, with a minimum impact on the environment elements – the biotechnologies.

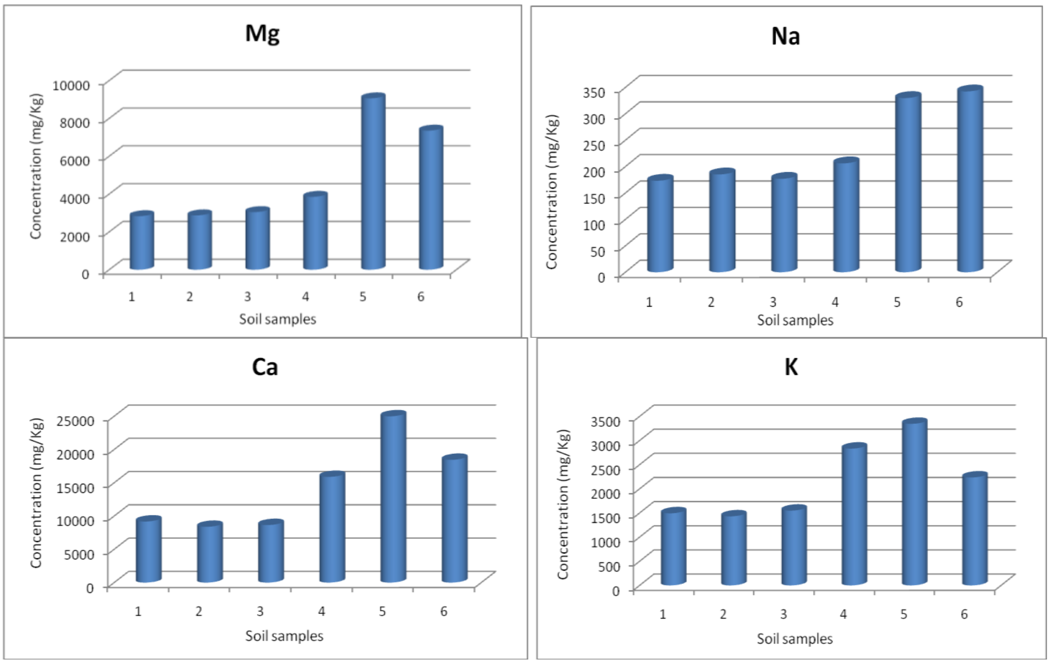


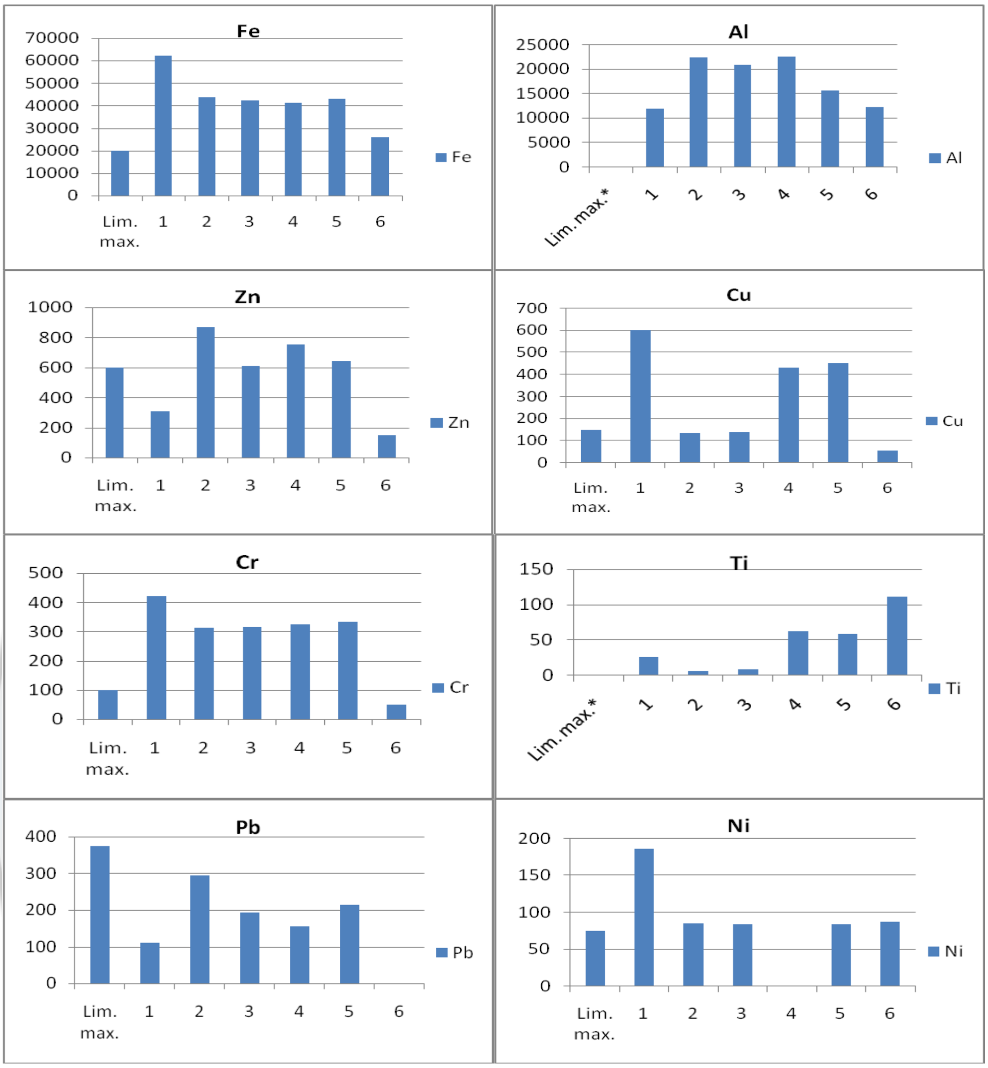
Figure 5 ***Soil concentration in Mg, Na, Ca and K – comparison between the concentration values in unpolluted soils (samples 1, 2, 3) and the concentration level in the soils from metallurgic zone of Dâmboviţa County (samples 4, 5, 6)***

From among the polluted areas bioremediation technologies, fitoremediation and mycoremediation are the two methods with great results in pollutants environment impact decreasing and in metals stabilization.

In these studies and research, the analyze concerning the possibility of metals accumulation in biosystems were done on wild growing species of *Plantae* and *Fungus*, from the industrial zone nearby of Targoviste. We chose these biosystems already adapted on the high polluted soils with metallurgic emissions, to establish the maxim capacity of that species in metals accumulation.

The previous studies, done on different wild growing macro fungus species, showed a content up 568-3904 mg/Kg dry matter for Fe [14], between 4.8 and 42.7 mg/Kg dry matter for Al [12], between 1.3 and 24.3 mg/Kg dry matter for Cr [7], between 0.90 and 9.71 mg/Kg dry matter for Mg [6], between 43.5 and 205 mg/Kg dry matter for Zn [12], between 9.23 and 107 mg/Kg dry matter for Cu [6] and a content of 0.9-2.6 mg/Kg dry matter for Pb [12].

By comparison with these data, the values in diagrams 7 to 14, showed the impact of high level of metals content in the soil on the biosystems, and their capacity to accumulate these metals up to a level which excel the normal levels (depending on the species) in them bodies.



* Maximum level wasn't induced

Figure 6 ***Heavy metals content of the soil from industrial zone of Târgovişte***

Also, these species of biosystems showed a high capacity of adaptation for polluted soil growing, without them nourishment characteristic to be changed; but they presents values 4-12 times higher for metals than the biosystems grow on unpolluted soils, which make them more dangerous for human and animals. The species from *Plantae Kingdom* demonstrate concentration much higher than the specie of *Fungus.*

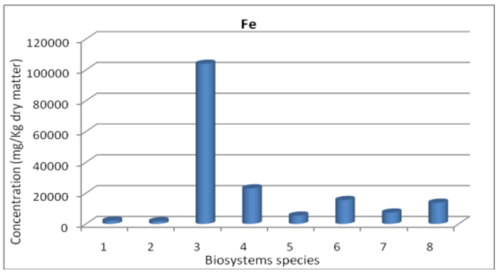


Figure 7 ***Concentration in Fe of different biosystems species from high polluted area***

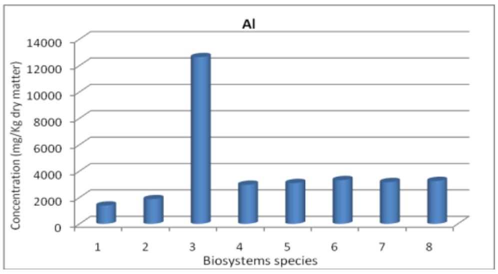


Figure 8 ***Concentration in Al of different biosystems species from high polluted area***

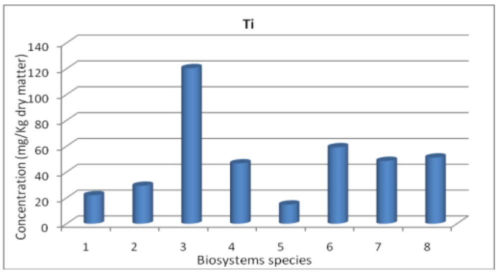


Figure 9 ***Concentration in Ti of different biosystems species from high polluted area***

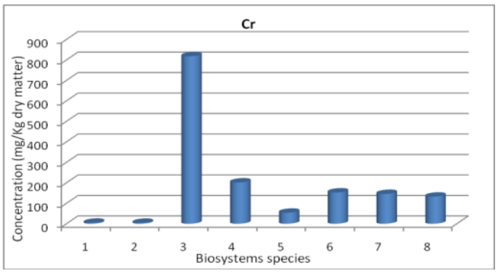


Figure 10 ***Concentration in Cr of different biosystems species from high polluted area***

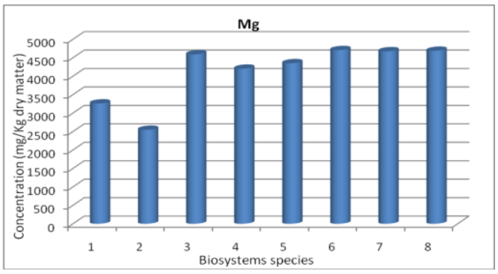


Figure 11 ***Concentration in Mg of different biosystems species from high polluted area***

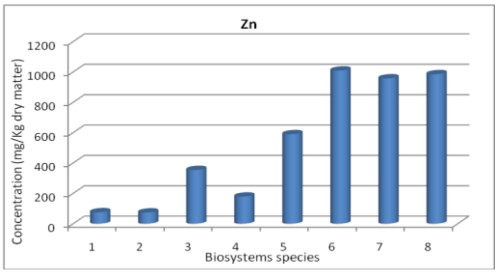


Figure 12 ***Concentration in Zn of different biosystems species from high polluted area***

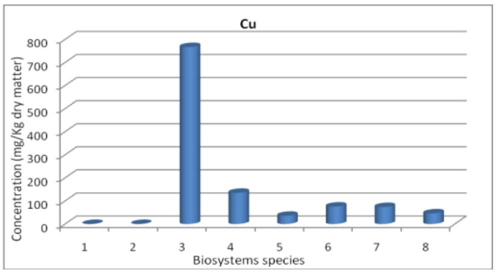


Figure 13 ***Concentration in Cu of different biosystems species from high polluted area***

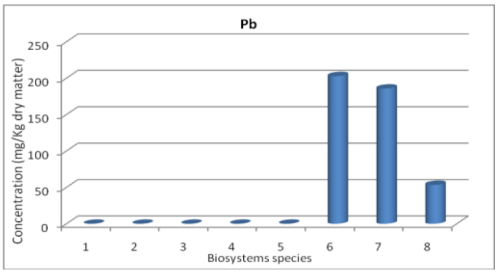


Figure 14 ***Concentration in Pb of different biosystems species from high polluted area***

1. ***Hypholoma capnoides (talie mare); 2. Hyph***
2. ***oloma capnoides (talie mică); 3.Thuidium abietinum; 4. Festuca pratensis; 5. Stipa capillata; 6. Lolium perene; 7. Luzula campestris; 8. Agrostis tenuis***

For many metals, the moss *Thuidium abietinum* showed a high capacity of accumulation even hyperaccumulation, so we can consider this specie the best bioindicator for metals, as well as a viable methods for metals extraction and contaminated soil remediation.
The mushrooms, next to the important metals accumulation capacity, they have a good capacity of ecological adaptation and can grow even of these soils with a high level of metals concentration.
For the species of *Plantae Kingdom, Festuca pratensis, Stipa capillata, Lolium perene, Luzula campestris, Agrostis tenuis,* we observed that the level of metals concentration is obviously higher that for the level in the mushrooms, this is because of them long period o vegetation.

Next to the metals accumulation level, we have to consider also the life period, the crop technology, and the impact on the environment parameters in the settlement of the best practice in bioremediation of metallurgic infested soils.

Conclusions

Conclusion (1). Each pollutant is characterized by an environment action influenced by the meteorological and topographic parameters, and also by the interaction with others pollutants elements. Analyzing these pollutants and them parameters we obtain an image of industrial process impact on the natural environment, and based on it we can take responsible decisions in environment remediation.
Conclusion (2). The optimization of natural environment quality is done by applying the ecological technologies, with minim energetically and starting matters consuming, with reduced pollutants emissions, and with a serious management of waste materials based on recycling and recirculation.
Conclusion (3). The bioremediation, being a natural process, require minimal supervision, which make the cheapest method of soil quality increasing and the field is faster restore to the agricultural system.
Conclusion (4). The biosystem's metals content is directly influenced by the characteristics of the ecosystem and of the soil on which they are growing. As the metals level in the soil is higher, as the biosystems, with high capacity of absorption, accumulate bigger quantities of metals. The mushrooms growing in high polluted areas showed a level of 4-12 times higher than the wild growing mushrooms.
Conclusion (5). Metals ions accumulation in the mushrooms is different than the accumulation in plants, influenced by the species characteristics, life period and environment parameters. The multiannual plants showed higher level of metals concentration that in the mushrooms, which has only 2 weeks of life period.

Conclusion (6). After the remediation process of the contaminated soils, are obtained biosystems charged with heavy metals, which can be extract and reuse in the industrial process.

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