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HEAVY METAL INFLUENCE ON AN ENVIRONMENT GENERATED BY THE MINING INDUSTRY: THE INFLUENCE OF COPPER, ZINC, LEAD, MANGANESE AND SILVER ON SOIL QUALITY IN THE MESTECANIŞ AREA (ROMANIA)

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Abstract. The mining activities from the northern area of Romania were carried out for years without a controlled measuring of pollution or any prevention actions. Thus, after 1995, an end was put to most of these activities. Suceava County, Romania, was highly polluted with heavy metals, especially copper resulted from mining activities. The current paper had the purpose to assess the influence of heavy metals generated in time by mining activities on the environmental quality of the studied area and, in order to do so, the method of global pollution index, in both its conventional and improved forms, was applied. The soil quality of the Mestecaniş area, namely the dump and its limits, was evaluated between 1996 and 2007, focusing on Cu, Zn, Pb, Mn and Ag. The main pollutants are heavy metals, especially copper, and the aim of this paper was to assess the influence of heavy metals on soil quality, so that the decision regarding further research could be made. Soil samples were analyzed between 1996 and 2007, during the mining activities and after these activities were stopped. The index of global pollution, calculated according to Rojanschi's method (1991) and that of Popa et. al. (2005), showed that the degree of pollution is within admissible limits. The final results illustrated that the environment has been modified by industrial activities within admissible limits, corresponding to class B, which is concordant with Rojanshi's method.

Keywords: mining industry, heavy metals, pollution, environmental impact and risk.

1. MINING INDUSTRY AND ENVIRONMENTAL COMPONENTS

The mining industry significantly contributes to the decrease of environmental quality by its waste, emission and associated environmental impacts. Some of the waste is inert and, hence, not likely to represent a significant pollutant threat to the environment, except for the smothering of riverbeds and a possible collapse if stored in large quantities, but other fractions, particularly those generated by the non-ferrous metal mining industry, may contain large quantities of dangerous substances such as heavy metals (Prasard,, 2001; Siegel, 2002; Mc Bride, 1989). Through extraction and subsequent mineral processing, metals and metal compounds tend to become chemically more available, which can result in the generation of acid or alkaline drainage. Moreover, the management of tailings is an intrinsically risky activity, often involving the processing of residual chemicals and elevated levels of metals. These impacts can have lasting environmental and socio-economic consequences and can be extremely difficult and costly to address through remedial measures. Waste from the extractive industries has, therefore, to be properly managed in order to ensure especially the long-term stability of disposal facilities and to prevent or minimize any water and soil pollution arising from acid or alkaline drainage and the leaching of heavy metals (Bennett, & Tributsh, 1978; Andráš, et al., 2008; Horaicu, et al., 2007).

In Romania, the studies focusing on the assessment of soil pollution from dumps with heavy metals located in mining areas (Lăcătuşu, 1995; Lăcătuşu, et al., 1998; Florea & Munteanu, 2003;

Damian, et al., 2008a and 2008b), as well as the studies dealing with the influence of heavy metals on the vegetation and dump rehabilitation (Damian, F., & Damian, Gh., 2006), took into consideration the European legislation that establishes the maximum level of pollutants in vegetation samples. These studies (Rojanschi, et al., 1991 and 1997; Popa, et al., 2005; Robu, et al., 2005 and 2007) showed that for impact and risk assessment it is fundamental to consider at least one environmental component or more environmental components such as air, water, soil etc.

The strategic objectives proposed for the mining sector are the following (Horaicu, et al., 2007; Macoveanu, et al., 2008):

- the development of mining products according to the demands of the market;
- the cutting down of the direct involvement of the national government in sustainable mining activities by gradually reducing the current state;
- the undertaking of mining activities in agreement with mining protection criteria;
- new funds for mine closures and environmental restoration, mitigation of social impact due to mine closure and redevelopment of mining area.

2. GEOLOGICAL DESCRIPTION OF EVALUATED SITE: THE MESTECĂNIŞ AREA

The main polymetallic mineralization associated to the epimetamorphic schists of the Eastern Carpathians, from NW to SE, are concentrated in the following metalliferous districts:

1) Borşa-Vişeu, with Novicior-Novăţ, Gura Băii-Burloaia and Dealul Bucăţii metalogenetic fields in the Maramureş Mountains;

2) Fundul Moldovei-Leşu Ursului with Fundul Moldovei and Leşu Ursului metalogenetic fields in the Bistriţa Mountains;

3) Hărlagia-Şumuleu;

4) Bălan-Fagul Cetăţii, with, Mediaş, Bălan Central, Fagul Cetăţii and Bălan Sud metalogenetic fields in the Giurgeu Mountains.

The Mestecăniş area is located in the Fundul Moldovei-Leşu Ursului district, characterized by two metalogenetic fields, Fundul Moldovei and Leşu Ursului, found in the Bistriţa Mountains.

The last lithostratigraphical classification of the Tulgheş lithogroup includes the following lithomembers: the Căboaia lithomember (Tg1), the Holdiţa lithomember (Tg2), the Leşu Ursului lithomember (Tg3) and the Arşita Rea lithomember (Tg4) (Savul, 1923; Kräutner, 1980; Vodă et al., 1996, 1996; Zincenco, 1994; Hârtopanu, 2004, etc). In the Mestecaniş area (view the map in Fig. 1), the metamorphic rocks are the following: porfirogeous rocks, chlorithic-sericitic schists, graphitic schists and black quartzites, and metamorphic quartzites with sulfides.

In the Mestecaniş area, Suceava County, the most important industrial activities were mining activities, mainly the underground extraction of metal ores. The exploration was made with drifts and drillings, and the exploitation with open panels.

The metal ores extracted from this area were: pyrite (FeS_2), chalcopyrite ($CuFeS_2$), blende (ZnS), galena (PbS), and, as epigenetic minerals resulted from primary sulfur alteration, chalcocite (Cu_2S) and very rarely copper (Cu), malachite [$CuCO_3Cu(OH)_2$] and azurite [$Cu_3(CO_3)_2(OH)_2$]; these minerals are found in the dumps (Fig. 4-5), but only rarely.

The mining activities in the Mestecaniş area were closed in 1998 (Fig. 2-3). As pointed out in the abstract, our evaluation was made after the closing of the Mestecanis mining perimeter. The project to close – rehabilitate the Mestecanis mine and mining perimeter consisted of the following: the closing down of the mining works linking the mine to the surface, which consisted in the embankment of the two slope galleries and the blocking of the entrances to the galleries using concrete dams; works meant to ensure the stability of the two tailings dumps through the execution of the following works: support walls made up of gabions filled with raw stones; a water-collecting ditch at the toe of dump no. 6, the planting of juvenile spruce and the building of small slope fences.

The highly acid mine waters (pH= 2, 5-3) go through a wastewater treatment plant, their flow being of approximately 31 l/s (the quality and efficiency of the plant is debatable).

Regarding the weathering of silicates and sulphides, the following can be mentioned: the compounds resulted from the weathering of silicates (carbonates, oxides, hydroxides, clay minerals) are the main mineral components of the soils. The weathering of silicates, which has several stages: Depletion of bases, Silicium removal, Argilisation and Destruction, may also enter buffering reactions with hydroxides. We merely mention these aspects, as they have not been dealt with in the present paper.

As far as the weathering of sulphides and the acid drainage are concerned, observations have been made, namely the following: the waters from the deposits, dumps or settling ponds of polymetallic sulphides are highly acid (Jambor, 1994, Herr & Gray, 1997, Iribar, et al., 2000, Forray, & Hallbauer, 2000, Hammarstrom, et. al., 2005., Stumbea, 2005, 2006, 2010). At Mestecanis, in the area of the dump, the value of the pH reaches 2,5-3.

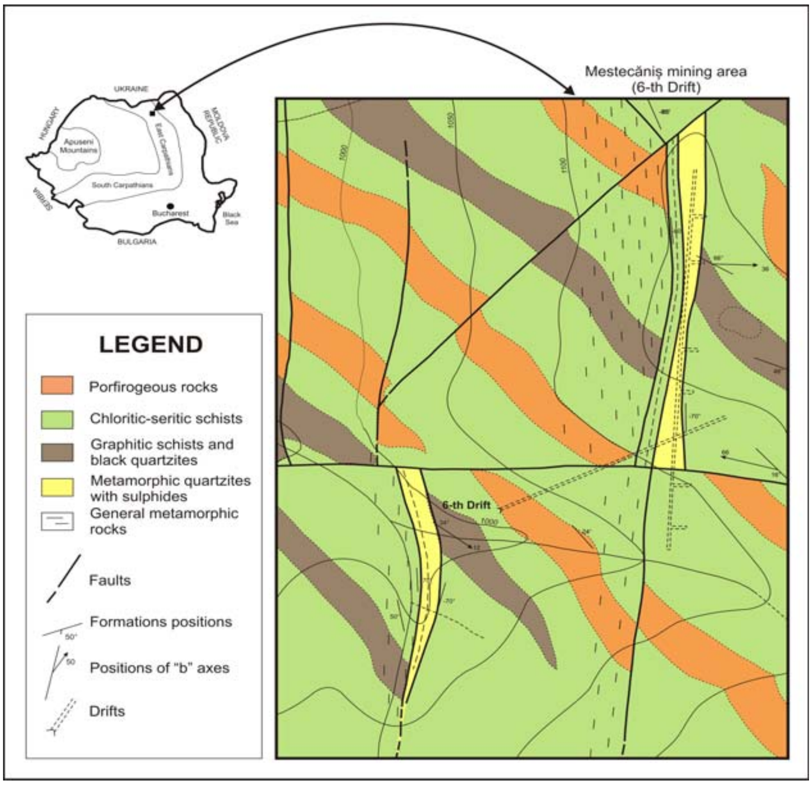

Figure 1. Map of the Mestecaniş area (Muşat, 1972, Archives of S.C."Geomold" S.A., Câmpulung Moldovenesc, Suceava County, completed by Florea and Horaicu, 2008)

Figure 2. Mine in the Mestecaniş area ,6th drift (General view)

Figure 3. Mine in the Mestecaniş area, 6th drift (Enclosure)

Figure 4. Dump of the Mestecaniş area, 6th drift (General view)

Figure 5. Dump of the Mestecaniş area, 6th drift (Detail)

Pyrite, which is and has been abundant in the deposit and, implicitly, in the dump, has formed, along with marcasite, upon contact with air and water, sulphides and sulphuric acid. Moreover, chalcopyrite, galena or blende has also formed, under oxidizing conditions, sulphides. Oxidation and oxidation-hydrolysis reactions, bacterial leaching or even buffering reactions are and have been present. Thus, the solubility of heavy metals has increased and their concentration in percolation waters is significant, leading to the pollution of groundwater and surface water, these waters being in immediate contact with the soils of the area.

The soils of the perimeter which was studied are part of the Obcina Mestecanisului. The group of the mountainous podzolic soils (Spodosols class) is the dominant one, with a very low degree of base saturation of the Iron humus Podsol type, which develops in the presence of rich precipitations and lower temperatures, as meteorological conditions, and in the presence of metamorphic rocks in the substratum as lithological condition. These rocks have a short profile, a reduced edaphic volume (a consequence of the large volume occupied by the skeleton), the humus is of Moder-Moor type, the acidity is high, the cationic exchange capacity is reduced and the quantity of bases is very small. A profile devised in the area highlighted the following horizons:

Depth (centimetres)	Horizon
0, 0 – 4	At
4 – 11	Aou
11 – 20	Bhs
20 – 38	Bs
38 – 57	BR

The Iron-Humus podzolization is a complex solification process through which the weathering of primary silicates from the upper part of the soil profile occurs, as well as the migration and accumulation of a part of the destruction products in the subjacent horizons, particularly that of iron and aluminium hydroxides, under the action of fulvic acids and other complex substances from the soil solution. Can form such a horizon iluvial Bhs and / or Bs, characteristic of the Lepti-entic Podzols, such as described above ground.

This type of pedogenetic evolution, which occurs primarily on a silicate substratum, causes the weathering through complexolysis of the minerals and the involving of Al and Fe ions as mobile organo-mineral compounds. The newly-formed compounds are soluble in water and they migrate from the upper part of the soil into horizon B. In draining environments, Al is more soluble than Fe and, therefore, is involving at an inferior level (at depth), whereas in the weakly draining ones Fe can be levigated and transferred, Al accumulating in the soil.

The precariousness of the conditions necessary for the neoformation of clay and the intense destruction of primary silicates determines, as far as the granulometric structure is concerned, the authoritarian predomination of coarse and medium textures. Soil Lepti-entic Podzols described above and belongs to the Spodosols class, it represents the dominant type of soil in the area.

The main restoration actions consisted in covering the land with vegetal soil up to 10 cm and planting various trees. Different studies (Dițoiu & Oseanu, 2007) showed that a period of at least 2 years is necessary for the environment to self-regenerate. The environmental quality of the area was assessed; soil samples were analyzed from depths of 5cm and 30 cm before and after restoration (Table 1). The conclusion was that the soil quality improved, especially regarding the pH (from values between 3.39-3.65 in 1998, to values between 5.00-5.02 in 2006), sulfurs (from values between 5091-6820 mg/l in 1998 to values of 280 mg/l in 2006) and copper (in 1998 the measured concentration was higher than the maximal allowable concentration, while in 2006 the measured concentration was lower than it) (Dițoiu & Oseanu, 2007).

3. HEAVY METAL INFLUENCE ON SOIL QUALITY

3.1. Experimental data

Soil samples from the Mestecaniş area were analyzed in 1996, 1999, 2005 and 2007 and the results are presented in Table 2. In 1998, the mining activities in this area were closed and remediation actions were developed through the planting of various trees. It was interesting to assess the situation during the mining activities and after replanting, especially the influence of the main pollutants generated on environmental quality.

Table 1. Soil characterization (Dițoiu and Oseanu, 2007)

Sample	Year	Depth (cm)	pH	Sulfur	Fe	Mn	Zn	Cu	Cd	Ni
				mg/kg						
Soil	1998	5	3.39	6820	13080	1500	67.88	720	2.1	129.5
		30	3.65	5091	12260	364	87.32	362	1.8	33.8
	2006	5	5	288	11482	1342	43.1	184	2.03	33.3
		30	5.02	280	6670	140	56	73	1.53	18.6

Table 2. Experimental results

Year	Cu	Zn	Pb	Mn	Ag
	mg/kg				
1996	41.02	39.05	27.58	180.29	0.40
1999	36.31	36.09	20.22	314.04	0.66
2005	29.53	39.16	30.00	267.61	0.64
2007	23.67	17.43	7.72	109.71	0.19
MAC^1*	200	600	100	2500	20
MAC^2*	500	1500	1000	4000	40
N.V.**	20	100	20	900	2

*Maximal Allowable Concentration, concordant with Romanian Order 756/1997

1- maximal allowable concentration for sensitive soil (e.g. arable land)

2- maximal allowable concentration for insensitive soil (e.g. industrial area)

** Values considered to be within normal limits, naturally present in soil.

It can be observed that copper and lead have the measured concentrations higher than the values considered to be within normal limits for sensitive soil (e.g. arable soil). As a result, further assessments were conducted in order to estimate the impact and associated risk for the environmental component: *soil.*

3.2. Impact assessment trough the method of global pollution index

3.2.1. Method description

The global pollution index method allows the *evaluation* of the environmental pollution degree induced in the environment by certain industrial activities, and its *quantification* using an index which considers the ideal and the real values of the quality indicators representative for the evaluated environmental components. This method, also known as Rojanschi's method (Rojanschi, 1991), is a complex estimation, based on the quality indicators for each environmental component, and a further correlation using a graphical representation. Thus, for each environmental component different evaluation grades are established within a scale from 1 to 10, considering the levels of quality indicators imposed by the national standards. On the scale, the evaluation grade 1 describes a very severe situation concerning environmental pollution, while the grade 10 describes the ideal situation, namely that in which the quality of the evaluated environmental component is not affected by human or industrial activities (Macoveanu, 2005; Robu, 2005; Rojanschi et al., 1997). The index of global pollution (***I_{GP}***) is defined by Rojanshi as in Eq. (1) (Rojanschi, 1991):

$$I_{PG} = \frac{S_i}{S_r} \quad (1)$$

where: S_i area of the ideal state of the environment,

S_r area that represents the real state (evaluated situation).

According to the literature (Macoveanu, 2005; Robu, 2005; Rojanschi, 1991), the value of I_{GP} can vary between 1 and 6 and each value corresponds to a real situation (Table 3). The global pollution index method has the following advantages:

- it offers a global overview of the environmental state and its quality;
- it allows a comparison between some regions, with the requirement that these regions have to be analyzed based on the same quality indicators;
- it allows a comparison between the environmental states of an area at different moments, offering the possibility to overview the evolution of the quality of environmental components and of the global quality of the environment.

The disadvantage of this method consists in the high degree of subjectivity generated during the calculation of evaluation grades, which greatly depends on the evaluator's experience. Moreover, this method can be applied only in the cases in which at least three environmental components are assessed.

Table 3. The values of the global pollution index (I_{GP})

Values of I_{GP}	***Class***	***Effects/ real situation***
$I_{GP} = 1$	A	Natural environment, not affected by industrial/human activities
$1 < I_{GP} < 2$	B	Environment modified by industrial activities within admissible limits
$2 < I_{GP} < 3$	C	Environment modified by industrial activities causing discomfort conditions
$3 < I_{GP} < 4$	D	Environment modified by industrial activities causing distress to life forms
$4 < I_{GP} < 6$	E	Environment modified by industrial activities, dangerous for life forms
≥ 6	F	Degraded environment, not proper for life forms

3.2.2. Improved global pollution index method

The improved method follows the same procedure as that developed by Rojanschi (1991). Thus, firstly, an evaluation scale for each environmental component assessed has to be established, considering the maximal allowed concentrations of quality indicators, according to the national legislation. After that, the environmental state can be assessed using the index of global pollution. As does Rojanschi's method, the improved method proposed by Popa et al. (2005) considers the *index of global pollution* (I_{GP}) as the ratio between the ideal state (S_i) and the real state (S_r) of the ecosystem. Thus, a graphical methodology based on concentric circles proposes the calculation of the *global pollution index* by using only the arithmetic mean of the evaluation grades $\left(\overline{b^2}\right)$ (Eq.2) (Popa et al., 2005; Robu, 2005):

$$I^*_{GP} = \frac{100}{\overline{b^2}} \qquad (2)$$

By applying this equation in order to calculate the *index of global pollution*, the global state of the assessed ecosystems may be quickly appreciated by using only the arithmetic mean of the evaluation grades. Popa et al. (2005) suggested a scale of the arithmetic mean values for the evaluation grades, correlated with the global state of the ecosystem (Table 4).

The proposed method defines the index of global pollution as the ratio between the surfaces of the concentric circles that correspond to the ideal and real states of the ecosystem, respectively leading to the final equation that allows the calculation of the global pollution index (Popa et al., 2005). This is one of the advantages of this improved method. Thus, the final information about the global state of the ecosystem is easier to be reached than in Rojanschi's method. Another advantage of this new method is that the global state of the ecosystem can be assessed by using only two environmental components, while Rojanschi's method can be applied only by taking into consideration at least three environmental components (Petruc et. al., 2006; Robu, 2005, Robu et. al., 2007).

The scales of evaluation grades were elaborated taking into account the maximal allowable concentrations, concordant with Romanian Order 756/1997, as well as the values considered to be within normal limits, values at which heavy metals are naturally present in soil, and their influence on the environment is not significant. The evaluation scales are presented in Table 5.

Table 4. Correlation between the arithmetic mean of the evaluation grades and the global state of the ecosystem (Popa et al., 2005)

Values of $\left(\overline{b^2}\right)$	***Values of*** I^*_{GP}	***Class***	***Effects/ real situation***
10	$I^*_{GP} = 1$	A	Natural environment, not affected by industrial/human activities
9.999 - 7.072	$1 < I^*_{GP} < 2$	B	Environment modified by industrial activities within admissible limits
7.071 - 5.774	$2 < I^*_{GP} < 3$	C	Environment modified by industrial activities causing discomfort conditions
5.773 - 5.001	$3 < I^*_{GP} < 4$	D	Environment modified by industrial activities causing distress to life forms
5 - 4.083	$4 < I^*_{GP} < 6$	E	Environment modified by industrial activities, dangerous for life forms
< 4.082	$I^*_{GP} \geq 6$	F	Degraded environment, not proper for life forms

Table 5. Evaluation scale proposed for sensitive soils, polluted with heavy metals (Cu, Zn, Pb, Mn, Ag)*

Evaluation grades	Cu	Zn	Pb	Mn	Ag
	mg/kg				
10	0-20	0-100	0-20	0-100	0-0.4
9	20-40	100-150	20-50	100-500	0.4-2
8	40-70	150-300	50-100	500-1500	2-4
7	70-100	300-500	100-250	1500-2000	4-8
6	100-150	500-750	250-500	2000-2500	8-10
5	150-300	750-1000	500-1000	2500-3000	10-20
4	300-500	1000-1500	1000-1500	3000-4000	20-40
3	500-750	1500-2000	1500-2000	4000-4500	40-50
2	750-1000	2000-2500	2000-2500	4500-5000	50-75
1	>1000	>2500	>2500	>5000	>75

* concordant with Romanian Order 756/1997.

4. ANALYSIS OF RESULTS

It has been mentioned that heavy metals could be accumulated in the soil and from the soil they could migrate into the vegetation chain. Thus, it proved necessary to calculate the index of global pollution by copper, zinc, lead, manganese and silver for the entire period (Eq.3) (fig. 6).

$$I_{PG} = 1.22 \qquad (3)$$

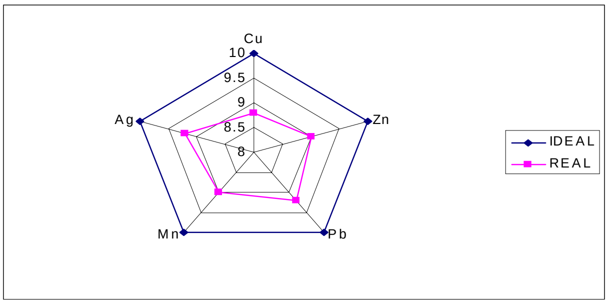

Figure 6. Global pollution with heavy metals, cumulated in the period between 1996-2007

The final result of the global pollution index (Ipg = 1.22) shows that the state of the environment modified by industrial activities is within admissible limits and it corresponds to class B. It can be observed that there is a significant influence on the soil due to the presence of heavy metals. In 1996, the pollution was greater than during other years. However, after the mining activities were closed, the soil pollution with heavy metals generated by these mining activities started to decrease with every year, and in 2007 the measured concentrations were lower than the values recommended by Romanian regulations (Order, 1997). The main pollutant in the studied area is copper and, thus, monitoring measures should be developed. The fact that the studied heavy metals have migrated from the soil into the groundwater and, due to biological processes, have been bio-accumulated in the vegetation chain must be taken into account. Nevertheless, further research should be conducted in order to estimate the impact not only on soil quality, but on vegetation ecosystems as well, in order to make the right decisions concerning the restoration actions necessary in the studied area.

5. CONCLUSIONS

Mining activities are the most important pollution sources for the evaluated area. The main pollutants are heavy metals, especially copper, and the purpose of this paper was to assess the influence of these pollutants on soil quality, so that the decision regarding further research could be made. Soil samples (from the dump and the limits of the Mestecaniş dump) were analyzed between 1996-2007, during the mining activities and after these activities are stopped (the global pollution index, calculated for the pollution with heavy metals that occurred during each evaluated year, from 1996 to 2007, was calculated for the first time for an ore deposit in Romania) The index of global pollution, calculated according to Rojanschi's method and that of Popa et al, (2005) showed that the pollution is within admissible limits, and that the environment modified by industrial activities within admissible limits corresponds to class B. Apart from this, the study underlined the fact that the main pollutant in the studied area was copper. It has to be taken into account that the studied heavy metals migrated from the soil into the groundwater, and, also, that, due to biological processes, heavy metals were bio-accumulated in the vegetation chain. This is a powerful argument in favor of the conducting of further research in order to estimate the impact not only on soil quality, but on the vegetation ecosystems as well, so that the right decisions concerning the restoration actions necessary in the studied area can be made.

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REFERENCES

Andráš, P., Adam, M., M. Chovan, M., Šlesárová, A., 2008. *Environmental hazards of the bacterial leaching of ore minerals from waste at the Pezinok deposit (Malé Karpaty Mts., Slovakia,* Carpathian Journal of Earth and Environmental Sciences, 3(1), 7-22.

Bennett, J.C., Tributsh, H., 1978. *Bacterial leaching patterns on pyrite crystal surfaces*, Journal Bacteriology, 134(1), 310-316.

Damian, Floarea, Damian, Gh., 2006. *Geochemical characterization of some old mine waste dumps from Baia Mare area and their influence on the natural vegetation*, Carpathian Journal of Earth and Environmental Sciences, 1(2), 63-72.

Damian, Floarea, Damian Gh., Lăcătuşu R., Macovei Gh., Iepure Gh., Năprădean, Ioana, Chira R., Kollar Lenuța, Rață Ioana, Zaharia Dorina Corina, 2008a. *Soils from Baia Mare zone and the heavy metals pollution,* Carpathian Journal of Earth and Environmental Sciences, 3(1), 85-94.

Damian, Floarea, Damian Gh., Lăcătuşu R., Iepure Gh., 2008 b. *Heavy metals concentration of the soils around Zlatna and Copşa Mică smelters Romania,* Carpathian Journal of Earth and Environmental Sciences, 3(2), 65-82.

Dițoiu, V., Osean, V., 2007. *Changes of soil quality by mining activities from Suceava county* (in Romanian), Annals of Grand Stefan University, Suceava, section Geography, XVI, 195-202.

Florea N., Munteanu I., 2003. *Romanian System of soils taxonomy (SRTS),* (in Romanian), Estfalia Ed., 182 p, Bucharest, Romania

Forray F.L., Hallbauer D.,K., 2000. *A study of the pollution of the Arieş River (Romania) using capillary electrophoresis as analytical technique*, Environmental Geology, 39(12), 1372-1384.

Hammarstrom J., M., Seal R., R., Meier A., L., Komfeld J., M., 2005. *Secondary sulfate minerals associated with acid rock drainage in the eastern US : recycling of metals and acidity in surficial environments,* Chemical Geology, 215, 407-431.

Hârtopanu Paulina, 2000. *Mineralo-geneese of manganesse belt from Bistrita Mountains (in Romanian),* Ed. Cartea Universitara, Bucharest

Herr C., Gray N.F., 1997. *Sampling riverine sediments impacted by acid mine drainage, problems and solutions,* Environmental Geology, 29(1/2), 37-45.

Horaicu C., Gabrian F., Robu Brînduşa, 2007. *Environmental risk management in extractive industry,* (in Romanian), Ed. TipoMoldova, 140 p., Iaşi, Romania

Iribar, V. et al., 2000, *Water contamination and remedial measures at the Troya abandoned Pb-Zn mine (The Basque Country, Northern Spain).* Environmental Geology, 39(7), 800-806.

Jambor, J.L., 1994. *Mineralogy of Sulfide-rich Tailings and Their Oxidation Products.*, in Environmental Geochemistry of Sulfide Mine-wastes, Mineralogical Association of Canada Short Course, 22, 59-102.

Kräutner H., G., 1980, *Litho-stratigraphic Correlation of Precambrian in the Romanian Carpathians*, Anuar of Geology and Geophysics Institute,Romania, LXVII, 229-296.

Lăcătuşu R., Răuță C., Avram N., Cârstea S., Medrea N., Kovacsovics Beatrice, Serdaru Maria, Lungu Mihaela, Rîşnoveanu I., Taină S., Mehedințu Carmen, Tănăsescu Veronica, 1998. *Heavy metals in soil-plant-water-animal system within the areas polluted by emissions from the non-ferrous metallurgical industry*. Soil Science, XXXII(1-2), 137-153.

Lacătuşu R., 1995. *Method for appraising the level of soil loading and pollution with heavy metals*, Soil Science , 29(2), 69-80.

Macoveanu, M., 2005. *Methods and procedures for environmental impact assessment*, EcoZone Ed.,Iasi,Romania, 264 p.

Mc Bride, M. B., 1989. *Reactions controlling heavy metal solubility in soils.* Advances in Soil Science 10, 1-56.

Order 756, 1997. *Order of Ministry of Waters, Forests and Environmental Protection for approval of roles for evaluation of environmental pollution*, published in Romanian Official Monitor no. 303, 1997.

Petruc, V, Robu, B., Macoveanu, M., 2006. *Improved global pollution index method applied for environmental impact assessment of a refinery,* Environmental Engineering and Management Journal, Iasi,Romania, 5, 51-62.

Popa, Camelia, Cojocaru, C., Macoveanu, M., 2005. *Geometrical correlation method for global estimation of the ecosystem state,* Environmental Engineering and Management Journal, Iasi, Romania, 4, 437-447.

Prasard M.N.V., 2001. *Metals in the Environment*, Marcel Dekker, New York – Basel. 481 p,

Robu Brindusa, 2005, *Environmental impact and risk assessment for industrial activities*, Ed. EcoZone, Iaşi, Romania,225 p.

Robu B., Caliman A. F., Betianu C., Gavrilescu M., 2007, *Methods and procedures for environmental risk assessment*, Environmental Engineering and Management Journal, Iasi, Romania, 6, 573-592.

Rojanschi V., Bran F., Diaconu Gh., 1997. *Environmental protection and engineering, (in Romanian),* Editura Economica, 497 p, Bucharest, Romania

Rojanschi V., 1991. *Posibilities for global evaluation of impact of pollution on ecosystems quality (in Romanian),* Mediul înconjurator, II(1-2), 45-52..

Savul M., 1923. *Les gisements de minerais de manganese au basin de Neagra Şarului,* Ann., Sci., Univ., Jassy, XII, 136-154.

Siegel Frederic R., 2002. *Environmental Geochemistry of Potentially Toxic Metals*, Springer-Verlag Berlin Heidelberg New York, 218p.

Stumbea D., 2005. *The acid rock drainage and its implications on the environment. (II) products of experimental alteration,* Anal. Ştiinț. ale Univ."Al. I. Cuza" Iaşi, Geologie, LI, 69-76.

Stumbea D., 2006. *Natural and artificial acid mine drainage products,* Romanian Journal of mineral-deposits and mineralogy, 82, 139-142.

Stumbea D., (2010) *Acid mine drainage related products in Negoiul Românesc quarrying waste deposits (Călimani Mts., Romania),* Carpathian Journal of Earth and Environmental Sciences, October 2010, **5**,(2), p. 9 – 18.

Vodă Al., Balintoni, I., 1996a. *Litho-stratigraphics correlation in crystalline of Oriental Carpathian* (in Romanian), Studia Univ. "Babes - Bolyai", Geologia, XXXIX (1-2), p. 61-66, Cluj-Napoca, Romania.

Vodă Al., Munteanu M., 1996b. *Lithostratigraphic, structural, and metallogenetic correlations in the East Carpathians Crystalline-Mesozoic Zone,* An., Inst., Geol., Rom., 69(I), 265-267.

Zincenco D., 1994. *Chronostratigraphic scale of the pre - Permian metamorphites and granitoids from Romanian Carpathians.* Carp. - Balk. Geol. Assoc. XV-th Congress, 4(2), 647 – 652.

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