This paper was peer-reviewed for scientific content.
Pages 817-820. In: D.E. Stott, R.H. Mohtar and G.C. Steinhardt (eds). 2001. Sustaining the Global Farm. Selected papers from the 10th International Soil Conservation Organization Meeting held May 24-29, 1999 at Purdue University and the USDA-ARS National Soil Erosion Research Laboratory.

Soil Pollution by Acid Rains and Heavy Metals in Zlatna Region, Romania

R. Lacatusu, M. Dumitru, I. Risnoveanu, C. Ciobanu, Mihaela Lungu, S. Carstea, Beatrice Kovacsovics and Carmen Baciu*

ABSTRACT

In the Zlatna area located in the Western Carpathian region of Romania, around an industrial complex involved in mining, metallurgical and chemical activities, the environment and particularly the soils are polluted due to the acid rains and heavy metals on 55,664 hectares. About 68% of the soils in the area affected by the emissions from these industrial activities present a high vulnerability to the impact of these pollution types. The increase of the natural soil acidity up to 3.6-3.9 pH values and soil loading with heavy metals at content levels exceeding up to 41 (Pb), 11 (Cu), 7 (Zn), 4 (Cd) times the maximum allowable limits contributed to soil base depletion, microbiological activity disturbance, organic matter degradation, soil structure deterioration, sheet and gully erosion, as well as landslides.

INTRODUCTION

The Western Carpathian region in Romania is well known for its Metalliferous Mountains, where an old mining activity is carried out in order to get the raw materials (polymetallic sulfide ores) for obtaining heavy metals.

The pollymetallic sulphide ores are mainly contained in the alpine magnetite including andesite, granite, rhyolite, and dacite, associated with basalt and gabrou. The alpine magnetite is associated with sedimentary rocks of Cretaceous age.

Zlatna, a little town located in this mining region, is particularly known due to its old polymetallic ores processing enterprise.

The primary (Cu and Zn) and secondary (Pb, Cd, As, Sn, and Sb) metallic sulfides are concentrated by floating technology and the metals are extracted by smelting procedures.

At the same time, in Zlatna there is also a chemical enterprise preparing different mineral salts of Cu, Zn, Pb, Bi, etc.

The daily sulphur emissions, together with dust loaded heavy metals, both discharged from smelter and the chemical enterprise, cause severe environmental pollution. The mean annual emissions into the atmosphere reach about 150,450 t SO_2 and 3,498 t dust loaded with heavy metals (Pb, Zn, Cu, Cd, Sb, Bi) and As (Serban et al., 1993).

Soil pollution is caused by acid rains and particles loaded with heavy metals, falling at the same time with the acid rains or blown from the sterile stockpiles resulted from floating and smelting processes. The area affected by these processes has a surface of 55,664 hectares.

This paper provides a study on the harmful effect of the air-born emissions on the soils.

MATERIAL AND METHODS

The sampling grid of soil profiles was irregular, having in view a higher number of soil profiles per hectare near pollution source - up to 4-5 profiles ha^{-1}. Soil types, land uses, and degree of soil and vegetation degradation were also taken into account.

Soil samples were collected mainly on genetic horizons, from 115 agricultural and forest soil profiles located in the area affected by the emissions of the above mentioned sources. Each soil profile was characterized by soil texture and basic chemical properties (pH, exchange capacity, content of humus, nitrogen, $CaCO_3$, mobile phosphorus and potassium, exchangeable hydrogen). Heavy metal (Cd, Cu, Cr, Co, Fe, Mn, Ni, Pb, and Zn) contents were also measured, by atomic absorption spectrometry procedure. On the basis of analytical data, the values of some indexes were computed, such as soil buffering capacity (Borlan, 1955), loading/pollution index[1] (Lacatusu, 1998) which, together with the proper analytical data, permitted to asses the degree of soil deterioration in the Zlatna area influenced by both the acid rains and heavy metal pollution.

RESULTS AND DISCUSSIONS

Soil vulnerability to pollution by acid rains and heavy metals

The polluted area is covered by various soils. Dystric and Eutric Cambisols are predominant (83.74%). In addition, there are Haplic and Vertic-Haplic Luvisols, Eutric Fluvisols, and Eutric Regosols (Table 1).

The vulnerability assessment of these soils, taking into account the values of the soil buffering capacity index, within the considered area, shows that soils with high vulnerability to the polluting impact represent 68%, while soils with moderate vulnerability represent 22% and soils with low vulnerability represent only 10% (Fig. 1). The ranking of soils according to the natural vulnerability to the impact of acid rains accompanied by heavy metals is presented in Table 2. The conclusion is that the nature of soils is largely prone to some increased effects of soil chemical and physical degradation.

*R. Lacatusu, M. Dumitru, I. Risnoveanu, C. Ciobanu, Mihaela Lungu, S. Carstea, Beatrice Kovacsovics, and Carmen Baciu, Research Institute for Soil Science and Agrochemistry B-dul Marasti 651, 71331 Bucharest 32, Romania. *Corresponding author: lacatusu@icpa.ro

Table 1. Intervals of topsoil pH_{H_2O} (1:2,5) values inside and outside the Zlatna polluted area.

Soil*	No. of soil samples	x_{min} Polluted area	x_{max} Polluted area	x_{min} Non-polluted area	x_{max} Non-polluted area	Δ pH
BO Dystric Cambisols	21	3.9	5.0	4.9	5.3	1.0 - 0.3
BP Haplic Luvisols	27	3.6	6.1	5.6	6.2	2.0 - 0.1
BD Vertic-Haplic Luvisols	34	4.3	5.1	5.0	6.2	0.7 - 1.1
BM Eutric Cambisols	18	4.7	6.9	5.2	7.1	0.5 - 0.2
SA Eutric Fluvisols	27	5.4	7.6	5.4	7.8	0.3 - 0.2
ER Eutric Regosols	9	4.6	5.3	4.9	5.7	0.3 - 0.4
ER Eutric Regosols	4	7.3	8.0	7.4	8.1	0.1 - 0.1
RS Eutric Regosols	14	5.2	6.6	6.4	7.9	1.2 - 1.3

* FAO/UNESCO classification

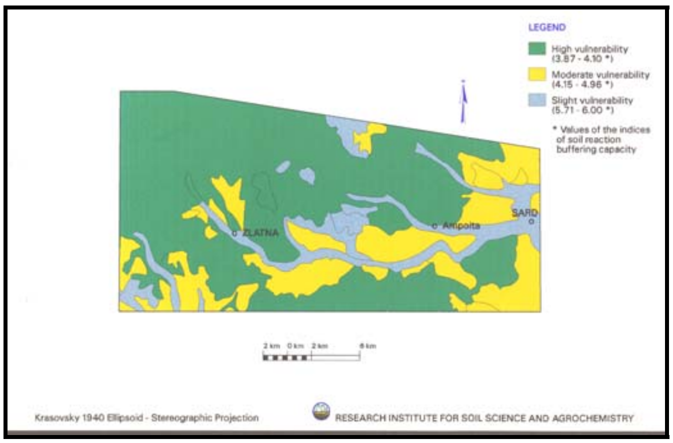

Figure 1. Map of soil vulnerability to pollution caused by acid rains and heavy metals within the Zlanta area. Scale is 1:200,000.

Table 2 Ranking of soils in the Zlatna area according to their vulnerability to the impact of acid rains accompanied by heavy metals

Vulnerability class	Soil type
1. very low	RS*
2. low	**RS***, **LS**, **ER**[1], SA, BM, BD
3. moderate	RS, ER[2], **SA**, **BM**, **BD**
4. high	**BO**, **BD**
5. very high	BD

*Bold letters mean prevalence of the respective vulnerability class for the considered soil type.
[1]Formed on acid rocks (rhyolite).
[2]Formed on basic rocks (basalte, diabase).

Degradation effects of soil pollution by acid rains and heavy metals

Natural acidity intensification

The acid rains, resulted by sulfur oxides transformation into acids, especially sulfuric acid, besides causing leaf burns, contribute to the acidity increase of naturally acid soils and to lowering the buffering capacity of base saturated topsoils. As a result, Dystric Cambisols and Haplic Luvisols presented the lowest pH_{H2O} values (3.6-3.9). The difference in pH values of these soils reaches up to 1-2 pH units, comparing polluted and non-polluted areas. The difference is very small, only 0.1-0.3 pH units for Eutric Cambisols, Eutric Fluvisols, and Eutric Regosols developed on basic rocks (Table 1).

The increase of natural acidity brings about the decrease of the percentage base saturation by removing Ca and Mg from the exchangeable complex and the increase of exchangeable H and Al content. So the percentage base saturation of the Dystric Cambisols and Haplic Luvisols decreases down to 20-25% and the exchangeable Al content increases up to 700-800 $mg \cdot kg^{-1}$.

Loading and pollution of soils with heavy metals

The emissions of heavy metals from the floating, smelting, and sterile stockpiles determined the topsoil loading with some chemical elements which considerably exceeded the maximum allowable limit (MAL), which are 100 $mg \cdot kg^{-1}$ for Pb and Cu, 300 $mg \cdot kg^{-1}$ for Zn, 3 $mg \cdot kg^{-1}$ for Cd (Kloke, 1980). These limits were exceeded 41 times by Pb, 11 times by Cu, 7 times by Zn, and 4 times by Cd. The calculation of the geometric mean values of the analyzed soil samples collected from the whole investigated area led to the conclusion that the major pollution is caused by Pb, Cd, and Zn. Fig. 2 and 3 present the mean depth distribution of selected metals in the studied soils, expressed by the geometric mean of measured values.

In order to assess the global loading or pollution level of soil with heavy metals, the loading/pollution index values were calculated for the topsoil samples collected from the entire area. The results were matched on the map and interpreted according to the already mentioned method (Figure 4). Four loading levels (from *low* to *very high*) and three pollution levels (from *slight* to *severe*) were outlined. It should be noticed that pollution occurred around the emission sources and along the Ampoiu Valley, where the winds are dominant. The presence of a stack for gas removal 400 m high from the land surface, and located on one of the highest hills within the area, permitted gas dispersion over a large area.

Polluted soils represent 33% of the whole investigated area and loaded soils represent 67%. The levels of heavy metals loading and pollution are referring to the five elements (Cd, Cu, Cr, Pb, Zn).

Other effects of soil pollution

As a result of soil pollution with heavy metals, a microbiological activity disturbance occurs, which is expressed by a significant depletion of bacteria and actinomycetes. Actually, dehydrogenase activity is decreased to a zero level (Mihailescu and Ciobanu, 1990).

Also, pollution with heavy metals caused a drastic depletion of the number of oribatidae and collembolles, while dipterous larvae population increased, revealing a very reduced bio-conversion activity of the organic substances.

The acidification and the micro-biological activity disturbance directly affect the quality of organic matter by the increase of fulvic acids weight up to 3.6 times to the prejudice of humic acids. A first effect of this process is heavy metals mobility intensification up to 3-4 times, as compared to the non-polluted soils.

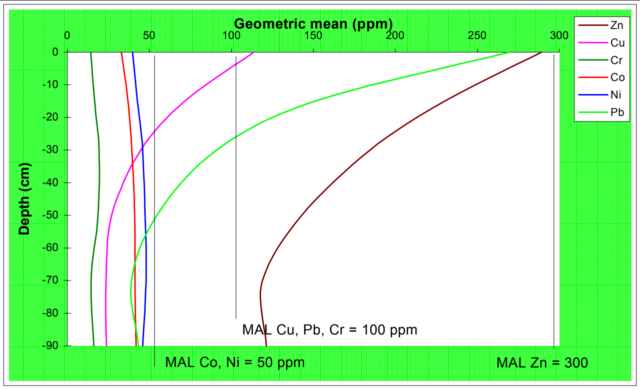

Figure 2 Geometric mean distribution of heavy metals (Zn, Cu, Cr, Co, Ni, Pb) contents (mobile forms) in soils within the area influenced by the emissions from the S.C. Ampellum S.A. in the Zlatna town

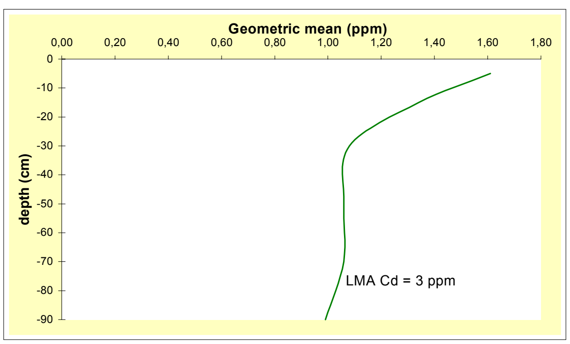

Figure 3 Distribution of geometric mean values of Cd contents in soils within the area influenced by the emissions from the S.C. Ampellum Zlatna S.A. in the Zlatna town

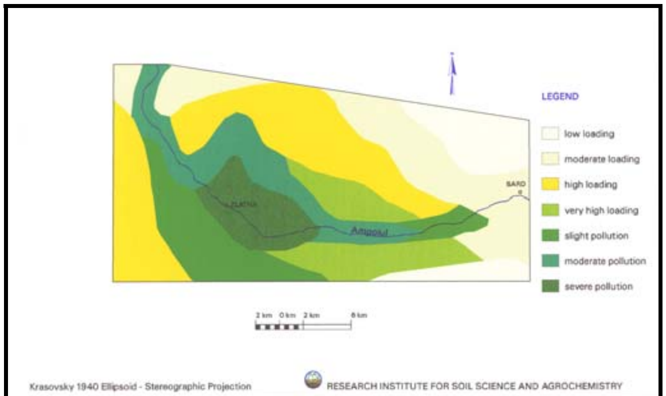

Figure 4. Map of topsoil loading and pollution with heavy metals (Cd, Cu, Cr, Pb, Zn) within the Zlatna area. Scale is 1:200,000.

The second effect is the decrease of the humification intensity, because the organic matter has a low nitrogen content and a high carbon content.

The loss of basic elements, especially calcium, from the colloidal complex, under the conditions of low organic matter contents causes soil structure deterioration.

All these processes taking place in the severely polluted soils on slopes, under conditions of reduced forest and grass vegetation, suit the sheet and gully erosion, as well as landslides, on large areas. This phenomenon is very accentuate east of Zlatna, on the left slope of the Ampoiu Valley, where about 40 hectares are in a precarious balance.

Soil degradation decreases the productivity of forest lands, grasslands, arable land and causes a severe alteration of the animal health. Cases of chronic pulmonary emphysema, saturnism, and chronic intoxication related to the presence of heavy metals were recorded.

CONCLUSIONS

1. The emissions from the floating of the polymetallic sulphide ores and from their smelting to extract non-ferrous metals and to obtain some chemical products, as well as the pollution from the waste stockpiles were the result of these inadequate technological processes. Therefore, the pollution of acid rains and heavy metals very negatively influenced an area of 55,664 hectares.
2. Soils in the area affected by these emissions have a high degree of natural vulnerability (68% of the total area) to the impact of the acid rains and pollution with heavy metals.
3. Natural reaction of soils in the area decreased with 1-2 pH units, reaching pH_{H2O} 3.6-3.9.
4. In the areas of maximum heavy metal impact, soil loading reached levels up to 41 (Pb), 11(Cu), 7 (Zn), 4 (Cd) times higher than the maximum allowable limits.
5. Soil pollution due to acid rains and heavy metals caused the micro-biological activity disturbance, organic matter degradation, soil structure deterioration, sheet and gully erosion, as well as landslides on about 10% of the whole area mainly affected by the emissions from the Zlatna factory.

REFERENCES

Borlan, Z., D. Stefanescu and D. Nebunelea. 1995. Indicatori ai capacitatii solurilor de tamponare pentru reactie, Stiinta Solului, XXIX, 1, 59-80.

Kloke, A. 1980. Richwerte ‘80, Orientierungsdaten für tolerierbare Gesamtgehalte einiger Elemente in Kulturböden, Mitt. VDLUFA, Nr.2, 9-11.

Lacatusu, R. 1998. Appraising levels of soil contamination and pollution with heavy metals, in: Developments for planning the sustainable use of land resources, Published by the European Soil Bureau, Joint Research Centre, 393-402.

Mihailescu, A. and C. Ciobanu. 1990. Poluarea industriala a solurilor si vegetatiei forestiere din zona Zlatna, Revista Padurilor, nr.3-4.

Serban, R., Fl. Stefanescu and I. Moroianu. 1993. Impactul uzinei Ampellum Zlatna asupra calitatii aerului. Prezent si perspective, Mediul Inconjurator, vol. IV, 1, 41-49.
Vasiliu, N., O. Ivan and M. Dumitru. 1995. Edaphic arthropods as bio-indicators of agricultural soil pollution with heavy metals and fluorine, Soil Science, vol. XXIX, 2, 81-90.

Endnote

[1]While the "pollution" is any undesirable change in the physical, chemical, or biological characteristics of the water, air, and soil that can harmfully affect health, survival, or activities of humans or other living organisms, the "contamination" refers to elevated presence of hazardous and undesirable elements or substances in water, air, or soil, due to the activities of man, that are not necessarily harmful, and the "loading" signifies the quantitatively expressed presence of such elements or substances, measured by different methods. The *loading/pollution index* represents the ratio between the content of one heavy metal, analytically measured in soil, and its reference loading value, determined by computation according to the Dutch system formulae (A value in the ABC series). The index values lower than 1 characterize the soil loading range, and those higher than 1 characterize the pollution range.