VULNERABILITY TO ACIDIFICATION OF SOILS OF THE ZLATNA AREA

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Abstract. In the period when the non-ferrous metallurgical plant of Zlatna was functioning, both sulfur dioxide and powder of metal sulphides and metal oxides were emitted in the air. Dioxide and trioxide sulfur in contact with rain water convert to sulfuric acid that leads to the formation of acid precipitation, which in contact with soils leads to its acidification. Soil cover in the Zlatna area is mainly represented by Eutric Cambisols (47.3%) Dystric Cambisols (29.5%) Luvisols (4.2 %), regosols (1.7 %), strongly eroded soils (3.3 %). Soil resistance to acidification depends on the soil fundamental characteristics such as reaction, texture, content and nature of humus, cation exchange capacity, etc. Based on the calculation of soil buffering capacity indicator for reaction, the vulnerability map to soil acidification in the Zlatna area, Budeni-Izvorul Ampoiului-Mets-Sard-Alba Iulia sector was drawn. Within this area, four classes of soil vulnerability to acidification were designated. Soils with high vulnerability are extended on a small area (2320 ha - 4,8%) and are represented by the following soils: Rhodic-dystric Cambisols, Lepti-rodic-dystric cambisols, Rhodic Cambisols, Rhodic-leptic Regosols, Albic-stagnic Luvisols, Stagnic Luvisols. The soils with high vulnerability are spread over large areas occupying 22 000 ha (45.5%). In this class, Dyistric Cambisols, Lepti-dystric Cambisols, Eutric Cambisols are included. Soils with medium vulnerability are spread over 41.4% of the area (20,000 hectares) and are represented by: Eutric Cambisols, Lepti-eutric Cambisols, Haplic Luvisols, Luvisols (eroded phase), Eutric Leptosol. *Soils with low vulnerability a*re found only on 8.3% of the area (4,000 hectares) and are represented by: Eutric Fluvisols, Fluvi-eutric Cambisols; Haplic Phaeozems, Eutric Gleysols, Calcaric Regosols, Calcaric-rhodic Regosols. The most affected soils were found near the pollution source and the effect was stronger in the case of natural acidity of soils.

Introduction

The old technological facilities that process metal polysulphides by thermal oxidation (conversion of sulphides into oxides: PbS, ZnS, CdS, Cu_2S in PbO, ZnO, CdO, Cu_2O) emit into the air sulfur dioxide, powder of metal sulfides and metal oxides (Borlan, 1998).

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Airborne and deposited sulphur and nitrogen compounds are the most important man-made constituents in relation to the ecological impact of acid precipitation (Dovland şi Semb, 1980).

Pollutants are removed from the atmosphere both during dry periods (sedimentation, absorption and impaction) and with precipitation (Fowler, 1980).

Dioxide and trioxide sulfur in contact with rain water converts to sulfuric acid that leads to the formation of acid precipitation.

Hydrogen ions of acidic substances (SO2, NO2,) dissolved in rain water determine strongly depletion of bases of clay-humus complex, passing in soil solution exchangeable bases that can be leached on soil profile. (Borlan, 1998).

The magnitude of leaching loss is in the same order as the cations are present in the soil: Ca^{2+}>Mg^{2+}>K^{+}>Na^{+} (Haynes & Swift, 1986).

Behavior of different soils to acidification depends on their ability to oppose the change of soil reaction, known as soil buffering capacity, that is determined by some soil properties (texture, humus content, cation exchange capacity, pH, degree of saturation in bases and carbonate content (Florea 1997).

In general, the soil capacity to oppose the decrease of soil pH caused by acid rain is greater as the T and V_{Ah} values are higher (Borlan, 1998).

The most vulnerable are sandy soils, poor in humus content and acid reaction, and the least vulnerable are those rich in carbonates (Florea 1997).

In Zlatna area, because of the activity of Ampellum S.A, as shown by Rauta et al., 1998, and Smejkal, 1982, large quantities of SO2, SO3, heavy metal oxides and sulfates were issued.

In this paper, soil vulnerability to acidification in the Zlatna area is studied.

1. Material and methods

The studied area is located in the Ampoi basin, in the south-eastern part of the Apuseni Mountains.

To evaluate the soil reaction buffering capacity, the main soil chemical properties have been determined: soil reaction, hydrolitical acidity, sum of exchangeable bases, cation exchange change, saturation degree.

The soil vulnerability to acidification in Zlatna area was evaluated using four interrelated and mutually correlating indices proposed by Borlan et al., (1995). Their formulae and functional definitions are as follows:

$$\textbf{I-RBCS (}^{\textbf{IRSA}}\textbf{)=lg } \frac{SBE}{Ah} \textbf{=lg} \left(\frac{T}{Ah}-1\right)$$

$$\textbf{I-RBS}^{\textbf{SBE}}\textbf{=lg}\frac{[SBE]echiv.kg^{-1}.0,4}{(H^{+})moli.l^{-1}}$$

$$\textbf{I-RBCS}^{\textbf{H}}\textbf{=lg}\frac{[Ah]moli.kg^{-1}.0,4}{(H^{+})moli.l^{-1}}$$

$$\textbf{I-RBCS}^{\textbf{CEC}}\textbf{=}\frac{[CEC].kg^{-1}.0,4equivalents}{(H^{+})moli.l^{-1}}$$

where: SEB, Ah and CEC are the sums of the exchangeable bases, hydrolytic acidity and cation exchange capacity of the soils, while (H^{+}) represents the proton activity in the soil solution

These indices were calculated for soils of the Zlatna area and they were interpreted according to table 1.

Tab. 1 - Border values for conventional interpretation of SRBC-I and significance of so separated domains for the soil resistance to acidification by exchangeable bases withdrawal

$SRBC^{IRSA}$	$ICTR^{SEB}$	$ICTR^{H}$	$ICTR^{CEC}$	Soil resistance to acidification	Soil vulnerability to acidification
>1,0	> 5,6	> 4,6	> 5,6	very high	very low
0,75-1,0	5,1-5,6	4,3-4,6	5,2-5,6	high	low
0,5-0,75	45-5,1	4,0-4,3	4,5-5,2	medium	medium
0,25-0,50	3,9-4,6	3,7-4,0	4,1-4,5	diminished	diminished
0,0-0,25	3,1-3,9	3,2-3,7	3,5-4,1	low	high
<0,0	< 3,9	< 3,2	< 3,5	very low	very high

2. Results and discussion

Normal rains have pH around 5.5, acid rain pH generally ranges between 4 and 4.5 (Brady & Weil, 2008). The mean pH of rainfall in the very heavily polluted area around Zlatna was of 4.81, while the minimum pH reached was 2.67 (Smejkal, 1982). In this area, acid rain affected the soil through progressive acidification, which determined the decrease of the soil's reaction, depletion of bases and the decrease of base saturation degree (Rizea et al., 2002). Lacatusu et al., 1998 shown a decrease of soil reaction in the Zlatna area by 1-2 pH units.

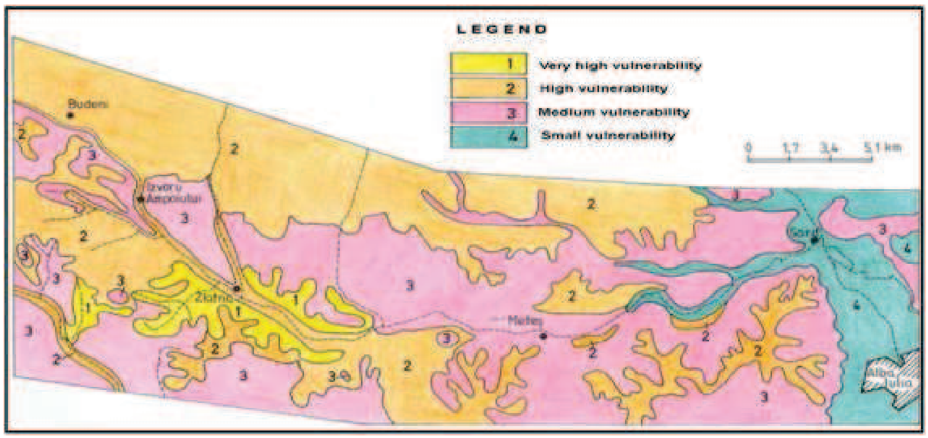

Fig. 1 - Map of soil vulnerability to acidification in Zlatna area

The main soil classes in the studied area are: Protisols, Cernisols, Cambisols, Luvisols, Hidrisols and Anthrisols. Most of the soils belong to Dystric Cambisols (29.5%) and Eutric Cambisols (47.3%).

Following the calculation of the indices proposed by Borlan at el. in the Zlatna area, four classes of soil vulnerability to acidification were delimited, which are shown in figure no 1.

Soils with very high vulnerability are spread over a small area (2320 ha-4, 8%) and are represented by the following soil types:

- Chromic-dystric Cambisols associated with Lepti-rodic-dystric Cambisols;
- Rodic Cambisols (eroded phase) associated with Lepti-dystric Cambisols;
- Alic-stagnic-albic Luvisols associated with Stagnic Luvisols.

Soils with high vulnerability are spread over large areas occurring 22 000 ha (45.5%). To this class belong:

- Dystric Cambisols associated with Lepti-dystric Cambisols and Dystri-lithic Leptosol;
- Eutric Cambisols associated with Lepti-eutric Cambisols, Dystric Cambisols and Lepti Dystricambisols.

Soils with medium vulnerability are extended on 41.4% of the territory (20,000 ha) and are represented by:

- Eutric Cambisols, including eroded phase, associated with Haplic Luvisols, including eroded phase, Luvisols (eroded phase) and Leptic Regosols (eroded phase);
- Eutric Cambisols associated with Lepti-eutric Cambisols and Dystric Cambisols associated with Lepti-dystric Cambisols and Eutric Leptosol;

- Haplic Luvisols, including eroded phase, associated with Luvisols (eroded phase).

Soils with low vulnerability are spread over 8.3% of the studied area (4,000 hectares) and are represented by:

- Eutric Fluvisols associated with Gleyic-eutric Fluvisols and Fluvi-eutric Cambisols

Eutric Gleysol associated with Eutric-mollic Gleysols Calcaric Regosols and Haplic Regosols associated with Rhodic calcaric Regosols

In the studied area, the effects of acidification on soil characteristics were expressed according to soil physical-chemical characteristic of soil and distance from pollution source.

The soils that belong to Phaeozems, Gleysols, Calcaric Regosols, Lepti-Endoleptic Regosols and some Fluvisols showed high resistance to the acidification due to the soil's moderately-slow alkaline reaction (pH_{H2O} 7.4-8.7) and the percentage of base saturation in the saturated field ($V_{8,3,}$% = 95-100).

The soils belong to Eutric Cambisols, including eroded phase, Haplic Luvisols and some Fluvisols of the Ampoi meadow shown moderate resistance to acidification; in this case, acid rains caused moderately strong acid reaction (pH H2O=4.4-5.6) and percentage of base saturation in the oligomesobasic field ($V_{8,3,}$% = 38-55) only in the upper horizons of the soil profile, which did not lead to changes in the taxonomic classification of these soils. In the lower soil horizons, these soils have moderately low reaction (pH 5.6-6.8) and eubasic percentage base saturation ($V_{8.3}$, % = 66-88).

Dystric Cambisols found at great distance from the pollution source showed no changes in their physical-chemical characteristics.

A special matter is represented by the Rhodic-Dystric Cambisols and Alic-stagnic-albic Luvisols located near the emission source that have very strong-strong acid reaction (pH = 3.3 to 4.9) and degree of base saturation ($V_{pH8.3}$,%) with values in the range of 4-28%. These values are specific to Podozols, but are not followed by morphological changes such as the presence of a Bhs horizon, which did not allow modification of the taxonomic classification.

According to Florea (1997), the most affected soils were found near the pollution source and the effect was stronger in the case of the natural acidity of soils.

Conclusion

The study of soil vulnerability to acidification in the Zlatna area showed the following:

- the vulnerability of the soil ranged from very high to low;

- the largest areas are represented by soils with high vulnerability (45.5%) followed by soils with medium vulnerability (41.4%);
- some soils were affected only in the first part of soil profile such as the Eutric Cambisols and some Fluvisols;
- the most sensitive soils are those natively acidic located near the source of pollution such as the Dystric Cambisols and the Luvisols.

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