

Control System of Soil Quality Status

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Abstract. This paper presents the monitoring system for the status of soil quality in Romania. This system is organized on three levels. The first level includes a fixed grid of 16x16 km and covers the whole country. In the monitoring system of the status of soil quality is important to determine the soil loading with elements and potentially polluting substances. The content of elements and potentially polluting substances in the soils is determined both by main characteristics of soils and of human actions. Some types of industrial pollution are the most aggressive pollution with heavy metals and oxides of sulphur which is found in Copșa Mică, Zlatna and Baia Mare. Are presented the concentrations of soluble heavy metals and sulphur in the three areas mentioned above and ecological reconstruction measures are proposed.

Keywords: monitoring, heavy metals, sulphur, soils, pollution.

1 Introduction

Urbanization, industrialization, agriculture, development of the circulation network and increase in energy, prime materials and materials required for new technologies consumption, have in addition positive and negative effects on soil quality status. They can lead to major changes in soil quality that may be irreversible.

It is therefore absolutely necessary to know in advance these changes to be evaluated their gravity.

So, came the need to establish a national monitoring system of soils in order to determine their current status and trend. (Răuță C., Cârstea St., 1983).

Monitoring system of the status of agricultural soils quality in Romania, as part of the National System of Environmental Quality, was founded in 1977. In 1992 they founded a new National System for Monitoring of Soil Quality in Romania, a system established in line with other European systems.

The system is characterized by the following elements:

- spatial distribution;
- network density;
- the set of indicators;
- frequency of measurements.

These items are detailed on three levels, namely:

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a). Level I consist of performing a minimum of investigation in all aspects of fixed networks for the determination of areas with soils in different stages and various processes of degradation. It seeks, regular, evolution of these soils through specific indicators.

b). Level II consists of details of investigations into certain points of the Level I network to identify the causes of soil degradation processes.

c). Level III includes detailed investigations to verify the hypothesis, analysis of soil degradation processes, making forecasts for recommendations to their remediation.

The frequency of measurements is 4 years for grid points without special problems of level I and 1 year for those with special problems.

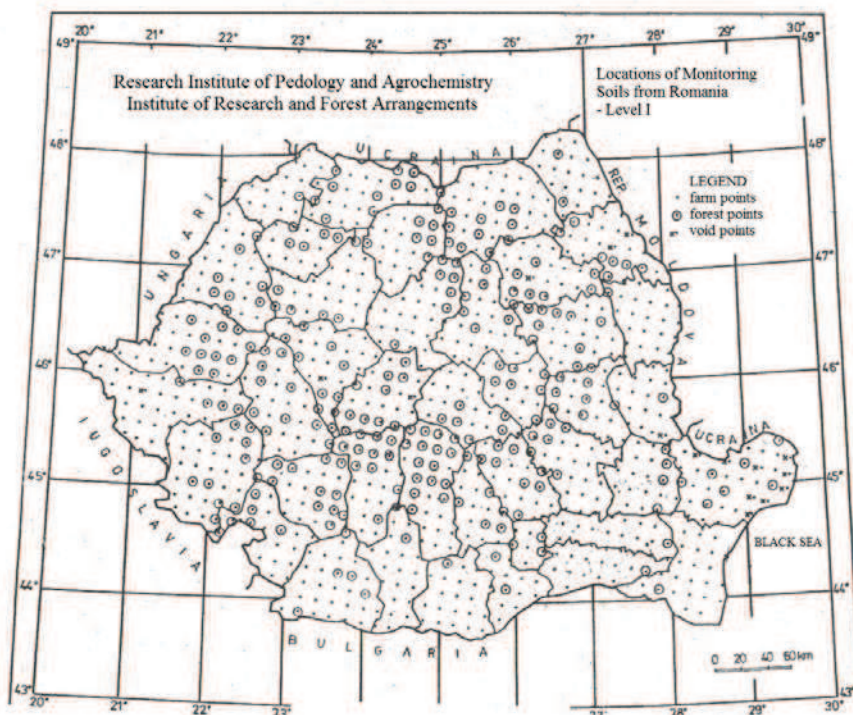


Fig. 1. The monitoring system of soils from Romania, Level I.

In Romania, the first level includes a fixed network 16x16 km covering the entire country. The network has 944 points of which 675 are in areas with agricultural soils and forest soils 269 territories. Points are located at each network node, the contents of a square of 400 m (Fig. 1). Soil profile description is based on a medium sample in modified structure consisting of 20-25 individual samples from the first 10 cm, three

individual samples for each horizon and four samples from each horizon in the natural structure according to the methodology presented in the "Monitoring the status of soils quality from Romania". (Răuță C. and collaborators, 1998, Dumitru M., 2000). The soil samples are centrally stored, soil tests are carried out, processed and interpreted data. Field and laboratory work for level I are almost 100% done.

The paper presents the soil load from monitoring sites of level I with potentially polluting elements and substances.

PPES contents in soils is determined by the main characteristics of soils (texture, pH, organic matter content), and human actions (fertilizer, phytosanitary treatments, pollution, etc.).

An important role in the concentration of pollutants in the soil it is relief, accumulative forms retaining a larger volume of polluting substances. Most sites in Romania are situated on horizontal land - very low pitched (50%) and the remaining land with different inclinations.

Approximately 50% of agricultural sites may suffer pollution by chemicalization works.

In terms of soil classes and soil types (Florea N., Munteanu I., 2003) on the Level I monitoring sites are:

- Chernozem, Kastanoziom, Phaeozem	23.14 %
- Cambisol Eutric, Cambisol Dystric	23.57 %
- Luvisol, Luvisol, Planosol	28.58 %
- Entic Podzols, Haplic Podzols	4.35 %
- Gleysols, Stagnic Luvisols	3.93 %
- undeveloped soils	14.82 %

Special issues related to retention and movement of pollutants in the soil raises Luvisol, Spodosols and Cambisols.

Related to soil texture, note the high percentage of Level I monitoring sites, clay soils (41.5%), clay loam (23.1%) and sandy loam (20.5%). Soils with slight texture not hold large PPES content, but favor strong mobilizing them. Fine textured soils retain high PPES content that can reach in the plants.

Soil reaction is of particular importance in terms of mobility PPES. Soils with weak alkaline reaction has very low-average vulnerability and the moderate and strong alkali are not vulnerable.

Vulnerability of soils to pollution with heavy metals is determined by soil characteristics listed above.

The most aggressive industrial pollution is heavy metal and sulfur oxides in Alba, Maramures, Sibiu counties with compounds of fluorine in Prahova Olt, Bacau, Tulcea counties.

Among the types of agricultural pollution, HCH and DDT residues pollution is important, wastewater, sludge livestock pollution.

2 Paper Preparation

2.1 Material and Methods

Soil indicators followed into the monitoring works are:

- joint analysis: texture (particle size composition), pH, humus, total nitrogen, mobile phosphorus, mobile potassium, moisture, apparent density, penetration resistance, hydraulic conductivity, total porosity, contraction index;
- specific analysis: the sum of exchangeable bases, hydrolytic acidity, exchangeable aluminum, total cation exchange capacity, base saturation degree, the total content of soluble salts, exchangeable sodium, total carbonates content;
- special analysis: heavy metal content, soluble sulphur content, soluble fluorine content, organochlorine pesticide content, the number of bacteria, mushrooms and dehydrogenate activity.

Methodologies used to determine the joint analysis are:

- Texture is determined by the sedimentation method and it is extracting a sample of suspension of a certain amount from depth h at time t, using the pipette Kubiena;
- Apparent density is determined on soil samples in the structure unchanged, using a metal cylinder from stainless material;
- Humidity is determined in the laboratory by oven drying method;
- Resistance to penetration was determined in the laboratory on soil samples collected in the cylinder, with humidity of 50% of the capacity of water, using a static penetrometer;
- Hydraulic conductivity in saturated medium is determined "in situ" through the "Auger Hole" method;
- Total porosity and the rate of contraction are determined by calculation;
- pH is determined potentiometrically in aqueous suspension 1:2.5;
- Humus is determined the modified method of Walkley-Black;
- Total nitrogen is determined by the method of Kjeldhal;
- Mobile phosphorus and potassium are determined by extraction solution of ammonium acetate-lactate (by Egner-Riehm-Domingo);

Regarding the specific analysis, the methodology applied is as follows:

- Sum of exchangeable bases is determined by the method of Kappen (0.1n HCl);
 - Hydrolytic acidity is determined by percolation with Na acetate or K 1n;
 - Exchangeable aluminum is determined by the method of Socolov;
 - Total capacity of cation exchange is determined by the method of Cernescu;
 - Degree of base saturation is determined by calculation;
 - The total content of soluble salts is determined by Conductivity;
 - The total content of carbonates is determined by gas volumetric method with Scheibler calcimeter;
 - Exchangeable sodium was determined by the method of Bower;
- Special analysis refers to:

- Heavy metals are determined spectrophotometrically by atomic absorption;
 - Soluble sulfur content is determined by gravimetric dosing;
 - Soluble fluoride content is determined by extraction in CuCl₂, microdiffusion Brewer;
 - Organochlorine pesticide content is determined chromatographic gaseous phase;
- Interpretations and size classes for most of the indicators listed above are those of the Development methodology of soil studies, vol. III (Florea N. and collaborators, 2003) and for special indicators are presented in Table 1.

Table1. Range concentration provisional of some potentially polluting elements and substances

POLLUTANT	DEGREE LOADING, PPM					NORMAL CONTENT	MAXIMUM AVAILABLE LIMITS
	LOW	MODERATE	HIGH	VERY HIGH	EXCESSIVE		
CU	21-40	41-100	101-200	201-400	>400	<21	100
PB	21-40	41-100	101-300	301-1000	>1000	<21	100
ZN	101-150	151-300	301-700	701-1500	>1500	<101	300
CD	1.1-2.0	2.1-3.0	3.1-7.0	7.1-20.0	>20	<1,1	3
Co	21-30	31-50	51-100	101-200	>200	<21	50
Ni	21-30	31-50	51-100	101-200	>300	<21	50
MN	901-1100	1101-1500	1501-2100	2100-2700	>2700	<901	1500
CR	31-50	51-100	101-200	201-400	>400	<31	100
SOLUBLE SULPHUR	151-300	301-500	501-700	701-1500	>1500	<151	-
SOLUBLE FLUORINE	1.1-5.0	5.1-10.0	10,1-25.0	25.1-75.0	>75	<1,1	10
DDT TOTAL	0.011-0.050	0.051-0.100	0.101-0.500	0.501-5.000	>5	<0,011	0.1
HCH TOTAL	0.011-0.050	0.051-0.100	0.101-0.500	0.501-5.000	>5	<0,011	0.1

Normal content: heavy metals – Adriano 1986; soluble sulphur – Răuță and collaborators 1998; soluble fluorine – Larsen and Widdowson 1971, Omuetti and Jones – 1980, total DDT and HCH – Răuță and collaborators, 1998.

Maximum available limits: heavy metals – Kloke, 1980; soluble sulphur – Răuță and collaborators, 1998; soluble fluorine – Larsen and Widdowson, 1971; Omuetti and Jones – 1980, total DDT and HCH – Răuță and collaborators, 1998.

2.2 Results and Discussions

One of the most important types of soil pollution in Copsa Mica, Baia Mare and Zlatna area is pollution with heavy metals and sulphur compounds.

The soil pollution in Copşa Mică area was determined by non-ferrous metallurgy industry. Pollution is given by heavy metals (Cu, Pb, Zn, Cd) and sulphur compounds. The area is characterized by a great geomorphologic complexity and a wide variety of soils (chernozem, phaeozem, nitisol etc.). In agricultural soils the accumulation of pollutants is achieved in the first cm of the soil, wherefrom through agricultural work the pollutants get into the whole horizon A (Table 2).

Table 2. The concentration of heavy metals and sulphur (Ciobanu, Mihăilescu, 2001)

Pollutant	Soil (0-5 cm)	Normal content	Maximum available limits
Cu	46	20	100
Pb	394	15	100
Zn	287	50	300
Cd	6,7	1	3
Soluble sulphur	215	100	

From table 2 results that lead exceeds four times the maximum available limits, two times the cadmium and zinc is close to this limit. Copper and sulphur content exceeding 2 times normal.

Soil pollution in Zlatna area was determined by non-ferrous minerals processing companies that eliminate annual significant quantities of SO₂, oxides and sulphates of lead, zinc, copper, arsenic, antimony and bismuth in air. These sediment particles were deposited on the ground. (Mihăilescu A., Ciobanu C., 2000). Pollution is given by heavy metals (Pb, Cu, Zn, Cd) and sulphur compounds (Table 3).

Table 3. The concentration of heavy metals and sulphur (Ciobanu, Mihăilescu, 2001)

Pollutant	Soil (0-5 cm)	Normal content	Maximum available limits
Cu	217	20	100
Pb	38	15	100
Zn	192	50	300
Cd	1.61	1	3
Soluble sulphur	608	100	

Polluted area is an area of hills and mountains, with varied soils (nitisol, luvisol, eutricambisol etc.) and with periods of calm atmosphere which promotes the stagnation of air masses and deposition of pollutants.

From table 3 results exceeding the maximum available copper limits by 2 times, and the normal lead content of 2.5 times, zinc 4 times and sulphur 6 times. Cadmium content is little high than normal.

In the area Baia Mare, mining companies of non-ferrous ores and their processing have been polluting factor. Soils pollution is given by heavy metals (Pb, Cu, Zn, Cd) and sulphur. The decisive role in the spread of pollutants is the relief. It is mountainous in the north constitute a barrier to pollution and is an alluvial plain in the south-west where the air currents allow the transport of heavy metal particulates. Lower meadows accumulate large quantities of heavy metals than higher landforms. (Lăcătușu R. and collaborators, 1997).

Also, the hydrological regime has an important role in heavy metal pollution. Surface water and groundwater contribute to the spread of pollutants and stagnant waters from micro depressions allow fixing of heavy metals on the surface of clay soils (Table 4).

Table 4. The concentration of heavy metals and sulphur (Ciobanu, Mihăilescu, 2001)

Pollutant	Soil (0-5 cm)	Normal content	Maximum available limits
Cu	113	20	100
Pb	749	15	100
Zn	224	50	300
Cd	4.44	1	3
Soluble sulphur	1450	100	

From table 4 results an excess of 7.5 times of maximum available limits of lead and a small excess of copper. Normal content is exceeded by 5.5 times of zinc and 4.4 times by cadmium. Normal content is exceeded the soluble sulphur by 14.5 times.

Important sources of soils pollution with sulphur compounds are emissions from power plants that do not apply desulphurization processes, from sulphuric acid power plants, from non-ferrous metallurgy, etc.

Oxides of sulphur coming from air pollution generates, after several chemical and biological transformations, SO_4^{2-} and H^+ - ions which contribute to soil acidification. This leads to fewer bacteria and microbiological activity disorder.

The objectives of the national monitoring system of soils quality in Romania are:

- a). systematic monitoring of quality characteristics of the soil;
- b). processing the information obtained to assess the quality status;
- c). elaboration of forecasts on the evolution of soil quality;
- d). warning agencies and makers on the situations in which appear the dangerous intensification phenomena of pollution, in order to prevent or limit harmful effects on soils;
- e). providing data needed to establish the main causes of soil pollution phenomena in order to build and improve prevention and improvement measures, including rehabilitation and / or recycling of waste substances usable and to avoid or mitigate damage to the economy;
- f). tracking dynamics of effectiveness of preventive measures against pollution of soils;
- g). providing information and data to establish technical and economic measures necessary to ensure the current and future stage, for consistency between the country's socio-economic development, protection of soil and environmental quality;

h). providing documentation necessary to support the national program of environmental protection;

i). using data on soils to achieve the national system of integrated environmental monitoring;

j). providing data of soils quality from Romania necessary to participation of the Romanian part to achieve International Reference System or other international programs.

For the reconstruction of agricultural soils contaminated with heavy metals and sulphur dioxide are necessary the works listed below:

a). general measures:

- reducing the emission of pollutants by upgrading polluting industries;

- attachment measures of waste dumps to prevent their scattering (Baia Mare);

- setting up perimeters of improvement of affected areas based on their mapping up-to-date;

- total or partial restructuring of uses in the areas affected.

b). specific measures:

- correcting acid reaction soil by applying calcareous amendments to bring the pH from a strong acid domain (pH < 5,8), into a moderately acid or weak acid domain (pH = 5,9-6,8). This reduces soil acidity so mobility of heavy metals and exchangeable aluminum concentrations. Doses of calcareous amendment are calculated using the formula:

$$D_{CaCO_3} = SBi = \left[\frac{Vd}{Vi} - 1 \right] \frac{100}{Cn} \quad \text{t/ha} \quad (1)$$

in which: Vd - desired degree of saturation;

Vi - initial degree of saturation;

SBi - sum of exchangeable bases;

Cn - neutralizing capacity of the amendment.

- fertilizing of soil with manure, which brings a surplus of nutrients in the soil (N, P, K);

$$D_G = \frac{0.4}{N} \left(15 + \frac{30}{IN} \right) \left(1.35 - \frac{8}{A} \right) \quad \text{t/ha} \quad (2)$$

in which: A- clay content with diameter of <0,002 mm, %;

N - nitrogen content of organic fertilizer, %;

IN - index of nitrogen according to the humus content and degree of base saturation.

-fertilization with nitrogen will consider cultivated plants and expected harvest and use nitro chalk,

- fertilization with phosphorus will be applying the relationship:

$$D_{P_{2O_5}} = \frac{50 - P_{Al}}{0,04 \times 6} - (Pg + PFg) \quad \text{kg s.a./ha} \quad (3)$$

in which: 50- optimal content of mobile phosphorus from soil ppm;

P_{Al} - initial content of mobile phosphorus from soil ppm;

0,04- average growth rate of mobile phosphorus content depending on the amount of P₂O₅ applied as fertilizer;

- 6 – number of years that apply phosphorus fertilization;
 - Pg – P₂O₅ contribution by organic fertilization;
 - PFg – P₂O₅ intake by amendment with phosphogypsum.
- potassium fertilization. The dose is calculated with relation:

$$D_{K_2O} = \frac{160 - K_{Al}}{0,05 \times 8} - Kg + Ccarb \quad \text{kg s.a./ha} \quad (4)$$

- in which: 160- optimal mobile potassium content ppm;
 K_{Al} – initial soil content in potassium mobile;
 0,05 – average growth rate of mobile potassium content per kg of K₂O applied through fertilization ppm;
 8 – number of years that apply ameliorative fertilization with K;
 Kg – K₂O intake of organic fertilization;
 Ccarb. – correction for carbonates
- afforestation of polluted areas function to intensity of pollution, namely: excessive heavily polluted area (acacia, black pine and bushes), the moderately polluted area (acacia, black pine, bushes, red oak), low polluted area (sessile, beech, hornbeam, mountain and plain maple, linden, cherry and bushes);
 - establishing waste dumps with fallow furrows and seeding grasses, planting acacia and vine.

2.3 Conclusions

The results of research conducted in Copșa Mică, Zlatna and Baia Mare, lead to the following conclusions:

- soils investigated are vulnerable soils to pollution processes by sulphur compounds and heavy metals;
- the main pollutants that affect agricultural ecosystems are the acidic sulphur compounds, Pb, Cu, Zn and Cd;
- pollution effects on soils were highlighted through acidification and depletion of bases of the adsorption complex;
- due to pollution with heavy metals and sulphur compounds disturbance microbiological activity takes place;
- the effect of pollution is destroying the soil structure;
- increasing the mobility of aluminum and heavy metals, with toxic effects on vegetation;
- changes of nutritional conditions leading to premature drying of vegetation and loss soil protection functions.

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