Study on Heavy Metal Accumulation Level of Soils from Zlatna Region

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Abstract: The present paper shows some of the research results of a Francophone Universitary Agency financed project. One of the research objectives was to establish the heavy metal soil contamination degree and the results clearly highlight a high level of heavy metal accumulation for the area under research. Modern research methods were used, namely spectrometric and stripping methods.

Keywords: soil pollution, heavy metals, spectrometric methods, stripping methods

1. Introduction

The soil is a dynamic system where short-term fluctuations occur, such as variations in humidity and pH levels, in redox conditions; it is also the place where the organic matter gradually decomposes as a consequence of changes in nature. These changes alter the shape and availability of metal ions and therefore they must be taken into account when making a decision on soil pollution or waste storage. Through field and laboratory tests, soils can be characterized from a physical, chemical and biological perspective.

The total metal content of soils is the result of varied metal input – parental material, atmospheric deposits, chemical fertilizers and improvements, organic fertilizers and other organic and inorganic polluting substances – minus metal output resulted from cropping or from leaching and volatilisation. All these factors can be quantified in relation [1]:

$$M_{total} = (M_p + M_a + M_f + M_{ac} + M_{ow} + M_{ip}) - (M_{cr} + M_l)$$

where:

M- represents heavy metals, p-parental material, a-atmospheric deposits, f-fertilizers, ac-agricultural chemical products, ow-organic waste, ip- other inorganic polluting substances, Cr-cropping losses, l- leaching and volatilisation losses.

Apart from the total heavy metal content of soils, the available concentrations depend on the chemical elements in the soil that control metal species; they also depend on elements of vegetation. While these polluting substances are harmless at low concentrations, the soil can turn into a polluting element for water or vegetation if a certain value is exceeded. [2]

2. Experimental

The soil samples were gathered from different depths depending on the vegetation of the respective soil: 0-20 cm for arable land and grass, 20-40 cm for orchards and vineyards.

For each material studied, we used the specific methods mentioned in our literature and complied with the experimental parameters and requirements of our study procedures [3]

We gave special attention to calibration. In order to determine metallic cations found in soil and vegetation samples by using atomic absorption spectrophotometric methods, we used the standards provided by AnalytikJena (which came with the equipment). Through proper dilution, we arrived at the optimum concentration (100 ppb) for GFAAS and 100 ppm for FAAS.

TABLE 1. Methods used for the analysis of soil heavy metal contamination

Method of analysis	Equipment used	Measured elements	Sample preparing methods
Atomic absorption spectrophotometry *applied to soil samples*	AAS *vario*2 FL, AAS *vario*5 GF, Germany	Cu^{2+}, Pb^{2+}, Cd^{2+}	Wet mineralization
Accumulation – dissolution methods, *applied to soil samples*	PTEA-Wagtech Computerized Electrochemical SystemBAS 100W;	Cu^{2+}, Pb^{2+}, Cd^{2+}	Wet mineralization
Titrimetry, *applied to soil samples*	Automatic burette SCHELLBACH, Germany	organic C (humus)	Wet oxidation
Colorimetry, *applied to soil samples*	SPEKOLL UV-VIS, Analytik Jena, Germany	Phosphorus (P)	Ammonium lactate acetate extraction
Flame photometry, *applied to soil samples*	FLAMFO 4, AnalytikJena, Germany	Potassium (K)	Ammonium lactate acetate extraction
Instrumental pH determination, *applied to soil samples*	INNOLAB, Germany	pH	In watery suspension

Methods and Equipment

Through the electrochemical method (stripping), determinations were conducted on mercury drop electrode using the computerized system BAS 100W. It is equipped with a classical cell, composed of three electrodes (EL- Hg drop; ER-Ag/AgCl; CE- Pt high surface spiral). All the samples were deaerated for 15 minutes before each determination. The measurements took place in the electrolyte mentioned in the specialty literature (HME): 117 g NaCl, 35.5 g ascorbic acid, 7.7 g NaOH, all dissolved in 500 mL ultrapure water. Water used for determination was obtained with the equipment for ultrapure water Mili Q, produced by USF Elga. The experimental parameters for HMDE analysis are as follows: Ei=-400mV; Ef=-100mV; sensitivity 100μA/V; scanning speed=20mV/s; accumulation time=400s; mercury drop size =10.

By using spectrometric methods, we intended both to obtain results close to the specialty literature and to compare the two methods. We used an AAS absorption spectrophotometer, model 6.

The analytical data on which we worked *for Cu* in the soil are: spectral line $\lambda = 324.7$nm; Φ (slit) = 0.5; strength of current = 10mA; flame type= air-acetylene; equipment sensitivity = 0.07 ppm. *For Pb*: spectral line $\lambda = 217$ nm; Φ (slit) = 1; strength of current = 5 mA; flame type= air-acetylene; equipment sensitivity = 0.12 ppm; *For Cd*: spectral line $\lambda = 228.8$ nm; Φ (slit) = 1; strength of current = 10mA; flame type = air-propane; equipment sensitivity = 0.03 ppm;

The obtained results [3] were compared to the allowed maximum limits, which, in the case of soils, must not exceed 100 ppm for copper, 100 ppm for lead and 3 ppm for cadmium.

Soil preparation in view of mineralization

The soil samples gathered were dried in a room with shelves for drying and with a ventilation system for steam exhaustion. After it dried, we removed from the soil the non-decomposed vegetal remains, foreign materials and gravel, and smashing the larger earth clods as much as possible.

The prepared samples were ground with a special laboratory mill.

Vegetation samples were ground and dried on clean surfaces in order to prevent a possible heavy metal contamination of the laboratory, or in order not to change the physical-chemical characteristics of the soil samples. They were subsequently passed through a sieve with a 2mm hole dimension and stored in sealed and labelled plastic boxes. On the label of each box, we mentioned the following:

- Sample name;
- Sample number;
- Date of gathering;
- Area where they were gathered;
- Depth of gathering;

Until they were analysed, the samples were kept in rooms where temperature and humidity were kept at not too high, constant levels.

Soil Mineralization

We prepared the extract from the soil sample by mineralization with hard acids (nitric acid, perchloric acid, sulphuric acid).

In a Berzelius glass, we placed 1 g of fine soil ground in a pestle mortar to which we added 15 ml of oxidating mixture: $HNO_3:HClO_4:H_2SO_4$ of proportion 2:1:0.2.

The Berzelius glass was passed to a sand bath (under the niche) until the dry evaporation of the mixture.

After cooling, to the obtained residue we added 5 ml of concentrated HCl, which was evaporated dry through sand bath.

The obtained residue was dissolved with HCL 0.5 N, filtered and then put in a 50 ml rated balloon flask. The filter was washed and the balloon was brought to a sign with a solution of HCl 0.5 N. The obtained extract was aspirated in AAS flame using a particular lamp for the dosed element.

A blank sample (in order to verify the reagents' pureness) and a set of standards were prepared for each element under the same conditions.

3. Results and Discussions

The effect of pollution is even higher as the soils initially had a more pronounced acidity and a weaker natural fertility [4], and the distance to the polluting source is smaller (table 2).

TABLE 2. Heavy metal levels depending on the distance to the polluting source

Distance, km	Heavy metal	min., mg/kg	max., mg/kg	average. mg/kg	σ
0,4 (on the premises of SC Ampelum)	Pb	463	887	685	194.63
	Cd	1.5	2.8	2.1	0.57
	Cu	143	211	182	27.83
	Zn	73	120	97	18.42
1,5 (Patrinjeni)	Pb	184	421	263	96.76
	Cd	1.2	1.8	1.5	0.22
	Cu	84	114	97	11.13
	Zn	46	87	63	15.41
3,0 (Valea Mică)	Pb	92	170	123	31.01
	Cd	0.9	1.7	1.2	0.33
	Cu	54.3	110	76	22.46
	Zn	27.4	69	54	16.47
3,0 (Valea Mică)	Pb	42.4	146	89	43.75
	Cd	0.6	1.1	0.8	0.21
	Cu	23.9	89	54	24.02
	Zn	25.2	54.5	37	12.35

Humified organic matter degrades and fulvic acids prevail qualitatively in its composition. From physical and physical-chemical points of view, we identified degradation processes for the mineral component from this excessively polluted soils as well, which, accompanying the destruction of humified organic substances leads to colloid degradation and dispersion.

In time, the absorptive complex lost its quality of binder for the soil aggregates, the structure degraded, and the previously installed erosion processes extended and became specific for the area.

The state of nutrition for the studied soil is under the optimum limits (table 3), the humus, phosphorous and potassium content are under the normal limits.

TABLE 3. State of nutrition of the studied soils

Sample	Depth of collection, cm	Humus, %	P, mg/kg	K, mg/kg
Soil TA 1	0 - 20	-	7.2	25.3
Soil TA 1	20 - 40	1.15	6.5	22.6
Soil TA 1	40 - 60	1.05	7.1	22.1
Soil TA 2	0 - 20	1.35	7.6	24.3
Soil TA 2	20 - 40	1.18	7.4	21.2
Soil TA 2	40 - 60	1.07	6.9	20.2
Soil TA 3	0 - 20	1.25	7.6	27.5
Soil TA 3	20 - 40	1.08	6.8	23.8
Soil TA 3	40 - 60	1.05	6.5	20.2
Soil TA 4	0-20	1.25	7.8	22.1
Optimum level	0 - 60	1.8 - 2.0	10 - 20	30 - 50

In general, heavy metal cations are the most mobile in acid conditions and their mobility and availability decreases when pH increases; anions of molybdenum (Mo) are an exception as they become more mobile when pH increases.

The pH values of soils are generally situated between 4.0 and 8.5, due to their buffering quality. In humid regions, the soil generally has acid values 5 –7, respectively 7 – 9 in arid regions; the extreme pH limits determined in the soil go from 2 to 10.5; the optimum pH for most arable lands is 6.5 for mineral soils and 5.5 for organic soils.

The allowed maximum limits in the case of soils are of 100 mk/kg for copper and lead and 3 mk/kg for cadmium. Comparing the obtained results, we find very high exceeding values, especially in the case of lead and copper. Cadmium reaches high values especially in the case of soils TA2 and TA3.
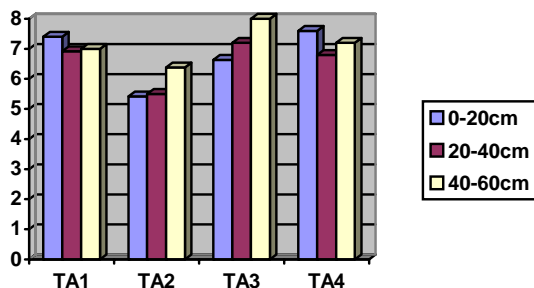

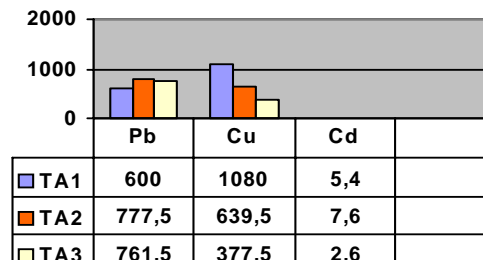**Figure 1.** pH variation depending on the depth of gathering

	Pb	Cu	Cd	
☐ TA1	600	1080	5,4	
☐ TA2	777,5	639,5	7,6	
☐ TA3	761,5	377,5	2,6	

Figure 2. Heavy metal contamination of the soil from the Zlatna region (mg/kg*)*

4. Conclusions

One of the most critical effects that acidifying industrial emissions cause is the destruction of the soil's organic matter, possibly leading to a significant blockage of humification processes, a phenomenon that has extremely serious repercussions on the general characteristics of soil ion exchange [5]. Mineral degradation of intensely and excessively polluted soils expresses the degradation and dispersion of colloids from the soils, especially in upper horizons, which in time, leads to the loss of the absorptive complex binding quality of soil aggregates. The structure degradation has lead to the installation and extension of erosion processes previously installed and specific to the area. The heavy metals retained by the organic and mineral part of the soil substantially limit the soil's biological activity, leading to the inhibition of nitrification processes, one of the essential conditions for soil fertility.

Acknowledgements:

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