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Soil pollution

ANALYTICAL INVESTIGATION CONCERNING THE METHODOLOGY FOR EXTRACTION OF EXCHANGEABLE FORMS OF HEAVY METALS FROM DIFFERENT TYPES OF SOILS

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Abstract. Mobile trace elements in soils can adversely affect the quality of food and fodder plants, the growth of plants, the activity of soil microorganisms and the quality of the groundwater. To establish the level of pollution inducted in the environment (transfer through solubilisation in groundwater, accessibility for plants), it is very important to know the content of heavy metals. The NF X 31-120/ 1992 standard can be used as a basis for assessment, as a sensitive instrument to detect soils with high amounts of potentially leachable elements. The experiments conducted led to obtaining conclusive and valuable data regarding the pollution of industrial activities on the environment.

Keywords: heavy metals, extraction method, mobile species, polluted soils, mining activities, industrial activities, agricultural soils.

AIMS AND BACKGROUND

The relative mobility of trace elements in soils is of major importance with regard to their availability and entry into the food chain and their potential for leaching down soil profiles to the groundwater. In view of the essentiality of certain trace elements including B, Co, Cu, Cr, Fe, Mn, Mo, Se and Zn for plants and/or animals, differences in mobility can result in deficient, adequate or even excessive supplies. Excess amounts of both essential trace elements and elements with not known essential function can have major toxic effects on living organisms and so their relative mobility is of major importance with regard to plant, animal and human toxicology. Due to polluted human activities (industrial, mining and agricultural activities, road transport) the level of heavy metals increases continuously. Heavy metals are part of the 'persistent substances with factor of risk', which tend to accumulated in the trophic chains, generating a significantly unwanted effect to alive organisms. The transfer of metals from soils to plants is important with regard to plant nutrition , and the contamination of crops with heavy metals.

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The international standard ISO/FDIS 14870/1999, adopted as a Romanian standard, proposed an extraction method of mobile species of heavy metals (Cu, Zn, Cd, Cr, Ni and Pb) accessible for plants from soils and sediments, using as buffer solution, a mixture of DTPA and TEA. The disadvantage of this standard consists in diminution the efficiency of extraction in the situations when the amounts of heavy metals in the soils are too high[1].

To solve this problem, it was necessary to find optimum extraction solutions for the studied types of soils: agricultural soils rich in humus, nitrogen and phosphorus, with normal level of heavy metals; soils from the neighbourhood of a waste dump mining and polluted soils from industrial activities, with high level of heavy metals.

During the experiments were used both standard[2-5] and non-standard methods[6], all of them being implemented with great success in national and international studies. The solutions used for extraction had in their composition substances like: ammonium acetate, ammonium nitrate, EDTA (ammonium or sodium salt) and magnesium chloride in buffer solution.

EXPERIMENTAL

Soil samples were drawn from unpolluted areas (clay soil), these being considered as control samples (2 samples from 0-10 and 30-40 cm depth), and polluted areas: 2 surface samples (C1, C2) drawn within a machine construction unit and 2 samples from 2 depths (0-10 and 30-40 cm) (Sa1, Sa2, Sb1, Sb2), drawn in the vicinity of a mining waste storage, with a distance of about 400 m between them and situated on different directions.

The samples, dried by air and screened by a screen for particles smaller than 0.2 mm, were mineralised using an acid mix ($HCl:HNO_3$, 1:3) in a microwave system type Milestone Ethos, in order to quantify the total concentration of heavy metals dissolved in aqua regia (Cu, Cd, Cr_{total}, Ni, Pb and Zn). These concentrations were measured by atomic absorption spectrometry in flame with a FAAS ATI UNICAM type 929. All soils analysed show a similar structure, argillaceous, the pH ranging between the following values: control samples pH $= 4.9 \div 5.1$; C1, C2 – pH $=7.3 \div 8.0$, Sa1, Sa2 – pH $= 4.65 \div 4.77$; Sb1, Sb2 – pH $= 4.4 \div 5.1$.

In order to quantify the concentrations of the mobile forms of heavy metals, four standardised and non-standardised analytical methods, utilised successfully in various research studies of various soil types (polluted and cleaned soils) were used.

Table 1 presents the types of solutions used for the extraction of mobile forms, the extraction conditions, the practicability of these methods and the bibliography references in which these methods are used (standards, publications).

Table 1. Analytical methods used for extracting exchangeable form of heavy metals

No	Method	Solutions utilised/conditions	Applicability	References
1	Standard ONORM L 1094-2/1994	1 M CH_3COONH_4, pH = 7±0.02, soil/solution = 1:10, shacked 2 h at 40 rot/min	Cd, Cu Cr, Fe, Mn, Ni, Pb, Zn	4, 7
2	Non-standard	1 M $MgCl_2$, pH = 7±0.2, soil/solution = 1:10, shaked 2 h at 40 rot./min	used for the extraction of sols/ sediments with high concentrations of heavy metals	6, 8, 9, 10
3	Standard DIN 19730/1997 ONORM L 1094-1/1994	1 M NH_4NO_3, pH = 7±0.02, soil/solution = 1:2.5, shaked 2 h at 40 rot./min	Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sn, Ti, V, Zn	3, 5, 11, 12
4	Standard NF X 31-120/1992	0.01 M EDTA + 1 M CH_3COONH_4, pH = 7± 0.02, soil/solution = 1:5, shaked 2 h at 40 rot./min	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	2, 13

The extraction solutions and the soil analysed were shaken by a shaker for 2 h at 40 rot./min, and then were left to settle for 15 min. They were filtered, and the first 5 ml of solution were dispensed. The filtered solution has been brought at a volumetric flask (25 and 50 ml, respectively), function of the liquid quantity used for extraction, and then the heavy metal (Cu, Cd, Pb, Zn, Cr_{tot}, Ni) contents were quantified by atomic absorption spectrometry in flame.

RESULTS AND DISCUSSION

The results obtained for the contents of metals totally dissolved in aqua regia have shown the alert (AL) and even interventions limits (IL) were exceeded for soils with less sensitive use (according to Order 756/97 concerning the reference values for trace of chemical elements in the soil in the Romanian legislation). These results are given in Tables 2, 3 and 4.

Table 2. Samples from within the machine construction unit

Heavy metal	Unit	C1	C2	Classification of the values according to the Romanian Order 756/97
Cu	mg/kg d.m.	654	879	C1, C2 > IL
Cr_{tot}	mg/kg d.m.	4201	3092	C1, C2 > IL
Ni	mg/kg d.m.	383	282	AL < C1, C2 < IL
Pb	mg/kg d.m.	54	162	NV < C1, C2 < AL, NV = normal value
Zn	mg/kg d.m.	607	645	NV < C1, C2 < AL

Table 3. Samples drawn from the south area of the mining waste storage

Heavy metal	Unit	Sa1 (0-10 cm)	Sa2 (30-40 cm)	Classification of the values according to the Romanian Order 756/97
Cu	mg/kg d.m.	371	334	AL < Sa1, Sa2 < IL
Cd	mg/kg d.m.	3.6	2.8	NV < Sa1, Sa2 < AL
Pb	mg/kg d.m.	3642	3506	Sa1, Sa2 > IL
Zn	mg/kg d.m.	806	720	AL < Sa1, Sa2 < IL

Table 4. Samples drawn from the south-west area of the mining waste storage

Heavy metal	Unit	Sb1 (0-10 cm)	Sb2 (30-40 cm)	Classification of the values according to the Romanian Order 756/97
Cu	mg/kg d.m.	490	569	AL < Sb1< IL, Sb2 > IL
Cd	mg/kg d.m.	1.5	17.4	Sb1≅NV
Pb	mg/kg d.m.	4538	5693	Sb1, Sb2 > IL
Zn	mg/kg d.m.	781	2136	AL < Sb1 < IL, Sb2 > IL

As it can be seen, the heavy metal contents place these soils in the category of strongly polluted soils, with the possibility of negative effects on the environment. This is why it is very important to know the mobility of these heavy metals in order to diminish and eliminate in time the toxic effect on the environment

As the SR ISO 14870/1999 method has a great disadvantage regarding the reduced capacity of complexation for high metal concentrations and the utilisation of successive extractions generates metal losses because of the repeated operations, as well as their redistribution between phases, was chosen the simple extraction method, in which the extraction agent is able to dissolve mobile concentrations. Four methods were used, which included various reagents, in order to reproduce the various conditions in the natural environment.

The standardised method NF X 31-120/1992 gave best results in the case of soils sampled in the area of the machine construction unit. Although the total Cr content was very high in both soils, exceeding by 5-7 times the maximum admitted intervention limit for soils with less sensitive use, this can not be easily released, as it is bound to other structures which are not reacting in the normal climatic conditions. The element Cu has proven to be the most mobile, being extracted in all four solutions, but the concentrations obtained are not significant, except for the method four, for which higher values were obtained (23 ppm and 128 ppm, respectively). For the soil C2, Pb is mobile to an extent of 20.6%, representing 33.4 mg/kg dried matter. The experimental data obtained for these soils using the method described in Ref. 2 are presented in Fig.1.

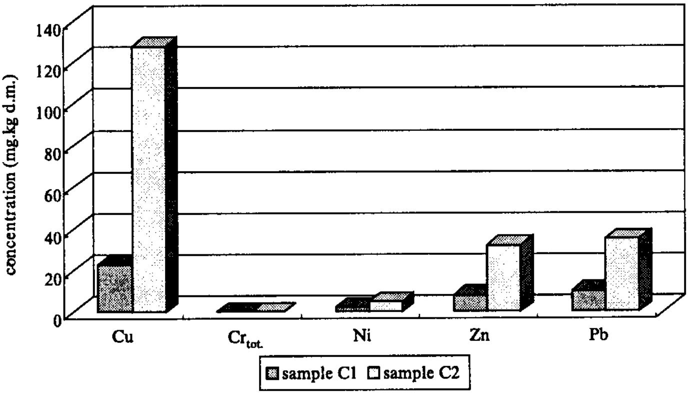

Fig. 1. Concentrations of mobile form of heavy metals using 4th analitycal method for C1, C2

These data allow us to conclude that in this case, even if the soils show high and very high contents of heavy metals totally dissolved in aqua regia, their mobility percentage is relatively low, excepting for Cu and Pb, but the values found do not imply serious consequences on the environment. The situation of the soils sampled in the proximity of a mining waste storage is unfortunately different. Thus, all four methods used confirmed the fact that the metals analysed in this case (Cu, Cd, Zn and Pb) are found in their mobile state. The percentages found were different, the method NF X 31-120/1992 giving in this case also the best results for all elements analysed. For the samples Sa1 and Sa2, the results found a percentage of approximately 19-20% mobility for Cu, a very high mobility for Pb (32-34%) and 20-21% for Zn. The major problem is given by the extremely high concentrations of mobile Pb (1247 ppm in Sa1, and 1118 ppm in Sa2, respectively), which represent a very high risk in the environment. These results are presented in Fig. 2.

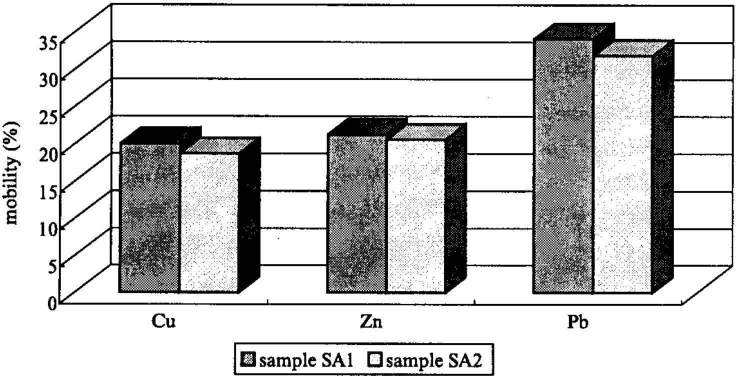

Fig. 2. Percent of mobility of heavy metals using 4th analitycal method for SA1, SA2

As for the samples Sb1 and Sb2, very high concentrations of metals in mobile state were found for Pb (2680 ppm – Sb1, 1294 ppm – Sb2), Zn (793 ppm – Sb2), Cu (190 ppm – Sb2), Cd (9.5 ppm – Sb2).

Figures 3 and 4 present the mobility percents obtained for the elements analysed in the samples Sb1, Sb2 by the four methods used.

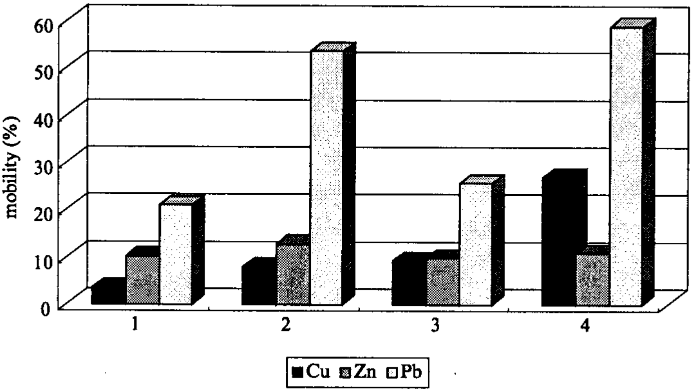

Fig. 3. Percent of mobility of heavy metals using all the analitycal methods from Table 1 for SB1

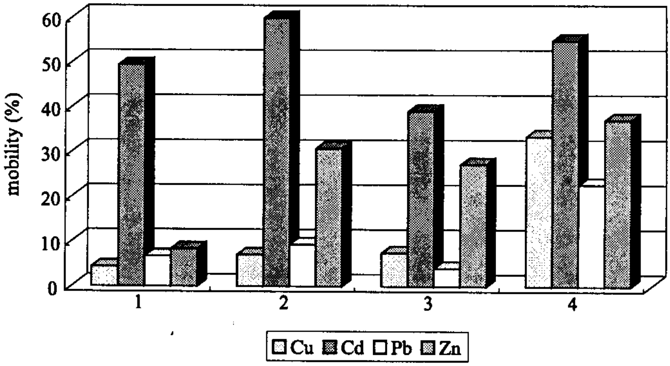

Fig. 4. Percent of mobility of heavy metals using all the analitycal methods from Table 1 for SB2

CONCLUSIONS

The standardised method NF X 31-120/1992 has proven extremely useful in these environmental studies, providing valuable information on the mobility of heavy metals in the analysed soils.

The control soils (agricultural soil) show low mobility, the concentrations found ranging in the heavy metal values necessary for the plant germination and growth (4-10 ppm Cu, 4-6 ppm Ni, 1-2 ppm Pb, 5-20 ppm Zn).

In the case of the soils in the area polluted by industrial activities, although show high concentrations of heavy metals (Cu, Cr_{tot}, Ni, Pb and Zn), the mobility is low or absent (for Cr_{tot}). Concentrations ranging between 1-3 ppm for Ni, 10-30 ppm for Pb, 35-128 ppm for Cu and 8-30 ppm for Zn were found.

The soils sampled in the vicinity of the area polluted by mining waste storage have a major impact on the environment because of the high mobility of the metals Cu, Cd, Pb and Zn, whose values are significant. Thus, very high concentrations were found for mobile Pb (1118, 1247, 1294, 2680 ppm), mobile Zn (148 ppm, 171 ppm, 793 ppm), mobile Cu (133 ppm, 190 ppm), mobile Cd (9.54 ppm).

High values were found both in the surface soil and in depth. The soils were sampled at a distance of 400 m between the sampling points on different directions, which leads to the conclusion that the pollution is not local, but on the entire area of the mining waste storage. The high concentrations of mobile heavy metals indicate that it is very possible that the underground water in the area might as well be polluted by these metals.

It is known that the acidity of the soil leads to the release of a higher quantity of heavy metals. Is the case of samples from the vicinity of the area polluted by mining waste storage, which has the values of pH between 4.4 and 5.1. The acid pH of these soils is an important factor which influenced their release. Unlike these soils, C1 and C2 have neutral or easy alkaline pHs which limit mobility to low concentrations for the heavy metals in their composition.

This study offers the possibility to obtain rapid information about the mobility of heavy metals from antrophic soils, without being necessary successive steps of extraction with DTPA and TEA, which are difficult to be performed, time-consuming and at the same time can conduct to the redistribution of heavy metals between phases.

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