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Soil pollution

OPTIMISED METHOD FOR EXTRACTION OF MOBILE SPECIES OF HEAVY METALS FROM POLLUTED SOILS

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Abstract. The paper proposed an optimised extraction method used for extraction of mobile forms of heavy metals (Cu, Cd, Pb and Zn) from different types of polluted soils with clay structure. This study presents a comparison between the results obtained using SR ISO 14870/1999 with 5 successive extractions and a ratio of soil:solution of 1:2 with the results obtained experimentally for one single chemical extraction and different ratios between soil and solution (1:5, 1:7, 1:10). The results obtained put in evidence similar concentration of mobile species and indicated that modified standard method (ratio 1:10) is a good analytical method for estimation of mobile species concentration of heavy metals from polluted soils. The total content and mobile forms of heavy metals were analysed with AAS technique, using an ATI UNICAM SOLAR equipment.

Keywords: extraction method, DTPA, mobile species, heavy metals, single extraction, AAS.

AIMS AND BACKGROUND

Pollution of soils became a major social, environmental and scientific problem, and trace metals such as lead, zinc and cadmium are common contaminants in polluted soils. Due to polluted human activities (industrial, mining and agricultural activities, road transport) the level of heavy metals increases continuously. Heavy metals are included in the category of 'persistent substances with factor of risk', which have the tendency 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.

Trace elements can not be transformed and degraded like organic molecules, they occur as different species, generally associated with major soil components: either complexed by humic substances, or more and less strongly adsorbed on mineral surfaces, or included in solids, e.g. as pure carbonates, sulphides, oxides or combined with other elements (Ca, Fe) within imperfect crystals.

Mobility can be defined as the ability for these elements to move from one form to another and mobilisation is observed when more soluble species appear in

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the soil – aqueous phase system. There are 5 different situations which give rise to the pronounced mobilisation of trace elements from solid phase into the liquid in soils. There are: acidification, changes in redox status, increased concentrations of organic complexing ligands, changes in the ionic composition of the soil solution and methylation[1].

The standard ISO 14870/1999 (Ref. 2) is an European method used for the extraction of mobile forms of heavy metals. This standard presents a great disadvantage, consisting in the diminution of the capacity of extraction at high concentration of the mobile forms of heavy metals in the soil or sediment.

This is produced because the standard uses a small ratio between extracting solution (a buffer solution at pH = 7.3 of DTPA, TEA and CaCl2) and soil (2:1). Successive steps of extractions conduct to material losses and redistribution of heavy metals between phases. For this reason, it is very important to extract all mobile species of heavy metals in a single chemical extraction.

EXPERIMENTAL

Soil samples were drawn from polluted areas: 2 samples from 2 depths (0-10 and 30-40 cm) (S1, S2), drawn in the vicinity of a mining waste dump storage, with a distance of about 400 m between them and situated on different directions.

The samples, dried on air and shaved by a shave 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 (Cu, Cd, Pb and Zn). These concentrations were measured by flame atomic absorption spectrometry with a FAAS ATI UNICAM type 929. All soils analysed show a similar structure, argillaceous, the pH ranging between the following values: S1 depth 0-10 cm, S1 (30-40 cm) – pH = 4.65 ÷4.77; S2 depth 0-10 cm, S2 (30-40 cm) – pH = 4.4 ÷5.1.

For the extraction of mobile forms of heavy metals was used a buffer solution at pH = 7.3 of 0.005 M DTPA, 0.1 M TEA and 0.01 M $CaCl_2$. The different ratios between soil and solution of extraction were used: 1:2, 1:5, 1:7 and 1:10. The solutions of soil were shaken 2 h at 40 rot./minute, and then were left to settle for 15 min. For the ratio 1:2 between soil and extraction solution were performed 5 successive steps of extractions on a single sub-sample.

They were filtered, and the first 5 ml of solution were dispensed. The filtered solutions were brought at a volumetric flask (25 and 50 ml, respectively), function of the liquid quantity used for extraction, and then the heavy metal concentration (Cu, Cd, Pb and Zn) were quantified by flame atomic absorption spectrometry.

Another extraction method used for the extraction of mobile forms of heavy metals is the French standard NF X31 – 120/1992 (Ref. 3).

The working conditions consisted in: 40 g of pre-treated sediment were mixed with 40 ml of buffer solution of 1M ammonium acetate and 0.01 M EDTA. The obtained suspension was shaken 2 h with 40 rot./min. The resulted solutions were filtered and after that analysed by AAS technique.

RESULTS AND DISCUSSION

The results obtained for the contents of metals totally dissolved in aqua regia have put in evidence that the alert (AL) and even the intervention 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) (Ref. 4). These results are presented in Tables 1 and 2.

Table 1. Samples drawn from the south area of the mining waste storage

Heavy metal (mg/kg d.m.)	S1 (0-10 cm)	S1 (30-40 cm)	Classification of the values according to the Romanian Order 756/97
Cu	371	334	AL < Sa1, Sa2 < IL
Cd	3.6	2.8	NV < Sa1, Sa2 < AL
Pb	3642	3506	Sa1, Sa2 > IL
Zn	806	720	AL < Sa1, Sa2 < IL

Note: NV – normal value according to the Romanian Order 765/97.

Table 2. Samples drawn from the south-west area of the mining waste storage

Heavy metal (mg/kg d.m.)	S2 (0-10 cm)	S2 (30-40 cm)	Classification of the values according to the Romanian Order 756/97
Cu	490	569	AL < Sb1< IL, Sb2 > IL
Cd	1.5	17.4	Sb1≅ NV
Pb	4538	5693	Sb1, Sb2 > IL
Zn	781	2136	AL < Sb1 < IL, Sb2 > IL

Note: NV – normal value according to the Romanian Order 765/97.

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.

The results obtained for mobile forms of trace elements from the analysed samples show:

- After 5 successive steps of extraction with DPTA (Ref. 2) the results for mobility were approximately the same with the values obtained with the French standard[3]. In case of high concentration of mobile trace elements in the soil, 5 successive steps of extraction are not enough for extracting all species (Fig. 3).
- For polluted soils with clay structure and high concentration of mobile forms of heavy metals the report between soil and solution of DTPA at 1:10 allows the extraction of all mobile species.
- The results obtained using a ratio 1:10 (Ref. 2) between soil and DPTA solution were similarly with the values resulted with the French standard (Figs 1, 2 and 3).

- For samples S1 at 0-10 cm and 30-40 cm depth, the results put in evidence 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 S1 (0-10 cm), and 1118 ppm in S1 (30-40), respectively), which represent a very high risk in the environment.
- Also for samples S2 (0-10 cm) and (30-40 cm) depth, very high concentrations of metals in mobile state were found for: Pb (2680 ppm in S2 (0-10), 1294 ppm in S2(30-40)), Zn (793 ppm in S2(30-40)), Cu (190 ppm in S2(30-40)), Cd (9.5 ppm in S2(30-40)).

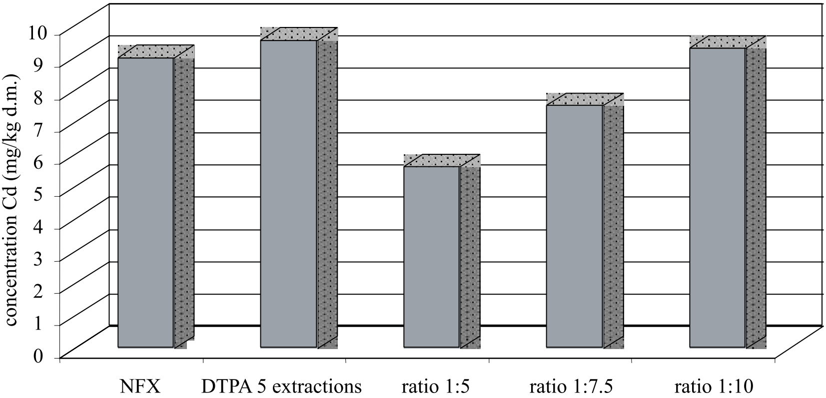

Fig. 1. Concentration of mobile forms of Cd with different extraction ratio (SR ISO 14870/9) of soil sample S2, depth 30-40 cm

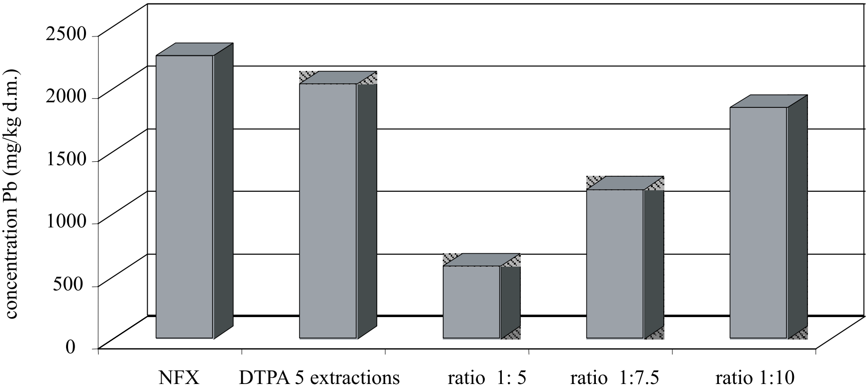

Fig. 2. Concentration of mobile forms of Pb with different extraction ratio (SR ISO 14870/9) of soil sample S1, depth 0-10 cm

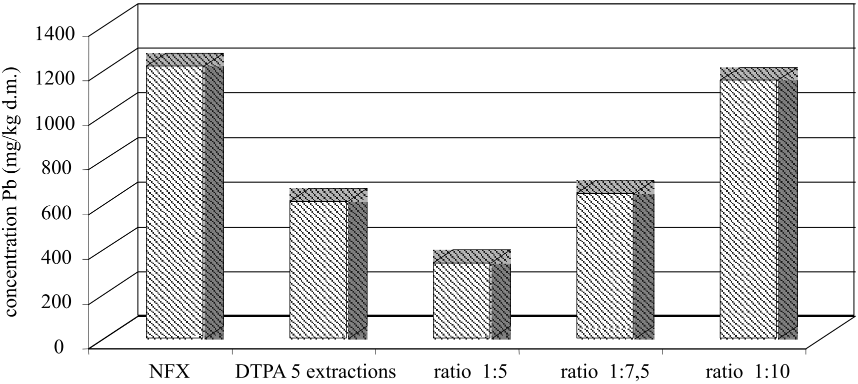

Fig. 3. Concentration of mobile forms of Pb with different extraction ratio (SR ISO 14870/9) of soil sample S2, depth 30-40 cm

CONCLUSIONS

The experimental data obtained put in evidence that it is necessary to improve the existing standard method SR ISO 14870/1999 by using a ratio of 1:10 between soil and solution of DTPA and one single chemical extraction for estimation of the concentration of mobile species of heavy metals from high polluted soils.

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. 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 the possibility 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. It is the case of these samples, which have the values of pH between 4.4 and 5.1. The pH of these soils is an important factor which influences the mobility of trace elements.

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