



## **SELECTIVE SEPARATION AND DETERMINATION OF HEAVY METALS (Cd, Pb, Cr) SPECIATION FORMS FROM HORTIC ANTROSOLS**

D. Bulgariu (1,3) and L. Bulgariu (2)

(1) Ȃl. I. Cuza University, Geology and Geochemistry, Iasi, Romania (dbulgariu@yahoo.com), (2) Technical University "Gh. Asachi" from Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, D. Mangeron, no. 71A, 700050, Iași (Romania), e-mail: lbulg@ch.tuiasi.ro, (3) Romanian Academies, Filial from Iași, Collective of Geography, Carol I, no. 18, 700506, Iasi (Romania)

The speciation, inter-phases distribution and biodisponibility of heavy metals in soils represent one of main problem of environmental geochemistry and agro-chemistry. This problem is very important in case of hortic antrosols (soils from glasshouses) for the elimination of agricultural products (fruits, vegetables) contamination with heavy metals. In soils from glass houses, the speciation and inter-phases distribution processes of heavy metals have a particular dynamic, different in comparison with those from non-protected soils. The predominant distribution forms of heavy metals in such soils types are: complexes with low mass organic molecules, organic-mineral complexes, complexes with inorganic ligands (hydroxide-complexes, carbonate-complexes, sulphate-complexes, etc.) and basic salts. All of these have high stabilities in conditions of soils from glass houses, and in consequence, the separation and determination of speciation forms (which is directly connected with biodisponibility of heavy metals) by usual methods id very difficult and has a high uncertain degree.

In this study is presented an original method for the selective separation and differentiation of speciation forms of heavy metals from glass houses soils, which is based by the combination of solid-liquid sequential extraction (SPE) with the extraction in aqueous polymer-inorganic salt two-phase systems (ABS). The soil samples used for this study have been sampled from three different locations (glass houses from Iasi, Barlad and Bacau – Romania) where the vegetables cultivation have bee performed by three different technologies. In this way was estimated the applicability and the analytical limits of method proposed by as, in function of the chemical-mineralogical and physical-chemical characteristics of soils. As heavy metals have been studied cadmium, lead and chromium, all being known for their high toxicity. The procedure used for the selective separation and differentiation of speciation forms of heavy metals from glass houses soils has two main steps: (i) non-destructive separation of chemical-mineralogical associations and aggregates from soils samples – for this the separation method with heavy liquids (bromophorme) and isodynamic magnetic method have been used; (ii) sequential extraction of heavy metals from soil fractions separated in the first step, by using combined SPE-ABS procedure. For the preparation of combined extraction systems was used polyethylene glycol (with different molecular mass: 2000, 4000 and 8000). As phase-forming inorganic salts and as selective extracting agents we have used different usual inorganic reagents. The type and concentration of phase-forming salts have been selected in function of, both nature of extracted heavy metals and chemical-mineralogical characteristics of soil samples. The experimental parameters investigated in this study are: molecular mass of polyethylene glycol and the concentration of polymeric solutions, nature and concentration of phase-forming salts, nature and concentration of extracting agents, pH in extraction system phase, type of extracted heavy metals, type of speciation forms of heavy metals and their concentrations. All these factors can influence significantly the efficiency and the selectivity of separation process.

The experimental results have indicate that the combined SPE-ABS extraction systems have better separation efficiency, in comparison with traditional SPE systems and ca realized a accurate discrimination between speciation forms of heavy metals from soils. Under these conditions, the estimation of inter-phases distribution and biodisponibility of heavy metals has a high precision. On the other hand, when the combined SPE-ABS systems are used, the concomitant extraction of the elements from the same geochemical association with studied heavy metals (inevitable phenomena in case of separation by SPE procedures) is significant diminished. This increases

the separation selectivity and facilitated the more accurate determination of speciation forms concentration. By adequate selection of extraction conditions can be realized the selective separation of organic-mineral complexes, which will permit to perform detailed studies about the structure and chemical composition of these.

#### Acknowledgments

The authors would like to acknowledge the financial support from Romanian Ministry of Education and Research (Project PNCDI 2-D5 no. 51045/07).