

TRACE ELEMENTS AND METAL BIOAVAILABILITY IN SOILS TREATED WITH INDUSTRIAL RESIDUES

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Abstract: *The aims of this paper are to present fundamental chemical reactions of metals in soils treated with industrial residues and to compare the two methods of trace elements phytoavailability estimation: sequential extraction method and plant bioassay method. Trace elements solubility and availability in land-applied industrial residues is governed by fundamental chemical reactions between metal constituent, soil and residual components. Organic matter, phosphates, carbonates, sulphides, iron, manganese and aluminium oxides are important sinks for trace elements in soil – residues system. The most important chemical property that govern trace elements availability, solubility, precipitation and sorption is pH of soil-residues system. Trace elements phytoavailability in soils treated with industrial residues is often estimated using soil /residues extraction methods. Spectroscopic studies shown that sequential extraction methods may not be accurate in soil-residues system. The best method to measure the effect of trace elements from industrial residues on phytoavailability seems to be plant bioassay. The key concepts use to describe phytoavailability are: the salt effect, the plateau concept and the soil plant barrier. Metals availability in soils from metal salts addition is higher than availability of metals from industrial residues. Metals content in plant show plateau at high residual loadings corresponding to the residuals metal concentration and sorption capacity. The soil plant barrier limits transmission of many trace elements through the food chain. Cadmium, an important human health concern, can bypass the soil-plant barrier. For trace elements phytoavailability estimation we used sequential extraction of trace elements from soil treated with mining steril (industrial residue), and plant bioassay method. Results of many studies that support these concepts provides a basis for understanding the relationship between trace elements chemistry and phytoavailability in industrial residues treated soils. Researches are needed to determine mechanisms for trace elements retention in soils and predict the long term bioavailability of trace elements in soil – industrial residue system.*

Key words: *trace elements, metal bioavailability, chemical extraction procedures, industrial residues,*

INTRODUCTION

In many industrial countries, soils are affected by mine waste disposal, acid deposition and sewage sludge use that could provide large inputs of pollutants and especially heavy metals to the soils. The impact of contamination on the environment should be of scientific concern, in order to minimize the threat of soil and groundwater contamination.

Heavy metals contamination of arable soils through industrial activities is a serious problem in the world.

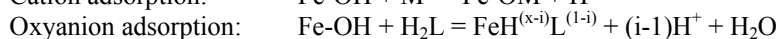
A variety of in-situ and ex-situ remedial methods have been used or proposed for the restoration of soil contaminated with heavy metals, which warrant investigating the extractability of heavy metals in soil. Chemical extraction procedures are able to predict the changes in the heavy metals mobility or bioavailability in soils.

Trace elements solubility and availability in land applied residues are governed by fundamental chemical reactions between metal constituent, soil and residual component. Organic matter, phosphates, carbonates, sulphides, iron, manganese and aluminium oxides are important sinks for trace elements in soil-residues system [1,2].

Trace elements reaction with iron and manganese oxides

Sorption is an important chemical process that regulates partitioning of trace elements between solution and solid phases in soil.

Trace elements sorption by the oxide surface is a highly pH depended process, described by the following chemical reactions:



Where: Fe-OH – is an iron oxide surface;

M^+ - trace element cation;

L^{2-} - oxyanion ligand.

Cationic trace elements absorption increase to almost 100% with pH increasing [3].

BROWN and PARKS, 2001, shows that Fe and Mn oxides have a much greater absorption capacity compared with Al oxides and other clay minerals. Molecular X-ray spectroscopic studies shown that the strong bonding of Pb, Cu, Co, Cr, Mn, Ni and Zn to these oxides surfaces is due to formation of metal hydroxide precipitate phases. New solids found after metal ion reaction with soil materials, including metal silicates and mixed double hydroxides with Al, can substantially reduce metal solubility and bioavailability [4,5,6].

Trace elements reaction with organic matter

Trace elements cations also sorb to soil organic matter and other forms of humified natural organic matter. Soft acid metals (Cd^{2+} , Hg^{2+}) prefer soft base ligands (SH^-), hard acid metals (Fe^{2+} , Mn^{2+}) prefer hard base ligands (HO^- , COO^-), borderline acids (Cu^{2+} , Zn^{2+} , Pb^{2+}) will form complexes with a weak or strong base [7].

Sorption of trace elements by organic matter increase with pH because metals preferentially bind with ionized functional groups formed with pH increased.

Proper evaluation of the effect of heavy metals on environment, is possible by knowing their chemical forms and binding soil, sediment, sludge or solid waste components.

Water soluble and exchangeable forms are considered mobile and available to plants, while metals incorporate into crystalline lattice of clays appear relatively inactive. The other forms, precipitate as carbonate, occluded in Fe, Mn and Al oxides or complexed with organic matter, could be considered relatively active or firmly bond.

Several reagents (CaCl_2 , NH_4OAc , NH_4NO_3 , EDTA) have been used to extract the mobile or bioavailable forms of heavy metals with single extraction procedure. Single and sequential extraction provides information on potential mobility as well as bioavailability and plant uptake of trace elements.

MATERIAL AND METHODS

Samples were taken from two kinds of sewage sludge: wet sludge (WS) from drying beds and dry sludge (DS) stored on Municipal waste water treatment plant lands, in Timisoara.

In order to determine the total concentration of heavy metals from WS and DS, we applied the modified method presented by Tessier et al, 1979. 0,2 g of each sample was weighed and then digested twice with a mixture (1:5, v/v) of 2 mL concentrated HClO_4 and 10 mL HF (the mixture was evaporated to near dryness each time). Finally, HClO_4 1mL alone was added and the sample was evaporated until the appearance of white fumes. The obtained residue was dissolved with $0,1 \text{ mol L}^{-1}$ HNO_3 , transferred into a volumetric polyethylene flask (25 mL) through $0,45\mu\text{m}$ filter and then diluted to the mark.

For sequential extraction was used Tessier method [8-12]. The protocol for selective sequential dissolution procedure is presented in Table 1.

Table 1

Protocol for selective sequential dissolution procedure							
Step no.	Fraction	Solid phase desired	Reagents	pH	Ratio solln/soil	T(°C)	time
1	EXC	Exchangeable	1 M NH ₄ NO ₃	7	25:1	25	30'
2	ERO	Easily reducible oxides	0,04M NH ₂ OH·HCl + 25% HOAc	2	25:1	25	30'
3	OM	Organic matter	30% H ₂ O ₂ 0,01M HNO ₃	2	25:1	80	3 h
4	RES	Residual	5:1, v/v HF, HClO ₄		25:1	180	30'

After each successive extraction, separation was accomplished by centrifuging at 5000 rpm for 30 minutes. The supernatant was removed, filtered and analyzed for heavy metals content.

The plant available metal fraction (EDTA extractable) was estimated using 0,5 M NH₄OAc + 0,5M HOAc + 0,02M EDTA (1:5 soil/extractant ratio, pH 4,65, shaken 2 hours) [13].

RESULTS AND DISCUSSIONS

Results of heavy metal total content of WS and DS presented in table 2, shows that Cd is relatively low, under the maximum admittance level (10 mg·kg⁻¹ d.m), Cr and Cu content are also above 500 mg·kg⁻¹ d.m input limit by law; Ni content (110 mg·kg⁻¹ d.m.) exceed limit with 10 units; Pb content (620 mg·kg⁻¹ d.m in WS and 813 mg·kg⁻¹ d.m in DS) is twice higher than maximum limit (300 mg·kg⁻¹ d.m) approximatively; Zn content in DS is relatively low, but in WS exceed the limit.

Table 2

Metal concentration in WS and DS and metal limits for land application in European Community and Romania

Metal	Metal content (mg·kg ⁻¹ d.m.)			
	WS	DS	Maximum admittance level	
			European Community ^{††}	Romania [†]
Cd	2,3	4,3	20-40	10
Cr	54	18	-	500
Cu	92	125	1000-1750	500
Ni	73	110	300-400	100
Pb	620	813	750-1200	300
Zn	2100	383	2500-4000	2000

† - Order 344 from 16.08.2004 [14]

†† - Limit Concentrations for Metals in European Community Directive 86/278/EEC (EC 2000) [15]

Values obtained for plant available metal fraction (EDTA extractable) in bulk sewages are presented in table 3.

Values obtained for plant available metal fraction of Cd, Cr, Cu, Ni and Pb in sewage sludges situate WS and DS in inert residues category. Zinc content from WS slowly exceed maximum admittance limit for inert residues and situate WS in non-polluting residues category.

Table 3

Plant available metal fraction (EDTA extractable) in sewages in comparison with maximum admittance level, for inert, nonpollutant and pollutant residues

Metal (mg·L ⁻¹)	WS	DS	Maximum admittance level (mg·L ⁻¹)**		
			Inert residues	Nonpollutant residues	Pollutant residues
Cd	udl*	udl*	0,1	0,2	0,5
Cr	0,151	0,041	0,5	2	5
Cu	0,03	1,19	2	5	10
Ni	0,046	0,147	0,5	1	2
Pb	0,24	0,20	0,5	1	2
Zn	2,6	0,66	2	5	10

udl* - under detection limit

** - values according with Landfill Directive 1999/31/EC [16]

Table 4

Results of chemical speciation of heavy metals from sludges

Metal	Sequential extraction results (mg·kg ⁻¹ d.m.)							
	1-st step		2-nd step		3-rd step		residual	
	WS	DS	WS	DS	WS	DS	WS	DS
Cu	0	0,322	1,84	0,537	87,4	3,09	2,76	0,344
Cr	1,62	4,25	30,8	2,77	17,8	7,02	3,8	3,96
Cd	0,48	2,08	0,89	2,21	0,92	0	0	0
Ni	15,3	23,65	21,2	61,38	9,5	13,53	27,1	11,44
Pb	74,4	58,90	223,2	424,7	248	85,56	62	50,84
Zn	525	37,53	1260	314,8	315	22,98	0	7,66

Analysing results of sequential extraction about Cu in WS respectively DS, we observed that copper was primary extracted in the 3-rd step (92% for WS, respectively 72% for DS), so this metal has the highest concentration in organic matter fraction. Because Cu forms specific complex combinations with organic matter, this seems to be a characteristic, released by organic matter and sulphides oxidation.

In analyzed samples, Zn is almost in exchangeable and easily reducible oxides, so it has a high mobility degree [17]. In WS Zn was found in exchangeable fraction (25%) and associated with Mn and Fe oxides (60%). This observation is important, because WS contain notable Zn quantities. So, we can affirm that Zn is in important amounts in plant available form (first step extractable fraction), being easily remobilised, but also strong influenced by reduction processes (2-nd step extractable fraction).

Pb is mainly associated with Mn and Fe oxides fraction, in a small degree bond with organic matter and in low amounts in exchangeable fraction. This fact induced low values of bioavailability, but with a considerable tendency in becoming available.

In WS samples, Ni was distributed between all fractions, about 20% of total amount was extracted in the first step. In DS, Ni was mainly determinate in residual fraction.

In WS Cr is associated with organic matter (33%) and with Fe and Mn oxides fraction (57%). In DS, Cr is homogeneous distributed between the four determinate fractions, predominating exchangeable fraction and bind to the organic matter.

Cd was extracted in high quantities in the first step, for both types of sewage sludge. This fact indicates that Cd is in plant availability form in most part, because the metals which are present in exchangeable fraction are usually weak absorbed and can be easily dissolute, becoming available for plants. This phenomenon may be extremely harmful for ecosystems and for Cd transfer in food chain.

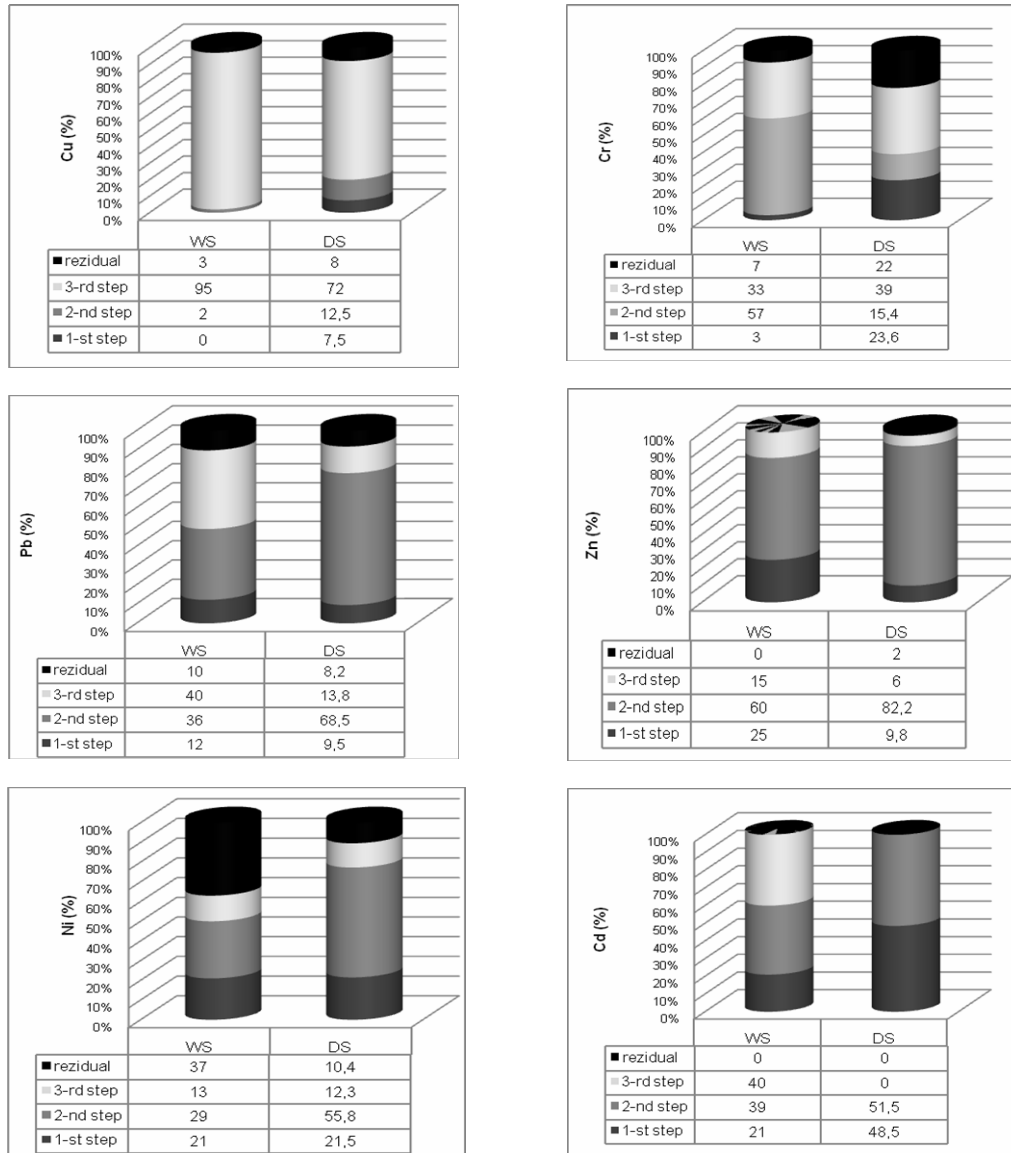


Figure 1: Chemical speciation (%) of Cu, Pb, Ni, Zn, Cr and Cd in WS and DS

CONCLUSIONS

In our days, the most part of sludge from water treatment plants are treated inadequate and stored on water treatment plants lands. Only a small part of them are used in agriculture. The legal framework for sewage sludge valorification in agriculture was created by the application of 86/278 Directive, concerning environment protection and in particularly, soil protection.

The use of high content heavy metals sewage sludge in agriculture has a long-term phytotoxic effect, due to excessive accumulation of heavy metals in plants.

Values obtained for Cd, Cu, Cr, Ni, Pb, Zn in plant available fraction (EDTA extractable), situated the two types of tested sludges in no pollutant residues category.

The total content of heavy metals determinate in WS and DS indicate the overflow of maximum admittance level for Ni, Zn and Pb.

BIBLIOGRAFY

1. BASTA, N.T. 2000. Examples and case studies of beneficial reuse of municipal byproducts. P.451-504. In J.F., Power and W.A. Dick Land application of agricultural, industrial and municipal byproducts. SSSA Book Ser.6.
2. BROWN, G.E., PARKS G.A. 2001. Orption of trace elements on mineral surfaces. Modern perspectives from spectroscopic studies and comments on sorption in the marime environment. *Int.Geol.Rev.* 49:963-1073.
3. ESSINGTON, M.E. 2004. Soil and water chemistry. An integrative approach. CRC Press, Boca Raton, FL.
4. European Community Directive 86/278/EEC (EC 2000).
5. FUENTES, A., LLORENS, M., SAEZ, I, SOLER, A, AGUILOV, M.I., ORTUNO J.F., MESENGUER, V.F. 2004. Simple and sequential extraction of heavy metals from different sewage sludges. *Chemosphere* 54(204), 1039-1044, www.elsevier.com.
6. HAN, F.X, ET ALL. New approach to studies of heavy metals distribution in soils. *Advances in Environmental Research* 8 (2003), p.113-120, www.elsevier.com.
7. KIDD, P.S., DOMINGUEZ-RODRIGUEZ, M.J, DIEZ, J., MONTEROSSO, C. Bioavailability and plant accumulation of heavy metals and phosphorus in agricultural soils amended by long-term application of sewage sludge. *Chemosphere* 66 (2007), p.1458-1467, www.elsevier.com.
8. MC BRIDE, M.B. 1994. *Environmental Chemistry of Soils*. Oxford University Press, New York.
9. MC BRIDE, M.B. 2003. Toxic metals in sewage sludge amended soils. Has promotion of beneficial use discounted the risk? *Adv. Environ. Res.* 8:5-19.
10. MC GRATH, S.P., GEGGARA, J. 1992. Chemical extractibility of heavy metals during and after long-term application of sewage sludge to soil. *J. Soil Sci.* 43:313-321.
11. MC KENZIE, R.M. 1980. The absorption of lead and other heavy metals on oxides of manganese and iron. *Aust. J. Soil Res.* 18:61-73.
12. NIREL, P.M.V. 1990. Pitfalls of sequential extraction. *Water Res.* 24:1055-1056.
13. Order 344/16.08.2004. Technical guidelines approbation concerning environment protection and soil, on agriculture use of municipal sludges.
14. SHECKEL, K.G., SPARKS D.L. 2001. Dissolution kinetics of nickel surface precipitateon clay mineral and oxide surfaces. *Soil Sci. Soc. Am. J.* 65:685-694.
15. SPARKS, D.L. 2003. *Environmental Soil Chemistry*. 2nd ed. Academic Press, San Diego CA.
16. TORRI, S.I., LAVADO, R.S. Dynamics of Cd, Cu and Pb added to soil through different kinds.. *Waste Management* (2007), doi10.1016/j.wasman.2007.01.020.
17. USEPA. 2003. Ecological Soil Screening Level, guidance and documents. www.epa.gov/