

ASSESSMENT OF TRACE METALS MOBILIZATION AND PARTITIONING IN SOIL COMPONENTS: BY ADSORPTION AND SEQUENTIAL EXTRACTION METHODS

S. Naeem, U. Zafar and S. F. Mahmood

Material Science Research Centre,
PCSIR Laboratories Complex, Lahore-PAKISTAN

ABSTRACT: Extraction techniques were used to establish the association of total concentration of six heavy metals in soil samples with their contents in the exchangeable, Carbonate, iron/manganese oxides and residual fractions. Heavy metals contents in the sediments were found to be significantly influenced by different physico-chemical parameters. The effect of these parameters can be arranged in the following order: Clay fraction > Carbonate > Silt fraction > Organic matter fractions. A sequential extraction procedure showed that the total concentrations of heavy metals were largely bound to the residual phase. A likely sequence of mobility in the investigated soil samples is as follows: Cadmium > Nickel > Copper > Chromium > Zinc > Lead. Soil cadmium was ready to be mobilized in all leaching solution at varied quantities. The results further verified that soil Cd is distributed among different fractions: water soluble, exchangeable and specifically adsorbed on the solid phase. Freundlich and Langmuir isotherms have been established for cadmium solid-phase partitioning.

INTRODUCTION

The suitability of a natural clay or soil as a barrier against the migration of contaminants towards the groundwater is usually assessed by evaluating material parameters such as mineralogical composition, specific surface area (SSA), and cation exchange capacity (CEC) (Roehi and Czurda, 1997). The actual form of fixation of sorbed contaminants to the components of the clay/soil is not considered (Barona and Romero, 1996). The objective of the presented laboratory study was to combine the evaluation of retardation processes of heavy metals in natural clays with the speciation of the sorbed metals by using sequential extraction procedures. Knowledge of chemical speciation is important in evaluating the mobility and toxicity of heavy metals. In general, the organic forms of metals are more toxic than their inorganic forms. In environmental samples such as soils or sediments, it is important to ascertain the availability and distribution of metals. Tessier *et al.* (1979) developed a method for sequential extraction that separates metals in sediments into five different metal fractions: (1) Exchangeable, (2) Bound to carbonates, (3) Bound to iron and manganese oxides, (4) Bound to organic matter and (5) Residual. Heavy metals present in each of these fractions have different (re) mobilization behaviors under specific environmental conditions. This well established method has been

adopted as is or modified by a number of researchers with different degrees of success (Maiz *et al.* 1997; Lam *et al.*; 1997 Ma and Rao 1997). Some bibliographic data on the sequential extraction of heavy metals present in soils and sediments have been given by Colvet *et al.*, 1990. The mobility of heavy metals in terms of leach ability depends not only on the total concentration in soil but also on soil properties and environmental factors. Soils containing much organic and mineral colloidal material, can sorb and immobilize these metals to a greater extent than soil poor in these reactive materials. Thus silicates, carbonates, phosphates, oxides and organic matter can all contribute to metal retention (Vahid *et al.*, 2003). Among the soil environmental factors, pH and organic matter are known to affect the trace metal transfer between soil phases, and thus metal solubility in many soils. Pueye *et al.*, 2003 have elucidated that soluble organic matter (fulvic acid), which can suppress heavy metal adsorption on Fe and Al oxides and silicate minerals at high pH, generally has a sufficiently strong affinity for metals such as Cu, Ni, Hg and Pb, that it promotes dissolution of these metals from adsorption sites on clay minerals.

The use of clay barrier is one of the common methods to prevent contaminant migration from the waste disposal facility to the ground water surface. In this regard the type of clay minerals

such as montmorillonite, illite and Kaolinite playgorskite make a major role. By and large, there are several mechanisms in which clay minerals prevent the migration of contaminant to the subsurface soil (Prost and Yaron 2001). In this regard, the evaluation of soil-contaminant interaction through the evaluation of adsorption characteristics of soil is a common method to evaluate the ability of soil for prevention of contaminant migration. In fact different clay minerals play different interactions mechanism with contaminants. K.W. Brown and associates (1980) developed a summary of the advantages and disadvantages of the use of various textured-soils for the treatment of hazardous industrial wastes (Table-1). In general, loam, silt loam, sandy loam, sandy clay loam, silty clay loam, silty clay, and sandy clay soils were identified as best suited for land treatment of hazardous wastes. Welp (1999) reported that the sorption and immobilization of toxic metals in soil is an effective detoxification process and thus an essential part of the buffer capacity of soil. There are several methods for immobilization of heavy metals in soil. Immobilization can be carried out by adding natural and synthetic oxides, aluminosilicates or coal fly ashes (Mench *et al.*, 1998). Clay minerals are among the major materials that interact with all almost all soil contaminants (Prost and Yaron, 2001). So solid speciation of heavy metals in clayey soils and fixation mechanisms of heavy metals is important parameter for the risk assessment of polluted soils. And these studies potentially can help to a better understanding of possible remobilization processes, and can also lead to more reasonable statements concerning the further use or the remediation methods of a heavy metal contaminated soil.

MATERIALS AND METHODS

Soil samples were collected locally in the vicinity of Material Research Centre at PCSIR Labs. Complex Lahore (Fig.1) from May-June 2005, as a part of in house R & D activity. The sampling site comprised of three different locations covering the whole length of the 250 m² wet land. Surface soil samples were collected using a scoop. In the laboratory, samples were dried at room temperature, ground and sieved through a -200 mesh before analysis. Drying sediments at higher temperature was avoided to ensure that organic matter content and the metal binding properties of the sediments remained intact. Care was taken

while sieving the sediments to prevent excess loss of the fine particles. All chemicals and acids used were of Analytical Reagent Grade (ARG), and were used without further purification.

Out of twenty samples, five were selected and were analyzed for cadmium, chromium, copper, nickel, lead and zinc concentration from the sampling area by Atomic Absorption Spectroscopy (AAS). Extraction techniques (Tessier *et al.*, 1979) were used to establish the association of the total concentration of the six metals in soil samples with their contents in the exchangeable, carbonates, iron/manganese oxides and residual fractions. Selected properties of the soil samples are summarized in Table-2. Freundlich & Langmuir isotherms were established for solid phase partitioning and high mobility of Cd in selected sampling area. Subsequently, sequential extraction was performed on Cd contaminated soil samples using a protocol (Table-3), (Roehi and Czurda 1997). Cd analysis was performed by AAS. Adsorption isotherm parameters were calculated for individual operational species according to a procedure reported by Salim *et al.*, 1996, using Freundlich and Langmuir isotherms.

Freundlich isotherm $q = K_f \cdot C^n$

q = Cd sorbed (meq/g)

C = Cd equil. Conc. (meq/l)

K_f , n = Freundlich parameters

Langmuir isotherm: $q = Q \cdot b \cdot c / 1 + b \cdot c$

Q = Langmuir sorption maximum

b = Langmuir affinity parameter

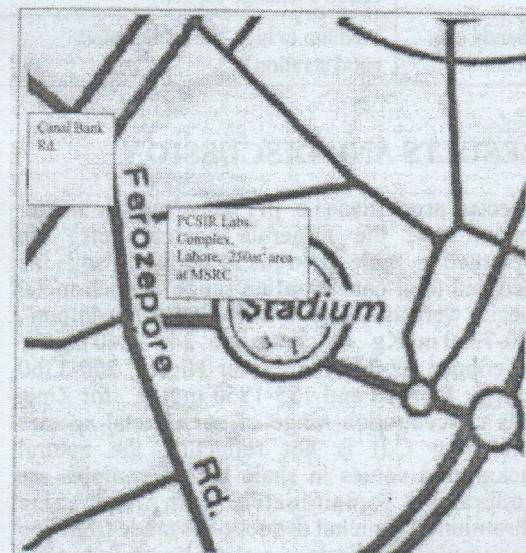


Fig.1: Map of the location

Table 1. Suitability of Various Textured Soils for Land Treatment of Hazardous Industrial Wastes
 (Courtesy: K.W. Brown and Associates 1980)

| Texture | Advantages | Disadvantages |
|-----------------|---|--|
| Sand | Very rapid infiltration; usually oxidized & dry; low runoff potential | Very low cation exchange capacity; very high hydraulic conductivity rate; low available water; little soil structure |
| Loamy sand | High infiltration; low to medium runoff | Low cation exchange capacity; moderate to high hydraulic conductivity rate; low to medium available water |
| Loam | Moderate infiltration; fair oxidation; moderate runoff potential; generally accessible; good cation exchange Capacity | Fair structure |
| Silt loam | Moderate infiltration; fair oxidation; moderate runoff potential; generally accessible; good cation exchange capacity | High crusting potential; poor structure; |
| Silt | Low infiltration; fair to poor oxidation; good cation exchange capacity; good available water | high runoff |
| Silty clay loam | Medium to low percolation; fair structure; high cation | potential Medium to low infiltration; some crusting |
| Silty clay | Good to high available water | Moderate runoff; often wet; fair oxidation |
| Clay loam | Medium-low percolation; good structure; medium to poor aeration; high cation exchange capacity; high available water | Medium to low infiltration; moderate to high runoff; often wet |
| Clay | Low percolation; high cation exchange capacity; high available water | Low infiltration; often massive structure; high runoff; sometimes low aeration |
| Sandy clay | Medium to low percolation; medium to high cation exchange capacity | Fair structure; moderate to high runoff |
| Sandy clay loam | Medium to high available water; good aeration | Medium infiltration |

RESULTS AND DISCUSSION

Selected properties (i.e. pH value organic matter content and the minerals contents etc) are presented in Table-2. In the investigated soils the recorded total concentration range of each metal species were as fellow: 0-20 mgKg for cadmium, 270-7250 mgKg for chromium, 240-2240 mgKg for copper, 52-210 mgKg for Nickel, 200-3360 mgKg for lead and 155-1750 mgKg for Zinc. This concentration range of each metal species (excluding Cd) is not reflecting the natural background values in shale but all samples are moderately contaminated with lead, zinc, chromium and nickel deduction is made from geo-accumulation index values), and higher concentration of lead is showing that soils components have relatively more affinity for Pb

(Joan&Bert.,1992). Aqua-regia extraction was then supplemented with sequential extraction. As reagent specificity is potentially desirable for sequential extraction procedures, the overall procedure (Tessier, 1979) finally adopted thus involves five successive extractions with: (i) $MgCl_2$ (pH 7.0); (ii) $NaOAc/HOAc$ (pH5.0) (iii) $NH_2OH.HCl$ in 25% $HOAc$ (pH2.0); H_2O/HNO_3 (pH 2.0) and subsequently NH_4Oac ; (v) HF and $HClO_4$. Heavy metals contents in the sediments were found to be significantly influenced by different physico-chemical parameters. The effect of these parameters can be arranged in the following order: Clay fraction> Carbonate> Silt fraction>

Table 2: Range of selected properties of the soil samples used in the laboratory study

| | | Unit | Method of Measurement |
|-------------------------------|---------|-----------|--|
| Quartz | 20-45 | % | x-ray diffraction |
| Feldspar | 3-5 | % | x-ray diffraction |
| Carbonate | 10-40 | % | volumetric, x-ray diffraction |
| Fe oxides | 10-20 | % | chemical extraction |
| Mn oxides | 0.1-0.5 | % | chemical extraction |
| Illite | 35-60 | % | x-ray diffraction |
| Kaolinite | 7-12 | % | x-ray diffraction |
| Montmorillonite | 2-5 | % | x-ray diffraction |
| Organic matter | 0.2 -.5 | % | Leco carbon analyzer |
| Clay fraction (< 2 μ m) | 15 -65 | % | sedimentation |
| Silt fraction (2 -63 μ m) | 30-75 | % | sedimentation |
| Sand fraction (> 63 μ m) | 8-10 | % | sedimentation |
| Soil pH (CaCl ₂) | 4.7-7.8 | - | 10 g soil/25 ml 0.01 M CaCl ₂ |
| CEC | 10-20 | meq/100 g | (Chhabra <i>et al.</i> 1975) |

Organic matter fractions. Sequential extraction procedure shows that the total concentrations of heavy metals are largely bound to the residual phase. A likely sequence of mobility in the investigated soil samples is as follows:

cadmium>nickel>copper>chromium>zinc>lead.

The solid-phase partitioning of Cd in soil sample used for the isotherm experiments generally showed the speciation was significantly dependent

on the sorbed metal concentrations, and showed a similar distribution of operational fractions as obtained in diffusion experiments (Roehi and Czurda 1997). A combination of sequential extraction analysis (Table-3) and adsorption isotherms Freundlich (Fig.2) and Langmuir (Fig.3) for Cd allowed the assessment of sorption capacities of individual fractions, and showing maximum adsorption on selected soil sample at exchangeable fraction.

Table 3: Sequential extraction procedure for Cadmium speciation.

| | |
|---|--|
| (1) Mobile fraction (MOB) | 1 g of air dry soil, 25 ml of 1M NH ₄ NO ₃ solution, 24 h at 20°C. |
| (2) Available fraction(AVL) | Residue from step 1, 25 ml of 1M NH ₄ OAc/HOAc solution, pH 6, 24 h at 20°C. |
| (3) Bound to Mn oxidesMnO ₄ | Residue from step 2, 25 ml of 0.1M NH ₂ OHHCl-HOAc solution, pH 6, 30 min at 20°C. |
| (4) Bound to organic matter (OM) | Residue from step 3, 25 ml of 0.025 M NH ₄ -EDTA solution, pH 4.6, 90 min at 20°C. |
| (5) Bound to amorphous Fe oxides (AFeO) | Residue from step 4, 25 ml of 0.2 M NH ₄ -oxalate-oxalic acid solution, pH 3.25, 4 h at 20°C. |
| (6) Bound to crystalline Fe oxides (CFeO) | Residue from step 5, 25 ml of 0.1 M ascorbic acid in 0.2 M NH ₄ -oxalate/oxalic acid solution, pH 3.25, 30 min at 96°C. |
| (7) Residual fraction (RES) | Residue from step 6, aqua regia extraction. |

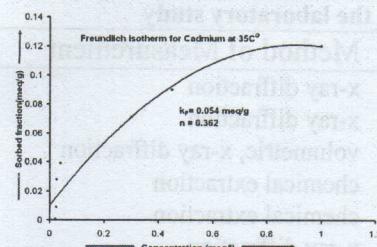


Fig.2: Freundlich isotherm for Cd adsorption at soil exchangeable fraction

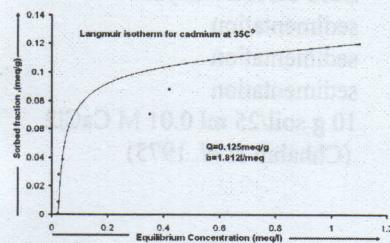


Fig.3: Langmuir isotherm for Cd adsorption at soil exchangeable fraction

CONCLUSION

The results presented in this study emphasize that sequential extraction procedures can contribute to the understanding of heavy metal retention phenomena in clay barriers by supplying information on the solid-phase partitioning of the contaminants.

REFERENCES

Barona, M., and F. Romero. Distribution of Metals in soils and relationships among fractions by principal components analysis. *Soil Technol.* 8:303-319 (1996).

Brown, K.W. and Associates. Hazardous Waste land treatment, Draft Edition. SW-874, U.S. Environmental Protection Agency, Cincinnati, OH.(1980).

Colvet, R., Bourgeois, and J.J. Msaky. Some experiments on extraction of heavy metals present in soil. *Intern.J. Environ. Anal. Chem.* 39:31-45(1990).

Joan, E.M. and E.B. Bert. U.S. EPA Ground water issue: Behavior of Metals in soil. EPA/540/S-92/018, U.S. Environmental Protection Agency, Washington DC. (1992).

Lam M.H.W., Tjia, A.Y.W., Chan, C.C., Chan, W.P., and W.S. Lee. Speciation study of chromium, copper and Nickel in coastal estuarine sediments polluted by domestic and industrial effluents. *Mar Pollut Bull* 34:259-264(1997).

Ma L.Q., G.N. Rao. Chemical fractionation of cadmium, copper, Nickel and Zinc in contaminated soils. *J Environ Qual* 26:259-264 (1997).

Maiz, I., Esnaola, M.V., and E. Millan. Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. *Sci Total Environ* 206:107-115.(1997).

Mech, M., J. Vangroennsveld., N. M. Lepp and R. Edwards. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments, in Vangroennsveld, J. And Cunningham, S.D (eds.) Metal contaminated soils: In situ inactivation and phytoremediation, spring and R.G. Landes. Berlin, pp 151-182(1998)

Porst, R., and B. Yaron. Use of modified clays for controlling soil environmental quality. *Soil Science* 166:880-894(2001).

Pueye, M. J. Sastre, E. Hernandez, M. Vidal, J. F. Lopez-Scanchez, and G. Rausel. Prediction of trace elements mobility in contaminated soils by sequential extraction. *J. Environ. Qual.* 32: 2054-2066 (2003).

Roehi, K.E and K. Czurda, Diffusion and solid speciation of Cd and Pb in Clay liners. *Appl. Clay Sci.* 12(5):387-402(1997).

Salim, L. A., C. J. Miller, J. L. Howard. Sorption Isotherm - Sequential Extraction Analysis of Heavy Metal Retention in Landfill Liners. *Soil Sci Soc Am J* 60:107-114(1996).

Schulthess, and C.P. Huang, Adsorption of heavy metals by silicon and aluminum oxide surface on clay minerals. *Soil Sci Soc Am J.* 54:679-688(1990).

Tessier, A., P.G.C. Campbell, M. Bisson, Sequential extraction procedures for the speciation of particulate trace metals. *Anal Chem* 51:844-851(1979).

Vahid, R., Q. Amir, R.G., and M. Sedighi, Relationship between Mineral Type and Sorption Characteristics of soil liner of Hamedan landfill. Proceeding of 2nd International Symposium on Contaminated sediments. 170-174: (2003).

Welp, G.. Inhibitory effects of the total and water-soluble concentrations of nine different metals on the dehydrogenase activity of a loess soil. *Biology and Fertility of Soils*, 30:132-139(1999).