

## Study on retention form of heavy metals in three polluted soil of North Maharashtra region

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### ABSTRACT

In the present investigation three soils contaminated by heavy metals were characterized as clay loam, loam and sandy clay loam. Their organic matter, pH and saturated hydraulic conductivity ( $K_s$ ) ranged from 5.4 to 9.9%, 4.2 to 6.3 and 1.1 to  $4.0 \times 10^{-4}$  cm/s, respectively. The metal content (in mg/kg) were, (1) Cr: 840, (2) Mn: 868, (3) Hg: 1280 and (4) Pb: 1664 with (5) Zn: 1029 for the sandy clay loam. As apposed in  $MgCl_2$  and  $CaCl_2$ ,  $BaCl_2$  was found to better exchange the heavy metals in all 3 soils. With  $BaCl_2$  31% to 70% of Cd and Zn were exchanged while only 17% to 20% of Hg & Pb were exchanged. By sequential extraction on all three soils, most of the heavy metals were found to be bound to Fe / Mn oxides and the organic fraction (30% to 40%) except for Cd and Zn which were mainly present on the exchangeable fraction (63% to 87%).

**Key words:** Sequential extraction, soil contaminated by heavy metals, characterization and metal retention in the soil.

### INTRODUCTION

The contamination of soil and ground water by heavy metals is an ongoing problem in developed and developing countries because of the current anthropogenic practices of mining and garbage land fillings. Subsoil polluted by heavy metals is subjected to leaching leading to the contamination of groundwater reservoirs and drinking water supplies. To be successful on a specific site, the remediation technique must be selected according to the form of retention of heavy metals on the soil particles. Sequential extraction of heavy metals from contaminated soil or sediments is used to identify the forms of heavy metals retained in the soils. This technique consists in submitting the soils to the successive action of a series of reagents with different chemical properties being capable of either creating weak acidic conditions, change in the redox potential of solution or oxidizing complexing agents. These agents extract a fraction of the heavy metal

linked to a specific form of retention. In recent years sequential extraction procedures have been used increasingly for environmental studies estimating the relative bonding strength of metals in different forms of retention. The knowledge obtained from such extraction indicates the mobility and the solubility of the metal in water. (Rule and Alden 1992, Dudka and Chlopecka, 1990).

The objective of the present study was to use sequential extraction procedure to characterize the forms of retention of various heavy metals in contaminated soils. The result of this study can be quite helpful in designing a remediation of site contaminated by heavy metal.

### MATERIAL AND METHODS

The experimental soil and their preparation: Soil samples were obtained from a site contaminated by various heavy metal. The moist

soil samples were air dried and sieved to remove the particles greater than 2mm. The soil samples were homogenized and kept in 1 plastic bags for further analysis.

Physical Chemical characteristic of soil: The experimental soils were characterized physically by determining their particle size (Hydro method and field method), bulk density (core method for disturb soil), particle density (pycnometer), porosity and saturated hydraulic conductivity, potassium (constant head method).

#### **The experimental soils were also analyzed chemically for-**

Water and Buffer pH, Electrical Conductivity, Bulk Density, Organic matter, Separation of particles, Heavy Metal Contents-(Cadmium, Nickel, Chromium, Zinc); Water Holding Capacity, Sodium, potassium

The pH and buffer pH of the soil measured by soaking them in deionised water. The electrical conductivity (E.C.: Ms/cm) of the soil supernatant in deionised water was also measured in electrical conductivity meter. The cation exchange capacity (CEC in mol (+)/kg) was calculated by exchanging heavy metals and other cations present in contaminated soil with Barium Chloride solution. Barium does not interfere with sulphate ion to form Barium sulphate, because of Lead / Mercury which forms very stable sulphate compound if soluble sulphate is present. All metals except sodium and potassium were determined by colorimetric method (NEERI 1995). Sodium and potassium were measured by flame emission spectrophotometer (Perkin Elmer).

The organic matter was measured by a wet dichromate oxidation technique except for cadmium, chromium, nickel and zinc. All metals extracted from the soil sample such as cadmium, chromium, nickel and zinc were determined by colorimeter.

Heavy metal exchangeable with  $MgCl_2$ ,  $CaCl_2$  and  $BaCl_2$ : One gram of experimental soil i.e. clay, loam and sandy was suspended in 25 ml 0.1M  $MgCl_2$ ,  $CaCl_2$  and  $BaCl_2$  separately in 35 ml polycarbonate tubes. The pH of each solution was

adjusted to 4-6 using dilute hydraulic acid. The resulting samples were shaken for 2 hours at 20°C and then centrifuge to separate the soil and liquid phase at 10,000 Rpm for 20 minutes. The supernatant was collected and analyzed for heavy metals. Similarly, the soil samples were also extracted in distilled water without addition of  $MgCl_2$ ,  $CaCl_2$  and  $BaCl_2$  solutions as a control experiment. All these experiments were carried out in triplicate.

## **RESULTS AND DISCUSSION**

Physical and chemical characterization of the soil: Both the hydrometer and field methods for soil particle size distribution indicated that the texture of the three experimental soils were clay loam, loam and sandy clay loam, respectively. The low particle density of all three soils ranged from 2.0 to 2.1 g/cm<sup>3</sup> and was explained in part by their high organic matter content ranging from 5.4 to 9.9%. The K<sub>s</sub> of each soil ranged from 1.1 to 4.0 x 10<sup>4</sup> cm/s and increased in parallel with their porosity and texture. All these soils were acidic in nature with a pH (in water) of 4.2, 5.1 and 6.3, respectively. Their EC decreased with pH probably as a result of soil particles binding strongly the metals and salts as soil pH increased. The results of the physical and chemical characterization of the contaminated soils are incorporated in Table 1.

The clay loam, loam and sandy clay loam contained 1088, 846 and 1467 mg/kg of total sulfur, of which 9.9, 13.6 and 5.1.8% was sulfide, respectively. The CEC varied from 2.0 to 12.2 cmol (+)/kg for the clay loam to the sandy clay loam. Clay loam has low CEC, may be because of exchangeable sites on soil surface is tightly occupied by heavy metals which is difficult to exchange with  $BaCl_2$  solution. The soil's heavy metal content was: i) for the clay loam, 840, 868, 1280, 1664 mg/kg of Cr, Mn, Hg and Pb, respectively, ii) for the loam, 2797 and 1821 mg/kg of Pb and Cd, respectively and iii) for the sandy clay loam, 1036, 794, 926 and 1029 mg/kg of Pb, Cd, Cu and Zn, respectively. All three experimental soils were found to contain levels of heavy metals and exceeding the permissible levels (MEFQ 1994). The fraction of heavy metals held by either form of sulfur is an indication of their fixation. Sulfates are insoluble when bound to Pb and Hg, but soluble when bound

**Table 1: Physical and chemical characterization of contaminated soils**

Soil Characteristic	Clay Loam	Loam	Sandy Clay Loam
Particle Size			
% Sand	29.0±0.6	49.5±0.5	53.5±0.9
% Silt	36.0±0.4	30.0±1.2	24.0±1.6
% Clay	35.0±1.0	20.7±0.7	22.7±0.7
Bulk Density (g/cm <sup>3</sup> )	08.0±0.0	09.0±0.0	09.0±0.0
Particle Density (g/cm <sup>3</sup> )	2.0±0.0	2.0±0.0	2.1±0.1
Total Porosity (%)	45.4±0.1	44.1±0.2	48.0±0.4
K (cm/s)	1.1±0.1x10 <sup>-4</sup>	1.3±0.1x10 <sup>-4</sup>	4.0±0.2x10 <sup>-4</sup>
EC (mS/cm)-water	9.2±0.2	8.0±0.2	2.3±0.2
PH-water	4.2±0.0	5.1±0.1	6.3±0.1
-CaCl <sub>2</sub>	4.3±0.1	5.2±0.1	6.0±0.0
CEC (cmol (+)/kg)	2.0±0.2	4.7±0.0	12.2±0.2
Sulfur (mg/kg)-total	1088.0±2.4	846.0±2.0	1467.0±19.5
-as SO <sub>4</sub> <sup>2-</sup>	980.0±4.8	731.0±4.8	705.6±10.5
-as S <sup>2</sup>	108.2±7.2	115.0±2.8	761.5±9.6
Organic Matter (%)	9.9±0.1	5.4±0.1	7.1±0.1
Heavy Metals (mg/kg)			
Cr (Total)	840	-	-
Mn	868	-	-
Hg	1280	-	-
Pb	1664	2797	1036
Cd	-	1821	794
Cu	-	-	926
Zn	-	-	1029

**Table 2: Heavy metal concentrations in the geo-chemical phase of soil**

Soil	Geo-chemical Phase (mg / kg)					Total
	Water	Ex	Fe-Mn Oxides	Organic Matter	Residual	
	<b>Clay Loam</b>					
Cr	2.1±0.5	67.0±7.0	190.6±7.0	486.9±7.2	84.0±3.5	832.2±13.0
Mn	183.0±6.6	10.0±6.4	392.2±12.0	198.9±12.3	84.3±2.8	868.1±2.6
Hg	48.0±1.5	71.7±6.0	266.0±10.0	766.0±8.4	123.0±2.0	1273.3±21.7
Pb	36.0±2.0	411.6±2.0	509.0±17.8	670.0±9.2	54.4±10.1	1624.3±26.1
	<b>Loam</b>					
Cd	276±10.1	1144.0±19.2	222.4±7.0	80.0±1.6	13.2±1.8	1736.0±28.0
Pb	22.4±1.5	731.5±9.5	1138.0±13.3	536.2±14.3	284.0±6.0	2721.4±32.5
	<b>Sandy Clay Loam</b>					
Cd	5.5±0.3	687.6±7.5	81.4±2.8	12.2±3.2	ND	786.8±3.2
Cu	17.5±1.2	256.1±6.6	273.2±8.5	287.0±13.5	78.2±3.8	913.0±24.3
Pb	46.6±1.9	96.1±10.3	431.8±16.0	415.1±6.2	8.7±2.0	998.4±21.4
Zn	9.8±0.3	687.0±8.1	178.2±6.4	42.0±8.5	97.0±7.6	1013.4±25.6

Water (W): water soluble, Ex: Acetic acid (HAc)-extractable, the values are the average of the triplicates.

to Cu, Zn and Cd. Thus, Pb and Hg are less mobile in the presence of sulfates. Metals have a strong affinity for sulfides and are therefore precipitated in the presence. Metal sulfide such as PbS, CuS, NiS, ZnS and AgS, are stable under anaerobic condition, but they become unstable and oxidize when exposed to air at the soil surface. The reaction under aerobic conditions produces sulfuric acid, which increases the solubility of heavy metals and promotes their mobility (Yong *et al.* 1992).

### Sequential extraction

The results of the sequential extraction of the three contaminated soils are incorporated in Table 2. Heavy metals retained in different fraction of soils are shown in Figure 2.

### Water soluble

For all 3 experimental soils, the water soluble fraction was generally small or almost nonexistent for Zn, Cu, Pb, Cr and Hg. Water extractable Mn in the clay loam was found to be 21.1 %, whereas for all other metals it was less than 3.7 %. 15.2% of Cd in the loam was water extractable, whereas Pb was found to be negligible (0.8%). Water extractable Pb, Cd, Cu and Zn from the sandy clay loam in water medium was found to be 4.5, 0.70, 1.9 and 0.95%, respectively (Table 2).

### Acetic acid-extractable

In the clay loam, the extractable fraction of Pb was found to be 25% of the Pb, but less than 8% of the other metals. With the loam, Cd was mainly bound in extractable (or exchangeable) fraction (63%), whereas 26% of the Pb was found in extractable fraction. The percentage of Cd, Cu, Pb and Zn in the sandy clay loam, bound to the extractable soil particle site was 87, 28, 9 and 67%, respectively (Figure 2) because Cd and Zn are chemically similar, their adsorption on the soil particles were similar, as expected (Mat *et al.* 1994).

### Metal oxide fraction

In the clay loam, the Fe/Mn oxides accounted for a major portion of the Cr, Mn, Hg and Pb, which were calculated to be 23, 45, 21 and 31%, respectively. In the loam, 40% of the Pb was found bound to Fe/Mn oxides, whereas only 12 % of the Cd was found on this fraction. In the sandy clay loam, the Fe/Mn oxides had bound 30% to 40%

of the Cu and Pb, whereas 15 and 17% of the Cd and Zn had been bound by this form (Table 2), Lead tends to have a high affinity for the Mn/Fe oxides in partially anaerobic condition (Mat *et al.* 1994). The oxides/hydroxides of Fe and Mn and organic fractions are considered to be the most important geochemical components for retaining heavy metals in soils and sediments (Tessier *et al.* 1985, Rule and Alden 1992, Young and Harvey, 1992). However, the adsorption of metals by these fractions is largely dependent on their overall abundance relative to each other (Young and Harvey, 1992).

### Organic fraction

High levels of heavy metals such as Cr, Mn, Hg and Pb were found on the organic fractions. In the clay loam, these levels were 58, 23, 60 and 40%, respectively. In the loam, the organic fraction held 32% of the Pb, but only 4% of the Cd. This fraction retained significant amounts of Cu (31%) and Pb (40%) in the sandy clay loam, but insignificant levels of Cd and Zn (Table 2). Most metals in anaerobic sediments are expected to be associated with the organic/sulfide fraction (Rule and Alden 1992).

The presence of high organic matter (5.4 to 9.9%), may increase anoxic conditions in sediments (Ahmad, 1993). Soils of this nature normally have high levels of hydrogen sulfides forming insoluble metal sulfides except for Mn and Fe, which are not easily exchangeable. For the three experimental soils, the organic/sulfide fraction contain a significantly high levels of Cu (31 %), Pb (40%) Hg (60%) and Cr (58%), reflecting its high affinity for heavy metals because of its ligands or groups that can form chelates with the metals (Yong *et al.* 1992). The relevant functional groups present in organic matter are amino, imino, carboxyl, phenolic, alcoholic, carbonyl and sulfhydryl. With increasing pH, the stability of the complexes is likely to increase because of the increased ionization of the functional groups. Nevertheless, Cu will maintain stable complexes over a wide range of pH (Jones and Jarvis, 1981). The order for the stability of heavy metals complexes is as follows:  $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$ . Heavy metals associated with sulfides can be available into reducible, carbonate and exchangeable fractions after an increase in the redox potential (Rule and Alden 1992).

### Residual fraction

Metals in this fraction are generally considered to be bound within lattice of silicate minerals and can become available only after digestion with strong acids at elevated temperature. This fraction is not considered to be significantly large and is important only in completing mass balance calculations. Heavy metals in the residual fraction were found to be less than 10% in all three soils. Cadmium was found to be undetectable, whereas Pb was found at levels of 10% (means 150-250mg/kg Pb bound in silicate mineral lattice that are still higher than clean up criteria of Pb for soil, which is 50mg/kg).

### Exchangeable fraction

Heavy metal in the exchangeable fractions is weakly bound and it is expected that this will easily leached out of the groundwater or absorbed by aquatic organisms. To extract the exchangeable fraction of heavy metals, ammonium acetate, sodium acetate and magnesium chloride have been used (Tessier *et al.*, 1979). Ammonium acetate has been used extensively in the analysis of soil and sediment to extract the carbonate bound heavy metals. Salts such as  $MgCl_2$ ,  $CaCl_2$ , and  $NaNO_3$  are commonly used as ion-displacing extractants to promote the release of metal ions physically bound by electrostatic attraction to the negatively charged sites on the soil particle surfaces. Metal ions present in the soil in this form are considered to be the most "available" to plants (Soon and Bates 1982). Magnesium chloride,  $CaCl_2$  and  $BaCl_2$  were used for exchangeable heavy metals from polluted soils at varying pH to predict the availability to plants and groundwater contamination.

In all 3 experimental soils, a lesser amount of exchangeable heavy metals was found with  $MgCl_2$  as compared to  $CaCl_2$ . A high amount of exchangeable heavy metals was found when using  $BaCl_2$  because Ba has a larger ionic size ( $1.34 \text{ \AA}$ ) than Ca ( $0.99 \text{ \AA}$ ) and Mg ( $0.66 \text{ \AA}$ ). Same valence with increasing ionic size gives greater replacing power (Yong *et al.* 1992). The concentration of exchangeable metals decreases as pH increases because metals especially Pb, become more tightly bound to the soil surface. Therefore, almost negligible amounts of Pb were found in the sandy clay loam, whereas about 17% Pb was found to be

exchangeable with  $BaCl_2$  in both the clay loam and the loam with a more acidic nature (pH 4.2-5.1). The concentration of Pb as well as those of other metals decreased as the pH increased. For a soil solution pH between 4 and 5, Pb was retained in an exchangeable form, but its adsorption decreases as the pH differed from this limit, to the benefits of the hydroxides and carbonates (Yong *et al.* 1992). A measure of this retention capacity is the cation exchange capacity.

### Summary and conclusions

To evaluate the possible remediation process, three textures of soils polluted by heavy metals were tested for forms of retention. The soils were initially characterized for particle size bulk and particle densities, porosity, k, electrical conductivity, pH, sulfur, organic matter and heavy metals. The soils were characterized as a clay loam, a loam and a sandy clay loam with an organic matter content of  $9.9 \pm 0.1$ ,  $5.4 \pm 0.1$  and  $7.1 \pm 0.1\%$ , respectively. These soils were acidic, with a pH between 4.2 and 6.3. The saturated and hydraulic conductivity varied between  $1.1$  to  $4.0 \times 10^{-4} \text{ cm/s}$ . Heavy metals content in the contaminated soils were (mg/kg):

- Clay loam. Cr: 840, Mn: 868, Hg: 1280 and Pb: 1664.
- Loam Cd: 1821 and Pb: 2797.
- Sandy clay loam. Cd: 794, Cu: 926, Pb: 1036 and Zn: 1029.

For each of the 3 soils, the heavy metals were extracted from each geo-chemical phase (soil fraction) through selective means using the appropriate reagents such as inert electrolytes ( $MgCl_2$ ,  $CaCl_2$  and  $BaCl_2$ ) for exchangeable metals, acetic acid for the extractable fraction, acidic hydroxylamine hydrochloride for the Fe/Mn oxides, acidic hydrogen peroxide for the organic fraction and strong acids ( $HCl-HNO_3$ ) for the residual fraction. From 30 to 40% of the heavy metals were bound to the Fe/Mn oxides and the organic fractions except for Cd and Zn, which were mainly present as exchangeable fractions. The heavy metals in the residual fraction were found to be less than oxides and organic matter.

Magnesium chloride exchanged Hg and Pb in the clay loam at levels of 20 and 5%,

respectively, whereas Cr and Mn were not exchanged. The exchangeable Hg and Pb in the clay loam were found to be 20 and 10% with  $\text{CaCl}_2$  and 20 and 17% with  $\text{BaCl}_2$ , respectively. Both Cr and Mn were not exchangeable with  $\text{CaCl}_2$  and  $\text{BaCl}_2$ . In the loam, 55 to 62% of Cd was exchanged and only 2.4 to 12.6% of Pb with either electrolytes,  $\text{BaCl}_2$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . In the sandy loam, 57 to 70% and 16 to 31.5% of Cd and Zn, respectively, were exchanged with these electrolytes. Magnesium chloride was less capable of exchanging Cd than

$\text{CaCl}_2$  and  $\text{BaCl}_2$ .  $\text{BaCl}_2$  exchanged a higher amount of Zn and Cd than  $\text{CaCl}_2$  while the least amount was exchanged with  $\text{MgCl}_2$ .

The sequential extraction of heavy metals proved a useful tool in understanding the retention mechanism of heavy metals in the soil. For designing the optimum remediation technique for a specific site, this method provides a means of assessing how strongly the contaminants are held in the soil.

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