

## Original Research Article

# Chemical Fractionation of Cadmium, Chromium, Copper and Lead In Petroleum Sludge

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## ABSTRACT

The degradation of environment due to discharge of sludge from industrial sources is real problem in several countries. Samples of sludge from the 3 petroleum refineries were collected and characterized for their pollution characteristics. This study attempted the fractionation of cadmium, chromium, copper and lead in petroleum sludges on the level of the geochemical background to compare the availability and the localization of heavy metals in the sludge samples using sequential extraction procedure. In the analyzed petroleum sludge samples Pb and Cu were the highest while Cd was in the lowest concentration. The highest content of Cu was associated with organic fraction, Cr with residual fraction, Cd and Pb with exchangeable fraction. The petroleum sludge samples from the 3 refineries vary in their physic-chemical Properties and total metal contents. Thus, the variation was also observed in concentration of Cd, Cr, Cu and Pb bound to different phases of sludge samples. The results from this study provide valuable information on the mobility of metals in sludge and may help us in predicting the behavior of sludge, if used for soil amendment and also for their disposal and

## Keywords

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Heavy metals,  
Sequential  
extraction,  
Mobility

## Introduction

Trace metals and metalloids have been used increasingly for the production of a wide variety of materials in the past few decades. Growing public concern has given importance to the fates and health effects of these waste elements in the environments (Takada *et al.*, 2006). The activities of oil producing companies affect the environment and the health of the people living within the immediate vicinity of the crude oil processing plants. The attendant hazards

may trigger processes that may have adverse effects on the ecosystem of such areas.

Petroleum sludge usually accumulates in refineries, because of pump failures, desalter failures, oil draining from tanks and pipelines ruptures. Sludge pits typically contain a semi emulsified mixture of oxidized crude oil, water and miscellaneous solids (together with whatever else has been dumped in them, corrosion product, sand, silt and clay) (Asia *et al.*, 2006).

Petroleum refineries are burdened with the problem of handling large sludge quantities. Around the world, thousands of pits were used as dumping sites for this type of wastes, and now these sites pose a serious risk to the people and surrounding environment because of their potential to contaminate groundwater by leaching through the soil and to migrate as an effect of dust weathering (Elektorowicz and Muslat, 2008 and Wong *et al.*, 2001). In India around 20,000 tons of sludge is generated every year. Around 0.002 to 0.1 % of total crude oil throughput goes as sludge. (Upreti, 2009).

The major limitation of soil application of sludge is the heavy metal contents and their bioavailability to the soil-plant system. It is, therefore, necessary to know the physical and chemical properties of any solid wastes before their disposal and particularly their elemental content, both in terms of total concentrations and the amount that is potentially biologically effective. However, the determination of specific chemical species or binding forms is difficult and often virtually impossible. For this reason, sequential extraction procedures are commonly applied, because they provide information about the fractionation of metals in the different lattices of the solid samples and give information on the environmental contamination risk (Vankateshwaran *et al.*, 2007 and Iwegbue *et al.*, 2007). The mobility of trace metals, their bioavailability and related ecotoxicity to plants depend strongly on their specific chemical forms or ways of binding. As a consequence, these are the parameters that have to be determined rather than the total elemental content in order to assess toxic effects and to study geochemical pathways (Kazi *et al.*, 2005 and Parkpain *et al.*, 2002).

The aim of our work was to apply a five-step sequential extraction procedure

proposed by Tessier *et al.* (1997), originally designed for sediment analysis, to sludge samples to fractionate cadmium, chromium, copper and lead in petroleum sludge on the level of the geochemical background for assessing mobility of potentially toxic elements and their movement into waterways or other components of ecosystem.

## **Materials and Methods**

### **Sample collection**

The petroleum sludge used was obtained from the bottom of effluent treatment plant (ETP) of three different petroleum refineries located in different parts of India. (Sludge I- Hindustan Petroleum Corporation Ltd. (HPCL), Mumbai; Sludge II- Reliance Petroleum Ltd. (RPL), Jamnagar Gujarat; Sludge-III Mangalore Refinery and Petrochemicals Ltd. (MRPL), Mangalore, Karnataka). Grab sample of sludge was collected in wide mouth polypropylene jars. The samples were dried, grounded and passed through 2 mm sieve and used for further analysis. All the reagents used for the analysis were of analytical grade (Merck, Darmstadt Germany) and the element's standard solutions used for calibration were prepared by diluting a stock solution of 1000 mg l<sup>-1</sup> of the given element supplied by Merck in 0.1 M HNO<sub>3</sub>.

### **Physico-chemical characterization**

Sludge samples were analyzed by the methods described by Jackson (1973) for various physico-chemical properties such as pH, electrical conductivity, organic carbon, soluble cations and total nitrogen. The pH and electrical conductivity was measured by preparing extract of sludge sample with distilled water (1:2). Organic carbon by wet dichromate oxidation with sulphuric acid (Walkley-Black method), total nitrogen was

determined by Kjeldhal method. The quantity of soluble calcium and magnesium was ascertained by EDTA titration and sodium and potassium by Flame photometric method.

The total metal content was determined after digesting the sludge samples with 1:3 ratio of conc. HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. For this 1g of sludge sample was weighed in a 100 ml beaker and was digested with 25 ml of acid mixture. The digestion was allowed to proceed for 16 hrs at 180<sup>o</sup>C. After digestion the solution was filtered into 50 ml flask. The residue on the filter paper was rinsed several times with distilled water making up the solution to 50 ml. Trace metals were analyzed on Atomic Absorption spectrophotometer (AAnalyst 800, Perkin Elmer).

#### **Sequential extraction**

Sequential chemical extraction of trace metals was undertaken using Sequential extraction procedure described by Tessier *et al.* (1979). Extraction was carried out progressively based on an initial weight of about 1.0 g of sludge. The operationally defined chemical fractions and extracting conditions and reagents used for sequential extraction and were as follows:

**Fraction 1: Exchangeable** – Sludge was extracted with 8 ml of 1 M MgCl<sub>2</sub> at pH 7.0 for 1 hr by continuous agitation at room temperature.

**Fraction 2: Bound to carbonate** – To the residue from step 1, 8 ml of 1 M NaOAc (adjusted to pH 5.0 with HOAc) was added and shaken for 5 hrs.

**Fraction 3: Bound to Fe–Mn oxides** – The residue from step 2 was extracted with 20 ml of 0.04 M NH<sub>2</sub>OH·HCl in 25% (v/v) HOAc

for 6 h. The extraction was performed at 960C with occasional agitation.

#### **Fraction 4: Bound to organic matter**

To the residue from step 3, 3ml of 0.02 M HNO<sub>3</sub> and 5ml of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0 with HNO<sub>3</sub>) was added. The sample was heated at 850C for 2 h with occasional agitation. A second 3 ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2.0 with HNO<sub>3</sub>) was then added, and the mixture was heated again at 850C for 3 h with intermittent agitation. After cooling, 5ml of 3.2 M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> were added, followed by dilution to a final volume of 20 ml with deionized water and then continuously agitated for 30 min.

**Fraction 5: Residual phase** – The residue from step 4 was digested with 4 ml Concentrated HNO<sub>3</sub> (70%), 2 ml HClO<sub>4</sub> (60%) and 15 ml HF (40%) to dryness.

The selective extraction was conducted in centrifuge tubes (polypropylene, 50ml) to minimize losses of solid material. Effective separation was achieved between each successive extraction by centrifugation at 8000 rpm for 30 min. The supernatant was removed with a pipette and analyzed for metals under study. After extracting sequentially the extract was analyzed on Atomic absorption spectrophotometer for cadmium, chromium, copper and lead.

An important consideration in the reliability of a sequential extraction data is the per cent recovery relative to a single digestion using a mixture of strong mineral acids for total metal concentration. Recovery is defined as follows:

$$\text{Recovery}_n = \left\{ \frac{\sum_n \text{Sequential extraction procedure}}{\text{Single digestion with strong acids}} \right\} \times 100$$

Where  $Recovery_n$  is the concentration of a given element in the single digestion with strong acids used for reference and the strong acid used for digestion was a mixture of strong acids used in the residual fraction digestion for each sequential extraction procedure.

## Results and Discussion

### Characterization of sludges

Physico-chemical analysis of sludge samples (Table 1) showed increase in pH values from 6.1 to 8.2. Among macroelements, sodium is abundant followed by calcium, magnesium and potassium in all sludge samples. With regard to nutrients organic carbon has shown high values whereas total nitrogen has shown moderate values. The sludge samples was rich in nutrients, as well as macroelements and also the pH of the sludge samples varied from slightly acidic to slightly alkaline which was favorable for the use of sludge for soil amendment. Organic matter and pH are most important factors that control the availability of heavy metals which is depicted in figure 1. The pH seemed to be the one of the promising factor which affects bioavailability and uptake of metals. Thus, pH effects were greater than that of metal complex formation by soluble organic matter. The variation in physico-chemical properties of sludge samples can be attributed to the difference in processing processes of different refineries.

### Total metal concentration

It can be seen that amongst the four metals concentration of Pb and Cu was higher than that of Cr and Cd. All the heavy metal values recorded for the sludges (Table 2) are within the maximum permitted concentration of heavy metals in sludge samples (European legislation, Directive 86/278/EEC).

Sludge sample from HPCL, Mumbai, having acidic pH and moderate organic carbon content, showed high concentration of Cu, Cr, Cd and Pb. In the sample from RPL, Jamnagar, having neutral pH and high organic carbon content, there was higher concentration of Cu and Pb than Cr and Cd. In the sample from MRPL, Manglore, having alkaline pH and low organic carbon content, showed high concentration of Cu, Cr, and Pb while that of Cr was low. It can be pointed out that in sample from RPL that even though the organic carbon content was high the concentration of all the four metals was lower than the sample from HPCL, where organic carbon content was low but the metal concentration was high. This can be attributed to the acidic pH of HPCL's sample. This indicates that pH has more influence on metal concentration in sludge samples than organic carbon content.

The Study by Sauve *et al.* (1997) showed that the activities of free metals were a function of soil acidity and total metal loadings in soil. The results are in agreement with the findings of Manceau *et al.* (2000), who observed that cation exchange reactions and complexation to organic matter are important in acidic conditions, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values. The total concentration of cadmium, chromium, copper and lead are compatible with the concentration obtained with the sequential extraction procedure (Table 2).

### Application of sequential extraction scheme

The main environmental hazards of the application of sludge to the soil are the unstable amounts of metals and the formation of combinations with various oxidation degrees of these metals. Their type

and character was established using the sequential extraction method. The different profiles of fractionation found in this paper are resulted indirectly from the geochemical character of each element.

Analysis of sludge samples using selective chemical extraction method to distinguish different phases reveals the data presented in table 3. Per cent distribution of Cd, Cr, Cu and Pb bound to exchangeable, carbonates, Fe/Mn oxides, organic matter and residual fraction of sludge samples is depicted in figure 2. Fractionation of Cd, Cr, Cu and Pb in petroleum sludge samples can be discussed considering the individual metal:

**Copper:** The highest content of Cu was associated with the organic fraction which averages 50.16% and the lowest with exchangeable fractions and averages 3.09%. Carbonate, Fe-Mn Oxides and residual fractions averages 7.13 %, 11.65 %, and 27.97 % respectively. The percentage of Cu fraction in HPCL's sample and RPL's sample follows the order as Organic > residual > Fe-Mn oxide > Carbonates > Exchangeable, whereas in MRPL sample it follows the order as Organic > residual > Carbonates > Fe-Mn oxide > Exchangeable. The presence of Cu in organic fraction was in strong agreement with that observed in many earlier studies in soil and street dusts by Ibrahim *et al.* (2009) and Yalcin *et al.* (2007). They reported presence of copper in organic fraction and was supported by the high formation constants of Cu-organic complexes.

**Chromium:** An average of 22.58% of Cr was associated with residual fraction and to a smaller extent with carbonate fraction (6.88%). concentration of Cr in exchangeable portion averages 22.58 % whereas in Fe-Mn Oxides and Organic fraction it was 18.53 % and 13.85 %

respectively. The distribution pattern of Cr in different fractions in HPCL's Sample was in the order of residual > Exchangeable > Fe-Mn oxide > Organic > Carbonates whereas in RPL's sample and MRPL's sample it was in the order of residual > Exchangeable > Fe-Mn oxide > Carbonates > Organic and residual > Fe-Mn oxide > Organic > Exchangeable > Carbonates respectively. Studies of stone and Marslek (1996) and Belzunce-Segarra *et al.* (1997) reported that Chromium was associated mainly with the residual fraction. The similar results were obtained for all the sludge samples.

**Cadmium:** Cadmium occurs mainly in two forms averaging 30.77 % and 25.40% as exchangeable and carbonates forms respectively. Organically bound cadmium averages 27.32 % whereas Fe-Mn oxides and residual content of Cd averages 16.67 % and 13.07% respectively. The Cd association with different fractions of all sludge samples followed the same order as Exchangeable > Carbonates > Fe-Mn oxide > Organic > Residual. Higher percentage of Cd was associated with exchangeable fraction. The results are similar to the findings of Li *et al.* (2001), who observed that the exchangeable fraction has special importance due to the high mobility of heavy metal from this fraction to the aqueous phase. The results have been widely recognized.

**Lead:** Lead was also distributed in all fractions but the prevailing one was exchangeable fraction which averages 38.73 %. This aspect was in contrast with the findings of the Belzunce-Segarra *et al.* (1997), who stated that the metal was mainly associated with residual fraction. This may be attributed to the high concentration of Pb in sludge samples. The lowest content of Pb was found to be in residual fraction and

averages 12.08 %. The average concentration of Pb occluded in carbonate, Fe-Mn Oxides and organic fraction was 12.15 %, 24.62% and 12.41 % respectively. Results show that the concentration of Pb in residual, carbonate and organic fraction was almost similar. Lead in HPCL's sample have showed the order of association as Exchangeable > Fe-Mn oxide > Organic> residual > Carbonates, whereas in RPL's sample and MRPL's sample followed the order of Exchangeable > Fe-Mn oxide> residual > Organic> Carbonates and Exchangeable > Fe-Mn oxide>Carbonates >residual >Organic respectively.

**Bio-available species:** The exchangeable and bound to carbonate species, corresponding to first two fractions, can release their metal loads by lowering the pH and are more mobile than the other phases, in this way taking the first two phases the results can be ascertained in terms of mobility and hence the bioavailability. Results showed the amounts of Cd, Cr, Cu, and Pb in bioavailable form namely 8.50 % Cu, 31.42 % Cr, 47.42 % Cd and 46.99 % Pb in HPCL's sludge sample, around 9.76 % Cu, 34.54 % Cr, 56.02 % Cd, 52.82 % Pb in Sludge sample of RPL and 12.39 % Cu, 22.40% Cr, 55.06 % Cd and 52.82 % Pb in Sludge sample of MRPL. A relatively high proportion of bio-available fraction of Pb was in the form of exchangeable species and that of Cd as carbonates. Cu was found to be least mobile. Based on this the order of comparative mobility of four metals they can be arranged as Cd > Pb > Cr > Cu.

The above mentioned results can be generalized as; the exchangeable metal fraction comprises metals adsorbed on the surface of the sludge. It is the most accessible, and metal migration from the solid phases to water can occur, e.g. after a change of ionic composition of water or as a

result of a shift of adsorption equilibrium in the system. It is known that the carbonates contain significant trace metal concentration. They can be released as a result of pH decrease. Metals bound to Iron and Manganese oxides fraction are sensitive to the redox potential changes and in anaerobic condition it is thermodynamically unstable. Metals bound to organic matter are temporarily inaccessible. With time passing, the processes of aerobic or anaerobic decomposition of organic matrix induce their release to water or other fractions. Once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

The exchangeable fraction was able to retain trace metals in the order of Pb > Cr > Cd > Cu and the carbonates were able to retain trace metals in the order of Cd > Pb > Cu > Cr. On the other hand, Fe-Mn oxides fraction was able to retain trace metals in the order Pb > Cd > Cu > Cr and the organic matter bounded fraction in the order of Cu > Cr > Cd > Pb. In the residual fraction Cr was predominant. Sequential extraction provides useful information for risk assessment since the amount of metals mobilizable under different changes in environmental conditions can be estimated. Follow-up of trace metal fractionation shows that mobility and bioavailability of trace metals is dependent on other physico-chemical properties of the medium besides total metal contents such as decomposition of organic matter, humic substance content, and pH as well as to the affinity of metals for various chemical forms. It can be seen clearly (Table 2) that the sum of five fractions was compatible with the total metal

concentration. The per cent recovery was satisfactory (90.39–96.11 %) indicating the reliability of the sequential extraction procedure.

The results indicate that the environmental impact of sequential speciation categories

depends on the ease of remobilization, therefore sludge should be dumped in land filling or its agricultural use should be done after stabilization to prevent the leaching of metals which in turn can prevent ground water contamination.

**Table.1** Physico-chemical characteristics of sludge samples

Sr. No	Sample	pH	EC (ds/m)	Ca <sup>++</sup> (mg/l)	Mg <sup>++</sup> (mg/l)	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Organic Carbon (%)	Total Nitrogen (%)
1	HPCL Sample	6.1	0.21	1.76	0.38	6.70	0.40	0.99	0.10
2	RPL Sample	7.2	0.78	2.80	1.24	9.50	1.40	1.59	0.14
3	MRPL Sample	8.2	1.68	5.10	3.44	10.9	1.60	0.13	0.13

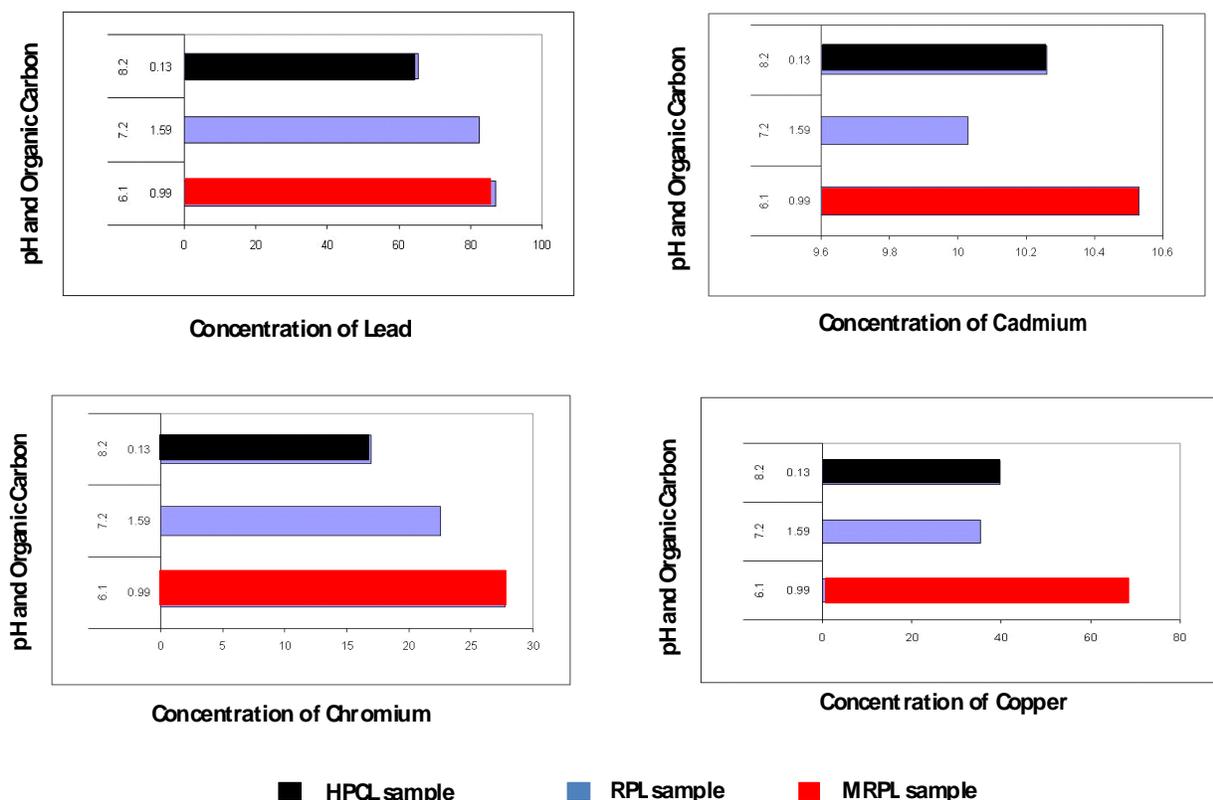
**Table.2** Total metal concentration and its comparison with sum of metal concentrations of five fractions of sludge samples

S.no	Sample	Metals	Total metal concentration (mg/Kg)	Sum of fractions (mg/Kg)	Recovery %
1.	HPCL Sample	Cu	67.82 ± 0.048	61.30	90.39
		Cr	25.73 ± 0.017	23.68	95.75
		Cd	10.53 ± 0.029	9.58	90.98
		Pb	86.97 ± 0.081	80.10	92.10
2.	RPL Sample	Cu	39.64 ± 0.009	36.66	92.48
		Cr	16.94 ± 0.011	15.98	94.33
		Cd	9.03 ± 0.006	8.46	93.69
		Pb	73.52 ± 0.014	70.40	95.75
3.	MRPL Sample	Cu	35.38 ± 0.024	32.12	90.79
		Cr	21.54 ± 0.078	20.00	92.85
		Cd	9.26 ± 0.024	8.90	96.11
		Pb	65.42 ± 0.024	60.92	93.12
<b>European Council Directive 86/278/EEC</b>					
	<b>Metals</b>	<b>Limit Values for Heavy- Metal Concentrations in sludge for use in Agriculture (mg/Kg)</b>			
	Cadmium	20 to 40			
	Copper	1000 to 1750			
	Lead	750 to 1200			
	Chromium	1000 to 1500			

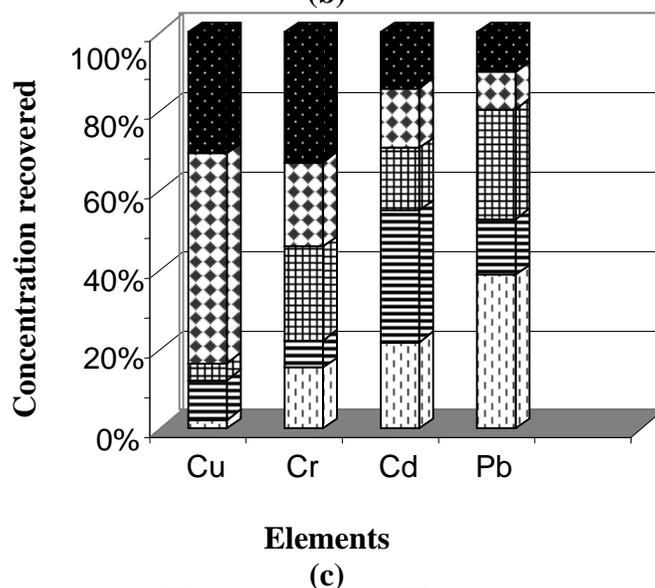
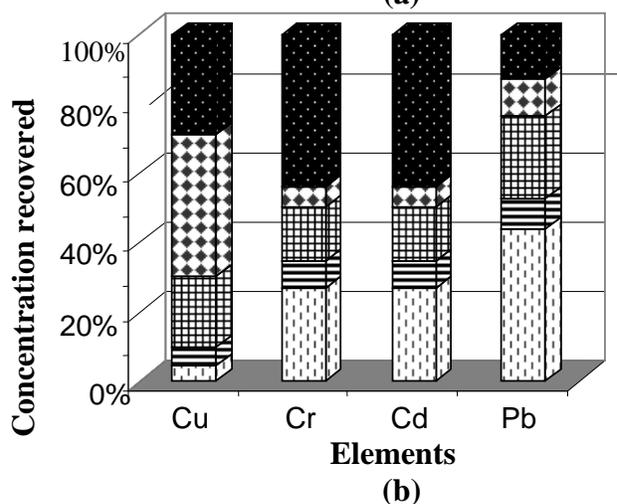
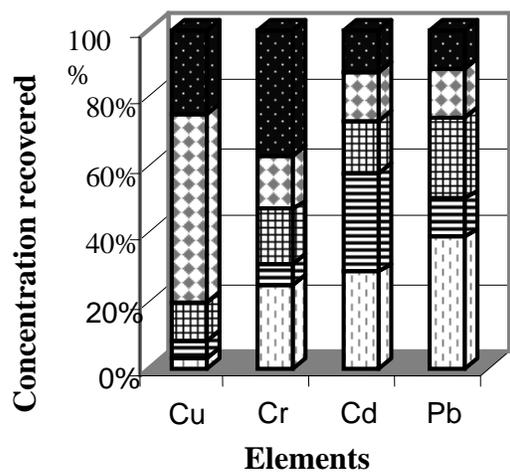
**Table.3** Metal concentrations bound to different phases of sludge samples

Fractions	Elements (mg/Kg)			
	Cu	Cr	Cd	Pb
<b>HPCL Sample</b>				
Exchangeable	1.71 ± 0.009	5.96 ± 0.019	2.72 ± 0.006	36.86 ± 0.081
Carbonates	3.50 ± 0.001	1.48 ± 0.005	2.54 ± 0.001	10.78 ± 0.025
Fe/Mn bound	6.83 ± 0.006	3.84 ± 0.023	1.44 ± 0.004	22.86 ± 0.057
Organic matter	33.92 ± 0.003	3.48 ± 0.004	1.40 ± 0.010	13.74 ± 0.009
Residual	15.34 ± 0.009	8.92 ± 0.004	1.20 ± 0.004	10.86 ± 0.006
<b>RPL Sample</b>				
Exchangeable	1.60 ± 0.008	4.34 ± 0.006	2.20 ± 0.007	30.92 ± 0.205
Carbonates	1.98 ± 0.003	1.18 ± 0.008	2.54 ± 0.001	6.28 ± 0.011
Fe/Mn bound	7.24 ± 0.019	2.52 ± 0.014	1.48 ± 0.003	16.7 ± 0.026
Organic matter	15.48 ± 0.004	0.92 ± 0.003	1.22 ± 0.004	7.62 ± 0.006
Residual	10.36 ± 0.004	7.02 ± 0.004	1.06 ± 0.004	8.88 ± 0.006
<b>MRPL Sample</b>				
Exchangeable	0.68 ± 0.011	3.08 ± 0.079	1.94 ± 0.009	23.6 ± 0.315
Carbonates	3.30 ± 0.106	1.40 ± 0.043	2.96 ± 0.018	8.58 ± 0.187
Fe/Mn bound	1.30 ± 0.000	4.72 ± 0.004	1.40 ± 0.006	16.96 ± 0.319
Organic matter	17.0 ± 0.010	4.22 ± 0.001	1.34 ± 0.008	5.64 ± 0.005
Residual	9.84 ± 0.008	6.58 ± 0.005	1.26 ± 0.008	6.14 ± 0.010

**Figure.1** Variation of total metal concentration as a function of pH and organic carbon content in petroleum sludge samples



**Figure.2** Fractionation of Cd, Cr, Cu and Pb in petroleum sludge, sample-I (a), sample-II (b), and sample-III (c)



Residual
  Organic matter
  Fe/Mn oxides
  Carbonates
  Exchangeable

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