



## ***In Situ Immobilization of Heavy Metals in Contaminated Soil Using Two Organic Waste Materials***

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### **Abstract**

Heavy metals contamination of soil may present potential risks to humans and the ecosystem. Risk assessment studies have shown the impacts of metals to be associated with the soluble and bio-available fractions of the metals rather than their total content in the soils. This has necessitated a new approach – in situ immobilization - in mitigating heavy metals' detrimental impacts. In situ immobilization relies on the addition of amendment(s) to a contaminated soil to effect a reduction in heavy metals' solubility and bioavailability in the soil without the arduous necessity to remove them from the soils. This study explore the utility of two natural wastes materials – rubber sludge (RS) and palm oil mill effluent (POME) – towards immobilization of heavy metals (Zn, Mn, Pb, Cu, Cr, and Cd) in soils. Contaminated soils from automobile workshops in Sapele, Delta State Nigeria, were thoroughly mixed with different doses of organic wastes, and amended samples were incubated for 20 days at ambient temperature before soils samples were analysed for geochemical forms according to procedure describe by Salbu et al. The result suggests that amendments decreases the soluble and bio-available fractions of heavy metals in soils compared to the un-amended control. The apparent order in which these metals were rendered inactive (dormant) was Cd >Pb> Cr > Cu>Mn> Zn with the palm oil mill effluent been relatively more effective than rubber sludge.

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### **Introduction**

Environmental pollution with heavy metals is global phenomenon as a result greater public attentions have been directed at the consequences of contaminated soil environment on human and animal health. Also, there has been ever-growing enthusiasm amongst the scientific community towards the development of technologies for remediation of contaminated sites (Bolan *et al.*, 2003a; Guo *et al.*, 2006; Garauet *et al.*, 2014) *In situ* immobilization (fixation) which relies on the addition of an amendment to a contaminated soil in order to reduce the fraction of toxic metals that is potentially mobile or bioavailable is however, becoming a promising technology for cleaning up contaminated soils and wastes (Zhou and Song, 2004;Guo *et al.*, 2006; Houben *et al.*, 2012). Metals

may be associated with various soil components in different ways, and these associations determine their mobility and bio-availability. Water soluble and exchangeable forms are readily mobile and bio-available, while those integrated into crystal lattices of clay are relatively inactive. The other forms such as those precipitated as carbonate, occluded in Fe, Mn, and Al oxides or complexed with organic matter could be relatively active or firmly bound depending on a combination of physical and chemical properties of soil (Kabala and Singh, 2001; Haung *et al.*, 2007).The need to improve on waste management, and increase resource efficiency, calls for the replacement of virgin resources in numerous applications with treated waste products (Cappuyns,

2015; Yang *et al.*, 2015). Thus, various waste materials such as fly ash, blast furnace slag, steel slag, red mud, bark/sawdust, composted wastes animal manure, industrial sludge and effluents etc have been trialed as immobilizing agents(Martin and

Rubby, 2004; Kumpiene *et al.*, 2008; Ashrafi *et al.*, 2014). This work seeks to explore the utility of two natural wastes materials – rubber sludge and palm oil mill effluent – towards immobilization of heavy metals in contaminated soils.

## Materials and Methods

Soil for the study was obtained from aggregate of top- soil (0-15cm) samples of automobile workshops in Sapele, Nigeria. The physico-chemical properties and total levels of metals in the soil sample are given in Table 1. The two organic amendments used for this study are rubber sludge (RS) and palm oil mill effluent (POME). The rubber sludge was obtained from a rubber factory while the POME was from a local palm oil mill plant at Ajemele, both in Sapele. The physico-chemical properties of the organic waste materials are given in Table 2.

Amendments were thoroughly mixed with soil samples (1Kg) placed in an incubating container at different loading rate; 2, 5, 10, 15, and 20% w/w. De-ionized water was added to each soil mixture to bring it to 60% of its water holding capacity. Amended samples were allow to stand with regular mixing and water losses throughout the incubation

period were compensated by adding fresh distilled water. After 20 days of incubation at ambient temperature, soils were analysed for geochemical forms using the procedure of Salbu *et al* (1998). The Salbu *et al* procedure, separate metals into six operationally defined fractions: reversibly physically sorbed as [F1] water extractable (water soluble metals); [F2] extractable with 1M NH<sub>4</sub>OAc at pH 7 (exchangeable); [F3] extractable with 1M NHOAc at pH 5 (specifically sorbed and carbonate bound); [F4] extractable with hydroxylamine (metals associated (sorbed or occluded) mainly on iron and manganese oxides); [F5] extractable with H<sub>2</sub>O<sub>2</sub> in 1M HNO<sub>3</sub> (strongly complexed by organic matter) and [F6] residual extracted with a mixture of HNO<sub>3</sub> and HClO<sub>4</sub> acid). The analyses were carried out in triplicates and the results are expressed as mean ± standard error of the mean.

Table 1: Physico-chemical properties of the aggregated heavy metals contaminated Soil from automobile workshops in Sapele, Delta state Nigeria

Parameters	Properties (Mean± SE)
pH	5.74± 0.006
Clay (%)	7.80± 0.318
Silt (%)	9.45±0.358
Sand (%)	82.75±0.145
TOC (%)	1.08±0.173
OM (%)	1.85± 0.173
P(mg/Kg)	32.01± 4.162
CEC(cmol/Kg)	11.21±0.260
Zn (mg/Kg)	745.30±7.451
Mn (mg/Kg)	181.61±3.780
Pb (mg/Kg)	42.40±1.798
Cu (mg/Kg)	103.73±2.988
Cr (mg/Kg)	61.80±2.965
Cd (mg/kg)	9.05 ±0.630

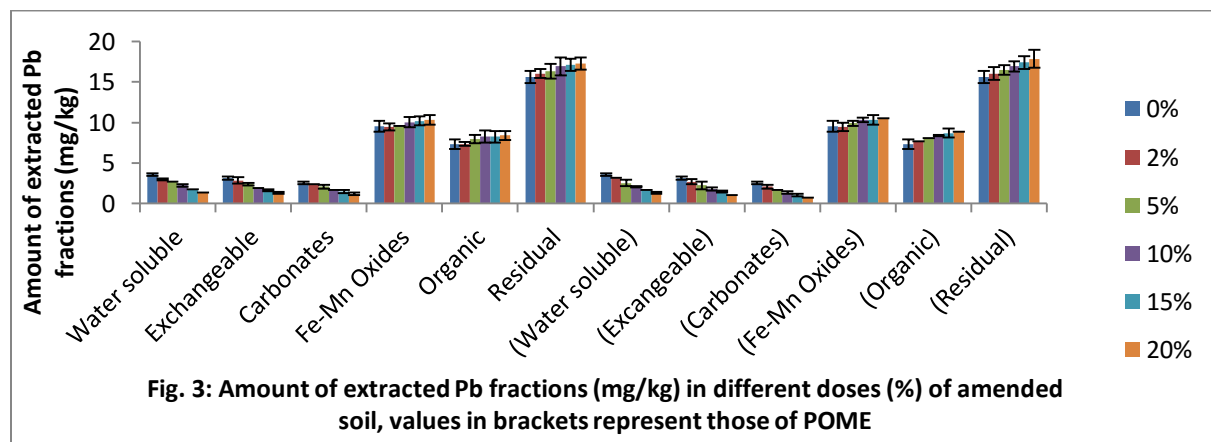
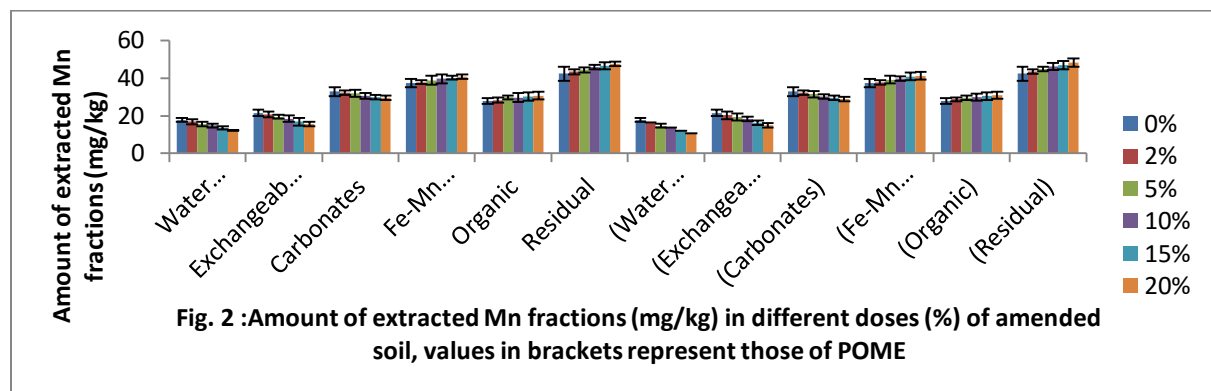
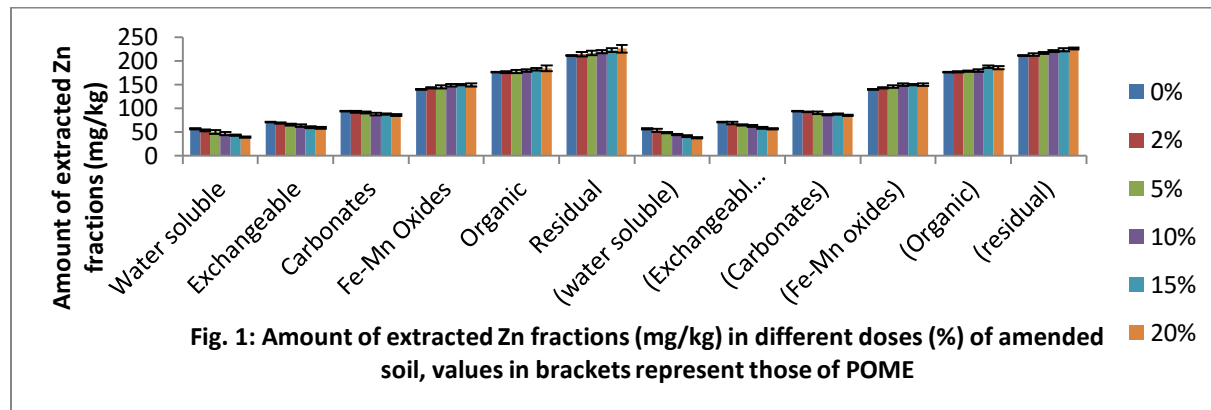
Table 2: Physico-chemical properties of Rubber sludge (RS) and palm oil mill Effluents (POME)

Parameters	Properties (Mean ± SE)	
	RS	POME
pH	4.90 ± 0.000	5.90 ± 0.000
N (%)	2.00 ± 0.231	0.29 ± 0.000
P (mg/kg)	53.02 ± 2.197	298.63 ± 3.121
K (%)	11.70 ± 0.173	27.20 ± 0.636
Mg (%)	3.10 ± 0.520	3.54 ± 0.173
Ca (%)	8.90 ± 0.231	9.60 ± 0.231
TOC (%)	2.20 ± 0.000	2.87 ± 0.231
Zn (mg/kg)	1.00 ± 0.058	3.20 ± 0.000
Mn (mg/kg)	0.10 ± 0.000	0.60 ± 0.058
Pb (mg/kg)	< 0.08	0.20 ± 0.000
CU (mg/kg)	1.20 ± 0.173	2.70 ± 0.173
Cr (mg/kg)	0.10 ± 0.000	0.10 ± 0.012
Cd (mg/kg)	< 0.01	< 0.01

## Results

The geochemical fractions of metals in the soils after treatment with the different doses of rubber sludge and palm oil mill effluent are shown in Fig. 1 – 6. The distribution of heavy metals in various fractions with accompanying treatment with RS and POME showed that metals were increasingly being transfer from the labile pools (water-soluble, exchangeable and carbonates bound fractions) to the more

recalcitrant, non-labile fractions (Fe-Mn oxides, organically complexed, and residual fractions) with added quantities of RS and POME. There was strong negative correlation between the amount of rubber sludge and palm oil mill effluents amendments added to soil and the mobility of the metals in soil (Table 3)



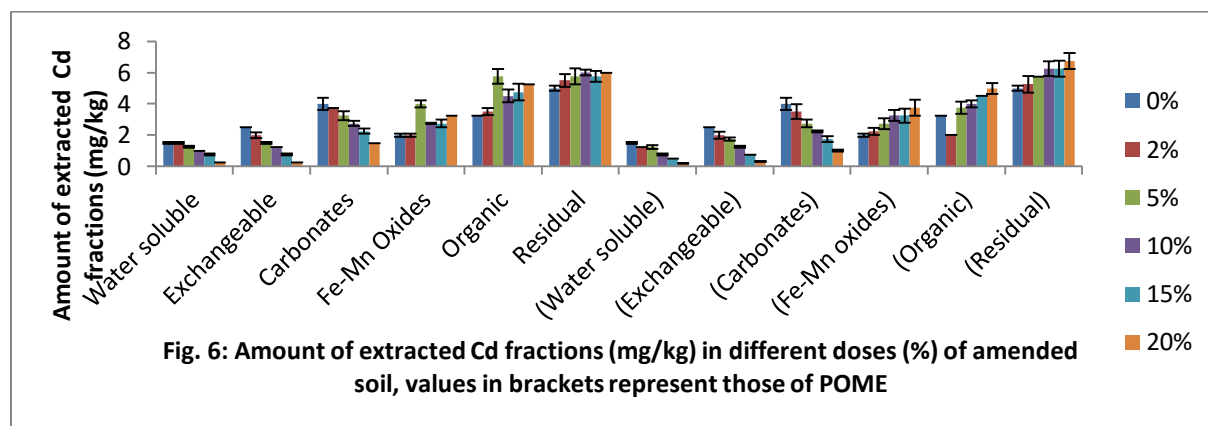
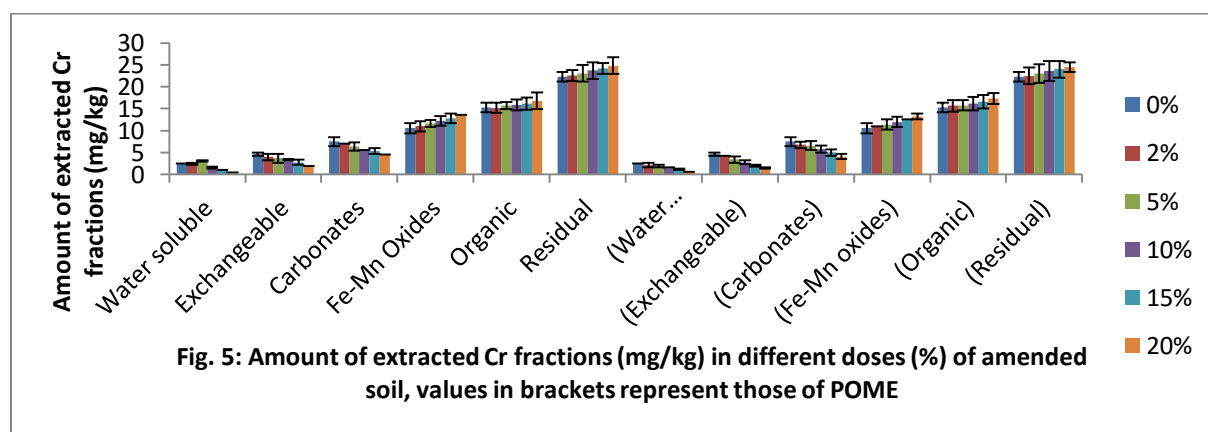
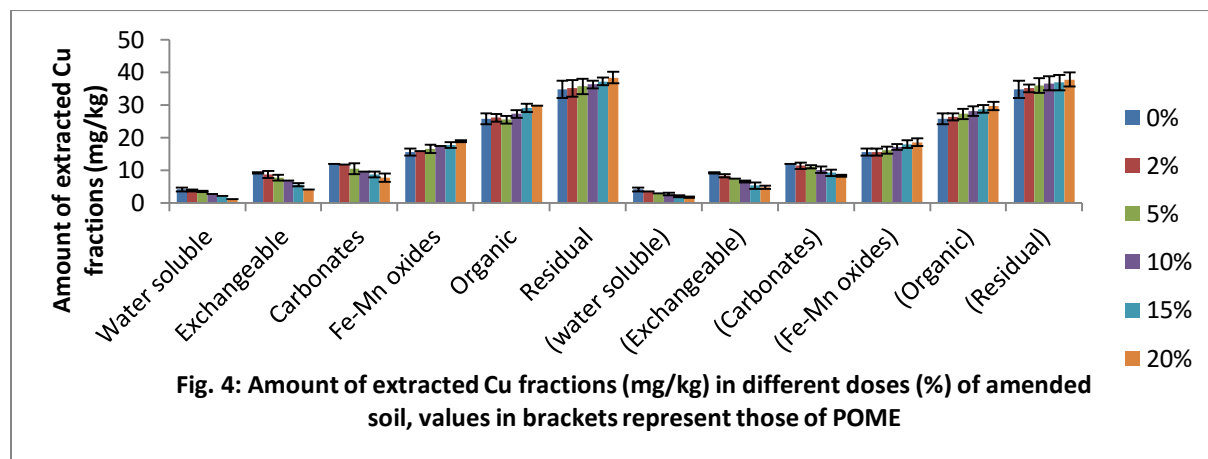


Table 3: Correlation coefficients between mobility index for each metal and amount of amendments added to the soil (values in brackets represent those of POME)

Amendments	Mobility index					
	Zn	Mn	Pb	Cu	Cr	Cd
	-0.9848*	-0.9908*	-0.9896*	-0.9989*	-0.9949*	-0.9923*
	(-0.9781*)	(-0.9895*)	(-0.9765*)	(-0.9934*)	(-0.9723*)	(-0.9953*)

\*significant at the %1 level

Table 4 & 5 show the variation of the values of mobility factor (Mf) and immobilization index (Mf/Mf<sup>o</sup>) with levels of amendments application for rubber sludge and palm oil mill effluents. The results show marked reduction in the mobility of the metals

up to 80% for Cd, 65% for Pb, 56% for Cr, 48% for Cu, 23% for Mn and 18% for Zn, following amendments application with palm oil mill effluent (POME) being relatively more effective than rubber sludge (RS) in fixing the metals in soil

Table 4: Relative mobility factor (Mf) of the heavy metals in the contaminated soil, amended with RS and POME. Values in brackets represent those of POME

Levels of amendments (%)	Zn	Mn	Pb	Cu	Cr	Cd
0	29.62 (29.62)	40.20 (40.20)	22.46 (22.46)	25.07 (25.07)	23.25 (23.25)	43.81 (43.81)
2	28.67 (28.66)	38.95 (38.73)	20.36 (19.34)	23.51 (23.28)	21.54 (21.15)	39.76 (39.05)
5	27.57 (27.36)	37.19 (36.58)	17.52 (15.75)	21.73 (21.36)	19.23 (19.29)	32.93 (32.00)
10	26.42 (25.85)	35.68 (34.94)	14.23 (12.82)	19.16 (19.23)	16.99 (13.55)	27.46 (24.04)
15	25.50 (25.12)	34.05 (33.03)	12.22 (10.33)	16.42 (16.72)	14.74 (13.36)	22.15 (17.72)
20	24.62 (24.19)	32.46 (31.16)	9.78 (7.80)	13.17 (14.84)	11.25 (10.13)	12.21 (8.81)

$$Mf = \frac{F1+F2+F3}{F1+F2+F3+F4+F5+F6} \times 100.$$

Table 5: Relative immobilization Index (Mf/Mf<sup>o</sup>) of the heavy metals in the contaminated soil, amended with RS and POME. Mf = mobility factor for amended soil, Mf<sup>o</sup> = mobility factor for unamended soil. Values in brackets represent those of POME.

Levels of amendments (%)	Zn	Mn	Pb	Cu	Cr	Cd
2	0.97 (0.97)	0.97 (0.96)	0.91 (0.86)	0.94 (0.93)	0.93 (0.91)	0.91 (0.87)
5	0.93 (0.92)	0.92 (0.91)	0.78 (0.70)	0.87 (0.85)	0.83 (0.83)	0.75 (0.73)
10	0.89 (0.87)	0.89 (0.87)	0.63 (0.57)	0.76 (0.77)	0.73 (0.58)	0.62 (0.55)
15	0.86 (0.85)	0.85 (0.82)	0.54 (0.46)	0.65 (0.67)	0.63 (0.57)	0.50 (0.40)
20	0.83 (0.82)	0.81 (0.77)	0.43 (0.35)	0.52 (0.59)	0.48 (0.44)	0.28 (0.20)

## Discussion

The results indicate potentials for RS and POME to immobilized heavy metals in this soil. Minerals and organic soil can bind metals to different degree. The water soluble, exchangeable, and to some extent the carbonate bound forms of metals are weakly bonded to soil and are thus easily released and made bio-available to plants. Organic matter, Fe and Mn hydrous oxides, and clay content are important soil

properties influencing sorption reactions (Bolan and Duraisamy, 2003). Other parameters such as: soil pH, cation exchange capacity (CEC), and redox potentials can also affect metals' mobility in soils (Zhao and Masaihiko, 2007; Lee *et al.*, 2013) In this present study with soil pH 5.74, contributory high pH (5.90) by POME will discourage availability, mobility and redistribution of the metals while contributing low

pH (4.90) by RS would promote availability, mobility and redistribution of the metals (Zn, Mn, Pb, Cu, Cr and Cd) in the various fractions. On the contrary, the presence of certain functional groups such as carboxylic (-COOH), amide (-NH-), hydroxyl (-OH-), and phenolic in the effluents favours complexation between RS/POME and the metals. The prevailing reaction is a function of the amount (treatment) of RS/POME applied to the contaminated soil and other soil physico-chemical properties. The observed trend of increasing concentration of heavy-metals in the Fe-Mn oxides, organic bound and residual fractions as associated with increasing amounts of amendments particularly rubber sludge (RS) suggests that the presence of abundant complexing/chelating sites in RS and POME complexing with the heavy metals ions followed by adsorption onto soil matrices.

The mobile pool of metals is operationally defined as the sum of the water soluble, exchangeable and carbonate bound fractions of the metals (Okieimen *et al.*, 2012). The ratio of this mobile pool to the sum of all fractions of metals in the soil is known as the mobility factor (Mf). High Mf values represent high mobility and potential availability of metals in soil. A soil treatment technique based on reducing the release and mobility/ availability of metal in soil represents a less invasive and effective detoxification process since the toxicity of the metals are related to their mobility and bioavailability. The effectiveness of soil amendment application in reducing subsurface mobility of metals in soil may be evaluated from the immobilization index, the ratio of mobility factor of metals in amended soil Mf, to the value in un-amended soil Mf<sup>0</sup>, (Mf/Mf<sup>0</sup>); the effectiveness of the immobilization process, increase with decrease in the value of the index (Okieimen *et al.*, 2012).

Table 4 & 5 show marked reduction in the mobility of the metals up to 80% for Cd, 65% for Pb, 56% for Cr, 48% for Cu, 23% for Mn and 18% for Zn, following amendments application with palm oil mill effluent (POME) being relatively more effective than rubber sludge (RS) in fixing the metals in soil. These results are indicative of the relative reactivity of the metals with active sites in the organic amendments. Assuming that mobility and availability of the heavy metals are related with their solubility and geochemical forms as reflected in their order of extraction sequence, then apparent mobility and potential availability in the soil after amendments

were Zn > Mn > Cu > Cr > Pb > Cd. The reverse is the case for apparent immobilization effectiveness (i.e., Zn < Mn < Cu < Cr < Pb < Cd). The interaction between clays and organic matter from RS/POME, with formation of organoclay, would have improved the soil adsorbing capacity. Rubber sludge and palm oil mill effluent were least effective in immobilizing Zn and Mn, probably due to ionic competition between them and other heavy metals ions present. Stabilization of multi-elements contaminated soil poses unique challenge as the metals may be present in different concentration and the presence of one contaminant may affect the stabilization efficiency of the other due to competition for sorption sites (Giuffré *et al.*, 2005). The enrichment of the soil in phosphorous, nitrogen, calcium, magnesium, and potassium due to application of RS and POME and consequent change in soil properties might have enhance the adsorption capacity of the soil. Okwute and Isu (2007) also showed an overall increase in CEC of POME soils over non-POME soils. The increase in CEC was attributed to the increase in the pH dependent charge as well as the addition of organic matter from the effluents. Several researchers have also reported increase in pH, potassium, calcium, magnesium and organic matter content on application of POME to soil (Onyia *et al.*, 2001; Iwara *et al.*, 2011; Iyakndue *et al.*, 2017). Phosphate-based materials are well known metal fixing agents in soil through adsorption by phosphate, phosphate anion induced adsorption and precipitation of metals as the phosphates (Cao *et al.*, 2001; Bolan *et al.*, 2003b). The observed difference in relative immobilization efficiency of POME over RS in this soil could be adduced to differences in pH, Phosphate content and other physico-chemical properties that tend to favour stabilization efficiency of POME than RS.

## Conclusion

Amendment of the heavy metals contaminated soil with two natural waste materials –rubber sludge and palm oil mill effluent - increased the stable fractions and decreased the soluble and bio-available fractions of heavy metals in soils. In situ immobilization with these waste materials may thus offer a cost –effective remediation technique for heavy metals contaminated soils. The long term effects on immobilization however need to be studied.

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