academicJournals

Vol. 7(5), pp. 249-258, May 2013
DOI: 10.5897/AJEST12.195
ISSN 1996-0786 ©2013 Academic Journals
http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Full Length Research Paper

Evaluation of copper and lead immobilization in contaminated soil by single, sequential and kinetic leaching tests

R. A. Wuana[1]*, S. G. Yiase[2], P. D. Iorungwa[1] and M. S. Iorungwa[1]

[1]Department of Chemistry, University of Agriculture, Makurdi, 970001, Benue State, Nigeria.
[2]Department of Chemistry, Benue State University, Makurdi, 970001, Benue State, Nigeria.

Accepted 8 May, 2013

The effectiveness of natural clay, calcium phosphate, poultry manure and rice husks as cheap and ecologically non-invasive amendments for immobilizing Cu and Pb in contaminated soil was assessed. A moderately contaminated soil was sampled from a cultivated field in the vicinity of an active waste dump, characterized and amended with the immobilizing agents at 5 to 20% w/w. Single (calcium nitrate), sequential (optimized European Communities Bureau of Reference, BCR method) and kinetic (ethylenediaminetetraacetic acid, EDTA) leaching tests were performed before and after soil amendments. Single extractions showed that metal immobilization efficiencies, E were generally high ($20 \le E \le 81\%$), increased as the agent dose and varied in the order: phosphate > natural clay > poultry manure > rice husks. BCR extractions showed that the agents attenuated Cu and Pb mobilities and induced changes in their fractionation patterns as most of the hitherto mobile fractions became associated with the less bioavailable forms. Two metal forms: readily labile and less labile, with apparent leaching rates k_1 (10^{-2} min^{-1}) and k_2 (10^{-3} min^{-1}), respectively were identified by fitting EDTA leaching data into a two-first-order model. The immobilizing agents suppressed both k_1 and k_2 for Cu and only k_2 for Pb. These agents may reduce risks resulting from Cu and Pb contamination in soil since metal mobility is related to its bioavailability.

Key words: Bioavailability, chemical extraction, contaminated soil, immobilizing agent.

INTRODUCTION

The disturbance and acceleration of nature's slowly occurring biogeochemical cycle of metals by anthropogenic activities have made most soils of rural, urban, agricultural and industrial areas to be contaminated by one or more of the toxic heavy metals (D'amore et al., 2005; Rajaganapathy et al., 2011; Corrochano et al., 2011). The term heavy metal has been widely adopted for a group of metals and metalloids and their compounds probably due to their toxicity in biological systems as well as contamination and persistence in environmental media (Bhat and Khan, 2011). Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, land tenure problems and economic losses (McLaughlin et al., 2000a, b; Suruchi and Khanna, 2011;

---

*Corresponding author. E-mail: raywuana@yahoo.com. Tel: +2348066645047.

Matini et al., 2011). Contamination of soil with heavy metals such as copper and lead particularly appears to be virtually permanent. Copper, for instance, is an essential heavy metal, but in high doses can cause anaemia, liver and kidney damage, stomach and intestinal irritation, while lead is a non-essential heavy metal that affects the functioning of the blood, liver, kidney and brains of human beings (Irmak, 2010; Sarma, 2011). Copper normally occurs in soil from horticultural preparations, copper pipes, irrigation water as well as from additives designed to control algal growth, while lead is a component of most industrial/domestic paints and leaded petrol in addition to untreated sewage from residential areas (Yap et al., 2008; Irmak, 2010). Increasing public concern about environmental and soil contamination has led to the promulgation of national and international regulations to reduce pollution and to remediate polluted sites. Consequently, over the last few decades a great deal of research has been carried out in order to develop strategies for the management of agricultural ecosystems (Chukwuka and Omotayo, 2008), as well as remediation of former industrial sites which have been exposed to diffuse pollution by toxic heavy metals (Finžgar et al., 2006; Belviso et al., 2010). Among the remediation technologies available for contaminated sites, *in situ* (in place) immobilization methods are relatively more advantageous since they are generally less expensive and disruptive to the natural landscape, hydrology and ecosystems than conventional excavation, treatment and disposal methods.

In situ immobilization refers to the reduction of metal bioavailability and leachability in contaminated soils using environment-friendly amendments. Since metal solubility is related to its mobility and bioavailability, metal immobilization may reduce environmental risk. Thus, the success of a strategy for in situ immobilization of metals can be evaluated by the ability to reduce contaminant solubility/extractability, which must also have a long-term effect (Alvarenga et al., 2008). Heavy metal-contaminated soils have classically been ameliorated using additives such as lime, phosphate, red mud, bone meal and organic matter and their effectiveness for field applications have already been demonstrated (Awodun, 2007; Fawzy, 2008; Gatimu et al., 2010a, b; Santos et al., 2010; Florido et al., 2011; Ogbo and Okhuoya, 2011). Most research efforts aimed at assessing the effectiveness of amendments for *in situ* immobilization have either employed one or combination of two single, sequential and kinetic extractions (Cao et al., 2003; Fawzy, 2008; Santos et al., 2010). In this study, single, sequential and kinetic extractions have been conjointly employed to assess the ability of some cheap, non-toxic agents- natural clay, phosphate salt, poultry manure and rice husks at immobilizing copper and lead in a contaminated soil. The study was carried out on a composite soil, sampled from a cultivated field in the vicinity of a waste dump at the Benue Industrial Layout, Makurdi, a rapidly growing city in the Lower Benue River Basin, a major agricultural zone in North-Central Nigeria from January to May, 2011.

MATERIALS AND METHODS

Materials

Multipurpose flask shaker (Model TT 12F, Techmel and Techmel, Texas, US), digitally operated high speed centrifuge (Model TGL-16G, Shanghai, China), pH meter (Fisher Hydrus 300 model), normal laboratory glassware (borosilicate), polyethylene vessels, electronic weighing balance (Gallenkamp 80) were used. A flame atomic absorption spectrophotometer (Buck Scientific Model 200A, Norwalk, Connecticut, US) was used for metal assay. Natural clay, phosphate salt [$Ca_3(PO_4)_2$], poultry manure and rice husks were used as immobilizing agents.

Sample collection, pre-treatment, characterization and amendment

Five top (0 to 20 cm) soil samples were collected at a cultivated field around an active waste dumpsite at the Benue Industrial Layout, Makurdi (7.44°N, 8.33°E), North-Central Nigeria. The soil samples were collected into polythene bags and taken to the laboratory, air-dried, ground and sieved to give <2 mm particle size and composited as the parent soil. Standard operating procedures were used to test soil properties: pH (1:25 soil/water ratio) (Maxted et al., 2007), bulk density (CDPRHAP, 1998), particle size distribution by the hydrometer method (Bouyoucos, 1962), organic matter by the Walkley-Black rapid acid dichromate oxidation (Schumacher, 2002), cation exchange capacity by the summation of Na, K, Ca and Mg (Jackson, 1962; Black, 1965), soil total metals by aqua regia digestion (ISO, 1995). Similarly, the immobilizing agents: natural clay, phosphate salt, poultry manure and rice husks were characterized, as the case may be, in terms of some of the afore-mentioned attributes and evaluated for their effectiveness at immobilizing Cu and Pb in contaminated soil. Different portions of a fixed mass of soil (1 kg) were separately put in polyethylene vessels and treated with 0, 52.6, 111.2 and 250 g (0, 5, 10 and 20% w/w) of the agent. Each treatment was performed in triplicate and incubated for 1 month at ambient temperature.

Single batch extractions

Portions of the unamended and amended soils were used. The single extractant was expected to leach the plant available metals. This scheme adopted the procedure of Mench et al. (1994). That is, 10 g of soil (<2 mm) was shaken with 0.1 M $Ca(NO_3)_2$ (50 mL) for 2 h at 20°C. Extracts were filtered through ashless filter paper. The 0.1 M $Ca(NO_3)_2$ extracts were acidified with 14 M HNO_3 (1.0 mL) to prevent metal adsorption.

BCR sequential extractions

The geochemical forms of Cu and Pb viz: extractable, M_1; oxide-bound, M_2; organic matter-bound, M_3 and residual, M_4 fractions in both the pre-amended and post-amended soil samples were assessed by the sequential extraction scheme proposed by the European Communities Bureau (BCR method) described by Ure et al. (1993).

Table 1. Physicochemical properties of the parent soil and immobilizing agents used for the study.

Property	Parent soil	Natural clay	Phosphate salt	Poultry manure	Rice husks
pH	5.7±1.3	6.0±0.7	8.1±0.1	6.9±0.0	6.5±0.5
Sand	34.8±2.5	34.8±2.5	-	-	-
Silt	22.0±2.2	10.0±2.0	-	-	-
Clay	31.0±3.1	55.2±4.6	-	-	-
OM (%)	5.8±0.3	0.9±0.1	-	45.3±1.3	-
CEC (meq/100 g)	10.6±2.2	13.0±0.5	-	7.9±1.0	-
Total Cu (mg/kg)	173.0±7.5	0.5±0.1	-	100.6±3.0	5.5±0.0
Total Pb (mg/kg)	133.0±6.7	0.9±0.0	-	1.5±0.0	1.5±0.1

Mean ± SD, n = 3.

Kinetic extractions

One gram portions of both the unamended soil and its sub-samples treated with the immobilizing agents (at 20% w/w) were separately transferred to 100 mL beakers provided. Aliquots of 50 mL of the extracting solution (0.05 M ethylenediaminetetraacetic acid, EDTA) were added to each of the beakers at a solid/solution ratio of 1:50 and the mixtures was stirred manually, homogenized with a vortex mixer, and then kept on a multipurpose flask shaker. At the elapse of selected time intervals: 10, 20, 30 min and 1, 2, 6, 10, 12, 16 h; the slurries were filtered through an ash less filter paper, centrifuged and kept for Cu and Pb assay.

RESULTS AND DISCUSSION

Physicochemical characteristics of parent soil and immobilizing agents

Some physicochemical properties of the parent soil and immobilizing agents are reported in Table 1. Textural analysis characterized the parent soil as sandy clay loam. The other properties were: pH (5.7), organic matter (5.8%), cation exchange capacity (10.6 meq/100 g). Soil total Cu and Pb were 171.0 and 133.0 mg kg^{-1}, respectively indicating moderate contamination with Cu and Pb. Mean values of the physicochemical attributes of natural clay were: pH (6.0), sand (34.8%), silt (10.0%), clay (55.2%), organic matter (0.9%), cation exchange capacity (13.0 meq/100 g). The only attribute measured for phosphate salt was pH value of 8.1. Poultry manure had the following attributes: pH (6.9), organic matter (45.3%), cation exchange capacity (7.9 meq/100 g) and total Cu and Pb, 100.6 and 1.5 mg/kg, respectively. The markedly high concentration of Cu in poultry manure may be attributed to its addition as a growth promoter to feed preparations (Wuana and Okieimen, 2011) and so during soil amendment, the manure needs to be scrupulously added at such doses that would not trigger short-term leaching pulses of the heavy metals in the soil. For rice husks, the parameters measured were: pH (6.5), total Cu and Pb (5.5 and 1.5 mg/kg, respectively). Rice husk is believed to be essentially composed of lots of silica, the organic compound constituent being mainly cellulose, hemicellulose and lignin (Okieimen et al., 2007). The efficiency of an agent to immobilize heavy metals in soil will be greatly influenced by the pH, organic matter content and cation exchange capacity.

Assessment of metal immobilization efficiency

The effectiveness of natural clay, calcium phosphate, poultry manure and rice husks as low-cost, non-toxic and ecologically non-invasive amendments for immobilizing Cu and Pb in contaminated soil was assessed by performing chemical leaching tests viz: single $Ca(NO_3)_2$ extractions to determine plant available metals, BCR sequential extractions and EDTA kinetic extractions before and after soil amendments.

Single calcium nitrate extractions

The results of $Ca(NO_3)_2$ extractions carried out on the unamended and post-amended soils are presented in Table 2. The immobilization efficiency, *E (%)* was calculated using Equation 1.

$$E\,(\%) = \left(\frac{M_o - M_e}{M_o}\right) \mathrm{x}\,100 \qquad (1)$$

Where, M_e = equilibrium extractable amount of metal in the amended soil (mg/kg); M_o = initial extractable amount of metal in the unamended soil (mg/kg). The results are illustrated in Figure 1.

Prior to amendment, pseudototal Cu and Pb concentrations in the parent soil were 173.0 and 133.0 mg/kg. With increased dosage of the immobilizing agents, however, these concentrations decreased generally after one month of equilibration. For natural clay, the range of immobilization efficiencies, *E* for Cu and Pb were $45.8 \leq E \leq 75.4\%$ and $38.9 \leq E \leq 77.5\%$, respectively.

Table 2. Calcium nitrate-extracted Cu and Pb concentrations (mg/kg) in soil before and after amendment with various doses of immobilizing agents.

Agent	Dose (% *w/w*)	Cu	Pb
Parent soil	0	135.7±9.5	90.4±7.5
Natural clay	5	73.5±7.9	55.2±9.8
	10	61.3±6.6	40.4±9.0
	20	33.4±6.0	20.3±3.6
Phosphate salt	5	60±5.2	40.5±8.6
	10	50.9±6.3	28.2±8.0
	20	25.4±7.5	18.4±5.0
Poultry manure	5	90.7±6.1	60.2±7.0
	10	80.3±5.7	50.4±5.4
	20	40.4±4.0	25.3±2.4
Rice husks	5	102.3±7.0	72.1±5.3
	10	90.2±7.3	51.4±5.0
	20	50.0±6.0	37.6±4.5

Mean ± s.d, n = 3.

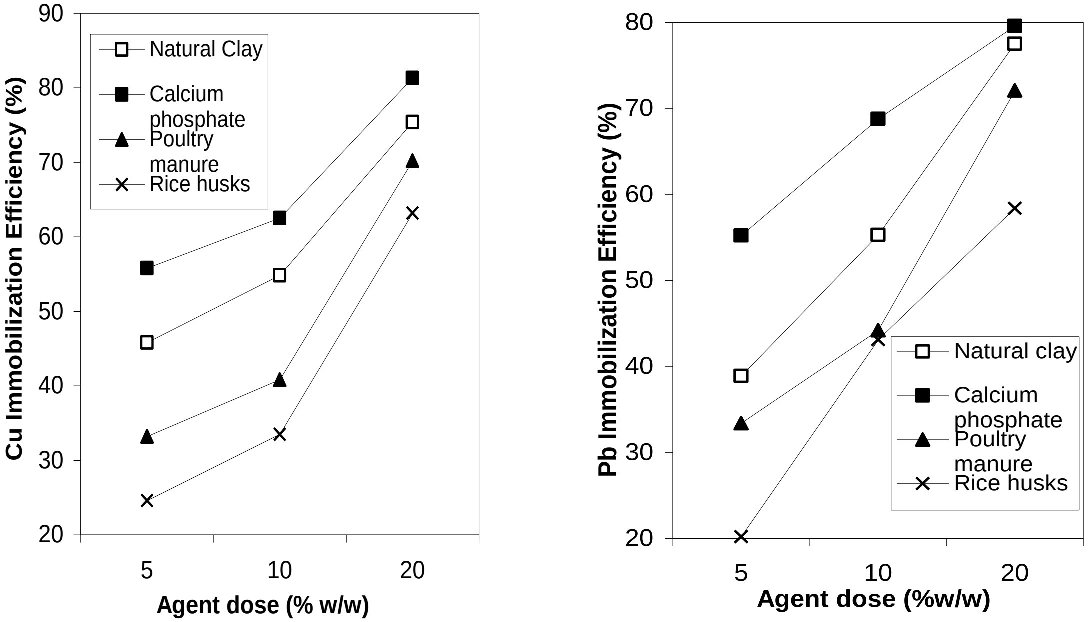

Figure 1. Efficiency of Cu and Pb immobilization in soil amended with different agents.

Natural clay consists mainly of clay mineral which is made up of silica (tetrahedral) layer alternating with one alumina (octahedral) layer held rigidly with hydrogen bonding. Clay may be generally described as 40% aluminum oxide, 46% silica oxide and 14% water. Soil amendment with clay will be more profitable at doses that bring the percentage clay to about 20% (Nara, 2010). Metal immobilization by this agent may occur through adsorption on the silica and alumina surfaces and/or through ion exchange.

Calcium phosphate showed immobilization efficiencies in the range of $55.8 \leq E \leq 81.3\%$ and $55.2 \leq E \leq 79.6\%$ for Cu and Pb, respectively. The mechanism of metal immobilization by calcium phosphate may be through adsorption onto the negative functional group on the phosphate ions (Cui et al., 2010).

The ranges of E values recorded for poultry manure were $33.2 \leq E \leq 70.2\%$ for and $33.4 \leq E \leq 72.1\%$ for Pb. The addition of poultry manure raises both the soil organic matter content and pH, increases the soil metal binding ability, thereby reducing their mobility and leachability.

Rice husks showed E values in the range of $24.6 \leq E \leq 63.2\%$ and $20.2 \leq E \leq 58.4\%$ for Cu and Pb, respecttively. Metal immobilization by rice husks may also be through adsorption as it consists of silica oxide and adsorbing organic compounds such as cellulose and hemicellulose.

Overall, E values ranged between $20.2 \leq E \leq 81.3\%$ and varied in the sequence: calcium phosphate > natural clay > poultry manure > rice husks for both Cu and Pb. The E values represent good efficiencies of the agents that can be recommended in field studies for Cu and Pb immobilization in contaminated soil.

Assessment of changes in Cu and Pb fractionation in soil

The extent of Cu and Pb incorporation in the amended soil was assessed by changes in their geochemical forms relative to the unamended soil as determined by the BCR sequential extraction procedure. Metal concentrations (mg/kg) in individual soil fractions extracted by the sequential procedure are presented in Table 3. The metal concentrations were converted to extraction yields (%) by using Equation 2 and the results are illustrated in Figure 2.

$$\text{Extraction Yield (\%)} = \frac{M_i}{\sum_{i=1}^{4} M_i} \text{ x } 100 \qquad (2)$$

Where, $\sum_{i=1}^{4} M_i = M_1 + M_2 + M_3 + M_4$; and M_1, M_2, M_3 and M_4 are the extractable, oxide-bound, organic-bound and residual metal pools (mg/kg), respectively. Since the first metal fraction is the most mobile, extraction yield in this fraction has been defined as the mobility factor, M_f.

BCR sequential extractions showed that the concentrations, hence extraction yields of Cu and Pb in the various soil fractions varied considerably with the nature and level of soil amendment (Figure 2a and b). Metal concentrations extracted by the first step of the sequential extraction procedure were somewhat comparable to the plant available fractions from calcium nitrate single extractions. Metal mobilities, M_f were reduced following amendment with the immobilizing agents. For instance, in the parent soil, M_f for Cu and Pb were 76.4 and 68.5%, respectively. Natural clay amendment at 5, 10 and 20% w/w lowered the M_f for Cu to 41.4, 34.9 and 18.2%, respectively; while corresponding values for Pb were 40.3, 30.5 and 15.9%. Calcium phosphate treatments at 5, 10, and 20% w/w gave M_f for Cu as 35.4, 30.5 and 15.6%, respectively; while corresponding values for Pb were 31.4, 20.0 and 15.0%. The M_f for Cu in soil amended with poultry manure at 5, 10 and 20% w/w were 53.5, 48.8 and 25.7%, respecttively; while corresponding values for Pb were 50.1, 39.7 and 23.1%. Treatment of soil at 5, 10 and 20% w/w with rice husks reduced Cu mobility to 60.8, 55.6 and 33.9%, respectively; while corresponding values in the case of Pb were 57.2, 41.6 and 31.8%. Depending on the M_f values, the ability of the treatments to immobilize the metals varied in the sequence: calcium phosphate > natural clay > poultry manure > rice husks. Additionally, M_f values for Cu were higher than those for Pb indicating the generally low mobility of Pb in natural soils (Pueyo et al., 2008). Reduced M_f recorded for both Cu and Pb following these treatments interprets the ability of the agents to attenuate metal mobility in soil via stabilization.

Metal extraction yields in the oxide-bound fraction of the amended soil were higher relative to the unamended soil, implying that some of the hitherto mobile metals were converted to the less bioavailable Fe/Mn-oxide form. This fraction contained as much as 11.8 - 18.3%, 29.5 to 36.3%, 12.3 to 19.5% and 12.1 to 22.5% of Cu in soils treated with natural clay, calcium phosphate, poultry manure and rice husks, respectively. Lead (Pb) was partitioned to the extent of 12.9 to 18.4%, 23.7 to 32.9%, 11.3 to 22.0% and 12.4 to 29.4% in soils treated with natural clay, calcium phosphate, poultry manure and rice husks, respectively. About 20.9 to 23.4, 16.8 to 18.9, 24.9 to 35.7 and 15.5 to 24.2% of Cu were found to be complexed and/or adsorbed to the organic matter-bound fraction for soils amended with natural clay, calcium phosphate, poultry manure and rice husks, respectively; whereas corresponding yields of Pb in this fraction were 23.2 to 24.2, 17.4 to 27.4, 25.5 to 38.2 and 9.6 to 20.9%. Apparently, Cu appeared to be associated with this fraction to a greater extent than Pb with poultry manure treatment seemingly recording the highest metal associations with the soil organic matter phase. The residual soil fraction retained Cu to the extent of 25.8 to 40.1, 18.4 to 29.2, 9.3 to 19.0 and 11.6 to 19.4% following natural clay, calcium phosphate, poultry manure and rice husks, respectively; while corresponding yields of Pb range was 23.7 to 41.4, 24.6 to 27.5, 13.2 to 16.7 and 17.9 to 20.7%, respectively. More Pb was, thus, in association with the residual soil fraction than Cu. It appeared that natural clay caused the

Table 3. BCR-extracted Cu and Pb (mg/kg) in fractions of soil before and after amendment with different doses of immobilizing agents.

Agent	Metal	Dose (% *w/w*)	M_1	M_2	M_3	M_4
Parent soil	Cu	0	130.5±9.5	10.4±0.5	10.8±2.1	19.1±1.0
	Pb	0	89.5±9.0	15.1±3.0	10.4±1.2	15.7±3.1
Natural clay	Cu	5	70.2±4.5	20.0±4.6	35.5±5.4	43.7±6.7
		10	58.3±4.7	25.7±4.8	40.3±6.6	42.5±6.6
		20	30.1±6.0	30.2±5.0	38.6±5.0	66.3±6.8
	Pb	5	52.3±5.0	16.7±2.4	30.1±3.3	30.7±4.0
		10	38.4±4.5	20.3±2.8	26.4±3.0	40.9±5.9
		20	20.1±3.2	23.2±2.5	30.5±4.0	52.2±6.0
Phosphate salt	Cu	5	60.0±4.6	50.0±5.2	28.5±5.4	31.2±4.0
		10	50.9±3.3	55.7±4.3	36.1±6.6	24.3±2.5
		20	25.4±2.0	59.1±5.9	30.7±4.8	47.5±6.9
	Pb	5	40.5±3.1	30.6±2.4	22.5±3.3	35.5±4.3
		10	28.2±2.3	36.7±3.0	28.5±3.7	34.6±5.0
		20	18.4±2.4	40.3±2.7	33.5±3.0	30.1±3.1
Poultry manure	Cu	5	88.0±5.0	20.3±2.1	41.0±4.0	15.3±3.2
		10	77.6±3.3	27.9±3.0	40.3±4.7	13.3±1.7
		20	40.0±2.0	30.3±2.7	55.5±4.4	29.6±6.9
	Pb	5	60.0±3.1	13.5±2.7	30.5±3.6	15.8±4.0
		10	49.1±2.3	17.6±2.0	37.5±4.2	19.5±2.1
		20	26.3±2.4	25.1±2.3	43.5±5.6	19.0±1.1
Rice husks	Cu	5	100.2±6.5	20.0±2.5	25.5±4.4	19.1±2.0
		10	90.0±5.3	25.5±3.3	31.1±4.7	15.4±2.5
		20	53.3±4.1	35.3±5.0	37.9±3.6	30.4±4.1
	Pb	5	71.5±3.3	15.5±2.1	12.0±3.0	26.1±4.0
		10	50.1±3.5	21.2±3.0	20.3±3.0	28.7±3.3
		20	36.0±3.0	33.3±3.2	23.6±2.3	20.2±3.5

M_1- acetic; M_2- hydroxylamine hydrochloride, pH 1.5; M_3- hydrogen peroxide, then ammonium acetate, pH 2 and M_4- aqua regia.

greatest metal redistributions in the residual fraction, probably due to additional supply of silicates to the soil matrix (Putwattana et al., 2010).

Assessment of changes in Cu and Pb leaching rates

Kinetic leaching experiments were designed to provide further information on the nature of bound metals in the soil and their degree of lability, hence bioavailability before and after amendments. A non-selective complexing agent, EDTA (0.05 M), capable of direct metal extraction from several soil compartments, such as metal bound to organic matter, carbonate and Fe/Mn (hydr)oxides was employed for this purpose. This concentration was previously established as furnishing optimal metal removal at pH 6.6 (Morera et al., 2001). Figure 3 illustrates the cumulative amounts of Cu and Pb leached by EDTA with time from the parent soil and its amended (20% *w/w*) sub-samples.

Apparently all the leaching curves show similar profiles. That is, the leached metal concentrations increased rapidly at short extraction times, and then reduced by the second hour into the experiment furnishing plateaux. The implication is that at short extraction time (1 h), metal extraction rates were very fast, mobilizing high

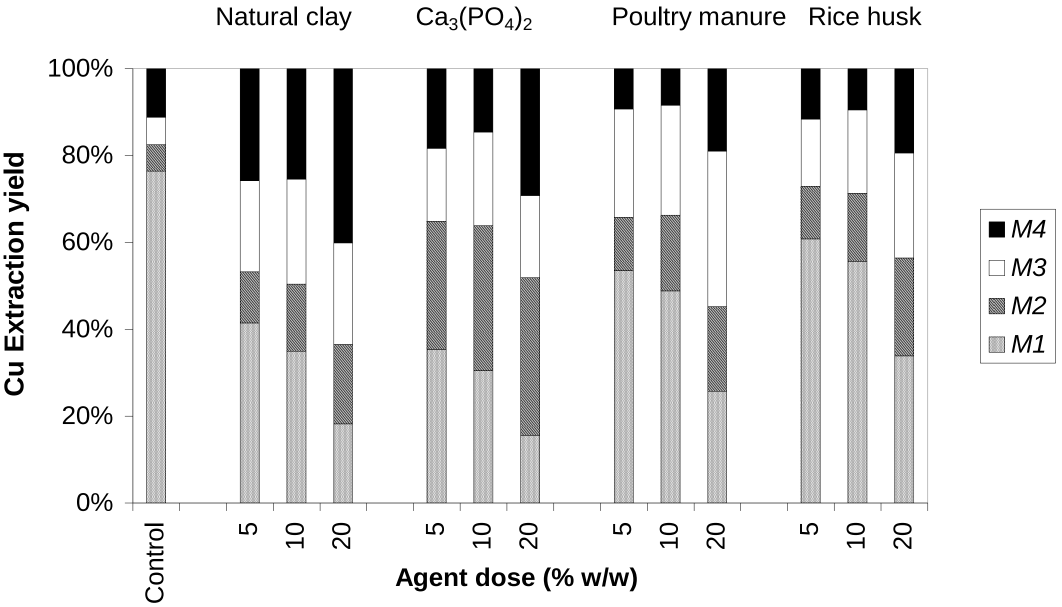

Figure 2a. Extraction yields (%) of Cu in operationally defined pools of contaminated soil amended with different immobilizing agents extracted by the BCR sequential procedure.

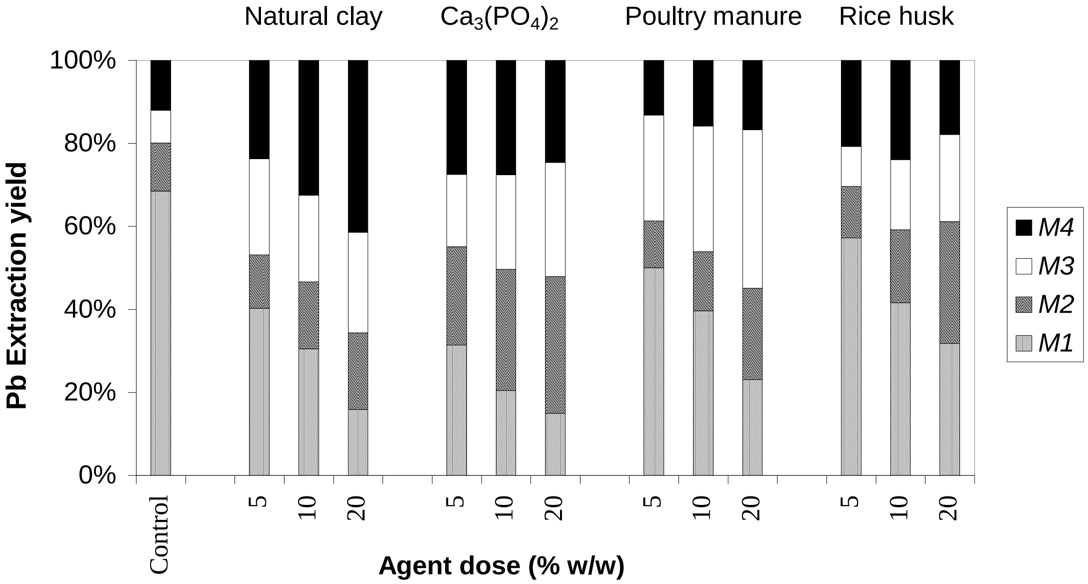

Figure 2b. Extraction yields (%) of Pb in operationally defined pools of contaminated soil amended with different immobilizing agents extracted by the BCR sequential procedure.

amounts of the metals. Plateaux observed for metal leaching implies that the soils had fixed sorption capacities that provided limited sites onto which the metals were originally sorbed (Thompson and Goyne, 2012). EDTA extracted amounts that were higher than those removed by any single step of the BCR sequential extraction method and represented more closely the sum of all the mobilizable metal fractions extracted by the BCR procedure. By the end of the 16 h extraction time, 86.0% Cu and 89.8% Pb were leached from the pre-amended soil relative to their pseudototal concentrations. Following amendments, 53.7, 68.0, 78.3 and 82.9% of Cu were respectively leached from soil treated with natural clay, calcium phos-phate, poultry manure and rice husks, respectively. Approximately 58.0, 57.2, 81.6 and 97.6% of Pb were respectively leached from the soil treated with natural clay, calcium phosphate, poultry manure and rice husks.

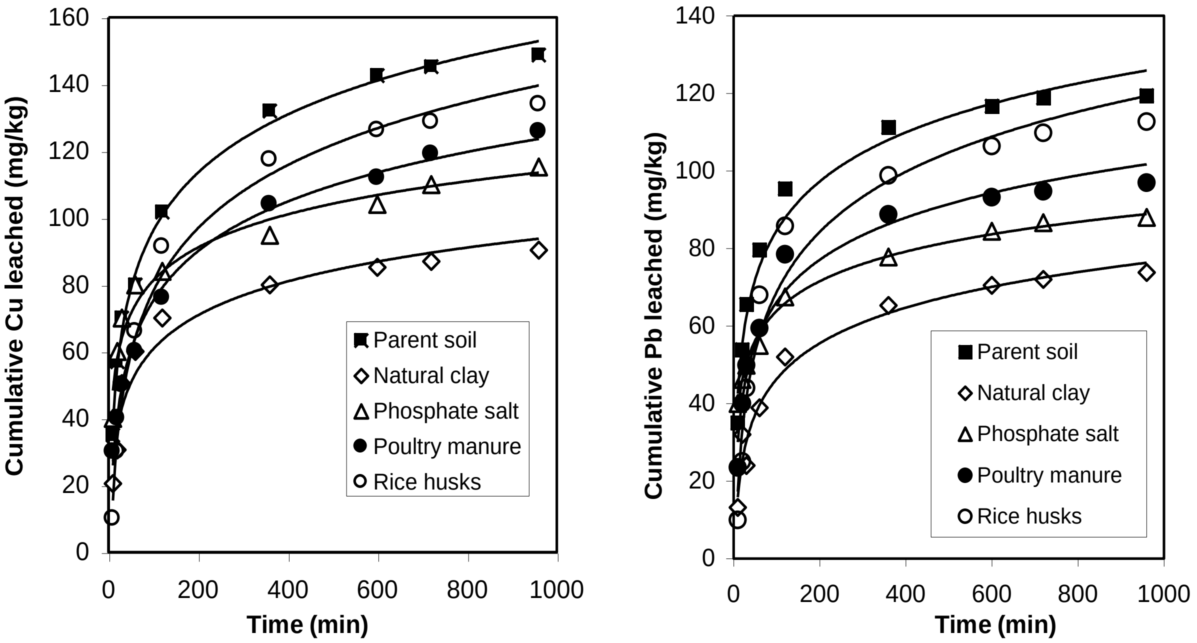

Figure 3. Cumulative Cu and Pb kinetically extracted with 0.05 M EDTA in the parent soil and its sub-samples amended (at 20% w/w) with different immobilizing agents.

Since chemical extractants cannot give information on metal forms in terms of a specific soil compartment unless each compartment presents a different kinetic behaviour, the EDTA kinetic data was fitted into a two-first-order-reaction (TFOR) model by adopting the approach of Labanowski et al. (2008) and Manoucherhi et al. (2011). Average removal rates per unit time, $R_M(t)$ (mg/kg soil/ min) (Equation 3) between t_i and t_{i-1} ($t_{i-1} < t < t_i$), for a given metal were calculated for each lag time and presented as semilogarithmic plots.

$$R_{M(t_i-1<t<t_i)} = \frac{M_{(t_i-1<t<t_i)}}{(t_i - t_{i-1})} \qquad 3)$$

Where, $M_{(t)}$ is amount of metal extracted at a given time. The evolution of $R_M(t)$ as two distinct linear segments of the semilogarithmic kinetic plots with different slopes and intercepts on the ordinate implied the simultaneous existence of two distinct, labile, M_1 and less labile, M_2 metal pools, each following a decreasing exponential function.

$$R_M(t) = R_{M1}(0)\, e^{-k_1 t} + R_{M2}(0)\, e^{-k_2 t} \qquad 4)$$

Where, $R_{M1}(0)$ and $R_{M2}(0)$ are the initial removal rates (at t = 0) of the two pools and k_1 and k_2 are their apparent rate constants. The metal leaching rates were apparently high at the start of the extraction, dominated by the $R_1(0)$ parameter characteristic of the first pool, but the contribution of this first pool decreased quickly to become insignificant (exponential decrease governed by k_1). Then, after a while, the contribution of the second pool became preponderant, with a clear slower extraction rate which still decreased with time (following k_2).

From Table 4, k_1 and k_2 for the leaching of Cu from the unamended (parent) soil were 4.71 x 10^{-2} and 4.00 x 10^{-3} min^{-1}, respectively; while corresponding values recorded for the amended soil were natural clay (k_1 = 4.00 x 10^{-2}/min; k_2 = 3.00 x 10^{-3}/min), phosphate salt (k_1 = 4.83 x 10^{-2}/min; k_2 = 1.20 x 10^{-3}/min), poultry manure (k_1 = 3.93 x 10^{-2}/min; k_2 = 2.60 x 10^{-3}/min) and rice husks (k_2 = 1.23 x 10^{-2}/min; k_2 = 3.30 x 10^{-3}/min). The leaching of Pb from the parent soil gave k_1 and k_2 as 3.84 x 10^{-2}/min and 5.10 x 10^{-2}/min, respectively. Following amendment with the immobilizing agents, these values were natural clay (k_1 = 1.92 x 10^{-2}/min; k_2 = 4.00 x 10^{-3}/min), phosphate salt (k_1 = 5.44 x 10^{-2}/min; k_2 = 3.30 x 10^{-3}/min), poultry manure (k_1 = 4.04 x 10^{-2}/min; k_2 = 3.30 x 10^{-3}/min) and rice husks (k_1 = 4.50 x 10^{-2}/min; k_2 = 3.70 x 10^{-3}/min). These observations indicate that the leaching rates for both the labile and the less labile Cu pools from the soil were apparently retarded for all the agents relative to the unamended soil. In the case of Pb, however, only the leaching rate for the less labile pool appeared to be suppressed upon amendment.

Conclusion

Single, sequential and kinetic leaching tests performed to assess the effectiveness of some cheap and non-toxic

Table 4. Rate constants, k_1 and k_2 for leaching of labile and less labile pools* of Cu and Pb from soil with 0.05 M EDTA before and after amendment with 20% w/w of immobilizing agents.

Agent	Metal	$k_1 \times 10^{-2}$/min	$k_2 \times 10^{-3}$/min
Parent soil	Cu	4.71	4.00
	Pb	3.84	5.10
Natural clay	Cu	4.00	3.00
	Pb	1.92	4.00
Phosphate salt	Cu	4.83	1.20
	Pb	5.44	3.30
Poultry manure	Cu	3.93	2.60
	Pb	4.04	3.30
Rice husks	Cu	1.23	3.30
	Pb	4.50	3.70

*Defined by two-first order reaction model.

agents at reducing the bioavailability of Cu and Pb in contaminated soil revealed that the immobilization efficiencies of the agents were high enough, increased with the level of amendment and varied in the sequence: calcium phosphate > natural clay > poultry manure > rice husks. The immobilizing agents retarded leaching rates for both the labile and the less labile pools of Cu but suppressed only the leaching rate for the less labile pool in the case of Pb. These agents may reduce risks resulting from Cu and Pb contamination in soil since metal mobility is related to its bioavailability.

REFERENCES

Alvarenga PMLF, Goncalves AP, Fernandes RMCSC, de Varennes APA, Duarte ECNFA, Vallini G, Cunha-Queda CF (2008). Effect of organic residues and liming materials on metal extraction from a mining-contaminated soil, Bioremediation J. 12(2):58-69.

Awodun MA (2007). Influence of sawdust ash on soil chemical properties and cowpea performance in Southwest Nigeria. Int. J. Soil Sci. 2(1):78-81.

Belviso C, Cavalcante F, Ragone P, Fiore S (2010). Immobilization of Ni by synthesising zeolite at low temperatures in a polluted soil. Chemosphere 78(9):1172-1176.

Bhat UN, Khan AB (2011). Heavy metals: An ambiguous category of inorganic contaminants, nutrients and toxins. Res. J. Env. Sci. 5(8):682-690.

Black CA (1965). Methods of Soil Analysis, Agronomy 9(2):63-67.

Bouyoucos GJ (1962). Improved hydrometer method for making particle size analysis of soils. Agron. J. 54:464-465.

California Department of Pesticide Regulation Environmental Hazards Assessment Program (CDPRHAP), (1998). Standard Operating Procedure, Sacramento, California. http://www.cdpr.ca.gov/docs/emon/pubs/sops/eqwa001.pdf

Cao RX, Ma LQ, Chenb M, Singh SP, Harris WG (2003). Phosphate-induced metal immobilization in a contaminated site. Environ. Pollut. 122(1):19-28.

Chukwuka KS, Omotayo OE (2008). Effects of Tithona green manure and water hyacinth compost application on nutrient depleted soil in South-Western Nigeria. Int. J. Soil Sci. 3(2):69-74.

Corrochano BG, Azcárate JA, Gonzalez MR (2011). Heavy metal chemical fractionation and immobilization in lightweight aggregates produced from mining and industrial waste. Int. J. Environ. Sci. Tech. 8(4):667-676.

Cui Y, Du X, Weng L, Van Riemsdijk WH (2010). Assessment of in situ immobilization of lead (Pb) and arsenic (As) in contaminated soils with phosphate and iron: solubility and bioaccessibility. Water Air Soil Pollut. 213:95-104.

D'amore JJ, Al-abed SR, Scheckel KG, Ryan JA (2005). Methods of speciation of metals in soils. J. Environ. Qual. 34(5):1707-1745.

Fawzy EM (2008). Soil remediation using in-situ immobilization techniques. Chem. Ecol. 24(2):147-156.

Finžgar N, Kos B, Leštan D (2006). Bioavailability and mobility of Pb after soil treatment with different remediation methods. Plant Soil Environ. 52(1):25-34.

Florido MC, Madrid F, Madrid L (2011). Effect of an organic amendment on availability and bio-accessibility of some metals in soils of urban recreational areas. Environ. Pollut. 159(2):383-390.

Gatimu E, Mwinyihija M, Killham K (2010a). Determination of the effect of red earth as an ameliorant for lead contaminated soils. Res. J. Environ. Toxicol. 4(3):151-161.

Gatimu E, Mwinyihija M, Killham K (2010b). Determination of the effect of bone meal as an ameliorant on lead contaminated soils. Res. J. Environ. Toxicol. 4(4):237-247.

International Organization for Standardization, ISO (1995). Soil quality: Extraction of trace elements soluble in aqua regia, ISO 11466:1995(E).

Irmak S (2010). Copper correlation of irrigation water, soils and plants in the Cukurova Region of Turkey. Int. J. Soil Sci. 5(3):185-195.

Jackson ML (1962). *Soil Chemical Analysis*, Prentice-Hall, New York.

Labanowski J, Monna F, Bermond A, Cambier P, Fernandez C, Lamy I, van Oort F (2008). Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate, Environmental Pollut. 152(3):693-701.

Manoucherhi N, Besancon S, Bermond A (2011). Kinetic characterizing of soil trace metal availability using soil/EDTA/chelex mixture. Chemosphere 83(7):997-1004.

Matini L, Ongoka PR, Tathy JP (2011). Heavy metals in soil on spoil heap of an abandoned lead ore treatment plant, SE Congo-Brazzaville. Afr. J. Environ. Sci. Technol. 5(2):89-97.

Maxted AP, Black CR, West HM, Crout NMJ, McGrath SP, Young SD (2007). Phytoextraction of cadmium and zinc from arable soils amended with sewage sludge using *Thlaspi caerulescens*:Development of a predictive model. Environ. Pollut. 150(3):363-372.

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL (2000a). Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Aust. J. Soil Res. 38(6):1037-1086.

McLaughlin MJ, Zarcinas BA, Stevens DP, Cook N (2000b). Soil testing for heavy metals. Commun. Soil. Sci. Plant Anal. 31(11-14):1661-1700.

Mench MJ, Didier VL, Löffler M, Gomez A, Masson P (1994). A mimicked *in situ* remediation study of metal-contaminated soils with emphasis on cadmium and lead. J. Environ. Qual. 23:58-63.

Morera MT, Echeverría JC, Mazkiarán C, Garrido JJ (2001). Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. Environ. Pollut. 113(2):135-144.

Nara S (2010). Structural development of clay soil with the amendment of coal combustion by-product FGD Gypsum in Lusatia Germany. Int. J. Soil Sci. 5(2):62-72.

Ogbo EM, Okhuoya JA (2011). Bio-absorption of some heavy metals by *Pleurotus tuber-regium* Fr. Singer (an edible mushroom) from crude oil polluted soils amended with fertilizers and cellulosic wastes. Int. J. Soil Sci. 6(1):34-48.

Okieimen FE, Okieimen CO, Wuana RA (2007). Preparation and characterization of activated carbon from rice husks. J. Chem. Soc. Niger. 32(1):126-136.

Pueyo M, Mateu J, Rigol A, Vidal M, López-Sánchez JF, Rauret J

(2008). Use of modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environ. Pollut. 152:330-341.

Putwattana N, Kruatrachue M, Pokethitiyook P, Chaiyarat R (2010). Immobilization of cadmium in soil by cow manure and silicate fertilizer, and reduced accumulation of cadmium in sweet basil (*Ocimum basilicum*). ScienceAsia 36(4): 349-354.

Rajaganapathy N, Xavier F, Sreekumar D, Mandal PK (2011). Heavy metal contamination in soil, water and fodder and their presence in livestock and products: A review. J. Environ. Sci. Technol. 4(3):234-249.

Santos S, Costa CA, Duarte AC, Scherer HW, Schneider RJ, Esteves VI, Santos EB (2010). Influence of different organic amendments on the potential availability of metals from soil: a study on metal fractionation and extraction kinetics by EDTA. Chemosphere 78(4):389-396.

Sarma H (2011). Metal hyperaccumulation in plants: A review focusing on phytoremediation technology. J. Environ Sci. Technol. 4(2):118-138.

Schumacher BA (2002). Methods for the determination of total organic carbon, TOC in soils and sediments. USEPA-NCEA-C-1282, EMASC-001, pp.1-21.

Suruchi Khanna P (2011). Assessment of heavy metal contamination in different vegetables grown in and around urban areas. Res. J. Environ. Toxicol. 5(3):162-179.

Thompson A, Goyne KW (2012). Introduction to the sorption of chemical constituents in soils. Nature Education Knowledge 4(4):7

Ure AM, Quevauviller PH, Muntau H, Griepink B (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of Commission of the European Communities. Intern. J. Environ. Anal. Chem. 51(1):5-151.

Wuana RA, Okieimen FE (2011). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology. pp.1-20.

Yap CK, Edward FB, Emila RAA, Ainey FI, Ismail A, Tan SG, Sharizat Y (2008). Determination of contamination and bioavailability of heavy metals (Cu, Cd, Zn, Pb, and Ni) in the Serdang urban Lake by using Guppy fish *Poecilia reticulate*. Trends in Applied Sci. Res. 3(1):69-75.