

MOBILIZATION OF LEAD AND CADMIUM INFLUENCED BY SOIL AMENDMENTS

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ABSTRACT

Activities such as mining and manufacturing and the use of synthetic products (especially chemical fertilizers and pesticides) result in heavy metal contamination of soil and water resources. The objectives of this research were to examine the effectiveness of soil organic and inorganic amendments on sorption or desorption Pb and Cd in soil and to explore the effects of soil amendments on soil physicochemical properties correlate with heavy metals (im) mobility on a contaminated soil under crop free environment. The effectiveness of different soil amendments viz., FYM, press mud, EDTA, lime, potassium humate and natural zeolite along with NPK fertilizers were tested for screening the best metal mobilizing and or immobilizing amendment for using in further field studies with hyper accumulating plant species. The experimental results revealed that application of 100 % RDF NPK plus EDTA mobilizing more DTPA extractable lead and cadmium in soil solution by charge specific chelation and cation exchange processes. Whereas 100 % RDF NPK plus FYM application showed lower soil available lead and cadmium by immobilization through influencing the soil physico-chemical properties.

KEY WORDS : Cadmium, DTPA, EDTA, Desorption, FYM, Immobilization, Lead, Sorption

INTRODUCTION

Soil contamination by heavy metals is one of the most serious ecological concerns all over the world. Basic sources of this contamination are the results of anthropogenic activities, like burning of fossil fuel, mining and metallurgy industry, waste incineration, releasing of toxic heavy metals by transport sectors, and use of fertilizers and agrochemicals, in addition to soils that are rich in heavy metals (Kaplan *et al.*, 2010). Further, increased industrialization and urbanization is resulting into continuous production of huge amounts of heavy metals containing in industrial effluents, sewage sludge and sewer water worldwide, which on reaching the agricultural fields get accumulated in soil at hazardous levels. Amongst heavy metals, which occur naturally in all soils, water and living organisms, many are essential for healthy life. However, when they are present in excessive concentrations, they may have

severe impact on the biological system manifesting in different types of ill effects on growth, respiration and other physiological activities. Heavy metals may also have an adverse effect on microbial population (Jordan and Lechevelier, 1973) and litter decomposition (Chaney *et al.*, 1978; Coughtrey *et al.*, 1979), which have a direct bearing on the process of nutrient transformation and mineralization of organic substrates. Polluting heavy metals are emitted from various sources as solid, liquid and as fine particles directly into atmosphere and ultimately deposited on the surface of land and water bodies. The dangers associated with heavy metals and toxic ions present in untreated effluents, sewage sludge and sewer water, causing phytotoxicity to crops and food chain contamination have become a matter of great social and scientific concern (Vassilev *et al.*, 2004). Thus, the issues of contamination of agricultural soils and chemical residues in agricultural produce have become

increasingly important in recent years due to increased public awareness and concern for food and land quality (Rizwan *et al.*, 2016b; Shaheen and Rinklebe, 2015). Here cadmium (Cd) and lead (Pb) gained more attention due to its wide spread and high toxicity to plant functions and lead inhibits metabolic process such as nitrogen assimilation, photosynthesis, respiration, water uptake and transcription, respectively. Cadmium (Cd), recognized as one of the most hazardous elements, is not essential for plant growth (Kabata-Pendias and Pendias, 2000). The main source of Cd contamination is industries involved in protective plating on steel and production of various alloys, pigments, stabilizers for plastic, Ni-Cd dry batteries and other miscellaneous items including photovoltaic cells and control rods for nuclear reactors. The other sources of Cd contamination are from mining, ore dressing and smelting of cadmium sulphide ore. Like Cd, excessive build up of Pb is due to mining, smelting, manure, sewage sludge and vehicle exhausts. During the past decades, the annual widespread release of heavy metals reached 22,000 t (metric ton) for Cd and 7, 38,000 t for Pb. Heavy metals in soil cannot be destroyed like some organic contaminants, but only be relocated from one place to another such as landfill (*ex-situ* decontamination), which is however a very expensive and often unacceptable from an ecological standpoint (McGrath *et al.*, 2001). Thus, significant alternative strategies are now addressing other approaches to reduce the risks associated with the presence of heavy metals in soils and to minimize potential impacts on plants, animals, water quality and consequently on a human health i.e., sustainable management of metal-polluted soils. The choice of suitable remediation strategy depends on many factors *viz.*, (i) size, location and history of the site, (ii) soil characteristics (structure, texture, pH etc.), (iii) type, physical and chemical state of contaminants, (iv) degree of pollution (contamination concentration and distribution), (v) desired final land use, (vi) technical and financial means available and (vii) environmental, legal and social issues. Many soils contaminated with organics can be decontaminated by *in situ* methods. Metals, on the contrary, are immutable and relatively immobile and so many of the low-cost options available for the remediation of organic contaminants are not effective for metal contaminated soils. Due to cost, time and logistical concerns relatively few options remain open. In

general, remediation techniques, whether *in-situ* or *ex-situ* do one of two things either they remove the contaminants from the soil *substratum* (site decontamination or cleanup techniques) or reduce the risk posed by the contaminants by reducing exposure (site stabilization techniques). The spread of contaminants in soil can be hindered by the soil stabilization technique, which is based on an application of suitable immobilizing agents. Adsorption of contaminants on mineral surfaces, formation of stable complexes with organic ligands, surface precipitation and ion exchange were identified as the main mechanisms responsible for the reduction of the metal mobility, leachability and bioavailability (Sabir *et al.*, 2013). Another approach directed towards real decontamination is metal phytoextraction, representing use of plants for metal removal from the soil by concentrating (phytoaccumulation) them in harvestable plant parts (Mandal *et al.*, 2014) by using the combination of plant and soil amendments. In agriculture, various amendments both organic and inorganic are frequently used to improve the soil properties such as microbial and enzyme activities or properties of soil organic matter and many of them significantly modify the mobility of metals in soil environment. Soil organic matter consists mainly of humic substances that plays a key role in governing complexation / immobilization / retention of trace metal ions (metal mobility) and hence their bioavailability (Piccolo, 1989; Almas *et al.*, 1995). Certain organic and inorganic amendments (FYM, press mud, zeolite, K-humate, lime, gypsum) can serve as immobilizing and phytoaccumulation agents for some heavy metals and EDTA has the capacity to alleviate or chelate the metals at different doses of application. Therefore, to get actual effect, soil type and other physico-chemical and biological changes studies are necessary. This information will help us in eco-friendly and sustainable management of soil fertility and reducing toxic heavy metal mingle into the food web through *in-situ* immobilization.

MATERIALS AND METHODS

An incubation experiment was conducted at research laboratory under controlled condition in the Department of Soil Science and Agricultural Chemistry, Faculty of Agriculture, Annamalai University, Annamalaiagar during March – April, 2017 to study the effect of different soil amendments

(FYM, press mud, EDTA, lime, Gypsum, potassium humate and natural zeolite) on the immobilization of heavy metals lead (Pb) and cadmium (Cd) amendments viz., along with NPK fertilizers were tested to screening the best metal mobilizer and or immobilizer for using in further field studies with hyper accumulating plant (sunflower). Bulk surface soil sample (< 20 cm depth) receiving the effluents of SIPCOT industrial area (northern part) in Cuddalore, Tamil Nadu, India, was collected. Soil was air dried and sieved through 2 mm sieve prior to use in the experiment. One kilogram of 2 mm sieved soil was filled in plastic containers of size 15 cm height and 22.5 cm diameter. After that, calculated quantities of fertilizers and amendments (w/w basis) were added as per treatments and mixed well (RDF, i.e. 60: 90: 60 kg of NPK ha⁻¹) used here as per the sunflower crop requirement for further studies). A completely randomized design was used with of eight treatments (seven amendments + one control) with three replications and maintained for 2 months (60 days). Thus, eight treatment combinations were set aside in 24 containers separately and maintained the soil moisture at about 60 per cent of the field capacity. The moisture level was maintained by adding water daily to compensate the loss due to evaporation. Soil samples were drawn at 20 days interval (20, 40

and 60 DAI) and dried under shade used for analysis of soil organic carbon content, pH, EC, CEC and heavy metals (DTPA extractable Pb and Cd). Analytical procedures followed for the analysis were given in Table 1.

RESULTS AND DISCUSSION

Influence of soil amendments on soil physico-chemical properties

Soil pH

The pH values recorded at 20, 40 and 60 days after incubation (DAI) ranging from 7.67 to 8.23, 7.31 to 8.26 and 7.3 to 8.26 at 20, 40 and at 60 DAI, respectively. The results were statistically non-significant (Table 2). However, the highest pH values of 8.23, 8.26 and 8.26 were recorded in RDF + lime (T₅) and this was followed by the treatments T₈ (RDF + zeolite), T₇ (RDF + K – Humate), T₃ (RDF + pressmud) and T₁ (control -100 % RDF alone) and the lowest pH values of 7.67, 7.31 and 7.30 were recorded in RDF + EDTA (T₄) at all the three stages of incubation, respectively. Soil pH was altered (increased or decreased) by the treatments when compared to initial soil pH level (7.81) at all stages of incubation. The pH values in different treatments at different stages (20, 40 and 60 DAI) ranged from

Table 1. Methods employed in the experimental soil analysis

Particulars	Method	Reference
pH (1:2.5 soil : water)	Using glass electrode in the “ELICO” pH meter	Jackson (1973)
EC (1:2.5 soil : water)	Using “ELICO” conductivity bridge	Jackson (1973)
Organic carbon	Chromic acid wet digestion method	Walkley and Black (1934)
Cation exchange capacity	Neutral normal ammonium acetate method	Jackson (1973)
Heavy metals (Pb and Cd)	0.005 DTPA using ICP-OES	Lindsay and Norvell (1978)

Table 2. Influence of Soil Amendments on soil pH, EC (dS m⁻¹), CEC (C mol (p⁺) Kg⁻¹) and soil organic carbon (SOC) content (g kg⁻¹) in heavy metal alleviated soil

Days of Incubation Treatments/Parameters	20 DAI				40 DAI				60 DAI			
	pH	EC	CEC	SOC	pH	EC	CEC	SOC	pH	EC	CEC	SOC
T ₁ -Control (100% RDF)	7.87	0.68	13.64	0.44	7.82	0.60	14.21	0.51	7.81	0.59	14.42	0.56
T ₂ -RDF + Farm yard manure	7.71	0.61	15.20	0.61	7.68	0.54	15.86	0.68	7.64	0.52	16.07	0.73
T ₃ - RDF + Pressmud	7.98	0.76	14.89	0.52	7.91	0.68	15.41	0.61	7.88	0.67	15.72	0.68
T ₄ - RDF + EDTA	7.67	0.38	13.03	0.37	7.31	0.31	13.70	0.43	7.30	0.29	13.98	0.47
T ₅ -RDF + Lime	8.23	1.01	8.45	0.09	8.26	0.88	8.03	0.07	8.26	0.88	7.78	0.06
T ₆ -RDF + Gypsum	7.79	0.52	12.27	0.21	7.70	0.47	13.05	0.27	7.67	0.42	13.25	0.35
T ₇ -RDF + Potassium humate	8.08	0.81	10.96	0.28	8.02	0.78	11.86	0.30	7.99	0.76	11.92	0.31
T ₈ -RDF + Zeolite	8.14	0.89	9.67	0.11	8.18	0.82	9.13	0.09	8.2	0.80	8.92	0.08
SEd±	0.06	0.03	0.37	0.016	0.15	0.025	0.380	0.012	0.15	0.024	0.385	0.013
CD (P=0.05)	NS	0.06	0.78	0.035	NS	0.052	0.81	0.026	NS	0.05	0.82	0.027

7.71 to 8.23, 7.68 to 8.26 and 7.64 to 8.26, respectively. Increased pH values were noticed in the treatments received RDF+ lime (T_5) and RDF + zeolite (T_8), whereas all other treatments showed a trend of decreased pH values from 20 to 60 days of incubation (Fig. 1A). The higher soil pH values were observed in the RDF+ lime (T_5) treatment at all the stages of incubation experiment. This may be attributed to the changes in electrochemical properties of soil by the addition of lime (CaCO_3) (Kirk, 2004; Saharwat, 2005) which generally added to soils for neutralizing the pH. The decrease or increase in pH over the period of aerobic incubation in this study may ascribed to the process of H^+ consumption or shift in the H^+/OH^- during soil reduction or oxidation influenced by the lime. The effect of lime on heavy metal contaminated soils duly increased soil pH which depends on pH of liming material and Ca^{2+} concentration in soil solution (Rehman *et al.*, 2015b) and also addition of lime have positive momentum of increasing soil pH.

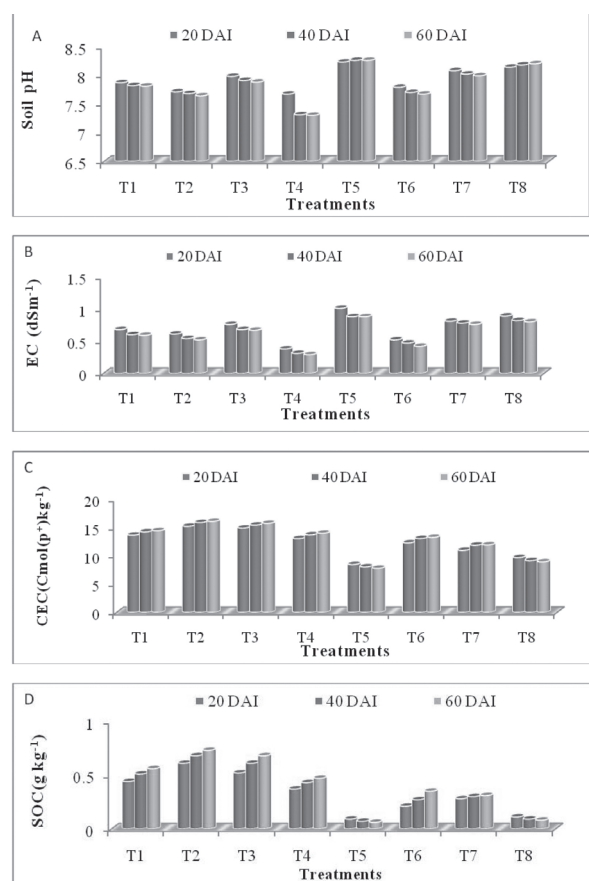


Fig. 1. Soil pH, electrical conductivity (EC) Cation exchange capacity (CEC) and soil organic carbon (SOC) at 20,40 and 60 DAI (A) CEC (B) SOC (C) CEC (D) SOC

With respect to the addition of RDF+ natural zeolite (T_8) in the study, which also showed an increasing trend of pH values like RDF +lime application (T_5) when compared to other treatments. This might be attributed due to the natural zeolite added in the experimental soil having the pH of 9.2 which possibly increased the pH of soil and also zeolite as a soil amendment could effectively ameliorate salinity stress (Al-Busaidi *et al.*, 2008). Further, zeolite (clay) is a class of alkaline porous aluminosilicate, with a negative charge (Mohamed, 2001), neutralized by introducing exchanged cations in the structure sites (Breck, 1974; Mondales *et al.*, 1995). In addition to that zeolites having more negatively charged (anionic) sites in it, hence able to adsorb positive charges which fluctuates the soil pH according to adsorbed cations, Mahabadi *et al.* (2007); Kulasekaran and Reddy, 2011) opined that the pH value of the loamy sand soil increased from 5.45 to 7.7 when 15 per cent zeolite was applied.

Except the treatments received RDF + lime and RDF + zeolite discussed earlier, remaining treatments tried in the experiment showed the trend of decreased pH values at all the stages of incubation in the order of RDF + K-humate > RDF + press mud > RDF alone > RDF + gypsum > RDF + FYM > RDF + EDTA. This may be attributed to the nature of soil amendments added and their behavior with contaminated soil in participating active acidity and buffer capacity of soil (Balaguravaiah *et al.*, 2005; Kim and Ong, 2007). Further, the bio-geochemical processes in soil and functions of certain amendments on soil reaction coupled with other soil physicochemical characteristics, which reduce the pH of soil solution (Kim *et al.*, 2003). The influence of different treatments were influenced the HMs contaminated soil pH was ably confirmed by significant positive correlation between pH with EC ($r = 0.956^*$, 0.958^* , 0.956^*) and negative correlation between pH with CEC and SOC ($r = -0.767^*$, -0.792^* , -0.797^* and $r = -0.650^*$, -0.688^* , -0.719) at 20,40 and 60 DAI, respectively (Table 3). The lower pH values were recorded by the treatment RDF +EDTA (T_4) over the whole period of incubation. This could be attributed to reduction of pH by EDTA due adsorption of divalent cations present in the soil solution (which may cause the pH to increase) and thereby reducing the soluble salt contents like Ca and Mg hitherto reducing EC of soil and pH (Dunne Jr. and Burd, 1992). Further, Nowack and Sigg (1995) opined that adsorption kinetics experiments revealed that the

Table 3. Simple correlation matrix showing relationships between pH, Electrical conductivity (EC), Cation exchange capacity (CEC) and Soil organic carbon (SOC)

	20 DAI				40 DAI				60 DAI			
	pH	EC	CEC	SOC	pH	EC	CEC	SOC	pH	EC	CEC	SOC
pH	1.000											
EC	0.956	1.000										
CEC	-0.767	-0.637	1.000									
SOC	-0.650	-0.477	0.952	1.000								
pH	0.955	0.981	-0.665	-0.550	1.000							
EC	0.958	0.991	-0.631	-0.477	0.986	1.000						
CEC	-0.792	-0.682	0.990	0.937	-0.702	-0.665	1.000					
SOC	-0.688	-0.530	0.974	0.995	-0.592	-0.529	0.963	1.000				
pH	0.960	0.980	-0.689	-0.577	0.998	0.982	-0.730	-0.620	1.000			
EC	0.956	0.994	-0.618	-0.451	0.978	0.998	-0.655	-0.506	0.975	1.000		
CEC	-0.797	-0.692	0.988	0.931	-0.712	-0.676	1.000	0.959	-0.739	-0.666	1.000	
SOC	-0.719	-0.572	0.987	0.982	-0.621	-0.570	0.981	0.995	-0.649	-0.551	0.978	1.000

complexes of divalent cations adsorb within few minutes by EDTA *i.e.* adsorption stoichiometric nature of EDTA influences the pH.

Electrical conductivity (EC)

The organic and inorganic amendments were significantly influenced the electrical conductivity of soil. The EC values recorded at 20, 40 and 60 days after incubation (DAI) ranging from 0.38 to 1.01, 0.31 to 0.88 and 0.29 to 0.88 dSm⁻¹, respectively (Fig. 1B). The highest EC of 1.01, 0.88 and 0.88 dSm⁻¹ were recorded in RDF + lime treatment (T₅) and it was followed by the treatments T₈ (RDF + zeolite), T₇ (RDF + K – Humate), T₃ (RDF + press mud) and T₁ (control). The lowest EC values of 0.38, 0.31 and 0.29 dSm⁻¹ were recorded in RDF + EDTA (T₄) received treatment at all the three stages of incubation, respectively. Electrical conductivity of incubated soil decreased with incubation period in all treatments. The higher EC values were observed in the RDF + lime (T₅) applied treatment at all the stages of incubation experiment. This may be attributed to the changes in electrochemical properties of soil by the addition of lime (CaCO₃) (Kirk, 2004; Saharwat, 2005) which generally added to soils for neutralizing the pH and have positive direct relation with EC. The decrease or increase EC over period of aerobic soil incubation in this study may ascribed due to the process of H⁺ consumption or shift in the H⁺/OH⁻ during soil reduction or oxidation influenced by the lime. The effect of lime on heavy metal contaminated soils duly increased soil pH which depends on pH of liming material and Ca⁺ concentration in soil solution (Rehman *et al.*, 2015b) and also addition of lime have positive

momentum of increasing soil pH. By increasing divalent calcium radicals or ions (salts) content in soil solution would causes the EC as increased. Further, addition of NPK fertilizers along with lime may increase the electrical conductivity of the soil (Argo and Biernbaum, 1996). EC values of all the treatments were followed same trend as observed in pH. Remaining treatments tried in the experiment showed the trend of EC values at all the stages of incubation in the order of RDF + zeolite > RDF+ K-humate > RDF+ press mud > RDF alone > RDF+ gypsum > RDF+FYM > RDF+EDTA. This may be attributed due to the nature of soil amendments added and their behavior with contaminated soil in participating active acidity and buffer capacity of soil (Kim and Ong, 2007; Balaguravaiah *et al.*, 2005). Further, the bio-geochemical processes in soil and functions of certain amendments on soil reaction coupled with other soil physicochemical characteristics, increases the EC of soil solution (Kim *et al.*, 2003). The lower EC values were recorded by the treatment RDF +EDTA (T₄) over the whole period of incubation. This could be attributed due to reduction of pH by EDTA due adsorption of divalent cations present in the soil solution (which may cause the pH to increase and increasing ionic content in soil solution) and thereby reducing the soluble salt contents like Ca and Mg hitherto reducing EC of soil and pH (Dunne Jr. and Burd, 1992). A significant decrease in EC was observed for this combination. Among the possible reasons, improvement in porosity and hydraulic conductivity, might have resulted in enhanced leaching of salts (Sharma *et al.*, 1983).

Cation exchange capacity (CEC $\text{Cmol(p}^+) \text{ kg}^{-1}$)

Values of CEC obtained at 20, 40 and 60 days after incubation (DAI) ranging from 8.45 to 15.20, 8.03 to 15.86 and 7.78 to 16.07 $\text{Cmol(p}^+) \text{ kg}^{-1}$ respectively. The highest CEC values of 15.20, 15.86 and 16.07 $\text{Cmol(p}^+) \text{ kg}^{-1}$ were recorded in RDF + FYM (T_2), which was on par with the treatment T_3 (RDF + pressmud) followed by T_4 , T_1 and T_6 which were on par with each other. Further T_6 was followed by treatments T_7 and T_8 and the lowest CEC values of 8.45, 8.03 and 7.78 $\text{Cmol(p}^+) \text{ kg}^{-1}$ were recorded in RDF + lime (T_5) at all the three stages of incubation respectively. CEC was altered (increased or decreased) by the treatments when compared to initial soil CEC level (13.52 $\text{Cmol(p}^+) \text{ kg}^{-1}$) at all stages of incubation. Increased CEC were noticed in all the treatments except RDF + lime (T_5) and RDF + zeolite (T_8) (Fig. 1C). Higher CEC values were observed in the RDF + FYM (T_2) applied treatment at all the stages of incubation experiment. In general, higher CEC observed in *Vertisol* is due to increased number of net negative charges on soil colloids with increase in finer fraction, while low CEC in *Entisol* might be due to their coarse texture leading to reduced number of negative charges for adsorption of cations on the exchange sites (Hazalton and Murphy, 2007). The FYM addition stimulate the soil biological activity, which consequently increases the organic matter content the soil (Zaller and Kopke, 2004) and increases the negative charges on the soil surface. Further, Hati *et al.*, (2007) opined that application of fertilizer alone or in conjunction with FYM induces increase in SOC. Which in turn, resulted increased adsorption sites by increasing net negative charges on the soil surface and reducing competing metal cations (Alamgir *et al.*, 2011). These are possible reasons that FYM treatment having higher CEC values compared to other treatments. Whereas, the lowest values of CEC were observed in RDF + lime applied treatment. This could be ascribed due to the fact that lime itself contained more calcium and increases the pH, where sources of negative charges in adsorbent site would be reduced by soil aggregation by lime and thus decreases the CEC.

Soil organic carbon (SOC)

The data associated to soil organic content was analyzed during incubation experiment at 20, 40 and 60 DAI and are furnished in Table 2. SOC content was significantly influenced by various soil

amendments and the values ranging from 0.09 to 0.61 at 20 DAI, 0.07 to 0.68 at 40 DAI and 0.06 to 0.68 g kg^{-1} at 60 DAI. Application of RDF + FYM (T_2) registered higher SOC of 0.61, 0.68 and 0.68 g kg^{-1} at all the stages of incubation and it was followed by the treatments RDF + press mud (T_3), T_4 , T_1 , T_6 , T_7 and T_8 . RDF + lime (T_5) treatment registered the lowest organic carbon content of 0.09, 0.07 and 0.06 g kg^{-1} at 20, 40 and 60 DAI, respectively. Increased SOC values were noticed in all the treatments except RDF + lime (T_5) and RDF + zeolite (T_8) treatments (Fig. 1D). SOC is an important soil chemical property of which decides the fertility of soil. It gives an indirect indication of nutrient status in soil. Higher organic carbon in *Vertisol* (Singh *et al.*, 2008; Thakur *et al.*, 2011) could be due to regular addition of organics and incorporation of stubbles in the soil. Low organic carbon in *Entisol* and *Alfisol* may be due to poor vegetation coupled with high rate of organic matter decomposition under hyperthermic temperature regime, which leads to extreme high oxidation condition. The SOC (g kg^{-1}) values were observed in the RDF + FYM (T_2) applied treatment at all the stages of incubation experiment of sandy loam soil. The RDF+FYM (T_2) added treatment proved its superiority in enhancing SOC over other organic and inorganic amendments tried (Table 2 and Fig 1D). This addition of organic carbon might be due to accumulation plant residual lignin in FYM, directly flows to the structural and metabolic soil carbon pool and increased biologically active soil organic carbon such as microbial biomass carbon and mineralizable carbon (Kanchikerimath and Singh., 2001). Further, the non-labile or residual SOC fraction constitutes the percentage of SOC under integrated application of manures and fertilizers; thus, it has the potential to considerably increase SOC in agricultural soils (Ghosh *et al.*, 2010). Whereas the treatment received application of RDF + lime (T_5) did not influence the carbon pool. Mando *et al.* (2005) reported in a similar fashion that manure was the most effective in increasing POM-C when compared with urea or without urea or other soil amendments. The N fertilization through organic manures stimulates microbial activity and enhances C turnover, which explains the negative values of C stabilization in the fertilizer N applied plots which was hindered by the RDF+ lime treatment at all the stages of incubation.

DTPA extractable lead (Pb) and cadmium (Cd)

To decrease the mobility of toxic heavy metals by

rendering them less mobile and more stable thereby decreasing their phytoavailability. One such method is *in-situ* chemical immobilization of heavy metals that decreases the concentration of dissolved contaminants by sorption and or precipitation (Basta and McGowen, 2004). Increasing adsorption of metals or decreasing its solubility can reduce the risk of plant uptake, pollutant transport and its redistribution from contaminated sites. Immobilization of metals can be accomplished by the addition of amendments to reduce contaminant solubility or bioavailability. The addition of soil amendments, such as organic matter, phosphates, alkalizing agents, and bio solid can decrease solubility of metals in soil and minimize leaching to groundwater (Khan *et al.*, 2012). Here, in the present study, organic and inorganic amendments were tried to immobilize the heavy metals (Pb and Cd) in an incubation experiment. The data in respect of DTPA extractable Pb and Cd are presented in Table 4. Application of various soil amendments along with RDF had significantly influenced the DTPA extractable Pb and Cd content in soil at 20, 40 and 60 days of incubation. Among the various organic and inorganic soil amendments tried, the highest DTPA extractable Pb was recorded by the treatment (T_4) RDF + EDTA (3.85 mg kg^{-1} at 20 DAI, 3.95 mg kg^{-1} at 40 DAI and 4.15 mg kg^{-1} at 60 DAI, and it was followed by RDF + K – Humate (T_7) $> T_8 > T_5 > T_6$ and T_1 . The lowest DTPA extractable Pb of 0.89 mg kg^{-1} at 20 DAI, 0.93 mg kg^{-1} at 40 DAI and 0.51 mg kg^{-1} at 60 DAI stages were recorded by the treatment RDF + FYM (T_2) and it was on par with the treatment RDF + pressmud (T_3)(Fig. 2A). With revere to DTPA extractable Cd, the same trend as in Pb was identified in Cd also. The highest extractable Cd in soil was registered by the treatment (T_4) RDF + EDTA (1.12 , 1.17 and 1.21 mg kg^{-1} at 20, 40 and 60

days of incubation, respectively) and it was followed by $T_7 > T_8 > T_5 > T_6$ and T_1 . The lowest values of Cd (0.63 , 0.59 and 0.55 mg kg^{-1} at 20, 40 and 60 days of incubation, respectively) was recorded by the treatment RDF + FYM (T_2) and it was on par with treatment T_3 (RDF + pressmud)(Fig. 2B). Each amendments used in the experiment were showed their significance in sorption, precipitation and or containing the heavy metals in the soil. Among the treatments tried, maximum values of DTPA extractable Pb and Cd (3.85 and 1.12 ; 3.95 and 1.17 ; 4.15 and 1.21 mg kg^{-1} at 20, 40 and 60 DAI

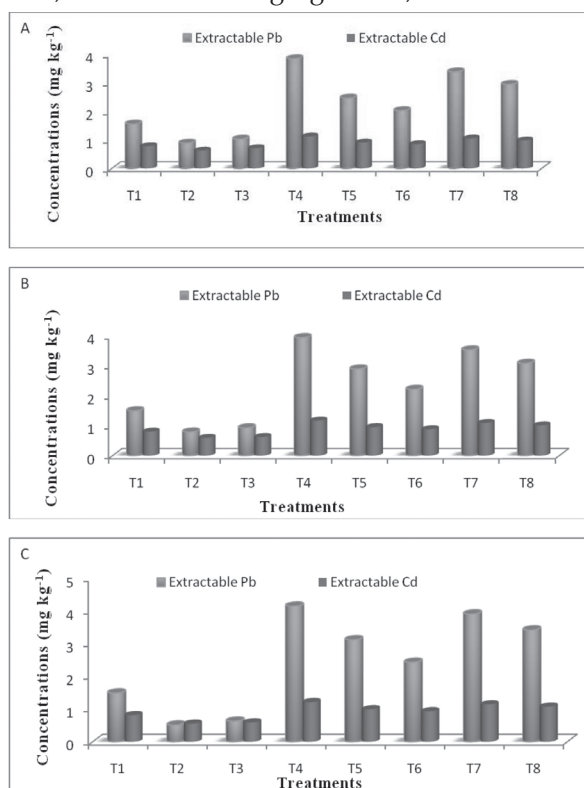


Fig. 2. DTPA extractable Lead (Pb) Cadmium (Cd) (A) 20 DAI (B) 40 DAI (C) 60 DAI

Table 4. DTPA extractable lead (Pb) and cadmium (Cd) (mg kg^{-1})

Days of incubation Treatments/Parameters	20 DAI		40 DAI		60 DAI	
	Pb	Cd	Pb	Cd	Pb	Cd
T_1 - Control (100% RDF)	1.56	0.78	1.50	0.80	1.49	0.81
T_2 - RDF + Farm yard manure	0.89	0.63	0.79	0.59	0.51	0.55
T_3 - RDF + Pressmud	1.03	0.71	0.93	0.62	0.63	0.59
T_4 - RDF + EDTA	3.85	1.12	3.95	1.17	4.15	1.21
T_5 - RDF + Lime	2.47	0.91	2.90	0.95	3.12	0.99
T_6 - RDF + Gypsum	2.03	0.85	2.22	0.88	2.43	0.93
T_7 - RDF + Potassium humate	3.39	1.05	3.54	1.09	3.91	1.14
T_8 - RDF + Zeolite	2.95	0.98	3.09	1.01	3.42	1.07
SEd±	0.07	0.02	0.08	0.03	0.08	0.02
CD (P=0.05)	0.16	0.05	0.17	0.06	0.18	0.05

respectively) were observed in the treatment receiving RDF + EDTA (T_4). This may be due to enhancement of metal leachability and metal liability in soil (Vassilev *et al.*, 2004) and increases the bioavailability of Pb and other heavy metals by forming water-soluble-chelate complexes (Huang *et al.*, 1997; Kos *et al.*, 2003). Further, Suthar *et al.* (2013) opined that the addition of chelating agent and the consequent formation of element-chelate complex prevent precipitation and sorption of elements in soil. Whereas, the minimum values of DTPA extractable Pb and Cd (0.89 and 0.63; 0.79 mg kg⁻¹ and 0.59; 0.51 and 0.55 mg kg⁻¹) were observed in the treatment amended with RDF+FYM (T_2) at 20, 40 and 60 DAI respectively, even though it registered low pH values compared to all other treatments except RDF+EDTA applied one (Table 4 and Fig.2C). However, it should be noted that in acidic soils, the increase in soil pH caused by the addition of the amendments may be considered as the main factor controlling the immobilization process in the soil (Janos *et al.*, 2010; Fan *et al.*, 2011) but in saline or alkaline soils, the addition of the amendments may not raise the soil pH, yet immobilize the heavy metal through other immobilizing mechanisms (De La *et al.*, 2011; Zhou *et al.*, 2012). This may be attributed due to increased sorption sites by FYM, through addition of organic carbon, enhancing the CEC and humic substances in soil. By which, HMs may get adsorbed, precipitated or more options of forming complex with Pb and Cd in sandy loam soil textures having pH < 8.5. The low cation exchange capacity of the soil attests to its low metal immobilization ability which may result in increase in leaching of elements. Further, higher values of CEC and SOC were observed in FYM treatment throughout the incubation period, which results in higher immobilization of lead and cadmium. These results are in agreement with those of Singh and Agrawal (2013), who envisages that the high cation exchange capacity of amendment (organic or inorganic) reveals its high capability in immobilizing the heavy metals in soil. However, a single factor rarely accounts for the immobilization of heavy metals in soils but also other immobilizing factors such as type of the soil, type of amendment, concentrations of heavy metal and metal speciation are also involved. The immobilization of Pb and Cd by organic and inorganic soil amendments tried in the experiment with respect to DTPA extractable Pb and Cd could be arranged in the order of RDF + EDTA > RDF + K-humate > RDF + zeolite > RDF +

lime > RDF + gypsum > RDF alone applied > RDF + press mud > RDF + FYM.

CONCLUSION

The DTPA extractable Pb and Cd were differed (in the soil amended with various amendments along with NPK addition based on the *soil associated factors* such as pH, EC, CEC and SOC) and also due to various mechanisms of amendments in soil duly at different stages of incubation analyses carried out. Immobilization of any metal in the soil described as the amount or concentration of metal adsorbed /solidified / leached out from soil solution or exchangeable sites of HMs. Keeping this in view, the treatment which allowed to extract lesser quantity /concentration of Pb and Cd was considered to be the best immobilizer in the sandy loam soil having slightly saline pH. According to the results, the percentage of immobilizing lead (Pb) and cadmium (Cd) by RDF + FYM (T_2) treatment were 66.07 %, 71.24 %, 75.64 % for Pb and Cd over RDF + EDTA amended treatment at 20, 40 and 60 DAI, respectively which registered lower immobility/ higher metal availability in soil. It can be concluded that, the decreasing trend of available concentrations of Pb and Cd in RDF + FYM amended soil is the best immobilizer by having lower Pb and Cd concentrations in soil solution compared to RDF + EDTA amended treatment which kept it high.

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