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REJUVENATION OF SOIL ORGANIC CARBON THROUGH SOIL AMENDMENTS: A NOVEL APPROACH TO MANAGING HEAVY METALS IN SOIL AND PLANTS

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Abstract: *Soil organic carbon (SOC) imparts better soil structural stability which in turn enhances the soil physical environment. Further, SOC plays a key role in maintaining soil health especially soils under stress. With aim of improving soil resilience under heavy metal stress, this study was formulated to find out the effect of soil amendments on rejuvenating soil organic carbon content under heavy metal stress. The field experiment was conducted in a farmer's field near SIPCOT industrial area, Cuddalore District, Tamil Nadu, India during June - September 2017. A randomized block design with seven amendments [Farmyard manure (FYM), Press mud (PM), Ethylene diamine tetraacetic acid (EDTA), Lime, Gypsum, Potassium humate (PH), Natural Zeolite (NZ)] and control were replicated thrice for assessing the effects on SOC enrichment in soil and its interventions with heavy metals in soil and plant using sunflower as a test crop. The outcome of the STUDY confirmed that the application of FYM and PM distinctively enriched the soil organic carbon (0.65 and 0.57 g kg^{-1}, respectively) content than the other amendments used from the initial SOC status (0.41 g kg^{-1}). Consequently, the organic amendments halt the heavy metals (lead and cadmium) progress in the soil thus bioavailability is reduced. In contrast, among inorganic amendments application of EDTA induces the mobility of heavy metals in soil (52.3 - 65.7 % over control) so increased the bioavailability and resulting in more uptake by sunflower plants.*

Keywords: *EDTA, FYM, Heavy metals mobility, Soil organic carbon, Sunflower*

INTRODUCTION

Heavy metals are importunate, non-biodegradable, and toxic when their accumulation is above the permissible limit in soil. Contamination of soils with toxic heavy metals has become one of the major causes of concern for living things. The existence is mainly anthropogenic sources from different industries and agricultural practices [1]. At present, inputs of heavy metals from anthropogenic sources exceed natural inputs due to amplified urbanization and industrialization. Industrial wastes deposition, industries, production sites from crowded cities, and other domestic wastes are among the major sources of heavy metals to get accumulated in more soils [2]. The bioavailability of heavymetals depends on certain physicochemical of properties soil like pH, EC, CEC, organic matter, soil texture, etc. Soil amendments play a key role in managing heavy metals. Organic amendments stabilize the heavy metals and reduce the bioavailability whereas inorganic amendments destabilize the same and increase its bioavailability [3].

Organic amendments like farmyard manure (FYM), press mud, poultry manure, and other compost helps not only improve soil properties and fertility but also involve altering the heavy metal availability in soil. On the other side inorganic amendments like ethylene diamine tetraacetic acid (EDTA), lime, gypsum, Zeolite, etc, are employed certain role in the mobility of heavy metals in soil. Metals like lead (Pb), and cadmium (Cd) reacted with soil organic matter by various mechanisms such as ion exchange, complexation, and precipitation reactions [4, 5]. The availability of heavy metals decreases with increasing retention of heavy metals either by silicate clays, calcite, and/or soil organic matter. Such retention of heavy metals is ascribed to reactions between metal ions and soils like adsorption, precipitation, and/or complexation. Further, the retention of metals (Pb & Cd) was greater with organic amendments than with inorganic. Stabilization or Immobilization of metals by interactionwith humic substances can trigger the formation of insoluble complexes or solid-phase complexationto humates present as coatings on soil solid surfaces [6]. To understand the effect of soil amendments for rejuvenating the soil organic carbon and other soil properties to manage the progress of heavy metals in soils and plants, detailed information is needed to halt the lethal effects of heavy metals in soils and make the contaminated soil productive. There are many studies are available in different aspects of managing heavy metals in a controlled soil environment but very few field studies are available in polluted sandy loam textured urban coastal soils. Therefore, the present field experiment was carried out to find out suitable soil amendments for rejuvenating soil organic carbon and its effect on the availability of certain heavy metals (Pb & Cd) in soil and plants using sunflower as a test cropin an industrially polluted coastal sandy loam soil.

MATERIALS AND METHODS

The experimental site, soil & design:

The field experiment was conducted in a farmer's field in sub-urban. Cuddalore; SIPCOT industrial estate area, it is geographically located at $11^0 39'$ N latitude and $79^0 45'$ E longitude with an altitude of 16.54 ft, to find out suitable soil amendments for rejuvenating soil organic carbon and its effect on the availability of certain heavy metals (Pb & Cd) in soil and plants using sunflower (*Helianthus annuus* L.) as a test crop during June – September,2017. Contaminated soil containing 69.1 mg kg^{-1} and 9.12 mg kg^{-1} of total lead and cadmium concentration and DTPA extractable concentration of Pb and Cd were 13.1 mg kg^{-1} and 0.82 mg kg^{-1}, respectively. The experimental soil was sandy loam in naturewith the pH, EC, CEC, and organic carbon status of 7.8, 0.73 d Sm^{-1}, 13.2 C mol (P+) kg $^{-1}$, and 0.41g kg^{-1}, respectively. The experiment was laid out in randomized block design (RBD), with seven soil amendments and one control as treatments and replicated thrice.

Crop management & amendments application:

Experimental plots were prepared with the dimension of 5 m × 4 m and soil was treated with different amendments [T_1 - Control),T_2 - Farmyard manure @ 12.5 t ha^{-1}, T_3 – Press mud @ 5 t ha^{-1}, T_4 – EDTA @ 1000 kg ha^{-1}, T_5 - Lime @ 2.5 t ha^{-1}, T_6 - Gypsum @ 2.5 t ha^{-1}, T_7 - Potassium Humate @ 100 kg ha^{-1}, T_8 - Zeolite @ 20 t ha^{-1}] selected for the study were applied as per the treatment schedule and seeds of sunflower variety KBSH1 were sown with a spacing of 60 × 30 cm and plants were thinned toa proper density at 4 - 5 leaf stage. Scheduled irrigation was given uniformly and regularly. The root and shoot weight were recorded at harvest.

Soil analysis:

Surface soil samples (15 cm depth) were collected (initial & post-harvest) and used for analyzing soil pH (1:2.5 soil: water using a glass electrode standardized with pH 4, 7, and 9.2 buffer tablets attached to an Ion analyzer), conductivity (conductivity meter), and cation exchange capacity was determined by neutral normal ammonium acetate method [6]. Organic carbon content was determined by the modified Chromic acid wet digestion titration method [7]

Analysis of heavy metals in soil and plant:
Soil and plant samples (1g) were digested after adding a tri-acid mixture (HNO_3, H_2SO_4, and $HClO_4$ in 5:1:1 ratio) at 80°C until a transparent solution was obtained [8]. The digested sample was filtered using Whatman no. 42 filter paper and the filtrate was finally made up to to 50 ml with distilled water. Concentrations of heavy metals in the filtrate of digested soil and plant samples were estimated by using an Inductively Coupled Plasma Optical Emission Spectrometer (Model-ICP-OES-5110, Agilent).

Statistical analysis:
The experiment was arranged in a Randomized Blocks Design (RBD) with three replicates. The data on soil properties and heavy metal contents in soil and plants were subjected to a one-way analysis of variance (ANOVA). Statistical tests were performed using SPSS software and the significant differences between the means were tested against the critical difference at a 5% probability level.

RESULTS AND DISCUSSION

Effect of soil amendments on the characteristics of polluted soil and availability of heavy metals
Soil amendments were added to the industrially polluted soil to investigate their effects on the soil properties and the availability of Pb and Cd. The results for the studied characteristics of sunflower-grown soil are depicted in Table 1. The soil pH was affected significantly ($p < 0.05$) by the different amendments. The pH and EC values ranged between 7.2 and 8.3; 0.34 and 0.87; the lowest significant value was found for EDTA, while the highest one was found for lime, respectively. The highest values of cation exchange capacity (CEC) and soil organic carbon (SOC) were found for the soil amended by FYM and it was on par with press mud. Soil amendments significantly ($p < 0.05$) affected the soil properties which in turn affected the bioavailability of Pb and Cd. Organic amendments decreased the availability of Pb and Cd by 42-50 %, and 28 - 37 % compared to the control, respectively. While inorganic amendments increased these values by 1.7 to 3 times compared to control treatment. FYM and press mud addition caused a decrease in the bioavailability of Pb and Cd approximately by 6 and 2.3 times compared to EDTA amended plots, respectively. The decrease in soil pH and EC with EDTA application was due to its nature and characteristics i.e. as a polyaminocarboxylic acid its ability of hydrogen bond donor count(2) and hydrogen bond acceptor count of (10) perpetuate the reduction in soil pH and EC by chelating the salty ions. As soil pH decreases, metals like Pb and Cd might have to compete with the extra positive charged ions for positions on the exchange sites and increase the solubility of these metals and a greater proportion was present as highly available free metal ions in the soil solution. Besides, Pb and Cd are, respectively, considered highly mobile and relatively mobile due to their small hydrated radius and large mass and therefore more absorption by EDTA [9]. Concerning soil organic carbon and its complexation mechanism had an immobilization effect on Pb and Cd in soil. The DTPA extractable Pb and Cd decreased significantly in FYM andpress mud applied plots Table 1. This might be attributed to the products such as humic and fulvic acids resulting from the decomposition of FYM and press mud with increased SOC compared to other amendments. Increased SOC formed stable organo-metallic complexes with Pb and Cd alone and in association with soil solids thus reducing the DTPA extractable Pb and Cd in soil solution. As fulvic and humic acids forms soluble as well as insoluble complexes depending upon the degree of saturationthus metal availability [10]. The importance of the organic matter in limiting Pb and Cd availabilityhas also been reported by [11, 12, 13]. Further, increased SOC content enhanced the CEC of soil in FYM and press mud amended plots which might have strengthened the organo-metal complex (O-M- C) formed with SOC and still reduced the DTPA extractable Pb and Cd.

Effect of soil amendments on the uptake of heavy metals (Pb &Cd) by sunflower
The addition of organic amendments decreased the bioavailability of Pb and Cd; on the other hand, inorganic amendments increased their availability in soil Fig 1 and 2. Soil application of inorganic amendments increased the bioavailability of Pb and Cd by 52.3 and 65.7 % compared to control, respectively. The availability of Pb and Cd in the FYM and press mud amended plots was decreased the plant uptake by 10-12 and 2 -3 times of Pb and Cd, respectively compared to control. Whereas, the

availability of these two metals in the EDTA amended plots were increased by three times over control. Organic amendments (FYM and press mud) were more effective than inorganic amendments in enhancing the immobilization of Pb and Cd in reducing metal bioavailability in soil. In contrast, inorganic amendments increase the bioavailability of Pb and Cd in the following order EDTA > K-humate > Zeolite >Lime >Gypsum to sunflower plants.

Table 1. Initial and post-harvest soil properties of the experimental site (Representative samples)

Soil samples	pH	EC (dSm^{-1})	CEC (c mol(P$^+$)kg^{-1})	SOC (g kg^{-1})	DTPA Pb (mg kg^{-1})	DTPA Cd (mg kg^{-1})
Initial Soil →	7.8	0.73	13.2	0.41	1.31	0.82
T_1 - Control	7.7^c	0.71^b	12.8c	0.51^c	1.42^f	0.79^f
T_2 - FYM	7.4^e	0.52^d	14.7a	0.65^a	0.71^g	0.52^h
T_3 - Press mud	7.6^d	0.63^c	14.3a	0.57^b	0.82^g	0.61^g
T_4 - EDTA	7.2^f	0.34^f	13.4b	0.43^d	4.21^a	1.23^a
T_5 - Lime	8.3^a	0.87^a	9.40f	0.17^f	2.94^d	1.14^b
T_6 - Gypsum	7.4^e	0.41^e	11.7d	0.24^e	2.51^e	0.93^d
T_7 - K - Humate	7.7^c	0.62^c	11.3d	0.28^e	3.96^b	1.04^c
T_8 - Zeolite	8.2^b	0.65^c	10.2e	0.19^f	3.13^c	0.98^{cd}
SEm±	0.03	0.02	0.37	0.02	0.08	0.03
(p=0.05)	0.05	0.06	0.82	0.05	0.17	0.07

pH-soil reaction, EC-electrical conductivity, CEC = cation exchange capacity, SOC = soil organic carbon. The available form of heavy metals was extracted by 0.005 M DTPA (diethylene triamine penta acetic acid). Mean (±standard deviation, n =3) with the same letters are not significantly different at p < 0.05; p values were determined by ANOVA.

Obviously, higher SOC content was recorded in the FYM and pres mud applied plots thus stabilized or immobilized the Pb and Cd in soil by forming O-M-C thus reduced uptake have realized by sunflower plants. Similar reports opined that organic amendments like composts, biochar have significantly reduced the availability of the metals compared to inorganic amendments [14, 15]. In contrast to that, inorganic amendments especially EDTA, destabilized or mobilized the Pb and Cd in soil solution by chelation effectively thus more availability of Pb and Cd. Consequently, the sunflower plants in contact with more metal cations of Pb and Cd and along with nutrients were well conducted and increased the uptake of said metals significantly (Figures 1 & 2). On the extraction capacity, EDTA depends on soil pH, EDTA concentration, major cationic content all coherently decides the metal mobility in soil and possible to increase the extraction efficiency of more than 60 % of total content [16].

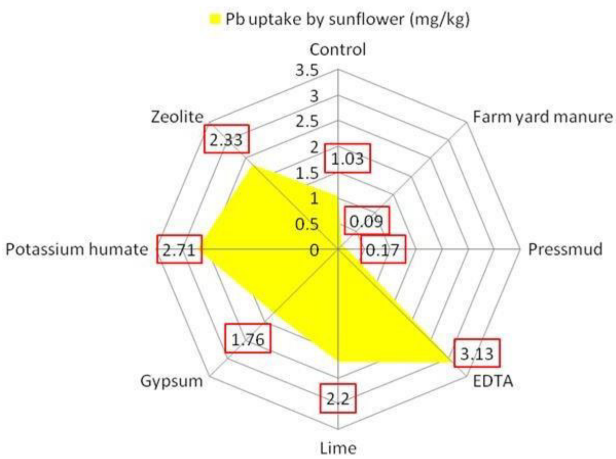

Figure 1. Effect of various soil amendments on lead (Pb) uptake by sunflower

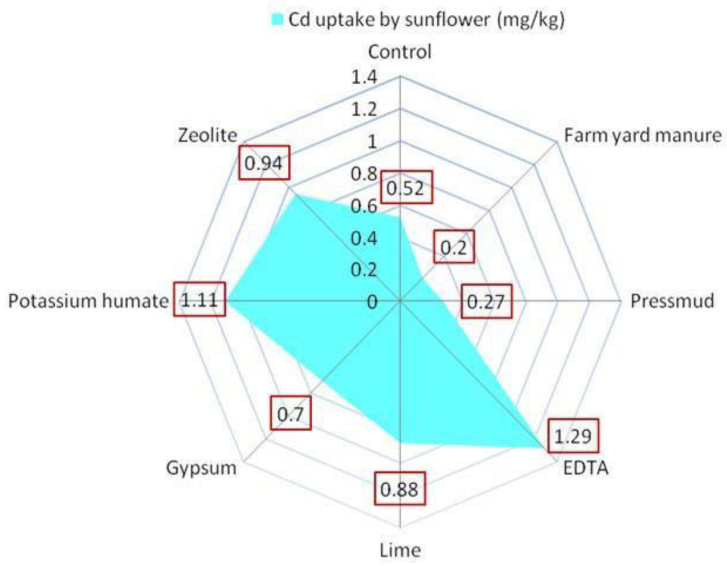

Figure 2. Effect of various soil amendments on cadmium (Cd) uptake by sunflower

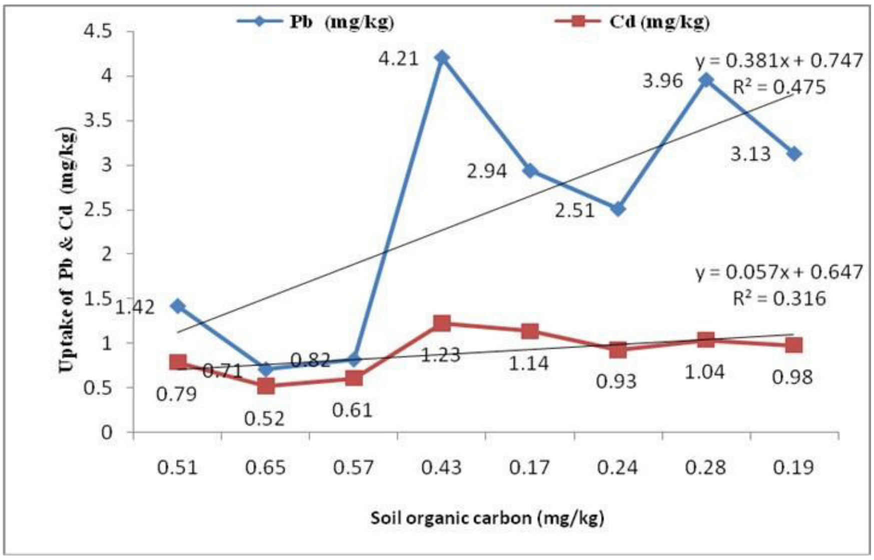

Figure 3. The Linear relationship between soil organic carbon and heavy metals uptake by sunflower

In addition, the above discussion was well supported by linear relationship between the SOC and heavy metals (Pb & Cd) uptake (Y= 0.381+ 0.747, R^2=0.475*; Y=0.057+0.647, R^2= 0.316*) respectively (Figure 3).

Such positive correlation of SOC plays a determining role in immobilizing heavy metals in soil organic matter complexes in sandy loam soils proved in this study i.e. increasing organic carbon content reduces the bioavailability of Pb and Cd in soil by FYM (T_2) and press mud (T_3).

It was the just opposite in the case of inorganic amendments that showed bioavailability of Pb and Cd in the diffused order due to their nature and characteristics which altered other soil properties especially pH.

Thus, uptake of these two metals majorly relied on SOC content and the nature of amendments too. Amongst the inorganic amendments EDTA registered higher uptake of Pb and Cd. This might be attributed due to its pH-dependent high cheating capacity with cations of equimolar concentration.

CONCLUSIONS AND RECOMMENDATIONS

From the outcome of the results, it can be concluded that the application of FYM or press mud to the industrially polluted soil could be a viable option for enriching the soil organic carbon content which in turn can halt the progress of Pb and Cd and improve the soil productivity. Whereas the application of EDTA significantly enhanced the Pb and Cd mobility in soil and improved their uptake bysunflower plants. Finally, we recommend that FYM / press mud can be applied to low-level contaminated soils as an in-situ immobilization to cut the mobility of Pb and Cd to plant nutrient cycle and thus food web. Whereas, EDTA can be recommended to highly polluted soils to effectively remove these metals from the soil through phytoextraction using hyper-accumulator plants like sunflower, and selection of the candidate for phytoextraction depends on the pedo-edapho- meteorological status of the regions.

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