Comparative Effects of Various Amendment Combinations on Cadmium and Lead Mobility in Soil and Its Uptake by Spinach Crop

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SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

By

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CERTIFICATE – I

This is to certify that the thesis entitled "**Comparative effects of various amendment combinations on cadmium and lead mobility in soil and its uptake by spinach crop"** submitted in partial fulfilment of the requirement for the degree of **MASTER OF SCIENCE** in **Agriculture (Soil Science and Agricultural Chemistry),** of the Rajmata Vijayaraje Scindia Krishi VishwaVidyalaya, Gwalior is a record of the bonafide research work carried out by **Mr. Jitendra Porwal, ID No. 17111301** under my or our guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee and the Director of Instruction.

No part of the thesis has been submitted for any other degree or diploma or has been published. All the assistance and help received during the course of the investigation has been acknowledged by the scholar.

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CERTIFICATE –II

This is to certify the thesis entitled "**Comparative effects of various amendment combinations on cadmium and lead mobility in soil and its uptake by spinach crop"** submitted by **Mr. Jitendra Porwal, ID No. 17111301** to the Rajmata Vijayaraje Scindia Krishi VishwaVidyalaya, Gwalior in partial fulfilment of the requirements for the degree of Master of Science in **Agriculture (Soil Science and Agricultural Chemistry)** has been accepted after evaluation by the External Examiner and approved by the Student's Advisory Committee after an oral examination on the same.

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(JITENDRA PORWAL)

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Legend
&	And
@	At the rate of
^{o}C	Degree Celsius
C.D.	Critical Difference
Cm	Centimeter
C.V.	Coefficient of Variation
DAS	Days after sowing
D.F.	Degree of Freedom
et al.	And others
etc	and the rest
Fig.	Figure (s)
G	Gram
ha	Hectare
HI	Harvest Index
i.e.	That is
K	Potassium
$Kgha^{-1}$	Kilogramme per hectare
L	Litre
MSS	Mean sum of square
Mg	Miligram
m	Meter (s)
N	Nitrogen
No.	Number (s)
NS	Non significant
P	Phosphorus
t	Tonnes
R.V.S.K.V.V.	Rajmata Vijayaraje Scindia Krishi Vishwa Vidyalaya
D.M.Y.	Dry Mater Yield
RH	Relative humidity
₹	Rupees
S.Em.±	Standard error of mean
S.S.	Sum of Square
Viz.	Namely
√	Square root
%	Percent

CHAPTER- I

INTRODUCTION

Agriculture productivity and production of good quality food is dependent on good quality soil, necessitating protection of fertile land area. In the recent years, soil pollution has emerged as a global issue due to increasing pressure on land resources caused by rapidly increasing population. Soil may become contaminated by the accumulation of pollutants through emission from industrial area, mine tailings, disposal of heavy metal wastes in improperly protected landfills, leaded gasoline, lead based paints, application of fertilizers, animal manures, bio-solids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals and atmospheric deposition (Zhang *et al.,* 2010). Among the pollutants, heavy metals are important because they are non-biodegradable, and persist for long durations in aquatic as well as terrestrial environments. Pb has a soil persistence period of 150– 5000 years, and has been reported to persist in soil for N150 years after sludge application (Nandakumar *et al.,* 1995). Similarly, Cd has a biological half-life of N18 years (Förstner *et al.,* 1995).

Metals, unlike other pollutants, remain in the atomic form, although their speciation can change in the time together with changes in the soil conditions. The long-lasting nature of contamination is dependent on the kind of the soil and its physiochemical properties. The most common heavy metals that occur in soil like iron (Fe), molybdenum (Mo), manganese (Mn), zinc (Zn), copper (Cu) and nickel (Ni) are essential for various physiological / metabolic functions in living cells while others like lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As) and uranium (U) are toxic even at very low concentrations (Kadem *et al.,* 2004; Meharg, 2005; Sun *et al.,* 2001). Heavy metals enter into the soil through pedogenic and anthropogenic sources (Park *et al.,* 2011). Naturally, concentration of heavy metals is low in soils but different anthropogenic activities lead to increased concentrations above critical limits (Facchinelli *et al.,* 2001; Manta *et al.,* 2002).

Among heavy metals Cd and Pb are most phytotoxic that inhibits plant growth and enter food chain through plant uptake from contaminated soil (Wang e*t al.,* 2018). Cadmium and Pb are categorized as most hazardous metals by United States Environmental Protection Agency (US-EPA) (Cameron *et al.,* 1992). Cadmium and lead accumulation in plants has a positive correlation with their availability and plant growth inhibition (Greger and Bertell *et al.,* 1992; Kibria *et al.,* 2006; Kibria *et al.,* 2007). Major source of Pb contamination in soil is the aerial emission of Pb from the combustion of petrol containing tetraethyl lead which contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Cd may also be added to soils adjacent to roads, the sources being tyros and lubricant oils (Smith *et al.,* 1995). Apart from minerals, sources of Pb are pesticides, fertilizer impurities, emissions from mining and smelting operations, and an atmospheric fall out from the combustion of fossil fuels. Similarly, application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Knox *et al.,* 2001).

In general heavy metals have toxic effects on living organisms when exceeding a certain concentration. Also, some heavy metals are being subjected to bioaccumulation and may pose a risk to human health when transferred to the food chain (Majid and Argue *et al.,* 2001; Zhou, 2003). Excessive metal concentration in contaminated soils might result in decreased soil microbial activity and soil fertility (over soil quality), yield loss (McGrath *et al.,* 1995) and possible contamination of the food chain (Hann and Lubbers *et al.,* 1983). Further heavy metals are reported to cause several disorders in humans including cardiovascular diseases, cancer, cognitive impairment, chronic anemia, damage of kidneys, ner-vous system, brain, skin, and bones (Jarup *et al.,* 2003). Therefore, it is imperative to deploy innovative and site-specific re- mediation technologies which could feasibly and efficiently remediate heavy metal contaminated soils.

Historically, there are several remediation technologies applied to contaminated soil like chemical treatment, soil flushing and washing, phytoremediation, bioremediation etc. (Salt *et al.,* 1995). The selection and adoption of these technologies being used at specific sites depends upon the extent and nature of the contaminant, characteristics of the contaminated site, cost of operation, availability of materials and relevant regulations.and soil type. The traditional method of dealing with this legacy of contamination is to excavate the soil and dump it into landfills which are generally not considered as cost effective or environmentally sustainable remediation practice (Boisson *et al.,* 1999). However, significant efforts have been made reasonably well to find alternative options which are regarded as less intrusive and more cost effective. One such technology that has received a considerable amount of attention is in situ immobilisation of heavy metals in soils by the addition of various amendments. In-situ stabilization of heavy metal in soil is often identified as a promising technology to have advantages in terms of cost-effective and environmentally friendly (Kumpiene *et al.,* 2008; Clemente and Bernal *et al.,* 2006; Lee *et al.,* 2011; Lopareva-Pohu *et al.,* 2011).

In-situ stabilization technique aims to decreases the concentration of dissolved contaminants through several processes such as metal adsorption through increased surface charge, formation of organic and inorganic metal complexes, sorption on Fe, Mn, and Al oxides, and precipitation (Ok *et al.* 2010). Hence, heavy metals become inaccessible for plant uptake, so their presence in the food chain is much lower, thus reducing the negative health and environmental effects. A large number of different amendments have been proposed and tested for in situ immobilisation of heavy metals in soils. Amendments have included agricultural products such as lime (Geeblen *et al.,* 2003), phosphate (Boisson *et al.,* 1999; Melamed *et al.,* 2003) and organic matter (biosolids) (Brown *et al.,* 2003, 2004; Farfel *et al.,* 2005), as well as various industrial products such as zeolites (Edwards *et al.,* 1999; Friesl *et al.,* 2003), birnessite (Mench *et al.,* 2000) and beringite (Boisson *et al.,* 1998). However, use of organic amendments for remediation of metal-contaminated soils is an economic approach ensuring better soil quality and fertility with an added benefit of safer environment through C sequestration.

A variety of organic materials can be used to immobilize metals in soils, including manures (farmyard, pig and poultry manure), composts of different origins, wood ash, saw dust and biosolids, sewage sludge, bark chips and wood chips (Karaca *et al.,* 2004b). The organic matter can affect metal availability due to the formation of complexes with metals or competition for sorption sites on soil matrix; OM could enhance metal adsorption by forming ligands having strong affinity with soil particles (Huang and Lin *et al.,* 1981). There have been a lot of attempts by several researchers to stabilize heavy metals in the contaminated soil by using organic or in organic amendments; however, combination of various amendments effect on remediation of multi-contaminated soil is very meagre.

Keeping this in view, the present study entitled "**Comparative effects of various amendment combinations on cadmium and lead mobility in soil and its uptake by spinach crop**" was undertaken with the following objectives.

1. To study the effect of various soil amendments levels on heavy metal stabilization in a Cd and Pb contaminated soil.
2. To study the effect of various soil amendments and its combination on soil fertility changes and spinach yield in a contaminated soil
3. To evaluate the effect of various soil amendments and its combination on heavy metal mobility in soil and its uptake by spinach crop.

CHAPTER-II

REVIEW OF LITERATURE

In this chapter, an attempt has been made to compile the available informations on the topic of investigation **"Comparative effects of various amendment combinations on cadmium and lead mobility in soil and its uptake by spinach crop"**. A brief account of the works done in past by various researchers is presented under appropriate heads.

2.1 Status of soil pollution in India

Soil is a dynamic living system on which every person's life, well being and fulfilment depend. It takes over thousands of years or even longer to develop one inch of soil. Agriculture productivity and production of good quality food is dependent on good quality soil. Every year in every country, soil resources are impaired and in some cases lost for productive use because of misuse, application of toxic materials, or poor land management systems. In India about 60% of the geographical areas occupied by agricultural land and most of which is facing one or more kind of degradation stresses. Soil pollution is one of the most sensitive environmental issues today. According to numerous studies, pollution in agricultural soils has become a growing concern in most of the developed and developing nations due to enhanced industrialization and urbanization.

Soil pollution can occur either by natural processes or man-made (anthropogenic) by the introduction of chemicals to the natural soil environment through industrial activity (industrial sector), chemicals used in agriculture (agricultural sector), or improper disposal of waste (urban sector). Natural processes can lead to an accumulation of toxic chemicals in the soil, for example, accumulation of higher levels of perchlorate in soil from the Atacama Desert in Chile is purely due to natural processes in arid environments. Mostly soil gets contaminated as a result of human action when the concentration of chemicals that are not originally found in nature, nutrients or elements in the soil exceeds naturally occurring levels. Soil pollution brings undesirable change in the physical, chemical or biological properties of the soil, which adversely affects crop production, soil quality, human nutrition, surrounding environment and there by causes huge disturbance in the ecological balance (Abrahams *et al.,* 2002).

In India industrial activities are mostly responsible for entry of pollutants into agricultural land. Soil pollution in the near by industrial area of several cities has caused loss of crop diversification due to deterioration of soil quality. Pollution of soil also drastically reduces the crop yields (15 to 25%) over the years and total cropped area decreases significantly.The Central Pollution Control Board (CPCB) in India identified critically polluted industrial areas and clusters or potential impact zone based on its Comprehensive Environmental Pollution Index (CEPI) rating. Forty three critically polluted zones were reported in the 16 states which have CEPI rating more than 70. Among the 43 sites, 21 sites exist in only four states namely Gujarat, Uttar Pradesh, Maharashtra and Tamil Nadu. In India industrial activities are mostly responsible for entry of pollutants into agricultural Land. The Central Pollution Control Board (CPCB) has identified 17 highly polluting industries, the majority of which are manufacturing industries like aluminum, cement, chlor-alkali, copper, distillery, dyes and intermediates, fertilizers, iron and steel, oil refineries, pesticides, petrochemicals, pharmaceuticals, pulp and paper, sugar, tannery, power plant, zinc smelters.

In India, heavy metal contamination in soil due to anthropogenic activity has been reported from different areas (Deka and Bhattacharyya*,* 2009). The total urban solid waste (MSW) generated in India is 68.8 million metric tons per year (TPY) or 1, 88, 500 metric tonnes per day (TPD) (Daniel and Perinaz*,* 2012). Studies have shown the buildup of heavy metals in the soils to a varying extent after repeated use of waste water for irrigation of crops.

2.2 Sources of cadmium and lead contamination in soil

The soil contaminants of heavy metals were studied in different parts of India. Heavy metals are naturally present in the deeper part of the earth from where they are being mined out and released into the biosphere in the form of waste either during the manufacturing process or after human use of the manufactured products. There are several industries and sources which release heavy metals in the environment, like mines, smelters, thermal power plant, metallurgical industries, electronics, textiles, phosphatic fertilizers, municipal solid wastes (MSW), sewage and industrial sludge etc.

Burning of fossil fuel at stationery sources (as in coal burning at power plants) contributed maximum emissions of Cr, Hg, Ni, V, Se; vehicular traffic contributed maximum for Pb; copper production contributed maximum for As, Cd and Cu; and zinc production contributed maximum for Zn. Among the heavy metals, Ni, Co, Cr and Cu are relatively more toxic to plants and As, Cd, Pb and Hg are relatively more toxic to higher animals (McBride*,* 1994).

(Raven *et al.,*1998). reported that application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg, and Pb. also observed that application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of Cd determines whether plant Cd uptake occurs to a significant degree.

(Jones and Jarvis 1998). Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for crop growth. The compounds used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which, after continued fertilizer,application may significantly increase their content in the soil.

(Basta *et al.,* 2005).The application of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se,Mo, Zn, Sb, and so forth, in the soil.

(Ratnakar and Shikha 2018) assessed the contamination level in soil samples from agricultural areas of in and around Lucknow city, Uttar Pradesh, India. It has been reported that Cd level in all the soil samples was found between 5.51 to 61.76 $mgkg^{-1}$, which was greater than the permissible limits (0.01–3.0 $mgkg^{-1}$). High Cd level in soil might be due to application of high doses of phosphate fertilizers and metal-based pesticides in agricultural crops.

2.3 Effect of cadmium and lead on crop yield, uptake and soil properties

The presence of heavy metals in soil affects the edaphological environment in several ways like contamination of food as well as a decrease in crop productivity and diminution of soil microbial activity . In long-term experiments, adverse effects on soil microbial biomass, as well as symbiotic N_2-fixation by blue-green algae and *Rhizobium* were observed due to heavy metals accumulation from sludge application (Brookes and McGrath*,* 1984).

(Mohan and Hosetti 1997,). Observed that Lead (Pb) is one of the most abundant toxic metal in the earth crust. Exposure to lead in the environmental and occupational settings continues to be a serious public health problem. Elevated Pb in soils may compromise soil productivity and even a very low concentration can inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption with toxic symptoms of dark leaves, wilting of older leaves, stunted foliage and brown short roots. The main consequences of Pb toxicity in plants are disruption of Ca metabolism, inactivation of various enzymes, reduced CO_2 assimilation and consequently suppression of photosynthesis. Relative mobility of Cd is higher than that of Pb.

(Shah and Dubey 1998).reported that of all toxic heavy metals, cadmium (Cd) ranks the highest in terms of damage to plant growth and human health. Cadmium is universally acknowledged to be a dangerous heavy metal and is toxic for human, animal and plant even at low concentrations. More over, its uptake and accumulation in plants poses a serious health thread to humans via the food chain.This is partly due to the ease with which it is taken up by plants but also to the relative speed with which it is translocated to the above ground parts. The presence of excessive amounts of Cd in soil commonly elicits many stress symptoms in plants, such as reduction of growth, especially root growth, disturbances in mineral nutrition and carbohydrate metabolism and may thus strongly reduce biomass production.

(Patra *et al.,* 2004) reported that elevated Pb in soils may compromise soil productivity and even a very low concentration can inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption with toxic symptoms of dark leaves, stunted foliage. Jaja and Odoemena*,* (2004) reported that at the evaluated Pb concentration: root/shoot and leaf growth, and fresh-dry biomass were significantly reduced in tomato. Kosobrukhov *et al.,* (2004) studied stoma density in *Plantago major* and found that stoma number in mm^2 was 194, 225, and 210 in the control, at 500 and 2000 mg kg^{-1} Pb, respectively. Also observed that stoma density decreased with 0 to 2000 mg l^{-1} Pb in Ipomoea lacunosa. Many researchers also reported a decline in the transpiration rate and water content in plants treated with Pb.

Khurana *et al.,* (2004) observed that in sewage water irrigated soil, the mean total Cd and Pb content was 1.03 to 5.18 times more than that in tube- well irrigated soils. It was also observed that under sewage irrigation near Amritsar the concentration of metals in the above ground parts of vegetables was also 1.6 to 6.6 times higher compared to those under normal water irrigation. They also found that in sewage fed soils the concentration of Pb of cauliflower, ladyfinger, brinjal, green-chillies and spinach was 5.0, 4.5, 5.0 and 6.30 µg/g dry matter, respectively. investigated that the average content of Cd, Ni and Pb in the sewage irrigated soil of Ahmadabad, India were 0.14, 0.56 and 27.20 µg/g respectively.

John *et al.,* (2008). indicated that the exposition of *Lemna polyrrhiza* to different concentrations of Cd and Pb results in an increase in growth, pigment content, proline, protein and sugar content at lower concentration; at higher concentrations their decrease was observed. Cd effect was more significant than that of Pb in hampering plant growth and development. Cd was accumulated more than Pb by L. polyrrhiza.

Sidhu and Khurana, (2010) conducted a pot culture experiment on a sandy loam soil amended with cadmium at the rate of 0, 5, 10, 20, 40 and 80 mg/kg soil. The results revealed that dry matter yield of shoots and roots of raya and spinach was decreased due to phytotoxic effect of Cd. The rate of Cd application at which significant reduction in dry matter yield of root and shoot occurred, varied depending on crop. Shoots for both the crops was significantly reduced at 20 mg Cd/kg soil level. However, roots of raya were found to be more tolerant to Cd toxicity than that of spinach as it was evident from significant decline in dry matter yield occurring at 20 and 10 mg Cd/kg soil, respectively.

Safarzadeh *et al.,* (2012) conducted a pot experiment to determine the effect of cadmium levels (0, 45 and 90 mg/kg soil) on dry matter yield, concentration, uptake and translocation of Cd in seven rice cultivars. Application of 45 mg Cd kg^{-1} soil decreased root and shoot dry weight. On an average, in all cultivars the Cd concentrations in shoot and root and its uptake is increased, whereas following the application of 45 mg Cd kg^{-1} the uptake of micronutrient was decreased.

Andresen and Kupper, (2013) stated that cadmium induced effects include oxidative stress, genotoxicity, inhibition of photosynthetic activity and inhibition of root metabolism are the major effect of cadmium in plant. Chlorosis, leaf rolls and stunting are the main and easily visible symptoms of cadmium toxicity in plants. observed that at higher metal concentration of Cd and Pb, total chlorophyll, protein and NR activity were reduced more during 7 days exposure period than 3 days exposure duration. Higher concentrations of Cd effected the growth and development of H. verticillata more significantly than higher concentration of Pb.

Saha *et al*., (2013).The toxicity of Cd is considered most hazardous among the heavy metals as it has several adverse impacts on soil microorganisms, plants, animal and human health. Heavy metals have a strong affinity for chelating substances, including the enzymes implicated in cellular metabolism and consequently by blocking these enzymes, they cause adverse physiological changes leading to even death of cell. These were found to affect soil microbial activity much earlier than their adverse effect on plant growth were expressed.

2.4 Availability of Pressmud, Steel slag, Fly ash and FYM in India and its composition.

2.4.1 Pressmud

India is the second largest producer and consumer of sugar in the world after Brazil. At the same time, annual by-product production through these industries is more than 8 Mt of press mud, 7.5 Mt of molasses, 43.8 Mt of bagasse, and 7.4 Mt bagasse ash (Murthy and Chaudhari , 2009).Among the several industries, sugar industry is the most important which not only contributes substantially to the economic development of the country, but also provides ample employment opportunities directly or indirectly. At present around 704 sugar mills has been established in India with estimated production up to 26 Mt sugar in 2015–16(Business Standard *et al.,* 2015). In India it is grown on an area of 4.94 million hectare with a production of 346.72 million tonne and an average productivity of 70.05 t ha^{-1}.India's share in the world sugar production was 17 per cent in 2014-15 (Singh and Katiyar*,* 2016).

Kumar *et al.,* (2017).Observed that Pressmud is a rejected waste material coming from sugarcane industries are classified as residue of the filtration of sugarcane juice. For every 100 tons of sugarcane crushed about 3 tons of pressmud cake is left behind as by-product i.e about 3% was produced from total quantity of cane crushed. Such huge accumulation of sugarcane byproducts are not being utilized in a productive manner. Build up of such waste with untreated discharge into the immediate waterbodies surrounding the sugar mills can strain the aquatic ecosystem. However, these byproducts had the great potential that can improve soil health, and sustainable agronomic productivity when mixed into agricultural soils as organic fertilizer. Government of India was encouraging the industries to set up distilleries to manufacture alcohol using molasses as raw material, while the press mud can be used for compost making and bagasse for power generation.

Mohamad *et al.,* (2017). Reported thatPressmud is a very soft, spongy, amorphous and dark brown material containing sugar, fiber and coagulated colloids including soil particles. It consists of 80% water and 0.9-1.5% sugar, organic matter, nitrogen, phosphorus, potassium, calcium, sulphur, coagulated colloids and other materials in varying amounts. also reported that moisture content of fresh pressmud is around 60% and oven dried pressmud contained 20% Organic C, 2.35% total N, 0.13% available P, 0.54% exchangeable K, 0.56% available S, 6.64% Ca, 0.46% Mg, 128 ppm Cu, 6300 ppm Fe, 308 ppm Mn and 883 ppm Zn.

Chogatapur *et al.* (2017). indicated that pressmud provides most of the essential elements and also used to reclaim the problematic soil. Press mud contained approximately 1.0 to 1.5 per cent N, 2.5 to 3.5 % P_2O_5 and 0.5 to 0.8 % K_2O and organic carbon of 35 to 37 %.

2.4.2 Steel slag

Steel slags are the main by-products generated during iron and crude steel production. The main raw materials are: iron ore, coal, limestone and recycled steel scrap. In general, steel production has the following two routes: i) using iron ore as raw material in Blast Furnace (BF) for iron making, basic oxygen steelmaking (BOF) for steel converting, and secondary metallurgical process (SMP) for steel refining; ii) using scrap based material in electric arc furnace (EAF) for steel making and secondary metallurgical process (SMP) for refining. confirmed that the main components of slag were oxides of iron and calcium through XRD study. It also reported that steel slag is a complex heterogeneous material mainly composed of total iron (43.14%), CaO (35.43%), SiO_2 (10.08%), Al_2O_3 (3.24%), MnO (2.52%) and MgO (2.06%). The Brunauer, Emmett and Teller (BET) results also showed that the specific surface area and pore size of steel slag is SBET= 12.56 m2/g and 794 nm, respectively. (iemkiewicz *et al.,* 1998)

Kalyoncu*,* (1999). The slag properties play a very important role in utilization. The physical characteristics, such as density, porosity, and particle size, area ffected by the cooling rates of the slag and its chemical composition. reported that the principal constituents of iron and steel slags are silica, aluminum, calcium, and magnesium, which together make up 95% of the composition. It contains several valuable components: CaO (40–60%), MgO(3–10%), Fe (2–8%), MnO(1–8%). Most slags also contain impurities of toxic elements, such as As, Pb, Cd, Co, Cr or Ni. Since these substances can be leached to some extent from the slags, possible environmental hazards cannot always be excluded.

(Das *et al.,* 2007). Reported that Slags can also be classified as three major types: BF slag, BOF slag and SMP slag. SMP slag is relatively less significant in terms of utilization due to the lower generated amount, where as BF slag accounts for about twice the amount of BOF slag.

(Gao *et al.,* 2011). In general the generation of steel melting slag is over 4 to 4.5 MT per annum. Out of this only 25% is being reused in India compared to 70-100% in other countries. reported that only 50% of slag has been used for the road project, for sintering and iron-making recycling in steel making plant.

(Hassan *et al.,* 2011). also reported that the slag is a complex material composed mainly of SiO_2, Al_2O_3, CaO, P_2O_5, TiO_2, MgO, FeO, MnO and sulphur compounds.

(Zhuo, *et al.* 2012) quantified the composition of stainless steel slag obtained from Taiyuan Iron and Steel (Group) Co., Ltd., Taiyuan, Shanxi. The results showed that the stainless steel slag was alkaline (pH13.96) with high concentrations of CaO (51.84%), SiO_2 (28.2%), MgO (9.74%), FeO (6.17%), Al_2O_3 (4.39%), TiO_2 (0.35%), MnO (0.29%) and S (0.18%). Ghataora (2015) observed that quantified the chemical composition of processed BOS slag aggregate and reported as: 42–44% CaO, 27–31% Fe_2O_3, 10–12% SiO_2, 5–6% MgO, 3–4% Mn_3O_4, 1–2% P_2O_5, 1–2% Al_2O_3, 0.5% TiO_2. BOF slag is usually di-calcium silicate (bredigite) (2CaO.SiO_2), containing tri-calcium silicate (3CaO.SiO2), free lime (CaO), wustite (FeO), calcium ferrite (also di-calcium ferrite and calcium aluminoferrite), and other elements up to 1–2% (e.g., Mn, Fe, Mg).

Pettinato et al. (2015) Thus the main by-products resulting by iron making and steelmaking are slags (that represent 90% of the total by-products), dusts and sludges. observed that steel slag has 16.20% porosity, 2.88 g cm^{-1} apparent density, 2.61 m_2 g^{-1}surface area and 1.72 μm−1most probable pore size.

2.4.3 Fly ash

Fly ash (a by-product from thermal power plants) has several chemical constituents and physical properties which can be beneficially utilized for improving soil physical and chemical environment, improving supply of some plant nutrients as well as enhancing fertilizer use efficiency. Rees and Sidrak, (1956) observed that the major matrix elements in flyash are Si, Al and Fe with significant percentages of Ca, K, Na and Ti; flyash contains highconcentrations of alkaline elements (4.48% CaO, 2.67% MgO).

(Abernathy, 1969). studied trace element composition of flyash of Eastern and Midwestern coal deposits and ashes from western states. He found that western coal (lignite and sub-bituminous) flyash had higher B content but were lower inother trace elements such as As, Cd, Co, Cr, Pb, Sb and Zn.

Yan *et al.*, (2001). elements such as As, Cd, Cu, Pb, and Zn are vaporized at intermediate temperature, and are found primarily in fly ash, Co, Cr,Cu and Ni remain associated with the iron oxidefraction and the elements with relatively low mobility(Cr, Cu, Pb and V) show affinity to silicates and glass fraction.

Nalawade *et al.,* (2015) characterized fly ash material and reported that are shown inThe SiO_2 ranges between 54.9 to64.03% with an average of 59.465%, Fe_2SO_3 ranges between 6.50 to 9.30% with an average 7.9%. The Al_2O_2, CaO, MgO are ranging between19.6 to 26.4%, 1.2 to 2.9% and 0.2 to 0.6% respectively, and average ranges between 23%, 2.05 % and 0.4 % respectively. In India, due to sulfur rich coal the pH was observed alkaline and the high salt content can increase the electrical conductivity (dsm^{-1}).The water holding capability of Indian fly ash is 35.6 to 48.6 percentand the organic carbon content is between 1.2 to1.9 percent. The relative abundance of total heavy metals in fly ash was found in order of As, Cu, Cd, Pb, Hg and Zn.The average content of these metals are 19.9, 24.1, 1.73, 19.5,1.50 and 23.5 $mgkg^{-1}$ respectively.

Mukhopadhyay and Mukherjee*,* (2016). Reported that Fly ash contains more of the oxides of Si, Al, Fe, P, Mn and Ca; it also contains lesser amount of Mg, Na, K, Zn, and S, and several trace elements. Highly volatile elements, such as Hg and Tl, are emitted almost totally in the vapor phase and thus are not found in significant amounts in fly ash.

Diatta *et al.,* (2017), observed that content of CaO in the fly ash was 16.3%as compared to the bottom ash of 6.7%. On the other hand, bottom ash could beconsidered for developing a higher reactive surface due to the allophonic properties of Si and Al oxides (i.e. SiO_2, Al_2O_3) as the prevailing chemical constituents. Thus the ratio of CaO to thesum of SiO_2 and Al_2O_3 was three times higher in fly ash (0.3) as compared to the bottom ash. The electrical conductivity particularly for the fly ash indicated a strong presence of soluble ions and chemical compounds.On this basis, it reveals that fly ash will display much stronger ameliorative as well as remediative features.

2.4.4 FYM

Farmyard manure refers to the decomposed mixture of dung and urine of farm animals along with litter and left over material from roughages or fodder fed to the cattle. On an average well decomposed farmyard manure contains 0.5 per cent N, 0.2 per cent P_2O_5 and .0.5 per cent K_2O. Application of farm yard manure (FYM) is known to maintain soil productivity longer than inorganic fertilizers (Flaig *et al.,* 1975).

Gattani *et al.,* (1976).observed that farm yard manure contains all the macro- and micronutrients required for plant growth but its main effect is due to nitrogen, phosphorus, and potassium. Maintenance of organic matter in soil is important for the improving nutrient and structural status of soils, particularly under tropical conditions as in India. Apart from its nutritional role, FYM controls the dynamics of all the macro- and micronutrients (Katyal, 1977).

Singh and Singh*,* (2014). Farm Yard Manure (FYM) which is the most commonly used organic manure in India is in short supply. A serious concern prevails on the availability of farm yard manure to meet the requirements of organic farming in India. Total farm yard manure available in the country is approximately 1200 million ton including availability of 268 million ton dung from livestock and 50% FYM is used to improve soil fertility while the remaining quantity is used for fuel.

Sharma *et al.* (2015).reported that on an average 1.5 - 4.5t ha^{-1} organic manure was available at farm level in the form of crop residues and animal dung in a survey conducted in low rainfall (below 500 mm $year^{-1}$) districts of Jodhpur, Nagaur, Pali and Balmer in Rajasthan. this is much lower than the recommended 5 to 7t ha-1 in dry areas where the rainfall is low (below 50 cm) . The shortage of organic manures is well documented. Against a requirement of 710 million tonnes of organic manure, only 105 million tonnes are available (Committee on Estimates 2015-16). The biggest constraint is the insufficiency of animal manure (The Indian Express 2016).

2.5 Utilization of Press mud, Steel slag, Fly ash and FYM as fertilizer source and soil conditioner

2.5.1 Press mud

Pressmud is a by-product of sugar industry is rich in micro and macro nutrients with organic carbon and it could be used in agricultural field as the fertilizing agent or soil conditioner. Like other organic manures, pressmud has great potential to supply nutrients in addition to its favorable effects on physicochemical and biological properties of soil. Thus, the beneficial effect of press mud for enhancing the soil fertility and thereby improving the crop productivity is well established (Laird *et al.,* 2001).

Partha and Sivasubramanian*,* (2006). Reported that several studies have been conducted on press mud for its suitability to use in agriculture and for energy production. stated that at time when cost of chemical fertilizers is increasing day by day and not affordable by farmers, pressmud has promise as a most economic source of plant nutrient for sustainable crop production and improvement in the physical (structure, texture, aeration, water-holding capacity, and porosity), chemical (pH, EC, CEC) and biological (microbial dyanamics) properties of the composts amended soil.

(Banulekha, 2007). Pressmud is used to maintain soil fertility and enhance crop production because it is rich in sugar and contains appreciable amount of essential plant nutrients viz., organic carbon, nitrogen, phosphorus, potassium, calcium and magnesium along with traces of micronutrients viz., Zn, Fe, Cu and Mn .

Bokhtiar *et al.,* (2015) in a study observed that pressmudis a good source of organic matter, NPK and important micronutrients and has established its importance in improving fertility, productivity and other physical properties of agricultural soils

(Kumar *et al.,*2017). The composition of press mud varies significantly on the soil conditions where it grows, cane varieties, period of supply of cane and geographical variations. the press mud contains 25-30% organic matter, major plant nutrients like N, P, K, Ca, Mg and S and minor elements like Fe, Zn, Mn, Cu, B and Mo. It improves the structure and water holding capacity of the soil as it contains fibrous material like decomposed coir waste and other Agriculture biomass.

2.5.2 Steel slag

A number of field and greenhouse studies have demonstrated that the use of steel slag as soil amendments to increase crop production and quality. Silicon (Si) is the most abundant element in the earth‘s crust. Although not classified as an essential plant nutrient, silicon (Si) is considered a beneficial nutrient for sugarcane *(Saccharumspp*.) and rice (*Oryza sativa L*) (Ma and Takahashi*,* 2002; Slags application may supply silicon which is considered a beneficial element to plants. Silicon may bring benefits to plants such as reduction of foliar diseases; improvement in pestcontrol; increase in photosynthetic capacity due to the silicon benefit to the architectural activity of the plant, leaving the leaves more upright; and improvementin the use of water by the plant (Silveira *et al.,* 2003).

Pereira *et al.,* (2004). Uptake depends upon the type of steel produced and on the type of furnace used to produce steel made a comparative study differences between silicon sources in relation to Si uptake. Among different Si-rich materials, metallurgical slags a byproduct of the high temperatures used in iron making and steelmaking processes release Si from crystalline form to reactive and as consequence more soluble forms, with the result to supply it to plants.

Xian and Sheng, (2006). evaluated steel slag as an iron fertilizer in Fe-deficient calcareous soils at different rates with corn. Results showed that application of steel slag increased the residual concentration of ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA) extractable Fe in the soils. The increase of extractable Fe was usually proportional to the application rate, and enhanced by the acidification of slag. At moderate rates (10 and 20 g kg^{-l}) of slag or acidified slag application corn dry matter yield and Fe uptake was substantially increased. Steel slag thus appeared to be a promising and inexpensive source of Fe to alleviate crop Fe chlorosis in Fe-deficient calcareous soils.

McCray and Ji, (2013). Observed that application of steel slag in sugar cane increased tonnage and sucrose yield. In responses to the calcium silicate slag application by broadcasting at 3.4 and 6.7 Mg ha^{-1} and banding at 1.1 Mg ha^{-1} showed significant increase in the sugar cane tonnage yield. Further, the leaf Si content is increased folloeiwing the application of electric furnace slag as compared to stainless steel slag, whereas the leaf Mg content was increased significantly greater in stainless steel slagcompared to electric furnace slag. Thus, magnesia slag being possible choices for supplying both Si and Mg however, its solubility is low.

Deus *et al.,* (2014). Correction of acidity with slag occurs similarly to the use of limestone. In addition to the decrease in acidity levels, Ca and Mg supply also occurs in soil with positive effects for crops such as potatoes, rice, black oats, beans, soybeans, alfalfa, coffee, and sugarcane, among others, making steel slag a sourcecapable of being used instead of limestone.

2.5.3 Fly ash

The idea of utilizing fly ash in agriculture has originally arisen as a result of their role as a nutrient supplement in soils low in Se, Mo, Cu, Zn, or B. Fly ash has alkaline characteristics and certain physical and chemical properties that might be useful as soil amendment acting as a liming agent to neutralize soil acidity (Taylor and Schumann, 1988).Since it is composed of mostly silt size particles, addition of fly ash to sandy soils could permanently alter soil texture, increase micro porosity and improve water retention capacity (Ghodrati *et al.,* 1995).

Kalra and Singh, (1997). Agricultural utilization of fly ash has been proposed because of its considerable content of K, Ca, Mg, S and P. Fly ash, a finely divided residue resulting from the combustion of bituminous coal of Thermal power Plant is regarded as an amorphous ferro- alumino – silicate mineral containing the naturally occurring essential elements similar to that of soil except humus and nitrogen (Tripathi and Sahu, 1997). Chemically, 90-99% of fly ash is comprised of Si, Al, Fe, Ca, Mg, Na and K with Si and Al forming the major matrix.

(Jala and Goyal, 2006). The coal combustion products (CCPs) in general and FA in particular have a considerable content of K, Ca, Mg, S and P which help in increasing plant growth and nutrient uptake.Fly ash might be supplying a part of K and micronutrients which might be useful in some deficient soils.In addition, the coal ash is consist of macro elements and micro elements such as Zn, Cu, B, Co and Mo etc that can effect to environment and human health.

(Bhattacharya and Chattopadhyay, 2006).reported that Fly ash is an abundant waste material which has a high total concentration of essential plant nutrients, but low bioavailability of the nutrients greatly limits its direct use in agriculture.

Srivastava *et al.,* (2016). Thus, fly ash can beincorporated with safe in soil as a soil ameliorates and also source of Ca, Mg and micronutrients particularly in acidic soil. Such utilization of fly ash in an integrated mannercan save chemical fertilizer to greater extent.

2.5.4 FYM

FYM is the source of primary, secondary and micronutrient to the plant growth. It is a constant source of energy for heterotrophic microorganisms, help in increasing the availability of nutrient quality and quality of crop produce. By using organic manures as organic fertilizer, agriculture can benefit from these manures and this can be a cheap way for society to conserve the environment. Organic matter inclusion in the form of farmyard manure has proven to enhance soil structure and water retention (Bhagat and Verma, 1991), It has been exhibited in most cases that the application of decomposed farmyard manure could increase the yields of crops grown on saline (Gaffar *et al.,* 1992). The soil quality could be improved with the application of organic manure and is more profitable in the environment protection in contrast to the application of chemical fertilizers alone (Conacher and Conacher, 1998).

(Yadav *et al.,* 1992).FYM supplies all major nutrients (N, P, K, Ca, Mg, S,) necessary for plant growth, as well as micronutrients (Fe, Mn, Cu and Zn). Hence, it acts as a mixed fertilizer. FYM improves soil physical, chemical and biological properties. Improvement in the soil structure due to FYM application leads to a better environment for root development. FYM also improves soil water holding capacity. The fact that the use of organic fertilizers improves soil structure, nutrient exchange, and maintains soil health has raised interests in organic farming. In general, the application of organic amendments such as crop residues and/or farmyard manure increases significantly SOC.

A traditional agricultural practice of applying nutrients was through organic manures such as green manures, farmyard manure (FYM). improved aggregate stability (Barzega *et al.,* 2002), decrease in the volume of micropores while increasing macropores (Hati *et al.,* 2006), Organic manure applications improved soil physical properties through increased soil aggregation , and improved soil water-holding capacity at both field capacity and wilting point (Hati *et al.,* 2007). and water infiltration rate, Several studies have reported that FYM plus inorganic N applications in irrigated systems resulted in reduced bulk density, higher SOC and hydraulic conductivity and improved soil structure and microbial communities (Bhattacharyya *et al.,* 2007).

2.5 Impact of Press mud, Steel slag, Fly ash and FYM on crop yield and soil properties

2.5.1 Pressmud

Additions of organic materials such as pressmud compost, municipal bio solids, animal manures and crop residues are of most important in maintaining the tilth, fertility and productivity of agricultural soils (Parmer and Sharma*,* 2002). Recently, press mud is being used as organic fertilizer source in agriculture and for crop production indicated that incorporation of press mud in crop field enhanced the soil quality parameters. The press mud was reported as a valuable plant nutrient and may affect physical, chemical, and biological properties of soil. (Kumar and Verma*,* 2002).

Dimitriu*,* (2004). reported that application of pressmud to sugarcane along with N, P and K fertilizers significantly increased the yield of cane and also quality of rice.

Shankaraiah and Kalyanamurthy*,* (2005). evaluated the effect of enriched press mud cake on growth, yield and quality of sugarcane.The result revealed that significant improvement in shoot population was observed with integrated use of press mud at 15 tonnes per hectare at recommended fertilizer level. Application of 10 tonnes of press mud cake per hectare with recommended P and K and PSB increased shoot population and number of millable canes. Continuous application of pressmud and nitrogenous fertilizer also significantly increased the cane and sugar yield of sugarcane.

Singh *et al.,* (2013). observed that application of pressmud and nitrogen alone or incombination did not affect the sucrose and purity of cane juice. However, they found that the yield of cane increased by 12.9 to 65.6% over that of control.

(Yang *et al.,* 2013). application of press mud also significantly improved soil C and N content. Lower C/N ratios in the amended soils indicated higher N mineralization by microbial activities Being an excellent source of nutrients adds organic matter; pressmud addition leads to better nitrogen nutrition and promotes cation exchange capacity (Bokhtiar *et al.,* 2015). observed that the pressmud compost application increased the phosphorus use efficiency by wheat (20-48%) and greengram (12-90%) as compared to single super phosphate.

Bokhtiar *et al.,* (2015) studied that soil fertility and productivity of sugarcan einfluenced by enriched pressmud compos twith chemical fertilizers. It was observed that soil organic C, total N, P, K and S were higher with pressmud application compared to non pressmud application. Application of enriched pressmud or raw pressmud with

50% RFD or 75%RFD recorded yields at par with 100% RFD as chemical fertilizers alone, respectively.

Mohamad *et al.,* (2017) stated that application of press mud in combination with natural soil can affect the physical, chemical and biological properties of soil. However, due to its bulky nature and high wax content,it is deemed problematic especially if it is directly applied to soil as manure. The wax content might deteriorate the soil physical properties such as permeability, aeration, soil structure and composition etc. and with the passage of time; the deterioration can be worsened.

2.5.2 Steel slag

Several alkaline slags have been used for crop production and improve soil properties such as pH, soil electrical conductivity (EC), cation exchange capacity (CEC), exchangeable Ca, Mg, and metal availability to plant, and increase the crop yield (Alva and Sumner*,* 1990).

Abou Seeda *et al.,* (2002) stated that the application of slag enhanced the nutrient uptake by radish plants and stimulated the plant growth. Slag with organic matter added at different rates stimulated the accumulation of nutrients (N, P, K, Fe and Zn) in both leaves and roots of the radish plant, due to the regulation of nutrients release from slag combined with organic matter, which play an important role for ensuring efficient utilization of nutrients.

Kuhn *et al.,* (2006) compared liming and fertilising effects of fine grained iron and steel slags. Investigations carried out on soil and yield have proven that the yields of experimental crops, in long term experiments by using iron and steel slags, were higher than those achieved after using different liming materials; on the other hand, pH has increased in the same way as a result of the use of both kind of materials. The use of basic slag in soil tests has produced the same fertilising effects, while the results of P content and soil pH has been higher, compared with super phosphate or rock phosphate use.

Lee *et al.,* (2011) reported that soil pH was increased from 5.22 to 8.10, 9.35, and 5.78 with the addition of 5% limestone, 5% red-mud, and 5% furnace slag, respectively. Similarly, soil EC was also increased from 151 to 326, 638, and 170 μS cm^{-1} following treatment with 5% limestone, 5% red-mud, and 5% furnace slag, respectively.These increases in soil pH and EC in all BS-amended soils likely resulted from the BS composition and in particular it has high Ca content. Silicon concentration in soil increased was by 1.3 times greater in treatments with stainless steel slag than in those with limestone.

Wang *et al.,* (2014 and 2015) also reported that application of 8 Mgha^{-1} of slag significantly increased grain yield from 8.09 ± 0.15 to 8.43 ± 0.09 Mgha^{-1} for the first early rice crop and from 7.46 ± 0.11 to 8.14 ± 0.48 Mg ha^{-1} for the late rice crop which could be due to the sources of many essential nutrients in slag for crop growth. Also an increase in the concentrations of soil nutrients, including available P_2O_5 from 53 to 96 mg kg^{-1}, and SiO_2 from 254 to1232 mg kg^{-1} was observed at the end of the first rice crop growth period in plots receiving 8 Mg ha^{-1} of steel slag when compared to the controls.

Ning *et al.,* (2016) conducted a consecutive early rice-late rice rotation experiment to test the impacts of steel slag on soil pH, silicon availability and rice growth in paddy soil. The results show that application of slag at a rate above higher or equal to 1 600 mg plant-available SiO_2 per kg soil increased soil pH, dry weight of rice straw and grain, plant-available Si concentration and Si concentration in rice shoots compared with the control treatment.

2.5.3 Fly ash

(Chang *et al.,*1977).There are several papers on the effect of flyash on soil-plant relationship indicating that many chemical constituents of flyash may benefit plant growth and can improve agronomic properties of soil. The limiting factors in flyash utilization on land are changes in the chemical equilibrium of soil affecting its pH,salinity, levels of certain toxic elements etc. Researchers have shown that by application of flyash to soil at the rate of 80% by weight, pH of calcareous soil was increased from 8.0 to 10.8 and that of acidic soil increased from 5.4 to 10.0.

(Nayak *et al.,*2012).Several research studies have been carried out on the application of flyash to improve the physical properties and swelling– shrinkage status of expansive clayey soils, as a potential soil amendment for improving poor physical characteristics of the clayey soil. Application of FA up to 2.5 % can be safely used without affecting the soil biological activity and there by improve nutrient cycling in agricultural soils.

Raja *et al.,* (2014) demonstrated in an experiment that dusting of 0.5 g m^{-2} day^{-1}flyash and above significantly reduced the photosynthesis, stomatal conductance, transpiration and albedo. A significant reduction of 12.3, 15.7 and 20.2 % in grain yield was recorded over control when fly ash was dusted at 0.5, 1.0 and 1.5 g m^{-2} day^{-1}, respectively.Fly-ash application to sandy soil could permanently alter soil texture, increase microporosity and improve the water-holding capacity. A gradual increase in fly-ash concentration in the normal field soil (0, 10, 20 and up to 100% v/v) was reported to increase the porosity, water-holding capacity, conductivity and cation exchange capacity.

Sett, (2017).observed that flyash application is not recommended for reclamation of acid soils, because by reducing acidity it causes deficiency of nutrients like phosphorus, zinc and copper while increasing levels of the trace elements viz. molybdenum, selenium and boron, which in turn become toxic to plant bodies.

2.5.4 FYM

Farm yard manure (FYM) is the conventional manure and is most easily available to farmers. It is a decomposed mixture of farm animals' dung and urine with straw and litter used as bedding for animals and residues of fodder fed to the farm animals. It is a rich source of plant nutrients, cellulose and crude fibre. Farmyard manure has played an important role in the continuous supply of well balanced diets of nutrients to crops and represents an important component of the nutrients cycle in agricultural ecosystems. FYM is the source of primary, secondary and micronutrient to the plant growth. It provides constant source of energy for heterotrophic microorganisms and helps in increasing the availability of nutrient quality and quality of crop produce.

Ali *et al.,* (2005).found that N, P and K contents in studied plant parts as well as yield components for both Tomato and Pea plants generally increased with application of organic manure (FYM and chicken manure) and natural minerals.

Sharma *et al.,* (2005a) reported that FYM application on equal N basis increased the shoot population, number of mill able canes and yield over others without remarkable change in sugar content of cane.

Gana and Busari*, (*2006). showed that cane yields were generally lower under the legume-treated soils *et al.,* (38.7-53.4 t ha^{-1}) when compared to yields recorded under FYM (58.6 -70.1 t ha^{-1}) or even inorganic fertilizers (55.7- 66.9 t ha^{-1}).

Yogananda *et al.,* (2014b), carried out research at VC farm Mandya and reported that the sugarcane responded positively with the increasing levels of FYM and Bio-digester liquid manure. Application of FYM equivalent to N recorded significantly superior yield (58.51 t $ha\text{-}^{1}$) over the control treatment

(Sinha *et al.,* 2014).Increase in the available nitrogen with application of bio-compost and farmyard manures may be attributed to the incorporation of organic matter which enhances the multiplication of microbes by incorporation of different organic sources for the conversion of organically bound N to in organic form .

2.6 Soil amendment for remediation of heavy metal contaminated soils

2.6.1 Pressmud

Ahmad *et al.,* (2016) evaluated the effect of combining pressmud and rice husk in the removal efficiencies of heavy metals in acidic synthetic wastewater. The ratios of pressmud to rice husk were varied at different percentages of weight ratio (0%, 20%, 40%, 60% 80% and 100%) and observation was made on the resultant removal of heavy metals concentrations. The result showed that the removal efficiency increased with the addition of pressmud up to 100%. By using only pressmud, almost 95% to 100% of heavy metals removal can be achieved where as the use of rice husk alone managed to remove merely 10% to 20% of heavy metals. As a conclusion, the soil-pressmud-Empty Fruit Bunch (EFB) mixtures are highly potential material, which can be a daily cover substitute due to the excellent heavy metals removal capability if compared to individual soil use. Amongst main contributing factor to the excellent performance is due to the high organic and fiber content present in pressmud and EFB.

A study was conducted by Harlina *et al.,* (2016) on suitability of laterite soil-pressmud as daily soil cover of landfill. The laterite soil samples were mixed with waste from sugar refinery process, namely pressmud at different percentages of weight ratio (10, 30 and 50%). The batch equilibrium tests were carried out and glaringly showed that the laterite soil-pressmud mixtures have the capability to remove more than 62% of

Cr, Cu, Mn, Ni, Pb and Zn concentration in leachate. Meanwhile, the removal efficiency of heavy metals from leachate in the laterite soil alone was lower than 50%. Pressmud alone however showed more than 53% removal. The laterite soil-pressmud mixtures, particularly at 30 and 50 percent of pressmud signify great potential as daily soil cover in reduction of heavy metals migration in landfill leachate.

2.6.2 Steel slag

Some investigations have been carried out to stabilize metals and metalloids, such as As, Cr, Cu, Pb, Cd and Zn in the contaminated soils following the addition of steel slags as soil amendments. Chemical stabilization with alkaline amendments could be an effective and stable soil remediation strategy for attenuating metal bioavailability and reducing plant metal uptake. Among recent studies, the use of slag with basic properties into a Cu-contaminated soil has led to relevant results in soil composition (Negim *et al.,* 2010). Because of its Ca and P content, the basic slag, on one hand, is a fertiliser, as it improves the physico-chemical properties of the soil and by increasing plant growth; on the other hand, it is a liming material, as it increases the precipitation and sorption of metals such as Cu.

Hassan *et al.,* (2011) demonstrated that alkaline soils contaminated with hexavalent chromium Cr (VI) can effectively be stabilized with furnace slag. The reduction capacity of the slag is attributed to its content of FeO, FeS, and SO_2 contained inthe slag in addition to its lower redox potential Eh and adsorption capacity. The presence of sulphate (usually present in iron slag) has also been shown to play a very important role in Cr(VI) immobilization by the formation of calcium aluminium sulphate chromate insoluble crystalline compounds. From the economical point of view, the iron slag is very cheap material as compared with other reduction agents of chromium-contaminated soils (e.g. zero-valent iron). Consequently, the treatment of soils contaminated with chromium by iron slag is both cost-effective and practical.

Hao *et al.,* (2012) investigated changes in available metal resulting from the application of fly ash and steel slag in a multi-metal (Zn, Pb, Cd, and Cu) contaminated acidic soil. Addition of steel slag (3 g kg^{-1}) and fly ash (20 g kg^{-1}) resulted in significant decrease in the concentrations of metals in soil solution and metal uptake by Oryza sativa L and also increases the soil pH. Significant decrease in the capability of metal resupply from solid to solution phase was observed in the fly ash and steel slag amended soils. Equilibrium modeling indicated that the soil amendments induced the precipitation of several Fe, Al and Ca minerals, which may play a positive role in metal stabilization.

Ning *et al.,* (2016) conducted a consecutive early rice-late rice rotation experiment to test the impacts of steel slag on metals-immobilization in paddy soil. The results show that the exchangeable fraction of Cd significantly decreased and cadmium concentrations in rice grains decreased significantly compared with the control treatment. In conclusion, application of steel slag reduced soil acidity, increased plant availability of silicon, promoted rice growth and inhibited Cd transport to rice grain in the soil-plant system.

2.6.3 Fly ash

Recently, coal combustion products in general and fly ash in particular has been used by several researchers for various environmental applications like (a) Phosphorus retention; (b) Heavy metal immobilisation; (c) Acid mine drainage (AMD) mitigation and mine site reclamation; and (d) Carbon sequestration. Their chemical composition makes then attractive for several goals, including the amelioration of soils and inactivation of heavy metals (Mohapatra and Rao, 2001).

Gu *et al.,* (2013) studied the remediation effects and mechanisms of the by-products of industry; fly ash and steel slag, on heavy metal contaminated acidic soil. The results indicated that the application of fly ash and steel slag significantly increased soil pH values, and the increments improved with the increasing amendment dosages. The treatments of fly ash added at 20-40 g kg^{-1} and steel slag at 3-6 g kg^{-1} had the pH values within 5.5-7.0.The addition of amendments substantially decreased the availability of heavy metals, and the higher amendment dosages resulted in the lower $CaCl_2$ extractable heavy metal concentrations. X-ray diffraction analysis indicated that the mobile metals were mainly deposited as their silicates, phosphates and hydroxides in amended treatments. These results demonstrated that the application of fly ash and steel slag might be a potential strategy to remediate heavy metal contaminated acidic soil.

Diatta *et al.,* (2017) observed that the content of CaO and derived compounds could be considered as the master factor responsible for the observed pH changes affecting or controlling heavy metals' inactivation. At relatively high soil pH, i.e. 7.5 and beyond, specific adsorption is often the predominant sorptive mechanism. but chemical sorption and precipitation are much more convincing processes that inactivate the heavy metals. The use of fly as well as bottom ashes for inactivation and remediation purposes should intrinsically consider to a greater extent the effect of pH and the specific physical properties of heavy metals. The rates of ashes and the degree of contamination may only lead to consolidated ash efficiency.

2.6.4 FYM

Application of organic manure to the metal contaminated soil may create a good environmental condition for mitigating the toxicity that is induced by high concentrations of soluble metal-ligand complexes in the soil solution and/or the toxicity of free chelators. Farm yard manure (FYM) positively influence crop production (Kaihura *et al.,* 1999) Farm yard manure can be a very effective amendment to reduce the accumulation of Cd and Pb in Amaranth and other crops growing on Cd and Pb contaminated soils. Organic matter with respective groups such as hydroxyl, phenolic and carboxyl effectively controls the adsorption and complexation of heavy metal and the activity of metal in the soil.

Clemente *et al.,* (2005) reported that both fresh cow manure and compost having a high maturity degree amendments favored Zn and Pb fixation in soil from a former Pb–Zn mine area at La Union (Murcia, Spain). The main objective was to explore the effect of organic matter on reducing the disruptive effect of heavy metal (loid)s, particularly Ni and Zn, on soil ecosystems. Manure application decreased plant tissue concentration of metals (Cu, Zn and Pb) compared with those grown in compost treated soil or control soil and it was attributed primarily to increase in soil pH due to manure application

Burgos *et al.,* (2006) concluded that the application of organic and inorganic amendment increased soil pH and total organic carbon content and decreased As, Cd, Cu, Pb and Zn, solubility.

Clemente *et al.,* (2007).Difference in pH of soil due to application of different organic amendments was possibly due to the differences in pH of applied amendments may increase soil pH due to release of basic cations and NH_3 into soils during decomposition microbially induced reducing conditions and displacement of hydroxyls ions fromsesquioxide surfaces by organic anions.

Paulsen *et al.,* (2000). Since the availability of Ni and other metals in soils is mainly controlled by the chemical equilibrium of metals in solid and solution phases, hence adsorption reactions are important to determine the availability of metals to plants and their mobility throughout the soil.

(Mahmood, 2010). Based on the results of the experiment, it could be concluded that application of FYM @ 20 t ha^{-1} significantly reduced Cd content in soil over no FYM application. Following the application of 2% farmyard manure, Ni concentration decreased by 39, 40, 45 and 35% in carrot, fenugreek, spinach, wheat grain, respectively.

Mostafa et al (2013). a that indicate mono and multi-metal sorption of Cd, Ni, and Zn enhanced with increase in organic amendment as cow manure with rates 0, 25, and 50 tons/ha.Sarra and Abutalib, (2014) found that compost addition significantly increased the sorption of cadmium, in linear correlation with the amount of compost added.

CHAPTER – III

MATERIAL AND METHODS

To fulfill the objectives of the present investigation, two separate experiments were conducted at Indian Institute of Soil Science (ICAR), Bhopal, Madhya Pradesh. The following is the brief description of the location, soil and climatic conditions of the farm, together with the nature and characteristics of the materials used and description of the methods followed during the study.

The first experiment under this investigation was incubation experiment aimed to study the various amendments (press mud, steel slag, fly ash and FYM) and rates (1, 2.5 and 5% dry w/w basis) on heavy metal (Cd and Pb) stabilization in a contaminated soil (artificially spiked soil with Cd and Pb).

The second experiment was a pot culture study, where the efficiency of various amendments and in combination with FYM were evaluated with respect to spinach yield, nutrient potential and remediation of heavy metal (Cd and Pb) contaminated soil.

3.1 Description of experimental site and climatic condition

The study was conducted at ICAR-Indian Institute of Soil Science Bhopal. ICAR-IISS is located at 23^{0}18'N; 77^{0}24' E, 485 M above mean sea level. The location falls under semi-arid and sub-tropical zone characterized by hot summer and cold winter. Mean minimum and maximum temperature being 26.4^{o}C and 44.1^{o}C in summer and 5.6^{o}C and 23.7^{o}C in winter, respectively, with wide diurnal variations. The average annual precipitations are about 710 mm of which about 80 per cent is normally received during a short span of three months from July to September.

3.2 Collection and processing of experimental soil

Soil for the experimental purpose was collected from the top 15 cm of an uncontaminated field from ICAR-IISS farm representing Vertisol (Typic Haplustert). Soil samples were drawn randomly from the farm with the help of an auger and a composite sample was obtained by mixing them thoroughly. Soil was air dried and ground to pass through a 2 mm sieve to separate dry roots, grasses and gravels, etc. A portion of the soil passed through 2 mm sieve was retained for laboratory analyses.

3.3 Physico-chemical properties of experimental soil

The processed bulk experimental soils which are used for incubation and pot culture study were analyzed for various physico-chemical properties. The data pertaining to the initial characterization of experimental soil are presented in the table 3.1. It indicates that the experimental soil was clayey in texture. The available N, P, K and organic carbon status of initial soil was 204.7, 13.2, 568.3 kg ha^{-1} and 0.71%, respectively. The chemical composition of soil indicates that the experimental soil was low in available nitrogen, medium in organic carbon and available phosphorus, and high in available potassium. The plant available micronutrient and heavy metal content of the experimental soil was 1.16, 8.32, 7.24, 0.65, 0.02, 0.83, 0.02, and 0.23 for Cu, Fe, Mn, Zn, Cd, Pd, Cr and Ni, respectively.

Table 3.1 Physico- chemical Properties of experimental soil

Sl.No.	Parameter	Value	Method/Reference
1.	pH (soil : water 1:2)	7.89	Jackson (1973)
2.	EC (soil:water 1:2) (dsm^{-1})	0.19	Jackson (1973)
3.	Mechanical analysis Sand (%) Silt (%) Clay (%) Textural Class	 35.4 21.9 42.7 Clayey soil	International pipette Method (Piper, 1967)
4.	Organic carbon (%)	0.71	Walkley and Black (1934)
5.	Av. N (kg ha^{-1})	204.73	Subbiah and Asija(1956)
6.	Av. P (kg ha^{-1})	13.17	Olsen et al. (1954)
7.	Av. K (kg ha^{-1})	568.34	Black (1965)

8.	Av. S (mg kg^{-1})	9.82	Chesnin and yien (1950)
9.	Total Heavy metals (***DTPA) (mgkg^{-1}) Cu Fe Mn Zn Cd Pb Cr Ni	Total\DTPA extract data 53.57 (***1.16) 38461 (8.32) 1016 (7.24) 67.92 (0.65) 0.89 (0.02) 25.93 (0.83) 50.40 (0.02) 58.71 (0.23)	Lindsay and Norvell (1978)

3.4 Collection and processing of various soil amendments

Various amendments like press mud, steel slag, fly ash and FYM were collected from different places for the experimental purpose. Pressmud was collected from the sugar mill Gayathri Sugar limited, Nizam Sugar Unit, Kamareddy district, Telangana. Steel slag sample was obtained from HARSCO India Pvt, Ltd, Hyderabad. Fly ash from obtained from National Thermal Power Corporation (NTPC) limited, Singrauli, Madhya Pradesh. Farm Yard Manure was collected from the research farm of ICAR-IISS, Bhopal. All the amendments used for experimental studies (incubation and pot culture experiment) wereair dried, sieved through 2 mm sieve and analyzed for their characteristics. The pH and EC for press mud, steel slag, fly ash and FYM was determined in a suspension with an amendment: water ratio of 1:5 using a pH meter and conductiviti meter, respectively. The total carbon, nitrogen, phosphorus, potassium and sulphur content in various amendments were analyzed using standard procedures (Chaudhury et al. 2005; Enamorado-Baez et al. 2013). Totalmicro nutrient and heavy metal contents were determined after wet digestion in hydrofluoric acid (HF) following standard protocol. Micronutrient and heavy metals (Cd, Cr Ni and Pb) in clear digests were determined usingInductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 2100 DV). The chemical composition of various amendments obtained by laboratory analysis following standard procedure are presented in Table 3.2.

Table 3.2 Chemical composition of press mud, steel slag, fly ash and FYM

Sl.No	Parameter	Amendments			
		Press mud	Steel slag	Fly ash	FYM
1.	pH (amendment : water 1:5)	7.47	10.15	7.68	6.58
2.	EC (dsm^{-1}) (amendment : water 1:5)	3.51	0.254	0.187	3.12
3.	Total organic carbon (%)	28.29	1.24	0.12	17.52
4.	Total nitrogen (%)	2.17	0.06	0.04	1.14
5.	Total phosphorus (%)	1.78	0.13	0.06	0.61
6.	Total potassium (%)	0.62	0.19	0.09	1.02
7.	Total sulphur (%)	1.04	0.18	0.71	0.62
8.	Total Fe (%)	1.34	11.05	6.62	3.06
9.	Total Heavy metals (mgkg^{-1})				
	Cu	96.77	11.38	36.56	66.27
	Co	3.93	7.48	18.65	18.38
	Mn	770.83	11165	1056	1020
	Zn	128.37	56.17	55.13	189.73
	Cd	0.56	0.42	0.67	0.43
	Pb	13.6	7.9	29.63	23.37
	Cr	20.61	268.74	57.22	56.67
	Ni	12.67	7.8	52.9	35.353

3.5 Incubation study

An incubation study was conducted under controlled laboratory condition using various soil amendments (press mud, steel slag, fly ash and FYM) to study its impact on stabilization of Cd and Pb in contaminated soil. The hypothesis of this experiment is to evaluate the quality of various amendments in terms of organic matter, oxide and hydroxides of metals and pH on heavy metal stabilization in soil. For this purpose, the processed bulk soil sample was spiked artificially with heavy metal (Cd and Pb) and different amendments were applied in order to study its impact on heavy metals stabilization in the contaminated soil. Incubation experiment with four different amendments (press mud, steel slag, fly ash and FYM) at three rates of application (1, 2.5 and 5% on dry w/w basis) along with absolute control was conducted. Therefore in total there were 13 treatments and all the treatments were replicated 3 times. The incubation studies were carried out in three soil type (uncontaminated, cadmium contaminated and lead contaminated soil) with same set of treatments (13) in each soil type. The treatment details are as follows

Soil Type: uncontaminated/Cd spiked/Pb spiked soil

T1: Control

T2: Press mud (1%)

T3: Press mud (2.5%)

T4: Press mud (5%)

T5: Steel slag (1%)

T6: Steel slag (2.5%)

T7: Steel slag (5%)

T8: Fly ash (1%)

T9: Fly ash (2.5%)

T10: Fly ash (5%)

T11: FYM (1%)

T12: FYM (2.5%)

T13: FYM (5%)

Bulk sample was collected from ICAR-IISS farm and after processing as described in section 3.2 was used for this incubation experiment and as well as for pot culture experiment. The soil samples were spiked with cadmium using cadmium nitrate salt to provide 100 mg Cd kg^{-1} soil.Similarly, lead was artificially spiked using lead nitrate salt to provide 1200 mg Pb kg^{-1} soil. The incubation study under controlled condition was conducted in plastic container of 1 kg capacity with a 500 gm soil. For artificial spiking of cadmium (cadmium contaminated soil) and lead(lead contaminated soil), the calculated amount of cadmium nitrate salt ($Cd(NO_3)_2.4H_2O$ and lead nitrate salt($Pb(NO_3)_2.4H_2O$) required for 500 gm soil was dissolved in 200 ml of distilled water and the entire solution was transferred to the plastic container containing 500 gm soil. After spiking, the soil in the container was allowed to dry and equilibrate for 30 days. After 30 days period, the spiked soil was transferred to the plastic tray and the required amount of amendments as per the treatment details were added and mixed thoroughly using hand gloves. Then, the entire soil containing amendments were transferred back to the plastic container and kept for incubation studies. Similarly, amendments were also added as per the treatment details in the uncontaminated/unspiked soil which is the original soil collected from ICAR-IISS farm. The plastic containers with loosely placed lids were then incubated for 4 weeks at 60% of the water-holding capacity of the soil at 25°C. Throughout the incubation period, water content was held constant by adding distilled water. After every week, soil samples were collected from each plastic container and analyzed for DTPA extractable heavy metal content (Cd and Pb) as described by Lindsay and Norvell, 1978. The Cd and Pb content in the extract was measured in the ICP-OES instrument.

3.6 Pot culture study

A pot experiment was conducted in a greenhouse at ICAR-IISS Bhopal with spinach as a test crop on clayey loam soil during kharif season 2018. The pot culture experiment was carried out in four soil type (uncontaminated, Cd contaminated, Pb contaminated soil and Cd + Pb contaminated soil) with same set of treatments (8) in each soil type. The experiment for uncontaminated soil is the original soil collected from ICAR-IISS farm. In case of Cd,Pb and Cd + Pb contaminated soil experiment; the original soil was artificially spiked with cadmium nitrate and lead nitrate salt. The cadmium and lead contamination level was 100 $mgkg^{-1}$ and 1200 $mgkg^{-1}$ representing Cd and Pb contaminated soil, respectively. Similarly, soil contaminated with Cd + Pb provides same level of contamination i.e. 100 ppm of Cd and 1200 ppm of Pb together in soil. Cadmium was applied at rate of 100 mg Cd kg^{-1} soil in solution form as $Cd(NO_3)_2.4H_2O$ and lead at the rate of 1200 mg Pb kg^{-1} soil in solution form as $Pb(NO_3)_2.4H_2O$. The experimental details are as follows:

Soil Type: uncontaminated/Cd spiked/Pb spiked soil/Cd + Pb spiked soil

T1: Control

T2: Press mud (5%)

T3: Steel slag (5%)

T4: Fly ash (5%)

T5: FYM (5%)

T6: Press mud (2.5%) + FYM (2.5%)

T7: Steel slag (2.5%) + FYM (2.5%)

T8: Fly ash (2.5%) + FYM (2.5%)

Total No. of treatments: 8 for each soil (uncontaminated, Cd, Pb and Cd + Pb contaminated soil)

No. of replication: 3

Total No. of pots: 24 for each soil

Design: CRD

Pot size: 7kg soil weight capacity

Crop: Spinach (variety: Selection 1)

3.6.1 Heavy metal spiking in soil and amendment addition

The pot culture experiment was conducted in a glazed earthen pot of 10 kg capacity filled with 7 kg of processed Vertisol (*Typic Haplustert*). For artificial spiking of cadmium (cadmium contaminated soil), the calculated amount of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) salt required for 7 kg soil to provide 100 mg Cd kg^{-1} soil is dissolved in 2 litre of distilled water and the entire solution is transferred to the pot containing 7 kg soil. After that the soil was allowed to dry for 30 days within the pot. Once the soil gets completely dried, the entire soil from the pot was transferred on a polythene sheet and mixed thoroughly with the help of hand gloves. After uniform mixing, the soil was carefully transferred to the respective pots. Similarly, artificial spiking of lead was done with lead nitrate salt ($Pb(NO_3)_2.4H_2O$). The required amount of lead nitrate salt required for 7 kg soil to provide 1200 mg Pb kg^{-1} soil is dissolved in 2 litre of distilled water and the entire solution is transferred to the pot containing 7 kg soil. After that, mixing and filling the pot is followed in the same way as described in cadmium spiked soil. Likewise in case of Cd + Pb contaminated soil, the required amount of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) and lead nitrate salt ($Pb(NO_3)_2.4H_2O$) together is dissolved in 2 litre of distilled water and the entire solution is transferred to the pot containing 7 kg soil . By this way, the Cd + Pb contaminated soil provides a cadmium and lead contamination level of 100 and 1200 mg/ kg soil, respectively. In case of uncontaminated soil, the original soil (7 kg) is filled as such in pots without any addition of heavy metal. In all the pots water was added at weekly interval for a period of one month. Each treatment was replicated thrice and the pots were arranged in randomized block design.

After 30 days period, the spiked soil was transferred to the plastic tray and the required amount of amendments as per the treatment details were added and mixed thoroughly using hand gloves. Then, the entire soil containing amendments were transferred back to the earthen pot for pot culture experiment. Similarly, amendments were also added as per the treatment details in the uncontaminated/unspiked soil which is the original soil collected from ICAR-IISS farm. Potted soils mixed with soil amendments and heavy metal was then allowed to equilibrate for another one week in moist condition prior to sowing of seeds.

3.6.2 Fertilizer addition and mixing

Uniform doses of N (75 kg N ha^{-1}), P (40 kg P_2O_5 ha^{-1}) and K (40 kg K_2O ha^{-1}l) were supplied in the form of urea, di-ammonium phosphate, and potassium chloride, respectively, in order to ensure adequate supply of nutrients. The entire dose of P, K, and half of the dose of N were applied as bassicly before sowing, while the remaining N was top-dressed 20 days after sowing. For basal application of nutrients, the soil from the pot was transferred on a polythene sheet. The calculated amount of each of the basal doses of fertilizer materials was added. After thorough mixing with hand gloves, the soil was carefully transferred to the respective pots. Later water was added in pots by gradual sprinkling to have the sufficient moisture content at the time of sowing.

3.6.3 Spinach seed treatment, sowing and after care

Before sowing, seeds of spinach variety Selection -1 were treated with Bavistin @ 2g kg^{-1} seed in order to avoid fungal infection. Ten healthy seeds of spinach were sown by making 2–3 cm deep holes equidistantly in the soil and then the holes were loosely covered with soil. After germination, all seedlings were allowed to grow for 10 days, after which they were thinned out to leave five healthy plants in each pot. Watering and weeding were done as and when required during the crop growth period.

3.6.4 Harvesting, processing and analysis of plant and soil samples

Sixty days after sowing, the above-ground portions (leaf) and roots of the spinach plants were harvested separately, washed with distilled water, and air dried. Roots were washed thoroughly with tap water to remove adhering soil particles, followed by washing with dilute hydrochloric acid (HCl) and then distilled water in sequence. The air-dried leaf and root samples were then oven-dried at 65 °C until their weights remained constant. Oven-dried plant parts (leaves and roots) were ground in a Willey mill and passed through a 2 mm sieve. Homogenized tissue samples were digested in a di-acid mixture containing nitric acid (HNO_3) and perchloric acid ($HClO_4$) (in the ratio 9:4 v/v) on a hot plate at 150–175 °C for about 2 h until a clear liquid was obtained.

Soil samples were collected separately from each pot for soil analysis after the harvest of the crop. The pH and electrical conductivity (EC) of post-harvest soil samples were measured in soil:water solution of 1:2 ratio, whereas soil organic carbon was estimated by following a wet oxidation method (Walkley and Black 1934). Soil samples were digested in the di-acid mixture (HNO_3/$HClO_4$ at 9:4 ratios) for total Cd and Pb content and plant-available soil Cd and Pb was extracted by the DTPA extractant (Lindsay and Norvell 1978). The concentrations of cadmium and lead in the digested samples (plant and soil) and in DTPA extractant were determined using an inductively coupled plasma optical emission spectrophotometer (Perkin Elmer Optima DV 2100).

3.7 Methods of soil analysis

Standard methods of analysis of soil samples were followed during the course of investigation, which are briefly mentioned below:

3.7.1 Mechanical analysis

Particle size distribution of soil was determined after passing the soil through 2 mm sieve and using Bouyoucos hydrometer method as described by Piper (1967) and from the per cent composition of sand, silt and clay, the textural class was found out with the help of the triangular diagram.

3.7.2 Soil reaction (pH)

The pH of the soil was determined in soil -water suspension (1:2.5 ratio) at 25^{o}C with the help of pH meter after intermittent stirring for 30 minutes as described by Jackson (1973).

3.7.3 Electrical conductivity (EC)

The electrical conductivity (a measure of concentration of soluble salts) was measured in the supernatant liquid of soil: water suspension (1:2.5) with the help of conductivity bridge as described by Jackson (1973).

3.7.4 Organic carbon

Organic carbon was determined by its oxidation with $K_2Cr_2O_7$ as per the method as described by Walkley and Black (1934).

3.7.5 Available nitrogen

The alkaline potassium permanganate oxidisable soil nitrogen as an index of N availability was estimated by the method given by Subbiah and Asija (1956).

3.7.6 Available phosphorus

For estimation of available phosphorus content of soil, Olsen's extractant i.e. 0.5 M $NaHCO_3$ adjusted to pH 8.5 (Olsen *et al.*, 1954) was used for the extraction of available phosphorus. Phosphate in the extract was determined colorimetrically using red filter (660 nm) after developing blue colours of reduced molybdo phosphoric acid following the procedure given by Dickman and Bray (1940).

3.7.7 Available potassium

Available potassium was estimated flame photometrically with the help of flame photometer after extracting with neutral normal ammonium acetate as described by Jackson (1973).

3.7.8 Available sulphur

Available sulphur content in soil was estimated through turbidimetric method using UV-VIS spectrophotometer at 420 nm wavelength as described by (chesnin and Yien, 1950).

3.7.9 Total and DTPA extractable heavy metal

Processed soil samples were digested in di-acid (HNO3/HClO4 at 9:4 ratio) and the available Cd and Cu in soil was extracted by the DTPA extractant (Lindsay and Norvell, 1978). The concentrations of heavy metal (Cd and Pb) in the soil digests and

DTPA solution were determined using inductively coupled plasma-optical emission spectrophotometer.

3.8 Plant Analysis

Oven dried plant parts (leaves and root) were ground in a Willey mill and passed through a 2 mm sieve before use. Homogenous tissue samples were digested in 9:4 $HNO_3:HClO_4$ (v/v) on a hot plate at 150-175ºC for about two hours until clear liquid was obtained. Heavy metals were determined using inductively coupled plasma-optical emission spectrophotometer. The concentration of P was measured using UV/VIS spectrophotometer at a wavelength of 430 nm and K concentrations were measured using a flame photometer.

3.9 Statistical analysis

The analysis of variance technique was carried out on each parameter in the laboratory studies, incubation studies and pot experiment as applicable to completely randomized design (Gomez and Gomez, 1984). To determine the significance of difference between means of two treatments, least significant difference was estimated at 5% probability level and Duncan‘s multiple range test was used for comparing the means.

CHAPTER – IV

RESULTS

The present investigation consists of two separate experiments under controlled condition (incubation and pot experiment). The first experiment (incubation study) was aimed to evaluate the impact of various amendment (press mud, steel slag, fly ash and FYM) and its application rates (1, 2.5 and 5%) on heavy metal (Cd and Pb) stabilization of contaminated soil (artificially spiked with Cd and Pb).The second experiment (pot culture study) was conducted to the study the effect of various amendment either alone or in combination with FYM on heavy metal (Cd and Pb) mobility in soil and its uptake by crop plant spinach.

Both the experiments were conducted in a cadmium (100 mg kg^{-1} soil) and lead spiked soil (1200 mg kg^{-1} soil). Both the experiments were carried out in clayey soil (vertisol) and the various amendments were applied as per the experimental/treatment conditions. In pot culture experiment, test crop spinach variety Selection - I seeds were sown and the recommended management practices were followed throughout the crop period including fertilizer application. The crop cutting (leaf) was done at 45 DAS and the root was separated from the soil. The leaf and root dry matter yield was recorded following standard protocol of sample washing and oven drying. The leaf, root and post-harvest soil samples were processed and analyzed for nutrient and heavy metal content.

The results generated from these two experiments were statistically analyzed, tabulated, and explained in succession of one experiment followed by the other as given below:

4.1. Experiment (I) – Impact of various amendments and its application rate on soil properties in a heavy metal spiked soil (Incubation experiment).

4.2. Experiment (II) - Impact of various amendments either alone or in combination with FYM on heavy metal mobility in soil and its uptake by spinach crop (Pot culture experiment).

4.1 Impact of various amendments and its application rate on soil properties in a heavy metal spiked soil

The results from the incubation study revealed that various amendments (HCl and HNO3) and its application rate (1, 2.5 and 5%) significantly influenced the pH, EC, SOC and DTPA extractable Cd and Pb content in soil (Table 4.1 to 4.4 and Figure 4.1 to 4.4).

4.1.1 Impact of various amendments and its application rate on soil pH, EC and SOC content.

The data pertaining to soil pH, EC and SOC content in a Cd and Pb contaminated soil amended with various amendments has been presented in table 4.1, 4.2 and 4.3. The results clearly indicate that application of press mud, steel slag, fly ash and FYM at 1, 2.5 and 5% application rate had significantly influenced the soil pH, EC and SOC at the end of incubation period of 30 days.

Irrespective of soil type (uncontaminated, Cd contaminated and Pb contaminated soil), steel slag application at 1, 2.5 and 5% rate showed significant increase in soil pH over control (Table 4.1). Among the various amendments, the increase in soil pH was found to be significantly highest in soil amended with steel slag followed by fly ash and press mud. The result also indicates that with increase in application rate of steel slag from 1 to 5% rate, the soil pH was also increased significantly. On the contrary, FYM application in a Cd and Pb contaminated soil resulted in significant decrease in soil pH over control.

The soil pH value at the end of 30 days of incubation period varied from7.67 to 9.00, 7.62 to 9.00 and 7.71 to 8.93, respectively in uncontaminated, Cd contaminated and Pb contaminated soil. In all the soil type (uncontaminated, Cd contaminated and Pb contaminated soil), significantly highest and lowest value of soil pH over control was observed in soil amended with steel slag and FYM at 5% rate, respectively at the end of 30 days of incubation period. The corresponding highest soil pH value in an uncontaminated, Cd contaminated and Pb contaminated soil at 5% rate of steel slag application was 9.00, 9.00 and 8.93, respectively. Similarly, the lowest soil pH value in an uncontaminated, Cd contaminated and Pb contaminated soil at 5% rate of FYM application was 7.67, 7.62 and 7.71, respectively.

From the result it is also clear that the soil pH was increased by 1.04, 1.14 and 1.09 unit over control following the application of steel slag at 5% rate in an uncontaminated, Cd contaminated and Pb contaminated soil. On the the other hand, the soil pH was decreased by 0.29, 0.24 and 0.13 unit over control following the application of FYM at 5% rate in an uncontaminated, Cd contaminated and Pb contaminated soil. Significant increase in soil pH over control was observed only at highest rate (5%) of press mud application.

Table 4.1 Effect of various amendments and its application rate on soil pH

Treatment	pH		
	Uncontaminated Soil	**Cd Contaminated Soil**	**Pb Contaminated Soil**
Control	7.96e	7.86e	7.84e
Press mud (1%)	7.92e	7.83ef	7.81ef
Press mud (2.5%)	7.86e	7.83fg	7.81fef
Press mud (5%)	7.82e	7.75g	7.75fg
Steel slag (1%)	8.40f	8.21c	8.35c
Steel slag (2.5%)	8.77c	8.61b	8.68b
Steel slag (5%)	9.00b	9.00a	8.93a
Fly ash (1%)	8.02a	7.83d	7.83e
Fly ash (2.5%)	7.97e	7.93de	7.85e
Fly ash (5%)	7.97d	7.96de	7.98d
FYM (1%)	7.90e	7.85f	7.72g
FYM (2.5%)	7.81f	7.72g	7.72g
FYM (5%)	7.67g	7.62h	7.71g
SEm(d)±	0.026	0.026	0.036
C.D. (5%)	0.057	0.060	0.075

The data pertaining to soil EC content measured at the end of incubation period is shown in Table 4.2. Among the various amendments, the increase in soil EC was found to be significantly highest in soil amended with press mud. Irrespective of soil type (uncontaminated, Cd contaminated and Pb contaminated soil), press mud application at 1, 2.5 and 5% rate showed significant increase in soil EC over control (Table 4.2). The result also indicates that with increase in application rate of press mud and FYM from 1 to 5% rate, the soil EC was also increased significantly. On the contrary, no clear trend was observed in soil EC following the application of steel slag and fly ash over control in an uncontaminated, Cd contaminated and Pb contaminated soil.

The soil EC value at the end of 30 days of incubation period varied from 0.33 to 1.04 dsm^{-1}, 0.40 to 1.20 dsm^{-1} and 0.49 to 1.37 dsm^{-1}, respectively in uncontaminated, Cd contaminated and Pb contaminated soil. In all the soil type (uncontaminated, Cd contaminated and Pb contaminated soil), significantly highest soil EC value was observed in soil amended with press mud at 5% rate at the end of 30 days of incubation period. The corresponding highest soil EC value in an uncontaminated, Cd contaminated and Pb contaminated soil at 5% rate of press mud application was 1.04, 1.20 and 1.37 dsm^{-1}, respectively.

A critical appraisal of data on soil organic carbon content at the end of incubation period of 30 days as influenced by various amendments and its application rate was presented in table 4.3. The SOC values ranged from 0.49 to 1.45%, 0.57 to 1.68% and 0.54 to 1.52% in the soil sample of uncontaminated, Cd contaminated and Pb contaminated Vertisol, respectively. Among the amendments, only press mud and FYM application resulted in significant increase in soil organic carbon (SOC) of soil samples of uncontaminated, Cd and Pb contaminated Vertisol over control. With increase in rate of application from 1 to 5% of press mud and FYM, the SOC content was also significantly increased. The highest increase in SOC content over control was observed in soil amended with press mud at 5% application rate followed by FYM.

Table 4.2 Effect of various amendments and its application rate on soil EC

Treatment	EC (dsm^{-1})		
	Uncontaminated Soil	**Cd Contaminated Soil**	**Pb Contaminated Soil**
Control	0.42fg	0.44fgh	0.51f
Press mud (1%)	0.58c	0.67c	0.77c
Press mud (2.5%)	0.71b	0.74b	1.05b
Press mud (5%)	1.04a	1.20a	1.37a
Steel slag (1%)	0.58j	0.31i	0.49f
Steel slag (2.5%)	0.33i	0.45fg	0.65e
Steel slag (5%)	0.39h	0.40h	0.75cd
Fly ash (1%)	0.34i	0.42gh	0.65e
Fly ash (2.5%)	0.41gh	0.48f	0.55f
Fly ash (5%)	0.45ef	0.56e	0.66e
FYM (1%)	0.43fg	0.55e	0.64e
FYM (2.5%)	0.47e	0.60de	0.68de
FYM (5%)	0.58d	0.64cd	0.80c
SEm(d)±	0.026	0.026	0.036
C.D. (5%)	0.058	0.051	0.081

The per cent increase in SOC content in the uncontaminated soil amended with pressmud at 1, 2.5 and 5% over control was 43.1, 91.4 and 150.0%, respectively. Simarly, in the Cd contaminated soil, the per cent increase in SOC content due to press mud application was 40.9, 104.9 and 175.4 %; whereas in the Pb contaminated soil it was 43.3, 90.1 and 153.3%, repectively at at 1, 2.5 and 5% application rate over control. Like wise, the per cent increase in SOC content in the uncontaminated soil amended with FYM at 1, 2.5 and 5% over control was 22.4, 53.5 and 84.5%, respectively. Simarly, in the Cd contaminated soil, the per cent increase in SOC content due to FYM application was 19.7, 49.2 and 19.1 %; whereas in the Pb contaminated soil it was 18.3, 50.0 and 88.3%, repectively at 1, 2.5 and 5% application rate over control. Over all the mean per cent increase in SOC content as result of pressmud and FYM application over control was 99.2 and 45.1%, respectively.

Table 4.3 Effect of various amendments and its application rate on SOC content

Treatment	SOC (%)		
	Uncontaminated Soil	**Cd Contaminated Soil**	**Pb Contaminated Soil**
Control	0.58e	0.61e	0.60e
Press mud (1%)	0.83c	0.86c	0.86c
Press mud (2.5%)	1.11b	1.25b	1.14b
Press mud (5%)	1.45a	1.68a	1.52a
Steel slag (1%)	0.57e	0.60e	0.60e
Steel slag (2.5%)	0.53e	0.61e	0.54e
Steel slag (5%)	0.53e	0.57e	0.56e
Fly ash (1%)	0.57e	0.59e	0.58e
Fly ash (2.5%)	0.52e	0.59e	0.55e
Fly ash (5%)	0.49e	0.59e	0.55e
FYM (1%)	0.71d	0.73d	0.71d
FYM (2.5%)	0.89c	0.91c	0.90c
FYM (5%)	1.07b	1.19b	1.13b
SEm(d)±	0.051	0.036	0.051
C.D. (5%)	0.106	0.072	0.106

From the SOC data, it was clearly evident that significant differences between press mud and FYM amended soil at their respective rate of application was recorded in all the soil type (uncontaminated, Cd contaminated and Pb contaminated soil). On the contrary, SOC content in the soil amended with steel slag and fly ash was found to be on par and statistically non significant. Slight decrease in SOC content was noticed in soil ameneded with 5% application rate of steel slag and fly ash over control. Irrespective of the amendments and its application rate, the SOC content was relatively higher in Cd contaminated soil followed by Pb contaminated soil and uncontaminated soil.

4.1.2 Impact of various amendments and its application rate on DTPA extractable Cd and Pb content in soil.

The data pertaining to DTPA extractable Cd and Pb in a contaminated soil amended with various amendments and its application rate has been presented in Figures 4.1, 4.2, 4.3 and 4.4. The results clearly indicate that significant effect was observed on DTPA extractable Cd and Pb in a contaminated soil amended with press mud, steel slag, fly ash and FYM during the incubation period of 30 days.

Soil amended with press mud, steel slag, fly ash and FYM significantly reduced the bioavailable form of heavy metal (DTPA) over unamended soil (control) of Cd (Figure 4.1 and 4.2) and Pb contaminated (Figure 4.3 and 4.4) vertisol. Irrespective of the treatment, the DTPA extractable Cd and Pb content decreased as the period of incubation period progress from 7 to 30 days. However, the reduction in DTPA extractable Cd and Pb was significantly greater during 7 to 15 days after incubation and thereafter the DTPA extractable Cd and Pb remains relatively stable till the end of 30 days period of incubation.

During the incubation period, the mean DTPA extractable Cd varied from 27.28 (soil amended with steel slag at 5% application rate) to 41.84 mg Cd kg^{-1} soil (unamended/control soil). Similarly, the mean DTPA extractable Pb varied from 185.9 (soil amended with press mud at 5% application rate) to 285.2 mg Pb kg^{-1} soil (unamended/control soil). Irrespective of the amendments, increase in the rate of application from 1 to 5% application, the DTPA extractable Cd and Pb content was also significantly reduced (Figure 4.1 and 4.3). Among the amendments used to remediate Cd contaminated soil, application of steel slag was proved to be significantly better in reducing DTPA extractable Cd content as compared to other amendments like press mud, fly ash and FYM (Figure 4.2). The relative efficiency of amendments for reduction in DTPA extractable Cd content following its application in a Cd contaminated soil was found in the order of steel slag > press mud > FYM > Fly ash (Figure 4.2). On the other hand, application of press mud was proved to be significantly better in reducing DTPA

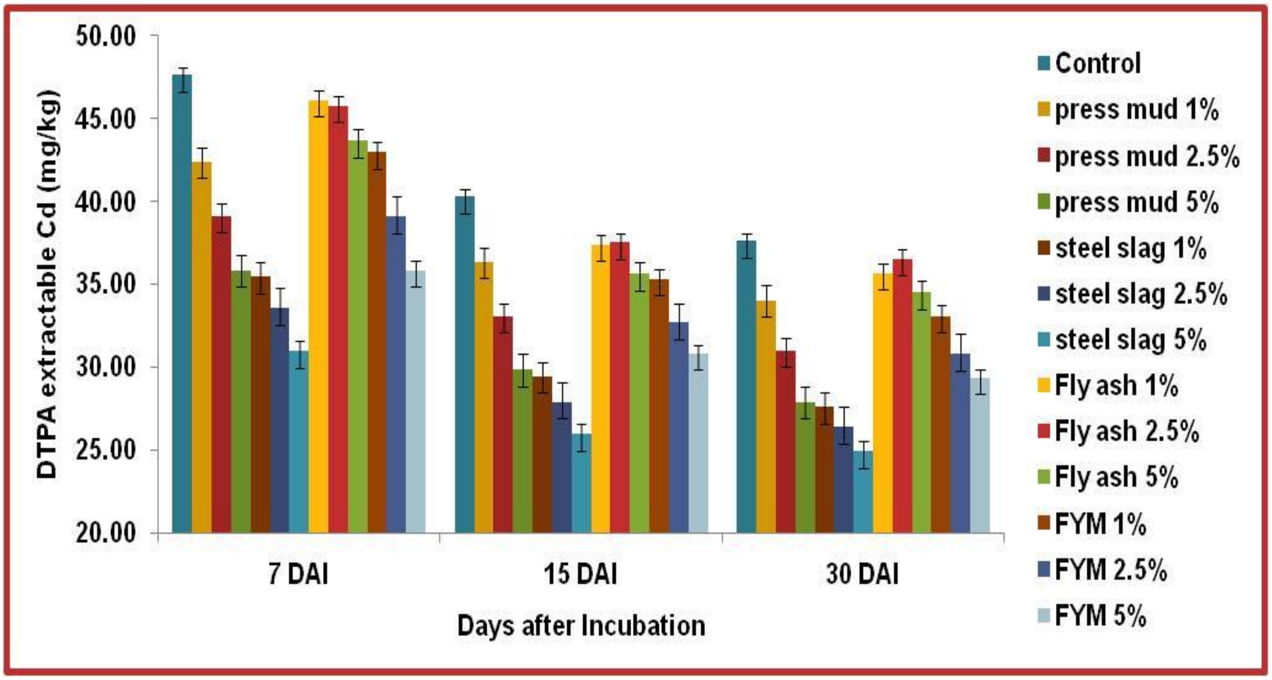

Fig. 4.1 Effect of various amendments and its application rate on DTPA extractable cadmium content in soil

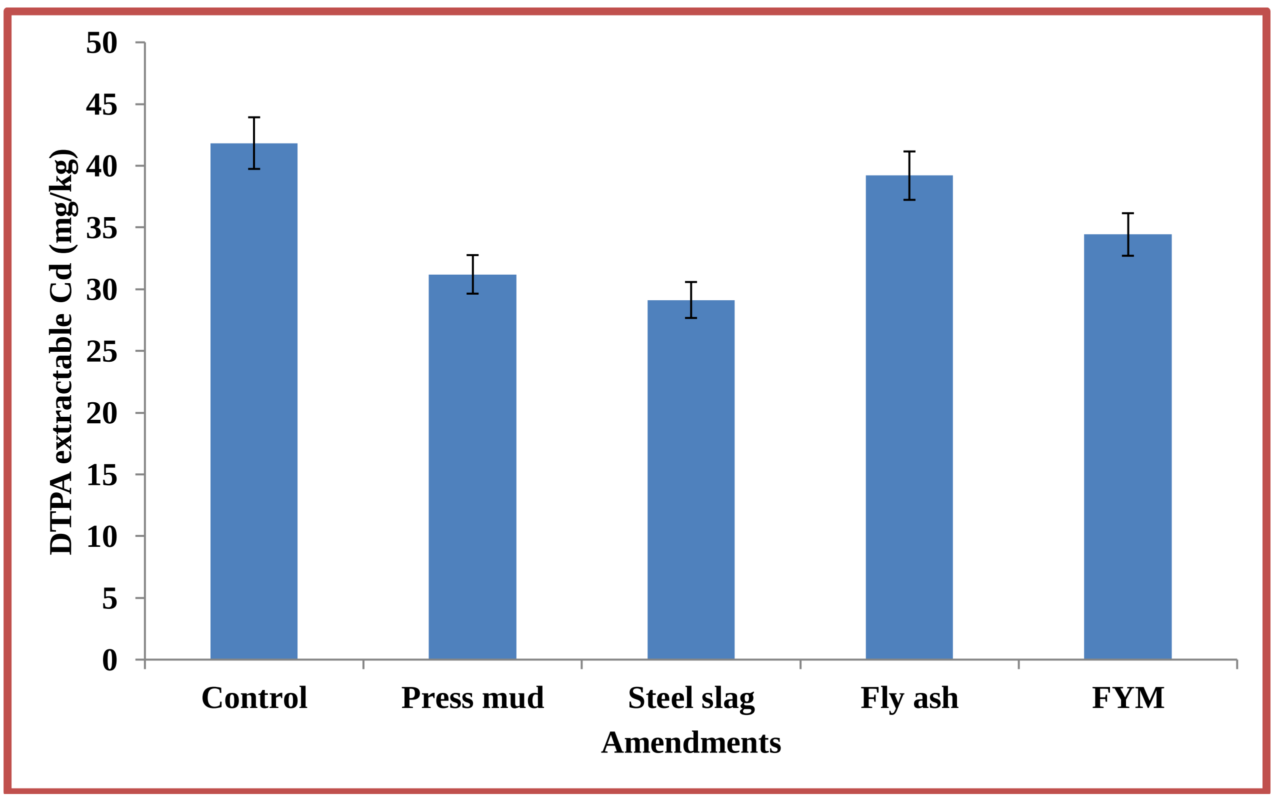

Fig. 4.2 Effect of various amendments on mean DTPA extractable cadmium content in soil

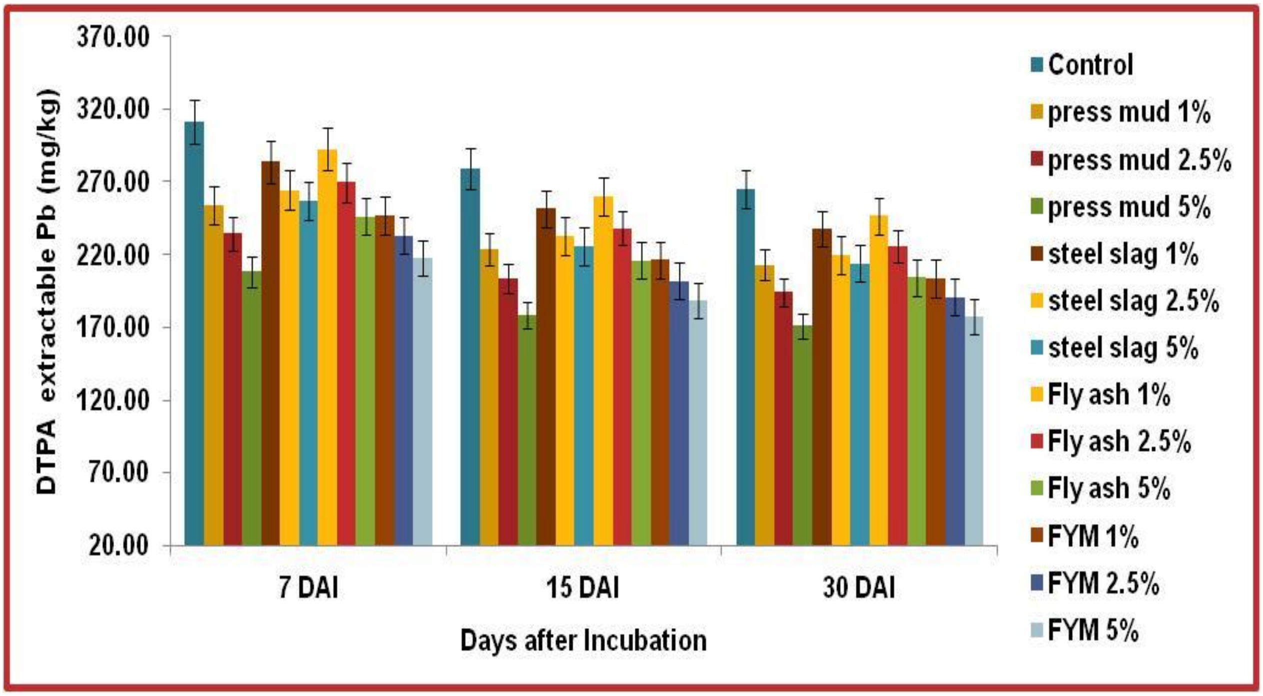

Fig. 4.3 Effect of various amendments and its application rate on DTPA extractable lead content in soil

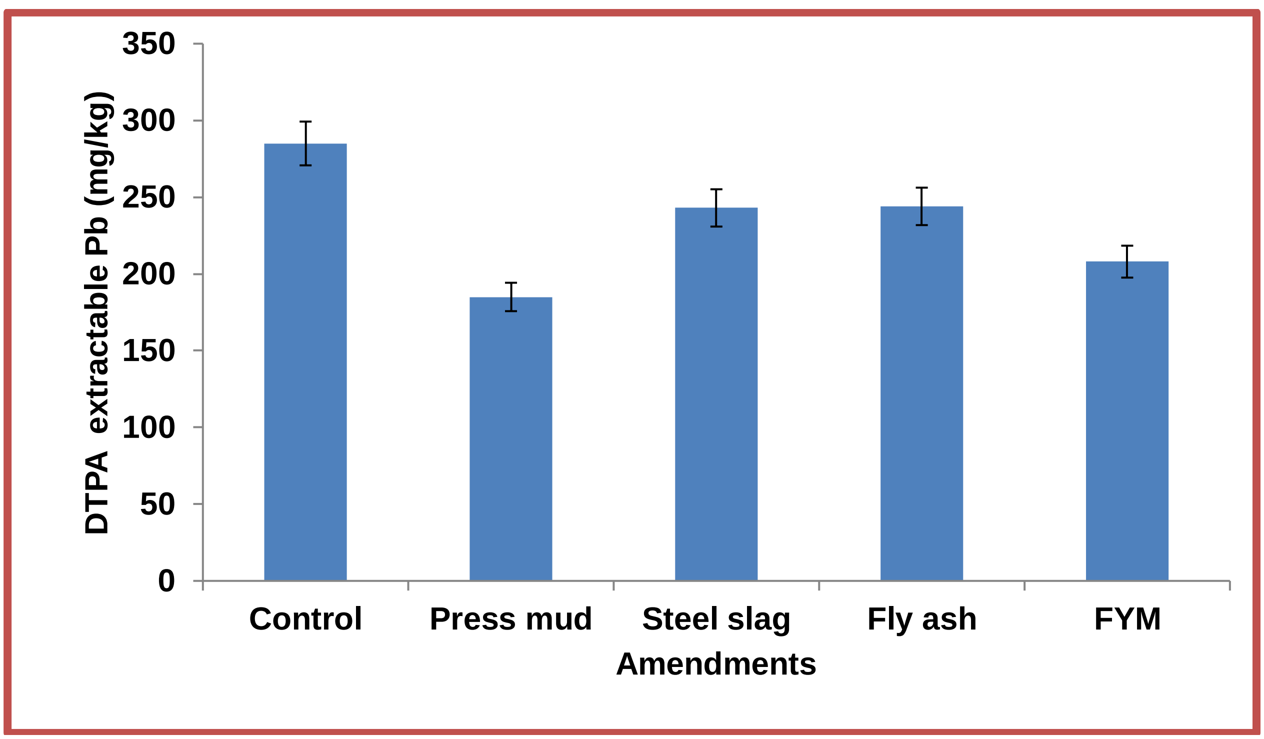

Fig. 4.4 Effect of various amendments on mean DTPA extractable lead content in soil

Table 4.4 Effect of various amendments and application rate on mean DTPA extractable cadmium and lead content in soil

Treatment	DTPA Extractable Heavy Metal content ($mgkg^{-1}$)			
	Uncontaminated Soil		Cd Contaminated Soil	Pb Contaminated Soil
	Cd	Pb	Cd	Pb
Control	0.02	1.00	41.84a	285a
Press mud (1%)	0.03	1.09	37.60c	230def
Press mud (2.5%)	0.02	0.99	34.41d	210g
Press mud (5%)	0.02	1.01	31.21f	185h
Steel slag (1%)	0.01	0.99	30.83f	257b
Steel slag (2.5%)	0.02	0.91	29.28g	238cd
Steel slag (5%)	0.02	0.81	27.28h	232de
Fly ash (1%)	0.02	1.01	39.74b	266b
Fly ash (2.5%)	0.02	1.12	39.95b	244c
Fly ash (5%)	0.02	0.92	37.92c	222f
FYM (1%)	0.02	1.02	37.12c	222ef
FYM (2.5%)	0.02	1.03	34.18d	208g
FYM (5%)	0.02	1.04	32.01e	194h
SEm(d)±	NS	NS	0.386	4.29
C.D. (5%)	NS	NS	0.801	10.08

extractable Pb content as compared to other amendments like steel slag, fly ash and FYM (Figure 4.4). The relative efficiency of amendments for reduction in DTPA extractable Pb content following its application in a Pb contaminated soil was found in the order of press mud > FYM > steel slag > Fly ash (Figure 4.4).

Further, the result clearly reveals that significant differences in DTPA extractable Cd and Pb were not observed between the unamended soil and soil amended with fly ash at lowest rate of application (1%). At the end of incubation study (30 days), the mean per cent reduction in DTPA extractable Cd and Pb ranged from 5.0% to 34.8% and 6.6% to 37.5%, respectively over control. The highest per cent reduction (34.8%) in DTPA extractable Cd was observed in the soil amended with steel slag at 5% application rate and the lowest reduction (5.0%) in the soil amended with fly ash at 1% application rate over unamended soil (control). Similarly, the highest per cent reduction (37.5%) in DTPA extractable Pb was observed in the soil amended with press mud at 5% application rate and the lowest per cent reduction (6.6%) in the soil amended with fly ash at 1% application rate over unamended soil (Table 4.4).

4.2 Impact of various amendments either alone or in comination with FYM on soil properties and heavy metal mobility in soil.

The results generated from the pot culture experiment are presented in the following heads:

4.2.1. Impact of various amendments either alone or in comination with FYM on soil properties and heavy metal mobility in soil.

4.2.2. Impact of various amendments either alone or in comination with FYM on dry matter yield of spinach crop

4.2.3. Impact of various amendments either alone or in comination with FYM on plant nutrient content and its uptake by spinach crop

4.2.3. Impact of various amendments either alone or in comination with FYM on Cd and Pb content and its uptake by spinach crop

4.2.1 Impact of various amendments either alone or in comination with FYM on soil properties and heavy metal mobility in soil.

A critical appraisal of data on soil pH, EC organic carbon, available nitrogen, phosphorus potassium and sulphur in post-harvest soil sample are presented in tables 4.5, 4.6, 4.7, 4.8, 4.9, 4.10 and 4.11. The data revealed that application of various amendments either alone or in combination with FYM showed significant effect on soil pH, EC, organic carbon, available nitrogen, phosphorus, potassium and sulphur over control.

Application of steel slag either alone or in combination with FYM significantly increased the soil pH over unamended soil (control) of uncontaminated, Cd, Pb and

Cd+Pb contaminated Vertisol (Table 4.5). On the other hand, soil amended with press mud and fly ash either alone or in combination with FYM resulted in significant decrease in soil pH over control soil (unamended). Further, the result clearly indicates that FYM application also significantly decreased ths soil pH of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Application of steel slag (2.5%) along with FYM (2.5%) significantly reduced the soil pH over the application of steel slag (5%) alone.

The soil pH values ranged from 7.74 to 8.85, 7.58 to 8.77, 7.38 to 8.84 and 7.38 to 8.77 in the post-harvest soil sample of uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol, respectively (Table 4.5). Among the various amendments used in pot culture experiment, the highest increase in soil pH value over unamended soil was recorded in soil amended with steel slag application alone at 5% rate. On the contrary, as a result of FYM application, the soil pH was decreased by 0.20, 0.27, 0.53 and 0.52 unit in the uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol, respectively over control.

Table 4.5 Effect of various amendments application on soil pH of post harvest soil sample of Vertisol

Treatment	Soil pH			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	7.94c	7.85c	7.91c	7.90c
Press mud (5%)	7.83de	7.81c	7.75d	7.74d
Steel slag (5%)	8.85a	8.77a	8.84a	8.77a
Fly ash (5%)	7.80de	7.89c	7.94c	7.97c
FYM (5%)	7.74e	7.58e	7.38f	7.38f
PM(2.5%)+FYM (2.5%)	7.85cd	7.71d	7.55e	7.67d
SS(2.5%)+FYM (2.5%)	8.65de	8.43b	8.34b	8.28b
FA (2.5%)+FYM (2.5%)	7.85cd	7.82c	7.45ef	7.54e
SEm(d)±	0.044	0.036	0.051	0.044
C.D. (5%)	0.090	0.081	0.114	0.099

The EC values ranged from 0.44 to 1.32 dsm^{-1}, 0.57 to 1.47 dsm^{-1}, 0.52 to 1.71 dsm^{-1} and 0.66 to 1.63 dsm^{-1} in the post-harvest soil sample of uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol, respectively. Irrespective of the treatments, the soil EC was significantly increased over control in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Among the various amendments used in pot culture study, significantly higher soil EC was observed in soil amended with press mud alone at 5% rate (1.32, 1.47, 1.71 and 1.63 dsm^{-1}) followed by press mud application in combination with FYM at 2.5: 2.5% rate (0.85, 1.15, 1.27 and 1.11 dsm^{-1}) in the uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol, respectively (Table 4.6). The result also clearly indicates that soil EC was not significantly different between the soils amended with fly ash or steel slag alone at 5% and unamended soil (control) in the uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated soil.

Table 4.6 Effect of various amendments application on soil EC of post harvest soil sample of Vertisol

Treatment	EC (dsm^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.44de	0.57de	0.52c	0.66c
Press mud (5%)	1.32a	1.47a	1.71a	1.63a
Steel slag (5%)	0.49cde	0.57e	0.66c	0.76c
Fly ash (5%)	0.52cd	0.58cde	0.69c	0.76c
FYM (5%)	0.83b	0.76cd	0.79c	0.79c
PM(2.5%)+FYM (2.5%)	0.85b	1.15b	1.27b	1.11b
SS(2.5%)+FYM (2.5%)	0.58c	0.76c	0.76c	0.81c
FA (2.5%)+FYM (2.5%)	0.58ce	0.67ce	1.14b	0.69c
SEm(d)±	0.057	0.089	0.159	0.073
C.D. (5%)	0.124	0.192	0.339	0.150

Data pertaining to soil organic carbon as influenced by various amendment application either alone or in combination with FYM in the uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol has been presented in table 4.7. The SOC values ranged from 0.53 to 1.53%, 0.57 to 1.61%, 0.54 to 1.61% and 0.52 to 1.61% in the post-harvest soil sample of uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated Vertisol, respectively. Among the treatments, except fly ash application alone at 5% rate all other amendments either alone or in combination with FYM resulted in significant increase in soil organic carbon (SOC) of post-harvest samples of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol over control. However, soil amended with fly ash (2.5%) along with FYM (2.5%) showed significantly higher value of SOC over unamended control and soil amended with fly ash alone at 5% rate.

Irrespective of soil type (uncontaminated, Cd contaminated, Pb contaminated and Cd+pb contaminated soil), the SOC content was increased in the following order of soil amended with press mud (5%) > press mud (2.5%) + FYM (2.5%) > FYM (5%) > fly ash (2.5%) + FYM (2.5%) > steel slag (2.5%) + FYM (2.5%) > steel slag (5%) > fly ash (5%). The per cent increase in SOC content of uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated soil amended with pressmud at 5% over control was 159.3, 159.7, 168.3 and 163.9%, respectively. Simarly, the per cent increase in SOC content of uncontaminated, Cd contaminated, Pb contaminated and Cd+Pb contaminated soil amended with FYM at 5% over control was 98.3, 88.7, 96.7 and 96.7%, respectively. Over all the mean per cent increase in SOC content as result of pressmud and FYM application over control was 162.8 and 95.1%, respectively.

From the SOC data, it was clearly evident that a significant difference between press mud and FYM amended soil at their respective rate of 5% application was recorded in all the soil type (uncontaminated, Cd contaminated and Pb contaminated soil). On the contrary, SOC content in the soil amended with steel slag and fly ash was found to be on par and statistically non significant. Slight decrease in SOC content of post harvest soil sample was noticed in soil ameneded with 5% application rate of steel slag and fly ash over control. Irrespective of the treatments, the SOC content was relatively higher in Cd contaminated soil as compared to uncontaminated soil. It is also clearly evident from the result that between the amendment application of either alone or in combination with FYM, only significant difference in SOC content of uncontaminated, Cd, Pb and Cd+Pb contaminated soil was recorded between press mud alone and press mud in combination FYM.

Table 4.7 Effect of various amendments application on SOC of post harvest soil sample of Vertisol

Treatment	SOC (%)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.59d	0.62d	0.60e	0.61e
Press mud (5%)	1.53a	1.61a	1.61a	1.61a
Steel slag (5%)	0.53e	0.57d	0.57e	0.58ef
Fly ash (5%)	0.58de	0.57d	0.54e	0.52f
FYM (5%)	1.17b	1.17b	1.18c	1.20c
PM(2.5%)+FYM (2.5%)	1.51a	1.59a	1.47b	1.53b
SS(2.5%)+FYM (2.5%)	0.87c	0.88c	0.83d	0.85d
FA (2.5%)+FYM (2.5%)	0.88c	0.90c	0.87d	0.88d
SEm(d)±	0.026	0.026	0.036	0.036
C.D. (5%)	0.046	0.064	0.085	0.074

The effect of various amendments application either alone or in combination with FYM on available nitrogen, phosphorus, potassium and sulphur content in uncontaminated, Cd, Pb and Cd+Pb contaminated soil were presented in the tables 4.8, 4.9, 4.10 and 4.11. In general, available nitrogen, phosphorus, potassium and sulphur status in the post harvest soil sample increased significantly over control in the soil amended with press mud either alone or in combination with FYM. Also FYM alone application resulted in significant increase in available nitrogen, phosphorus, potassium and sulphur status over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

The available nitrogen content of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 197.77 to 258.16 kg ha^{-1}, 194.51 to 256.11 kg ha^{-1}, 194.32 to 256.29 kg ha^{-1} and 193.57 to 255.08 kg ha^{-1}, respectively (Table 4.8). The highest and lowest value of available nitrogen was noticed in the soil amended with press mud (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Among the treatments, significant differences were not observed between unamended control and soil amended with steel slag (5%) or fly ash (5%) alone application on available nitrogen content of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. However, aplication of steel slag and fly ash in combination with FYM showed significant increase in available nitrogen content in post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.8 Effect of various amendments application on available nitrogen in post harvest soil sample of Vertisol

Treatment	Available Nitrogen (Kgha^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	205.61e	205.71d	204.59e	205.24e
Press mud (5%)	258.16a	256.11a	256.29a	255.08a
Steel slag (5%)	200.76e	200.85de	202.07e	201.04ef
Fly ash (5%)	197.77e	194.51e	194.32f	193.57f
FYM (5%)	228.67c	225.31c	229.60c	226.67c
PM(2.5%)+FYM (2.5%)	237.91b	239.31b	238.56b	236.88b
SS(2.5%)+FYM (2.5%)	218.21d	219.43c	215.69d	215.60d
FA (2.5%)+FYM (2.5%)	215.69d	216.53c	215.77d	214.46d
SEm(d)±	4.31	4.86	3.55	3.58
C.D. (5%)	9.15	10.31	7.55	7.60

Critical appraisal of data pertaining to available phosphorus in the post-harvest soil samples of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol has been presented in table 4.9. The available phosphorus content of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 13.63 to 37.00 kg ha^{-1}, 13.29 to 35.48 kg ha^{-1}, 12.62 to 33.87 kg ha^{-1} and 12.62 to 38.87 kg ha^{-1}, respectively (Table 4.9). Like available nitrogen content, the highest and lowest value of available phosphorus was noticed in the soil amended with press mud (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Among the treatments, significant differences were not observed between unamended control and soil amended with steel slag (5%) or fly ash (5%) alone application on available phosphorus content of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, aplication of steel slag and fly ash in combination with FYM showed significant increase in available phosphorus content over control in post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.9 Effect of various amendments application on available phosphorus in post harvest soil sample of Vertisol

Treatment	Available Phosphorus (Kgha^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	13.80e	13.46c	13.29c	12.87d
Press mud (5%)	37.00a	35.48a	33.87a	38.87a
Steel slag (5%)	16.33de	15.67c	16.15c	15.50d
Fly ash (5%)	13.63e	13.29c	12.62c	12.62d
FYM (5%)	26.00c	26.95b	26.44b	25.59bc
PM(2.5%)+FYM (2.5%)	31.67b	30.06ab	30.48ab	30.57b
SS(2.5%)+FYM (2.5%)	18.04d	18.04c	18.63c	18.46cd
FA (2.5%)+FYM (2.5%)	17.61de	16.77c	16.43c	17.19d
SEm(d)±	1.89	2.62	2.92	3.41
C.D. (5%)	4.04	5.53	6.19	7.25

The available potassium content of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 582.12 to 774.48 kg ha^{-1}, 529.76 to 712.32 kg ha^{-1}, 504.56 to 711.20 kg ha^{-1} and 496.72 to 709.52 kg ha^{-1}, respectively (Table 4.10). Unlike available nitrogen and phosphorus content, the soil ameneded with FYM (5%) alone showed significantly highest content of available potassium content in the post harvest sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. The highest and lowest value of available potassium was noticed in the soil amended with FYM (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Significant differences were not observed between soil amended with steel slag (5%) and fly ash (5%) alone application on available potassium content of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. However, aplication of steel slag and fly ash in combination with FYM showed significant increase in available potassium content over control in post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.10 Effect of various amendments application on available potassium in post harvest soil sample of Vertisol

Treatment	Available Potassium (Kgha^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	616.84e	585.76e	570.36d	535.08e
Press mud (5%)	686.22c	674.81bc	668.08b	677.88b
Steel slag (5%)	600.04ef	548.83f	519.96e	523.60e
Fly ash (5%)	582.12f	529.76f	504.56e	496.72f
FYM (5%)	774.48a	712.32a	711.20a	709.52a
PM(2.5%)+FYM (2.5%)	713.72b	694.45ab	682.08b	690.48ab
SS(2.5%)+FYM (2.5%)	654.64d	649.32cd	613.48c	637.84c
FA (2.5%)+FYM (2.5%)	647.08d	626.08d	592.76cd	613.76d
SEm(d)±	10.95	13.31	11.72	10.91
C.D. (5%)	23.20	28.23	24.82	23.13

Data pertaining to available sulphur in the post-harvest soil samples of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol has been presented in table 4.11. The available sulphur content of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 9.89 to 20.39 kg ha^{-1}, 9.98 to 19.66 kg ha^{-1}, 9.70 to 20.45 kg ha^{-1} and 10.38 to 19.77 kg ha^{-1}, respectively (Table 4.9). Like available nitrogen content, the highest of available sulphur content was noticed in the soil amended with press mud (5%) in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, unlike available nitrogen and phosphorus content, soil amended with fly ash in an uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol resulted in significant increase in available sulphur content over control. Among the treatments, significant differences were not observed between soil amended with steel slag and fly ash in combination with FYM of post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, it is evident from the result that significant differences on available sulphur content was observed between aplication of steel slag and fly ash alone in post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.11 Effect of various amendments application on available sulphur in post harvest soil sample of Vertisol

Treatment	Available Sulphur ($Kgha^{-1}$)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	9.89f	9.98f	9.70f	10.38e
Press mud (5%)	20.39a	19.66a	20.45a	19.77a
Steel slag (5%)	11.51e	10.46f	10.81e	10.66e
Fly ash (5%)	12.78de	13.05d	12.56d	12.37cd
FYM (5%)	14.22c	13.66c	13.55c	13.66c
PM(2.5%)+FYM (2.5%)	16.58b	16.03b	16.91b	16.85b
SS(2.5%)+FYM (2.5%)	12.47de	11.80e	12.70d	12.24d
FA (2.5%)+FYM (2.5%)	13.53cd	12.72d	13.30cd	13.04cd
SEm(d)±	0.65	0.27	0.37	0.61
C.D. (5%)	1.39	0.58	0.80	1.31

The data pertaining to DTPA extractable Cd and Pb in a Cd, Pb and Cd+Pb contaminated soil amended with various amendments either alone or in combination with FYM has been presented in table 4.12 and 4.13. The results clearly indicate that significant effect was observed on DTPA extractable Cd and Pb in a contaminated soil (Cd, Pb and Cd+Pb contaminated soil) amended with press mud, steel slag, fly ash and FYM.

Irrespective of the treatments, the DTPA extractable Cd content was relatively higher in the cadmium contaminated soil as compared to Cd+Pb contaminated soil (Table 4.12). Similarly, DTPA extractable Pb content was also relatively higher in the lead contaminated soil as compared to Cd+Pb contaminated soil (Table 4.13). Further , the result reveals that soil amended with press mud, steel slag, fly ash and FYM significantly reduced the bioavailable form of Cd and Pb heavy metal (DTPA extractable) over unamended soil (control) of Cd, Pb contaminated and Cd+Pb contaminated soil vertisol. Application of various amendments either alone or in combination with FYM showed no significant difference in DTPA extractable Cd (Table 4.12) and Pb (Table 4.13) content over control of unamended Vertisol.

The DTPA extractable content of Cd varied from 24.69 (soil amended with steel slag alone at 5% application rate) to 37.92 mg Cd kg^{-1} soil (unamended/control soil) in a cadmium contaminated soil; whereas it varied from 18.62 (soil amended with steel slag alone at 5% application rate) to 31.38 mg Cd kg^{-1} soil (unamended/control soil) in a Cd+Pb contaminated soil (Table 4.12). Similarly, the mean DTPA extractable Pb varied from 225.85 (soil amended with press mud alone at 5% application rate) to 282.25 mg Pb kg^{-1} soil (unamended/control soil) in a lead contaminated soil; whereas it varied from 199.48 (soil amended with steel slag alone at 5% application rate) to 254.12 mg Cd kg^{-1} soil (unamended/control soil) in a Cd+Pb contaminated soil (Table 4.13).

Among the amendments used to remediate Cd and Cd+Pb contaminated soil, application of steel slag was proved to be significantly better in reducing DTPA extractable Cd content as compared to other amendments like press mud, fly ash and FYM (Table 4.12). The relative efficiency of amendments for reduction in DTPA extractable Cd content following its application in a Cd contaminated soil was found in the order of steel slag > press mud/FYM > Fly ash (Table4.2). Similar trend on reduction in DTPA extractable Cd content was also observed in a Cd+Pb contaminated soil. On the other hand, application of press mud was proved to be significantly better in reducing DTPA extractable Pb content as compared to other amendments like steel slag, fly ash and FYM in a Pb and Cd+Pb contaminated vertisol (Table 4.13). The relative efficiency of amendments for reduction in DTPA extractable Pb content following its application in a Pb contaminated soil was found in the order of press mud > FYM > steel slag > Fly ash. Similar trend on reduction in DTPA extractable Pb content was also observed in a Cd+Pb contaminated soil.

Further, the result clearly reveals that significant differences in DTPA extractable Cd were not observed between the soil amended with press mud (5%) and FYM (5%) in a Cd and Cd+Pb ccontaminated soil. However, in a lead contaminated soil significant difference in DTPA extractable Pb content was observed in soil amended with press mud (5%) and FYM (5%) alone.

The mean per cent reduction in DTPA extractable Cd content as a result of amendment addition ranged from 10.26% to 34.89% and 2.14% to 40.66%, respectively in a Cd and Cd+Pb contaminated soil (Table 4.12). Similarly, the mean per cent reduction in DTPA extractable Pb content over as a result of amendment addition ranged from 11.09% to 56.41% and 5.99% to 21.50%, respectively in a Pb and Cd+Pb contaminated soil (Table 4.13). The highest per cent reduction (34.9%) in DTPA extractable Cd was observed in the Cd contaminated soil amended with steel slag (5%) alone application and the lowest per cent reduction (10.3%) in the soil amended with fly ash (5%) alone application over unamended control soil. Similarly, the highest per cent reduction (40.7%) in DTPA extractable Cd was observed in the Cd+Pb contaminated soil amended with steel slag (5%) alone application and the lowest per cent reduction (2.14%) in the soil amended with fly ash (5%) alone application over unamended control soil.

On the contrary, the highest per cent reduction (56.4%) in DTPA extractable Pb was observed in the Pb contaminated soil amended with press mud (5%) alone application and the lowest per cent reduction (11.1%) in the soil amended with fly ash (5%) alone application over unamended control soil. Similarly, the highest per cent reduction (21.5%) in DTPA extractable Pb was observed in the Cd+Pb contaminated soil amended with press mud (5%) alone application and the lowest per cent reduction (6.0%) in the soil amended with fly ash (5%) alone application over unamended control soil. The result also clearly indicates that the performance of fly ash (2.5%) application along with FYM (2.5%) proved to be better in reducing the bioavilable content of Cd and Pb content in a contaminated soil than the application of fly ash (5%) alone.

Table 4.12 Effect of various amendments application on DTPA extractable cadmium content in post harvest soil samples of Vertisol

Treatment	DTPA extractable cadmium content in soil ($mgkg^{-1}$)		
	Uncontaminated Soil	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.02	37.92a	31.38a
Press mud (5%)	0.02	31.01c	26.83d
Steel slag (5%)	0.03	24.69e	18.62f
Fly ash (5%)	0.02	34.03b	30.71ab
FYM (5%)	0.02	30.99c	27.16cd
PM(2.5%)+FYM (2.5%)	0.02	33.16b	27.82cd
SS(2.5%)+FYM (2.5%)	0.03	28.64d	23.97e
FA (2.5%)+FYM (2.5%)	0.02	31.49c	28.97bc
SEm(d)±	NS	0.71	0.89
C.D. (5%)	NS	1.62	2.05

Table 4.13 Effect of various amendments application on DTPA extractable lead content in post harvest soil samples of Vertisol

Treatment	DTPA extractable lead content in soil ($mgkg^{-1}$)		
	Uncontaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	1.04	282.25a	254.12a
Press mud (5%)	1.08	225.85d	199.48e
Steel slag (5%)	1.05	266.08b	230.71bc
Fly ash (5%)	0.09	267.49b	238.89b
FYM (5%)	1.02	238.68c	222.85cd
PM(2.5%)+FYM (2.5%)	0.08	228.11d	215.75d
SS(2.5%)+FYM (2.5%)	1.03	246.40c	231.88bc
FA (2.5%)+FYM (2.5%)	1.08	271.16b	225.93cd
SEm(d)±	NS	3.35	4.14
C.D. (5%)	NS	8.38	10.62

4.2.2 Impact of various amendments either alone or in comination with FYM on dry matter yield of spinach crop.

Spinach Leaf

Application of various amendments significantly influenced the dry matter yield of spinach leaf (Tables 4.14; photo 1 and 2). In a Cd, Pb and Cd+Pb contamintated soil, the dry matter yield of spinach leaf was significantly increased following the application of press mud, steel slag, fly ash and FYM over control. Further, application of press mud, steel slag and fly ash in combination with FYM also increased the spinach leaf dry matter yield significantly over control. Irrespective of soil contamination (Cd, Pb and Cd+Pb contaminated soil) and in uncontaminated Vertisol, the dry matter yield of spinach leaf was highest in the FYM amended soil followed by press mud and steel slag or fly ash application. Further, the result reveals that application of steel slag (2.5%) and fly ash (2.5%) along with FYM (2.5%) significantly increased dry matter yield over the application of steel slag (5%) and fly ash (5%) alone.

The dry matter yield of spinach leaf ranged from 9.33 to 12.48 g pot^{-1}, 5.94 to 8.14 g pot^{-1} 6.25 to 9.05 g pot^{-1} and 6.06 to 8.40 g pot^{-1} in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol, respectively. Among the soil type (uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol), the dry matter yield of spinach leaf was relatively highest in uncontaminated soil followed by Pb contaminated soil, Cd+Pb contaminated soil and Cd contaminated soil. The per cent increase in dry matter yield of spinach leaf ranged from 4.39 to 33.76%, 5.22 to 37.04%, 11.68 to 44.80% and 11.72 to 38.13% as a result of application of amendments either alone or in combination with FYM in the uncontaminated, Cd, Pb and Cd+Pb contaminated soil. The highest per cent increase in dry matter yield of spinach leaf in a uncontaminated soil was observed in press mud (5%) alone amended soil; whereas in a Cd and Pb contaminated soil it was noticed in PM (2.5%) + FYM (2.5%) amended soil. On the other hand, the highest per cent increase in dry matter yield of spinach leaf in a Cd+Pb contaminated soil was noticed in soil amended with FYM (5%) alone treatment.

Spinach Root

The dry matter yield of spinach root as influenced by application of various amendments either alone or in combination with FYM was presented in table 4.15. Like spinach leaf, significant increase in the dry matter yield of spinach root was also observed in soil amended with various amendments over control (Tables 4.14). In a Cd, Pb and Cd+Pb contamintated soil, the dry matter yield of spinach root was significantly increased following the application of press mud, steel slag, fly ash and FYM over control. Further, application of various amendments (press mud, steel slag and fly ash in combination with FYM also increased the spinach root dry matter yield significantly over control. Irrespective of soil contamination (Cd, Pb and Cd+Pb contaminated soil) and in uncontaminated Vertisol, the dry matter yield of spinach root was highest in the FYM amended soil followed by press mud and steel slag or fly ash application. Unlike spinach leaf, significant differences on dry matter yield of spinach root was observed between soil amended with steel slag and fly ash application of uncontaminated and Pb contaminated soil. Similar trend were also observed in spinach root where application of steel slag (2.5%) and fly ash (2.5%) along with FYM (2.5%) significantly increased the dry matter yield over the application of steel slag (5%) and fly ash (5%) alone.

The dry matter yield of spinach root ranged from 1.52 to 2.04 g pot^{-1}, 1.09 to 1.51 g pot^{-1} 1.37 to 1.83 g pot^{-1} and 1.27 to 1.72 g pot^{-1} in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol, respectively. Among the soil type (uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol), the dry matter yield of spinach root was relatively highest in uncontaminated soil followed by Pb contaminated soil, Cd+Pb contaminated soil and Cd contaminated soil. The per cent increase in dry matter yield of spinach root ranged from 3.9 to 34.2%, 11.9 to 38.5%, 3.6 to 33.6% and 5.5 to 35.4% as a result of application of amendments either alone or in combination with FYM in the uncontaminated, Cd, Pb and Cd+Pb contaminated soil. The highest per cent increase in dry matter yield of spinach root in an uncontaminated, Cd and Pb contaminated soil was observed in FYM (5%) alone amended soil; whereas in a Cd+Pb contaminated soil it was noticed in PM (2.5%) + FYM (2.5%) amended soil.

Table 4.14 Effect of various amendments application on dry matter yield of spinach leaf

Treatment	Dry matter yield of Spinach Leaf (g pot^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	9.33e	5.94g	6.25d	6.06e
Press mud (5%)	12.48a	7.77bc	8.86a	8.05b
Steel slag (5%)	9.84de	6.25f	7.14c	6.77d
Fly ash (5%)	9.74e	6.72e	6.98c	6.83d
FYM (5%)	12.41a	8.07ab	9.03a	8.40a
PM(2.5%)+FYM (2.5%)	11.60b	8.14a	9.05a	8.35ab
SS (2.5%)+FYM (2.5%)	10.84c	7.63cd	8.50b	8.11ab
FA (2.5%)+FYM (2.5%)	10.34cd	7.42d	8.17b	7.70c
SEm(d)±	0.258	0.141	0.163	0.163
C.D. (5%)	0.559	0.312	0.345	0.336

Table 4.15 Effect of various amendments application on dry matter yield of spinach root

Treatment	Dry matter yield of Spinach Root (g pot^{-1})			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	1.52f	1.09d	1.37f	1.27g
Press mud (5%)	2.01ab	1.50a	1.80a	1.60bc
Steel slag (5%)	1.70d	1.22c	1.50d	1.42ef
Fly ash (5%)	1.58e	1.26bc	1.42e	1.34fg
FYM (5%)	2.04a	1.51a	1.83a	1.70ab
PM(2.5%)+FYM (2.5%)	2.00b	1.50a	1.81a	1.72a
SS(2.5%)+FYM (2.5%)	1.83c	1.35b	1.63b	1.56cd
FA (2.5%)+FYM (2.5%)	1.71d	1.25bc	1.54c	1.46de
SEm(d)±	0.012	0.032	0.012	0.032
C.D. (5%)	0.037	0.115	0.035	0.108

4.2.3 Impact of various amendments either alone or in comination with FYM on plant nutrient content and its uptake by spinach crop.

The effect of various amendments application either alone or in combination with FYM on nitrogen, phosphorus, potassium and sulphur content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated soil are presented in the tables 4.16, 4.17, 4.18 and 4.19. In general, nitrogen, phosphorus, potassium and sulphur content in spinach leaf increased significantly over control in the soil amended with press mud either alone or in combination with FYM. Also FYM alone application resulted in significant increase in nitrogen, phosphorus, potassium and sulphur content in spinach leaf over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.16 Effect of various amendments application on nitrogen content in spinach leaf

Treatment	Nitrogen content in Spinach Leaf (%)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	2.07d	1.76e	1.83d	1.83c
Press mud (5%)	2.33c	2.07bc	2.15b	2.03abc
Steel slag (5%)	2.10d	1.90d	2.06bc	1.96bc
Fly ash (5%)	2.07d	1.76e	1.84d	1.81c
FYM (5%)	2.61a	2.26a	2.34a	2.27a
PM(2.5%)+FYM (2.5%)	2.58ab	2.19ab	2.29a	2.24a
SS(2.5%)+FYM (2.5%)	2.40bc	1.97cd	2.08bc	2.08ab
FA (2.5%)+FYM (2.5%)	2.26cd	1.86de	1.99c	1.96bc
SEm(d)±	0.096	0.057	0.068	0.115
C.D. (5%)	0.203	0.128	0.145	0.242

The nitrogen content in spinach leaf from uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 2.07 to 2.61 %, 1.76 to 2.26 %, 1.83 to 2.34 % and 1.83 to 2.27 %, respectively (Table 4.16). The highest and lowest value of spinach leaf nitrogen content was noticed in the soil amended with press mud (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Among the treatments, significant differences were not observed between unamended control and soil amended with fly ash (5%) alone application on nitrogen content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. However, aplication of fly ash in combination with FYM showed significant increase in nitrogen content in spinach leaf over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Further the result also reveals that significant increase in nitrogen content of spinach leaf was observed in soil amended with steel slag and fly ash along with FYM as compared to steel slag and fly ash application alone.

Critical appraisal of data pertaining to phosphorus content in the spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol has been presented in table 4.17. The phosphorus content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 0.26 to 0.37%, 0.21 to 0.36%, 0.21 to 0.35% and 0.20 to 0.35%, respectively. Like nitrogen content, the highest and lowest value of phosphorus was noticed in the soil amended with press mud (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Unlike nitrogen content, among the treatments significant differences were observed between unamended control and soil amended with fly ash (5%) alone application on phosphorus content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Application of steel slag and fly ash in combination with FYM showed significant increase in phosphorus content over control in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. The result also reveals that significant increase in phosphorus content of spinach leaf was observed in soil amended with steel slag and fly ash along with FYM as compared to steel slag and fly ash application alone.

The potassium content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 2.48 to 3.09%, 2.19 to 2.74%, 2.21 to 2.77% and 2.23 to 2.79%, respectively (Table 4.18). Unlike nitrogen and phosphorus content in spinach leaf, the soil ameneded with FYM (5%) alone showed significantly highest content of potassium content in the spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. The highest and lowest value of potassium in spinach leaf was noticed in the soil amended with FYM (5%) and fly ash (5%), respectively in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Significant differences were not observed between soil amended with steel slag (5%) and fly ash (5%) alone application on potassium content in spinach leaf of uncontaminated and Cd+Pb contaminated Vertisol. However, aplication of steel slag and fly ash in combination with FYM showed significant increase in potassium content in spinach leaf over control in post harvest soil sample of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Table 4.17 Effect of various amendments application on phosphorus content in spinach leaf

Treatment	Phosphorus content in Spinach Leaf (%)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.26e	0.21e	0.21d	0.20e
Press mud (5%)	0.37a	0.36a	0.36a	0.35a
Steel slag (5%)	0.31c	0.29c	0.31ab	0.28c
Fly ash (5%)	0.28de	0.24d	0.26c	0.23d
FYM (5%)	0.35ab	0.34a	0.35a	0.32b
PM(2.5%)+FYM (2.5%)	0.37a	0.36a	0.35a	0.34ab
SS(2.5%)+FYM (2.5%)	0.33bc	0.31b	0.33ab	0.33b
FA (2.5%)+FYM (2.5%)	0.31cd	0.31b	0.29bc	0.29c
SEm(d)±	0.012	0.012	0.026	0.012
C.D. (5%)	0.033	0.023	0.051	0.022

Critical appraisal of data pertaining to sulphur content in the spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol has been presented in table 4.19. The sulphur content in spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 0.38 to 0.43%, 0.31 to 0.41%, 0.34 to 0.41% and 0.32 to 0.41%, respectively. Like nitrogen content in spinach leaf, the highest sulphur content in spinach leaf was noticed in the soil amended with press mud (5%) in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, unlike nitrogen and phosphorus content in spinach leaf, soil amended with fly ash in an

Table 4.18 Effect of various amendments application on potassium content in spinach leaf

Treatment	Potassium content in Spinach Leaf (%)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	2.48d	2.19e	2.21e	2.25c
Press mud (5%)	2.80c	2.59bc	2.60bc	2.50abc
Steel slag (5%)	2.52d	2.38d	2.50cd	2.42bc
Fly ash (5%)	2.48d	2.20e	2.23e	2.23c
FYM (5%)	3.13a	2.83a	2.83a	2.79a
PM(2.5%)+FYM (2.5%)	3.09ab	2.74ab	2.77ab	2.76a
SS(2.5%)+FYM (2.5%)	2.88bc	2.46cd	2.51cd	2.56ab
FA (2.5%)+FYM (2.5%)	2.71cd	2.32de	2.41d	2.41bc
SEm(d)±	0.115	0.077	0.081	0.141
C.D. (5%)	0.244	0.160	0.176	0.298

Table 4.19 Effect of various amendments application on sulphur content in spinach leaf

Treatment	Sulphur content in Spinach Leaf (%)			
	Uncontaminated Soil	Cd Contaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.38e	0.31d	0.34c	0.32e
Press mud (5%)	0.42bc	0.41ab	0.41a	0.40ab
Steel slag (5%)	0.39e	0.36c	0.37b	0.36d
Fly ash (5%)	0.42c	0.38bc	0.40a	0.41a
FYM (5%)	0.41cd	0.40ab	0.39a	0.38bc
PM(2.5%)+FYM (2.5%)	0.43ab	0.40ab	0.41a	0.41a
SS(2.5%)+FYM (2.5%)	0.40d	0.40ab	0.40a	0.38cd
FA (2.5%)+FYM (2.5%)	0.43a	0.42a	0.41a	0.41a
SEm(d)±	0.008	0.012	0.009	0.012
C.D. (5%)	0.013	0.030	0.020	0.021

uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol resulted in significant increase in sulphur content in spinach leaf over control. It is also evident from the result that significant differences on sulphur content in spinach leaf was observed between aplication of steel slag and fly ash alone in uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

The effect of various amendments application either alone or in combination with FYM on nitrogen, phosphorus, potassium and sulphur uptake by spinach leaf of uncontaminated, Cd, Pb and Cd+Pb contaminated soil are presented in the tables 4.5, 4.6, 4.7 and 4.8. In general, nitrogen, phosphorus, potassium and sulphur uptake by spinach leaf increased significantly over control in the soil amended with press mud either alone or in combination with FYM. Also FYM alone application resulted in significant increase in nitrogen, phosphorus, potassium and sulphur uptake by spinach leaf over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

The data also reveals that nitrogen, phosphorus, potassium and sulphur uptake by spinach leaf of uncontaminated soil was relatively higher as compared to contaminated soil (Cd, Pb and Cd+Pb). The nitrogen uptake by spinach leaf from uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 193.2 to 323.7 mg pot^{-1}, 104.2 to 182.5 mg pot^{-1}, 114.1 to 211.6 mg pot^{-1} and 110.7 to 190.3 mg pot^{-1}, respectively (Figure 4.5). Similarly, phosphorus uptake by spinach leaf from uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 24.4 to 46.7 mg pot^{-1}, 12.2 to 29.3 mg pot^{-1}, 12.8 to 31.7 mg pot^{-1} and 12.3 to 28.4 mg pot^{-1}, respectively (Figure 4.6). The potassium uptake by spinach leaf from uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 231.8 to 388.4 mg pot^{-1}, 130.8 to 228.1 mg pot^{-1}, 138.1 to 256.1 mg pot^{-1} and 136.2 to 234.1 mg pot^{-1}, respectively (Figure 4.7). On the other hand, sulphur uptake by spinach leaf from uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol varied from 35.3 to 50.9 mg pot^{-1}, 18.6 to 32.6 mg pot^{-1}, 21.4 to 37.1 mg pot^{-1} and 19.6 to 34.5 mg pot^{-1}, respectively (Figure 4.8). The highest nitrogen and potassium uptake by spinach leaf was noticed in the soil amended with FYM (5%) alone in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, highest phosphorus uptake by spinach leaf was noticed in the soil

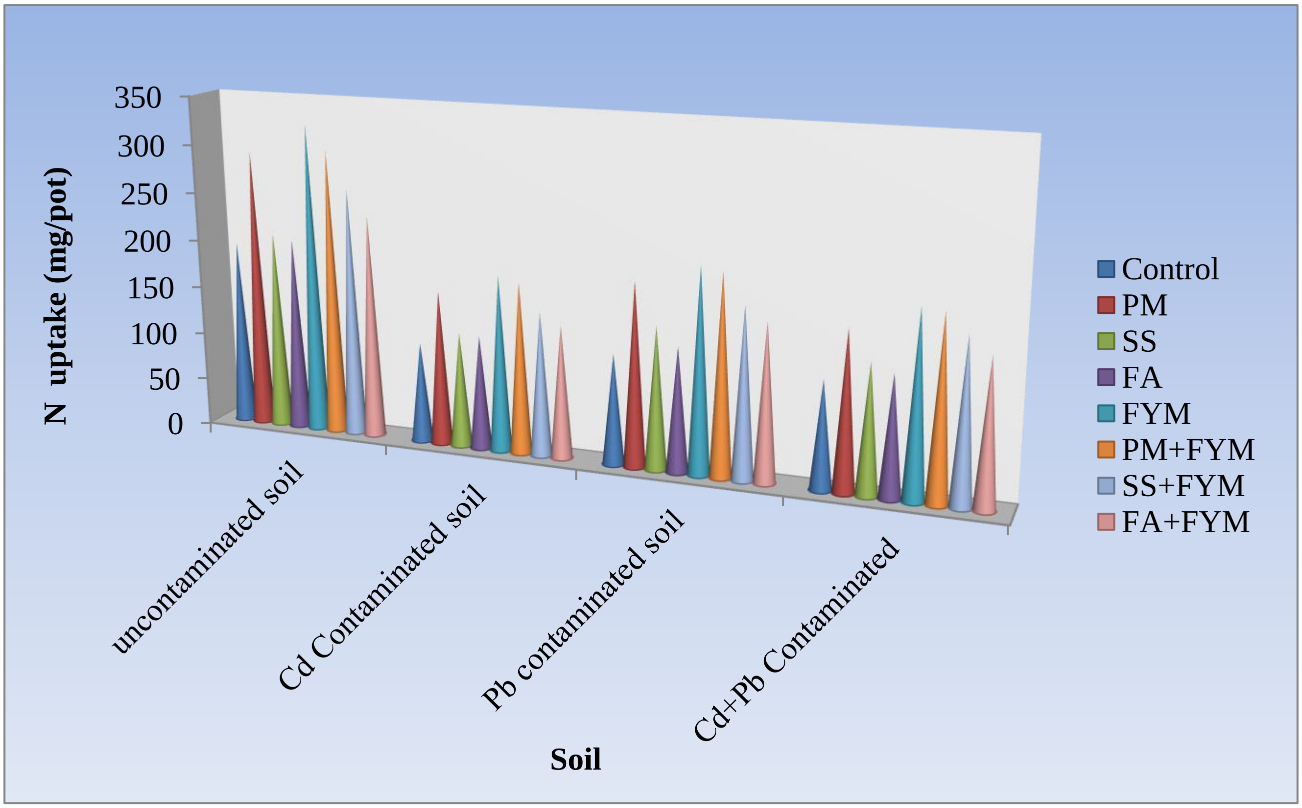

Fig. 4.5 Effect of various amendments application on N uptake by spinach leaf

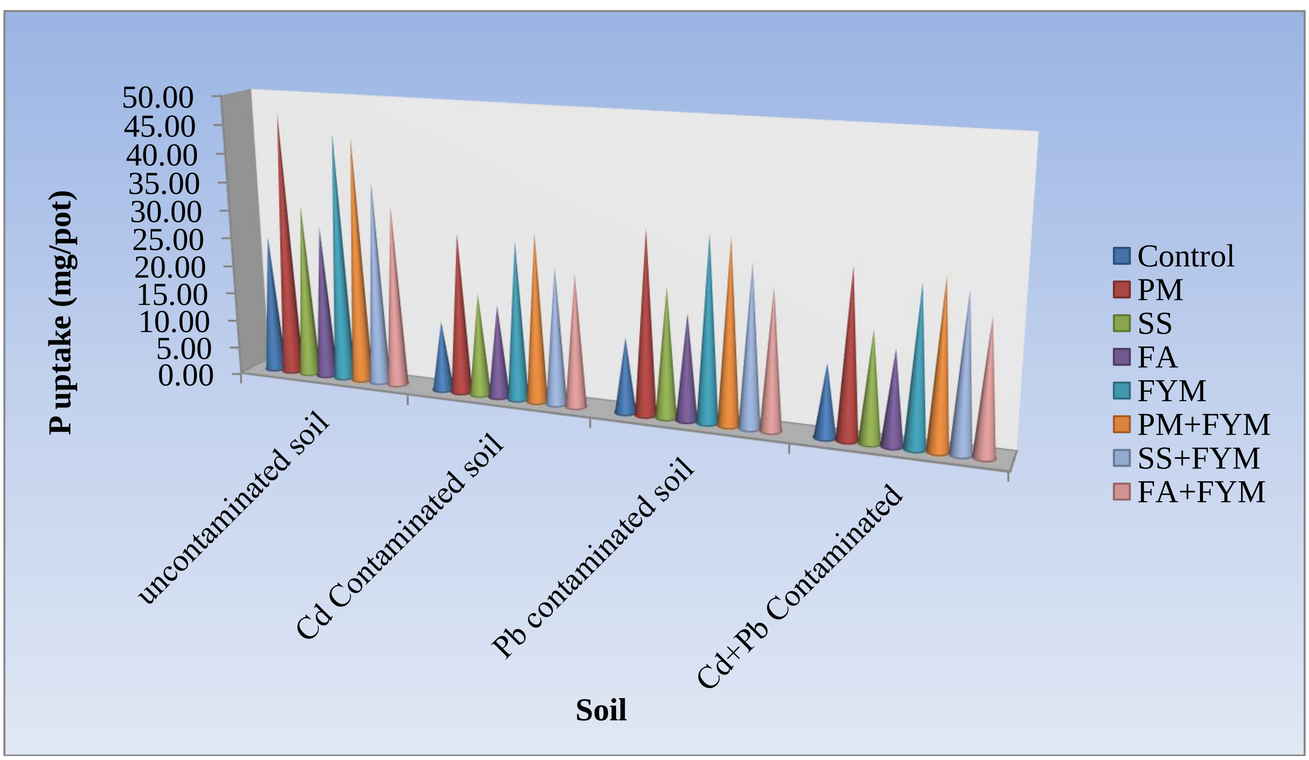

Fig. 4.6 Effect of various amendments application on P uptake by spinach leaf

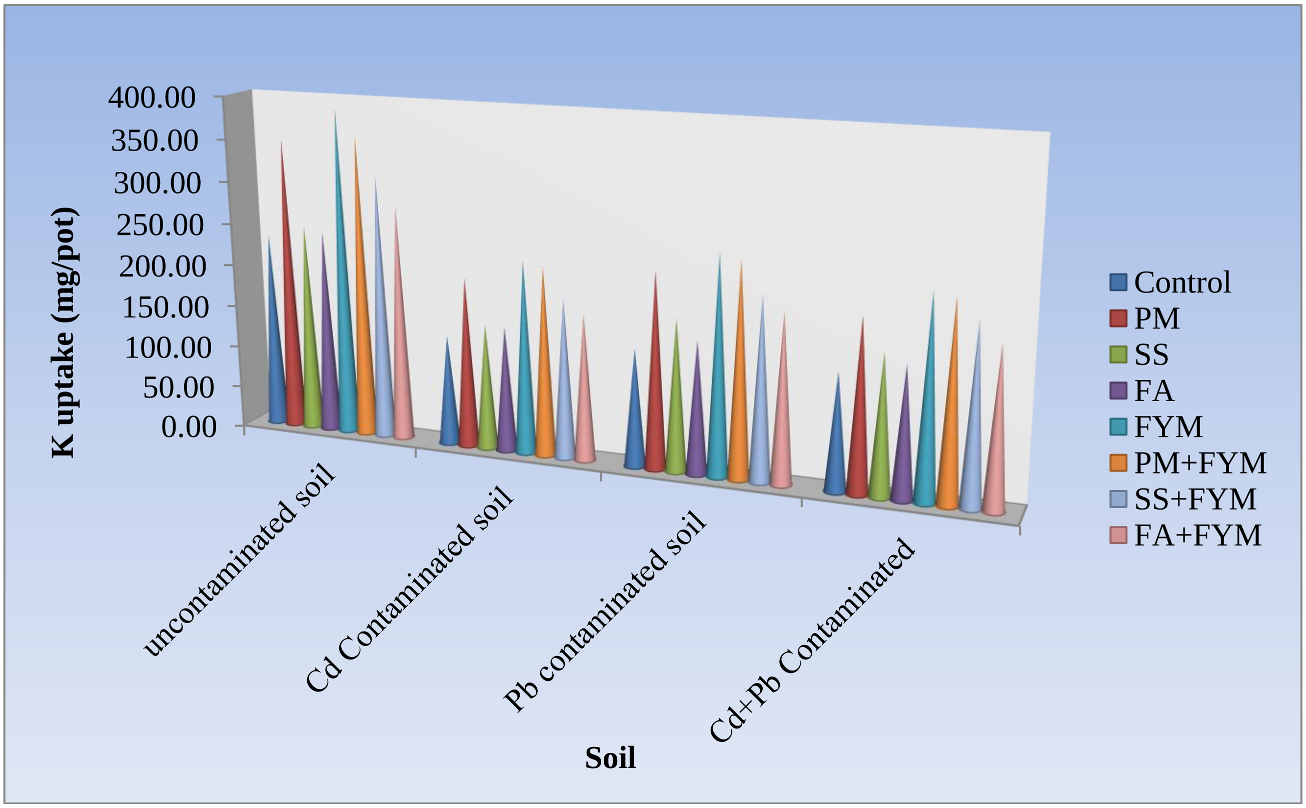

Fig. 4.7 Effect of various amendments application on K uptake by spinach leaf

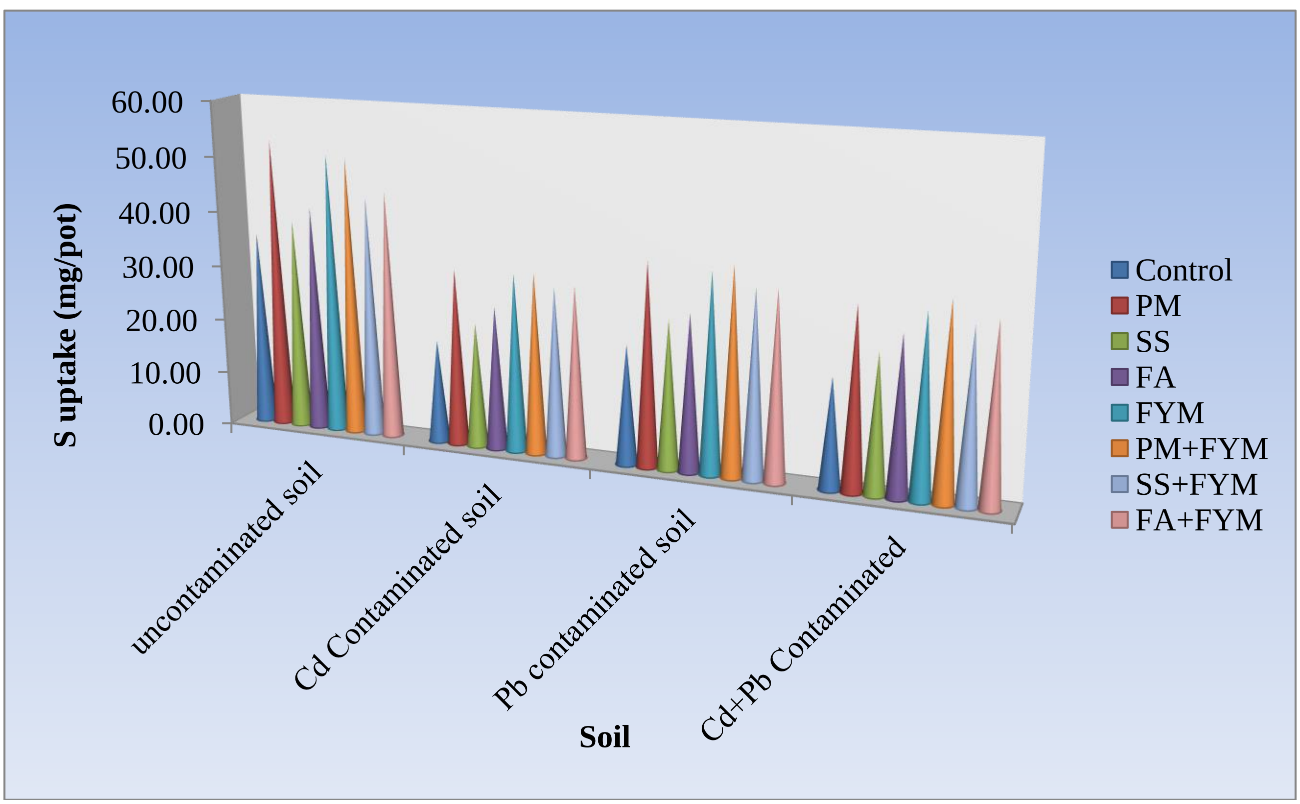

Fig. 4.8 Effect of various amendments application on S uptake by spinach leaf

amended with press mud (5%) alone in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. The lowest nitrogen, phosphorus and potassium uptake by spinach leaf was noticed in the soil amended with fly ash (5%) alone in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. However, significantly lowest sulphur uptake was observed in soil amended with steel slag (5%) alone in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Overall application of soil amendments along with FYM showed significantly higher uptake of nitrogen, phosphorus, potassium and sulphur as compared to application of amendments without FYM in the uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

4.2.4 Impact of various amendments either alone or in comination with FYM on Cd and Pb content and its uptake by spinach crop.

Spinach leaf

Soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly influenced the cadmium and lead content in spinach leaf and their uptake (Tables 4.20, 4.21, 4.22 and 4.23). Irrespective of the treatment, cadmium and lead content and its uptake by spinach leaf was observed to be statistically non significant in the uncontaminated soil. The addition of soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly decreased the cadmium and lead content in leaf. The cadmium content ranges from 163.0 to 287.0 μg g^{-1} and 142.33 to 242.3 μg g^{-1} in the spinach leaf in the Cd and Cd+Pb contaminated soil, respectively (Table 4.20). Similarly, the spinach leaf lead content ranged from 47.0 to 108.0 μg g^{-1} and 35.7 to 85.7 μg g^{-1} in the Cd and Cd+Pb contaminated soil, respectively (Table 4.21). The cadmium content in spinach leaf was relatively higher in cadmium contaminated soil as compared to Cd+Pb contaminated soil. Similar trend was also observed in spinach leaf that lead content in spinach leaf was relatively higher in lead contaminated soil as compared to Cd+Pb contaminated soil.

Among the treatments, the lowest cadmium content in spinach leaf was observed in soil amended with steel slag (5%) alone in the Cd and Cd+Pb contaminated soil. On the contrary, the lowest lead content in spinach leaf was observed in soil amended with press mud (5%) alone in the Cd and Cd+Pb contaminated soil. Steel slag application in a Cd and Cd+Pb contaminated soil resulted in 43.2 and 32.4% reduction in spinach leaf cadmium content over control, respectively. On the other hand, press mud application in a Pb and Cd+Pb contaminated soil resulted in 56.5 and 58. 4% reduction in spinach leaf lead content over control, respectively. Application of FYM also significantly reduced the cadmium and lead content in spinach leaf of Cd and Cd+Pb contaminated soil over unamended soil.

The addition of soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly decreased the cadmium and lead uptake by spinach leaf. The cadmium uptake by spinach leaf ranges from 1018.7 to 1705.0 µg pot $^{-1}$ and 964.1 to 1468.4 µg pot $^{-1}$ in the Cd and Cd+Pb contaminated soil, respectively (Table 4.22). Similarly, the spinach leaf lead uptake ranged from 416.1 to 675.3 µg pot $^{-1}$ and 286.5 to 519.4 µg pot $^{-1}$ in the Cd and Cd+Pb contaminated soil, respectively (Table 4.23).

Table 4.20 Effect of various amendments application on cadmium content in spinach leaf

Treatment	Cadmium content in spinach leaf (µgg^{-1})		
	Uncontaminated Soil	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.001	287.00a	242.33a
Press mud (5%)	0.001	187.33de	163.67d
Steel slag (5%)	0.001	163.00f	142.33e
Fly ash (5%)	0.002	224.67b	193.33b
FYM (5%)	0.001	194.67d	164.67d
PM(2.5%)+FYM (2.5%)	0.002	185.00e	165.00d
SS(2.5%)+FYM (2.5%)	0.002	165.67f	137.33e
FA (2.5%)+FYM (2.5%)	0.002	207.67c	184.67c
SEm(d)±	NS	4.24	3.044
C.D. (5%)	NS	9.08	6.46

Table 4.21 Effect of various amendments application on lead content in spinach leaf

Treatment	Lead content in spinach leaf (μgg^{-1})		
	Uncontaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	1.54	108.00a	85.67a
Press mud (5%)	2.12	47.00g	35.67f
Steel slag (5%)	1.90	74.33c	64.33bc
Fly ash (5%)	1.87	86.67b	72.67ab
FYM (5%)	2.21	58.33e	50.33de
PM(2.5%)+FYM (2.5%)	2.21	51.00f	44.67ef
SS(2.5%)+FYM (2.5%)	2.30	67.67d	56.00cde
FA (2.5%)+FYM (2.5%)	2.33	72.33c	60.00bcd
SEm(d)±	NS	1.67	6.35
C.D. (5%)	NS	3.55	13.48

Table 4.22 Effect of various amendments application on cadmium uptake by spinach leaf

Treatment	Cadmium uptake by spinach leaf (μgpot^{-1})		
	Uncontaminated Soil	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.007	1705.0a	1468.4a
Press mud (5%)	0.012	1455.9c	1317.2c
Steel slag (5%)	0.008	1018.7e	964.1e
Fly ash (5%)	0.019	1508.9bc	1320.5c
FYM (5%)	0.012	1570.6b	1382.9abc
PM(2.5%)+FYM (2.5%)	0.023	1506.0bc	1377.9bc
SS(2.5%)+FYM (2.5%)	0.022	1264.6d	1113.9d
FA (2.5%)+FYM (2.5%)	0.021	1541.1b	1422.5ab
SEm(d)±	NS	39.70	42.68
C.D. (5%)	NS	84.38	90.50

Table 4.23 Effect of various amendments application on lead uptake by spinach leaf

Treatment	Lead uptake by spinach leaf (μgpot^{-1})		
	Uncontaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	20.72	675.3a	519.4a
Press mud (5%)	23.02	416.1e	286.5c
Steel slag (5%)	20.45	530.3c	436.7ab
Fly ash (5%)	20.45	605.6b	496.3a
FYM (5%)	25.09	527.0c	422.6ab
PM(2.5%)+FYM (2.5%)	22.86	461.7d	372.4bc
SS(2.5%)+FYM (2.5%)	23.16	575.1b	455.2ab
FA (2.5%)+FYM (2.5%)	23.50	590.8b	462.5ab
SEm(d)±	NS	19.36	52.48
C.D. (5%)	NS	41.06	112.27

The cadmium uptake by spinach leaf was relatively higher in cadmium contaminated soil as compared to Cd+Pb contaminated soil. Similar trend was also observed in spinach leaf that lead uptake by spinach leaf was relatively higher in lead contaminated soil as compared to Cd+Pb contaminated soil.

Among the treatments, the lowest cadmium uptake by spinach leaf was observed in soil amended with steel slag (5%) alone in the Cd and Cd+Pb contaminated soil. On the contrary, the lowest lead uptake by spinach leaf was observed in soil amended with press mud (5%) alone in the Cd and Cd+Pb contaminated soil. Application of FYM also significantly reduced the cadmium and lead uptake by spinach leaf of Cd and Cd+Pb contaminated soil over unamended soil.

Spinach root

Soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly influenced the cadmium and lead content in spinach root and their uptake (Tables 4.24, 4.25, 4.26 and 4.27). Irrespective of the treatment, cadmium and lead content and its uptake by spinach root was observed to be statistically non significant in the uncontaminated soil. The addition of soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly decreased the cadmium and lead content in spinach root. The cadmium content in spinach root ranges from 207.0 to 362.4 µg g $^{-1}$ and 180.8 to 306.8 µg g $^{-1}$ in the Cd and Cd+Pb contaminated soil, respectively (Table 4.24). Similarly, the spinach root lead content ranged from 54.5 to 146.2 µg g $^{-1}$ and 41.4 to 120.5 µg g $^{-1}$ in the Cd and Cd+Pb contaminated soil, respectively (Table 4.25). The cadmium content in spinach root was relatively higher in cadmium contaminated soil as compared to Cd+Pb contaminated soil. Similar trend was also observed in spinach root that lead content in spinach root was relatively higher in lead contaminated soil as compared to Cd+Pb contaminated soil. Among the treatments, the lowest cadmium content and uptake by spinach root was observed in soil amended with steel slag (5%) alone in the Cd and Cd+Pb contaminated soil (table 4.26). On the contrary, the lowest lead content and uptake by spinach root was observed in soil amended with press mud (5%) alone in the Cd and Cd+Pb contaminated soil (Table 4.27). Application of FYM also significantly reduced the cadmium and lead content in spinach root of Cd and Cd+Pb contaminated soil over unamended soil.

Table 4.24 Effect of various amendments application on cadmium content in spinach root

Treatment	Cadmium content in spinach root (µgg^{-1})		
	Uncontaminated Soil	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.004	362.38a	306.78a
Press mud (5%)	0.004	217.32f	189.86d
Steel slag (5%)	0.004	207.03g	180.76de
Fly ash (5%)	0.006	283.04b	243.60b
FYM (5%)	0.004	253.71d	214.59c
PM(2.5%)+FYM (2.5%)	0.004	233.10e	207.87c
SS(2.5%)+FYM (2.5%)	0.004	214.82fg	178.08e
FA (2.5%)+FYM (2.5%)	0.004	271.35c	241.30b
SEm(d)±	NS	4.77	4.30
C.D. (5%)	NS	10.13	9.13

Table 4.25 Effect of various amendments application on lead content in spinach root

Treatment	Lead content in spinach root (μgg^{-1})		
	Uncontaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	2.18	146.72a	120.55a
Press mud (5%)	2.42	54.52g	41.39e
Steel slag (5%)	2.24	94.42c	81.74bc
Fly ash (5%)	2.18	109.22b	91.57b
FYM (5%)	2.42	76.04e	65.60cd
PM(2.5%)+FYM (2.5%)	2.45	64.26f	56.28de
SS(2.5%)+FYM (2.5%)	2.58	87.75d	72.68cd
FA (2.5%)+FYM (2.5%)	2.52	94.51c	78.39bc
SEm(d)±	NS	2.54	8.33
C.D. (5%)	NS	5.39	17.68

Table 4.26 Effect of various amendments application on cadmium uptake by spinach root

Treatment	Cadmium uptake by spinach root (μgpot^{-1})		
	Uncontaminated Soil	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.006	393.55a	391.05a
Press mud (5%)	0.008	326.65c	303.32e
Steel slag (5%)	0.007	251.68e	256.35c
Fly ash (5%)	0.009	355.54bc	326.40b
FYM (5%)	0.008	383.26ab	365.87c
PM(2.5%)+FYM (2.5%)	0.008	349.14c	358.21d
SS(2.5%)+FYM (2.5%)	0.007	289.65d	277.80c
FA (2.5%)+FYM (2.5%)	0.007	338.79c	351.50c
SEm(d)±	NS	15.22	11.63
C.D. (5%)	NS	32.29	9.65

Table 4.27 Effect of various amendments application on lead uptake by spinach root

Treatment	Lead uptake by spinach root (µg/pot)		
	Uncontaminated Soil	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	3.314	200.50a	153.65a
Press mud (5%)	4.863	98.30e	65.64c
Steel slag (5%)	3.802	141.27d	115.94b
Fly ash (5%)	3.445	155.53c	122.69b
FYM (5%)	4.938	139.15b	111.82b
PM(2.5%)+FYM (2.5%)	4.903	116.55b	96.95b
SS(2.5%)+FYM (2.5%)	4.725	143.32d	113.80b
FA (2.5%)+FYM (2.5%)	4.299	145.08b	114.18b
SEm(d)±	NS	4.55	13.02
C.D. (5%)	NS	24.67	27.60

Transfer coefficient value for cadmium and copper from soil-plant system

Transfer coefficient was calculated as the ratio of the concentration of metal in a plant to the total concentration of metal in soil. A higher transfer coefficient indicates a greater mobility of metal from soil into plant. Transfer coefficient was significantly influenced by the addition of various amendments either alone or in combination with FYM (Table 4.28 and 4.29).

The results clearly indicate that the mobility of heavy metal in soil and its subsequent uptake by crop plant was significantly reduced in the amended soil as it was evident from lowest values of transfer coefficient over the unamended soil (control). Further it was evident from the data that in a Cd contaminated soil, the transfer coefficient value for cadmium was lowest in the steel slag (5%) alone amended soil (1.63); whereas the transfer coefficient value for cadmium in a Cd+Pb contaminated soil amended was with steel slag (5%) alone was 1.42 (Table 4.28). The lowest transfer coefficient value of Cd in the steel slag amended soil indicates greater reduction in mobility of heavy metal (Cd) from soil to plant system as compared to other treatments. Among the amendments, fly ash application in a Cd and Cd+Pb contaminated soil showed highest transfer coefficient value of Cd indicating lowest reduction in mobility of heavy metal (Cd) from soil to plant system as compared to other treatments.

Table 4.28 Effect of various amendments application on transfer coefficient value of cadmium from soil to plant system

Treatment	Transfer coefficient value of cadmium from soil to plant system	
	Cd Contaminated Soil	Cd + Pb Contaminated Soil
Control	2.87a	2.42a
Press mud (5%)	1.87de	1.64d
Steel slag (5%)	1.63f	1.42e
Fly ash (5%)	2.25b	1.93b
FYM (5%)	1.95d	1.65d
PM(2.5%)+FYM (2.5%)	1.85e	1.65d
SS(2.5%)+FYM (2.5%)	1.66f	1.37e
FA (2.5%)+FYM (2.5%)	2.08c	1.85c
SEm(d)±	0.003	0.001
C.D. (5%)	0.090	0.065

Crtical appraisal of data on transfer coefficient value of lead clearly indicate that the mobility of lead in soil and its subsequent uptake by crop plant was significantly reduced in the amended soil as it was evident from lowest values of transfer coefficient over the unamended soil (control). Further it was evident from the data that in a Pb contaminated soil, the transfer coefficient value for lead was lowest in the press mud (5%) alone amended soil (0.04); whereas the transfer coefficient value for lead in a Cd+Pb contaminated soil amended with press mud (5%) alone was 0.03 (Table 4.29).

The lowest transfer coefficient value of Pb in the press mud amended soil indicates greater reduction in mobility of heavy metal (Pb) from soil to plant system as compared to other treatments. Among the amendments, fly ash application in a Cd and Cd+Pb contaminated soil showed highest transfer coefficient value of Cd indicating lowest reduction in mobility of heavy metal (Pb) from soil to plant system as compared to other treatments. Among the heavy metal (Cd and Pb), the mean transfer coefficient value of cadmium was significantly higher as compared to lead indicating the mobility of Cd metal from soil into plant system was relatively higher than Pb (Figure 4.9).

Table 4.29 Effect of various amendments application on transfer coefficient value of lead from soil to plant system

Treatment	Transfer coefficient value of lead from soil to plant system	
	Pb Contaminated Soil	Cd + Pb Contaminated Soil
Control	0.12a	0.10a
Press mud (5%)	0.04g	0.03f
Steel slag (5%)	0.06c	0.05bc
Fly ash (5%)	0.07b	0.06b
FYM (5%)	0.05e	0.04de
PM(2.5%)+FYM (2.5%)	0.04f	0.04ef
SS(2.5%)+FYM (2.5%)	0.06d	0.05cde
FA (2.5%)+FYM (2.5%)	0.06c	0.05bcd
SEm(d)±	0.001	0.001
C.D. (5%)	0.003	0.011

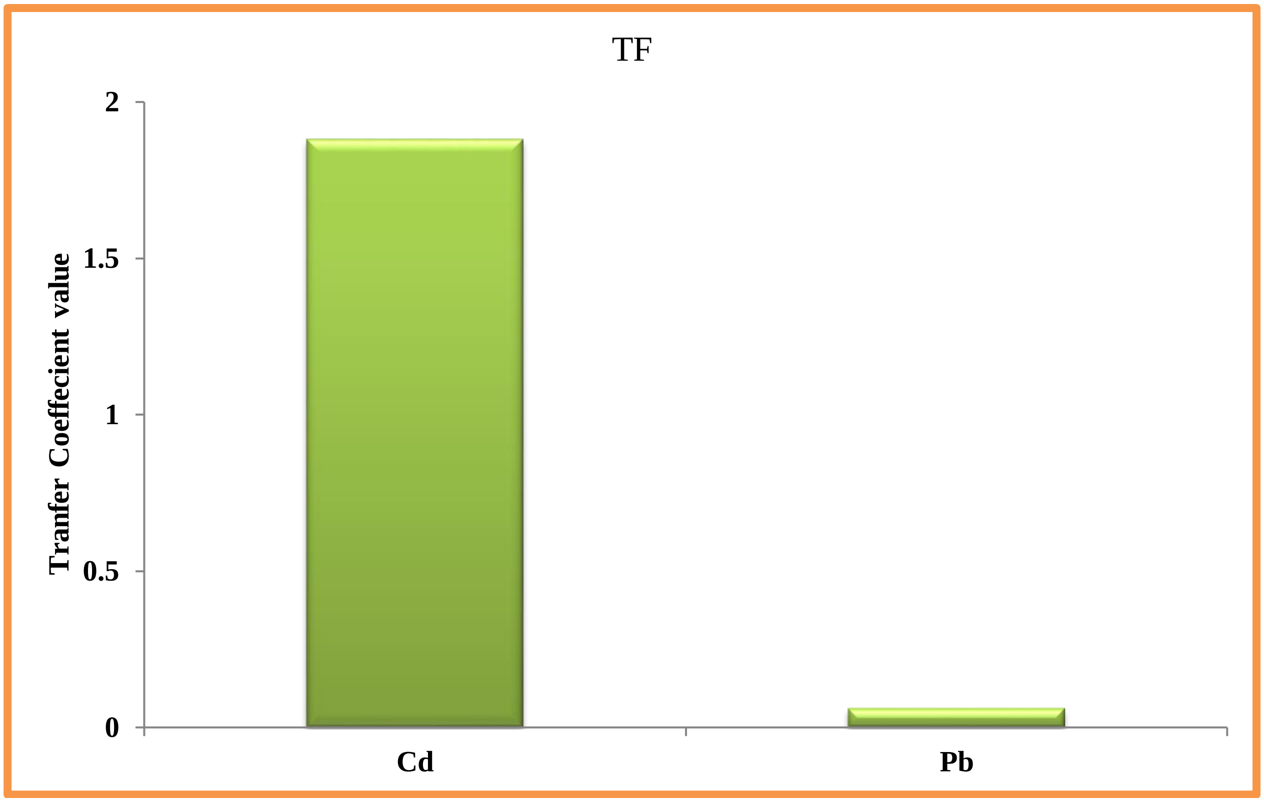

Fig. 4.9 Effect of various amendments application on mean transfer coefficient value of cadmium and lead from soil to plant system

CHAPTER – V

DISCUSSION

Remediatiation of cadmium and lead contaminated Vertisol was carried out in a two separate experiments under controlled condition (incubation and pot culture experiment). The results obtained from these two experiments are discussed simultaneously in this chapter, under the following sub-heads:

5.1. Impact of various amendments and its application rate on soil properties in a heavy metal spiked soil (Incubation experiment).

5.2. Impact of various amendments either alone or in comination with FYM on heavy metal mobility in soil and its uptake by spinach crop (Pot culture experiment).

5.1. Impact of various amendments on soil properties in a heavy metal spiked soil

Remediation technologies for heavy metal contaminated soils are mainly divided into two groups: namely immobilization, such as in situ chemical fixation, and separation/ concentration, such as soil washing. The metal mobility in soils can be effectively reduced by the chemical immobilization via adsorption, complexation, precipitation/co-precipitation, or a combination thereof (Ok et al. 2010). To sufficiently reduce the metal mobility and improve the soil quality on severely metal-contaminated sites, where most metals exist as labile forms, a large amount of immobilizing agents is often required. .Of the numerous immobilizing agents used for in-situ stabilization of contaminants, organic materials such as biosolids, manures and composts, rich in organic matter, have proved successful at reducing the mobility of contaminants in multi-metal polluted soils (Clemente and Bernal, 2006).

5.1.1 Impact of various amendments and its application rate on soil pH, EC and SOC content.

Additions of organic materials such as pressmud compost, municipal bio solids, animal manures and crop residues are of most important in maintaining the tilth, fertility and productivity of agricultural soils (Parmer and Sharma 2002). Soil amendments (press mud, steel slag, fly ash and FYM) used in the present study had positive effects on the soil chemical properties like soil pH, EC and SOC content after the end of incubation period of 30 days. Irrespective of soil type (uncontaminated, Cd contaminated and Pb contaminated soil), steel slag application at 1, 2.5 and 5% rate showed significant increase in soil pH over control. Lee et al. (2011) also reported that soil pH was increased with the addition of furnace slag. The increases in soil pH in slag amended soils likely resulted from the slag composition and in particular it has high Ca content.

On the contrary, FYM application in a Cd and Pb contaminated soil resulted in significant decrease in soil pH over control. Ali et al. (2005) also indicated that pH values were slightly decreased with FYM application at rate of 2 or 3% to sandy soilafter harvesting maize. The decrease in pH of the soil amended with FYM might be due to the release of organic acids from the manure. The decrease in soil pH with the application of FYM was also reported by Sinha and Sakal (1993). Press mud was reported as a valuable plant nutrient and may affect physical, chemical, and biologicalproperties of soil (Kumar and Verma 2002; Nehra and Hooda 2002; Rangaraj et al. 2007). In our study only at highest rate (5%) of press mud application significant increase in soil pH over control was observed. Among the various amendments, the increase in soil EC was found to be significantly highest in soil amended with press mud and FYM. Our results corroborates with the findings of Negim et al. (2010), who reported that slag addition increased soil pH, soil conductivity, and plant growth compared to the untreated soil.

Among the amendments, only press mud and FYM application resulted in significant increase in soil organic carbon (SOC) of soil samples of uncontaminated, Cd and Pb contaminated Vertisol over control.The reason might be due to presence of huge amount of organic matter content in FYM and pressmud which was evident from the initial characterization of the material. The total organic carbon (TOC) content of the materials used in the present study estimated by TOC analyzer reveals the presence of huge amount of total carbon in press mud (28.3%) and FYM (17.5%) as compared to other amendments like steel slag (1.24%) and fly ash (0.12%). Increasing the rate of application from 1 to 5% of press mud and FYM, the SOC content was also significantly increased.The mean per cent increase in SOC content due to press mud application was 94% in the uncontaminated soil; wheras the mean per cent increase in SOC content due to FYM application is 53%. Kumar et al (2017) also observed that the press mud contains 25-30% organic matter and its application resulted in increase in SOC in post harvest soil sample. The more organic carbon in FYM and pressmud-amended soil might be due to the high organic nature of the FYM and pressmud.

5.1.2 Impact of various amendments and its application rate on cadmium and lead mobility in soil

The amendment of soils for heavy metal contaminated soil remediation is a promising technique with the aim of reducing the risk of pollutant transfer to the ecosystem well being. Organic materials are a popular choice for this as they are derived from biological matter and often require little pre-treatment before they may be directly applied to soils. Additionally the practice of soil amendment may also be a convenient route to the disposal of organic residues surplus to requirement.

Soil amended with press mud, steel slag, fly ash and FYM significantly reduced the bioavailable form of heavy metal (DTPA) over unamended soil (control) of Cd. Among the amendments used to remediate Cd contaminated soil, application of steel slag was proved to be significantly better in reducing DTPA extractable Cd content as compared to other amendments like press mud, fly ash and FYM. Chemical stabilization with alkaline amendments like slag could be an effective and stable soil remediation strategy for attenuating metal bioavailability and reducing plant metal uptake. Gu et al. (2013) in his study reported that addition of steel slag as soil amendments substantially decreased the availability of heavy metals, and the higher amendment dosages resulted in the lower $CaCl_2$ extractable heavy metal concentrations. X-ray diffraction analysis indicated that the mobile metals were mainly deposited as their silicates, phosphates and hydroxides in amended treatments. The release of alkaline element like Ca, Na and Mg together with Fe and Si from the original slag following its application together with contaminants (Cd) might have involved in chemical reaction like precipitation of Cd as carbonates and oxy-hydroxides, ion exchange and formation ternary cation–anion complexes on the surface of Fe and Al oxyhydroxides (Kumpiene et al., 2008; Negim et al., 2010).

Adding steel slag, which typically have a pH of 10.5, to soils will result in an increase in the soil pH and a concurrent decrease in the mobility of cationic metals in soils due to reduced competition between H ions and metal ions for cation exchange sites either directly on the surface of biochar or as a general liming effect on the soil matrix (Beesley et al. 2011). In our incubation studies also at higher rate of press mud application the soil pH was increased that might have resulted in decrease in the mobility of Cd in soil.

On the other hand, application of press mud was proved to be significantly better in reducing DTPA extractable Pb content as compared to other amendments like steel slag, fly ash and FYM. At the end of incubation study (30 days), the highest per cent reduction (34.8%) in DTPA extractable Cd was observed in the soil amended with steel slag at 5% application rate and the lowest per cent reduction (5.0%) in the soil amended with fly ash at 1% application rate over unamended soil (control). Similarly, the highest per cent reduction (37.5%) in DTPA extractable Pb was observed in the soil amended with press mud at 5% application rate and the lowest per cent reduction (6.6%) in the soil amended with fly ash at 1% application rate over unamended soil. Our experimental result also corroborates with Ahmad *et al.,* (2016) who reported that with the help of pressmud almost 95% to 100% of heavy metals removal can be achieved whereas the use of rice husk alone managed to remove merely 10% to 20% of heavy metals.

The addition of phosphorus rich press mud material and FYM as soil amendments might have resulted in the formation lead phosphate precipitate or complex formation which leads to reduction in bioavailable content of lead in soil. In addition to phosphorus, press mud also rich in organic carbon that might have also resulted in formation organic metal chelate resulting in decrease in bioavailable content of Pb in soil. Singh *et al.* (1999) and Ibrahim *et al.* (1993) also reported increased available P in soil due to press mud incorporation. The phosphorus build up in soil due to press mud application might have resulted in formation of stable complex of lead phosphate. Several authors have also previously been reported that amending soils with highly organic materials like FYM and press mud can generate large concentrations of soluble organic matter to which free ions like Cd and Pb can complex and reduce its mobility in soil (Bernal et al., 2007). Therefore, one of the mechanisms suggested by the several authors was that the FYM and press mud may reduce Pb mobility by the precipitation of insoluble Pb-phosphates.

5.2. Impact of various amendments either alone or in combination with FYM on soil properties and plant nutrient uptake

Maintenance of soil organic matter is important for the long-term productivity of agroecosystems. For this reason, the application of organic wastes rich in organic matter to soil, such as animal manure, sewage sludge, compost, crop residues, by-products with high organic matter content, etc. is a current environmental and agricultural practice for maintaining soil organic matter, reclaiming degraded soils and supplying plant nutrients.

5.2.1 Impact of various amendments either alone or in combination with FYM on soil pH, EC, SOC and available nutrient content in soil

Additions of organic materials such as pressmud compost, municipal bio solids, animal manures and crop residues are of most important in maintaining the tilth, fertility and productivity of agricultural soils (Parmer and Sharma 2002). In our pot culture experiment, application of steel slag either alone or in combination with FYM significantly increased the soil pH over unamended soil (control) of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. On the other hand, soil amended with press mud, FYM and fly ash either alone or in combination with FYM resulted in significant decrease in soil pH over control soil (unamended). Among the various amendments used in pot culture experiment, the highest increase in soil pH value over unamended soil was recorded in soil amended with steel slag application alone at 5% rate.

Among the various amendments used in pot culture study, significantly higher soil EC was observed in soil amended with press mud alone at 5% rate followed by press mud application in combination with FYM at 2.5: 2.5% rate in the uncontaminated, as well as in contaminated soil (Cd, Pb and Cd+Pb)Vertisol. Among the treatments, except fly ash application alone at 5% rate all other amendments either alone or in combination with FYM resulted in significant increase in soil organic carbon (SOC) of post-harvest samples of uncontaminated and contaminated soil (Cd, Pb and Cd+Pb)Vertisol over control. Over all the mean per cent increase in SOC content as result of pressmud and FYM application over control was 162.8 and 95.1%, respectively.

Lee et al. (2011) also reported that soil pH was increased with the addition of furnace slag. The increases in soil pH in slag amended soils likely resulted from the slag composition and in particular it has high Ca content. In an another experiment it was reported that the pH values were slightly decreased with FYM application at rate of 2 or 3% to sandy soil after harvesting maize (Ali et al. (2005) . The decrease in pH of the soil amended with FYM might be due to the release of organic acids from the manure. The decrease in soil pH with the application of FYM was also reported by Sinha and Sakal (1993). Our results corroborates with the findings of Negim et al. (2010), who reported that slag addition increased soil pH, soil conductivity, and plant growth compared to the untreated soil. Presence of huge amount of organic matter content in FYM and pressmud which was evident from the initial characterization of the material might have been the reason for increase in SOC of post harvest soil samples. The total organic carbon (TOC) content of the materials used in the present study estimated by TOC analyzer reveals the presence of huge amount of total carbon in press mud (28.3%) and FYM (17.5%) as compared to other amendments like steel slag (1.24%) and fly ash (0.12%). Kumar et al (2017) also observed that the press mud contains 25-30% organic matter and its application resulted in increase in SOC in post harvest soil sample. The more organic carbon in FYM and pressmud-amended soil might be due to the high organic nature of the FYM and pressmud.

Available nitrogen, phosphorus, potassium and sulphur status in the post harvest soil sample increased significantly over control in the soil amended with press mud either alone or in combination with FYM. Also FYM alone application resulted in significant increase in available nitrogen, phosphorus, potassium and sulphur status over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol.

Among the various amendments studied, press mud application proved to be a better amendment in increasing the available nitrogen, phosphors and sulphur content in the post harvest uncontaminated soil as well as in the contaminated soil (Cd, Pb and Cd+Pb contaminated Vertisol). Pressmud is a by-product of sugar industry is rich in micro and macro nutrients with organic carbon and it could be used in agricultural field as the fertilizing agent or soil conditioner. Like other organic manures, pressmud has great potential to supply nutrients in addition to its favorable effects on physicochemical and biological properties of soil. Application of press mud also significantly improved soil C and N content. Lower C/N ratios in the amended soils indicated higher N mineralization by microbial activities (Yang et al 2013; Razzaq 2001). Being an excellent source of nutrients adds organic matter;pressmud addition leads to better nitrogen nutrition and promotes cation exchangecapacity(Bokhtiar e al 2015).Mishra et al (1982) observed that the pressmud compost application increased the phosphorus use efficiency by wheat (20-48%) and greengram (12-90%) as compared to single super phosphate.

On the other hand, FYM is better among the amendements studied in increasing the available sulphur content in soil apart from available N, P and K. FYM is the source of primary, secondary and micronutrient to the plant growth. Generally, press mud and FYM used in the present study were rich in plant nutrients like N, P, K and S which is evident from the initial characterization of material determined for the total nutrient content prior to the experiement. Application of such plant nutrient rich material in soil will certainly increase the available nutrient status of post harvest sample. Application of nutrient poor (N, P and K) steel slag and fly ash in soil showed no significant improvement in the available nutrient (N, P and K) status in post harvest soils of contaminated soil (Cd, Pb and Cd+Pb contaminated) as well as uncontaminated Vertisol.

If the nutrient poor amendments like fly ash and steel slag is added along with FYM, the available N, P, K and S was increased to a greater extent as compared to application of steel slag and fly ash alone. The reason might be due to additive effect of nutrient rich FYM when applied in combination with steel slag and fly ash resulted in increase in available nutrient status in soil. Increase in the available nitrogen, phosphorus, potassium and sulphur with application farm yard manures may be attributed to the incorporation of organic matter which enhances the multiplication of microbes by incorporation of different organic sources for the conversion of organically bound nutrient to inorganic form (Sinha *et al.,* 2014). Sarwar et al. (2010) also indicated that incorporation of press mud in crop field enhanced the soil quality parameters. The press mud was reported as a valuable plant nutrient and may affect physical, chemical, and biological properties of soil (Kumar and Verma 2002; Nehra and Hooda 2002; Rangaraj et al. 2007).

2.5.2 Impact of various amendments either alone or in combination with FYM on bioavailable fraction of Cd and Pb in a contaminated soil

Soil amended with press mud, steel slag, fly ash and FYM significantly reduced the bioavailable form of Cd and Pb heavy metal (DTPA extractable) over unamended soil (control) of Cd, Pb contaminated and Cd+Pb contaminated soil Vertisol. Among the amendments used to remediate Cd and Cd+Pb contaminated soil, application of steel slag was proved to be significantly better in reducing DTPA extractable Cd content as compared to other amendments like press mud, fly ash and FYM. The relative efficiency of amendments for reduction in DTPA extractable Cd content following its application in a Cd and Cd+Pb contaminated soil was found in the order of steel slag > press mud/FYM > Fly ash.

On the other hand, application of press mud was proved to be significantly better in reducing DTPA extractable Pb content as compared to other amendments like steel slag, fly ash and FYM in a Pb and Cd+Pb contaminated vertisol. The relative efficiency of amendments for reduction in DTPA extractable Pb content following its application in a Pb and Cd+Pb contaminated soil was found in the order of press mud > FYM > steel slag > Fly ash. The mean per cent reduction in DTPA extractable Cd content as a result of amendment addition ranged from 10.26% to 34.89% and 2.14% to 40.66%, respectively in a Cd and Cd+Pb contaminated soil. Similarly, the mean per cent reduction in DTPA extractable Pb content over as a result of amendment addition ranged from 11.09% to 56.41% and 5.99% to 21.50%, respectively in a Pb and Cd+Pb contaminated soil.

The stabilization technique is based on the incorporation of amendments, in order to minimize metals and metalloids, such as As, Cr, Cu, Pb, Cd and Zn that can be found in contaminated soils. This technique is able to enhance one or several processes such as metal adsorption through increased surface charge, formation of organic and inorganic metal complexes, sorption on Fe, Mn, and Al oxides, and precipitation (Bolan and Duraisamy, 2003; Raicevic et al., 2005; Kumpiene et al., 2008). Gu et al. (2013) in his study reported that addition of steel slag as soil amendments substantially decreased the availability of heavy metals, and the higher amendment doses resulted in the lower $CaCl_2$ extractable heavy metal concentrations. X-ray diffraction analysis indicated that the mobile metals were mainly deposited as their silicates, phosphates and hydroxides in amended treatments. The release of alkaline element like Ca, Na and Mg together with Fe and Si from the original slag following its application together with contaminants (Cd) might have involved in chemical reaction like precipitation of Cd as carbonates and oxy-hydroxides, ion exchange and formation ternary cation–anion complexes on the surface of Fe and Al oxyhydroxides (Kumpiene et al., 2008; Negim et al., 2010).

Adding steel slag, which typically have a pH of 10.5, to soils have resulted in an increase in the soil pH and a concurrent decrease in the mobility of cationic metals in soils due to reduced competition between H ions and metal ions for cation exchange sites either directly on the surface of biochar or as a general liming effect on the soil matrix (Beesley et al. 2011). In our incubation studies also at higher rate of press mud application the soil pH was increased that might have resulted in decrease in the mobility of Cd in soil. The addition of phosphorus rich press mud material and FYM as soil amendments might have resulted in the formation lead phosphate precipate or complex formation which leads to reduction in bioavailable content of lead in soil. In addition to phosphorus, press mud also rich in organic carbon that might have also resulted in formation organic metal chelate resulting in decrease in bioavailable content of Pb in soil.

The phosphorus build up in soil due to press mud application might have resulted in formation of stable complex of lead phosphate. Several authors have also previously been reported thatt amending soils with highly organic materials like FYM and press mud can generate large concentrations of soluble organic matter to which free ions like Cd and Pb can complex and reduce its mobility in soil (Bernal et al., 2007). Therefore, one of the mechanisms suggested by the several authors was that the FYM and press mud may reduce Pb mobility by the precipitation of insoluble Pb-phosphates.

5.2.3 Impact of various amendments either alone or in combination with FYM on dry matter yield of Spinach

Organic soil amendments (e.g. compost, biosolids, manure) are widely used to promote crop growth in agriculture due to their positive effect on soil nutrient content and a range of soil biophysical and chemical properties (Jones and Healey, 2010). A correct management of the application of amendments in soil remediation relies mainly on two aspects: efficient increase of the soil organic matter and adequate match of the release of mineral nutrients to vegetation demand.

In a Cd, Pb and Cd+Pb contamintated soil, the dry matter yield of spinach leaf was significantly increased following the application of press mud, steel slag, fly ash and FYM over control. Further, application of press mud, steel slag and fly ash in combination with FYM also increased the spinach leaf dry matter yield significantly over control. The dry matter yield of spinach leaf was highest in the FYM amended soil followed by press mud and steel slag or fly ash application. The per cent increase in dry matter yield of spinach leaf ranged from 4.39 to 33.76%, 5.22 to 37.04%, 11.68 to 44.80% and 11.72 to 38.13% as a result of application of amendments either alone or in combination with FYM in the uncontaminated, Cd, Pb and Cd+Pb contaminated soil.

Press mud is being used as organic fertilizer source in agriculture and for crop production (Kumar and Verma 2002; Singh et al 2007). Dimitriu (2004) reported that application of pressmud of sugarcane along with N, P and K fertilizers significantly increased the yield of cane and also quality of rice. On the contrary, Singh et al. (2013) observed that application of pressmud and nitrogen alone or incombination did not affect the sucrose and purity of cane juice. Singh et al. (2013) studied the effect of press mud application on crop yield and soil properties. The result indicated that application of pressmud increased the maize and wheat yield by 129.4 and 62.2% respectively. Fantaye et al. (2016) reported that combined application of 5 tonnes of pressmud and 5 tonnes of FYM significantly increased sunflower seed yield, seed protein and oil contents as compared to control without pressmud

Farm yard manure (FYM) is the conventional manure and is most easily available to farmers. It is a decomposed mixture of farm animals’ dung and urine with straw and litter used as bedding for animals and residues of fodder fed to the farm animals. It is a rich source of plant nutrients, cellulose and crude fibre. Farmyard manure has played an important role in the continuous supply of well balanced diets of nutrients to crops and represents an important component of the nutrients cycle in agricultural ecosystems. FYM is the source of primary, secondary and micronutrient to the plant growth. It provides constant source of energy for heterotrophic microorganisms and helps in increasing the availability of nutrient quality and quality of crop produce. It is hoped that the use of FYM alone or in combination with fertilizers will gradually improve and sustain soil productivity over the years (Mwangi, 2010).

Wafaa et al (2006) reported that applied FYM at the rate of 3% significantly affected the dry matter of both shoots and roots of wheat crop as well as their content of N, P and K. Clemente et al., 2007 reported that increase in biomass of Beta vulgaris and Beta maritima was recorded with application of cow manure compared to the control and in olive husk treated contaminated soil (pH 7.7–8.1,EC 0.13 dsm^{-1}, OM 6.3 %) which was attributed to the decreased availability of metals in soils thus improving plant growth. High biomass production by addition of FYM could be due to additional supply of macronutrients, increased OM content, biological activity, improved nutrient cycling, increased CEC and buffering capacity (Paulsen et al., 2007; Stewart et al., 2000).

5.2.4 Impact of various amendments either alone or in combination with FYM on nutrient content in spinach and its uptake

In general, nitrogen, phosphorus, potassium and sulphur content in spinach leaf increased significantly over control in the soil amended with press mud either alone or in combination with FYM. Also FYM alone application resulted in significant increase in nitrogen, phosphorus, potassium and sulphur content in spinach leaf over unamended soil of uncontaminated, Cd, Pb and Cd+Pb contaminated Vertisol. Significant increase in nitrogen content of spinach leaf was observed in soil amended with steel slag and fly ash along with FYM as compared to steel slag and fly ash application alone. Similar trend were also observed wih respecte to N, P, K and S uptake by spinach leaf. The obvious reason is that the FYM and press mud are rich in plant nutrients like N, P, K and S. Hence application of these amendments resulted in increase in nutrient content in spinach leaf and their uptake by spinach. FYM is the source of primary, secondary and micronutrient to the plant growth. It provides constant source of energy for heterotrophic microorganisms and helps in increasing the availability of nutrient quality and quality of crop produce.Application of FYM along with steel slag and fly ash resulted in significant increase in N, P, K and S content in spinach leaf and their uptake as a result of additive effect of nutrient content in FYM. Like other organic manures, pressmud has great potential to supply nutrients in addition to its favorable effects on physicochemical and biological properties of soil. Thus, the beneficial effect of this press mud for enhancing the soil fertility and thereby improving the crop productivity is well established (Laird et al 2001).

Application of press mud also significantly improved soil C and N content. Lower C/N ratios in the amended soils indicated higher N mineralization by microbial activities (Yang et al 2013; Razzaq 2001). Being an excellent source of nutrients adds organic matter;pressmud addition leads to better nitrogen nutrition and promotes cation exchangecapacity(Bokhtiar e al 2015).Mishra et al (1982) observed that the pressmud compost application increased the phosphorus use efficiency by wheat (20-48%) and greengram (12-90%) as compared to single super phosphate.

5.2.5 Impact of various amendments either alone or in combination with FYM on nutrient heavy metal content and its uptake by spinach leaf

Organic amendments like compost, farmyard manure (FYM), bio-solids or bio-solid compost may effectively reduce the bio-availability of heavy metals in soils due to its high content of organic matter and high concentrations of P and Fe (Brown et al. 2003). The effect of manure on heavy metal availability is due to the introduction of organic matter to the soil, which may retain Cd in the soil against both leaching and crop uptake (Jones and Johnston 1989). In our study, soil amendments (press mud, steel slag, fly ash and FYM) application either alone or in combination with FYM significantly influenced the cadmium and lead content in spinach leaf and their uptake. The addition of soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly decreased the cadmium and lead content in leaf. The cadmium content in spinach leaf was relatively higher in cadmium contaminated soil as compared to Cd+Pb contaminated soil. Similar trend was also observed in spinach leaf that lead content in spinach leaf was relatively higher in lead contaminated soil as compared to Cd+Pb contaminated soil.The artificial spiking of Vertisol by Cd and Pb for the experimental to create artificial contamination will oboviously results in increased Cd and Pb content in spinach leaf as compared to uncontaminated soil.

Immobilization of metals can be accomplished by the addition of amendments to reduce their solubility and/or bioavailability for plants (Kwiatkowska-Malina, 2015a; De Tendera et al., 2016). The addition of soil amendments, such as organic matter, phosphates, alkalizing agents, and biosolid can decrease solubility of metals in soil thus minimize their leaching to groundwater (Kwiatkowska, 2006; Kwiatkowska-Malina, 2011; Shahid et al., 2014; Sharma1 and Archana, 2016). The protective role of soil organic matter (SOM) for plants lies in its high cation exchange capacity (CEC), and the ability to form simple and chelate compounds with heavy metals ions in soil (Kinniburgh et al., 1999). Among the treatments, the lowest cadmium content in spinach leaf was observed in soil amended with steel slag (5%) alone in the Cd and Cd+Pb contaminated soil. On the contrary, the lowest lead content in spinach leaf was observed in soil amended with press mud (5%) alone in the Cd and Cd+Pb contaminated soil. Steel slag application in a Cd and Cd+Pb contaminated soil resulted in 43.2 and 32.4% reduction in spinach leaf cadmium content over control, respectively. On the other hand, press mud application in a Pb and Cd+Pb contaminated soil resulted in 56.5 and 58. 4% reduction in spinach leaf leads content over control, respectively. Application of FYM also significantly reduced the cadmium and lead content in spinach leaf of Cd and Cd+Pb contaminated soil over unamended soil. Similar trend was also observed in Cd and Pb uptake by spinach leaf in a contaminated (Cd, Pb and Cd + Pb contaminated soil) as result of amendment addition.

Sarra and Abutalib (2014) also found that compost addition significantly increased the sorption of cadmium, in linear correlation with the amount of compost added. Under contaminated soil conditions, Yassen et al (2007) found that application of Farm yard manure (FYM) significantly decreased Cd concentration (41to 31%) in spinach plant. In grain rice Cd content was significantly reduced by 27% by farm yard manure and 62% by farm yard manure mixed with lime. Burgos et al. (2006) concluded that the application of organic and inorganic amendment increased soil pH and total organic carbon content and decreased As, Cd, Cu, Pb and Zn, solubility. The results by

Mostafa et al (2013) indicate mono and multi-metal sorption of Cd, Ni, and Zn enhanced with increase in organic amendment as cow manure with rates 0, 25, and 50 tons/ha.

Like spinach leaf, the addition of soil amendments (press mud, steel slag, fly ash and FYM) either alone or in combination with FYM significantly decreased the cadmium and lead content in spinach root and their uptake. The cadmium and lead content in spinach root is relatively higher than the spinach leaf. The cadmium content in spinach leaf and root was relatively higher in cadmium contaminated soil as compared to Cd+Pb contaminated soil. Similarly, the lead content in spinach leaf and root was relatively higher in lead contaminated soil as compared to Cd+Pb contaminated soil. In a multi contaminated soil where co-existence of Cd and Pb in the contaminated soil resulted in reduction in bioavailability of Cd and Pb as compared to presence of individual Cd or Pb contamination. This might have have resulted in lower Cd and Pb content in spinach leaf as well as in root from multi contaminated soil (Cd+Pb) as compared to Cd or Pb alone contaminated soil. The results generated from the present investigation cooroborates with the findings reported by (Walker et al., 2003). Phosphate and soluble salt contents of cow manure might lead to low metal availability in soil and thus low metal concentration in plants. Farm yard manure enhanced spinach fresh weight by decreasing Cd and Pb concentration in spinach leaves in a contaminated soil. Decreased Cd and Pb in spinach leaves could be due to its decreased mobility in soil owing to its adsorption onto soil organic matter as well as due to formation of stable complex with other other elements like P, Ca, Fe and Mn (Yassen et al., 2007). Similar results were also reported by (Zaniewicz- Bajkowska et al., 2007) that vegetables (celeriac and leek) accumulated less Cd in farm yard manure treated soil (pH 5.7, OM 1.5%) compared to the control soil.

The studies reported by Walker et al. (2003) confirmed that low DTPA-extractable metals (Fe, Zn, Pb, Cu) in the organic manure treated soil was due to precipitation of metals with P and other salts released during decomposition of OM (Kabata-Pendias and Mukherjee, 2007). Complexation of OM with metals might be prevented due to high pH and calcareous nature of the soil thus decreasing DTPA-extractable metals (Jahiruddin et al., 1985). Vácha et al. (2002) compared various organic amendments and concluded that the efficiency is strongly dependent on the quality of the organic matter. Application of FYM is found to decrease the concentration of Zn, Cu and Ni in wheat grain and show (Singh, 1994, Gupta et al. 1989). In our present studies also the quantity and quality of organic matter composition in the amendements played a major role in stabilizing Cd and Pb following its application in a Cd, Pb and Cd=Pb contaminated soil.

5.2.6 Impact of various amendments either alone or in combination with FYM on transfer coefficient of Cd and Pb from soil to plant system

Transfer coefficient was calculated as the ratio of the concentration of metal in a plant to the total concentration of metal in soil. A higher transfer coefficient indicates a greater mobility of metal from soil into plant. Transfer coefficient was significantly influenced by the addition of various amendments either alone or in combination with FYM.

The mobility of heavy metal in soil and its subsequent uptake by crop plant was significantly reduced in the amended soil as it was evident from lowest values of transfer coefficient over the unamended soil (control). Further it was evident from the data that in a Cd contaminated soil, the transfer coefficient value for cadmium was lowest in the steel slag (5%) alone amended soil (1.63). The lowest transfer coefficient value of Cd in the steel slag amended soil indicates greater reduction in mobility of heavy metal (Cd) from soil to plant system as compared to other treatments. Chen et al. (2000) evaluated chemical amendments (calcium carbonate (CC), steel sludge (SS) and furnace slag (FS) on the growth and uptake of cadmium (Cd) by wetland rice, Chinese cabbage and wheat grown in a red soil contaminated with Cd. Among the three amendments, FS was the most efficient at suppressing Cd uptake by the plants, probably due to its higher content of available silicon (Si). Results showed that soil amended with CC, SS and FS decreased Cd uptake by wetland rice, Chinese cabbage and wheat by 23–95% compared with the unamended control. The mechanisms of stabilization by silicon-rich amendments of cadmium, zinc, copper and lead in a multi-metal contaminated acidic soil and the mitigation of metal accumulation in rice were also investigated by Gu et al (2011). These results demonstrated steel slag could be effective in mitigating heavy metal accumulation in rice grown on multi-metal contaminated acidic soils.

Similarly, the transfer coefficient value for lead was lowest in the press mud (5%) alone amended soil (0.04). The lowest transfer coefficient value of Pb in the press mud amended soil indicates greater reduction in mobility of heavy metal (Pb) from soil to plant system as compared to other treatments. Among the heavy metal (Cd and Pb), the mean transfer coefficient value of cadmium was significantly higher as compared to lead indicating the mobility of Cd metal from soil into plant system was relatively higher than Pb. Mench et. al. (1994a) reported that the addition of Thomas phosphate basic slag lowered the bioavailable lead content in the metal contaminated soils. Phosphate and phosphate - containing minerals have been shown to reduce bioavailable Pb in soils. The application of alkaline materials, organic matters, phosphates, alumino-silicates, iron grit, basic slag (3.9%) and compost of sewage sludge (5%) combined with iron grit are the most efficient to promote shoot production and limit foliar Cu accumulation in dwarf beans cultivated in a highly Cu-contaminated soil (Bes and Mench, 2008).The Ca and P contents in BS make it a potential liming agent to increase the precipitation and sorption of metals such as Cu and a potential fertilizer promoting plant growth and improving physico-chemical properties of the soil.

Significant decrease in the capability of metal resupply from solid to solution phase was observed in the steel slag amended soils. Equilibrium modeling as reported in the literature from previous studies indicated that the soil amendments induced the precipitation of several Fe, Al and Ca minerals, which may play a positive role in metal stabilization. Some investigations have been carried out to stabilize metals and metalloids, such as As, Cr, Cu, Pb, Cd and Zn in the contaminated soils following the addition of steel slags as soil amendments. Chemical stabilization with alkaline amendments could be an effective and stable soil remediation strategy for attenuating metal bioavailability and reducing plant metal uptake. Because of its Ca and P content, it acts as a liming material and it increases the precipitation and sorption of metals.

The addition of phosphorus rich press mud material and FYM as soil amendments might have resulted in the formation lead phosphate precipate or complex formation which leads to reduction in bioavailable content of lead in soil. In addition to phosphorus, press mud also rich in organic carbon that might have also resulted in formation organic metal chelate resulting in decrease in bioavailable content of Pb in soil. Singh *et al.* (1999) and Ibrahim *et al.* (1993) also reported increased available P in soil due to press mud incorporation. The phosphorus build up in soil due to press mud application might have resulted in formation of stable complex of lead phosphate. Several authors have also previously been reported thatt amending soils with highly organic materials like FYM and press mud can generate large concentrations of soluble organic matter to which free ions like Cd and Pb can complex and reduce its mobility in soil (Bernal et al., 2007). Therefore, one of the mechanisms suggested by the several authors was that the FYM and press mud may reduce Pb mobility by the precipitation of insoluble Pb-phosphates.

CHAPTER – VI

SUMMARY, CONCLUSIONS AND SUGGESTION FOR FUTURE WORK

Anthropogenic sources of heavy metal contamination are evident due to intensive agricultural practices such as herbicide and pesticide application, waste water irrigation, municipal solid waste and even chemical fertilizer. Several technologies exist for the remediation of metal contaminated soil. Among various technologies, immobilization of heavy metals in soil by in-situ technique may provide a cost-effective and sustainable solution for remediation of contaminated soils (Mench et al., 2000).

Immobilization normally refers to decrease in metal mobility, bioavailability and bioaccessibility of heavy metas in soil through complexation, precipitation and adsorption reactions by adding immobilizing agents to the contaminated soils. Of the numerous amendments used for in-situ stabilization of contaminants, amendments rich in organic carbon, phosphates and silicates have proved successful for remediation of heavy metal pollution due to its porosity, large surface area, and good absorptivity. It is also well known that organic materials such as biosolids, manures and composts rich in organic matter is important for the retention of metals by soil solids through adsorption reactions or forming stable complexes thus decreasing its mobility and bioavailability in soil.Hence, the present investigation entitled "Comparative effects of various amendment combinations on cadmium, lead mobility in soil and its uptake by spinach crop" were carried out at Indian Institute of Soil Science, Bhopal with the objectives to assess the performance of press mud, steel slag, fly ash and FYM on Cd and Pb stabilization in soil and its uptake by crop plant spinach. The findings of the study have been summarized as follows:

Incubation Study

- Application of various amendments like press mud, steel slag, fly ash and FYM significantly reduced the bioavailable form of heavy metal (DTPA) in a Cd and Pb Vertisol.

- At the end of incubation study (30 days), the per cent reduction in DTPA extractable Cd and Pb ranged from 4.5% to 35.8% and 6.6% to 35.2%, respectively over control.
- The incubation study result also reveals that with increase in level of amendment application from1% to 5% on w/w basis, the percent reduction in bioavailable Cd and Pb was also significantly reduced over control.
- The per cent reduction in biovaialbe Cd content was significantly greater (35.8%) in the soil amended with steel slag at 5% application rate. On the other hand, soil amended with press mud at 5% application rate showed significantly greater reduction in bioavialble Pb content at the end of incubation period of 30 days.
- Initially at 7th day of incubation period the Cd and Pb content was higher and subsequently it reduces over the period of incubation and almost get stabilized at the end of incubation priod of 30 days.
- The per cent reduction in bioavailable cadmium and lead content at the end of 30 days of incubation period was found to be significantly lowest in soil amended with fly ash at 1% application rate.
- The result also indicates that at the end of incubation period of 30 days, application of various amendment and its rate had significantly influenced the soil pH, EC and SOC content over control.
- Irrespective of soil type (uncontaminated, Cd contaminated and Pb contaminated soil), the pH was significantly highest in soil amended with steel slag and lowest in soil amended with FYM
- The pH at the end of 30 days of incubation period ranges from 7.67 (FYM 5%) to 9.00 (Steel slag 5%), 7.62 (FYM 5%) to 9.00 (Steel slag 5%) and 7.71 (FYM 5%) to 8.93 (Steel slag 5%) respectively in uncontaminated, Cd contaminated and Pb contaminated soil.
- Application of steel slag at 5% level had significantly increased the soil pH by 1.04, 1.14 1nd 1.09 over control in the uncontaminated, Cd contaminated and Pb contaminated soil. However, the EC was significantly highest in soil amended with press mud and lowest in soil amended with Fly ash in the uncontaminated, Cd contaminated and Pb contaminated soil.

- At the end of 30 days of incubation period, application of press mud and FYM amendment and its rate from 1% to 5% had significantly influenced the SOC content. On the other hand soil amended with steel slag/ fly ash showed no significant difference in SOC content at the end of 30 days period of incubation.
- The SOC content at the end of 30 days of incubation period ranges from 0.49% (Fly ash 5%) to 1.45 %(Press mud5%), 0.57% (Steel slag 5%) to 1.68% (Press mud 5%) and 0.55% (steel slag 5%) to 1.52% (Press mud 5%) respectively in uncontaminated, Cd contaminated and Pb contaminated soil.
- The per cent increase in SOC at the end of 30 days of incubation period was found to be significantly highest in soil amended with press mud at 5 % application rate followed by FYM at 5% application r.ate.
- The incubation study reveals that at the application rate of 5% steel slag was found to be better source of amendment for Cd stabilization in soil contaminated with Cd due to high pH and presence of oxides and hydroxides of FE and Al in steel slag amendment.
- On the contrary the Press mud and FYM application at 5% proved to be better amendment in stabilizing lead in lead contaminated soil due high phosphorus content and TOC content in press mud and FYM.

Pot Culture Study

Impact of press mud, steel slag, fly ash and FYM on dry matter yield, plant available nutrient and heavy metal uptake by spinach crop

- Significant increase in dry matter yield of spinach leaf and root was observed in the Cd, Pb and Cd + Pb contaminated soil amended with press mud, steel slag, fly ash and FYM at 5% application rate. However, in the uncontaminated soil, steel slag and fly ash showed no significant difference in DMY of spinach leaf and root over control.
- Irrespective of the soil type (uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil), steel slag and fly ash performance on DMY of spinach leaf and root were found to be similar with no significant difference between the treatment.

- Irrespective of soil contamination (Cd and Pb spiked soil) and in uncontaminated vertisol, the dry matter yield of spinach leaf and root was highest in the FYM followed by press mud amended soil with no significant difference between the treatment.
- The per cent increase in DMY yield of spinach leaf in the soil amended with FYM over control was 33.01, 35.92, 44.49 and 38.61% in uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil, respectively.
- Application of various amendments alone and its combination with FYM is found to be significantly different with respect to DMY of spinach leaf and root. Moreover, its effect was more pronounced in case of steel slag and fly ash, where application of steel slag and fly ash in combination with FYM showed higher yield than without FYM application.
- Similar trend was also observed in DMY of spinach root with per cent increase in DMY yield of spinach root over control was 34.21, 38.53, 33.58 and 33.86% in uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil, respectively.
- Plant nutrient content (N, P, K and S) in spinach leaf and their uptake followed the same trend. Irrespective of the soil type (uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil), steel slag and fly ash performance on plant nutrient content and their uptake by spinach leaf found to be similar with no significant difference between the treatment.
- Irrespective of soil contamination (Cd and Pb spiked soil) and in uncontaminated vertisol, the nutrient content (P) and its uptake by spinach leaf was highest in the press mud followed FYM amended soil with no significant difference between the treatment.
- The plant Cd content and its uptake was significantly reduced in the soil amended with press mud, steel slag and FYM either alone or in combination with FYM.
- The cadmium and lead content and its uptake by spinach leaf was relatively higher in the soil contaminated with either Cd or Pb as compared multi element contaminated soil (Cd + Pb). In other words in a multi contaminated (Cd + Pb)

soil, the cadmium content and its uptake was reduced by the presence of Pb and vice versa.

- In Cd and Cd + Pb contaminated soil, the highest per cent reduction in cadmium content of spinach leaf to the tune of 42.51 and 41.26 % was observed in steel slag amended soil.
- On the contrary, in Pb and Cd + Pb contaminated soil, the highest per cent reduction in lead content of spinach leaf to the tune of 56.49 and 58.36 % was observed in press mud amended soil. Similar trend was also observed in cadmium and lead content and its uptake by spinach root

- Among the various amendments used for stabilization heavy metal in soil, the per cent reduction in cadmium and lead content, and its uptake by spinach leaf and root was significantly lowest in soil amended with fly ash.
- Irrespective of soil contamination (Cd, Pb, and Cd + Pb contaminated soil), spinach root accumulates greater cadmium and lead content than spinach leaf. The cadmium and lead contamination to spinach leaf and root was higher in Cd and PB contaminated soil than uncontaminated soil.
- The pot culture experimental result clearly indicates that application of various amendment like press mud, steel slag, fly ash and FYM either alone or in combination with FYM had significantly influenced the soil pH, EC and SOC content over control.
- Irrespective of soil type (uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil), the pH was significantly highest in soil amended with steel slag and lowest in soil amended with FYM.
- Application of steel slag had significantly increased the soil pH by 0.91, 0.92, 0.93 and 0.87 unit over control in the uncontaminated, Cd contaminated, Pb contaminated and Cd + Pb contaminated soil, respectively.
  - In the post harvest soil samples amended with various amendment, the EC was significantly highest in soil amended with press mud and lowest in soil amended with Fly ash in the uncontaminated, Cd contaminated and Pb contaminated soil.

- Press mud and FYM amendment soil showed significant increase in SOC content of post harvest soil samples. On the other hand, soil amended with steel slag/ fly ash showed no significant difference in SOC content.
- The per cent increase in SOC in the post harvest soil sample was found to be significantly highest in soil amended with press mud followed by FYM. Further the result also reveals that among the various amendments used, application of carbon rich amendments like press mud and FYM significantly increased SOC over carbon poor amendments like steel slag and fly ash.
- However, when steel slag/fly ash was applied in combination with FYM, the SOC content was significantly increased as compared to application of steel slag /fly ash alone.
- Like SOC, similar trend were also observed in soil available nutrient status (N, P K & S) in the post harvest soil sample.

- In a contaminated Vertisol (Cd, Pb and Cd + Pb contaminated soil), significant reduction in the bioavailable form of heavy metal (DTPA extractable Cb & Pb) was observed in soil amended with press mud, steel slag, fly ash and FYM over control
- The per cent reduction in DTPA extractable Cd ranged from 10.26% to 53.58% and 2.13% to 40.66%, over control in the Cd and Cd+Pb contaminated soil, respectively.
- Similarly, the per cent reduction in DTPA extractable Pb ranged from 3.93% to 19.98% and 5.99% to 21.50%, over control in the Pb and Cd+Pb contaminated soil, respectively.
- The per cent reduction in bioavailable Cd content was significantly greater (53.38%) in the soil amended with steel slag. On the other hand, soil amended with press mud showed significantly greater reduction (21.50%) in bioavailable Pb content of post harvest soil sample.
- The transfer coefficient value (ratio of plant Cd/Pb content to total soil Cd/Pb content) was comparatively higher for Cd (1.37 to 2.87) than Pb (0.04 to 0.12), indicating the mobility of Cd from soil to plant was greater than Cd.

CONCLUSIONS

- To sum up, the study from the incubation and pot culture experiment studies clearly implicate that the application of phosphorus and organic carbon rich soil amendments like press mud/ FYM/ press mud + FYM in combination has greater potential in reducing the mobility of Pb in soil contaminated with lead. Similarly, silica and alkaline rich amendment like steel slag application either alone or in combination with FYM has greater potential in reducing the mobility of cadmium in soil contaminated with cadmium.
- In a multi contaminated soil where Cd and Pb co-exist, application of press mud/ FYM/press mud + FYM in combination has greater potential in reducing the mobility of Cd and Pb in soil contaminated as evidenced by reduction in DTPA extractable Cd & Pb content and lower transfer coefficient value in a Cd + Pb Contaminated soil (artificially spiked soil).
- Therefore, press mud and steel slag either alone or in combination with FYM was proved to be a better management option for sustainable crop yield and simultaneously reducing the transfer of potentially toxic heavy metal (Cd and Pb) to edible plant parts (leaf) in a Cd and Pb contaminated

SUGGESTION FOR FUTURE WORK

Under long term experiments, heavy metal release from the adsorbed phosphate and organic carbon rich amendments like press mud and FYM needs to be investigated in details before making recommendation for its use as soil amendments to remediate Cd and Pb contaminated Vertisol. Also the possible mechanisms involved in the steel slag use for cadmium stabilization in a cadmium contaminated soil needs to be explored further.

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Appendix- I

Value of Mean Sum of Square for Soil pH, and EC after 30 days period of Incubation

Source of Variation	D.F.	pH			EC		
		UCS	Cd CS	Pb CS	UCS	Cd CS	Cd CS
Treatments	12	0.471	0.461	0.476	0.173	0.149	0.170
Errors	26	0.001	0.001	0.002	0.001	0.001	0.002
Total	38	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Soil SOC and DTPA extractable Cd and Pb after 30 days period of Incubation

Source of Variation	D.F.	SOC			DTPA Extractable Cd/Pb	
		UCS	Cd CS	Pb CS	Cd CS	Cd CS
Treatments	12	0.264	0.357	0.286	45.99	780.66
Errors	26	0.004	0.002	0.004	0.052	27.66
Total	38	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Appendix- II

Value of Mean Sum of Square for Soil pH and EC of post harvest soil sample

Source of Variation	D.F.	pH				EC			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	0.558	0.483	0.725	0.592	0.292	0.359	0.479	0.320
Errors	16	0.003	0.002	0.004	0.003	0.005	0.012	0.038	0.008
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Soil SOC of post harvest soil sample

Source of Variation	D.F.	SOC			
		UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	0.496	0.554	0.517	0.549
Errors	16	0.001	0.001	0.002	0.002
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Soil available N and P of post harvest soil sample

Source of Variation	D.F.	Available nitrogen				Available phosphorus			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	1261	1258	1289	1229	230.7	213.4	199.3	264.8
Errors	16	27.9	35.5	19.0	19.3	5.4	10.3	12.8	17.5
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Soil available K and S of post harvest soil sample

Source of Variation	D.F.	Available potassium				Available sulphur			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	1216	13660	17090	20436	31.98	29.87	35.41	30.56
Errors	16	180.4	266.1	206.1	178.7	0.647	0.112	0.21	0.576
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Soil DTPA extractable Cd and Pb of post harvest soil sample

Source of Variation	D.F.	DTPA Extractable Cd and Pb content			
		Cd CS	Pb CS	Cd+Pb CS	
		Cd	Pb	Cd	Pb
Treatments	7	129.3	9625	176.5	14886
Errors	16	0.77	16.9	1.21	25.8
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for dry matter yield of spinach leaf and root

Source of Variation	D.F.	Dry Matter yield of Leaf				Dry Matter yield of Root			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	16.88	12.65	16.32	13.65	0.019	0.007	0.012	0.009
Errors	16	0.10	0.03	0.04	0.04	0.001	0.001	0.001	0.001
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for N and P content in spinach leaf

Source of Variation	D.F.	N content in spinach leaf				P content in spinach leaf			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	0.144	0.108	0.106	0.086	0.005	0.009	0.008	0.008
Errors	16	0.014	0.005	0.007	0.020	0.001	0.001	0.001	0.001
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for K and S content in spinach leaf

Source of Variation	D.F.	K content in spinach leaf				S content in spinach leaf			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	0.208	0.168	0.155	0.130	0.002	0.003	0.003	0.004
Errors	16	0.020	0.009	0.010	0.030	0.001	0.001	0.001	0.001
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for N and P uptake by spinach leaf

Source of Variation	D.F.	N uptake by spinach leaf				P uptake by spinach leaf			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	7446	17427	23676	19611	1094	449.6	565.9	452.3
Errors	16	146.2	28.4	39.6	59.3	3.4	0.962	3.1	0.908
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for K and S uptake by spinach leaf

Source of Variation	D.F.	K uptake by spinach leaf				S uptake by spinach leaf			
		UCS	Cd CS	Pb CS	Cd+Pb CS	UCS	Cd CS	Pb CS	Cd+Pb CS
Treatments	7	76046	27230	34789	29670	1599	657	821	701
Errors	16	129.5	44.4	58.0	89.7	1.40	1.04	0.66	0.79
Total	23	-	-	-	-	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Cd and Pb content in spinach leaf

Source of Variation	D.F.	DTPA Extractable Cd and Pb content			
		Cd CS	Pb CS	Cd+Pb CS	
		Cd	Pb	Cd	Pb
Treatments	7	4787	1888	3333	754
Errors	16	27.08	4.2	13.9	60.6
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Cd and Pb content in spinach root

Source of Variation	D.F.	DTPA Extractable Cd and Pb content			
		Cd CS	Pb CS	Cd+Pb CS	
		Cd	Pb	Cd	Pb
Treatments	7	7885	2460	5538	1701
Errors	16	34.2	9.68	27.8	104.3
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Cd and Pb uptake by spinach leaf

Source of Variation	D.F.	DTPA Extractable Cd and Pb content			
		Cd CS	Pb CS	Cd+Pb CS	
		Cd	Pb	Cd	Pb
Treatments	7	134905	20433	87581	16313
Errors	16	23.7	562.7	2733	4132
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

Value of Mean Sum of Square for Cd and Pb uptake by spinach root

Source of Variation	D.F.	DTPA Extractable Cd and Pb content			
		Cd CS	Pb CS	Cd+Pb CS	
		Cd	Pb	Cd	Pb
Treatments	7	6622	2648	6486	1820
Errors	16	347.6	31.1	203.2	254.4
Total	23	-	-	-	-

UCS: uncontaminated soil; Cd CS: Cd contaminated soil; Pb CS: Pb contaminated soil

VITA

The author of this thesis Mr. Jitendra Porwal S/o Shri Banshi Lal Porwall was born on 25th January 1993 at Vill.-Muravar , Post-Muravar, Teh.-Jawar, Dist-Sehore (M.P.). He completed his primary education from Govt. primary school, Muravar ,High School (10th) from S.V.M.H.S. School, Dewas and H.S.S.C. (12th) from S.V.M.H.S.School Dewas (M.P.)

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(JITENDRA PORWAL)