

Effects of co-composted cow manure and poultry litter on the extractability and bioavailability of trace metals from the contaminated soil irrigated with wastewater

Bushra Haroon, Amjad Hassan, Arshad Mehmood Abbasi, An Ping, Shao Yang and Muhammad Irshad

ABSTRACT

It is generally recognized that agricultural soils accumulate toxic metals after long-term wastewater irrigation. The removal of trace metals (TMs) from the soil is not possible. Therefore, this study investigated the effects of the addition of manure on the extractability and bioavailability of TM from the contaminated soil after wastewater irrigation. Soils samples were treated with co-composted cow manure (CM) and poultry litter (PL) at 10 and 20 t ha⁻¹. The study showed that addition of manure enhanced fenugreek biomass and reduced TM uptake depending on the combination of composted manures used. TM concentrations in the fenugreek shoots varied in the order of Pb > Ni > Zn > Cu > Cd. A higher amount of manure mixture especially composted with the privet and cypress residues decreased the extractability of TM from the contaminated soil. Soils amended with PL reduced TM concentrations more than CM; this is also true for the plant uptake. The variation of TM in plants was positively associated with their concentrations in the soil and adversely related to the plant biomass. This study confirmed that the combined use of composted manure with plant residues can be an effective addition for ameliorating the TM pollution in soils and crops.

Key words | arid region, bioavailability, contaminated soil, cow manure, heavy metals, poultry litter

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INTRODUCTION

The benefits of treated wastewater reuse for integrated water resources management and its role for water cycle management and solving water scarcity issues have been emphasized (Kalavrouziotis *et al.* 2015). The metal pollution in soils and vegetation has become a significant environmental and ecological issue of the world (Satashiya 2017). Wastewater irrigation, the disposal of solid waste, the application of sludge, vehicle emissions and industrial activities have been reported among major contributors of trace

metals (TMs) in soil (Majeed *et al.* 2018) and impaired the quality and safety of food (Alghobar & Suresha 2017). Edible crops in the Hattar industrial area of Pakistan were found to be accumulated with TMs, and these metals were present beyond permissible limit in agricultural soils (Irshad *et al.* 2015). Sarwar *et al.* (2017) reported the importance of TM monitoring in the environment due to food-chain contamination.

Abdel-Shafy & Mansour (2018) reported the successful remediation of contaminated soils using phytoremediation technology. However, the remediation of the soil contaminated particularly with TMs has also been reported a complicated phenomenon (Liu *et al.* 2017). TMs cannot be

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removed from soils, but can only be changed from one state to another oxidation state (Ullah *et al.* 2015). Plants are unable to uptake the total pool of metals that exist in the growth medium. The fraction of the metal which a plant can uptake and absorb is known as a bioavailable fraction. The accumulation of TM in plant tissues depended on the type of plant species and the ability of different plants to uptake metals had been assessed by the uptake of plant and the transfer factor of metal ions from soil to plant (Abbaslou & Bakhtiari 2017). In soils and bio-waste, TMs exist in variable forms such as exchangeable metals, organic matter-associated metal, metals associated with secondary minerals, phosphates, carbonates and oxides, and ions present on the crystals of primary minerals (Theobald 2017). The fraction of the soluble metals that exist in soil solution is easily available for plant absorption, while other metal pools of soil are less bioavailable. Soil factors that affect the bioavailability of metals involve the presence of total metal ions in the soil, soil pH, the content of clay and hydrous oxide, the percentage of organic matter and reduction state (Murtaza *et al.* 2017).

Pedrero *et al.* (2010) reported the fundamentals of agricultural irrigation and reuse of treated municipal wastewater and elaborated the effects of wastewater reuse on soils and plants in Greece and Spain. In view of the effects of wastewater irrigation in agricultural fields, effective management approaches are required for the sustainable use of soils polluted with wastewaters. The application of organic-rich material as a soil amendment in agricultural practices provides an approach for converting organic wastes into useful resources (Rosazlin *et al.* 2010). Organic waste can help to improve the soil structure, increase the content of soil organic matter, prevent the growth of soil-borne plant pathogens and stimulate plant growth (Xiong *et al.* 2017). The beneficial use of animal manure via land application has been well recognized by the farmers. The addition of manure to the soil alters properties such as the availability of plant nutrient, amount of organic matter, cation exchange capacity and tilth of the soil. Livestock manures are believed to be helpful in the degradation of soil contaminants and alleviate the uptake of contaminants by the plant. Two studies have reported the concentrations of TMs in polluted soils and plants after the addition of manure (Irshad *et al.* 2015; Shazia *et al.*

2016). However, metals from polluted soils and their bioavailability to a crop after the application of co-composted manures have not been well reported. Therefore, the current study was conducted to investigate the extraction of metals and the uptake response of fenugreek in the contaminated soil after discrete treatment with composted cow manure (CM) and poultry litter (PL) with privet and cypress residues.

MATERIALS AND METHODS

Polluted soil samples were collected (0–20 cm) randomly from 10 adjacent wastewater-irrigated fields of the Hattar area, District Haripur, Pakistan. Samples were air-dried, sieved and then kept in plastic bags. These samples were thoroughly mixed and analyzed for the physico-chemical properties (texture, total carbon, electrical conductivity (EC), pH and extractable TM). Total carbon content was measured by using a dry combustion method (Nelson & Sommers 1982). The pH of compost suspension with soil: water at the ratio of 1:5 was measured by using a pH meter (Model: HANNA HI 8520). The EC of the soil suspension was determined with an EC meter (Model: 4320 JENWAY). Soil texture was determined using a pipette method (Gee & Bauder 1986). Selected properties of soil are given in Table 1. Industrial wastewater samples collected from the drain (used for irrigation) were also analyzed for chemical properties (Table 1; Bushra *et al.* 2018).

Composting process

CM and PL samples were collected from local farms and brought to the laboratory. Leaf residues of broad-leaved privet (*Ligustrum lucidum*) and Italian cypress (*Cupressus sempervirens*) were collected after trimming from the local areas of Abbottabad. CM and PL were air-dried. Leaf residues were dried and chopped into small pieces about 2–3 inches. Manures were co-composted with residues of broad-leaved privet and Italian cypress at the ratio of 1:0, 1:1 and 1:2 (animal manure:plant residues) in the plastic buckets, and these were placed under the shade. Samples were moistened occasionally and aerated equally during the co-composting process, moisture content was

Table 1 | Average values of the soil and water quality parameters of wastewater used for irrigation, along with standard limits of drinking water by NSDWQ-Pak and irrigation water by the USA (Radojevic & Bashkin 2010; Bushra et al. 2018)

Parameters	Unit	Present study (mean)	NSDWQ-Pak	US irrigation water quality	Soil properties
pH	–	9.20 ± 0.3	6.5–8.5	6.5–8.4	8.1 ± 0.2
EC	µS cm ⁻¹	1,124 ± 26	–	<700	636. ±10.2
COD	mg L ⁻¹	459 ± 14	–	–	–
Pb	mg L ⁻¹	2.50 ± 0.31	0.05	5.0	47.5 ± 1.6 mg kg ⁻¹
Ni	mg L ⁻¹	1.64 ± 0.23	0.02	0.2	6.2 ± 0.8 mg kg ⁻¹
Mn	mg L ⁻¹	0.98 ± 0.14	>0.5	0.2	2.3 ± 0.5 mg kg ⁻¹
Fe	mg L ⁻¹	0.72 ± 0.1	–	5.0	2.1 ± 0.1 mg kg ⁻¹
Zn	mg L ⁻¹	1.51 ± 0.1	5.0	2.0	2.2 ± 0.1 mg kg ⁻¹
Cu	mg L ⁻¹	0.81 ± 0.02	2.0	0.2	8.0 ± 0.6 mg kg ⁻¹
Cd	mg L ⁻¹	0.32 ± 0.02	0.01	0.01	1.6 ± 0.1 mg kg ⁻¹
K	mg L ⁻¹	0.72 ± 0.10	–	–	–
Ca	mg L ⁻¹	4.10 ± 0.31	–	–	–
Mg	mg L ⁻¹	0.91 ± 0.02	–	–	–
Na	mg L ⁻¹	6.81 ± 0.42	–	–	–
Total C	g kg ⁻¹	–	–	–	32.2 ± 1.4
Clay	%	–	–	–	6.8 ± 0.3
Silt	%	–	–	–	7.0 ± 0.4
Sand	%	–	–	–	86.2 ± 2.3

maintained at about 40%, and the temperature was maintained according to the requirement of the experiment and composted for 100 days. The composted samples were collected, air-dried and ground into powder form, sieved and then stored in plastic bags. Selected properties of composted CM and PL supplemented with privet and cypress residues are given in Figures 1 and 2.

Soil incubation

Polluted soil samples were amended with the addition of manure at two levels: 10 and 20 t ha⁻¹ (based on 2 million kg soil per plow layer in ha). A 500 g sample of soil was weighed and mixed with manure samples. The experiment was a factorial combination of 2 × 2 × 3 × 2 (two manure types, two types of plant residues, three mixing ratios and two application rates) replicated three times arranged into a completely randomized design. The moisture content of the soil was kept at 30% in plastic buckets. Samples were incubated for 8 weeks at room

temperature. Concentrations of extractable metals, namely lead (Pb), nickel (Ni), zinc (Zn), copper (Cu) and cadmium (Cd) in the manure-amended soils, were determined by a modified procedure of Amacher (1996), i.e., metals were extracted with 0.1 mol L⁻¹ Mg(NO₃)₂ and shaken for 2 h at about 80 cycles/min. Soil weighing 5 g was extracted. After extraction, the solution was centrifuged and filtered and finally used for the determination of TM concentrations using an atomic absorption spectrophotometer (AAS) (Model: Analyst 700, Perkin Elmer).

Greenhouse study

Fenugreek (*Trigonella foenum-graecum*) was grown in a greenhouse. For this purpose, plastic pots were filled with the contaminated soil (5 kg per pot). Soil samples were brought from the Hattar industrial estate area. The contaminated soil was treated with the above-composted manures. An equal number of seeds was sown in each pot at a depth of 2 cm. After 1 week of germination, plants were

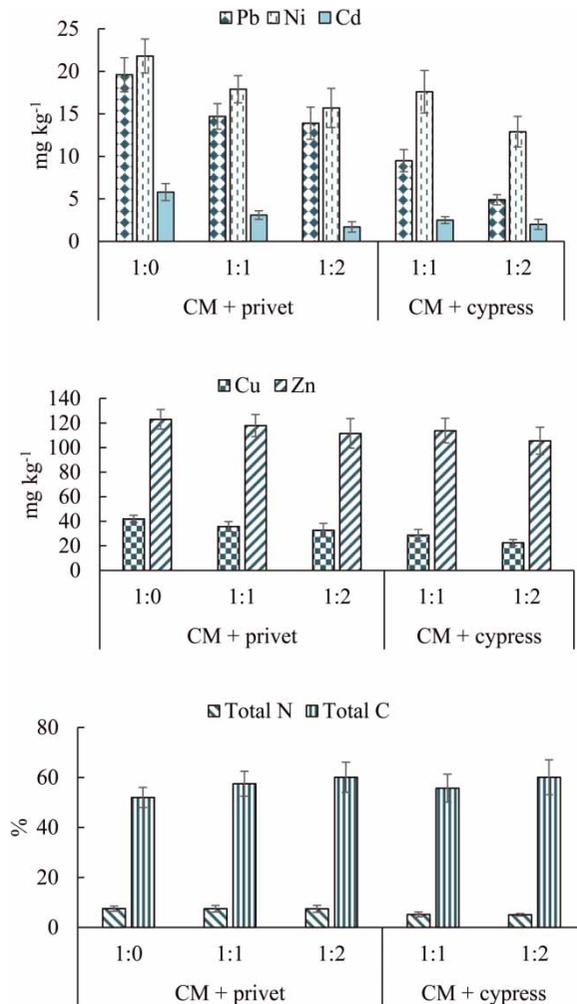


Figure 1 | Chemical properties of CM composted with privet and cypress plant residues. For this and subsequent figures, 1:0, 1:1 and 1:2 indicate the ratios of manure mixture with privet and cypress residues.

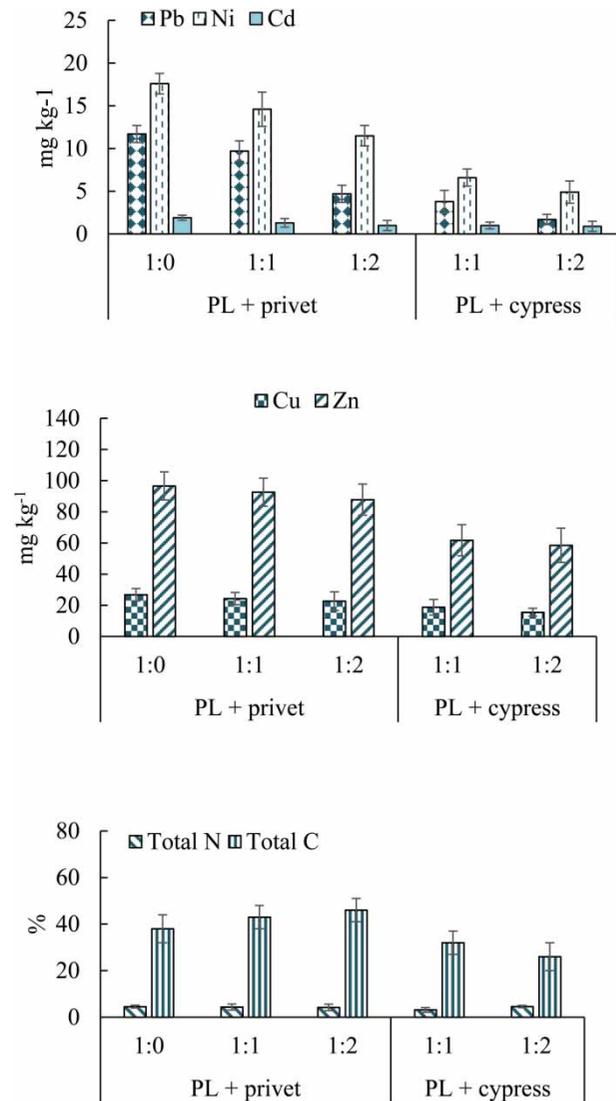


Figure 2 | Chemical properties of PL composted with privet and cypress plant residues.

thinned to 20 seedlings per pot. A basal dose of nitrogen and phosphorus at the rate of 100 kg ha⁻¹ in the form of urea and diammonium phosphate was applied to boost the initial plant growth. Experimental setup for the pot experiment consisted of the amended treatments as detailed above. The experiment was a factorial combination of 2 × 2 × 3 × 2 (two manure types, two types of plant residues, three mixing ratios and two application rates) units. It was arranged into a randomized complete block design with three replications. Irrigation was applied according to the field capacity. The field capacity of the soil was measured based on the water weight held in the sample versus the dry weight of the soil sample. After 8 weeks, vegetable

plants were harvested, washed with distilled water and dried at 65 °C in an oven for about 48 h to determine dry biomass. Milled shoot samples of plants weighing 0.5 g were digested within a mixture (1:3) of per chloric (HClO₄) and nitric (HNO₃) acids for the determination of total concentrations of trace elements (Miller 1998). TM contents in the shoots were determined using the AAS. Biological accumulation coefficient (BAC) was calculated as the ratio of TM in shoots to that in soil (Yoon *et al.* 2006). The uptake of metal ion plant and their transfer factor from soil to plant is determined by the BAC.

Data analyses

Data were statistically analyzed using the Stat-view software (SAS 1999). The level of significance among treatments was determined using an analysis of variance. A separation of means was done using a least significant difference (LSD) at $P < 0.05$. Regression equations and determinant (R^2) explaining the relationship of TM concentrations in soils to the TM uptake by plants were determined.

RESULTS AND DISCUSSION

Soil incubation

Soil samples contained higher concentrations of TM due to long-term wastewater irrigation (Table 1). Extractable TM concentrations in the soil varied as $Pb > Ni > Cu > Cd > Zn$. Results showed that the application of composted material to soil reduced the extractability of TM depending upon the type and ratio of composted manure applied

(Table 2). TM concentration in soils reduced significantly as compost application rates increased and decreased as the amount of privet and cypress wastes in the compost increased. Mixing of soil with manure containing cypress residues reduced TM concentrations more than the composted material containing privet residues. PL combined with plant residues was found more effective in mitigating the concentrations of TM in soil than CM treatments.

Lead (Pb)

Soil samples treated with manure apparently reduced the concentration of Pb in the soil extract. Both CM and PM co-composted with cypress reduced Pb concentration in the soil extract when compared with manure + privet residues. At an application rate of 10 t ha^{-1} , the composted CM + privet at the ratio of 1:2 reduced Pb by 12.5% as compared to CM (1:0), i.e., without plant residues. The soil treated with composted CM along with privet at the ratio of 1:2 obviously reduced Pb concentration by 21% than control soil. It was noticed that the composted CM and PM combined with

Table 2 | Extractable heavy metals (mg kg^{-1}) in the contaminated soil amended with CM and PL composted with plant residues

Manure/application rate	Plant residues	Manure mixture	Pb	Ni	Cu	Cd	Zn	pH	EC ($\mu\text{S m}^{-1}$)
Control		0.0	27.2	7.2	8.5	2.8	2.41	8.10	636.8
CM 10 t ha^{-1}	Privet	1:0	24.2	6.9	6.5	2.3	1.93	7.15	619.2
		1:1	21.5	6.6	5.0	1.9	1.72	7.35	623.6
		1:2	21.3	5.7	3.9	1.1	1.15	7.55	626.5
	Cypress	1:1	22.9	5.8	3.6	1.5	1.85	7.26	625.5
		1:2	19.7	4.8	3.2	0.9	1.72	7.45	629.0
PL 10 t ha^{-1}	Privet	1:0	15.5	5.9	4.0	1.5	1.38	6.73	593.0
		1:1	14.4	5.3	3.6	1.4	1.19	6.77	595.5
		1:2	12.7	3.5	2.9	1.0	0.94	6.85	600.6
	Cypress	1:1	14.6	4.7	3.8	1.4	0.86	6.82	597.5
		1:2	11.2	4.0	2.4	1.2	0.70	6.86	606.2
CM 20 t ha^{-1}	Privet	1:0	17.5	5.5	3.6	0.8	0.60	7.35	839.2
		1:1	15.4	5.3	3.2	0.7	0.56	7.65	842.5
		1:2	14.5	4.8	2.8	0.6	0.57	7.85	847.1
	Cypress	1:1	14.4	4.9	2.2	0.5	0.65	7.80	840.5
		1:2	11.5	4.2	1.8	0.5	0.50	7.90	844.0
PL 20 t ha^{-1}	Privet	1:0	9.8	4.8	1.6	0.5	0.22	7.15	810.0
		1:1	8.1	4.6	1.1	0.4	0.15	7.41	817.0
		1:2	6.9	3.8	1.1	0.4	0.11	7.45	823.1
	Cypress	1:1	9.2	4.3	0.9	0.3	0.16	7.33	815.5
		1:2	7.8	3.8	0.7	0.3	0.15	7.55	820.0
		LSD (0.05)		0.9	0.3	0.1	0.1	0.05	0.2

cypress reduced Pb concentration more than privet addition. At 20 t ha^{-1} , CM composted with cypress (1:2) reduced Pb by 34.2% than composted CM (1:0). The results indicated that composting of plant residues with animal manure decreased the extractability of TM from polluted soils. Shazia *et al.* (2016) reported a reduced availability of TM from polluted soils after amendment with manure. Brown *et al.* (2003) reported the immobilization of Pb concentration in soil due to the application of biosolid compost. The use of additional organic matter in soils decreased the bioavailability of TM and associated TM fractions with organic matter, oxides of metal and carbonates (Walker *et al.* 2004).

Nickel (Ni)

Significant changes in the Ni concentration of soil samples applied with composted CM and PM were observed (Table 2). A higher concentration of Ni was found (6.9 mg kg^{-1}) in soil treated with CM samples without plant residues. Nickel concentration apparently decreased due to the addition of manure mixture with plant residues. For instance, composted CM with privet residues at the application of 10 t ha^{-1} showed the Ni concentration of 6.9, 6.6 and 5.7 mg kg^{-1} at the ratio of 1:0, 1:1 and 1:2, respectively. Nickel concentrations were 5.8 and 4.8 mg kg^{-1} in the soil treated with CM + cypress residues at the ratio of 1:1 and 1:2, respectively. Increasing the manure application rate also reduced more Ni concentration from the soil. Composted manure with plant waste relatively decreased the release of Ni than manure without plant waste. It has been reported that organic matter after a composting process supported binding sites in soil, which reduced TM uptake by plants (Silveira *et al.* 2003). Singh *et al.* (2015) reported a reduced availability of heavy metals to plants after the application of cattle manure mixed with rice husk. The mobility of TM decreased in the composted manure than fresh manure, and manure application beneficially reduced the TM pollution in soils (Shazia *et al.* 2016).

Copper (Cu)

The concentration of Cu reduced in the amended soil according to the manure application (Table 2). Increasing the application rate of manure reduced more Cu concentration in the soil. The concentrations of Cu in soil treated

with CM + privet residues were 6.5, 5.0 and 3.9 mg kg^{-1} in 1:0, 1:1 and 1:2 ratios, respectively, at 10 t ha^{-1} . The decreased amount of extractable Cu due to the increasing ratio of plant residues was partially linked to the variations in the organic matter content of the soil. The release of Cu in a lower amount from the manure-treated soil might be related to the humification process of organic matter, which may generate stabilized complexes of Cu with humic substances (McLaren & Clucas 2001). Poultry manure and other additional manure had been reported for the Cu optimization in the contaminated soil (Thomas & Dauda 2015). The release of phosphate, carbonates and other salts after the application of composted manure may transform into metal insoluble compounds and decreased metal solubility (Walker *et al.* 2003).

Cadmium (Cd)

Changes in the extractable Cd were observed when the soil was treated with CM and PL composted with or without plant residues (Table 2). Higher Cd contents were found in the soil amended with CM and PL without plant waste (1:0). The composted material with a higher ratio of plant residues reduced Cd concentration in polluted soils. Cadmium concentration reduced from 1.5 to 1.0 mg kg^{-1} after soil treatment with PL + cypress (1:2) at the application rate of 10 t ha^{-1} . The treatment of PL + cypress (1:2 mixture) reduced Cd concentration from 0.8 to 0.6 mg kg^{-1} with the application rate of 20 t ha^{-1} . The permissible limit of Cd in soil was reported 5 mg kg^{-1} (Dudka *et al.* 1994). Zobia *et al.* (2018) reported that the addition of plant residues along with the animal manure reduced the extractability of metallic elements in soils. Lower TM solubility in soil treated with manure compost was due to the organic matter humification and soil pH (Gupta & Sinha 2007). Manured soil enhanced the organic matter content, which may help for the attachment of metal ions and decrease their bioavailability (Liu *et al.* 2009). Biosolid addition formed binding sites in soils and reduced the uptake of TM in plants (Silveira *et al.* 2003).

Zinc (Zn)

Reduction in Zn concentration was observed in the soil after the addition of manure (Table 2). In other words, composted

manure with privet and cypress residues immobilized Zn in the soils. Zinc concentration in the soil decreased by 42.1% and 10.5% when treated with CM + privet (1:2) and CM + cypress residues, respectively, at 10 t ha⁻¹ than CM without privet residues (1:0). A reduced availability of TM in the soil treated with composted manure was reported (Irshad *et al.* 2014). Bast *et al.* (2005) reported that poultry manure contained TM sorbents capable of reducing TM solubility and enhancing immobility in the soil. The availability of TM in the soil was affected by the amount and the quality of organic matter which may interact with the TM, forming complexes and chelates of varying stability (Leita *et al.* 1999).

pH and EC

The pH of the soil was higher with composted manure added with plant residues (Table 2). pH values of soil were higher in cypress + CM/PL treatments than privet + manure mixtures. Overall, the pH values of CM containing soil were higher than the PM-amended soil. The PL + privet compost amended soil showed pH that ranged from 6.73 to 6.85, while pH values of soil were 6.82 and 6.86 after amendments with 1:1 and 1:2 mixture of PL + cypress residues. It showed that the pH of the soil slightly increased due to the addition of composted CM with plant residues. Soil higher pH was reported after the application of composted animal manures (Scharenbroch 2009). Loper *et al.* (2010) also reported soil lower pH after compost amendment. Incubating the soil with different animal manures resulted an increased in soil pH (Roy & Kashem 2014).

The EC of soil enhanced with a higher application rate of composted manure (Table 2). The result showed that the soil treated with PL compost having a lower EC value as compared to CM compost. EC values of soil were higher after amendment with composted manure with plant residues. Cypress-containing manure enhanced EC values of the soil more than privet-containing manure. The higher application rate of compost to the polluted soil indicated higher EC values. Increasing the application rate of animal manure gave a higher EC of the soil (Dikinya & Mufwanzala 2010). Greater EC values were reported in manured soils by Loper *et al.* (2010) and Wolka & Melaku (2015).

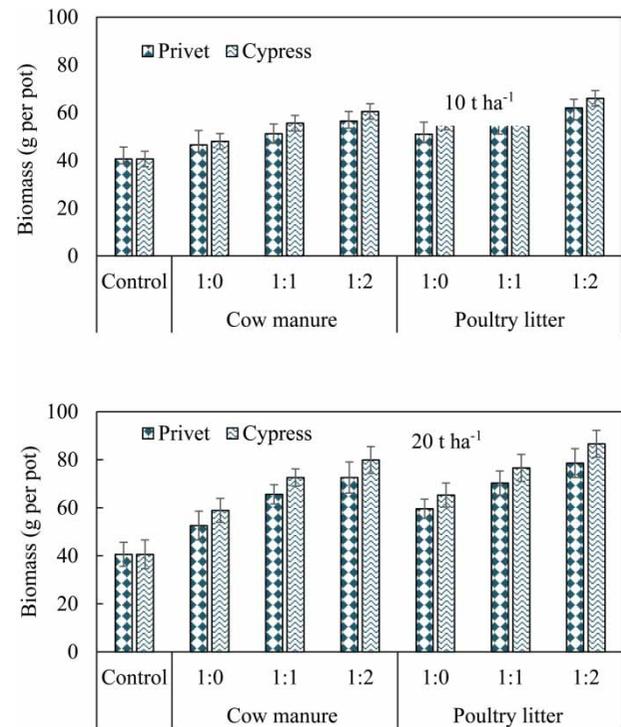


Figure 3 | Fenugreek dry biomass as affected by the application of composted CM and PL in the contaminated soil.

Plant growth and TM concentration

The application of composted manure significantly ($P < 0.05$) increased fenugreek biomass (Figure 3). Polluted soils amended with composted CM and PL enhanced biomass production. Among the treatments, the highest biomass of shoots was obtained with manure composted with plant residues and the lowest biomass was obtained in control soil. The shoot biomass of fenugreek increased more under PL amendment as compared to CM. The superior biomass yield after treatment with composted manure could possibly be due to the appropriate bioavailability of major plant nutrients (Shazia *et al.* 2016). The addition of composted manure with a higher application rate in the polluted soil decreased the uptake of TM from the soil by fenugreek. The concentration of TM in the shoots varied in the order of Pb > Ni > Zn > Cu > Cd (Figures 4–8).

The variations of TM in fenugreek shoots were directly related to their concentrations in the amended soils (Figures 4 and 5). In control soil (without manure addition),

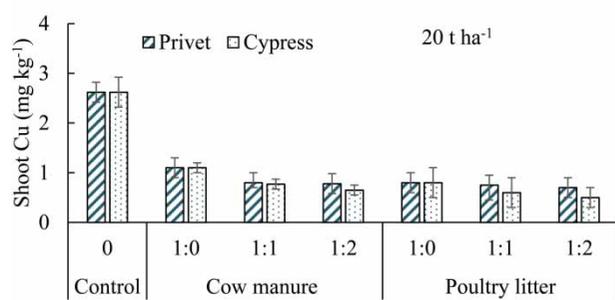
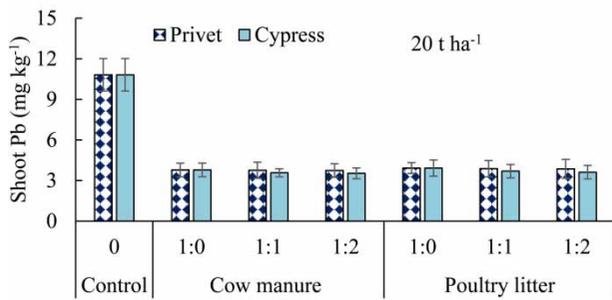
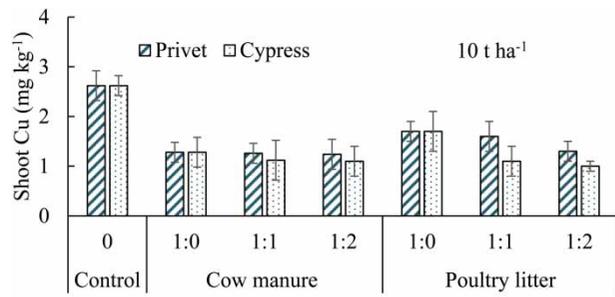
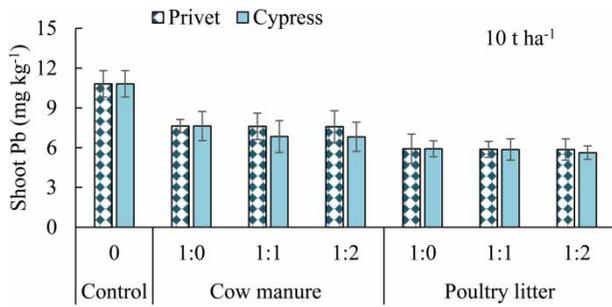


Figure 4 | Lead concentrations in the shoots of fenugreek as affected by composted CM and PL application.

Figure 6 | Copper concentrations in the shoots of fenugreek as affected by composted CM and PL application.

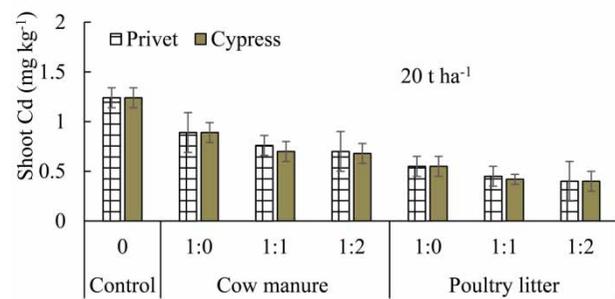
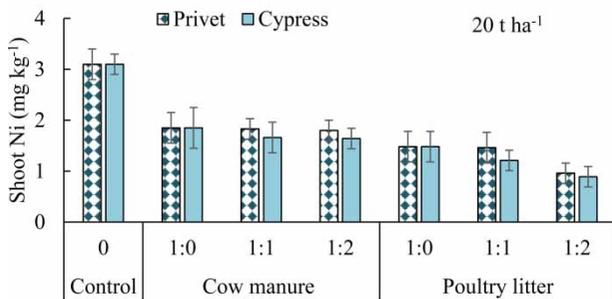
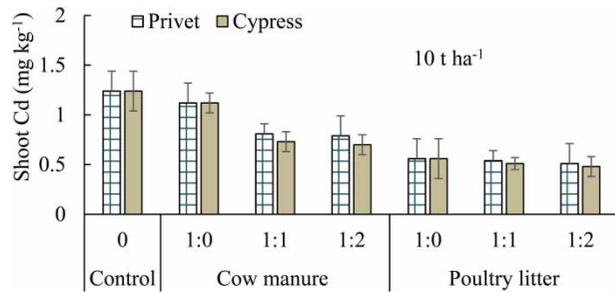
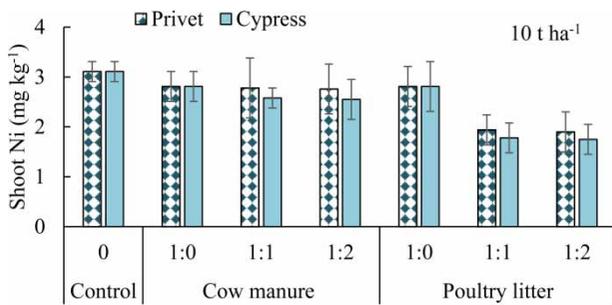


Figure 5 | Nickel concentrations in the shoots of fenugreek as affected by composted CM and PL application.

Figure 7 | Cadmium concentrations in the shoots of fenugreek as affected by composted CM and PL application.

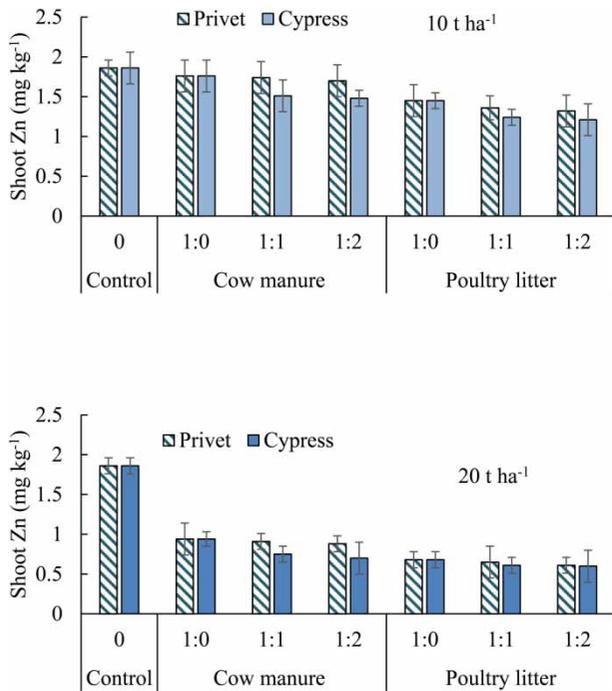


Figure 8 | Zinc concentrations in the shoots of fenugreek as affected by composted CM and PL application.

the concentration of Pb was 10.8 mg kg^{-1} in shoots and reduced to 7.6 mg kg^{-1} when the soil was mixed with the composted CM (at 10 t ha^{-1}). The changes in the availability of TM were sufficiently related to the alterations of these elements in the manure-amended soil (Figures 9 and 10). The development of complexes between the organic matter and Pb may reduce the availability of Pb from the soil with additional manure. Organic amendments with high pH may further reduce the solubility of Pb (Albuquerque *et al.* 2011).

Nickel concentrations in the plant shoots varied with additional manure ratios of $1:0 > 1:1 > 1:2$ (Figure 5). Nickel concentration was higher in shoots with the manure-amended soil as compared to the unamended soil. The concentration of Ni reduced by 9.6% in the shoots of fenugreek with composted CM (1:0) than untreated soil. It was reported that a higher concentration of humic acid and fulvic acid in compost was capable of binding metals (Forja *et al.* 2017).

The contents of Cu in shoots were relatively altered like other TM with additional manure (Figure 6). The combination of CM/PM with cypress residues reduced more Cu content in the shoots than privet waste. The level of

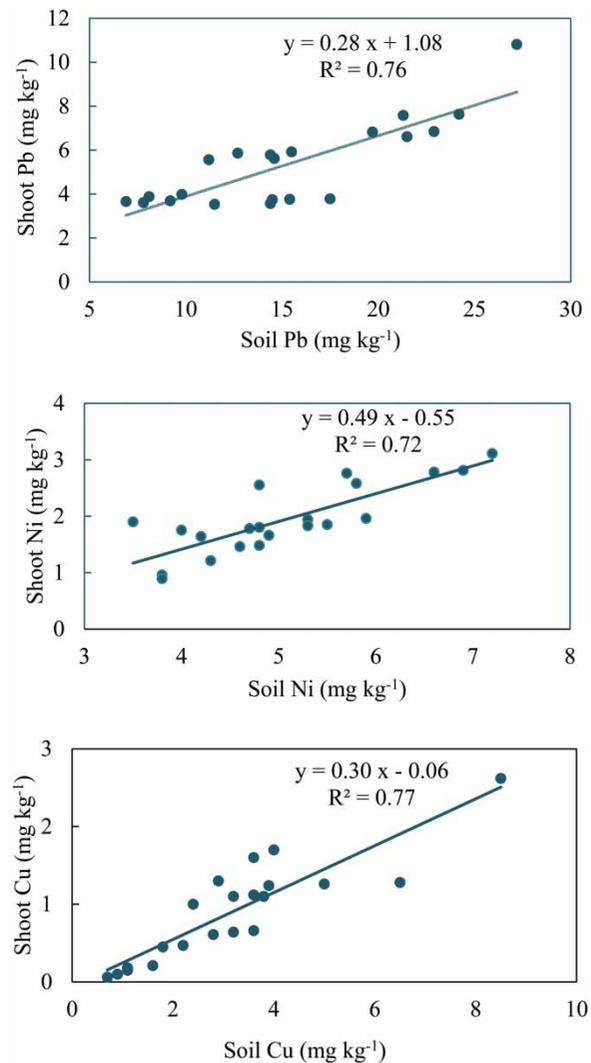


Figure 9 | Relationship of Pb, Ni and Cu in fenugreek shoots versus concentrations of these heavy metals in the soil after the addition of manure.

Cu in the shoots had reduced by 23.5% and 41.1% with PL + privet and PL + cypress residues (at 1:2) at 10 t ha^{-1} . The major part of Cu may attach to the stable portion dominated oxides of manganese, iron and stable organic complexes (Senkondo 2014). The greater affinity of Cu to the compost matrices may lead to a lower available fraction of Cu (Tella *et al.* 2016).

The amount of Cd varied in fenugreek shoots according to the type of manure mixture applied to the soil (Figure 7). Poultry manure was found to be more efficient in reducing the concentration of Cd in the shoots. The lower extraction of metals from the manured soil has been reported

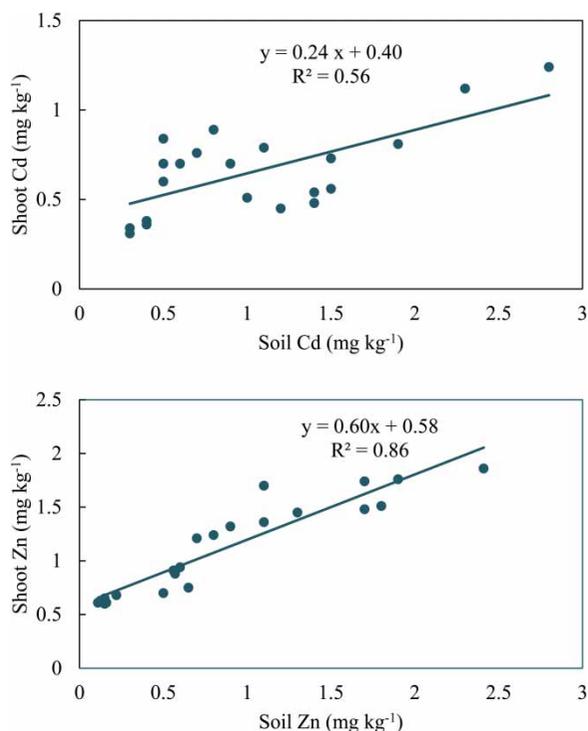


Figure 10 | Relationship of Cd and Zn in fenugreek shoots versus concentrations of these heavy metals in the soil after addition of manure.

elsewhere. Phosphates, organic minerals and aluminum compounds present in organic additives retained more TM and therefore reduced the extractability (Khan *et al.* 2017). The organic matter of the soil changes the solubility and exchangeability of Cd into organic bond fraction and thus decreases the bioavailability (Han-Song *et al.* 2010). The amount of organic matter in the contaminated soil enhanced the accessibility of binding sites (Beesley *et al.* 2014).

The zinc concentration of plant shoots reduced after addition of co-composted CM and PM with plant residues (Figure 8). CM + privet inoculated soil at the ratio of 1:0, 1:1 and 1:2 showed Zn concentrations of 0.94, 0.91 and 0.88 mg kg⁻¹, respectively, while in PL + privet treatments, the Zn concentrations were 0.68, 0.65 and 0.61 mg kg⁻¹ with an application rate of 20 t ha⁻¹. A lower bioavailability of TMs was reported due to the greater content of soil organic matter and CEC (Sanvong & Suppadit 2016).

The BAC for TM also showed that TM accumulation in fenugreek plants was ameliorated with the addition of

Table 3 | BAC for heavy metals contents in fenugreek grown in the contaminated soil amended with composted manure

Manure/application. rate	Plant residues	Manure mixture	Pb	Ni	Cu	Cd	Zn
Control		0:0	0.39	0.43	0.31	0.44	0.77
CM 10 t ha ⁻¹		1:0	0.31	0.40	0.19	0.48	0.92
	Privet	1:1	0.35	0.42	0.25	0.42	1.02
		1:2	0.35	0.48	0.31	0.71	1.54
		Cypress	1:1	0.29	0.44	0.31	0.48
		1:2	0.34	0.53	0.34	0.77	0.87
	Poultry manure 10 t ha ⁻¹		1:0	0.38	0.33	0.42	0.37
Privet		1:1	0.40	0.36	0.44	0.38	1.23
		1:2	0.46	0.54	0.44	0.51	1.46
		Cypress	1:1	0.38	0.37	0.28	0.34
		1:2	0.49	0.43	0.41	0.37	1.72
CM 20 t ha ⁻¹			1:0	0.22	0.11	0.18	1.11
	Privet	1:1	0.24	0.12	0.20	1.09	1.63
		1:2	0.26	0.12	0.22	1.17	1.54
		Cypress	1:1	0.25	0.12	0.21	1.68
		1:2	0.31	0.14	0.25	1.40	1.40
	Poultry manure 20 t ha ⁻¹		1:0	0.40	0.15	0.13	1.20
Privet		1:1	0.48	0.18	0.16	0.95	4.33
		1:2	0.56	0.14	0.14	0.90	5.55
		Cypress	1:1	0.40	0.13	0.11	1.13
		1:2	0.46	0.11	0.09	1.03	4.00
		LSD (0.05)		0.12	0.02	0.03	0.21

manure after the co-composting process (Table 3). The regression analysis showed that shoot Pb concentration was related to the Pb concentration of soil by the following equations: $y = 0.28x + 1.08$ and $R^2 = 0.76$. Nickel concentration in fenugreek shoots was related to the Ni concentration of soil by the equations: $y = 0.49x - 0.55$ and $R^2 = 0.72$ (Figures 9 and 10). The higher values of R^2 indicated that the shoot concentration of TM was highly influenced by the metal concentrations of soil. The concentrations of TM (Pb, Ni and Cd) in fenugreek shoots were adversely related to the biomass production in the contaminated soil. The biomass yield reduced with

the higher amount of these TM in the shoot tissues (Figure 11).

CONCLUSIONS

The study showed that the addition of manure enhanced fenugreek biomass and reduced TM uptake depending on the treatment of the manure. The TM concentrations in fenugreek shoots decreased after the application of composted CM and PL. TM in the plant shoots differed in the order of $Pb > Ni > Zn > Cu > Cd$. The addition of CM and PL combined with plant residues reduced the extractability of TM from the contaminated soil. The variation of TM in plant tissue was positively associated with their concentrations in soil and adversely related to the biomass production. This study ascertained that the combined use of plant and animal waste in contaminated soils can be a good source of soil improvement of TM in soils and crops.

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REFERENCES

- Abbaslou, H. & Bakhtiari, S. 2017 Phytoremediation potential of heavy metals by two native pasture plants (*Eucalyptus grandis* and *Ailanthus altissima*) assisted with AMF and fibrous minerals in contaminated mining regions. *Pollution* 3 (3), 471–486.
- Abdel-Shafy, H. I. & Mansour, M. S. M. 2018 Phytoremediation for the elimination of metals, pesticides, PAHs, and other Pollutants from wastewater and soil. In: *Phytobiont and Ecosystem Restitution* (V. Kumar, M. Kumar & R. Prasad, eds). Springer, Singapore.
- Albuquerque, J. A., De La Fuente, C. & Bernal, M. P. 2011 Improvement of soil quality after 'alperujo' compost application to two contaminated soils characterised by differing heavy metal solubility. *J. Environ. Manage.* 92 (3), 733–741.
- Alghobar, M. A. & Suresha, S. 2017 Evaluation of metal accumulation in soil and tomatoes irrigated with sewage water from Mysore city, Karnataka, India. *J. Saudi. Soc. Agric. Sci.* 16 (1), 49–59.

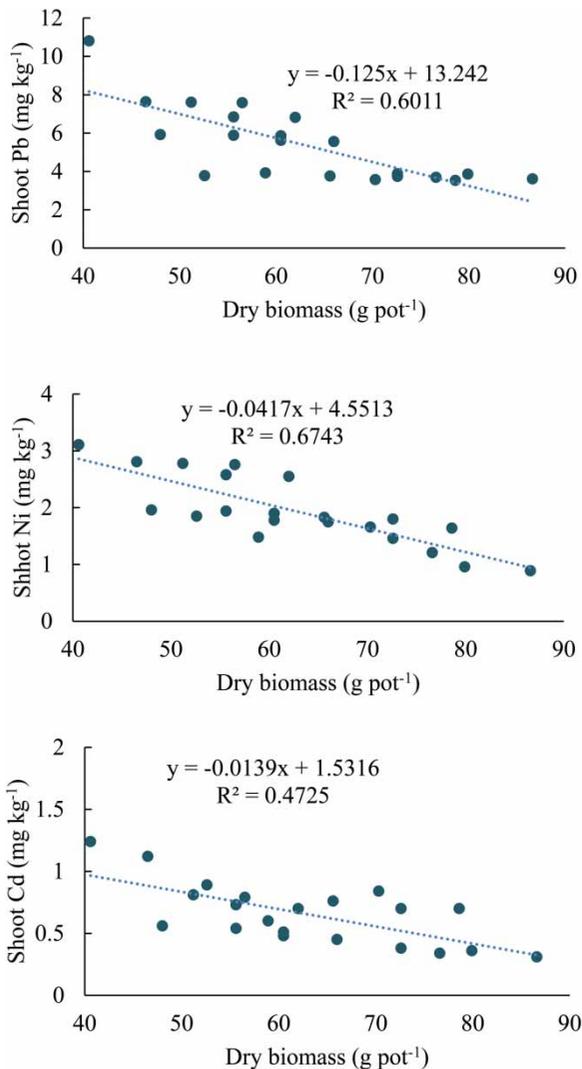


Figure 11 | Relationship of heavy metals in fenugreek shoots versus biomass yield after the addition of manure.

- Amacher, M. C. 1996 Nickel, cadmium, and lead. In: *Methods of Soil Analysis, Part 3: Chemical Methods* (D. L. Spark, ed.). SSSA Book Series No 5, SSSA and ASA, Madison, WI, pp. 739–768.
- Bast, N. T., Ryan, J. A. & Chaney, R. L. 2005 Trace element chemistry in residual-treated soil. *J. Environ. Qual.* **34** (1), 49–63.
- Beesley, L., Inneh, O. S., Norton, G. J., Moreno-Jimenez, E., Pardo, T., Clemente, R. & Dawson, J. J. 2014 Assessing the influence of compost and biochar amendments on the mobility and toxicity of metals and arsenic in a naturally contaminated mine soil. *Environ. Pollut.* **186**, 195–202.
- Brown, S., Chaney, R. L., Hallfrisch, J. & Xue, Q. 2003 Effect of biosolids processing on lead bioavailability in an urban soil. *J. Environ. Qual.* **32** (1), 100–108.
- Bushra, H., Ping, A., Pervez, A. & Faridullah, I. M. 2018 Characterization of heavy metal in soils as affected by long-term irrigation with industrial wastewater. *J. Water Reuse Desal.* **9** (1), 47–56.
- Dikinya, O. & Mufwanzala, N. 2010 Chicken manure-enhanced soil fertility and productivity: effects of application rates. *J. Soil. Sci. Environ. Manage.* **1** (3), 46–54.
- Dudka, S., Piotrowska, M. & Chlopecka, A. 1994 Effect of elevated concentrations of Cd and Zn in soil on spring wheat yield and the metal contents of the plants. *Water Air Soil Pollut.* **76** (3–4), 333–341.
- Forja, R., Asensio, V., Guedes, R. S., Rodríguez-Vila, A., Covelo, E. F. & Marcet, P. 2017 Remediation of soils polluted with inorganic contaminants: role of organic amendments. In: *Enhancing Clean-up of Environmental Pollutants*. Springer, Cham, pp. 313–337.
- Gee, G. W. & Bauder, J. W. 1986 Particle-size analysis. In: *Methods of Soil Analysis, Part 1, Agronomy Series No. 9* (A. Klute, ed.). American Society of Agronomy, Soil Science Society of America, Inc., Madison, WI, USA, pp. 383–441.
- Gupta, A. K. & Sinha, S. 2007 Phytoextraction capacity of the plants growing on tannery sludge dumping sites. *Bioresour. Technol.* **98** (9), 1788–1794.
- Han-Song, C. H. E. N., Huang, Q. Y., Li-Na, L. I. U., Peng, C. A. I., Liang, W. & Ming, L. I. 2010 Poultry manure compost alleviates the phytotoxicity of soil cadmium: influence on growth of pakchoi (*Brassica chinensis* L.). *Pedosph.* **20** (1), 63–70.
- Irshad, M., Gul, S., Eneji, A. E., Anwar, Z. & Ashraf, M. 2014 Extraction of heavy metals from manure and their bioavailability to spinach (*Spinacia oleracea* L.) after composting. *J. Plant Nutr.* **37** (10), 1661–1675.
- Irshad, M., Naureen, R. & Faridullah, F. 2015 Assessing selected heavy metals in vegetables and soils irrigated with wastewater at Haripur, Pakistan. *Minerva Biotecnol.* **27**, 99–105.
- Kalavrouziotis, I. K., Kokkinos, P., Oron, G., Fatone, F., Bolzonella, D., Vatyliotou, M., Fatta-Kassinou, D., Koukoulakis, P. H. & Varnavas, S. P. 2015 Current status in wastewater treatment, reuse and research in some Mediterranean countries. *Desal. Water Treat.* **53** (8), 2015–2030.
- Khan, M. A., Khan, S., Khan, A. & Alam, M. 2017 Soil contamination with cadmium, consequences and remediation using organic amendments. *Sci. Total Environ.* **601**, 1591–1605.
- Leita, L., De Nobili, M., Mondini, C., Muhlbachova, G., Marchiol, L., Bragato, G. & Contin, M. 1999 Influence of inorganic and organic fertilization on soil microbial biomass, metabolic quotient and heavy metal bioavailability. *Biol. Fert. Soils* **28**, 371–376.
- Liu, L., Chen, H., Cai, P., Liang, W. & Huang, Q. 2009 Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. *J. Hazard. Mater.* **163** (2–3), 563–567.
- Liu, S. H., Zeng, G. M., Niu, Q. Y., Liu, Y., Zhou, L., Jiang, L. H. & Cheng, M. 2017 Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: a mini review. *Bioresour. Technol.* **224**, 25–33.
- Loper, S., Shober, A. L., Wiese, C., Denny, G. C., Stanley, C. D. & Gilman, E. F. 2010 Organic soil amendment and tillage affect soil quality and plant performance in simulated residential landscapes. *HortScience* **45** (10), 1522–1528.
- Majeed, S., Rashid, S., Qadir, A., Mackay, C. & Hayat, F. 2018 Spatial patterns of pollutants in water of metropolitan drain in Lahore, Pakistan, using multivariate statistical techniques. *Environ. Monitor. Assess.* **190** (3), 128.
- McLaren, R. G. & Clucas, L. M. 2001 Fractionation of copper, nickel, and zinc in metal-spiked sewage sludge. *J. Environ. Qual.* **30** (6), 1968–1975.
- Miller, R. O. 1998 Nitric-perchloric acid wet digestion in an open vessel. In: *Handbook of Reference Methods for Plant Analysis* (Y. Kalra, ed.). CRC Press, Washington, DC.
- Murtaza, G., Usman, Y., Niazi, N. K., Usman, M. & Hussain, T. 2017 Bioaccumulation of potentially toxic elements in cereal and legume crops: a review. *CLEAN–Soil Air Water* **45** (12), 1700548.
- Nelson, D. W. & Sommers, L. E. 1982 Total carbon, organic carbon and organic matter. In: *Methods of Soil Analysis. Part 2 Chemical and Microbiological Properties* (A. L. Page, R. H. Miller & D. R. Keeney, eds). American Society of Agronomy, Soil Science Society of America, Madison, WI, pp. 539–579.
- Pedrero, F., Kalavrouziotis, J., Alarcón, J. J., Koukoulakis, P. & Asano, T. 2010 Use of treated municipal wastewater in irrigated agriculture- review of some practices in Spain and Greece. *Agric. Water Manage.* **97** (9), 1233–1241.
- Radojevic, M. & Bashkin, V. N. 2010 *Practical Environmental Analysis*, 2nd edn. RSC Publishing, UK.
- Rosazlin, A., Fauziah, C. I., Wan Rasidah, K. & Rosenani, A. B. 2010 Leaching of heavy metals (Cu, Mn, Zn, Ni, Pb and As) after six months application of raw and composted recycled paper mill sludge. In: *Proceedings of the 19th World Congress of Soil Science: Soil Solutions for a Changing World*, pp. 1–6.

- Roy, S. & Kashem, M. A. 2014 Effects of organic manures in changes of some soil properties at different incubation periods. *Open J. Soil. Sci.* **4** (3), Article ID: 43613, 6 pages.
- Sarvong, C. & Suppadit, T. 2016 The use of soybean plants to evaluate the efficacy of broiler litter biochar as a treatment for cadmium contaminated soil. *Tropic. Agric.* **93**, 1–19.
- Sarwar, N., Imran, M., Shaheen, M. R., Ishaque, W., Kamran, M. A., Matloob, A. & Hussain, S. 2017 Phytoremediation strategies for soils contaminated with heavy metals: modifications and future perspectives. *Chemosphere* **171**, 710–721.
- SAS. 1999 In: *Statistical Analysis System User's Guide* (A. A. Ray, ed.). SAS Institute, Inc., Cary, NC.
- Satashiya, K. F. 2017 *Phytoremediation Potential of Flowering Plants for Cd, Ni and Pb Contaminated Soils*. Doctoral Dissertation, Soil Science and Agricultural Chemistry, NM College of Agriculture, Navsari Agricultural University, Navsari.
- Scharenbroch, B. C. 2009 Organic materials and impacts on soil, tree, and environmental properties. *J. Arboric. Urban Forest.* **35** (5), 221–231.
- Senkondo, Y. H. 2014 *Mobility and Plant Availability of Copper Contamination in Coffee Plantations in Arusha and Kilimanjaro, Tanzania*. Doctoral Dissertation, Ghent University, Belgium.
- Shazia, G., Naz, A., Khan, A., Nisa, S. & Irshad, M. 2016 Phytoavailability and leachability of heavy metals from contaminated soil treated with composted livestock manure. *Soil Sed. Contam. Inter. J.* **25** (2), 181–194.
- Silveira, M. L. A., Alleoni, L. R. F. & Guilherme, L. R. G. 2003 Biosolids and heavy metals in soils. *Scien. Agric.* **60** (4), 793–806.
- Singh, W. R., Pankaj, S. K. & Kalamdhad, A. S. 2015 Reduction of bioavailability and leachability of heavy metals during agitated pile composting of *Salvinia natans* weed of Loktak lake. *Inter. J. Recycl. Org. Waste Agric.* **4** (2), 143–156.
- Tella, M., Bravin, M. N., Thuriès, L., Cazeviell, P., Chevassus-Rosset, C., Collin, B. & Doelsch, E. 2016 Increased zinc and copper availability in organic waste amended soil potentially involving distinct release mechanisms. *Environ. Pollut.* **212**, 299–306.
- Theobald, T. 2017 *Regional Phosphorus Management in Berlin-Brandenburg*. Lebenswissenschaftlichen Fakultät der Humboldt-Universität zu Berlin, Germany.
- Thomas, E. Y. & Dauda, S. O. 2015 Comparative effects of compost and poultry manure on bioavailability of Pb and Cu and their uptake by maize (*Zea mays* L.). *New York Sci. J.* **8** (7), 23–34.
- Ullah, A., Heng, S., Munis, M. F. H., Fahad, S. & Yang, X. 2015 Phytoremediation of heavy metals assisted by plant growth promoting (PGP) bacteria: a review. *Environ. Exp. Bot.* **117**, 28–40.
- Walker, D. J., Clemente, R., Roig, A. & Bernal, M. P. 2003 The effects of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. *Environ. Pollut.* **122** (2), 303–312.
- Walker, D. J., Clemente, R. & Bernal, M. P. 2004 Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere* **57** (3), 215–224.
- Wolka, K. & Melaku, B. 2015 Exploring selected plant nutrient in compost prepared from food waste and cattle manure and its effect on soil properties and maize yield at Wondo Genet, Ethiopia. *Environ. Syst. Res.* **4** (1), 9–12.
- Xiong, W., Guo, S., Jousset, A., Zhao, Q., Wu, H., Li, R. & Shen, Q. 2017 Bio-fertilizer application induces soil suppressiveness against *Fusarium* wilt disease by reshaping the soil microbiome. *Soil Biol. Biochem.* **114**, 238–247.
- Yoon, J., Cao, X., Zhou, Q. & Ma, L. Q. 2006 Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. *Sci. Total Environ.* **368**, 456–464.
- Zobia, A., Irshad, M., Ping, A., Hafeez, F. & Yang, S. 2018 Water extractable plant nutrients in soils amended with cow manure co-composted with maple tree residues. *Int. J. Agric. Biol. Eng.* **11** (5), 167–173.

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