Biological Forum – An International Journal 13(2): 336-344(2021)

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Effect of Modified Steel Slag Application as Soil Amendment on Soil Quality and Spinach Yield in a Copper Contaminated Vertisol

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(Received 07 April 2021, Accepted 12 June, 2021)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: In recent years, soil pollution caused by heavy metals has emerged as a global issue. Several industrial by-products like red mud, flyash and steel slag have been potentially used as soil amendments for remediation of contaminated soil. A study was conducted under controlled green house condition to evaluate the effects of modified steel slag (acid modified steel slag, ACMSS and spent wash modified steel slag, SWMSS) application on soil quality and spinach yield in a Cu contaminated Vertisol. The dry matter yield of spinach leaf and root was recorded during 2015-16 and 2016-17 and the post harvest soil sample was analyzed for bioavailable Cu content. The results revealed that steel slag (SS) or modified steel slag application showed significant effect on soil properties over control. Among the treatments, SWMSS and spent wash (SW) application resulted in significant increase in soil organic carbon (SOC) over control. DTPA extractable Cu was significantly reduced by 28.8%, 21.9% and 9.8% in the soil amended with ACMSS, SS and SWMSS, respectively. The alkaline phosphatase activity (70.01 µg PNP g^{-1} soil h^{-1}), dehydrogenase activity (4.61 µg TPF^{-1} g^{-1} hr^{-1}) and mean dry matter yield of spinach leaf (8.78 g pot^{-1}) and root (4.34 g pot^{-1}) was highest in the SWMSS amended soil. To conclude from the present study, ACMSS has greater potential in reducing the mobility of heavy metal in soil and its subsequent transfer to spinach leaf.

Keywords: Modified steel slag, Spent wash, Spinach crop, Copper contaminated soil, Phosphatase activity, Dehydrogenase activity.

INTRODUCTION

Increasing pressure on land resources caused by industrial and urban activities across the globe has resulted in various types of soil degradation. Every year due to inappropriate disposal of hazardous materials, or poor land management systems, soil resources are getting damaged and in severe cases soil becomes unproductive. In India, agricultural land area occupies nearly two-third of the geographical area and the greater part of it is experiencing various kind of degradation stresses. Among the various soil degradation, soil pollution is one of the most sensitive environmental issues faced across the globe. Soil pollution may be caused due to presence of organic and inorganic pollutants beyond the baseline concentration in the soil resource. Soil pollution caused by heavy metals are vital because of its perseverance and toxicity to almost all kind of organisms (Khan *et al.*, 2008; Zhang *et al*., 2010). In general, heavy metals are transported to various plant parts through root absorption from the contaminated soil, which eventually enters to human via food chain contamination and poses greater risk to human health. Lead, copper, zinc, arsenic, cadmium, chromium, cobalt, nickel, selenium, silver, and mercury are the prevalent heavy metals mostly in soil. Among these potentially hazardous heavy metals, the presence of copper in soil beyond the baseline concentration poses a greater risk to ecosystem service. Emissions from major industries and their associated activities like pesticides, fertilizers, petroleum-refinery, metallurgy, electroplating, copper mining, explosive, paints and dyes resulted in increased concentration of copper levels in the surrounding environment. Copper mainly from mining and smelting activities is one among the heavy metals which is highly toxic to soil biota and plant (Tang *et al.,* 2006). Elevated levels of Cu in the environment have generated attention of environmentalist because it poses serious threat to soil micro-organisms, fauna, and human health (Shrivastava 2009). High levels of copper in soil due to various anthropogenic activities are toxic to soil microorganisms and enzyme activities and can create serious ecological problems.

In India, several researchers have reported that in India most of the cities nearby to the industrial areas resulted in soil pollution and the subsequently caused deterioration in soil quality which ultimately leads to crop diversification loss. Over the years, crop yield was reduced by 15 to 25% as a result of soil pollution and total cropped area was also decreased significantly. Hence, a greater attention is necessary to restrict heavy metals reaching to soil (source level) and also to remediate heavy metal contaminated soil (sink level). Historically, landfill as a remediation techniques to excavate the hazardous materials and dumping to abandon place is considered environmentally unsafe and economically impractical (Salt *et al.,* 1995). Heavy metals stabilization by processes of adsorption, binding or co-precipitation through addition of soil amendments in a contaminated soil has been widely accepted as a potential measures to remediate contaminated sites (Kumpiene *et al*., 2008; Clemente and Bernal, 2006; Coumar *et al.* 2016). Among the various amendments used for contaminants stabilization in soil, organic matter rich materials likebiosolids, biochar and composts or inorganic waste materials or by products from industry like slag, press mud and fly ash have proved to be successful in reducing the heavy metal mobility in multi-element contaminated soils (Clemente and Bernal, 2006; Coumar *et al*., 2016a).

Various industrial inorganic by products like red mud, flyash, steel slag, etc have been projected as soil amendments because of their low cost and environmental safety (Lombi *et al.*, 2002; Lee *et al.*, 2011). During the steel refining process, steel slag is generated in huge quantities which are usually used in road pavement, as a building material and for cement production. Calcium oxides, calcium silicates, calcium aluminates, iron oxide, magnesium oxide, and other silicates and oxides are the major compositions of steel slag (Kim *et al*., 2008; Cobo *et al.*, 2009). Also a silicon rich alkaline by-product of steel industry, steel slag has been widely used as fertilizer (Wang and Cai, 2006), acid liming material (Bhat *et al*., 2010). Due to its porosity, large surface area, and good absorptivity, the steel slag has been recommended for remediation of heavy metal pollution in acid soil (Gu *et al*., 2011).

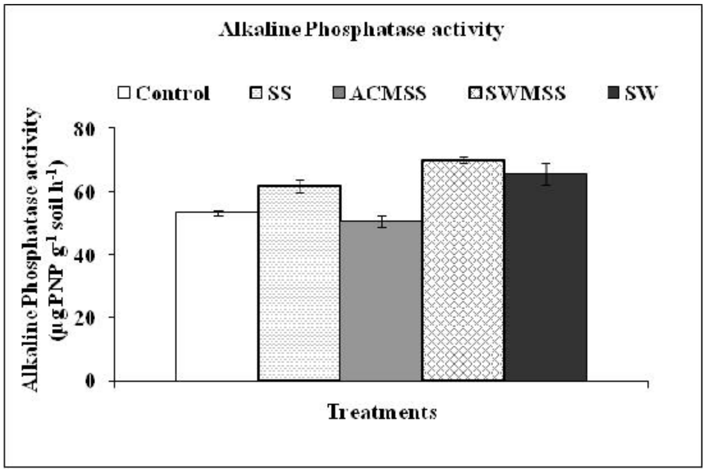
Some studies have shown that steel slag is a good adsorbent of heavy metals, mostly via precipitation and adsorption of the metal oxide on the slag surface (Gupta *et al.,* 2006; Kim *et al.,* 2008). It has also been widely reported that application of steel slag on heavy metal contaminated acid soil results in soil pH alteration thereby reduces heavy metal mobility in soil. Further, silica which is a major constituent of slag serves as an adsorption site for heavy metal thereby reduces its mobility in soil and thus the translocation of heavy metal to crop plant is reduced. Therefore, more than a pH effect may be involved in the reduction of metal bioavailability. However the dominant mechanisms of action of these materials have not been conclusively established. Further, remediation of heavy metal contaminated through slag application was so far reported in acid soil and still there is a paucity of data on remediation of contaminated black soil (alkaline soil) by steel slag application. In view of this, the present investigation aims to study the effect of modified steel slag on soil microbial activity and spinach yield in a copper contaminated Vertisol.

MATERIALS AND METHODS

A. Experimental site and materials used

Greenhouse experiment was conducted at ICAR-Indian Institute of Soil Science, Bhopal under controlled condition to evaluate the effects of modified steel slag application on soil microbial activity and spinach yield in a Cu contaminated Vertisol. Steel slag sample was ground into a fine powder and the pH and EC being determined in a 1:2.5 slag: water ratio suspension. The chemical composition of the steel slag is analyzed following standard procedure and the result is presented in Table 2. The raw spent wash was collected from M/s Som Distilleries, located at the outskirt of Bhopal, Madhya Pradesh. Nutrient and heavy metal contents were determined after wet digestion in a di- acid mixture (HNO_3: $HClO_4$) in 10: 1 ratio. Micronutrient and heavy metals (Cd, Cr Ni and Pb) were determined in clear digests by ICP-OES and the results were presented in Table 2.

The soil for the experimental purpose was collected from a uncontaminated field (15 cm) of ICAR-IISS farm representing Vertisol (Typic Haplustert). Soil samples were drawn randomly from different locations with the help of an auger and mixed thoroughly to have composite soil sample. Dry roots, grasses and gravels were removed from the air dried soil sample by passing through 2 mm sieve. The processed soil sample was analyzed for A portion of various physico-chemical properties and the results were presented in the Table 1. The results indicate that the soil of experimental site was clayey soil in texture had pH 8.25 and electrical conductivity (EC) 0.22 dSm^{-1}. The soil is medium in soil organic carbon status (0.56%), low in available N (167.0 kg ha^{-1}), medium in P (15.2 kg ha^{-1}) and high in K (428.6 kg ha^{-1}) fertility status. The diethylene triamine pentaacetic acid (DTPA)-extractable heavy metal content was 1.52, 0.003, 0.41, 0.07 and 0.53 mg kg^{-1} for Cu, Cd, Pb, Cr and Ni, respectively (Table 1).



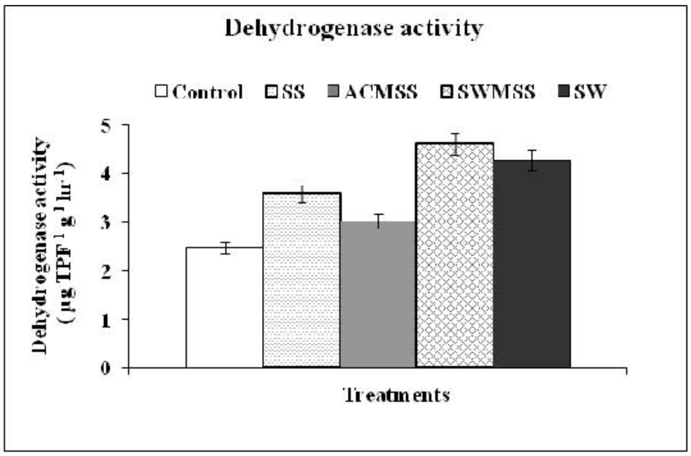


Fig. 1. Effect of modified steel slag application as soil amendment in a copper contaminated soil on soil microbial enzymatic activity at the end of second year (2016-17) after harvest of spinach crop.

Table 1: Physico- chemical Properties of experimental soil.

Parameter	Value	Method/Reference
pH (soil : water 1:2)	**8.25**	Jackson (1973)
EC (soil: water 1:2) (dSm^{-1})	**0.22**	Jackson (1973)
Mechanical analysis Sand (%) Silt (%) Clay (%) Textural Class	 **35.4** **21.9** **42.7** **Clayey Soil**	International pipette Method (Piper, 1967)
Organic carbon (%)	**0.56**	Walkley and Black (1934)
Available nitrogen (kg ha^{-1})	**167.00**	Subbiah and Asija(1956)
Available phosphorus (kg ha^{-1})	**15.2**	Olsen et al. (1954)
Available potassium (kg ha^{-1})	**428.6**	Black (1965)
Available sulphur (mg kg^{-1})	**11.4**	Chesnin and yien (1950)
Total Heavy metals (***DTPA extractable) (ppm) Cu Cd Pb Cr Ni	 **87.70 (***1.52)** **00.10 (0.003)** **28.037 (0.41)** **29.10 (0.07)** **71.04 (0.53)**	Lindsay and Norvell (1978)

Table 2: Chemical composition of steel slag and spent wash.

Parameter	Value	
	Spent wash	Steel slag
pH	4.8	10.44
EC (dSm^{-1})	20.6	0.275
Total organic carbon (%)	2.8	0.5
Total nitrogen (%)	0.17	0.08
Total phosphorus (%)	0.02	0.16
Total potassium (%)	0.95	0.21
Total sulphur (%)	0.32	0.14
Total Heavy metals (ppm)		
Cu	2.9	5
Cd	0.32	ND
Pb	0.22	15
Cr	0.48	57
Ni	0.08	7
Zn	3.4	20

B. Greenhouse experiment and treatment details

Pot culture experiment under greenhouse condition was carried out with spinach as a test crop in a cu contaminated clayey soil of Vertisol. Heavy metal spiking method was followed to artificially contaminate the soil with copper using Cu salts at rate of 300 mg Cu kg^{-1} soil in solution form as $CuSO_4.5H_2O$. The artificially contaminated experimental soil of 5 kg was filled in a wide-mouthed glazed pot of 7 kg capacity. The treatment details for Cu contaminated Vertisol was designed with five treatments as control (no amendments), original steel slag (SS), acid modified steel slag (ACMSS), spent wash modified steel slag (SWMSS) and spent wash alone (SW). Each treatment was replicated thrice and the experiment was conducted in a randomized block design.

Preparation of modified steel slag was done using original steel slag material and treating with 5 N HCl at slag: acid ratio of 1:1. Exact amount of 140 gm of steel slag was weighed in a 1 litre glass beaker and then 140 ml of 5 N of HCl was added to it. After addition of acid, steel slag acid slurry was allowed to remain for thirty minutes with intermittent stirring using glass rod. Similarly, spent wash modified steel slag was prepared using spent wash instead of 5N HCl. The slurry thus prepared represents modified steel slag which was added to each pot (containing 7 kg soil) immediately after the reaction time (half an hour after acid addition). In all the treatment, the steel slag used was 20 gm steel slag kg^{-1} soil. After the addition of slurry addition it was mixed thoroughly with soil. In the SS treatment, original steel slag was added to soil without any acid or spent wash treatment. In the SW treatment, only spent wash added at the rate of 20 ml kg^{-1} soil (equal amount of spent wash that was used as in SWMSS). The potted soil mixed with amendments (SS, ACMSS, SWMSS, and SW) was kept under field capacity for two week prior to spinach sowing.

C. Fertilizer addition, sowing and after care

Basal application of half dose of recommended nitrogen (75 kg N ha^{-1}), entire does of phosphorus (40 kg P_2O_5 ha^{-1}) and potash (40 kg K_2O ha^{-1}) was done before sowing. The remaining half dose of nitrogen was applied twenty days after sowing. Nitrogen, phosphorus and potassium was applied in the form of urea, DAP and potassium chloride, respectively. Irrigation was given at sowing and during crop growth by gradual sprinkling using tap water. To avoid fungal infection, spinach seed (*var. Selection-1*) was treated with Bavistin @ 2g kg^{-1} seed before sowing. Ten healthy seeds of spinach were sown in holes at 2-3 cm depth made equidistantly in a circular fashion in the pots. After germination, the entire seedling was allowed to grow for ten days and then thinned out to maintain five plants in each pot.

D. Biomass harvesting, sample processing and analysis

The spinach crop was sown during September 2015 and 2016. Spinach crop was grown for 60 days for both the years and plants were harvested at two different stages, 1st leaf cutting at 30 days after sowing (DAS) and 2nd cutting at 60 DAS for the year 2015 and 2016. During 2nd cutting (2015 and 2016), roots were also separately collected from the soil. Leaf and roots were washed thoroughly with tap water first to remove adhering soil particles and then with distilled water. Oven dry (at 65°C to constant weight) weights of leaf and root were recorded. The dry matter yield of spinach leaf reported in the result section is the mean of 1st and 2nd cuttings. Oven-dried leaves 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.

The concentrations of Cu in the digested plant sample (1st cutting leaf, 2nd cutting leaf and root) for both the years (2015 and 2016) were analyzed separately using an inductively coupled plasma-optical emission spectrophotometer (Optima DV 2100, PerkinElmer, USA). The result related to Cu content in plant leaf and their uptake reported in the result section was mean value of 1st and 2nd cuttings Cu content and their uptake.

At the end of second year (2016) after spinach crop harvest, soil samples were analyzed for chemical and biological properties. Soil pH and electrical conductivity was measured in a 1:2 soil: water suspension. Soil organic carbon was estimated through wet oxidation method by following Walkley and Black, 1934 method. Alkaline phosphatase and Dehydrogenase activity was determined following the method of Tabatabai (1982) and Casida *et al.*, (1964), respectively. Soil samples were also extracted for bioavailable Cu content using a DTPA extractant (Lindsay and Norvell 1978). The concentrations of Cu in the DTPA extractant were determined using an ICP-OES instrument (Optima DV 2100, PerkinElmer, USA).

E. Statistical analysis

All measurements are mean values of three replicates. Data were subjected to one-way analysis of variance (ANOVA) using SPSS version 9.0 statistical package. The mean values were grouped for comparisons based on least significant differences among them at $p < 0.05$ confidence level.

RESULTS AND DISCUSSION

A. Soil chemical properties and bioavailable fraction of copper content in soil

Application of steel slag (SS) and spent wash modified steel slag (SWMSS) significantly increased the soil pH over unamended soil (control) of Cu contaminated Vertisol (Table 3). On the other hand, soil amended with acid modified steel slag (ACMSS) and spent wash application alone resulted in significant decrease in soil pH over control soil (unamended) in the post harvest soil sample at the end of second year (2016-17) of spinach crop. The soil pH values ranged from 7.48 to 8.62 and significantly lowest in soil amended with ACMSS as compared to unamended soil.

At the end of second year (2016-17) of spinach crop, soil EC was significantly increased over control and ranged from 0.392 to 0.947 dsm^{-1} in a Cu contaminated Vertisol. Significantly higher soil EC was observed in soil amended with ACMSS (0.947, dsm^{-1}) followed by spent SWMSS (0.780 dsm^{-1}), SW (0.671 dsm^{-1}) and SS application (0.519 dsm^{-1}). The SOC values ranged from 0.51 to 0.69%, Cu contaminated Vertisol, respectively (Table 3). Among the treatments, SWMSS and SW application resulted in significant increase in soil organic carbon (SOC) over control. The per cent increase in SOC of soil amended with SW and SWMSS was 32.7% and 30.7%, respectively over control in a Cu contaminated Vertisol (Table 3).

Table 3: Effect of modified steel slag application as soil amendment in a copper contaminated soil on soil parameters at the end of second year (2016-17) after harvest of spinach crop.

Treatment	Soil Parameters						
	pH	EC (dsm^{-1})	SOC (%)	DTPA Cu (mg kg^{-1})	Available N (kg ha^{-1})	Available P (kg ha^{-1})	Available K (kg ha^{-1})
Control	8.25b	0.392e	0.52b	106.31b	213.83cd	15.33c	416.57c
SS	8.62a	0.519d	0.53b	83.01d	219.40c	16.20b	421.30c
ACMSS	7.48d	0.947a	0.51b	75.67e	207.37d	16.42b	506.13b
SWMSS	8.53a	0.780b	0.68a	95.84c	238.30b	18.97a	557.27a
SW	7.83c	0.671c	0.69a	128.44a	250.90a	19.47a	549.93a
SEm(±)	0.089	0.045	0.037	2.847	4.284	0.376	3.634
C.D. (5%)	0.271	0.105	0.059	6.342	9.545	0.838	8.097

Available nitrogen, phosphorus and potassium content in the post harvest soil sample ranged from 207.4 to 250.9 kg ha^{-1}, 15.3 to 19.47 kg ha^{-1} and 416.6 to 557.3 kg ha^{-1}, respectively in the post-harvest soil sample of Cu contaminated Vertisol (Table 3). Soil amended with SWMSS or SW resulted in significant increase in available nitrogen, phosphorus and potassium content of post-harvest samples of Cu contaminated Vertisol over control. On the other hand, soil amended with ACMSS decreased the SOC of the post-harvest sample of Cu contaminated Vertisol.

Application of SS, ACMSS and SWMSS significantly reduced the DTPA extractable Cu over control in a Cu contaminated soil.

The DTPA extractable Cu values ranged from 75.67 to 128.44 mg kg^{-1} in the post-harvest soil sample of Cu contaminated Vertisol. At t he end of second year of spinach crop growth, DTPA extractable Cu was significantly reduced in the soil amended with ACMSS, SS and SWMSS by 28.8%, 21.9% and 9.8%, respectively in the post harvest soil sample.

Improvement in soil properties like pH, EC, cation exchange capacity (CEC) and reduction in heavy metal mobility in soil has been reported following the application alkaline slag material in a contaminated acid soil (Alva and Sumner, 1990). However, our study is in alkaline Vertisol which was artificially contaminated with Cu and used steel slag either untreated (original steel slag) or acid (HCl/spent wash) modified to evaluate its impact on heavy metal mobility in soil, soil properties and crop yield. As the raw spent wash used in our experiment had pH 4.8, we hypothesized that spent wash treated with steel slag may solubilize the Si and other elements like Fe, Ca and Al in similar way as in case of slag treated with mineral acid (HCl). The results from the present study revealed that steel slag or modified steel slag application showed significant effect on soil pH, EC, organic carbon, available nitrogen, phosphorus and potassium over control (unamended soil). 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. Lee *et al.,* (2011) also reported that application of limestone, red-mud and furnace slag increased soil pH and EC significantly.

The silica together with other impurities like Ca, Fe, Al and Mg is released from the original steel slag (Yoo *et al*., 2004) which is also evident from our result that increased extractable Si in the soil amended with acid treated slag was observed over the untreated slag. In addition to Si, other impurities like Fe, Al and Ca might have released which results in precipitation of Cu 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) and thereby the mobility of Cu (DTPA extractable fraction) in the soil amended with ACMSS was reduced considerably over the SS amended soil. Further, DTPA extractable copper in the soil amended with SW was significantly higher than the unamended soil which might be due to presence of substantial amount Cu in the raw spent wash.

B. Soil microbial enzymatic activities

Modified steel slag applications significantly influenced the alkaline phosphatase and dehydrogenase activities in the post harvest soil sample at the end of second year (2016-17) spinach crop (Figure 1). In all the treatments, except ACMSS amended soil, alkaline phosphatase activity was increased significantly over control. The alkaline phosphatase activity was highest in the SWMSS amended soil (70.01 µg PNP g^{-1} soil h^{-1}) followed by SW (65.61 µg PNP g^{-1} soil h^{-1}) and SS amended soil (61.82 µg PNP g^{-1} soil h^{-1}). The dehydrogenase activity was highest in the SWMSS amended soil (4.61 µg TPF^{-1} g^{-1} hr^{-1}) followed by SW (4.27 µg TPF^{-1} g^{-1} hr^{-1}), SS amended soil (3.57 µg TPF^{-1} g^{-1} hr^{-1}) and ACMSS amended soil (3.02 µg TPF^{-1} g^{-1} hr^{-1}). Among the treatments, the alkaline phosphatase and dehydrogenase activity was highest in the soil amended with SWMSS (70.01 µg PNP g^{-1} soil h^{-1} and 4.61 µg TPF^{-1} g^{-1} hr^{-1}) and lowest in the ACMSS(50.58 µg PNP g^{-1} soil h^{-1}). Similarly, the dehydrogenase activity was highest in the soil amended with SWMSS (4.61 µg TPF^{-1} g^{-1} hr^{-1}) and lowest in the control (2.48 µg TPF^{-1} g^{-1} hr^{-1}).

The per cent increase in alkaline phosphatase activity in the soil amended with SS, SW and SWMSS was 15.9, 23.1 and 31.3%, respectively over control in a Cu Vertisol. Similarly, 21.8, 43.9, 72.2 and 85.9% dehydrogenase activity in a Cu contaminated Vertisol were noticed due to application of ACMSS, SS, SW and SWMSS, respectively over control. The result further clearly indicates that the dehydrogenase activity is highly sensitive to Cu stress and amendment (SS, ACMSS, SPMSS and SW) addition as compared to alkaline phosphatase activity. Several authors have reported that due to toxic metals exposure to soil microorganisms, microbial diversity and enzymatic activities in soil has been significantly reduced (Lasat 2002; McGrath *et al*., 2001). Moreover, adverse impact of Cu on phosphatase activities (Todorova and Topalova 2013; Wang *et al*., 2007) and dehydrogenase activities (Xie *et al.*, 2009; Kizilkaya *et al.*, 2004) could be considered as potential indicators for metal toxicity.

C. Dry matter yield of spinach crop

Steel slag and modified slag amendments significantly influenced the dry matter yield of spinach leaf at both the harvest stage and year of cultivation (Table 4). In all the treatments, except HCl treated slag the mean (average of 1^{st} and 2^{nd} cutting) dry matter yield of spinach leaf was increased significantly over control during 2015-16 and 2016-17. The mean dry matter yield of spinach leaf during 2015-16 and 2016-17 was highest in the spent wash modified steel slag (SWMSS) application followed by spent wash (SW) and steel slag (SS) amended soil. The mean dry matter yield of spinach leaf ranged from 3.90 to 8.98 g pot^{-1} and 4.03 to 8.78 g pot^{-1} during 2015-16 and 2016-17, respectively. Among the treatments, the mean dry matter yield of spinach leaf was highest in the soil amended with spent wash modified steel slag (SWMSS) and lowest in the acid modified steel slag (ACMSS). During the first year (2015-16), the per cent increase in mean dry matter yield of spinach leaf in the soil amended with SS, SW and SWMSS was 22.2, 35.9 and 47.7%, respectively over control (unamended soil) in a Cu Vertisol. Similarly, 16.4, 20.9 and 26.3% increases in mean dry matter yield of spinach leaf in a Cu contaminated Vertisol were noticed due to application of SS, SW and SWMSS, respectively over control during 2016-17. The result further clearly indicates that the increase in dry matter yield of spinach leaf during the second year (2016-17) was significantly lower than the first year (2015-16) spinach crop.

Table 4: Effect of modified steel slag application as soil amendment in a copper contaminated on dry matter yield of spinach crop.

Treatment	Dry matter yield of spinach crop (g pot^{-1})			
	Leaf		Root	
	2015-16	2016-17	2015-16	2016-17
Control	6.08d	6.95c	2.05c	1.75c
SS	7.43c	8.09b	3.02b	2.83b
ACMSS	3.90e	4.03d	1.60c	1.31c
SWMSS	8.98a	8.78a	4.92a	4.34a
SW	8.26b	8.40ab	4.61a	4.02a
SEm(±)	0.270	0.288	0.396	0.359
C.D. (5%)	0.602	0.640	0.881	0.799

The result from the spinach root mean dry matter yield showed soil amended with steel slag and modified slag in Cu contaminated soil significantly influenced the dry matter yields of spinach root at both the year (2015-16 and 2016-17) of spinach crop. The dry matter yield of spinach root during 2015-16 and 2016-17 ranged from 1.60 to 4.92 g pot^{-1}, and 1.31 to 4.34 g pot^{-1}, respectively. The dry matter yield of spinach root was highest in the soil amended with SWMSS and lowest in the ACMSS. During 2015-16, the per cent increase in dry matter yield of spinach root in the soil amended with SS, SW and SWMSS was 47.3, 124.9 and 139.5%, respectively over control (unamended soil) in a Cu contaminated Vertisol. Similarly, the per cent increase in dry matter yield of spinach root observed during 2016-17 in the soil amended with SS, SW and SWMSS was 61.7, 129.7 and 148.0%, respectively over control (unamended soil) during 2016-17.

The dry matter yield of spinach leaf and root at both the years clearly indicated that it was highest in the soil amended with spent wash modified steel slag (SWMSS) and lowest in the acid modified steel slag (ACMSS) which is apparently due to the presence of plant nutrients in spent wash (Rajukkannu and Manickam, 1997; Zalawadia and Raman, 1994; Pathak *et al.*, 1999) and steel slag (Wang and Cai, 2006; Stroehlin and Berger, 1963; Anderson and Parkpian, 1984) together makes the crop yield to increase, whereas, the low soil pH and high EC in the ACMSS might have resulted in reduction in crop yield. On the contrary from the present study, an investigation by Anderson and Parkpian (1984) showed that the dry matter yield of sorghum was increased following the application of a slag as fertilizer material to alkaline soils.

D. Heavy metal content and its uptake by spinach crop

Soil amendments significantly influenced the copper content of spinach leaf and root at the end of both the years of spinach crop. The addition of SS or SWMSS in a Cu contaminated soil significantly decreased the copper content in spinach leaf and root over control (Table 5).The copper content ranges from 45.71 to 70.16 and 38.71 to 65.49 mg kg^{-1} in the spinach leaf at first year (2015-16) and second year (2016-17), respectively. Similarly, the spinach root copper content ranged from 66.37 to 113.14 mg kg^{-1} and 60.04 to 106.48 mg kg^{-1} during first year (2015-16) and second year (2016-17) spinach crop growth. The reduction in leaf and root copper content over control was more in the ACMSS than the untreated steel slag (SS) and found to be statistically significant. In general, copper content was more in root as compared to leaf at their corresponding treatments.

Table 5: Effect of modified steel slag application as soil amendment in a copper contaminated on copper content in spinach crop.

Treatment	Copper content in spinach crop (mg kg^{-1})			
	Leaf		Root	
	2015-16	2016-17	2015-16	2016-17
Control	70.16a	65.49a	96.15b	91.80b
SS	50.87c	45.86b	72.52d	68.19cd
ACMSS	45.71d	38.71c	66.37d	60.04d
SWMSS	60.61b	62.11a	82.61c	75.94c
SW	67.31a	65.06a	113.14a	106.48a
SEm(±)	1.787	1.955	3.705	5.875
C.D. (5%)	3.982	4.356	8.256	13.09

At both the period (2015-16 and 2016-17) of spinach crop growth, copper uptake by spinach leaf and root was significantly lowest in the soil amended with SS and ACMSS over unamended (control) Cu contaminated soil. The copper uptake ranges from 179.57µg pot^{-1} to 552.02 µg pot^{-1} and 156.82 to 545.75 µg pot^{-1} in the spinach leaf at first (2015-16) and second (2016-17) year of spinach crop growth (Table 6). Further, the result clearly indicates that significant differences in the copper uptake by spinach leaf and root at both the year (2015-16 and 2016-17) were observed between the soils amended with SS and ACMSS.

The release of alkaline element like Ca, Na and Mg together with Fe and Si from the original slag as a result of acid treatment in steel slag (Yoo *et al*., 2004; Fang *et al.*, 2014; He *et al.*, 2012) and its subsequent addition in our experimental Cu contaminated soil might have stabilized the Cu in soil. Such element together with contaminants (Cu) involved in chemical reaction like precipitation of Cu 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). Thus the mobility of Cu was substantially reduced in soil amended ACMSS (as evidenced from decreased DTPA extractable Cu in soil) and as a result the copper content and its uptake in spinach leaf and root was reduced significantly over unamended soil.

Table 6: Effect of modified steel slag application as soil amendment in a copper contaminated on copper uptake by spinach crop.

Treatment	Copper uptake by spinach crop (µg pot^{-1})			
	Leaf		Root	
	2015-16	2016-17	2015-16	2016-17
Control	428.04b	455.17b	103.99d	161.97bc
SS	375.61c	370.92c	169.02c	190.75b
ACMSS	179.57d	156.82d	55.81e	78.52c
SWMSS	538.34a	545.50a	328.27b	333.21a
SW	552.02a	545.75a	404.11a	427.75a
SEm(±)	15.88	19.42	18.53	42.82
C.D. (5%)	35.38	43.27	41.29	95.39

CONCLUSION

Heavy metal contaminations in soil due to anthropogenic activities are evident and become global issues in recent years. Historically, several technologies exist to remediate heavy metal contaminated soil; however, the most promising technology for remediation of contaminated sites is contaminants stabilization particularly heavy metals by the incorporation of organic or inorganic amendments in soil. To conclude from the present study it clearly implicate that steel slag treated with HCl (acid modified steel slag) has greater potential in reducing the mobility of heavy metal in soil and its subsequent transfer to edible plant parts (spinach leaf) as evidenced by reduction in DTPA extractable Cu in the post harvest soil sample of a Cu Contaminated Vertisol. Further studies on heavy metal release from the adsorbed steel slag or modified slag under long term experiments needs to be evaluated.

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How to cite this article: Coumar, M.V., Sharma, M., Jain, R.C., Saha, J.K., Gupta, S.C., Rajendiran, S. and Patra, A.K. (2021). Effect of Modified Steel Slag Application as Soil Amendment on Soil Quality and Spinach Yield in a Copper Contaminated Vertisol. *Biological Forum – An International Journal*, *13*(2): 336-344.