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EFFECT OF APPLICATION OF SOME ORGANIC AMENDMENTS ON SOIL PROPERTIES, EXTRACTABLE MICRONUTRIENTS AND THEIR CHEMICAL FRACTIONS IN A SANDY LOAM SOIL

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Abstract. In a 120-day incubation study, farmyard manure (FYM), mushroom compost (MC), poultry manure (PM), vermi-compost (VC), biogas slurry (BS) and biochar from *Lantana sp*.; a common weed (BC) each added at 15 t ha^{-1} significantly increased soil electrical conductivity and organic C content, however, only VC failed to increase soil organic C content significantly but increased soil pH when compared with the control sample. Among organic amendments, FYM, MC, VC and BS increased DTPA-extractable Zn and Mn in soil significantly when compared with the control sample, while BC was significantly effective in regard to increasing both DTPA-extractable Mn and hot water soluble B when compared with the control sample. Application of FYM and MC significantly increased DTPA-extractable Cu and Fe, respectively when compared with the control sample. Simple correlation and path coefficient analysis were performed to identify key chemical fractions of micronutrients in soil having the direct and indirect effects on availability of micronutrients in organically amended soils. Based on soil extractable concentrations of micronutrients in organically amended soils, FYM appeared to be the best source of Zn, Cu and Mn, while MC could serve as the best source of Fe. Biochar from *Lantana sp*. may serve as a good source of B.

Keywords: chemical fractions, micronutrients, organic amendments, soil properties

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INTRODUCTION

Organic amendments are widely used in agriculture to maintain soil productivity by promoting good soil physical conditions suitable for plant growth (Weber *et al.* 2007), serving as a source of plant nutrients for plants growth (Watson *et al.* 2002) and enriching the microbial biodiversity of agricultural system (Hole *et al.* 2005). Plants acquire nutrients from soil solution which is always in equilibrium with the nutrient associated with soil solid phase which consists of both organic and inorganic colloids, carbonates, sesquioxides and other primary and secondary minerals (Adriano 2001). Organic amendments being carbonaceous in nature are subjected to microbial decomposition and depending upon their chemical composition these organic amendments produce a variety of water soluble organic acids and many natural chelating/complexing agents which alter the intensity of different chemical fractions of nutrients associated with soil solution, soil exchange complex, organic matter, soil carbonates and sesquioxides and other soil minerals (Huang and Cobran 2005). The ease with which these chemical fractions equilibrate with soil solution also varies widely. The addition of different organic amendments as an agronomic practice changes soil properties and also the intensities of different chemical pools of micronutrients to influence the availability of both macro- and micro-nutrients in soil. The present investigation was undertaken to examine the way in which different organic amendments influence the general soil properties, the concentration of extractable soil micronutrients and their different chemical pools in a sandy loam soil to understand the build-up of micronutrients in soil upon application of different organic amendments/manures.

MATERIALS AND METHODS

A bulk (10 kg) sample of surface (0–15 cm) soil was collected from E1 plot of Norman E. Borlaug Crop Research Centre of Govind Ballabh Pant University of Agriculture and Technology, Pantnagar (India). The geographical location of the field is at 29°01.450'N, 79°28.723'E and altitude of 214 m above mean sea level. Soil sample was dried under shade, crushed with a wooden roller and passed through a 2-mm sieve. Soil sample was analyzed for general properties following the standard methods (Page *et al.* 1982). The experimental soil had 69.2% sand, 20% silt and 10.8% clay and, according to the classification of International Society of Soil Science, it had sandy loam texture (Geea and Bauder 1986), 7.35 pH and 0.051 dS m^{-1} specific soil conductance in 1:2 soil water suspension, 4.6 g organic C, 19.2 mg Olsen's P, 222.5 mg ammonium acetate extractable K, 3,300 mg exchangeable Ca, 120 mg exchangeable Mg, 37.4 mg 0.15% $CaCl_2$ extractable S and diethylenetriaminepentaacetic acid (DTPA) extractable 0.32 mg Zn; 1.06 mg Cu; 6.17 mg Fe and 3.36 mg Mn and 0.06 mg hot water soluble B kg^{-1} soil.

Farmyard manure (FYM) and vermi-compost (VC) were collected from Instructional Dairy Farm of the university at Nagla. Mushroom compost (MC) was collected from Mushroom Research & Training Centre (Pantnagar). Poultry manure (PM) was collected from Poultry Farm (Nagla). Biogas slurry (BS) was collected from Integrated Farming System Model Farm, N.E. Borlaug Crop Research Centre. Biochar (BC) was prepared by incineration of *Lantana camara* (a bush weed) under limited O_2 supply. All the samples of organic amendment were air-dried. The sample was crushed with a pestle and mortar to make it a fine and homogeneous powder. All organic amendments were analyzed in duplicate for pH, electrical conductivity in 1:10 solid water suspension and for total C and N concentration using CHN analyzer. All organic amendments were digested in di-acid (HNO_3: $HClO_4$, 9:4 v/v) and analyzed for Zn; Cu; Fe and Mn by atomic absorption spectrophotometry (GBC Avanta M model) following the procedure outlined by Page *et al.* (1982). These organic amendments were also subject to the dry ash procedure in an electric muffle furnace at 550°C for 3 h, ashes were dissolved in 2 N HCl and analyzed for B by the azomethine H method.

Incubation study

Three hundred grams of soil, on oven dry weight basis, were separately treated with 2 g of FYM, MC, PM, VC, BS and BC with a control in duplicate. After thorough mixing, the treated soil was filled in fourteen plastic containers (8 cm diameter × 14 cm length) which were provided with a basal 1-cm glass wool pad over the drainage holes. A battery of cation (IRC 86, H^+ form, 4 milliequivalent) and anion-exchange resins (IRA 96, NO_3^- form, 4 milliequivalent) spread over a basal glass wool pad in a separate plastic container was fitted below each soil-filled plastic pot. The lowest plastic pot, having no drainage holes, was also fitted below the ion-exchange resin battery container to collect the drained solution. Treated soil in each plastic container was first moistened to field capacity moisture regime by adding the requisite volume of distilled water. The weight of whole assembly was initially recorded and used to maintain soil moisture regime near field capacity by weighing and adding distilled water twice a week throughout the incubation period. The incubation was done in the laboratory (maximum temperature – from 26.0 to 27.5°C and minimum temperature – from 24.0 to 22.0°C, R.H. 40–56%).

Treated soil was subjected to periodic leaching by adding 20 ml distilled water after 10, 20, 30, 50, 70, 90 and 120 d (days) of incubation to quantify the displaceable mineralized inorganic fraction of the micronutrients during incubation. The leachate was passed through the beds of cation- and anion-exchange resins. Next day, 12.5 mL of 0.01 M HNO_3 was allowed to gradually pass through cation- and anion-exchange resins twice and the extract was collected, pooled. The total volume of the extract was measured. The Zn, Cu, Fe, Mn and B in extracts were analyzed following the procedures described in the preceding paragraph. The values recorded at different time intervals during incubation were summed up and reported as displaceable fraction of these micronutrients.

At the end of 120 d incubation period, soil contained in all the plastic containers was removed from the container and separately air-dried, mixed and pulverized. Soil sample pertaining to each replicate was analyzed for soil pH and electrical conductance in 1:2 soil water suspension, readily oxidizable soil organic C content and DTPA extractable micronutrient cations (Zn, Cu, Fe and Mn) and hot water soluble B following the standard procedures. These soil samples were sequentially extracted for different chemical fractions of micronutrient cations and B according to the modified sequential extraction scheme proposed by Ahnstrom and Parker (1999). Two of air dry soil samples were taken in a polypropylene centrifuge tube and it subjected to sequential extractions twice in 15 mL of 0.1 M strontium nitrate (water soluble and exchangeable fraction, F1) for 2 h at 180 rpm, once in 30 mL of 1 M sodium acetate (pH 5.0) (carbonate bound fraction, F2) for 2 h at 180 rpm, thrice in 5 mL of 5% sodium hypochlorite solution (pH 8.5) (organically bound fraction, F3) for 30 min. at 180 rpm and twice in 20 mL of solution of 0.2 M Oxalic acid + 0.2 M Ammonium oxalate + 0.1 M Ascorbic acid (pH 3.0) (reducible/iron oxide bound fraction, F_4) for 30 min. at 180 rpm. After each equilibration, clear supernatants were obtained by centrifugation at 7,000 rpm for 10 min. The extracts of different fractions (F1 to F4) were acidified with two drops of concentrated HCl. After the collection of supernatant of F4, soil pellet was removed from centrifuge tube, air dried for 5 d and finely crushed with a pestle and mortar. An aliquot of 0.2 g of finely crushed soil was digested in HF-$HClO_4$ following the procedure outlined by Page *et al.* (1982). The digests of HF-$HClO_4$ were analyzed for micronutrients as residual fraction (F5).

The data on the properties of organic amendments and effect of different organic amendments on soil properties and extractable micronutrients were statistically analyzed by Duncan's multiple range test. The data on different chemical fractions of micronutrients were log transformed and statistically analyzed as factorial completely randomized block design according to statistical procedure outlined by Snedecor and Cochran (1967) with the help of the Standard Computer Program software developed by the Department of Mathematics, Statistics, and Computer Science of G.B. Pant University of Agriculture and Technology. The test of significance was conducted at $p \leq 0.05$. Path coefficient analysis was also performed following the procedure outlined by Li (1956).

RESULTS AND DISCUSSION

Some properties of organic amendments used in the study are presented in Table 1. The pH of VC and FYM was nearly neutral (6.97 and 7.21), while MC and PM had slightly alkaline pH (7.53 and 7.60). The pH of BS (8.92) and BC (8.29) was alkaline. Rout *et al*. (2012) reported that cattle manure and poultry manure had higher pH than VC. The pH of VC was very close to the standard range (6.5–7.5) reported by Manna (2004). Malav *et al.* (2015) also noted that BS had a pH of 7.9. The observed variations between the values recorded in the present study and values reported in the literature could be ascribed to many factors such as the age of organic amendments, their preparation method and storage conditions. The electrical conductivity (EC), an index of the concentration of soluble salts in any soil amendments showed wide variations; the highest EC value (0.673 dS m^{-1}) was observed in FYM, followed by PM (0.419 dS m^{-1}), BS (0.414 dS m^{-1}), VC (0.282 dS m^{-1}), MC (0.230 dS m^{-1}) and BC (0.118 dS m^{-1}). Uz *et al*. (2016) also observed a higher EC value for FYM (4325 µS cm^{-1}) as compared to VC (1558 µS cm^{-1}). Considering the upper threshold value of EC as 4 dS m^{-1} for a good quality manure (Manna 2004), all these organic amendments could be rated as suitable for soil application. The highest total C was noted in BC (475.8 g C kg^{-1}), while the lowest value of C was recorded in MC (179.4 g C kg^{-1}). Among organic amendments, MC had the highest concentration of Fe (1985.5 mg kg^{-1}) and Mn (244.9 mg kg^{-1}) but the lowest concentration of B (14.9 mg kg^{-1}). Biogas slurry (BS) had the highest concentration of Zn (193.0 mg kg^{-1}) and Cu (145.6 mg kg^{-1}). Biochar (BC) prepared from *Lantana* weed had the highest concentration of B (33.4 mg kg^{-1}) but the lowest concentration of Zn (24.7 mg kg^{-1}), Fe (968.7 mg kg^{-1}), and Mn (61.9 mg kg^{-1}).

Table 1. Some properties of organic amendments

Properties		Organic amendment					
		Farmyard manure (FYM)	Mushroom compost (MC)	Poultry manure (PM)	Vermi-compost (VC)	Biogas slurry (BS)	Biochar (BC)
pH value (1:10)		7.21^{a}	7.53^{b}	7.60^{b}	6.97^{a}	8.92^{e}	8.29^{d}
EC (dS/m) (1:10 at 25°C)		0.553^{e}	0.189^{b}	0.344^{d}	0.231^{c}	0.340^{d}	0.097^{a}
Total C (g kg^{-1})		276.9^{c}	179.4^{a}	226.2^{b}	271.1^{c}	411.5^{d}	475.8^{e}
Total micronutrients (mg kg^{-1})	Zn	135.5^{c}	108.1^{b}	179.8^{d}	155.6^{c}	193.0^{d}	24.7^{a}
	Cu	23.9^{a}	23.7^{a}	17.4^{a}	21.1^{a}	145.6^{b}	24.1^{a}
	Fe	1129.9^{b}	1985.5^{d}	1182.7^{b}	1622.7^{c}	1201.1^{b}	968.7^{a}
	Mn	152.2^{b}	244.9^{e}	157.9^{b}	204.5^{d}	181.3^{c}	61.9^{a}
	B	16.3^{a}	14.9^{a}	19.5^{b}	15.8^{a}	16.7^{a}	33.4^{c}

The numerical values followed by a dissimilar letter in the superscript in a row are significantly different at ($p \leq 0.05$) by Duncan's multiple range test.

Effect of organic amendments on soil properties

The data on the effect of different organic amendments on some general properties of soil, extractable concentrations of micronutrients after 120 days of incubation are presented in Table 2. Among different organic amendments, application of only VC increased soil pH significantly when compared with the control sample, while other organic amendments did not bring any significant change in soil pH. Similar observation was made by Angelova *et al.* (2013). Application of all organic amendments brought a significant increase in electrical conductivity (EC) of soil owing to the release of soluble ions upon their mineralization. The highest increase in the EC was noted in case of MC, while the lowest increase in EC was recorded in the case of BS amendment which could be attributed to the production of organic acids during decomposition causing removal of inorganic ions by exchange/complexation and subsequent removal by leaching/displacement. Eteng (2015) also showed that organic amendments increased soil pH regardless of types of manure. Dikinya and Mufwanzala (2010) reported that the application of chicken manure irrespective of application rate did not change the pH of amended soil, while EC increased with the increase in application rates. Azeez and Averberke (2012) also found that EC of soil significantly increased with the application of poultry, cattle and goat manure and potential of manure induced by soil salinization was very high in poultry manure and goat manure compared with cattle manure. Uz *et al.* (2016) reported that application of FYM decreased pH more than VC, which is similar to our observations and they also noted an increasing trend of electrical conductivity with all organic amendments. However, the EC values obtained in the current study were well below the threshold level to cause any salinity problem. Several researches (Sutton 1994, Garg *et al.* 2009) had also reported that organic manures do not cause salinity when applied at moderate levels.

Application of all organic amendments except VC increased the content of soil organic C significantly over the control. The highest increase was recorded with PM, while the lowest but statistically significant increase was recorded with BS amendment. Several studies have proved that the addition of organic residues increased the soil organic carbon level (Usman *et al.* 2004, Hadad 2015). Ragheb *et al.* (2017) also noted the highest organic C level in PM-amended soil. Bakayoko *et al.* (2009) found that poultry and cattle manure treatments significantly increased the soil organic matter content from 0.46 to 2.8 and 1.1%, respectively. Application of FYM increased the concentration of DTPA-extractable Zn, Cu and Mn significantly when compared with the control sample, while that of MC increased the concentration of DTPA-extractable Zn, Fe and Mn significantly. Application of VC and BS increased the concentration of DTPA-extractable Zn and Mn significantly when compared with the control sample. Application of BC increased the concentration of DTPA-extractable Mn and hot water soluble B significantly when compared with the control sample.

Table 2. Effect of different organic amendments on some soil properties after 120 d of incubation

Organic amendment	Soil properties			DTPA extractable (mg kg^{-1} soil)				Hot water sol. B (mg kg^{-1} soil)
	pH (1:2)	EC (dS/m^{-1}) (1:2) at 25°C	Organic C (g kg^{-1})	Zn	Cu	Fe	Mn	
Control	6.56^{ab}	0.210^{a}	4.88^{a}	0.42^{a}	1.05^{ab}	8.65^{bc}	26.80^{ab}	0.20^{ab}
Farmyard manure (FYM)	6.60^{b}	0.245^{b}	8.48^{c}	0.97^{c}	1.23^{c}	11.32^{bcd}	30.13^{c}	0.28^{bc}
Mushroom compost (MC)	6.32^{a}	0.293^{c}	6.53^{b}	0.90^{c}	1.15^{bc}	16.21^{d}	28.81^{bc}	0.25^{b}
Poultry manure (PM)	6.41^{ab}	0.284^{c}	8.68^{c}	0.57^{a}	1.15^{bc}	13.28^{cd}	25.90^{a}	0.15^{a}
Vermi-compost (VC)	6.98^{c}	0.250^{b}	6.14^{ab}	0.80^{b}	1.16^{bc}	7.70^{b}	29.11^{c}	0.17^{a}
Biogas slurry (BS)	6.58^{b}	0.244^{b}	6.34^{b}	0.74^{b}	1.04^{a}	6.07^{a}	29.42^{c}	0.25^{b}
Biochar (BC)	6.43^{ab}	0.245^{b}	8.58^{c}	0.54^{a}	1.02^{a}	6.14^{b}	29.57^{c}	0.43^{c}

The numerical values followed by a dissimilar letter in the superscript in a column are significantly different at ($p \leq 0.05$) by Duncan's multiple range test

Chemical fractions of micronutrients in soil

The scheme adopted for studying chemical fractions of micronutrients (Ahnstrom and Parker 1999) involved the use of 1 M sodium acetate (pH 5.0) to extract carbonate bound fraction of micronutrients. Though some organic amendments like BS and BC which had alkaline pH (>8.0) might carry some micronutrients as carbonates yet the post-incubation pH of treated soil (6.32 to 6.98) ruled out the significant accumulation of carbonates upon the use of alkaline organic amendments. Joshi *et al*. (2015) reported that the soil extracts obtained with the use of 1 M sodium acetate (pH 5.0) in sequential extraction scheme carried some fulvates as well, therefore, the observed concentration of micronutrients in this chemical fractions could be ascribed to the fraction of micronutrients associated with fulvic acid in soil.

Zinc

The data on effect of organic amendments addition on different chemical fractions of Zn in soil are presented in Table 3. On an average the most dominant fraction of Zn was residual fraction followed by iron oxide-bound, carbonate-bound, organically-bound, water soluble and exchangeable (Yadav *et al.* 2013, Katyal and Rattan 1993) and displaceable fraction. On an average, application of MC and PM increased the average content of Zn in soil by 22.1 and 20.6%, respectively, in comparison with the control sample. The interaction effect of Zn fractions and organic amendments indicated that none of the organic amendments could increase the content of displaceable, water soluble and exchangeable-, organically-bound and residual fraction of Zn in soil significantly when compared with the control sample. Among different organic amendments, the use of PM and BC significantly increased the carbonate bound fraction nearly 2.5 times when compared with the control sample. However, Zahedifar (2017) observed that wheat straw derived biochar (3%) shifted the Zn distribution from exchangeable and carbonate fractions to the organic matter fraction in agricultural soil, while Zn associated with carbonates showed a statistically significant increase (about 49%) as 1.5% biochar was applied to rangeland soil. The variation in the findings of this study and that of Zahedifar (2017) could be ascribed to the variation in the nature of biochar and soil under study. Application of PM, VC and BS significantly increased the iron oxide bound fraction of Zn nearly 2.0 times as compared to control. Hokayem and Azzi (2014) reported that with the application of cow manure rich in Zn, almost 50% of Zn was in non-mobile residual fraction, while 31% of Zn was bound to oxide fraction.

Table 3. Different chemical fractions of Zn as influenced by application of organic amendments. Bold values indicate percent fraction of total soil Zn content

Amendments	Displaceable	Water soluble + exch.	Carbonate-bound	Organically-bound	Iron oxide -bound	Residual	Mean
Control	0.11^{a}	0.22^{a}	1.87^{ab}	1.35^{abc}	2.69^{a}	46.06^{ab}	8.72^{a}
	0.20	**0.42**	**3.58**	**2.58**	**5.14**	**88.08**	
Farmyard manure (FYM)	0.08^{a}	0.39^{a}	1.45^{a}	0.89^{a}	2.74^{a}	55.19^{b}	10.12^{a}
	0.14	**0.64**	**2.39**	**1.47**	**4.51**	**90.86**	
Mushroom compost (MC)	0.29^{a}	0.32^{a}	2.76^{ab}	1.00^{ab}	4.82^{ab}	54.69^{b}	10.65^{b}
	0.46	**0.50**	**4.32**	**1.57**	**7.54**	**85.61**	
Poultry manure (PM)	0.26^{a}	0.32^{a}	4.63^{c}	2.35^{c}	5.80^{b}	49.75^{ab}	10.52^{b}
	0.41	**0.51**	**7.34**	**3.72**	**9.19**	**78.84**	
Vermi-compost (VC)	0.09^{a}	0.23^{a}	3.03^{bc}	2.47^{c}	5.38^{b}	34.69^{a}	7.65^{ab}
	0.19	**0.50**	**6.60**	**5.38**	**11.72**	**75.60**	
Biogas slurry (BS)	0.07^{a}	0.16^{a}	3.67^{bc}	2.12^{bc}	5.14^{b}	33.31^{a}	7.41^{ab}
	0.16	**0.36**	**8.25**	**4.77**	**11.56**	**74.90**	
Biochar (BC)	0.13^{a}	0.11^{a}	4.77^{c}	1.19^{abc}	3.58^{ab}	33.13^{a}	7.15^{a}
	0.30	**0.26**	**11.12**	**2.77**	**8.34**	**77.21**	
Mean	0.15^{A}	0.25^{A}	3.17^{C}	1.62^{B}	4.31^{D}	43.83^{E}	
	0.28	**0.47**	**5.94**	**3.04**	**8.08**	**82.19**	

* numerical values in a column having a dissimilar small letter in the superscript are significantly different at $p \leq 0.05$.

**numerical values in a row having a dissimilar capital letter in the superscript are significantly different at $p \leq 0.05$.

Copper

The data on different chemical fractions of Cu as influenced by different organic amendments are presented in Table 4. On an average, the most dominant fraction of Cu was residual fraction followed by iron oxide-bound, organically-bound, carbonate-bound, water soluble and exchangeable and displaceable fraction (Table 4). On an average, application of MC, BS, BC, VC and PM increased the average content of Cu in soil significantly by 41.8, 59.4, 60.7, 145.7 and 171.5%, respectively in comparison with the control sample. The interaction effect of Cu fractions and organic amendments indicated that none of the organic amendments could increase the content of displaceable, water soluble and exchangeable, carbonate-bound, organically-bound and iron oxide-bound fraction of Cu in soil significantly when compared with the control sample. Among different organic amendments, the use of PM and VC significantly increased the residual fraction more than 3.0 times, while BS and BC increased it significantly more than 1.7 times when compared with the control sample. Hokayem and Azzi (2014) reported that with the application of cow manure rich in Cu, almost 50% of Cu was bound to the non-mobile residual fraction but 30% of Cu was found in the

Table 4. Different chemical fractions of Cu as influenced by application of organic amendments. Bold values indicate percent fraction of total soil Cu content

Amendments	Dis-placeable	Water soluble + Exch.	Car-bonate-bound	Organ-ical-ly-bound	Iron oxide-bound	Residual	Mean
Control	0.02[a*]	0.05[a]	0.67[ab]	1.55[ab]	3.06[a]	9.38[a]	2.45[a]
	0.11	**0.34**	**4.55**	**10.53**	**20.78**	**63.70**	
Farmyard manure (FYM)	0.01[a]	0.08[a]	0.39[a]	1.20[a]	4.57[a]	12.57[ab]	3.14[ab]
	0.07	**0.42**	**2.07**	**6.37**	**24.28**	**66.78**	
Mushroom compost (MC)	0.02[a]	0.07[a]	1.07[b]	1.98[ab]	4.13[a]	13.57[ab]	3.47[bc]
	0.10	**0.34**	**5.13**	**9.50**	**19.82**	**65.11**	
Poultry manure (PM)	0.02[a]	0.05[a]	1.27[b]	2.64[b]	3.24[a]	32.69[c]	6.65[d]
	0.05	**0.13**	**3.18**	**6.61**	**8.12**	**81.91**	
Vermi-compost (VC)	0.02[a]	0.06[a]	1.11[b]	2.32[b]	2.92[a]	29.69[c]	6.02[cd]
	0.04	**0.17**	**3.07**	**6.42**	**8.09**	**82.21**	
Biogas slurry (BS)	0.02[a]	0.05[a]	1.17[b]	2.35[b]	3.77[a]	16.07[b]	3.91[cd]
	0.10	**0.21**	**4.99**	**10.03**	**16.09**	**68.58**	
Biochar (BC)	0.01[a]	0.07[a]	0.90[ab]	1.82[ab]	3.13[a]	17.69[b]	3.94[bc]
	0.06	**0.30**	**3.81**	**7.70**	**13.25**	**74.88**	
Mean	0.02[A]	0.06[A]	0.94[B]	1.98[C]	3.55[D]	18.81[E]	
	0.07	**0.24**	**3.71**	**7.81**	**14.00**	**74.18**	

* numerical values in a column having a dissimilar small letter in the superscript are significantly different at $p \leq 0.05$.

** numerical values in a row having a dissimilar capital letter in the superscript are significantly different at $p \leq 0.05$.

organically-bound fraction. The variations in the observations of this study and that of Hokayem and Azzi (2014) could be ascribed to differences in experimental set up, organic amendment and soil type used in both studies.

Iron

The data on different chemical fractions of Fe as influenced by different organic amendments are presented in Table 5. The data presented in Table 5 indicated that on an average the most dominant fraction of Fe was residual fraction followed by iron oxide-bound, organically-bound, carbonate-bound, water soluble and exchangeable and displaceable fraction. On an average, application of VC and BS significantly decreased the average content of Fe in soil by 14.5 and 12.1% in when compared with the control sample. The interaction effect of Fe fractions and organic amendments indicated that none of the organic amendments could increase the content of displaceable, iron oxide-bound and residual fractions of Fe in soil significantly when compared with the control sample. Among different organic amendments, the use of PM and VC significantly increased the carbonate bound fraction nearly 2.0 times, while the use of BS

Table 5. Different chemical fractions of Fe as influenced by application of organic amendments. Bold values indicate percent fraction of total soil Fe content

Amendments	Displaceable	Water soluble + exch.	Carbonate-bound	Organically-bound	Iron oxide-bound	Residual	Mean
Control	0.53^{a}	1.11^{bc}	7.55^{a}	52.19^{d}	1375.9^{a}	10347.8^{a}	1964.2^{c}
	0.004	**0.009**	**0.06**	**0.44**	**11.67**	**87.80**	
Farmyard manure (FYM)	0.32^{a}	1.34^{bc}	7.13^{a}	45.12^{cd}	1347.8^{a}	9756.5^{a}	1859.7^{bc}
	0.003	**0.012**	**0.06**	**0.40**	**12.08**	**87.44**	
Mushroom compost (MC)	0.44^{a}	1.60^{c}	7.06^{a}	34.83^{bc}	1379.8^{a}	10058.8^{a}	1913.8^{c}
	0.004	**0.014**	**0.06**	**0.30**	**12.02**	**87.60**	
Poultry manure (PM)	0.46^{a}	1.32^{bc}	16.79^{b}	28.37^{ab}	1378.2^{a}	9774.7^{a}	1866.6^{bc}
	0.004	**0.012**	**0.15**	**0.25**	**12.31**	**87.28**	
Vermi-compost (VC)	0.50^{a}	0.81^{ab}	14.87^{b}	24.98^{a}	1404.5^{a}	8634.2^{a}	1680.0^{a}
	0.005	**0.008**	**0.15**	**0.25**	**13.93**	**85.66**	
Biogas slurry (BS)	0.36^{a}	0.56^{a}	9.26^{a}	21.89^{a}	1422.3^{a}	8905.9^{a}	1726.7^{ab}
	0.003	**0.005**	**0.09**	**0.21**	**13.73**	**85.96**	
Biochar (BC)	0.36^{a}	0.79^{ab}	8.58^{a}	26.35^{ab}	1465.1^{a}	10142.2^{a}	1940.6^{c}
	0.003	**0.007**	**0.07**	**0.23**	**12.58**	**87.11**	
Mean	0.42^{A}	1.08^{B}	10.18^{C}	33.39^{D}	1396.2^{E}	9660.0^{F}	
	0.004	**0.010**	**0.09**	**0.30**	**12.58**	**87.02**	

* numerical values in a column having a dissimilar small letter in the superscript are significantly different at $p \leq 0.05$.

** numerical values in a row having a dissimilar capital letter in the superscript are significantly different at $p \leq 0.05$.

amendment significantly decreased the content of water soluble and exchangeable fraction of Fe nearly to half as compared to the control. The use of MC, PM, VC, BS and BC also registered a significant decrease in organically-bound fraction of Fe in soil when compared with the control sample. Similar observation was made by Dhaliwal *et al.* (2012).

Manganese

The data on different chemical fractions of Mn as influenced by different organic amendments are presented in Table 6. On an average, the most dominant fraction of Mn was iron oxide-bound fraction followed by residual, water soluble and exchangeable, carbonate-bound and organically-bound- and displaceable fraction. The main effect of amendments had no statistically significant influence on different chemical fractions of Mn in soil. The interaction effect of different chemical Mn fractions and organic amendments indicated that none of the organic amendments could increase the content of displaceable, water soluble and exchangeable and iron oxide-bound fraction of Mn in soil when compared with the control sample. Among different organic amendments, the use of

Table 6. Different chemical fractions of Mn as influenced by application of organic amendments. Bold values indicate percent fraction of total soil Mn content

Amendments	Displaceable	Water soluble + exch.	Carbonate-bound	Organically-bound	Iron oxide-bound	Residual	Mean
Control	0.10^{a}	2.71^{a}	0.51^{a}	0.39^{ab}	42.39^{a}	47.52^{c}	15.6^{a}
	0.10	**2.89**	**0.54**	**0.42**	**45.28**	**50.76**	
Farmyard manure (FYM)	0.07^{a}	2.82^{a}	1.14^{ab}	1.59^{c}	44.68^{a}	21.46^{a}	11.96^{a}
	0.10	**3.93**	**1.59**	**2.22**	**62.26**	**29.91**	
Mushroom compost (MC)	0.09^{a}	3.05^{a}	1.01^{ab}	0.83^{bc}	34.52^{a}	36.68^{bc}	12.7^{a}
	0.12	**4.00**	**1.33**	**1.09**	**45.31**	**48.15**	
Poultry manure (PM)	0.12^{a}	2.96^{a}	0.46^{a}	0.92^{bc}	29.61^{a}	29.42^{abc}	10.58^{a}
	0.19	**4.66**	**0.72**	**1.45**	**46.64**	**46.34**	
Vermi-compost (VC)	0.05^{a}	3.38^{a}	1.92^{bc}	0.68^{abc}	37.25^{a}	25.11^{ab}	11.4^{a}
	0.07	**4.94**	**2.81**	**0.99**	**54.47**	**36.72**	
Biogas slurry (BS)	0.08^{a}	3.26^{a}	2.78^{c}	0.42^{ab}	42.46^{a}	20.74^{a}	11.62^{a}
	0.11	**4.67**	**3.99**	**0.60**	**60.89**	**29.74**	
Biochar (BC)	0.07^{a}	3.45^{a}	2.45^{c}	0.11^{a}	30.46^{a}	24.43^{ab}	10.16^{a}
	0.12	**5.66**	**4.02**	**0.18**	**49.96**	**40.07**	
Mean	0.08^{A}	3.09^{D}	1.47^{C}	0.71^{B}	37.34^{F}	29.34^{E}	
	0.12	**4.29**	**2.04**	**0.99**	**51.84**	**40.73**	

* numerical values in a column having a dissimilar small letter in the superscript are significantly different at $p \leq 0.05$.

** numerical values in a row having a dissimilar capital letter in the superscript are significantly different at $p \leq 0.05$.

specifically VC, BS and BC significantly increased the carbonate bound fraction nearly 3.8, 5.5 and 4.8 times, respectively when compared with the control sample. The use of FYM significantly increased organically bound fraction of Mn nearly 4.0 times, while the use of FYM, VC, BS and BC significantly decreased residual fraction of Mn when compared with the control.

Boron

The data on different chemical fractions of B as influenced by different organic amendments are presented in Table 7. The data presented in Table 7 indicated that on an average the most dominant fraction of B was residual fraction followed by iron oxide-bound, organically-bound, carbonate-bound, displaceable and water soluble and exchangeable fraction. On an average, application of FYM, MC, PM and BC increased the average content of B in soil by 11.9, 29.5, 25.3 and 12.2%, respectively when compared with the control sample. The interaction effect of B fractions and organic amendments indicated that none of the organic amendments could increase the content of displaceable, water soluble and exchangeable fraction of B in soil significantly when com-

Table 7. Different chemical fractions of B as influenced by application of organic amendments. Bold values indicate percent fraction of total soil B content

Amendments	Displaceable	Water soluble + exch.	Carbonate-bound	Organically-bound	Iron oxide-bound	Residual	Mean
Control	0.07^{a}	0.05^{a}	0.40^{b}	3.38^{a}	8.66^{a}	82.56^{bc}	15.85^{a}
	0.07	**0.05**	**0.42**	**3.55**	**9.10**	**86.80**	
Farmyard manure (FYM)	0.08^{a}	0.09^{a}	0.27^{ab}	3.55^{ab}	9.82^{ab}	92.60^{cd}	17.73^{bc}
	0.07	**0.08**	**0.25**	**3.34**	**9.23**	**87.03**	
Mushroom compost (MC)	0.08^{a}	0.07^{a}	0.13^{a}	3.58^{ab}	10.53^{bc}	108.77^{e}	20.53^{c}
	0.07	**0.06**	**0.11**	**2.91**	**8.55**	**88.31**	
Poultry manure (PM)	0.09^{a}	0.05^{a}	0.40^{b}	3.95^{abc}	11.42^{cd}	103.20^{de}	19.85^{bc}
	0.08	**0.04**	**0.34**	**3.32**	**9.59**	**86.64**	
Vermi-compost (VC)	0.07^{a}	0.05^{a}	0.60^{c}	4.45^{cd}	10.00^{b}	76.42^{ab}	15.26^{a}
	0.07	**0.05**	**0.66**	**4.86**	**10.92**	**83.44**	
Biogas slurry (BS)	0.07^{a}	0.05^{a}	0.67^{c}	4.59^{d}	12.14^{d}	68.61^{a}	14.36^{a}
	0.08	**0.06**	**0.78**	**5.33**	**14.09**	**79.66**	
Biochar (BC)	0.10^{a}	0.08^{a}	0.40^{b}	4.12^{bcd}	10.00^{b}	92.04^{cd}	17.79^{bc}
	0.09	**0.07**	**0.37**	**3.86**	**9.37**	**86.23**	
Mean	0.08^{A}	0.06^{A}	0.41^{B}	3.94^{C}	10.37^{D}	89.17^{E}	
	0.08	**0.06**	**0.39**	**3.79**	**9.97**	**85.72**	

* numerical values in a column having a dissimilar small letter in the superscript are significantly different at $p \leq 0.05$.

** numerical values in a row having a dissimilar capital letter in the superscript are significantly different at $p \leq 0.05$.

pared with the control sample. Among different organic amendments, the use of; VC and BS significantly increased the carbonate bound fraction nearly 1.5 times, while MC significantly decreased this fraction of B in soil by 3.0 times when compared with the control sample. The use of VC, BS and BC significantly increased organically-bound fraction of B by 31.7, 35.8 and 21.9% when compared with the control sample. Application of MC, PM, VC, BS and BC significantly increased the iron oxide-bound fraction of B in soil by 21.6, 11.8, 15.5, 40.2 and 15.5% when compared with the control sample. Residual fraction of B in soil was significantly increased with the application of MC and PM but this fraction was significantly decreased with the use of BS.

Relationships of different chemical fractions of micronutrients and soil extractable micronutrients

Simple correlation analysis among soil properties, soil extractable micronutrients and chemical fractions of micronutrients in soil revealed that only water soluble + exchangeable fraction of Fe was significantly and positively correlated with DTPA-extractable Fe (r = 0.959, significant at $p \leq 0.01$ [data not presented here]). Since the availability of micronutrients was likely to be affected by their different chemical fractions independently and also due to their intricate inter-relationships among themselves, simple correlation analysis might not reveal the relationship between soil extractable micronutrients and their chemical fractions in the soil. Therefore, a path coefficient analysis was also performed to obtain further insight into the inter-relationship among different chemical fractions of Zn and their effects on soil extractable micronutrients (Fig. 1). The direct effect indicated the direct contribution (single causal path) of a chemical fraction of micronutrient to soil extractable micronutrient concentration. The weight of a positive direct P indicated that the dependent variable (soil extractable micronutrient concentration) was expected to increase by that many times of its standard deviation from its mean when the independent variable (a given chemical fraction of micronutrient) increased by one standard deviation from its mean while holding all other relevant chemical fractions constant. The indirect effect of a specific chemical fraction indicated that it could contribute to soil extractable micronutrient by influencing another chemical fraction of the concerned micronutrient. In Fig. 1, the direct effects of all chemical fractions of a micronutrient on extractable soil micronutrient are shown, while the indirect effects of only those chemical fractions are shown whose numerical value was positive and significant over their individual direct effects.

A close inspection of path coefficients (P) for DTPA-extractable soil Zn revealed that water soluble + exchangeable Zn fraction showed the highest positive and direct effect on DTPA-extractable Zn (P = 1.923) followed by iron oxide-bound Zn fraction (P = 1.090). Residual fraction of Zn contributed through water soluble + exchangeable Zn fraction. Organically-bound, and carbonate-bound fractions of Zn contributed through residual Zn fraction because their indirect *P* value through residual Zn fraction was greater than their direct *P* value. Joshi *et al.* (2014) also noted that the water soluble and crystalline Fe oxide occluded fraction showed the highest positive and direct effect on Zn uptake by maize plants.

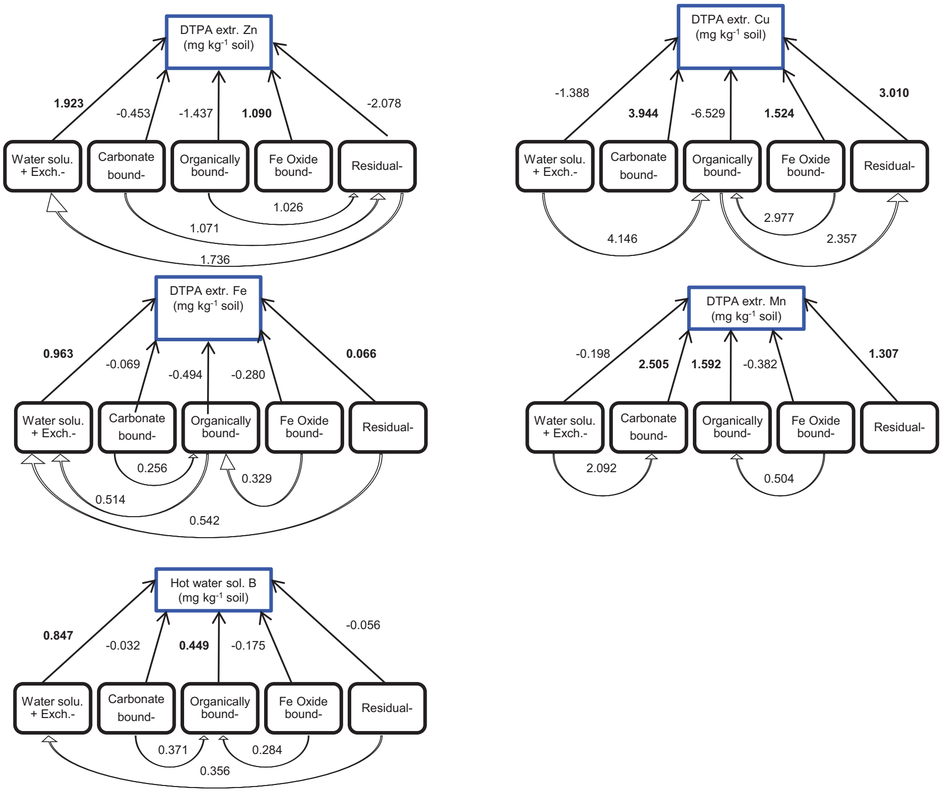

Fig. 1. Path diagrams between soil extractable micronutrients and different chemical fractions of micronutrients in soil treated with organic amendments. The values of residual factor were 0.021 for DTPA extr. Zn, 0.106 for DTPA extr. Cu, 0.018 for DTPA extr. Fe, 0.103 for DTPA extr. Mn and 0.357 for hot water soluble B. Dominant direct effects are indicated as numerical values in bold

In the case of DTPA-extractable soil Cu, *P* values indicated that carbonate-bound (*P* = 3.944) followed by residual- (*P* = 3.010) and iron oxide-bound (*P* = 1.524) fractions had positive and direct effect on DTPA-extractable Cu. Water soluble + exchangeable and iron oxide-bound fraction contributed through organically-bound fraction. Organically-bound fractions of Cu contributed through residual fraction. Joshi *et al.* (2015) also reported that in acidic soils, the DTPA (pH = 7.3) and AB-DTPA (pH = 7.6) extractable Cu showed a significant and positive correlation with organically complexed (Pb-displaceable) Cu; acid soluble Cu and crystalline Fe oxide occluded Cu fractions.

In the case of DTPA-extractable Fe, *P* values indicated that water soluble + exchangeable fractions ($P = 0.963$) followed by residual fractions ($P = 0.066$) had a positive and direct effect on DTPA-extractable Fe. Residual-and organically-bound fractions contributed through water soluble + exchangeable fraction of Fe, while iron oxide-bound and carbonate-bound fractions contributed through organically-bound fraction of Fe

In the case of DTPA-extractable Mn, *P* values indicated that carbonate-bound ($P = 2.505$) followed by organically-bound ($P = 1.592$) and residual ($P = 1.307$) fractions had a positive and direct effect on DTPA-extractable Mn. Obrador *et al.* (2007) also found a significant correlation between Mehlich-3 extractable soil Mn and organically-bound Mn fraction. Iron oxide-bound fraction contributed through organically-bound fraction of Mn. Interestingly, water soluble + exchangeable fraction of Mn contributed through carbonate bound fraction. These results indicated that Mn associated with low molecular weight organic acids and also organic matter could be easily mobilized for plant availability.

In the case of hot water soluble B, *P* values indicated that water soluble + exchangeable fractions ($P = 0.847$) followed by organically-bound ($P = 0.449$) fractions had a positive and direct effect on hot water soluble B. Carbonate-bound and iron oxide-bound B fractions contributed indirectly through organically-bound fractions of B. Residual fraction of B contributed indirectly through water soluble + exchangeable fraction of B.

These results indicated the existence of a partially reversible dynamic equilibrium among the different chemical fractions of micronutrients like Zn (Joshi *et al.* 2014) and Mn (Joshi *et al.* 2017) in the organically amended soil.

In general, this study showed that in organically amended soil the residual fraction was the highest, followed by the remaining fractions in the following order: oxide-bound > carbonate-bound > organically-bound > water soluble and exchangeable fraction as reported by Jaloud *et al.* (2013). Hosseinpur and Motaghian (2017) also observed that the effect of cow dung and vermi-compost treatments on Zn associated with Fe-Mn oxides and organic matter was significant ($p < 0.05$). In their study, they noticed a significant correlation of DTPA-TEA- and AB-DTPA-extractable Zn and Cu with Fe-Mn oxides fraction indicating bioavailability of oxide-bound fractions.

CONCLUSIONS

Thus, different organic amendments vary in their properties and also in their micronutrient contents. Application of these organic amendments to soil alter some mutable soil properties and also differentially influence the intensities of different chemical fractions of micronutrients in soil. The availability of micronutrients in organically amended soils is controlled by mutually interacting different chemical fractions of micronutrients as evident from their significant direct and indirect effects in path analysis. Based on the changes in the levels of DTPA-extractable micronutrient cations and hot water soluble B in treated soil, FYM appeared as the best source of Zn, Cu and Mn, while MC seemed to be the best source of Fe. Biochar from *Lantana sp*. was a good source of B. Hence, different organic amendments based on their specific micronutrient supplying capacities could be provided singly or in combination to supply key critical micronutrient(s).

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