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Assessment of micronutrients fractionations and mobility in soils of eastern Uttar Pradesh

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ABSTRACT

In the present investigation, an attempt has been made to assess the various chemical forms and mobility factor (MF) for zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) in different soils of eastern Uttar Pradesh. For this purpose, surface soil (0–15 cm) samples from two different locations were collected under Entisol, Inceptisol, Vertisol and Alfisol during 2019–20 and analysis was done in the laboratory of Department of Soil Science and Agricultural Chemistry, BHU, Varanasi. The modified Tessier sequential extraction procedure was used to determine the chemical pools of Zn, Cu, Fe and Mn in each soil. Results indicated that total metal content follows the order of Fe>Mn>Zn>Cu across the soil orders, whereas mobility factor of micronutrients arranged as: Mn>Cu>Zn>Fe. The highest exchangeable (F1), carbonate bound (F2), Fe–Mn oxides bound (F3), organically bound (F4) and residual (F5) fraction were recorded in Inceptisol, Vertisol, Alfisol, Inceptisol and Alfisol, respectively for micronutrients, i.e. Zn, Cu, Fe and Mn. The mean percentage value of various micronutrients fractions were in the order of F5>F3>F4>F2>F1, except Mn, whose chemical forms follows the order of F3>F5>F4>F2>F1. The Zn and Cu were highly mobile in Vertisol while Fe and Mn in Entisol.

Keywords: Fractionation, Micronutrients, Mobility factor, Soil orders, Uttar Pradesh

Zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) are essential micronutrients, which serve as a co-factor for several enzymes involved in the metabolism of carbohydrates, lipids, proteins and nucleic acids (Barker and Pilbeam 2015). Micronutrients exist in soils in various forms, varying in their availability to plants. Sharma *et al.* (2016) postulated the occurrence of micronutrients in distinct chemical pools, i.e. water soluble, easily exchangeable, adsorbed, precipitated with secondary minerals, and held onto primary minerals. The nature and amount of various forms of micronutrients depend upon the variation in soil texture, pH, calcium carbonate, and organic matter (OM) content of soil. Therefore, chemical speciation of soil micronutrients through single and sequential extraction have been extensively applied using a variety of extractants (Xiao *et al.* 2017). Sequential selective extraction procedures are commonly used to understand and predict the bioavailability, leaching, transformation and chemical forms of nutrients in agricultural soils (Mahmoud *et al.* 2015). This technique varies in the number of fractions extracted as well as the order and kind of reagents used. In general, the fractionation schemes start with the weakest extractants and end with the strongest, most aggressive extractants, and separate five to seven metal fractions (Golui *et al*. 2020). One of the main drawbacks of these techniques is that they are rather laborious and time consuming.

In Uttar Pradesh intensive rice-wheat cropping system causing large-scale depletion of micronutrients for the past few decades (Singh *et al.* 2016). This may further deteriorate the already exploited soils. Until now, most of the studies have been conducted to estimate DTPA extractable Zn, Cu, Fe and Mn in surface soil of various soil orders, but very few studies have focused on the distribution of different forms of Zn, Cu, Fe and Mn in four major taxonomic orders of eastern Uttar Pradesh. Therefore, the cardinal objective of the present investigation was to generate scientific information on the distribution of Zn, Cu, Fe and Mn pools in four major soil orders in eastern Uttar Pradesh and their mobility factor.

MATERIALS AND METHODS

Location and collection of soil samples: The GPS based surface soil samples (0–15 cm) were collected from four major taxonomic orders of eastern Uttar Pradesh, i.e. Entisol, Inceptisol, Vertisol and Alfisol. For each soil orders, two soil samples were collected from two separate locations.

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Entisol was collected from lower bank of the river Ganga, one from Shikhar block of Mirzapur (25°13' N and 82°87' E) which was designated as Entisol-I and another from Pindra block of Varanasi (25°31' N and 83°02' E) which was designated as Entisol-II. Inceptisol was sampled from agricultural land of Shikhar block, Mirzapur (25°15' N and 82°87' E) and Agricultural Research Farm at Institute of Agricultural Sciences, Banaras Hindu University, Varanasi (25°25' N and 82°99' E) and labeled as Inceptisol-I and Inceptisol-II, respectively. Agricultural land of Nagar city (25°10' N and 82°50' E) and Shikhar (25°80' N and 82°47' E) block of Mirzapur was chosen for the collection of Vertisol and tagged as Vertisol-I and Vertisol-II, respectively. The Alfisol-I was collected from agricultural land of Chakia block of Chandauli (25°01' N and 83°21' E) and Alfisol-II was collected from Agricultural Research Farm at Rajiv Gandhi South Campus, Banaras Hindu University, Mirzapur (25°05' N and 82°60' E).

Processing and analysis of soil samples: Soil samples were collected and analyzed for micronutrients fractions during 2019–20 in the Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi. Soil samples were air-dried at room temperature followed by grounding in wooden mortar and pestle and passed through a 2 mm sieve and homogenized properly and further grounded to pass through 0.5 mm sieve for chemical fractions analysis. The modified Tessier sequential extraction procedure was used to determine the chemical fractionation of Zn, Cu, Fe and Mn in each soil order by atomic absorption spectroscopy (AAS) (Tessier *et al.* 1979). The exchangeable fraction (F1), carbonate bound fraction (F2), Fe–Mn oxides bound fraction (F3), organically bound fraction (F4) and residual fraction (F5) were estimated in different soils. The total Zn, Cu, Fe and Mn content in the soil samples were determined by the summation of all five fractions (F1–F5). The mobility factor (MF) of Zn, Cu, Fe and Mn was calculated based on the content of micronutrients in the mobile fractions to the sum of all fractions (Gusiatin and Kulikowska 2015).

$$\text{Mobility factor (MF)} = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100$$

The F1–F5 are the micronutrients content in each fraction (mg/kg) according to the modified Tessier sequential extraction procedure. This equation shows the potential mobility of trace elements in the soil.

The data were statistically analyzed with one-way analysis of variance (ANOVA) using SPSS version 16.0 software. Duncan's multiple range test (DMRT) was performed to test the significance of the difference between the treatments at $P \leq 0.05$.

RESULTS AND DISCUSSION

Zinc fractions and its mobility factor: The concentration of each chemical form of Zn in soil is shown in Table 1. The highest exchangeable pool was recorded in Inceptisol-II (0.19 mg/kg) and the lowest in Entisol-I (0.06 mg/kg). Moreover, the highest F2, F3, F4 and F5 fraction was documented in Vertisol-I (1.37 mg/kg), Alfisol-I (12.6 mg/kg), Inceptisol-II (6.95 mg/kg) and Alfisol-I (67.6 mg/kg), respectively. On an average, the maximum proportion of the extracted Zn of total Zn was associated with the F5 (70.6%) followed by F4 (21.4%), F3 (6.70%), F2 (1.11%) and F1 (0.16%) fraction. A significantly high proportion of Zn was associated with Fe–Mn oxides bound and residual fraction, which is in agreement with other workers (Beygi and Jalali 2019). In case of total Zn content, Alfisol-I (93.3 mg/kg) recorded the maximum value, whereas the lowest in Entisol-I (57.3 mg/kg). Bhattacharya *et al.* (2020) reported that total Zn content was higher in Alfisol as compared to Inceptisol and Entisol. Zinc was highly mobile in Vertisol-I, as it observed the highest MF 1.81% (Table 1) and the mobility factor of Zn follows the order of Vertisol>Inceptisol>Entisol>Alfisol. However, it has been reported that Zn is mostly associated with the low molecular weight organic acids and low adsorption capacity of Zn in sand particles increased its mobility (Brunetto *et al.* 2018).

Copper fractions and its mobility factor

The F1, F2, F3, F4 and F5 fractions of Cu in soils ranged from 0.13–0.58, 0.67–2.13, 4.65–12.5, 4.11–7.69 and 34.7–53.4 mg/kg, respectively (Table 1). The maximum F1 was recorded in Inceptisol-II, F2 in Vertisol-I, F3 in Alfisol-I, F4 in Inceptisol-II and F5 in Alfisol-I. A major portion (7.18–13.4%) of Cu was present in organically bound fraction due to its high affinity towards humic substances, which resulted in the formation of the complex with OM (Sun *et al.* 2019). Thus, Inceptisol containing high OM documented the highest organically bound Cu fraction. The mean percentage value of Cu pools of total Cu were in the order of F5 (74.8%)>F3 (12.4%)>F4 (10.1%)>F2 (2.06%)>F1 (0.64%). The highest concentration of total Cu was in Alfisol-I (72.2 mg/kg), whereas the minimum in Entisol-I (44.4 mg/kg). The findings of the present investigation were lined with the findings of Bhattacharya *et al.* (2020). The mobility of Cu in various soil orders represent as: Vertisol-I>Vertisol-II>Inceptisol-I>Inceptisol-II>Entisol-II>Entisol-I>Alfisol-I>Alfisol-II (Table 1). Due to strong adsorption of Cu with soil organic and inorganic components (Fe–Mn oxides), the mobility and availability of Cu would be expected to be low in Inceptisol and Alfisol (Golui *et al.* 2020).

Iron fractions and its mobility factor: The Inceptisol-I recorded the maximum F1 (9.84 mg/kg) and F4 (1060 mg/kg) Fe fraction among the soil orders (Table 2). The F2 pool was the highest in Vertisol-I (30.1 mg/kg) and the lowest in Alfisol-I (13.4 mg/kg). Alfisol-I documented the highest F3 (3933 mg/kg) and F5 (13170 mg/kg) Fe pool. The highest percentage of Fe out of total Fe was associated with the residual fraction (65.4%) across the soil orders. About 25.0% of total Fe was associated with Fe–Mn oxides bound, while only 0.08% of total Fe occurred with exchangeable fraction. It has also been reported (Xu *et al.* 2019) that the lowest content of Fe is found in the exchangeable form, and

Table 1 Distribution of zinc and copper (mg/kg) in different soil fractions and its mobility factor

Soil type	Zinc							Copper						
	F1# (mg/kg)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	F5 (mg/kg)	Total (mg/kg)	MF (%)	F1 (mg/kg)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	F5 (mg/kg)	Total (mg/kg)	MF (%)
Entisol-I	0.06c (0.10)*	0.64b (1.12)	12.6c (22.0)	3.15d (5.49)	40.9c (71.3)	57.3c	1.23b	0.13e (0.29)	0.82bcd (1.85)	4.65c (10.5)	4.11c (9.25)	34.7d (78.1)	44.4g	2.16c
Entisol-II	0.07bc (0.11)	0.67b (1.06)	14.9bc (23.6)	3.83cd (6.07)	43.6bc (69.1)	63.1bc	1.17b	0.24de (0.50)	0.95bcd (2.00)	4.69c (9.87)	4.48bc (9.42)	37.2d (78.2)	47.5f	2.52bc
Inceptisol-I	0.17a (0.22)	1.05a (1.33)	16.2abc (20.6)	6.85a (8.68)	54.6abc (69.2)	78.9ab	1.56ab	0.55ab (1.01)	1.24bc (2.28)	5.80c (10.7)	7.12a (13.1)	39.7cd (73.0)	54.4e	3.30ab
Inceptisol-II	0.19a (0.23)	1.10a (1.31)	16.6abc (19.8)	6.95a (8.31)	58.9ab (70.4)	83.7a	1.57ab	0.58a (1.01)	1.30b (2.26)	6.36c (11.0)	7.69a (13.4)	41.7bcd (72.3)	57.6d	3.27ab
Vertisol-I	0.15ab (0.18)	1.37a (1.62)	17.8ab (21.1)	5.73ab (6.76)	59.7ab (70.4)	84.7a	1.81a	0.41c (0.66)	2.13a (3.40)	7.63bc (12.2)	6.26ab (10.0)	46.2abc (73.7)	62.6c	4.07a
Vertisol-II	0.16a (0.18)	1.19a (1.37)	18.3ab (21.1)	6.32ab (7.30)	60.6a (70.0)	86.6a	1.57ab	0.43bc (0.65)	1.81a (2.73)	8.22bc (12.4)	6.39ab (9.65)	49.3ab (74.5)	66.2b	3.39ab
Alfisol-I	0.12abc (0.13)	0.51b (0.55)	20.2a (21.6)	4.84bc (5.19)	67.6a (72.5)	93.3a	0.69c	0.37cd (0.51)	0.73cd (1.01)	12.5a (17.3)	5.18bc (7.18)	53.4a (74.0)	72.2a	1.53c
Alfisol-II	0.11abc (0.13)	0.45b (0.52)	18.6ab (21.3)	5.06bc (5.79)	63.1a (72.2)	87.3a	0.65c	0.33cd (0.47)	0.67d (0.96)	10.8ab (15.5)	5.92abc (8.50)	52.0a (74.6)	69.7a	1.45c
Mean	0.13 (0.16)	0.87 (1.11)	16.9 (21.4)	5.34 (6.70)	56.1 (70.6)	79.4	1.28	0.38 (0.64)	1.21 (2.06)	7.58 (12.4)	5.89 (10.1)	44.3 (74.8)	59.3	2.71
SEm (±)	0.02	0.13	1.43	0.48	5.05	6.55	0.16	0.04	0.16	1.18	0.58	2.55	0.91	0.35
CD (P≤0.05)	0.07	0.38	4.30	1.43	15.1	19.6	0.47	0.13	0.48	3.53	1.74	7.65	2.73	1.04

*Data in parentheses indicates proportion of each fraction in total Zn and Cu present in soil, respectively. #F1; exchangeable fraction, F2; carbonate bound fraction, F3; Fe–Mn oxides bound fraction, F4; organically bound fraction and F5; residual fraction, and MF; mobility factor.

Table 2 Distribution of iron and manganese (mg/kg) in different soil fractions and its mobility factor

Soil type	Iron							Manganese						
	F1# (mg/kg)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	F5 (mg/kg)	Total (mg/kg)	MF (%)	F1 (mg/kg)	F2 (mg/kg)	F3 (mg/kg)	F4 (mg/kg)	F5 (mg/kg)	Total (mg/kg)	MF (%)
Entisol-I	4.63c (0.09)*	19.4bc (0.36)	1442d (27.0)	621c (11.6)	3252d (60.9)	5338d	0.46a	5.12c (1.92)	14.3cd (5.37)	118d (44.4)	23.7e (8.89)	105d (39.4)	267e	7.36a
Entisol-II	5.65bc (0.09)	19.9bc (0.31)	1529d (23.7)	727bc (11.3)	4169d (64.6)	6450d	0.41a	5.06c (1.64)	16.9bcd (5.49)	138cd (44.8)	27.5de (8.92)	121cd (39.1)	308e	7.19a
Inceptisol-I	9.84a (0.13)	21.5abc (0.28)	2094cd (27.4)	1060a (13.9)	4451d (58.3)	7636d	0.42a	7.03ab (1.85)	18.7abc (4.93)	155cd (40.8)	58.8a (15.5)	140bcd (36.9)	380d	6.83a
Inceptisol-II	10.1a (0.12)	22.3abc (0.26)	2132cd (24.6)	1025a (11.8)	5481cd (63.2)	8671cd	0.38a	8.21a (1.87)	19.0abc (4.34)	187c (42.8)	62.9a (14.4)	160bc (36.6)	438c	6.26a
Vertisol-I	8.68ab (0.08)	30.1a (0.28)	2817bc (25.7)	811abc (7.41)	7279c (66.5)	10946c	0.36a	6.14bc (1.22)	25.0a (4.99)	250b (49.7)	50.8abc (10.1)	170b (33.9)	502b	6.27a
Vertisol-II	8.04ab (0.07)	25.8ab (0.23)	2872bc (25.6)	913ab (8.15)	7379c (65.9)	11199c	0.31ab	6.40bc (1.16)	23.7ab (4.31)	287ab (52.1)	54.5ab (9.91)	179b (32.5)	550b	5.53a
Alfisol-I	6.30bc (0.04)	13.4c (0.07)	3933a (21.9)	833abc (4.64)	13170a (73.3)	17956a	0.11c	2.73d (0.44)	13.2cd (2.13)	328a (52.9)	39.9cd (6.42)	237a (38.1)	621a	2.60b
Alfisol-II	5.99bc (0.04)	16.7bc (0.12)	3462ab (23.9)	845abc (5.83)	10160b (70.1)	14490b	0.16bc	2.66d (0.50)	10.3d (1.93)	298ab (55.7)	42.7bc (7.98)	181b (33.9)	535b	2.46b
Mean	7.41 (0.08)	21.1 (0.24)	2535 (25.0)	854 (9.33)	6918 (65.4)	10336	0.33	5.42 (1.33)	17.7 (4.19)	220 (47.9)	45.1 (10.3)	162 (36.3)	450	5.56
SEm (±)	0.95	3.07	301	78.1	753	1031	0.06	0.55	2.36	18.2	4.38	12.7	17.6	0.80
CD (P≤0.05)	2.85	9.20	902	234	2256	3090	0.18	1.64	7.09	54.7	13.1	38.0	52.8	2.39

*Data in parentheses indicates proportion of each fraction in total Fe and Mn present in soil, respectively. #F1; exchangeable fraction, F2; carbonate bound fraction, F3; Fe–Mn oxides bound fraction, F4; organically bound fraction and F5; residual fraction, and MF; mobility factor.

the highest in the residual form. The order of association between total Fe content and different soil orders could be arranged as: Alfisol>Vertisol>Inceptisol>Entisol. Shakeri and Saffari (2020) also found a similar association of Fe. The highest amount of total Fe (17956 mg/kg) was recorded in Alfisol-I and the lowest in Entisol-I (5338 mg/kg). In case of mobility factor, the maximum 0.46% was noted in Entisol-I and the minimum 0.11% in Alfisol-I (Table 2). The mobility factor of Fe in different soils follows the order: Entisol>Inceptisol>Vertisol>Alfisol. It has been reported by Zahedifar (2020) that Fe has a high affinity for Fe–Mn oxides and this finding suggested that Fe was held in a more stable fraction in which the movement of Fe in the soil profile would be negligible. Therefore, Alfisol recorded the lowest mobility factor (MF) for Fe.

Manganese fractions and its mobility factor: Soil Mn has mainly associated the Fe–Mn oxide bound fraction across the soil orders (47.9% of the total extracted Mn), while smaller values in the exchangeable (1.33%) and carbonate (4.19%) bound fractions. Manganese mostly co-precipitates with Fe–Mn oxides and associated with the mineral crystal structure (Joshi *et al.* 2017). Therefore, Fe–Mn oxides bound Mn pool recorded the maximum Mn content among the different Mn fractions. The maximum F1 (8.21 mg/kg), F2 (25.0 mg/kg), F3 (328 mg/kg), F4 (62.9 mg/kg) and F5 (237 mg/kg) Mn pools were recorded, respectively in Inceptisol-II, Vertisol-I, Alfisol-I, Inceptisol-II and Alfisol-I (Table 2). In case of total Mn content, Alfisol-I (621 mg/kg) had the maximum value, whereas the lowest in Entisol-I (267 mg/kg). This result was supported by the observations made by Sharma *et al.* (2016). The Entisol-I noted the maximum MF 7.36% for Mn, however Alfisol-II recorded the lowest 2.46% (Table 2). The mobility factor of Mn across the soil orders appeared in the order of Entisol>Inceptisol>Vertisol>Alfisol. The preceding researches (Borah *et al.* 2020) have mentioned that Mn has a high affinity for Fe–Mn oxides and residual fractions, therefore very less mobile in crystalline Fe oxide rich Alfisol.

Evaluation of various chemical forms of Zn, Cu, Fe and Mn in four major taxonomic orders of eastern Uttar Pradesh revealed that Mn content was highest in Fe–Mn oxides bound fraction, whereas other micronutrients in residual pool irrespective of soil orders. The total metal content follows the order of Fe>Mn>Zn>Cu across the soil orders whereas the mobility factor of micronutrients could be arranged as: Mn>Cu>Zn>Fe. The bioavailable, i.e. exchangeable pool of Zn, Cu, Fe and Mn was maximum in Inceptisol. The mean percentage value of various micronutrients fractions were in the order of F5>F3>F4>F2>F1, excerpt Mn whose chemical fractions follows the order of F3>F5>F4>F2>F1. The Zn and Cu were highly mobile in Vertisol while Fe and Mn in Entisol.

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