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Micronutrient Distribution in Arid and Semi-arid agricultural Soils of Central India

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Abstract—*Copper, iron, manganese and zinc are the micronutrients which are essential for proper growth and reproduction of all organisms including plants. There phyto-available (labile) concentration is the most important factor, which determines the toxicity or deficiency of elements in the environment and governs soil fertility status. Thus, the present study was conducted to identify the status and distribution pattern of total and DTPA extractable (plant available) concentrations of Cu, Fe, Mn and Zn in the arid and semi-arid, rural agricultural soils of Central India. The total and DTPA extractable micronutrient contents followed the descending order as: Fe > Mn > Zn > Cu. The results obtained from multivariate statistical analysis indicated anthropogenic source of DTPA extractable micronutrients, specifically agriculture and allied activities which was confirmed by close association of DTPA extractable Cu, Fe, Mn and Zn concentrations with soil organic carbon and moisture content. Whereas mineral enriched geology of the area is responsible for high total content. Micronutrient distribution showed maximum soil organic carbon and DTPA extractable Cu, Fe, Mn and Zn in the intensively cultivated agricultural areas where more human settlement was present. However, high values of total micronutrient content were reported in the areas dominated by extensive agricultural activities and forest land. The study revealed that intensive agricultural management can alter the natural cycling of minerals in soil which may pose Fe/Mn toxicity and/or Cu/Zn deficiency problems.*

Keywords*: Micronutrients, Multivariate analysis, Agricultural soils, Geogenic enrichment.*

1. INTRODUCTION

With a predicted population of 1.5 billion by the year 2050, India needs to increase its current food production by 5 Mt as compared to 3.1 Mt per year achieved during the past 4 decades [1]. But the area under cultivation is limited, and to meet the challenge and fulfil the demand/supply of staple foods, vegetables, cash crops, fibres and fuels at local and regional scale, adequate nutrient reserves, particularly soil micronutrients are necessary. According to Ar non and Stout [2], absence of micronutrient leads to hindered growth and reproduction of organism because of their direct and specific action, which cannot be replaced by any other element. However, Epstein [3] concluded that, these are the components of molecules known to be as an essential metabolite which are either derived from the soil parent material or from several anthropogenic activities [4].

Micronutrients are not regularly added to agricultural soils along with other common fertilizers, but their removal from the soils has been going on for centuries through many processes including natural and anthropogenic activities, without any systematic replacement [5]. All soils contain approximately every naturally occurring element of the periodic table with varying concentrations. However, Copper (Cu), Iron (Fe), Manganese (Mn) and Zinc (Zn) are those micronutrients which are essential for proper growth and reproduction of all organisms including plants, thus are of main concern of the present study. These elements can be divided into 'total' and 'plant available', later is the fraction of total metal content which is potentially available to the plants. This plant available (labile) concentration is the most important factor, which determines the toxicity or deficiency of elements in the environment.

'Total' micronutrient concentration include all forms of an element present in a soil (i.e. ions bound in the crystalline structure of primary and secondary mineral, adsorbed on the surface of secondary clay, oxides and carbonate minerals, bound to humus and organic matter, free ionic forms, as well as soluble organic and inorganic complexes in the soil solution) and will show whether the soil is contaminated/ geochemically enriched or deficient to provide necessary nutrients for adequate agricultural activities [6].

Several extract ants have been used to quantify total and plant available concentration of soil micronutrients. Diethylenetriaminepentaacitic acid (DTPA) is one of the most common soil extract ant for evaluating plant available micronutrients [7].

The aim of the present was to identify the distribution pattern of total and DTPA extractable concentrations of Cu, Fe, Mn and Zn in agricultural soils and to study the relationships of micronutrients among themselves and with other physico-chemical properties of agricultural soils.

2. MATERIALS AND METHODS

2.1 Study area

The Sidhi district is situated on the north-eastern boundary (between 22° 47.5' and 24° 42.10' North latitude and 81° 18.40' and 82° 48.30' East latitude) of the Madhya Pradesh State, India. The area is characterized by low hill with extensive plateaus and Son river valley. The average elevation of the area is 311 m with a tropical monsoon type climate. The average rainfall is 1100 mm [8]. The total population of the area is 1.12 million [9]. The Sidhi district covers a total area of 4,720 km^2 out of which the land used for agricultural purpose is approximately 45%. The soils are comprised of Mollisol, Alfisols, Entisols, Inceptisols and Vertisol with alluvial, red and black soil types. The major crops grown are rice, maize, barley, wheat, mustard and lentil.

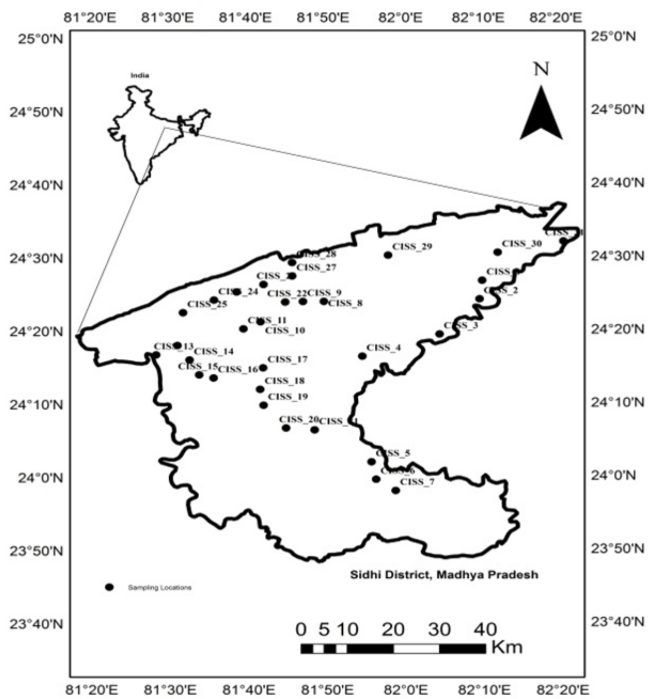

Fig. 1: Map of the study area showing sampling locations

2.2 Sample collection and storage

A total of thirty one soil samples (0-30 cm depth) were collected from agricultural field in December, 2014 (Fig. 1). Sampling was done by means of stratified random sampling. Each sample was a composite mixture of 5 sub-samples collected from one hectare plots with stainless steel soil cores. Geographical information of all the sampling locations were recorded with GPS. After removing top vegetation, roots and litter, collected samples were pooled and homogenized. Samples were air-dried at 24°C temperature for three days, and then passed through 2 mm nylon sieve. About 100 g of all the samples were oven dried at 105 °C, crushed with mortar-pestle and passed through 0.2 mm sieve and then stored in polypropylene bottles for laboratory analysis.

2.3 Physico-chemical and micronutrient analysis of soil sample

Determination of soil pH and electrical conductivity (EC) were done with 1:2 and 1:5 soil water ratio (W/V) suspension, respectively using a standardized pH meter with buffer solution and standardized EC meter with reference solution. Soil Organic Carbon (SOC) was estimated by the Walkley and Black [10] rapid dichromate wet oxidation method. Moisture content of soil was determined by gravimetric method [11].

Total Cu, Fe, Mn and Zn content was obtained by microwave digestion of 0.25 g of soil sample with reagent mixture of nitric acid, hydrofluoric acid, hydrochloric acid and hydrogen peroxide in a ratio of 9:3:2:1, respectively in the high performance microwave digester [12].

The DTPA extractable or plant available fraction of Cu, Fe, Mn and Zn were assessed by extracting 10 g of each soil sample with 20 ml of diethylenetriamine penta-acetic acid (DTPA) extractant (0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M triethanolamine, pH adjusted to 7.3) [13].

All extracts were filtered with Whatman-42 filter, made up the final volume up to 50 ml with Millipore water (Milli-Q system, Millipore) and stored in polypropylene bottles at 4°C in refrigerator. The same extract of each sample was used to determine the concentration of the CU, Fe, Mn and Zn using flame atomic absorption spectrophotometer (FAAS-GBC Avanta, Australia) at their respective wavelength.

2.4 Multivariate statistical analysis

For assessment of soil quality, the descriptive statistics were calculated with statistical software package SPSS version 21.0. Specific multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis (CA) were used to determine the relationship among micronutrients in the environment and their possible sources of origin [14]. For analyzing the relationship among observed variables, PCA reduces and extracts the data into a smaller number of independent factors known as principal components, this method is widely used in soil and sediment studies [15]. Varimax rotation was applied to enhance the interpretation of results by minimization of number of variables with a high loading on each component.

Cluster analysis is a pattern recognition technique which produces partitioning of similar type of variables. The results of CA are produced in a tree like structure, known as dendogram. The data obtained from micronutrients and soil properties was first standardized by means of z-scores before calculating the CA and Euclidean distances for similarities in the variables. The hierarchical clustering was done by applying Ward's method on the standardized dataset.

3. RESULTS AND DISCUSSIONS

3.1 Soil physico-chemical properties

Descriptive statistics of soil properties analyzed in the study area are presented in Table 1. Soil pH varied between 6.06 and 8.16, with an average of 7.29, indicating the agricultural soils are slightly acidic to slightly alkaline in nature. The EC of agricultural soils ranges from 14.26 to 157.9 µS/cm. Moisture content of soils also showed a large spatial variation ranging from 2.62 to 6.47%. SOC showed significant spatial variation ranging from very low to very high SOC with an average concentration of 0.97%.

3.2 Soil micronutrient status

Details of concentration of total and available micronutrients are presented in Table 1. The mean concentration of total Cu, Fe, Mn and Zn are found to be 50.80, 35743.95, 574.29, 62.04 mg/kg and DTPA extractable Cu, Fe, Mn and Zn are found to be 3.45, 160.25, 18.64 and 4.06 mg/kg respectively, following the descending order as: Fe>Mn>Zn>Cu. High standard deviations in micronutrient concentration is observed due to great heterogeneity in the soil parent material and land use pattern. The mean concentrations of the total and DTPA extractable micronutrients are higher in agricultural soils of the study area than the benchmark soils of India reported by Katyal [16]. Total content of these micronutrients is lower than the crustal average [17], but falling in the range of Indian soils, reported by Singh [1]. All the soils had significant amount of DTPA extractable micronutrients considering the critical limits suggested by Lindsay and Norvell [13].

Table 1: Soil physico-chemical properties and micronutrient concentrations

	Unit	Range	Mean
pH	-	6.06-8.16	7.29±0.6
EC	µS/cm	14.26-157.90	66.93±38
MC	%	2.62-6.47	4.73±0.8
SOC	%	0.16-1.92	0.97±0.4
DTPA Cu	mg/kg	0.37-6.87	3.45±1.6
DTPA Fe	mg/kg	30.06-395.55	160.15±99.5
DTPA Mn	mg/kg	14.37-23.10	18.64±2.5
DTPA Zn	mg/kg	0.70-8.50	4.06±2.1
Total Cu	mg/kg	14.13-144.27	50.80±32.3
Total Fe	mg/kg	16757-71170 7	35743±12759
Total Mn	mg/kg	144.27-1044.20	574.29±195.3
Total Zn	mg/kg	32.33-110.93	62.04±19.2

3.2.1 Copper

The average concentration of Cu in the earth's crust is 60 mg/kg and its background concentrations in soils depend on geology and typically vary between 2 and 50 mg/kg [4]. Predicted no effect concentrations (PNECs), protecting 95% of all plant and microbial species of soil, vary between 10 and 200 mg/kg [4]. Total Cu content in the study area ranged from 14.13 to 144.27 mg/kg with a weighted mean of 54.48 mg/kg. These values for total Cu seem to be higher than those reported on a variety of soils whereas, Katyal [16] reported the total Cu concentration in the benchmark soils of India ranged between 11 and 148 mg/kg with a weighted mean of 41 mg/kg. DTPA-extractable Cu ranged from 0.37 and 6.87 mg/kg soil with a weighted mean value of 3.45 mg/kg soil. DTPA-extractable Cu was significantly correlated with soil organic carbon and other DTPA extractable micronutrients under study. According to McBride and Basiak [18], Cu shows high affinity towards organic complexing, which govern the bioavailability and mobility of Cu in soils. No significant relation was observed between total and DTPA Cu concentrations. Allen [19] also reported that the behaviour, bioavailability and toxicity of Cu is independent of its total concentration.

3.2.2 Iron

Total Fe in the study area varied from 16,757.53 and 71,170.67 mg/kg with an average value of 35,742.95 mg/kg. DTPA-Fe ranged from 30.06 and 395.55 mg/kg soil with a mean value of 160.15 mg/kg soil. The grand mean of total Fe content for world soils is 35,000 mg/kg [6]. Association between DTPA-Fe and pH indicates that Fe deficiency would be a serious problem in alkaline and calcareous soils [20]. According to Kabata-Pendias and Mukherjee [17], the major factors governing the mobilization and fixation of Fe are; oxidizing or alkaline soil conditions which enhances Fe precipitation, and acidic or reducing soil conditions increases the solubility of Fe compounds in the soils. With a decrease in soil organic matter content, Fe deficiency would be further increased, as organic matter is reported to be the main resource of plant available forms of micronutrients in soils [21, 22].

3.2.3 Manganese

Total Mn varied from 144.27 and 1,044.20 mg/kg among the soils of the study area with the weighted mean of 574.29 mg/kg. The grand mean of total Mn content for world soils is 488 mg/kg and its highest level occurs in loamy soils [6]. Sampling site 6, have loamy textured soil and show the similar trend. Total Mn was correlated with total Cu, Fe and Zn but it was not correlated with DTPA-Mn. Lack of association between total and DTPA-Mn indicates that the availability of Mn, like availability of Cu, Fe and Zn in soils is dependent upon factors other than their total contents [23]. DTPA-extractable Mn varied from 14.37 and 23.10 mg/kg with an average of 18.64 mg/kg. Hodgson [24], reported the Mn solubility in soil solutions is mainly affected by complexing with organic matter. According to Lindsay and Cox [25], pH is one of the major factor influencing the Mn availability in soils. The micronutrient absorptive capacity of soils increases with increasing pH [26, 27]. In the study area, soils with high pH exhibited the lowest DTPA-Mn. Both total and plant available (DTPA extractable) Mn distribution in soils were not uniform and it was found to be concentrated at certain points which are usually enriched with total and available Fe, Zn and Cu, respectively. Fe-Mn antagonism is widely known and is observed in several studies world-wide [6].

3.2.4 Zinc

The total Zn contents in surface soils ranged from 32.33 to 110.93 mg/kg with a weighted mean value of 62.04 mg/kg. The positive relation among these micronutrient indicates the influence of geogenic factors on their distribution in soils. High concentration of one of these micronutrients is found to be rich in concentration of the remaining ones and vice versa. It may be because of the role of Fe and Mn oxides and hydroxides in binding Zn with soils [28]. No relation between total Zn and DTPA-Zn shows that total Zn is not responsible for plant availability of Zn in soils, similar conclusions were made by Alloway [7]. DTPA-Zn varied between 0.70 and 8.50 mg/kg soil with an average of 4.06. Unlike total Zn, DTPA-Zn was highly correlated with the soil pH and organic matter, supporting that Zn availability in soils decreases with increasing in pH [6] and increases with increasing organic matter content [23]. Kabata-Pendias and Mukherjee [17] found that soil organic compounds hold Zn quite strongly at near neutral and alkaline regions, irrespective of its readily mobile nature. Hodgson [24] suggested that the complexing agents generated by organic matter increases the Zn availability in soils. DTPA-Zn was positively correlated with DTPA extractable Cu, Fe and Mn. Follet and Lindsay [23] suggested the interrelationship among micronutrients and variation in their distribution pattern is dependent on common soil factors and parent material. Alloway [4], concluded that the main factors governing and regulating the bioavailability of zinc are very close to those for Cu, Mn and Fe but, Zn deficiency or toxicity problems arises due to its easily soluble nature.

3.3 Multivariate statistical analysis

3.3.1 Principal component analysis

The results of principal component analysis by applying Varimax rotation with Kaiser Normalization for micronutrients and other soil properties are shown in Table 2. Three principal components with eigen value greater than 1 were extracted. PCA reduced the initial dimension of the dataset to three components which explains 79.228 % of the data variation. Therefore these three factors play significant role to explain micronutrient status in the soils of the study area. The graphical representation of the three components is also shown in Fig. 2.

Table 2: Rotated component matrix

	PC1	PC2	PC3
pH	-.89	-.11	.08
EC	.05	.01	.95
MC	.73	-.09	-.40
SOC	.93	-.09	-.09
DTPA Cu	.77	-.05	.25
DTPA Fe	.75	-.32	.12
DTPA Mn	.89	-.01	-.02
DTPA Zn	.87	-.06	.14
Total Cu	.21	.88	.01
Total Fe	-.25	.90	-.11
Total Mn	-.44	.72	-.02
Total Zn	.05	.94	.13
Eigen value	5.21	3.11	1.19
% variance	43.35	25.92	9.96
Total % variance	43.35	69.27	79.23

The first principal component (PC1) explains 45.134 % of the total variation and loads heavily on pH, moisture content, soil organic carbon, and DTPA extractable Cu, Fe, Mn and Zn. Loading of soil organic carbon (0.91) is maximum and that of EC is minimum (0.47). High variation in the loading pattern of variables indicate the quasi-independent nature of micronutrients within the group. The second principal component (PC2), dominated by total content of Cu, Fe, Mn and Zn accounts for 24.14 % of the total variance, indicating the abundance of micronutrients is due to presence of nutrient rich parent material in the soil [29]. The third principal component (PC3) is strongly correlated with EC which has a high loading value (0.95) and accounting for 9.95% of the total variation.

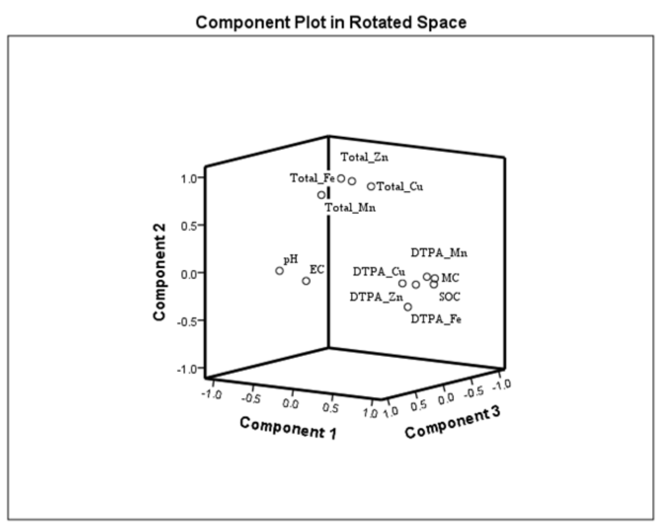

Fig. 2: Bi-plot of principal components

3.3.2 Cluster analysis

Hierarchical clustering solution and squared Euclidean distance (values of the distances between clusters) are represented in the dendogram (Fig.3). The figure displays two clusters: (1) SOC - DTPA extractable Z - DTPA extractable Mn - MC - DTPA extractable Cu - DTPA extractable Fe; (2) Total Cu - total Zn - total Fe - total Mn - pH - EC. CA is in good agreement with PCA results, suggesting availability of at least two sources of micronutrients in agricultural soils.

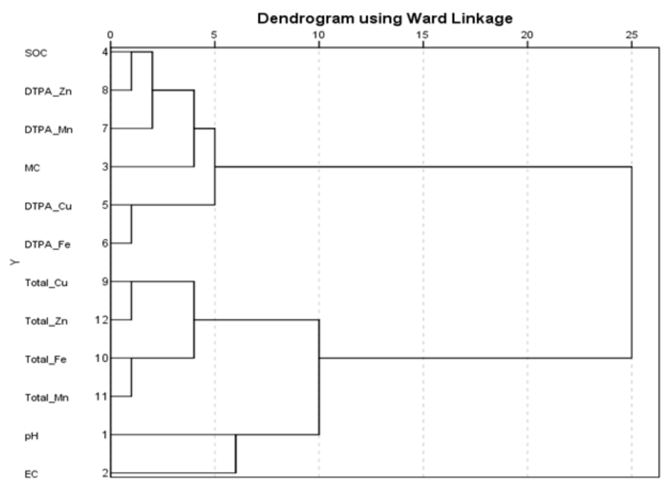

Fig. 3: Hierarchal dendrogram showing a clustering of micronutrients and soil properties using Ward's method

4. CONCLUSIONS

Distribution of total and DTPA extractable micronutrient concentrations (Cu, Fe, Mn and Zn) and physico-chemical properties in agricultural soils of arid and semi-arid regions of Central India were studied. The results shows that the DTPA extractable micronutrients are highly correlated with soil organic carbon and moisture content. However, concentration of total micronutrients do not show any relation with DTPA extractable micronutrients. Principal component analysis and hierarchical cluster analysis revealed two possible sources of micronutrient inputs in the soils. DTPA extractable Cu, Fe, Mn and Zn mainly come from agricultural activities whereas, total content of micronutrients are closely associated with the soil parent material. Soil pH is found to be negatively correlated with bioavailability of micronutrients. Results indicate that the soils are not contaminated but mineral rich geology and indiscriminate use of agrochemicals may alter natural cycling of micronutrients, resulting in Cu/ Zn deficiency and Fe/ Mn toxicity problems.

5. ACKNOWLEDGEMENT

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