Distribution of DTPA-extractable micronutrient cations (Zn, Fe, Mn, and Cu) and its relationship with physico-chemical properties in soils of Birbhum district, West Bengal

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Abstract
The present investigation was carried out for evaluation of the status of DTPA- Zn, Fe, Mn, and Cu in relation with physico-chemical properties in soils of Birbhum district, West Bengal. Total 90 surface soil samples were collected from three different blocks namely Md. Bazar, Nalhati and Bolpur. Collected soil samples were analyzed for pH, electrical conductivity, organic carbon, textural class, Available P and DTPA- extractable micronutrients using standard analytical methods. In general, textural class ranged from sandy loam to sandy clay loam. Soils were strong to moderately acidic in reaction. Electrical conductivity was found in normal range. Soil organic carbon status ranged from 0.24 to 0.81% and was low in available P status. The status of available Zn was sufficient to high level while status of available Fe, Mn and Cu was high. The DTPA-extractable zinc content in the surface soils under study varied from 0.37 to 1.28 mg kg\(^{-1}\) with an average value 0.856 mg kg\(^{-1}\). The available iron, manganese and copper contents in soils ranged from 36.8-45.1, 15.1-17.9 and 2.5-3.2 mg kg\(^{-1}\) respectively. From the correlation study it was found that soil pH significantly and negatively correlated with available zinc (r= -0.233*), iron(r= -0.42**) and manganese(r= -0.324*) whereas non- significantly with available copper (r= -0.132) content. Soil organic carbon showed significant and positive correlation with all the micronutrients except copper content. Non-significant and negative correlation was found between electrical conductivity and available micronutrients. Clay content correlated significantly and negatively with available Mn (r= -0.172*) and positively with available Zn (r=0.535**). Significant and negative correlation showed between available P with available Zn and Fe.

Keywords: Correlation, micronutrients, physico-chemical properties, DTPA, Birbhum district

Introduction
Soil is one of the most important natural resources which is crucial for life on earth. Soil is the base of the life, which support all the living organisms of the earth. Plant depends upon the nutritional status of the soil for their growth and completion of the life cycle. The optimum plant growth and crop yield depends not only on the total amount of nutrients present in the soil at a particular time but also on their availability which in turn is controlled by physical and chemical properties of soil. Along with macronutrients (nitrogen, phosphorus, potassium, sulphur), micronutrients (zinc, iron, manganese, copper) are of immense importance in order to maintain soil health, hence by increasing productivity of crops. Because of imbalanced and inadequate fertilizer use coupled with low efficiency of other inputs, the response (production) efficiency of chemical fertilizer nutrients has declined tremendously under intensive agriculture in recent years.

Micronutrients such as zinc (Zn), copper (Cu), manganese (Mn) and Iron (Fe) are essential nutrients required in very small quantities for normal plant growth by involving in various enzymes and other physiological process including gene expression, biosynthesis of proteins, nucleic acids, growth substances, chlorophyll and secondary metabolites, metabolism of carbohydrates and lipids, stress tolerance etc. (Rengel, 2007 and Gao et al., 2008) \[25, 8\]. Furthermore Zn is essential for protein and auxin production, cu is a constituent of cytochrome oxidase, Fe helps in photosynthesis while Mn is essential for photosynthesis, carbon assimilation and nitrogen metabolism.
Total amount is rarely indicative of the nutrient availability to the plant, because availability influenced by numerous soil parameters like, soil pH, organic content, adsorptive surfaces and other physical, chemical and biological conditions in the rhizosphere zone (Pati and Mukhopadhyay, 2011) [22]. According to (Zende, 1984) [36] the nutrient supply in soils is depends on the level of organic matter, calcium carbonate, degree of microbial activity, change in pH, types and amount of clay and status of soil moisture. Micronutrient availability is greater in soils with heavy texture, high organic matter content and lower pH whereas, coarse textured soils such as sand have fewer reserve and tend to get depleted rather quickly (Yadav and Meena, 2009) [15].

Due to use of HYV's and intensive cropping along with application of high analysis primary nutrient fertilizers leads to decline micronutrient status in our soil system (Mathur et al., 2006) [17]; Somasundaram et al., 2009 [30]; Sharma et al., 2009) [27]. Keeping these in view and also lack of information on micronutrients status to identify the emerging micronutrient deficiency or toxicity in the soils of Birbhum district, therefore a comprehensive study was undertaken for evaluation of DTPA-extractable micronutrient cations (Zn, Cu, Mn, Fe) and its relationship with physico-chemical properties in soils of Birbhum district, West Bengal, which will be useful in judging the deficiency of various element and thereby use of efficient fertilizer management practices.

Materials and Methods

Study area

The present study was conducted on the soils of different blocks of district Birbhum in West Bengal state. The geographical area of the district is 4545 sq. Km with 5.12% of the total area of the state. It is the 9th biggest district by area in the state. The district is situated between 23°30' 30' north latitude and 87° 5' 25" and 88° 1' 40" east longitudes. Geographically, this area lies at the north eastern end of the Chota Nagpur Plateau, as it slopes down and merges with the alluvial plains of the Ganges. The climate on the western side is dry and extreme but is relatively milder on the eastern side. During summer, the temperature can shoot well above 40 °C (104 °F) and in winters it can drop to around 10 °C (50 °F). Rainfall is higher in the western areas as compared to the eastern areas.

Soil sampling

Thirty soil samples (0-15 cm) were collected from the farmer’s field from each three blocks namely Md. Bazar, Nalhati and Bolpur of Birbhum district, were air dried, ground in a wooden mortar, passed through 2 mm sieve and stored in polythene bags for various analysis.

Soil analysis

Soil samples were analyzed for texture using Hydrometer method by using sodium hexa meta phosphate as a dispersing agent as described by Bouyoucos (1927). Soil reaction (pH) was measured in 1:2.5 soil: water suspension with a digital glass electrode pH meter (Jackson 1973) [11]. Electrical conductivity was measured using conductivity meter as outlined by Jackson (1973) [11] under suitable measuring conditions. Walkley and Black’s (1934) [34] wet oxidation method was used for determination of organic carbon (OC). Available phosphorus was extracted with Bray No-1 solution as extractant (Bray, 1945) [3] and using spectrophotometer at wave length of 660 nm. Plant available (DTPA-extractable) cationic micronutrients via Zn, Cu, Mn, and Fe in soils were extracted using DTPA (0.005 M DTPA + 0.01 M CaCl2 + 0.1 M TEA, pH 7.3) at 1:2 soil to extractant ratio as described by Lindsay and Norwell (1978) [15] and determined on atomic absorption spectrophotometer. Based on the available soil micronutrient status, the soils were grouped into three categories as, deficient, sufficient, and high (Table.1). The relationship between various soil properties and cationic micronutrient distribution were established by using simple correlation coefficient.

Result and Discussion

Physicochemical properties

The values of physico-chemical properties with range and average for the different blocks of the district are presented in Table 2. Particle size distribution study revealed that the texture varied from sandy loam to sandy clay loam. Dominant fraction in these soils was sand, which might be due to high rainfall and the parent material from which the soil was derived. The results of the study were in conformity with the findings of Sathyarayana and Biswas (1970) [20]. The pH of most of the soils was strong to moderately acidic in nature. The type of parent material and leaching of basic cations might be the reason for that. Similar finding was reported by Chakravarti et al., (1957) [4]. Electrical conductivity in the soils under study and was found to be normal with respect to plant growth. Soil organic carbon status in soils of three different blocks ranged from 0.24 to 0.73%, 0.28 to 0.76% and 0.25 to 0.81% respectively. Soils from Md. Bazar block showed low amount of organic carbon content. This might be due to intensive cropping and improper soil management. Available P content varied from 12.04 to 42.4 kg ha⁻¹ with a mean value of 27.09 kg ha⁻¹, which indicates that most of the soils under study came under low available P status. Acidic soil reaction might be the reason for low P content in these soils. This result agrees with findings of Deshmukh (2012) [7], Pandit et al., (2016) [20] and Das et al., (2010) [6].

Status of available micronutrients

The data revealed that DTPA-extractable zinc content in the surface soils under study, varied from 0.37 to 1.28 mg kg⁻¹ with an average value 0.856 mg kg⁻¹. Out of ninety samples only 18% of the samples were comes under deficient. Soils of Nalhati block were found to contain higher amount of DTPA-extractable zinc which may due to the high organic carbon content as like findings of Krishnamurthy and Srinivasasamurthy (2001) [12] and Chidanandappa et al., (2008) [5] and Kamar et al., (2017) [13].

The DTPA-extractable Fe content of the soils ranged from 28.9-36.4, 46.3-55.6 and 35.2-43.4 mg kg⁻¹ in blocks of Md. Bazar, Nalhati and Bolpur respectively. All the soil samples under study were found to be having high iron levels. Among three blocks, soils of Nalhati were showed that highest amount of Fe levels. The high amount of Fe content in these soils might be due to the leaching of exchangeable bases from the surface soils (Hrangbung et al., 2018) [10] and presence of high organic matter content as reported by Prasad and Sakal (1991) [23] and Sunandana et al., (2019) [11].

The DTPA-extractable Manganese content of the soils were found to contain high available manganese value. Mn content of soils under study varied from 15.1-17.9 mg kg⁻¹ with an average value of 16.53 mg kg⁻¹. The lowest (12.5 mg kg⁻¹) value of Mn was recorded in soils of Md. Bazar block while highest (19.6 mg kg⁻¹) value of Mn content was observed in soils of Nalhati block. The higher content of Mn in these soils are usually associated with the higher content of organic matter and presence of sand which have fewer reserve and tend to get depleted rather quickly (Yadav and Meena, 2009) [15].

Soils of Nalhati block. The higher content of Mn in these soils is greater in soils with heavy texture, high organic matter content and lower pH whereas, coarse textured soils such as sand have fewer reserve and tend to get depleted rather quickly (Yadav and Meena, 2009) [15].

According to (Zende, 1984) [36] the nutrient supply in soils is depends on the level of organic matter, calcium carbonate, degree of microbial activity, change in pH, types and amount of clay and status of soil moisture. Micronutrient availability is greater in soils with heavy texture, high organic matter content and lower pH whereas, coarse textured soils such as sand have fewer reserve and tend to get depleted rather quickly (Yadav and Meena, 2009) [15].
might be due to high acidity and chelating of organic compounds released during the decomposition of organic matter. These results were confirmatory with results obtained by Mandavgade et al., (2015) [16] and Sunandana et al., (2019) [33].

The data presented in table 2 showed that DTPA-copper varied from 2.5 to 3.2 mg kg⁻¹ with a mean value of 2.85 mg kg⁻¹. The result is in conformation with the finding of Meena et al., (2017) [18] and Bharteezy et al., (2017) [17]. Out of total 90 soil samples collected from farmer’s field more than 90% soils found high in Cu content. This is in confirmation with the finding of Pandey et al., (2013) [19] and Singh et al., (2015) [29].

**Relationship between DTPA extractable micronutrients and soil physico-chemical properties**

The current study showed that, DTPA extractable zinc exhibit positive and significant correlation with clay content (r = 0.535**) and organic matter (r = 0.362**), whereas negative and significant correlation with soil pH (r = -0.233*) and available P (r = -0.588**), table 3. The negative correlation with pH may be attributed to their precipitation as hydroxides and carbonates consequently making them immobile and unavailable to the plants. Similar results were obtained by Shinde (2007) [28]. The positive correlation between available zinc and clay content indicates that available zinc status increases with increasing fineness similar observation was made by Kumar et al., (2011) [14] and Meena et al., (2017) [18]. The positive correlation between available zinc and organic carbon content indicates that zinc forms soluble complexes (Chelates) with soil organic matter component as reported by Mandavgade et al., (2015) [16]. DTPA extractable iron showed significant and negative correlation with soil pH (r = -0.42**) and available P (r= -0.24**). The negative correlation with pH indicates that solubility of iron in soil decreases along with increasing pH by the formation of insoluble precipitate. Similar results were also reported by Gupta (2003) [30] and Yadav and Meena et al., (2009) [35]. While negative correlation with available P may due to the precipitation of sparingly soluble iron-phosphate compounds in the soil. The available Fe significantly increased with increase in organic carbon (r = 0.425**). The positive correlation of Fe with soil organic carbon might be due to the formation of the relatively more soluble Fe-organic chelates (Talukdar et al. 2009 and Ray et al., 2016) [32, 24].

Correlation study showed that like other micronutrients, availability of Mn also decreased with increase in soil pH (r = -0.324*) which may due to the formation of insoluble higher valent oxides of manganese at higher pH. It is confirmatory with findings of Patel et al., (2019) [21] and Sunandana et al., (2019) [31]. The availability of manganese in these soils reduced with increase in clay content (r = -0.172*) which may due to absorption of metal ions by clay particles. The similar results were studied by Vijayakumar et al., (2011) [33], Ray et al., (2016) [24] and Patel et al., (2019) [21]. The availability of manganese in these soils enhanced with increase in OM content of the soil (0.523**) as reported as Sunandana et al., (2019) [31]. Available copper in soils under study correlated non-significantly and negatively with pH (r = -0.132) and organic carbon (r = -0.023). Negative correlation with pH indicates that at higher pH copper precipitates as copper hydroxide Cu(OH)₂ which is not readily available to the plants. High OM content reduces availability of Cu which may due to formation of complex formation with organic matter, similar findings also reported by Vijayakumar et al., (2011) [33].

**Table 1: Rating limits for soil test values used in India**

| Elements | Deficient | Sufficient | High |
|----------|-----------|------------|------|
| Fe       | < 4.5     | 4.5-9.0    | >9.0 |
| Mn       | < 3.5     | 3.5-7.0    | >7.0 |
| Cu       | < 0.2     | 0.2-0.4    | >0.4 |
| Zn       | < 0.6     | 0.6-1.2    | >1.2 |

**Table 2: Physico-chemical characteristics in the soils of Birbhum district**

| Block | pH | EC (dS m⁻¹) | Organic C (%) | Available P (Kg/ha) | DTPA-Zn (mg/kg) | DTPA-Fe (mg/kg) | DTPA-Mn (mg/kg) | DTPA-Cu (mg/kg) | Textural Class |
|-------|----|-------------|---------------|---------------------|----------------|----------------|----------------|----------------|----------------|
| Md. Bazar | 4.35-5.84 | 0.01-0.08 | 0.24-0.73 | 9.08-43.31 | 0.33-1.30 | 28.9-36.4 | 12.5-16.8 | 2.9-3.7 | SCL |
| Mean | 4.90 | 0.04 | 0.47 | 26.38 | 0.84 | 32.65 | 14.65 | 3.3 | |
| Nalhati | 5.91-6.94 | 0.01-0.07 | 0.28-0.76 | 18.02-42.89 | 0.35-1.26 | 46.3-55.6 | 17.8-19.6 | 2.2-2.8 | SCL |
| Mean | 6.47 | 0.03 | 0.56 | 29.72 | 0.88 | 50.95 | 18.7 | 2.5 | |
| Bolpur | 4.66-5.75 | 0.01-0.07 | 0.25-0.81 | 9.21-41.0 | 0.45-1.28 | 35.2-43.4 | 15.2-17.3 | 2.4-3.1 | SCL |
| Mean | 4.92 | 0.03 | 0.49 | 25.8 | 0.85 | 39.3 | 16.25 | 2.75 | |

**Table 3: Correlation in between DTPA-extractable micronutrients and physico-chemical properties in soils of Birbhum district**

| Soil Properties | Zn | Fe | Mn | Cu |
|----------------|----|----|----|----|
| pH             | -0.23** | -0.42** | -0.24* | -0.132 |
| EC             | -0.023 | -0.04 | -0.142 | -0.032 |
| OC             | 0.362** | 0.425** | 0.523** | -0.023 |
| Clay           | 0.535** | 0.23 | -0.172* | 0.118 |
| Available P    | -0.588** | -0.24** | 0.34 | 0.021 |

* - Significant at 5% ** - Significant at 1%

**Conclusion**

The soil analytical data of Birbhum district clearly indicates that soils are were strong to moderately acidic in reaction with normal soluble salt content. The content of organic carbon classified as normal to high category, The status of available Zn was sufficient to high level while status of available Fe, Mn and Cu was high. From the correlation study it was found that soil pH significantly and negatively correlated with available zinc, iron and manganese, whereas non-significantly with available copper content. Electrical conductivity correlated non- significantly and negatively with DTPA extractable micronutrients. Organic carbon content correlated significantly and positively with all the available micronutrients except copper. The information of the present study could be useful in micronutrient fertilization strategy in soils of Birbhum district, West Bengal.

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