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Categorization of DTPA extractable micronutrients using GIS techniques in tehsil Muzaffargarh, Punjab, Pakistan

Aftab Ahmad Sheikh[1], Muhammad Akram Qazi[1], Naveed Iqbal Khan[1], Anam Farooq[1], Farah Umar[1], Rehman Gul[1], Maryam Shafique[1], Haseeb ur Rehman[2], Zafar Kalyar[1], Khurram Shehzad[1], Abdul Waheed[1], Abdul Manan Saeed[1], Zahid Hassan Tarar[1], Hafeez-u-Rehman[1], Muhammad Salik Ali Khan[3*], Muhammad Shoaib Aslam[1], Sher Afzal[1] and Annum Sattar[1]

[1]Soil Fertility Research Institute, Punjab, Pakistan
[2]Muhammad Nawaz Shareef University of Agriculture, Multan
[3]Provincial Reference Fertilizer Testing Laboratory, Raiwind, Lahore

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Abstract

Soil health in terms of plant available nutrients is crucial to estimate the yield potential of agricultural land in an area. Based on the availability of soil health data, it is possible to set yield targets using various yield prediction models. This study was initiated to estimate the concentration of DTPA-extractable micronutrients in Tehsil Muzaffargarh and to develop a database that can be used to develop predictive models. Soil samples (n=11537) were collected from Muzaffargarh (0-15 cm depth). The latitude and longitude values of sampling points were recorded for the purpose of georeferencing the soil samples. Micronutrients such as zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) were extracted with diethylenetriamine penta-acetate (DTPA) extraction solution and their concentrations were determined with atomic absorption spectrophotometer. Water soluble boron (B) was determined spectrophotometrically using Azomethine-H as colour developing reagent. Critical limits established by the National Agricultural Research Center (NARC) Islamabad, Pakistan, were used as a benchmark for grading micronutrient status. The ordinary kriging technique was used to visualize the micronutrient status in the surveyed area and digital maps were prepared using Quantum Geographic Information System (QGIS) software. Results showed that the range of DTPA-extractable micronutrients Zn, Fe, Mn, and Cu ranged from 0.10-5.92, 0.01-12.51, 0.09-10.00 and 0.03-8.08 µg/g, respectively. Boron concentration ranged from 0.02-1.98µg/g. Most of the soils in the studied area had adequate levels of Zn (61.9%) and Cu (48.6%) while 45.8, 43.3 and 55.4 % of the soil samples fell into the marginal category in terms of Cu, Mn, and B, respectively. The results revealed the widespread deficiency of DTPA-extractable Fe (< 4.5mg kg^{-1} in 74% soil samples) in Tehsil Muzaffargarh. The digitized maps developed from this study would serve as primary source to locate micronutrient deficient areas and also set site-specific yield targets along with other biophysical factors. However, these maps need ground truthing after crop harvest each year.

Keywords: Plant available micronutrients; critical limits; kriging; digitized maps

Introduction

Agriculture sector has a major contribution (21% of GDP) in the economy of Pakistan. Almost 48% of employment is linked directly or indirectly with this sector. Punjab is the most populated province of Pakistan and covers 20.63 million hectares (Hussain *et al.*, 2015). As a populous and agricultural province, it should not only meet its own food needs, but is also obliged to supply the whole country with agricultural products. The prerequisite to increase agricultural yield per unit area is the availability of primary information of all biophysical and chemicals factors related to crop yield in a specific area. The primary information may include variability in soil macro- and micronutrients, microclimate, land use, soil topography, management practices and others (Whetton *et al.*, 2021).

Although all factors are crucial for optimum yield, but among all of these factor part of plant nutrients has indispensable place and their deficiency could reduce quantity and quality of produce. In present era of high

***Email:**-msalikali786@gmail.com
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population where food security is a major constrain we cannot comprise with low yield. Every nutrient (micro and macro) has a well-established and unique behavior in soil with respect to its plant availability. Hence, soil analysis data has undoubtedly gained significant weightage in predicting site-specific yield potential. A number of survey studies have been carried out globally to monitor soil nutrients status. However, a significant part of soil data is unused (Ghasemi *et al.*, 2009).

In developing countries like Pakistan where population is increasing day by day and this increasing population demanding a huge amount of food from agriculture sector that is directly linked with soil nutrients availability (United Nations, 2012). On the same time malnutrition due to deficiency of micronutrients is also a though provoking issue in countries (Karimizarchi *et al*., 2014) i.e., Pakistan, Nepal, Sri lanka, Nigeria and India etc.

In soil numerous factors are responsible for micronutrient availability and among these soil chemical properties such as pH and calcium carbonate are most imperative which are antagonistically correlated with availability of micronutrients (Niaz *et al*. 2007). Generally, 80% soils of Pakistan are alkaline in nature with pH ranging from 7.5 to 8.5 (hmed *et al*., 2020: Muhammad *et al*. 2008; Rashid *et al.*, 1997a). This alkaline nature of soil strongly restricts the bio-availability of micronutrients to plants especially 100 folds for zinc (Khan *et al.*, 2010; Khan *et al.*, 2013) and 1000 folds for iron with each unit increase in pH. Addition to soil pH in Pakistan, high cropping intensity (Rashid *et al*., 2006) introduction of new high yielding varieties and predominant application of macronutrients (N,P,K) are other important reasons for deficiency of micronutrients. Most of crops are more susceptible to micronutrient deficiencies than macronutrients (Tariq *et al*., 2014; Imtiaz *et al*., 2006) which negatively effects the crop yield.

Micronutrients has a key role in plant growth (Souri and Aslani 2018a; Souri and Bakhtiarizade, 2019b) and their deficiency may effects growth, yield, reproduction (Malakouti, 2007) and different physiological and metabolic process (Gurjar *et al*., 2015, Gao *et al*., 2008). Zinc plays a role in enzymatic activities and act as a cofactor (Phillips 2004), manganese is crucial for photosynthesis and net assimilation rate of plants (Dutta and Dhua 2002). Boron deficiency is a serious common problem in Pakistan (Ahmed *et al*. 2011), Iron has an important role in chlorophyll contents of plants and fruit quality as well (Tagliavini *et al.*, 2000; Souri *et al*., 2018a) and Copper is imperative for the metabolic process (Ilyas *et al*., 2015).

Deficiency of micronutrients is observed in many crops such as serious yield reduction in rice is observed by Zn deficiency in Asian countries (Rehman *et al*., 2012), yield and growth reduction in Chickpea (Mehboob *et al*., 2021) yield reduction in alfalfa, sugar beets, and legumes (Sarkar *et al*., 2012) and low yield and fiber quality of cotton due to boron deficiency (Atique-ur-Rehman *et al*., 2020).

Addition to crops micronutrient are requisite for humans, a daily intake of 10-60 mg for Fe, 2-3 mg for Cu and 15 mg for Zn for young adult (Imtiaz *et al*., 2010) is compulsory for normal physiological processes. Deficiency of micronutrients can cause serious health hazardous such as impaired immune system (Brown and Wuehler, 2000), baby-killer diseases such as pneumonia and diarrhea due to Zn deficiency (Bhargava *et al*., 2001) and anemia due to deficiency of Fe (Ramzani *et al*., 2016; WHO, 2010).

The deficiency of micronutrients is reported in many regions of Pakistan, 26.6% deficiency of Zn and 80% deficiency of B in district Bhimber of Azad Jammu and Kashmir (Ahmad *et al.*, 2010) and 50% deficiency of Boron, 57% defiance of Zn, and 21% deficiency of Fe is reported in Punjab (PHDEB 2005). Agricultural lands in Chakwal and Jhelum districts were also found to be deficient in plant-available B (Rashid *et al.*, 1997b).

Keeping in view the whole scenario, micro-nutrient indexing in tehsil Muzaffargarh and developing digitized maps could potentially be used to adopt variable-rate (VR) technology in coming years. Variable-rate applicators are controlled by computers and apply fertilizer in the field after getting information from digitized maps. Variable-rate is a better fertilizer management technology over the uniform - rate fertilization (Wittry and Mallarino, 2004). It reduced up to 41% less P fertilizer application and also reduced the Soil-Test-P variability in the area. It is estimated that the damage to global ecosystem due to unwise use of chemical fertilizers is approximately $170 billion annually (Sutton *et al.*, 2013). Hence, site-specific application of agricultural inputs is essential to minimize the environmental and economic repercussions of fertilizer use.

This survey study was conducted with the objectives to; (1) categorize the agricultural land of tehsil Muzaffargarh into different classes depending on the concentration of DTPA-extractable micronutrients using GIS techniques and (2) develop maps showing spatial distribution of micronutrients in tehsil Muzaffargarh. The analysis results were compared with criteria set by Ryan *et al.* (2001) and surveyed area was categorized into low, marginal and adequate classes depending upon the concentration of available micronutrients. This study could help farmers to determine the spatial patterns of micronutrients in soil of tehsil Muzaffargarh and avoid over- or under-application of micronutrients and also setting yield-targets.

Materials and Methods

Study area

Muzaffargarh region falls in arid climate zone with hot summer and mild winter. The recorded temperature ranged from 540ºC to -10ºC with an average annual rainfall of 127mm (Akram *et al.*, 2014). The major crops grown include sugarcane, wheat, and cotton. Main fruit trees are dates, mangoes, pomegranate, and citrus.

Soil Sampling

The surveyed area was divided into grids of 10-acres each (40469 m^2) (GOP, 2018). A total of 11553 soil samples were collected, one sample collected from each grid at a depth of 0-15cm. Samples were air-dried, and sieved through 2mm sieve and analyzed for micronutrient (Lindsay and Norvell, 1978). The georeferenced soil sampling points of

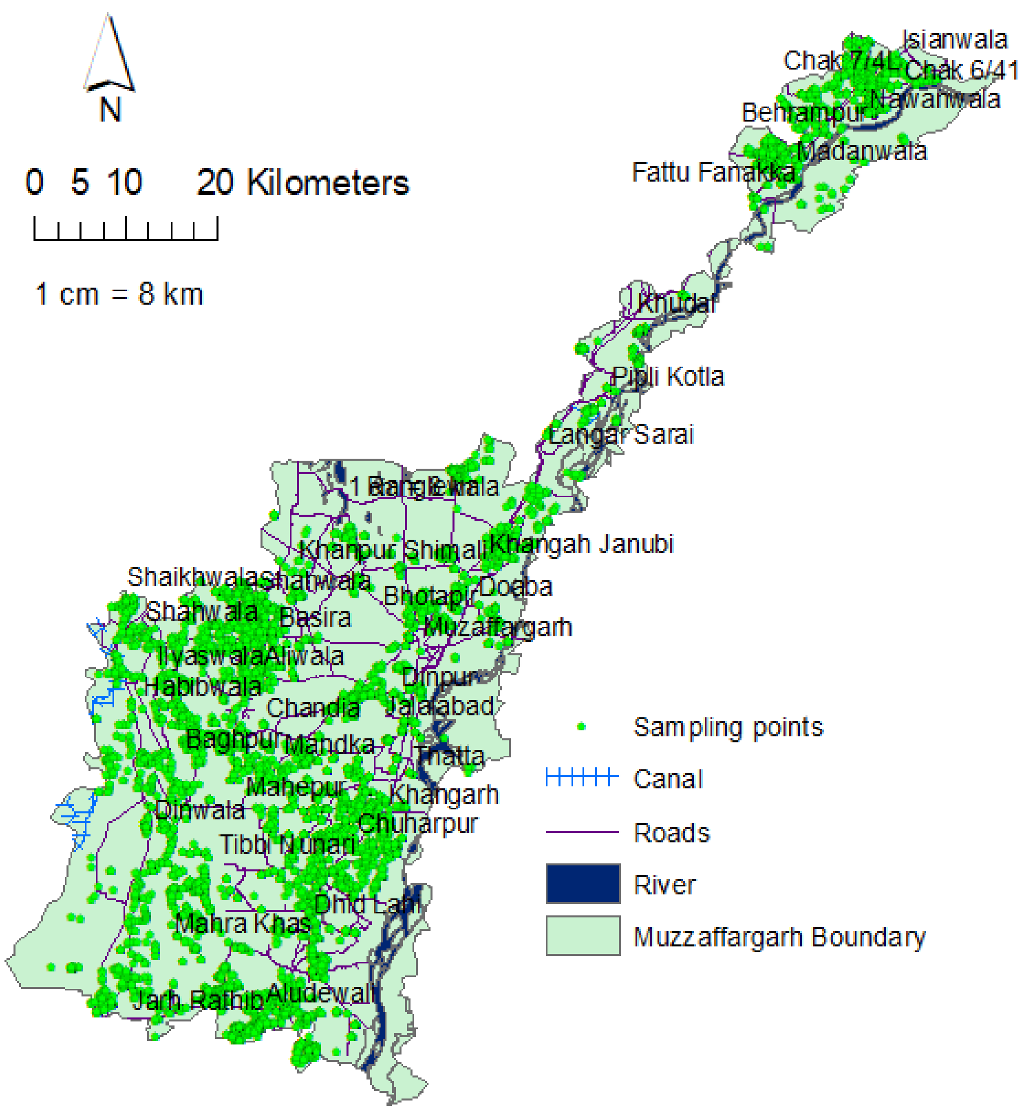

Figure 1: Soil sampling points (green dots) along with georeferenced locations of roads, canal, and river in tehsil Muzaffargarh

tehsil Muzaffargarh along with geographic positions of roads, canal and river is shown in Figure 1.

Table 1: Fertility criteria of DTPA-Extractable zinc, copper, iron, manganese and water-soluble boron and their percent distribution in tehsil Muzaffargarh

Micronutrient (mg kg^{-1} soil)	Class	Status	Count (n=11537)	Percent distribution
	< 0.5	Low	1427	12.4
Zinc	0.5 - 1.0	Marginal	2965	25.7
	> 1.0	Adequate	7145	61.9
	< 4.5	Low	8541	74.0
Iron	-	-	-	-
	≥ 4.5	Adequate	2996	26.0
	< 0.2	Low	647	5.6
Copper	0.2 - 0.5	Marginal	5284	45.8
	> 0.5	Adequate	5606	48.6
	< 1.0	Low	3662	31.7
Manganese	1.0 - 2.0	Marginal	5000	43.3
	> 2.0	Adequate	2875	24.9
	< 0.5	Low	4005	34.7
Boron	0.5 - 1.0	Marginal	6386	55.4
	> 1.0	Adequate	1146	9.9

Source: (Ryan *et al.*, 2001)

Estimation of micronutrients

The (DTPA) extraction methodology is considered appropriate for estimation of micronutrients in soils of Pakistan (Tarar *et al.*, 2020) therefore, it was followed in this study. The pH of extraction solution (mixture of 0.005 M DTPA; 0.01 M $CaCl_2$ and 0.10 M triethanolamine) was adjusted at 7.3. Soil samples and extraction solution (20 g soil and 40 mL extraction solution) were shaken on reciprocating mechanical shaker for 2 hours and filtrate was obtained using Whatman 42 filter paper. Micronutrients were determined using Atomic Absorption Spectrophotometer (AAS) following its operating manual. The instrument was calibrated by Pakistan Council of Scientific and Industrial Research (PCSIR) which is an accredited calibration body (PNAC accredited calibration lab. No. 002). The working standards for Zn, Cu, Fe, and Mn were prepared from Certified Reference Material (CRMs) traceable to National Institute of Standards and Technology (NIST).

Boron was analyzed using Azomethine-H as colour developing reagent. The soil extract was taken by shaking soil sample (10 g) with 0.05N HCl (20 mL) for 5 minutes. The filtrate was used to develop the colour using buffer solution and azomethine-H colour reagent. A series of standard solutions containing 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg L^{-1} boron were prepared from CRM. The absorbance was measured at 420 nm and boron concentration in soil samples were determined from calibration curve (Ryan *et al*., 2001).

Visualization of micronutrients distribution

The analytical results were used to visualize the spatial distribution of micronutrients in the agricultural land of tehsil Muzaffargarh. The projected coordination system WGS 1984 UTM was used to overlay the sampling points on the digitized map of tehsil Muzaffargarh. The ordinary kriging technique was used for interpolation and prediction of micronutrient status between two sampling points. Kriging interpolation transforms soil data points into continuous fields of concerned soil attribute and generate the accurate estimate values for specific area based on measured values.

Classification of soil data

The guidelines for DTPA-extractable micronutrients and soil boron set by National Agricultural Research Center (NARC) Islamabad, Pakistan were used to classify the surveyed area into low, marginal and adequate areas based on the analysis data (Table 1). Quantum Geographic Information System (QGIS) software was used to represent these classified zones in the form of maps.

Statics

The data was analyzed statistically for this purpose, computer software R was used and means were compared.

Results and Discussion

Spatial distribution of DTPA-extractable zinc

Results revealed that 62% soil samples of Muzaffargarh tehsil have adequate amount of DTPA-extractable Zn (>1.0 mg kg^{-1}). Whereas 25.7% soil samples have marginal and 12.4% soil samples showed low concentration of Zn (Table 1; Figure 2). Analysis data when represented in the form of kriged map did not show Zn deficiency. However, 12.4% soil samples fell in the category of low Zn. Overall, surveyed area is free from Zn deficiency except localized spots of deficiency (Figure 3). It might be due to that, mostly, in Pakistan rice growing soils are deficient from Zn (*Rehman et al.*, 2018a; Nadeem and Farooq, 2019) and about 25-50% reduction in rice yield is reported due to its deficiency (Zafar *et al.*, 2022). Zinc is most important nutrient after N, P, K and about 49% soils are deficient from Zn worldwide (Suganya 2015). Zn deficiency is major micronutrient deficiency in Pakistan due to alkaline nature of our soils (Rehman *et al.*, 2020). Higher fixation of Zn reduce its bioavailability (Takkar and Walker, 1993), especially, in rice growing areas (flooded conditions) (Rahmathullah *et al.*, 1976). Performance of Zn fertilizers is not too good (Tahir *et al.*, 1991) and fertilizer use efficiency of Zn fertilizers is < 3.5% which was attributed to the variations in the Zn adsorptive capacity of the soils (Suganya 2015). Although, Zn deficiency is major constrain in Pakistan but Paddy soil conditions are more prone to Zn deficiency compared to other upland crops like wheat (Kausar *et al.*, 1976) and Muzafargarh is not a rice growing area that's might be reason, Zn deficiency observed in small patches only and 12.5% soil is showed low Zn concentration.

Spatial distribution of DTPA-extractable iron

Iron in the studied area ranged from 0.01 to 12.51 mg kg^{-1} soil. The analysis data showed that almost 74% surveyed area is low in Fe and remaining 26% area has adequate concentration of Fe for optimum plant growth (Table 1). Red shaded area in kriged map showed the iron-

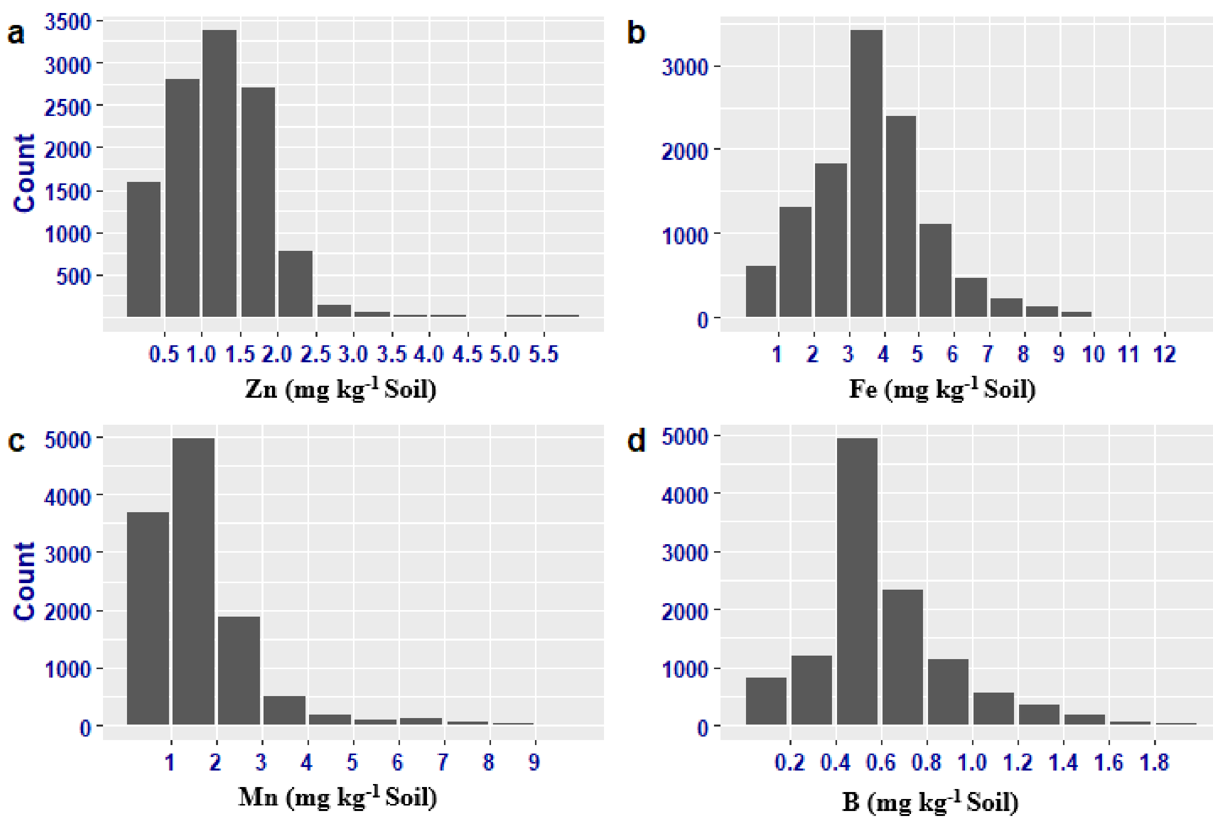

Figure 2: Frequency distribution of DTPA-extractable Zinc, Iron, Manganese and Boron in agricultural land of tehsil Muzaffargarh. Total number of soil samples analyzed were 11537

deficient areas in tehsil Muzaffargarh (Figure 4). About of 80% of Pakistani soils are alkaline in nature with high pH which is a foremost constrain behind low availability of micronutrient including Zn, Fe, B, Mn, Cu, (Rehman *et al*., 2018a; Nadeem and Farooq, 2019). Iron is more sensitive to pH change compared to other micronutrients and one unit increase in pH cause 1000 fold decrease in Fe availability.

Another reason of low Iron availability in soil is that Fe primarily present as oxide, hydroxide of iron and in the form of less soluble ferric iron (Fe^{3+}) mineral (Sarwar *et al*., 2020) especially in calcareous soils. Higher bicarbonate content enhanced the pH and reduce the Fe availability and known as lime-induced iron (Fe) deficiency (Jelali *et al*., 2010; Sarwar *et al*., 2020). Although, plant itself tried to reduce the deficiency of Fe, two strategies are reported through which plants can reduce the iron availability (Altomare and Tringovska 2011; Guerinot 2010). 1st strategy is rhizosphere acidification through extrusion of protons to solubilize the insoluble Fe^{3+} minerals (Santi & Schmidt, 2009), reduction of iron Fe^{3+} to iron Fe^{2+} (Ding *et al*., 2009), 2nd Strategy involves the release of phytosiderophores from roots which form complexes with Fe and made them easily available for plants (Prasad & Djanaguiraman, 2017). But these strategies are failed to mitigate the problems of iron availability in alkaline or calcareous soils of Pakistan, so, application of Fe in plant available form is best option to meet the plant requirement. But in our conditions pH is major constraint which resists the availability of nutrients especially micronutrients to plants and Fe is more sensitive to a change in pH. That's why its deficiency is frequently observed in all type of soil and also reported in present study.

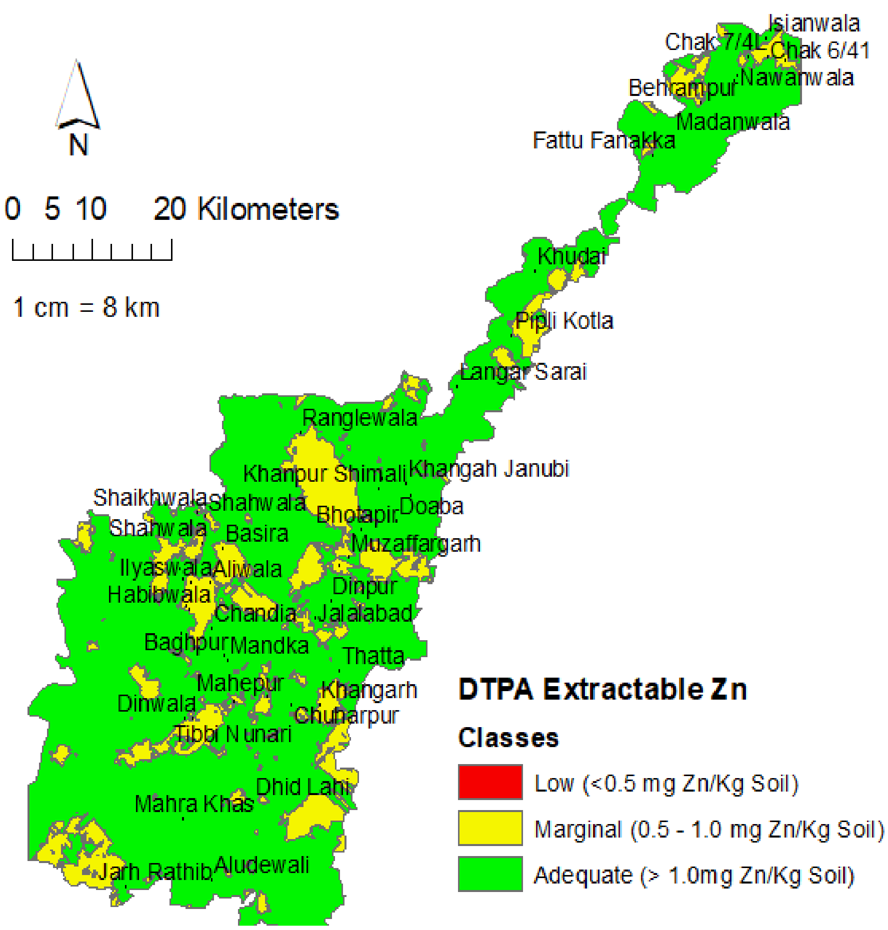

Figure 3: DTPA-extractable zinc in tehsil Muzaffargarh

Spatial distribution of DTPA-extractable copper

Copper concentration ranged from 0.03 to 8.08 with mean of 0.59 mg kg^{-1} soil (Figure 5). Considering the critical limits set by NARC, Islamabad, the 48.6% area falls in adequate range followed by 45.8% area within marginal class regarding the DTPA-extractable Cu. The 5.6% samples

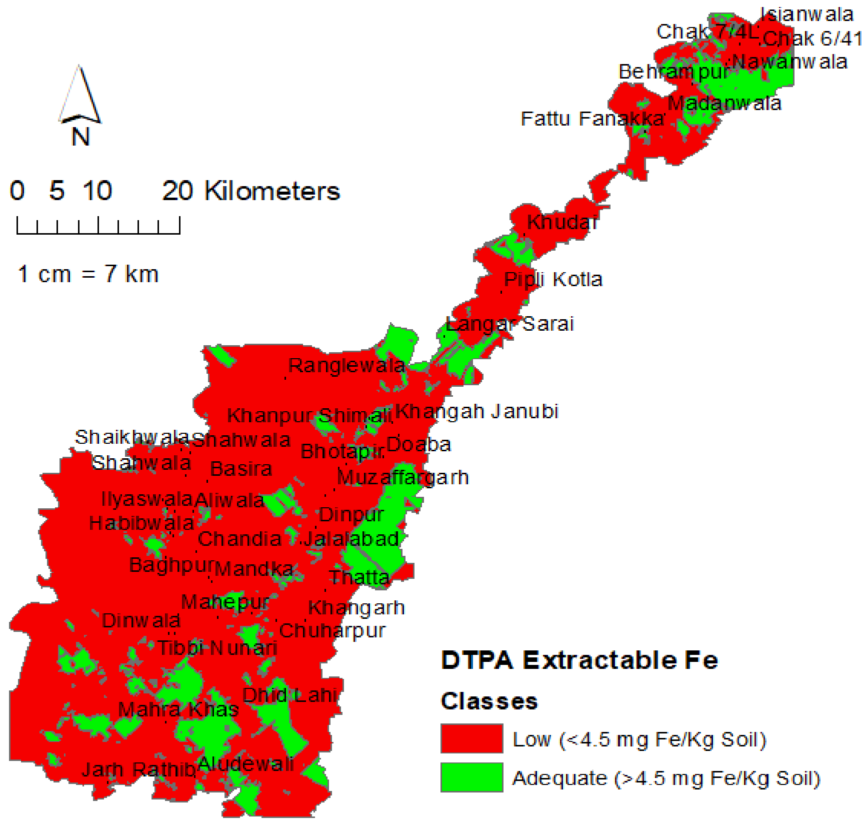

Figure 4: DTPA-extractable iron in tehsil Muzaffargarh

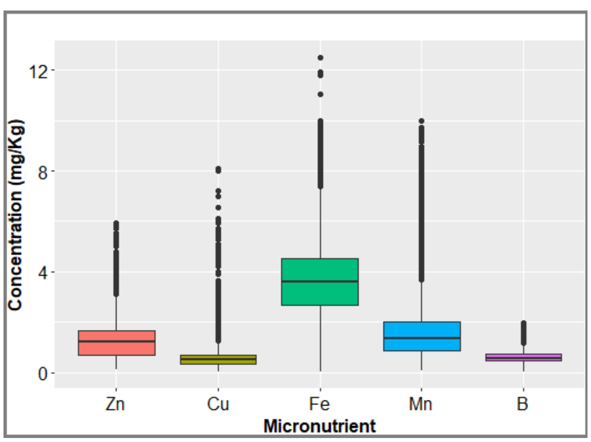

Figure 5: Boxplot representing minimum, maximum and mean values of DTPA-extractable micronutrients in tehsil Muzaffargarh

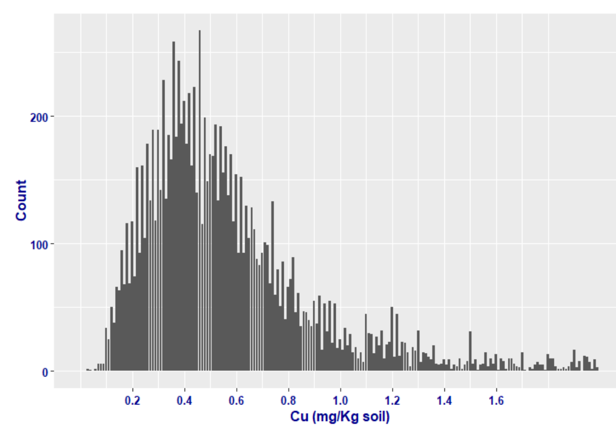

Figure 6: Frequency distribution of DTPA-extractable copper in agricultural land of tehsil Muzaffargarh. Total number of soil samples analyzed were 11537

represented low concentration of Cu (Table 1). The frequency distribution of Cu concentration revealed that majority of soil samples fall within interval of 0.3 to 0.5 mg kg^{-1} soil (Figure 6). The kriged map of spatial distribution of Cu illustrated the marginal concentration in villages Aludewali, Thatta, eastern side of Khanpur, and Pipli Kotla (Figure 7). Copper is another essential micronutrient in plants its deficiency generally observed in peat soils (contain high organic matter) in course sandy soils and in alkaline calcareous soils where pH is more than 7.5 (Mengel *et al.*, 2001). In Pakistan due to alkaline nature of our soils Copper is found deficient in many areas (Kausar, 2022). In above study only small portion of Muzafagarh district (5.6%) is found deficient from Cu, 45.8% fall marginal zone and 48.6% area falls in adequate range. 45.8% area which fall in marginal area is might be due to the presence of $CaCo_3$ and high pH of our soils.

Spatial distribution of DTPA-extractable manganese

The manganese concentration ranged from 0.09 to 10.0 with mean value of 1.62 mg kg^{-1} soil (Figure 5). The analysis data showed 24.9% area as adequate for DTPA-extractable

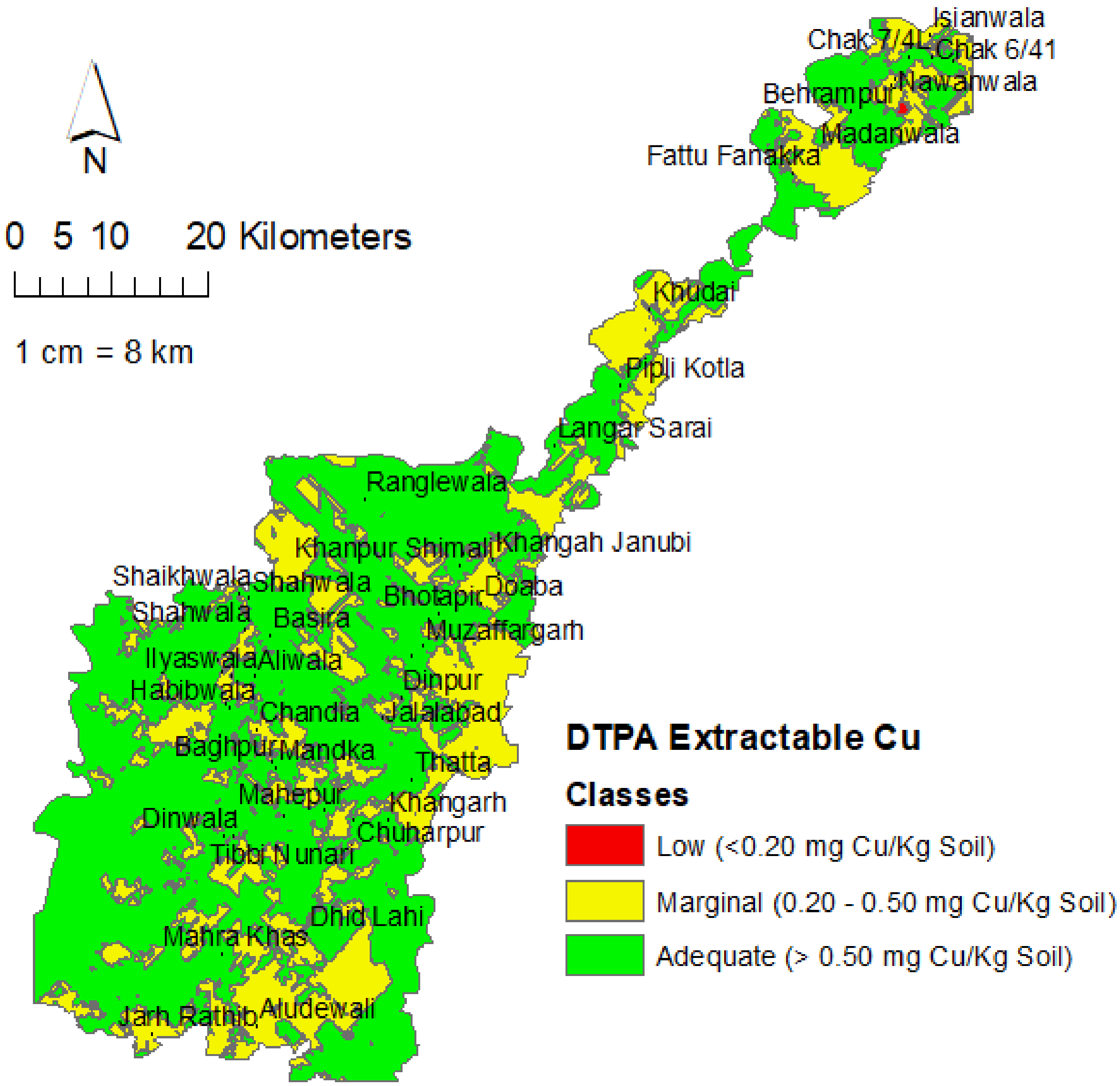

Figure 7: DTPA-extractable copper in tehsil Muzaffargarh

Mn whereas 43.3 % area falls in marginal class. The 31.7 % soil samples showed low concentration of Mn (Table 1). Most of the soil samples (~5000) were in the range of 1 to 2 mg Mn kg^{-1} soil (Figure 2). The spatial distribution map showed village Dinpur, Chandia, Shahwala and portion of Khanpur Shimal as deficient in DTPA-extractable Mn (Figure 8). Manganese is one of the 17 essential elements for plant growth. Although, it is needed in small quantities but it is as critical as the other nutrients. It is involve in photosystem II (PSII) as an essential element of the metalloenzyme cluster of the oxygen-evolving complex (Broadley *et al.*, 2012). In alkaline and calcareous soils due to strong immobilization crop response to Mn fertilizers is unpredictable. Manganese is also pH dependent micronutrient in our soil its bioavailability is major constrain (Babar *et al.*, 2022). In present study 31.7 % samples showed low concentration of Mn which might be due to the presence of $CaCo_3$ and high pH.

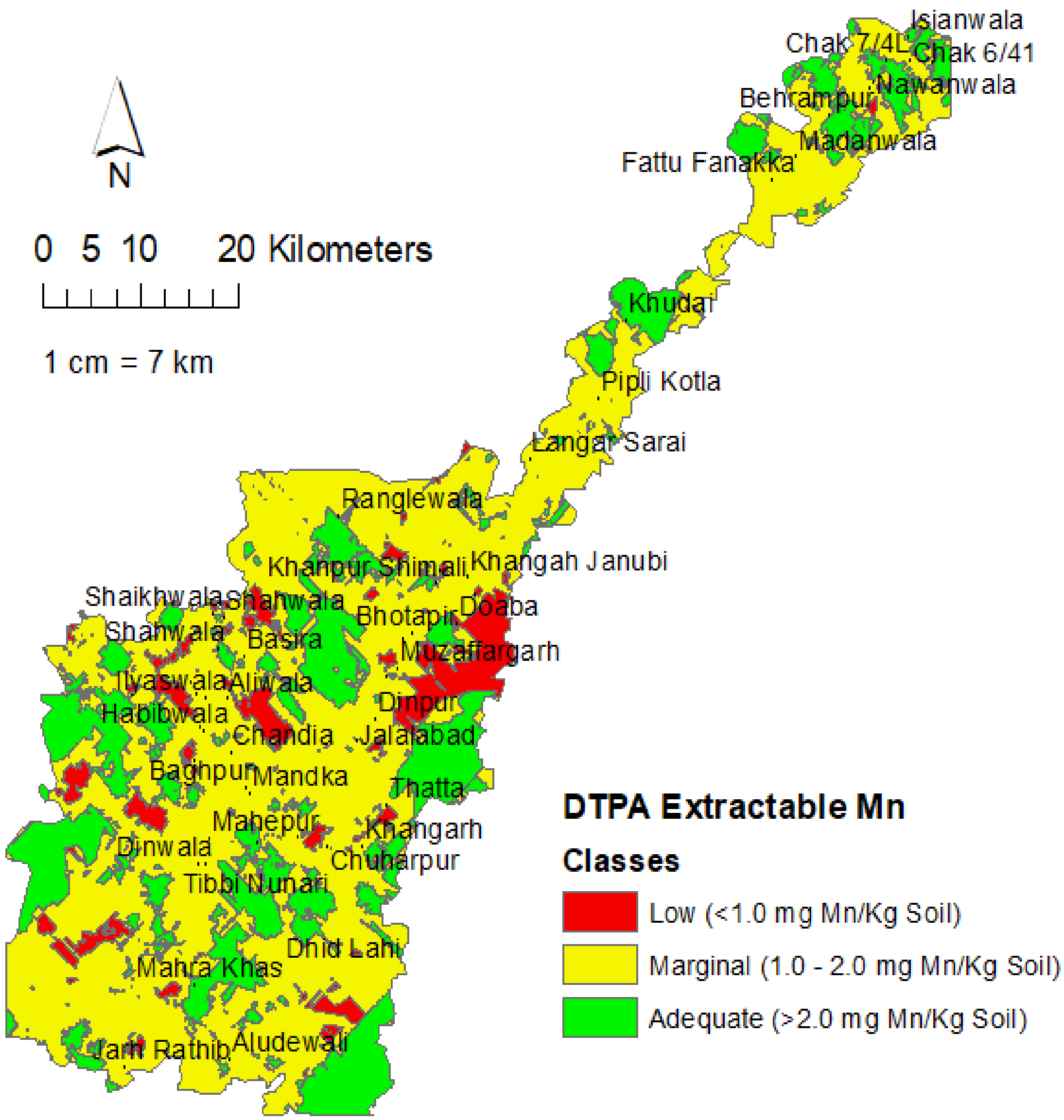

Figure 8: DTPA-extractable manganese in tehsil Muzaffargarh

Spatial distribution of boron

The boron concentration in soils of tehsil Muzaffargarh ranged from 0.02 to 1.98 mg kg^{-1} soil. The average value was 0.61 mg B/kg soil (Figure 5). The frequency distribution showed that most of the samples (~5000) fell within interval of 0.4 to 0.6 mg B/kg soil (Figure 2). The 34.7% soil samples showed low concentration of B whereas, only 9.9 % samples were adequate with respect to critical level of B (Table 1). Low availability of Boron is a serious common problem in Pakistan (Ahmed *et al.*, 2011) it is 2nd most deficient micronutrient after Zn (Rashid, 2006). Boron bioavailability is depend upon various factors including water quality, Temperature, plant species and agronomic practices (Bhupenchandra *et al*., 2020). Further Boron deficiency in Pakistani also related to high pH because B has a high adsorption in alkaline soils (Shorrocks *et al*., 1997; Shorrocks *et al*., 2010). Another reason of B deficiency is our arid to semi-arid climate high temperature and low organic matter. Boron deficiency in our soil is widespread influence the

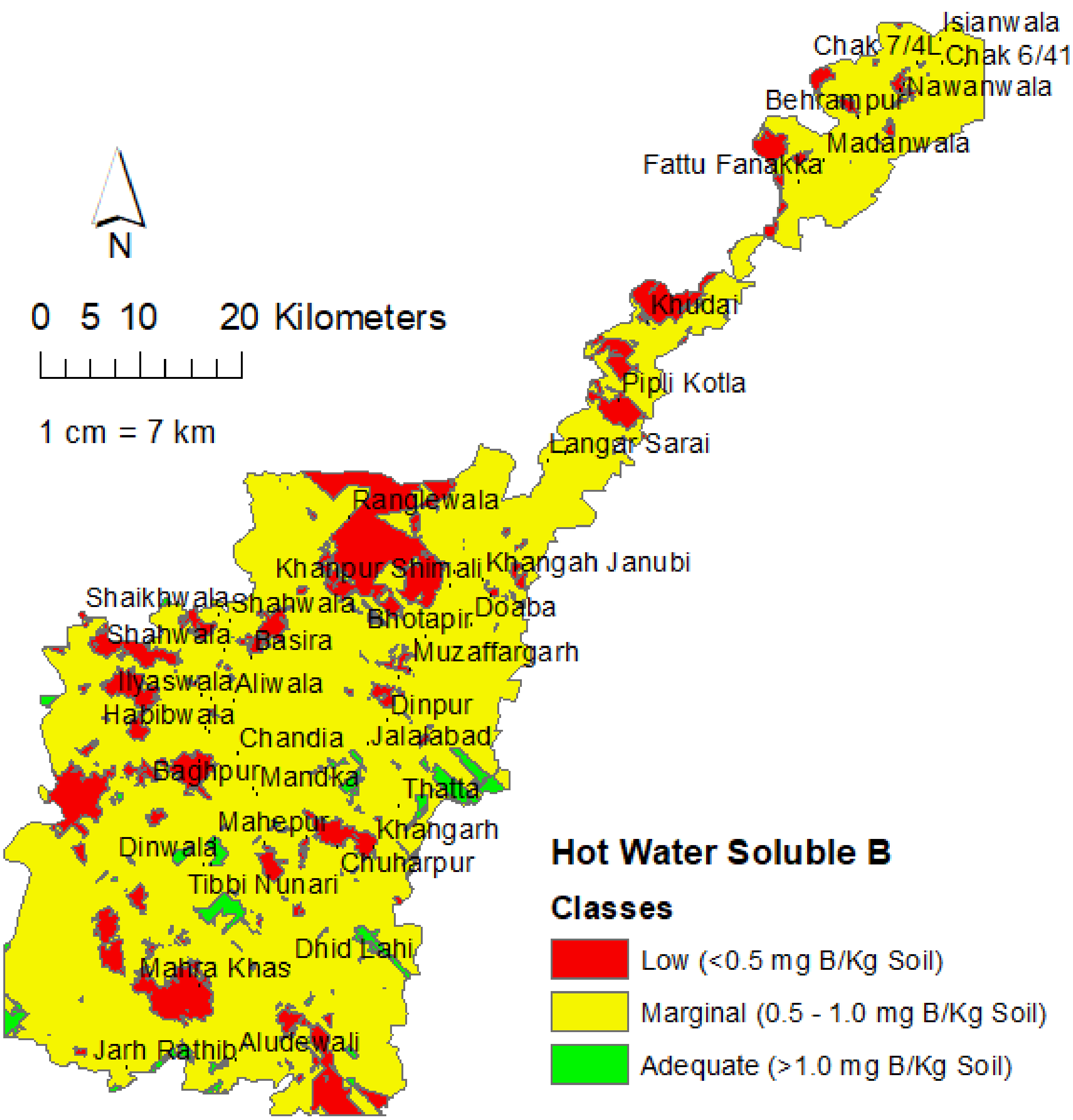

Figure 9: Hot Water-soluble boron in tehsil Muzaffargarh

growth of major filed crops like maize, cotton, wheat, rice, potato, sugarcane, mustard and rapeseed (Tariq and Mott, 2007; Mehboob *et al*., 2021; El-Naggar *et al*., 2015; Haider*et al*., 2021; Kumar *et al*., 2016). Boron deficiency is frequently observed in Typic Haplocambid soils of cotton growing belt of Pakistan (Qamar *et al*., 2020) and half of the cotton-growing area is deficient of B (Ahmed *et al*., 2013) and Muzaffargarh is cotton growing area. Moreover, B-deficiency is a common problem in tropical soils, which have low organic matter and clay contents (Qamar *et al*., 2020; Rosolem *et al*., 2001; Niaz *et al*., 2016) which might be the reason of low B contents in these soils.

Conclusion

Overall status of plant available zinc, copper, manganese was found satisfactory however, the plant available iron and Boron was found deficient in agricultural land of tehsil Muzaffargarh. Iron deficiency is almost observed in all soils and B is also found deficient in Cotton growing areas. The analysis data did not reveal geographical trend of plant available micronutrients in the study area. The georeferenced digital maps developed in this research work could serve best for site-specific application of micronutrients in the study area.

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