MAPPING BORON AND BENEFICIAL HEAVY METAL IONS FOR WHEAT-CULTIVATING SOILS IN TURKEY'S BORON-MINING ZONE

GULMEZOGLU, N.[1*] – AYTAC, Z.[2] – KUTLU, I.[3] – KULAN, E. G.[2] – GOZUKARA, G.[4]

[1]*Eskişehir Osmangazi University, Agricultural Faculty, Department of Soil Science and Plant Nutrition, 26160, Eskişehir, Turkey. (phone: +90-222-324-2991; fax: +90-222-324-2990)*

[2]*Eskişehir Osmangazi University, Agricultural Faculty, Department of Field Crops, 26160, Eskişehir, Turkey. (phone: +90-222-324-2991; fax: +90-222-324-2990)*

[3]*Eskişehir Osmangazi University, Agricultural Faculty, Department of Biosystem Engineering, 26160, Eskişehir, Turkey. (phone: +90-222-324-2991; fax: +90-222-324-2990)*

[4]*AkdeniziUniversity, Agricultural Faculty, Department of Soil Science and Plant Nutrition, 07070, Antalya, Turkey. (phone: +90-0242-310-3748; fax: +90-242-227-4564)*

**Corresponding author*
e-mail: dgulmez@ogu.edu.tr

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Abstract. The mapping of boron (B) and beneficial heavy metals in the agricultural soils of mining zones is essential to evaluating the deficiencies and toxicity of those elements. Given its high annual production of boron, the Kırka Boron Mine (KBM) ranks among the largest mining complexes in Turkey. There, this research was conducted to determine the variation of some properties of soil with B and beneficial heavy metal ions (i.e., Fe, Zn, Mn, and Cu) according to great soil groups and to map their ions in wheat-cultivating soils at different distances from KBM. Results showed that the B, Fe, Cu, Mn, and Zn contents of wheat-cultivated soils changed according to soil group and distance from KBM. The Fe content of soils decreased as the distance from KBM increased, and B content reached toxic values at a distance of 20–30 km. Mn and Zn contents were low, though B and Fe contents were toxic, whereas Cu content was sufficient for wheat cultivation. Available B and beneficial heavy metal maps can be useful in confirming B and Fe pollution and in recommending fertiliser use in mining zones.
Keywords: *great soil groups, fertiliser, Kırka, microelements, pollution*

Introduction

Via special mechanisms, plants intake certain concentrations of beneficial heavy metal ions such as iron (Fe), zinc (Zn), copper (Cu), and manganese (Mn), as well as boron (B), a non-metal ion, from soil. When those ions appear in the soil in adequate amounts, they support the growth of crops by activating various enzymes and supporting cell metabolism (Broadley et al., 2012). Recent research (Nowack et al., 2008; Dwivedi et al., 2012; Gupta et al., 2015; Marathe and Sawant, 2016) has focused on the enrichment of nutrients with nutritional elements, most commonly Fe and Zn, to show that an overabundance of beneficial heavy metals and B in soil is toxic for plants (Alloway, 2013). Those ions appear in agricultural soils at inadequate or excessive concentrations due to industrial processes or the decomposition of the bedrock (Altan et al., 2016). The chief cause of those ions' appearance at excess levels in soil is their presence in mineral reserves found in geological bedrock.

A staggering 72% of the world's boron reserves are in Turkey, among which the Kırka Boron Mine (KBM), given its high annual boron production, is the primary boron mine in the world (Helvacı and Orti, 2004). Kırka is a neighbourhood of Seyitgazi in the district of Eskişehir in Central Anatolia, and though KBM bears a slightly hilly terrain, the agricultural area around Kırka is flat. Most of the cultivated area around the mining zone is composed of soil from the Brown Forest great soil group (BFGSGr) and Brown great soil group (BGSGr) (Anonymous, 2001). Wheat, as a major field crop cultivated in Central Anatolia, yields less (2.5 ton/ha) on average annually there than the wheat yield mean (5.0 ton/ha) of developed countries, and farmers in the region have complained that local boron mines make their fields unproductive (Çiçek ve Gence 2001). Research conducted to determine B toxicity in irrigation water, soil, and plants has shown that levels of B fluctuated in irrigation water, yet were not excessive, whereas the topsoil exhibited B pollution (Emiroğlu et al., 2010; Cetin et al., 2011). Although the amount of B found in the leaf tissue of crops in the area was not toxic, no research has shown the levels of beneficial heavy metal ions in the region's soils. In response, this study aimed to determine the variation of some soil properties with B and beneficial heavy metal ions (i.e., Fe, Zn, Mn, and Cu) according to great soil groups and different distances from KBM, to map those ions in wheat-cultivated soils, and to analyse any correlations among soil properties with B and grain yield.

Materials and Methods

Site conditions

Kırka is located at 39° 16' 59.9" N and 30° 31' 59.9" E at an altitude of 1,053 m and is 23 km from Seyitgazi in the Central Anatolia Region of Turkey (*Figure 1*). The study area covered approximately 156,884 ha, in a region with a hard, semiarid continental climate characterised by dry, hot summers and mostly cold, snowy winters. The total annual precipitation and monthly average temperature in the study area were 311.5 mm and 9.0 °C, respectively, for the last 30 years and 354 mm and 8.2 °C, also respectively, for 2011–2012's wheat cultivation season. The soils of the site mostly consisted of BFGSGr and BGSGr, classified per the US Department of Agriculture's (USDA) soil taxonomy system (Anonymous, 2001; Dinç et al., 2001).

Sampling, analyses, and mapping

Wheat cultivation fields were selected for soil sample collection because wheat is commonly grown in the region. Samples were taken at distances of 0–20, 20–30, and 30–40 km from KBM at a depth of 0–30 cm (180 points) in October 2011 before wheat sowing, and coordinates of the sampling points were measured using the Magellan Triton 400 GPS device (Magellan, North America). Samples included soils of the BFGSGr and BGSGr, as well as a few other soil types, determined by using soil taxonomy maps (Anonymous, 2001).

Samples were dried, sieved through a 2-mm stainless sieve, and subjected to analyses for pH (1:2.5 soil:water), electrical conductivity (EC, 1:2.5 soil:water), lime using a Scheibler calcimeter, organic matter using the Walkley–Black (1934) method, and texture using a hydrometer method. Plant-available beneficial heavy metal (Fe, Cu, Mn, and Zn) concentrations were assessed using methods described by Lindsay and Norwell (1978) via extraction with diethylenetriaminepentaacetic acid (pH 7.3) with an atomic

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absorption spectrometer (Analytik Jena novAA 350, Jena, Germany). After samples were extracted with hot water, B was determined colourimetrically per the azomethine-H method (Wolf, 1971). To gauge related elemental measurements, reference-available nutrients of agricultural soil that were certified reference material from the National Institute of Standards and Technology (Gaithersburg, MD, USA) were used. Readings of pH, lime, (EC), organic matter, available in beneficial heavy metals (i.e., Fe, Cu, Mn, and Zn), and B were classified according to Richards (1954), Ulgen and Yurtsever (1995), Smith and Weldon (1941), Linsay and Norwell (1978) and Berger and Trough (1940), respectively. Wheat grain yields from farmers' fields in the area (ton/ha) were determined by weighing after harvest.

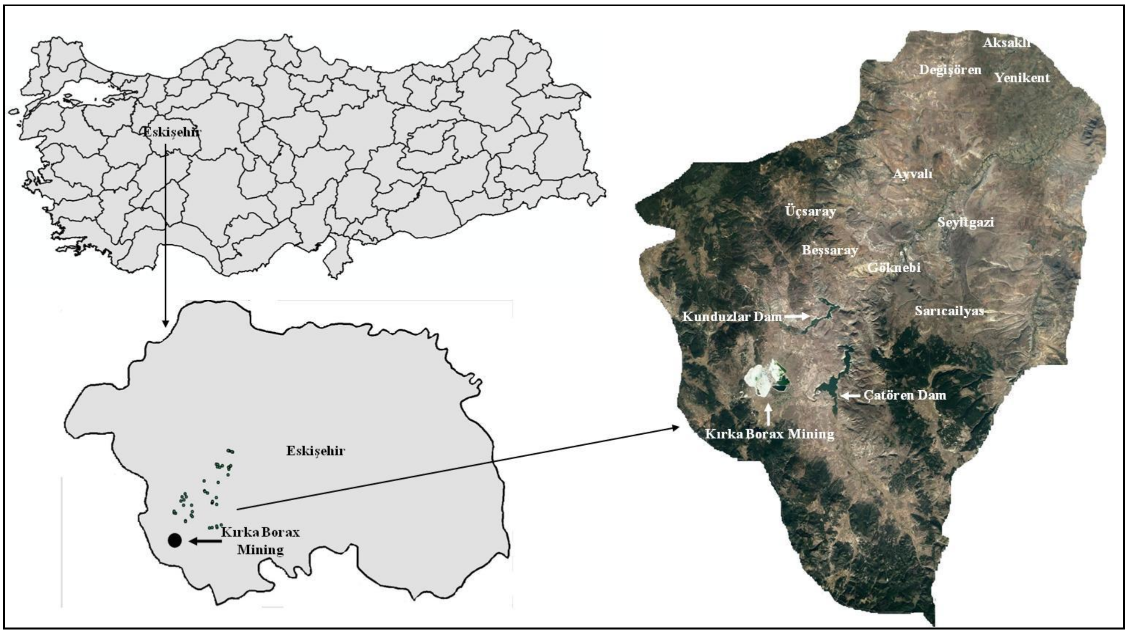

Figure 1. *Location map of the study area and sampling sites*

The dataset representing the samples was evaluated according to descriptive statistics—namely, the minimum, maximum, mean, coefficient of variation (CV), skewness, and kurtosis coefficients—for each variable. CV, a significant indicator of change, in the samples was classified as low (<15%), moderate (15–35%), or high (>35%) (Mulla and Mc Bratney, 2000), whereas skewness and kurtosis values indicated whether data could be generalised with normal distribution. The skewness coefficient revealed how data distribution strayed to the right or left of the norm; a negative result showed that the sample was below the average median, whereas a positive one indicated that it was above the median. If the mean was greater than the median, then the distribution skewed to the right (positive). If skewness is ±2 or less, then it was deemed normal. By contrast, the kurtosis coefficient showed the perpendicularity and oblateness of the normal distribution curve; a positive result meant that the slope was more perpendicular than normal, whereas a negative one indicated that the slope was more oblate than normal. To calculate skewness and kurtosis values, Equation 1 and Equation 2 were used, respectively (Stein, 2002):

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$$\sum_{i=1}^{n} \frac{(y_i - \bar{y})^3 / n}{s^3} \quad \text{(Eq.1)}$$

$$\sum_{i=1}^{n} \frac{(y_i - \bar{y})^4 / n}{s^4} \quad \text{(Eq.2)}$$

in which $\bar{y}$ is the mean, s is the standard deviation, and n is the number of data points.

Relationships between samples with B content and wheat yield were determined by Pearson correlation analysis. All statistical analyses were performed using the SPSS 20.0 (IBM, Armonk, NY, USA). Spatial analyses of B, Zn, Mn, and Fe concentrations in the soils for mapping were performed randomly by inverse distance weighting using ArcGis 10.2 (ESRI Inc., Redlands, USA).

Results

Physical and chemical properties of the soils

Descriptive statistics describing some of the physical and chemical properties of samples from the site appear in *Table 1* and *2*. The vast majority of BGSGr soil had a clay texture (60%), whereas that of BFGSGr had sandy (36%). The pH classification of BGSGr ranged from neutral (pH > 6.9) to slightly alkaline (pH < 8.18), whereas that of BFGSGr was exclusively slightly alkaline (pH 7.97–8.33); the pH of BFGSGr (8.12) was generally higher than that of BGSGr (7.75). The mean lime content of BGSGr samples (11.4%) was far greater than that of BFGSGr (5.7%); whereas the majority of BGSGr had moderate lime content (44%), BFGSGr had less (35%). The organic matter of BGSGr samples (2.49%, low) was less than that of BFGSGr (3.29%, medium), and soil salt concentrations were quite low in both soil groups. The coefficients of skewness and kurtosis indicated that the soil properties were normally distributed; however, the CV of lime content in both group's soils was largely variable and ranged from 70.37% for BGSGr to 127.92% for BFGSGr (*Table 1*).

Table 1. *Descriptive statistics of texture (%), pH, lime ($CaCO_3$)(%), organic matter (OM) (%) and EC (dS/m) of brown forest and brown great soil groups*

Great soil groups	Parameter	Texture			pH	Lime	OM	EC
		Sand	Silt	Clay				
Brown-Forest	Min.	29.30	4.90	14.20	7.97	0.45	2.21	0.17
	Max.	78.70	24.50	62.10	8.33	28.00	4.80	0.44
	Mean	45.64	17.40	36.96	8.12	5.70	3.29	0.24
	CV%	27.85	28.02	28.65	1.37	127.92	23.42	26.48
	Skewness	1.28	-1.12	-0.07	0.24	2.01	0.28	1.73
	Kurtosis	1.46	1.10	0.33	-1.28	3.95	-1.05	3.99
Brown	Min.	27.40	11.00	17.60	6.90	1.13	1.33	0.17
	Max.	58.60	47.70	61.60	8.18	27.40	4.75	0.64
	Mean	37.85	21.90	40.27	7.75	11.44	2.49	0.30
	CV%	20.98	50.57	36.19	4.96	70.37	28.34	33.12
	Skewness	0.85	1.40	-0.26	-0.94	0.75	1.34	1.74
	Kurtosis	0.97	0.88	-1.18	-0.25	-0.53	3.29	3.91

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In the evaluation by distance from KBM, 52% of samples were sandy at up to 20 km. Moreover, 47% of the samples were clay between 20 and 30 km, whereas 43% were clay between 30 and 40 km. The mean lime content, pH, and EC values of the samples increased with distance from KBM up to 40 km (*Table 2*). However, soil salinity (<4 dS/m) was not high for wheat cultivation. Approximately 40% of the samples were low in lime up to 20 km, whereas 33% and 53% of the samples had moderate lime at 20–30 km and 30–40 km, respectively. Approximately 40% of the samples also had high organic matter up to 20 km, 67% low organic matter at 20–30 km, and 60% moderate organic matter at 30–40 km. the CV of lime values of samples decreased with distance from KBM (*Table 2*).

Table 2. *Descriptive statistics of texture (%), pH, lime ($CaCO_3$)(%), organic matter (OM) (%) and EC (dS/m) of distance (km) from Kırka Boron Mine*

Distance	Parameter	Texture			pH	Lime	OM	EC
		Sand	Silt	Clay				
0-20	Min.	30.40	4.90	14.20	6.90	0.45	2.21	0.17
	Max.	78.70	47.70	42.60	8.18	28.00	4.80	0.44
	Mean	51.70	23.18	25.14	7.70	5.98	3.38	0.24
	CV%	25.03	56.84	28.82	5.50	137.24	24.00	29.52
	Skewness	0.73	0.67	0.83	-0.62	1.87	0.01	1.79
	Kurtosis	0.71	-0.50	1.00	-1.03	2.94	-1.08	3.68
20-30	Min.	27.40	11.00	24.70	7.67	0.82	1.33	0.17
	Max.	58.60	21.20	61.60	8.33	25.55	4.04	0.31
	Mean	36.96	16.16	46.90	8.04	9.28	2.38	0.24
	CV%	22.05	18.23	21.10	2.02	86.91	28.22	15.34
	Skewness	1.24	-0.39	-0.39	-0.50	0.96	0.84	0.27
	Kurtosis	2.41	-0.37	-0.38	1.02	-0.44	1.44	0.01
30-40	Min.	29.30	8.60	33.50	7.97	1.13	1.94	0.23
	Max.	49.30	23.30	62.10	8.28	27.40	4.75	0.64
	Mean	37.89	18.89	43.25	8.12	11.41	2.78	0.35
	CV%	12.72	19.84	15.97	1.33	68.45	25.65	30.56
	Skewness	0.72	-1.55	1.21	-0.01	1.07	1.60	1.52
	Kurtosis	1.25	3.03	3.31	-1.51	0.65	3.42	2.89

Microelement contents of the soils

The descriptive statistics of the B, Fe, Cu, Mn, and Zn contents of both soil groups and the distance from KBM appear in *Tables 3* and *4*. The available B and beneficial heavy metal maps of the samples by distance from KBM appear in *Figure 2*. The B, Fe, Cu, Mn, and Zn contents of wheat-cultivated soils changed depending on the soil group and distance from KBM. The maximum (4.26 mg/kg) and mean (1.48 mg/kg) of B content of samples were greater in BGSGr than in BFGSGr (*Table 3*). BFGSGr samples were rich with Fe and Mn, and high B and Zn contents were also detected in BGSGr samples. B and beneficial heavy metal contents except for Cu (CV <35%) showed high variations in both soil groups. The Fe content (3.35) of BFGSGr and Zn content (2.29) of BGSGr were also greater than the acceptable skewness limit (±2), as *Table 3* shows.

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Table 3. *Descriptive statistic of B (mg/kg), Fe (mg/kg), Mn (mg/kg), Cu (mg/kg), Zn (mg/kg) and grain yield (ton/ha) of brown forest and brown great soil groups*

Great soil groups	Parameter	B	Fe	Mn	Cu	Zn	Grain yield
Brown-Forest	Min.	0.63	2.34	2.47	0.42	0.17	1.80
	Max.	2.26	22.78	48.10	1.89	1.30	4.80
	Mean	1.03	5.99	16.14	1.21	0.44	3.20
	CV%	36.29	72.42	86.46	31.47	73.02	26.12
	Skewness	1.96	3.35	0.98	0.13	1.99	0.21
	Kurtosis	5.64	12.86	-0.14	-0.09	3.40	-0.79
Brown	Min.	0.41	1.61	0.15	0.57	0.14	2.50
	Max.	4.26	6.02	37.70	1.82	2.8	5.00
	Mean	1.48	3.25	10.43	1.22	0.58	3.58
	CV%	75.71	36.92	85.90	27.10	119.86	20.22
	Skewness	1.45	1.02	1.98	-0.22	2.29	0.50
	Kurtosis	1.13	0.15	4.43	-0.78	4.46	-0.60

Table 4. *Descriptive statistic of B (mg/kg), Fe (mg/kg), Mn (mg/kg), Cu (mg/kg), Zn (mg/kg) and grain yield (ton/ha) of distance (km) from Kırka Boron Mine*

Distance	Parameter	B	Fe	Mn	Cu	Zn	Grain yield
10-20	Min.	0.63	2.34	2.73	0.42	0.17	3.00
	Max.	2.26	22.78	48.10	1.89	1.30	4.80
	Mean	1.08	5.94	17.16	1.16	0.47	3.61
	CV%	37.94	82.32	88.51	35.66	75.58	16.63
	Skewness	1.75	3.30	0.91	0.38	1.77	0.55
	Kurtosis	4.49	11.78	-0.56	-0.16	2.22	-0.81
20-30	Min.	0.41	1.61	2.47	0.57	0.14	2.10
	Max.	4.13	9.82	24.94	1.69	2.18	4.70
	Mean	1.49	4.27	9.75	1.09	0.46	2.84
	CV%	81.52	48.13	65.22	26.24	110.67	22.89
	Skewness	1.09	1.44	1.57	0.21	3.04	1.64
	Kurtosis	-0.10	2.90	2.06	0.16	10.04	4.17
30-40	Min.	0.57	2.22	0.15	1.16	0.19	3.00
	Max.	4.26	6.02	37.70	1.68	1.98	5.00
	Mean	1.27	3.19	12.00	1.43	0.45	3.90
	CV%	69.21	40.79	93.56	10.27	103.82	15.66
	Skewness	3.23	1.52	1.38	-0.31	2.91	0.42
	Kurtosis	11.18	1.09	1.54	0.04	8.72	-0.23

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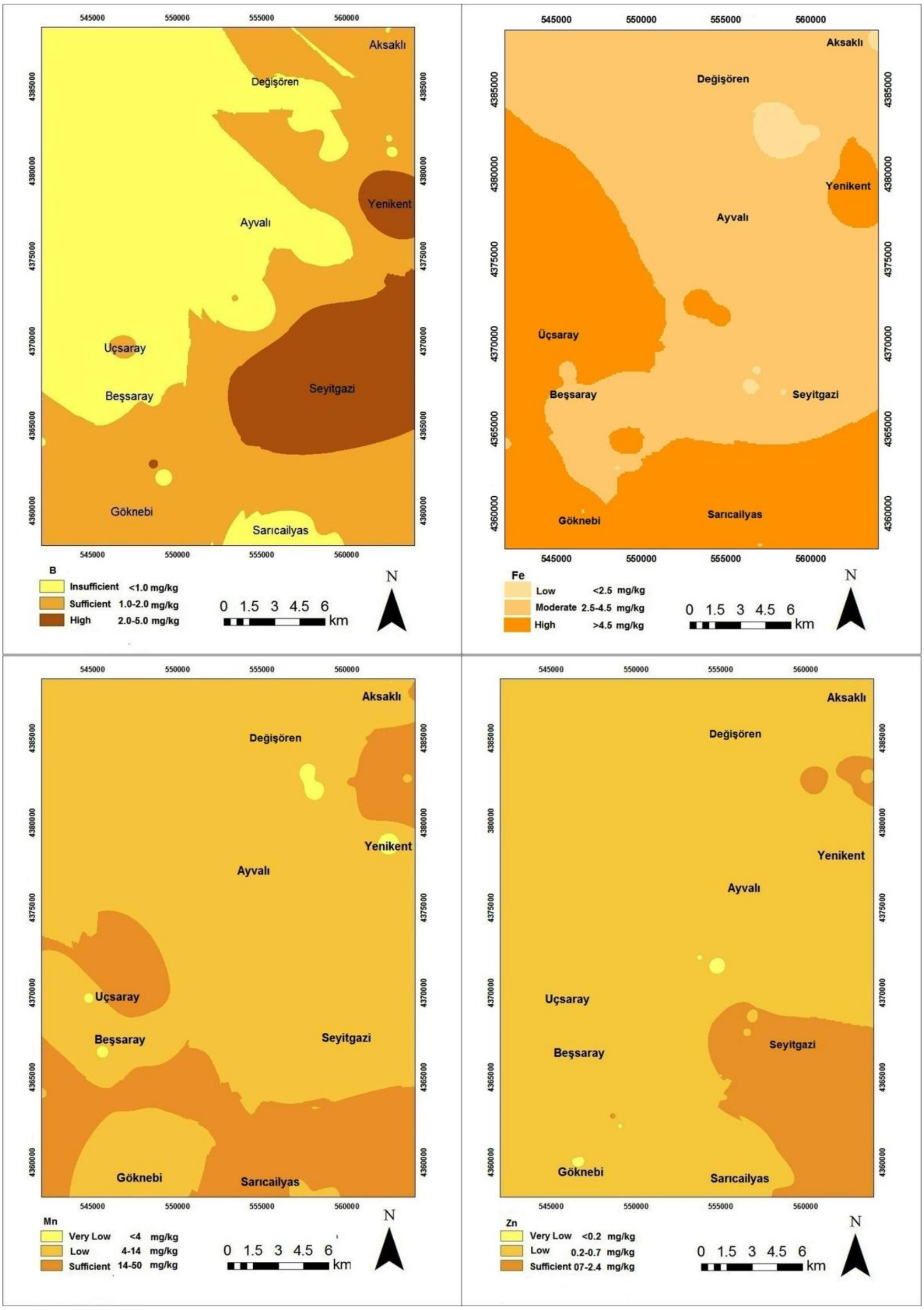

Figure 2. *Spatial distribution maps of avalible B, Fe, Mn and Zn concentrations of samples by distance from Kırka Boron Mine*

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As the distance from KBM increased, so did B levels in the soil (*Table 4*, *Figure 2*). Whereas Fe content decreased with distance, mean Zn content was nearly the same at each distance. Mn and Cu contents demonstrated no regular relation to distance. Although only slight variation in Cu content (CV <35%) appeared at different distances from KBM, all other elements showed high CV. Deviations from the normal distribution of skewness coefficients were as follows: up to 20 km for Fe (3.30), between 20 and 30 km for Zn (3.04) and between 30 to 40 km for B (3.23) and Zn (2.91), as shown in *Table 4*.

Wheat yield varied from 1.8 to 4.8 ton/ha in BFGSGr soil, yet changed between 2.5 and 5.0 ton/ha in BGSGr soil. Understandably, yield showed moderate variation, as supported with CV values of roughly 26% in BFGSGr and 20% in BGSGr (*Table 3*). The mean yield of wheat was 3.61 ton/ha up to 20 km, 2.84 ton/ha between 20 and 30 km, and 3.9 ton/ha between 30 to 40 km from KBM. The CV of the wheat yield by distance showed a mid-level change, and the values distributed normally regarding the skewness coefficient (*Table 4*).

Correlations between soil physical and chemical properties with B and wheat yield

Significant positive and negative relationships between soil physical and chemical properties with B and wheat yield according to soil group and distance from KBM appear in *Table 5*. In BGSGr soil, a positive correlation between B and Zn and a negative one between B and lime emerged. In that soil group, though the effects of sand and lime contents in soil on yield were negative, the Cu and clay contents of soil affected the yield positively. In BFGSGr soil, a significant, positive correlation emerged between B with lime and organic matter, though a negative one occurred between B and Cu. In that soil group, increasing amounts of silt negatively affected yield, whereas increasing amounts of clay benefitted it, as it did in BGSGr soil (*Table 5*).

Table 5. *Correlation coefficients between soil properties with B and wheat yield*

Relationships	Great Soil Groups		Distance (km)		
	Brown	Brown-Forest	0-20	20-30	30-40
B-Fe	-	-	-	-	0.567*
B-Cu	-	-0.492*	-0.484*	-	-
B-Zn	0.36*	-	-	0.741**	-
B-Clay	-	-	-0.460*	0.693**	-
B-Lime	-0.401*	0.585**	0.637**	-	-
B-OM	-	0.490*	-	-	-
Yield-B	-	-	-	0.600**	-
Yield-Fe	-	-	-	-0.515*	-
Yield-Cu	0.530**	-	-	-	-
Yield-Sand	-0.650**	-	-	-	-
Yield-Silt	-	-0.646**	0.499*	-0.599**	-
Yield-Clay	0.640**	0.538**	-	0.819**	-
Yield-Lime	-0.434*	-	-	-	-0.611**

*Significant at $p < 0.05$, ** Significant at $p < 0.01$.

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In the assessment based on distance, negative correlations between B with Cu and clay surfaced at up to 20 km away, whereas a positive correlation emerged between B and lime. Silt content and yield correlated positively at up to 20 km and negatively between 20 and 30 km. By contrast, positive correlations between B with clay and Zn in the area appeared between 20 and 30 km. Correlations between yield with B and clay were positive between 20 and 30 km, whereas yield with Fe was negative. Between 30 and 40 km, a positive correlation between B with Fe and negative correlation to lime with yield was observed (*Table 5*).

Discussion

The pH, sand, and organic matter contents of BFGSGr soils was high, whereas BGSGr soils contained high amounts of clay, lime, and EC. According to the USDA soil taxonomy, BGSGr belongs to light-coloured soils in arid regions' subordo of zonal soils, whereas BFGSGr belongs to the calcimorphic subordo of intrazonal soils (Dinç et al., 2001). In general, BGSGr soils consist of 1.0–1.5% organic matter, lime, and clay and are alkaline. BFGSGr soils consist of moderate organic matter with low-level clay and less lime content than BGSGr (Bayramin, 2015). Most soil up to 20 km from KBM was sandy, after which it became clay at 20–40 km. The EC, pH, and lime content of the soils near KBM were low, whereas organic matter content was high. The soil properties of BFGSGr and BGSGr were compatible with general characteristics since all soil properties examined were normally distributed (skewness coefficient ≤2) (Webster, 2001).

Low B content (<1 mg/kg) was found in 55% of BFGSGr samples and 40% of BGSGr samples. However, high B content (>2 mg/kg) was seen in 24% of BGSGr soils and in values of 2–5 mg/kg in the area 20–30 km from KBM (*Figure 2*). Important factors that decrease the benefits of B in the soil are pH, clay minerals, humidity, lime, oxides, and organic matter (Broadley et al., 2012). A previous study reported that B content in the irrigated soil of the region was 0.08–3.40 mg/kg, in a fluctuation due to the study site's proximity to KBM (Cetin et al., 2011). Emiroğlu et al. (2010) also determined that the B content of the irrigation water was greater than the standards of the Turkish Environmental Guidelines (>1 mg/L) and counterparts in Europe (>0.6 mg/L).

Whereas 5% of BFGSGr samples had low Fe content (<2.5 mg/kg), 65% had high Fe content (>4.5 mg/kg). However, 40% of BGSGr had low Fe content and 24% high Fe content. BGSGr soil contained Fe content toxic to plants, though the Fe content of soils up to 40 km from KBM decreased. Taban et al. (1997) and Eyüpoğlu et al. (1998) found that 73% of soils in Turkey had high Fe content, which the current results corroborate.

Approximately 10% of BFGSGr soil had low Mn content and 50% sufficient in terms of Mn, whereas 75% were very low and 15% sufficient in terms of Zn content. With respect to the Mn content of BGSGr, 16% of the soils were very low and 64% sufficient. Regarding the Zn content of BGSGr soils, 68% were very low and 16% sufficient. For both soil groups and at all distances, Cu content was sufficient. Mn content was sufficient up to 20 km, yet low at 20–40 km. The mean Zn content of soils did not change depending on distance (*Figure 2*). Eyüpoğlu (1999) indicated Mn deficiency of 44% in Turkish soils, especially due to the high pH values. The availability of Mn decreases due to the high oxidation of Mn^{+2} to Mn^{+4} as a result of high bacterial activity occurring at around 6.5 and 8.0 pH. Moreover, Mn is affected by

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not only pH, but also Ca, Mg, Fe, Zn, and NH_4 ions at increased concentrations (Sparrow and Uren, 2014). Available Zn concentration changes between 0.1 and 0.6 mg/kg in soils of Central Anatolia given the presence of lime, high pH levels, low organic matter, and low precipitation (<300 mm/year) (Çakmak et al., 1996).

Wheat yields varied according to soil groups and distance from KBM, and those differences could be due to the variation of soil features along with cultivar differences and cultural activities such as irrigation and fertilisation.

It is critical to determine correlations among texture, lime, organic matter, and B, Fe, Zn, Cu, and Mn contents in soils with wheat yields. Reportedly, if the clay content of soil is high, then wheat yield is better. The high water-holding capacity of clay soil could provide a significant increase in wheat yield (Nouri et al., 2016). The soil should have less than 1 mg/kg of B, 5 mg/kg of Fe, 1mg/kg of Mn, 0.5 mg/kg of Zn, and 0.5 mg/kg of Cu, since wheat cultivation requires fertilisation with these minerals (Jacobsen et al., 2003; Wang et al., 2016). By contrast, other studies have reported that Zn application to soil increases wheat yield by 260%, especially where Zn content in the Central Anatolian Region is less than 0.5 mg/kg (Yılmaz et al., 1997).

In sum, the mean of wheat yield and B and Zn contents in BGSGr soils, as well as mean Fe and Mn contents in BFGSGr soils, were high. Fe content in the soils decreased as the distance from KBM increased, and B content reached toxic values at 20–30 km. Mn and Zn contents were found to be low, B and Fe contents were toxic, and Cu content was sufficient for wheat cultivation in the examined soils. Available B and beneficial heavy metal mapping might be useful to confirm B and Fe pollution or recommend the use of fertiliser in the mining zone.

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