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Scientific Research

Determination of Indicator Plants for Boron in the Kırka (Eskişehir/Turkey) Boron Deposit Area

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ABSTRACT

The amount of elements in plants is important for biogeochemical explorations. Some plants which were accumulated extremely elements, are called indicator plants. In this study, the 11 plant species and soil samples were collected boron deposits area in Kırka (Eskişehir). Boron is determinated in plants (leaves and twigs) and soil samples. Additionally, statistical relations were established between the boron values of plant and soil samples and three plants were only found. The boron in twigs of *Puccinellia intermedia* (n = 17, r = 0.7274), twigs of *Genista aucheri* (n = 26, r = 0.8581) and leaves of *Pinus nigra* (n = 16, r = 0.6805) species are found 119, 81 and 115 mg/kg respectively. This species was reflected boron in soil and their used indicator plant for boron. The indicator plants could be successfully used for biogeochemical prospecting and environmental monitoring.

KEYWORDS

Biogeochemistry; Boron; Indicator Plant; Kırka (Eskişehir/Turkey)

1. Introduction

The Turkish borate deposits (Bigadiç, Sultançayırı, Kestelek, Emet and Kırka) are approximately 75% - 85% of the world reserves that contain some borate minerals such as coleminite, ulexite borax, etc. The Kırka (Eskişehir/ Turkey) deposit which is one of the most important borate minerals, is the largest boron deposit not only in Turkey but also in the world (**Figure 1**) [1,2].

In the literature, many geochemical and geophysical methods have been used to explore the new mining deposits. The resistivity and seismic methods are used in the gravity and magnetic geophysical researches, particularly for borate deposits created by sedimentary filling. On the other hand, the drilling method with geological mapping is one of the most suitable methods in order to explore the new mining deposits in the world [3,4].

Recently, the biogeochemical prospecting methods are successfully used for detection of the new mining deposits. These methods include the determination elements in different organs of plants such as leaves, twigs or roots and soil. In generally, the relationship between the amount of elements in plant and soil is used for determine the indicator plants. In the literature, several indicator plants are found for Au and Fe, Mn, Zn, Cu, and other elements [4-20].

Boron is metalloid and essential for plant functions. When presented in suboptimal or in excess amount, it may become nutritional deficiency or toxic [21,22]. However, some plant species extremely accumulated or tolerated boron. It was reported that only the *Eurotia ceratoides*, *Limonium suffruticosum and Salsola nitraria* species in Russia were accumulated boron [5].

In this study, the amount of the boron is determinated in plant and soil samples in Kırka (Eskisehir-Turkey) borate deposits and investigated plant-soil relationships for each plant species organs. The indicator plant species which are found could be used as guidelines in order to determine the borate deposits and environmental moni-

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toring in future studies.

2. Geology and Location of Borate Deposits

There are three coeval assemblages in the west of Central Anatolia (from West to East) in the youngest Alpine magmatism (Miocene to Quaternary). They are the Western Anatolian Volcanic assemblage, the N-S trending Kırka-Afyon-Isparta Alkaline Volcanic assemblage and the Central Anatolian Volcanic Provinces [23]. All of the Turkish borate deposits are classified as volcanic related deposits. The borate deposits in Bigadiç, Sultançayırı (Balıkesir), Kestelek (Bursa), Emet (Kütahya) and Kırka (Eskişehir) were created in the playa-lake sediments during Miocene volcanism. The borate minerals are formed within the sequence consisting of conglomerate, sandstone, claystone, shale, marl, limestone and tuff intercalation [24].

Figures 1 and **2** show that Kırka B deposits area were composed of the lithology from old to young, respectively the Zahrendere Travertine Formation (composed of yellow-white limestone), the Lepçekdere Formation (claystone, limestone, borate in marl), the Salihiye Formation (opal in limestone), the Karaören Formation (clayey tuff, claystone, limestone and opal) and the Kırka Formation (tuff, claystone, limestone, borate and opal) [25].

The Kırka borate deposit (Miocene, Western Turkey), is the most important B_2O_3 producer in the world at present. It exhibits a symmetrical zonation in a lateral sense. It is comprised of a central body of Na borate (borax), an intermediate zone of Na-Ca borate (ulexite), and a marginal zone of Ca borate (colemanite). This mineral zonation is also developed in a vertical sense, while it shows an asymmetrical zonation because of the presence of a discontinuous Mg borate horizon overlying the central body of borax [24].

3. Materials and Methods

The natural plant species and representative soil samples were collected from the Boron mining areas especially in Kırka and Bigadiç, Emet borate deposits. The surface soil samples were collected in the depth range of 15 - 20 cm and stored in plastic bags. The plant species were identified from study [26], and then plant samples were separated into twigs, leaves, spikes and barks.

Digested of Plant Samples: the plant samples were washed with water and than dried in the oven-dried at 80˚C for 24 h. The 0.20 g of the dry grounded plant samples were placed into the porcelain crucible and fired up to 550˚C in the muffle furnace with a heating rate of 50˚C/h for 7 h. Then, the ashes were taken and evaporated with 2 ml 0.1 M HCl (1/3) at 45 - 50˚C by using a hot-plate. The residue was dissolved in 25 ml of deionized water and filtrated by using filter papers [27,28].

Extraction Boron from Soil Samples: The soil samples were oven-dried at 80˚C for 10 h and than were ground and then sieved under 80 mesh. The 5.00 g of dried soil samples and 20.00 ml of extraction solutions (0.01 M Mannitol + 0.01 M $CaCl_2$) were shake for 16 h into shaker. The mixture was filtrated using filter paper and the boron determinate in soil extract solutions [27,29,30].

Boron Analysis: The B concentrations in the digested plant and soil extract solutions were determined according to the method suggested [27-30]. The 12.5 ml of the extract plant and soil extract solutions were transferred into a 25 ml flask, The 2.5 ml ammonium acetate tampon solution with the pH of 8 and the 2.5 ml of 0.3% 3,4-Dihydroxyazomethine-H solution in 1% ascorbic acid and the solution completed to 25 ml by deionised water. The solution are mixed and kept for 90 min. in dark and then the absorbance of the solution was measured at 420 nm by Genesys 20 model Spectrophotometer.

The 20 $mg \cdot ml^{-1}$ stock standard boron solutions were prepared by dissolving sodium borate. Then, some of these stock solutions with different volume were taken and diluted with distillated water in order to prepare diluted solutions with certain concentrations (from 2 $mg \cdot ml^{-1}$ to 8 $mg \cdot ml^{-1}$). The absorbance of these freshly diluted solutions was measured and then the calibration graph was obtained.

The measurements of the water samples taken from waste water pool (in the surface water) in the Kırka and the Emet deposit areas were performed directly.

Other Element Analysis: Determination of Sr, Li, Cu, Zn, Mn, Co, and Ni in soil samples were analyzed by Flame Atomic Absorption Spectrophotometer [31].

4. Results and Discussions

The plant species such as *Gypsophila perfoliata* L., *Pinus nigra* Arn, *Chrysopogon gryllus* (L.) Trin., *Juniperus oxicedrus* L. subsp., *Juniperus foetidissima* Willd., *Apera intermedia* Hackel, *Quercus trojana* P.B. Webb, *Puccinellia intermedia* (Schur) Janchen, *Alyssum sibiricum* Willd, *Genista aucheri* Boiss and *Euphorbia hirsuta* L. are grown widely in Kırka and Emet, Bigadiç borate deposits. A few plant, soil and water samples were taken from Emet and Bigadiç (not water) in order to comparate with Kırka area. The maximum, minimum and the average B values of all plant and soil samples which were taken from these deposits are given in **Table 1** for leaves, twigs, spikes and barks.

The B values of soil samples taken from the Kırka borate deposit varies between 1 ppm and 723 ppm, while the B values of the soil samples taken from Emet and Bigadiç varies between 1 ppm to 130 ppm. The B values of the natural soil samples are in the range of 0.10 - 80

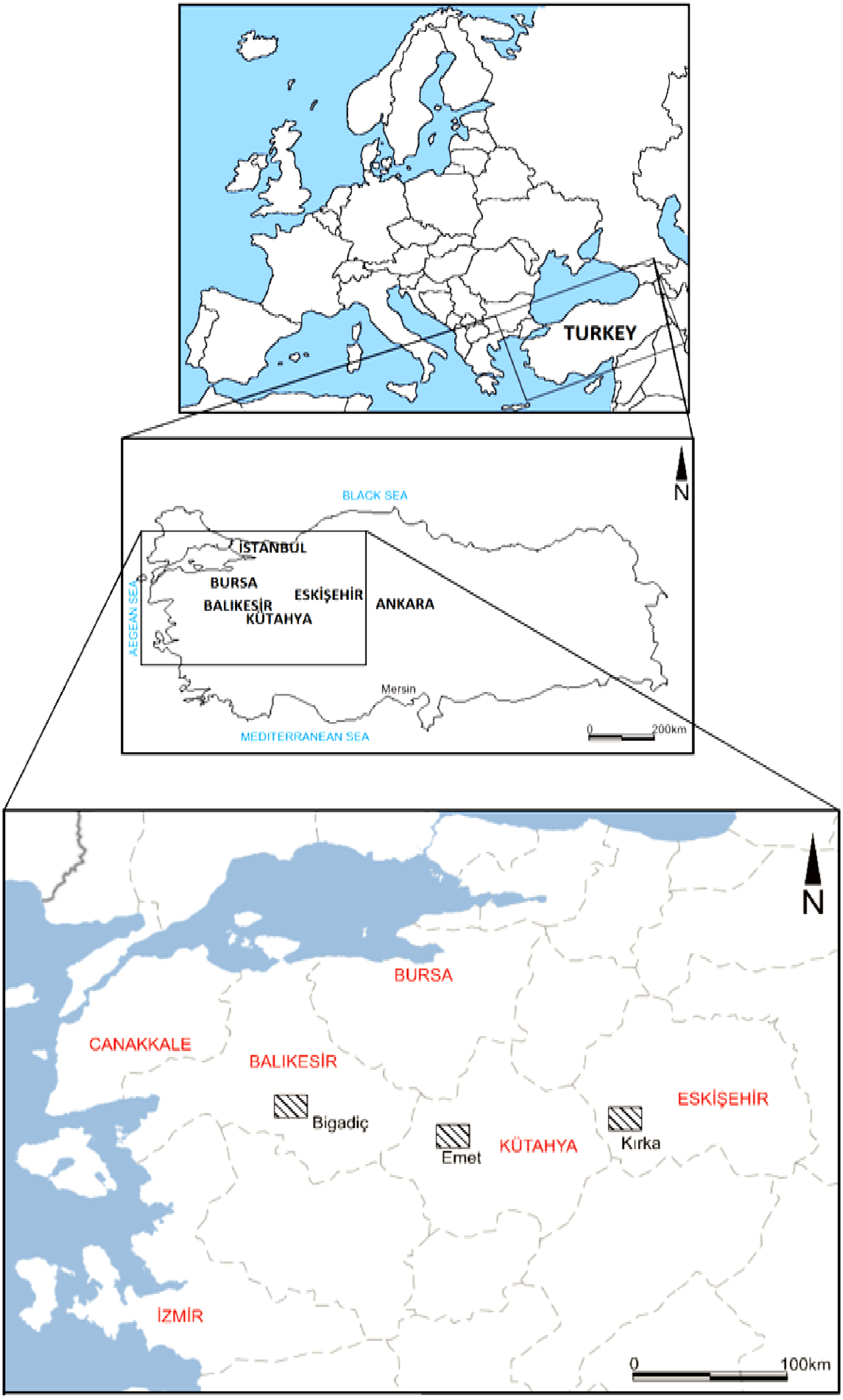


Figure 1. **Location map of study area.**

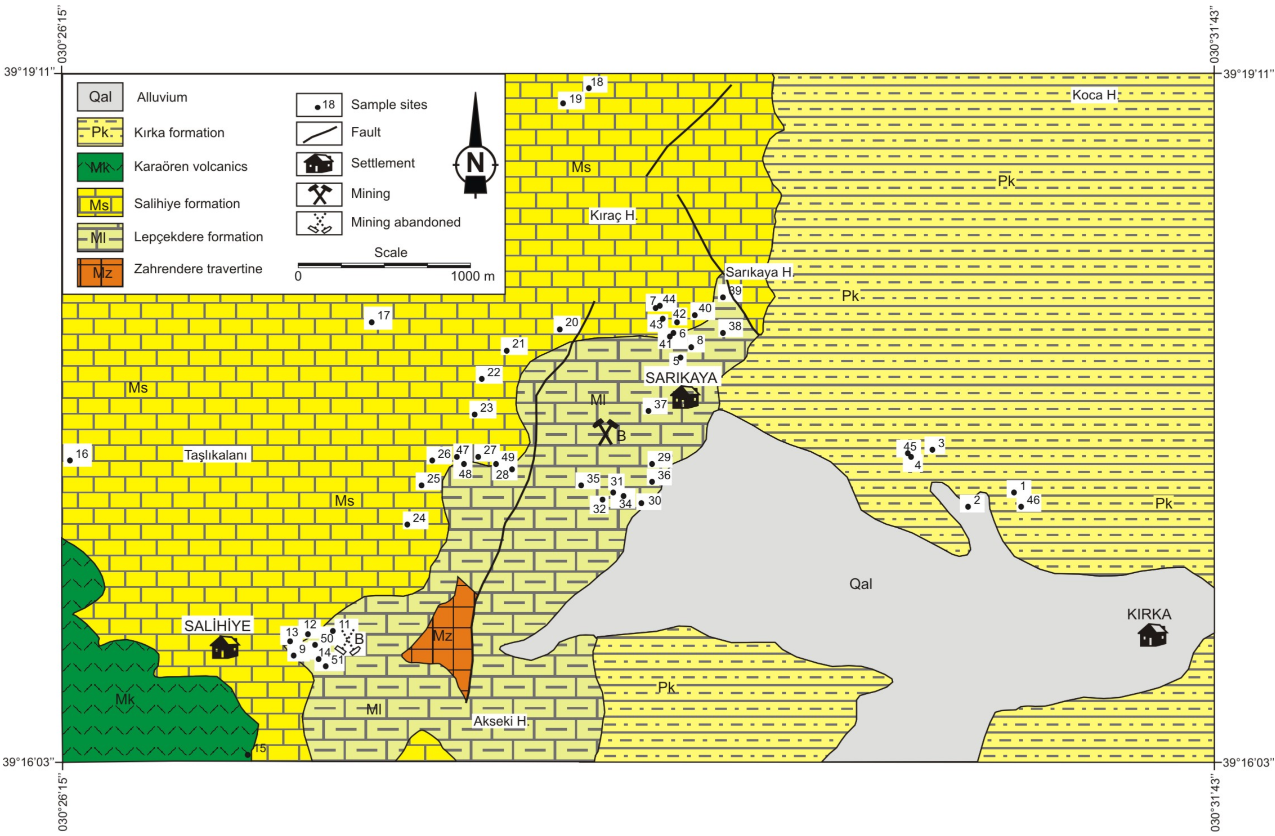


Figure 2. Geological map of the Kırka (Eskişehir) area (simplified from Gök *et al*., 1979).

Table 1. Boron concentrations in various plants and their organs and in soils from Kırka (Eskişehir) boron deposits.

The plant species		n	B content in the soil (μg/g)			B content in the plant (μg/g)		
			Min.	Max.	Average	Min.	Max.	Average
Alyssum sibiricum Wılld	Twigs	9	5	21	9	38	188	76
	Leaves	9	5	21	9	50	325	160
Chrysopogon gryllus (L.) Trin	Twigs	8	1	16	6	31	51	43
	Leaves	9	1	18	7	48	736	181
	Barks	5	3	8	4	33	87	54
Gypsohila perfoliata L.	Twigs	23	9	723	162	43	243	130
	Leaves	22	9	723	162	95	1102	526
Puccinellia intermedia (Schur) Janchen	Twigs	17	8	462	219	36	190	119
	Spikes	18	8	462	216	99	641	285
	Barks	19	8	462	216	88	445	255
Quercus trojana PB Webb	Twigs	28	2	15	5	43	119	72
	Leaves	28	2	15	5	45	423	191
Genista aucheri Boiss.	Twigs	27	1	21	6	39	188	81
	Leaves	14	1	21	6	71	250	142
Juniperus Oxycedrus L. Subsp	Twigs	27	1	16	5	36	308	77
	Leaves	28	1	16	5	37	204	89
Pinus nigra Arn.	Twigs	24	1	16	5	38	602	180
	Leaves	16	1	10	4	44	223	115
Juniperus foetidissima Willd	Twigs	3	5	15	9	78	434	231
	Leaves	2	6	15	10	63	103	83
Apera intermedia Hackel	Twigs	2	321	390	355	850	1160	1005
	Spikes	2	321	390	355	700	1197	948
Euphorbia hirsuta L.	Twigs	23	2	15	5	47	115	68
	Leaves	21	2	15	5	62	220	119

ppm [5,21,32,33]. The B values of the three borate deposits are higher than the values of the natural soil samples. Thus, these values can be accepted as anomaly values.

On the other hand, the boron in the water samples of Kırka borate deposits area at 1, 2, 4, 14 and 50 stations are 272 ppm, 326 ppm, 510 ppm, 295 ppm, 195 ppm, respectively (**Figures 1** and **2**). The boron value of the water samples of Emet borate deposit at one station is 590 ppm. The value of B is 10 ppb in the natural water [5]. The B values of the water samples taken from borate deposit areas are higher than the values of the natural water samples, and these values can be accepted anomaly values.

Predominantly, the high B content of the soils is reflected in the parts of the plant species. The B values of the plant species are ranged from 31 ppm to 1197 ppm and the B values of the natural plant samples are ranged from 0.1 ppm to 1 ppm. However, these values are up to 230 ppm in the contaminated area [5,21,32,33]. The B values of the plant species of the borate deposits region are higher than the natural plant samples. Therefore, these values can be accepted anomaly values.

The B content of the soil and the plant samples given in **Table 1** was plotted. It was observed that the correlation between B in the part of the plants (*G. perfoliata* (r < 0.413 for twigs, r < 0.423 for leaves), *C. gryllus* (r < 0.707 for twigs, r < 0.666 for leaves and r < 0.878 for barks), *J. oxicedrus* (r < 0.380 for twigs, r < 0.468 for leaves), *J. foetidissima* (r < 0.997 for twigs), *Q. trojana* (r < 0.372 for twigs, r < 0.372 for leaves), *A. sibiricum* (r < 0.666 for twigs, r < 0.666 for leaves) and *E. hirsute* (r < 0.413 for twigs, r < 0.433 for leaves, for n > 3) and soil were not significant at 95% (P > 0.05) confidence level. Because the slope of the regression (r) line of the experimental is lowest than theoretical regression (r) line. Furtermore, *J. foetidissima* (for leaves), and *A. intermedia* (*for* twigs and leaves) are insufficient samples, for n < 3.

In contrast to that a statistically significant plant/soil relationship was observed for the B in the twigs of *G. aucheri*, in the twigs of *P. intermedia*, and in the leaves of *P. nigra* and presented in **Figures 3-5**, respectively. The slope of the regression (r) lines was 0.8581 (for 26 samples), 0.7274 (for 17 samples) and 0.6805 (for 16 samples), respectively. All of the relationships are highly significant (99% confidence level, P < 0.01).

The sensitivity of the *P. nigra*, *G. aucheri* and *P. intermedia* plant species is shown in **Figure 6**. It is clear in **Figure 6** that *P. nigra* is the most sensitive and *G. aucheri* is more sensitive than *P. intermedia*. Therefore, it is better to prefer to start with the most sensitive one for biogeochemical prospecting in the future. Morever, bioconcentration factor (BF, B plant/Bsoil); P. *nigra* 16.0 > *G. aucheri* 6.3 > *P. intermedia* 0.9.

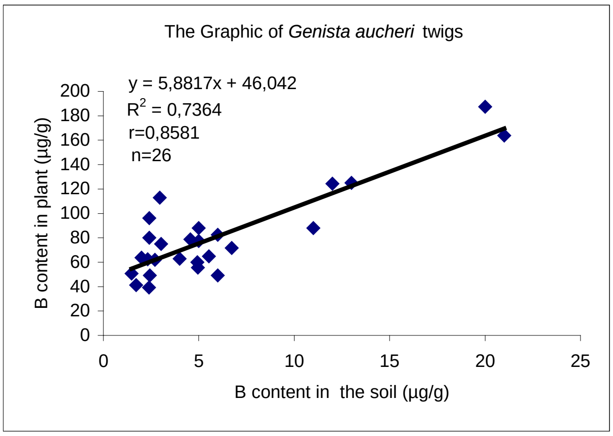


Figure 3. **The relationship between the concentration of B in the soil and B in the *Genista aucheri* twigs.**

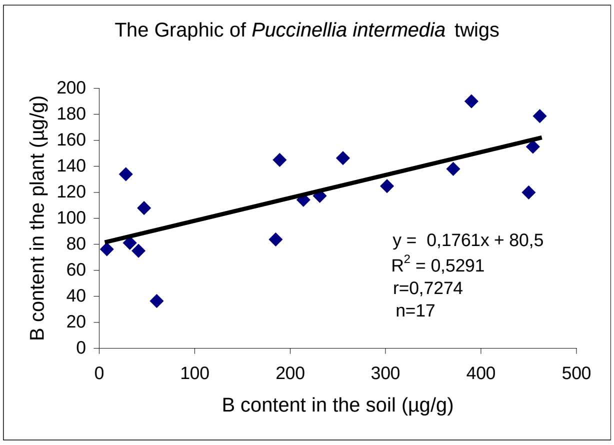


Figure 4. **The relationship between the concentration of B in the soil and B in the *Puccinellia intermedia* twigs.**

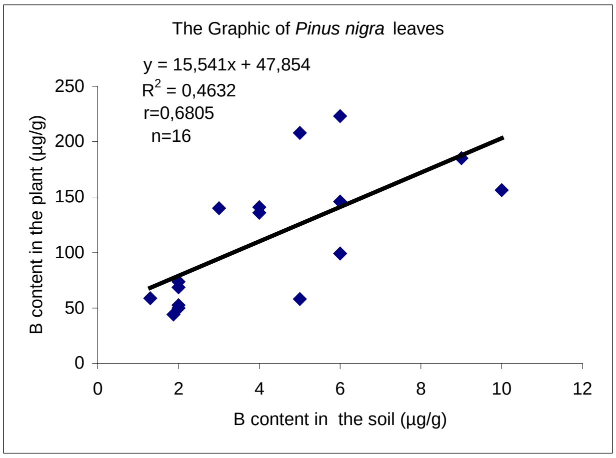


Figure 5. **The relationship between the concentration of B in the soil and B in the *Pinus nigra* leaves.**

The inter-elemental relationship between the B concentration of the indicator plants and some other elements (B, Sr, Li, Cu, Zn, Mn, Co and Ni) of the soil was

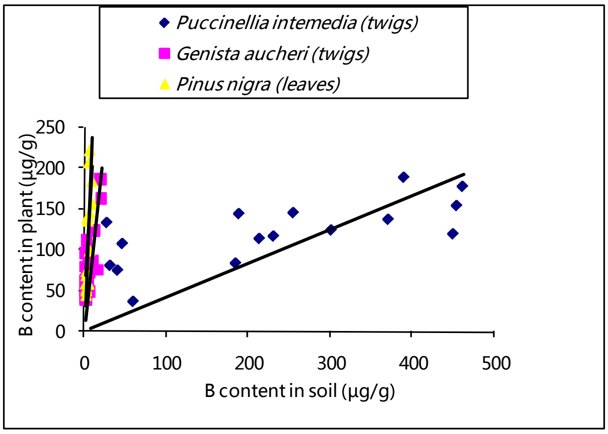


Figure 6. The correlation between the B contents of the *Puccinellia intermedia* (twigs), *Genista aucheri* (twigs), *Pinus nigra* (leaves) and the soil.

shown in **Table 2**.

As it was seen in **Table 2**, there was relationships of B concentration in the twigs of *G. aucheri*, in the twigs *of P. intermedia*, in the leaves of *P. nigra* and the Sr, Li, Cu, Zn, Mn, Co and Ni elements in the soil are not significant (95% confidence level, $P > 0.05$). Therefore, B in the plants has been independent to Sr, Li, Cu, Zn, Mn, Co and Ni in the soil. In addition, it is obvious that the B concentration in the indicator plants depends on the B concentration in the soil.

5. Conclusions

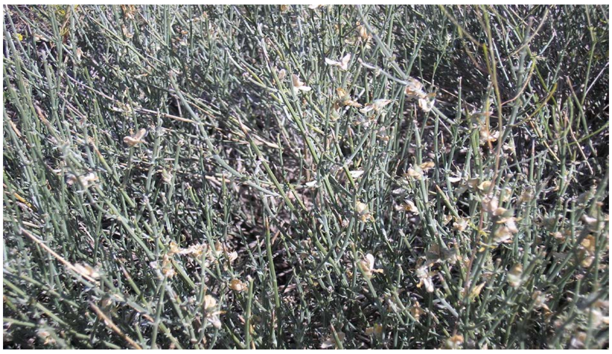
In the present study, the elemental contents of the plants (*G. perfoliata*, *P. nigra*, *C. gryllus*, *J. oxicedrus*, *J. foetidissima*, *A. intermedia*, *Q. trojana*, *P. intermedia*, *A. sibiricum*, *G. aucheri*, *E. hirsuta*), soil, and water taken mainly from Kırka and also from Emet and Bigadiç borate deposit areas are chemically analyzed. The B concentrations in the samples were compared with the B concentrations of the natural plant, soil and water. It was investigated that the B concentrations of all the samples regardless whether it is plant or soil or water are anomaly. However, it was observed that there was a relation between the B concentration of only the twigs of *G. aucheri*, the twigs of P. *intermedia* and the leaves of *P. nigra* plants and the B concentration of the soil (**Figures 7(a)-(c)**, respectively). Therefore, these plant species are determined as indicator plants. Besides, the B concentration of these indicator plants is independent to the concentration of the Sr, Li, Cu, Zn, Mn, Co, and Ni elements in the soil. This means that the indicator plant can take B from the soil regardless it has these elements or not.

It is concluded that the B content in the twigs of *G. aucheri*, in the twigs of P. *intermedia* and in the leaves of *P. nigra* yielded good indications for biogeochemical prospecting and could be successfully used as environmental monitor for environmental pollution studies.

Table 2. Results of correlation analysis for inter-elemental relationships between soil and plants.

B in the Indicator plants		Elements in the soil							
		B	Sr	Li	Cu	Zn	Mn	Co	Ni
Puccinellia intermedia (Schur) Janchen	Twigs	**S**	NS	NS	NS	NS	NS	NS	NS
Genista aucheri Boiss	Twigs	**S**	NS	NS	NS	NS	NS	NS	NS
Pinus nigra Arn.	Leaves	**S**	NS	NS	NS	NS	NS	NS	NS

S: highly significant ($p < 0.01$). NS: not significant ($P > 0.05$).


(a)


(b)


(c)

Figure 7. The photographs of the plant species; (a) *Genista aucheri*, (b) *Puccinellia intermedia*, and (c) *Pinus nigra.*

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