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Boron Concentration in Water, Sediment and Different Organisms around Large Borate Deposits of Turkey

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Abstract Boron is an essential nutrient for plants and an essential element for many organisms, but can be toxic to aquatic and terrestrial organisms above certain concentrations. The aim of this research was to determine boron concentrations in water, sediment and biotic samples (Gammaridae spp.-Crustacea, *Helix* sp.-Gastropoda, *Donax* sp.-Bivalvia, *Helobdella* sp.-Hirudinae, Ephemeroptera nymph, Chrinomidae larvae, Tipulidae larvae-Insecta, *Rana* sp.-Amphibia, *Natrix* sp.-Serpentes, fish sample *Leiscus cephalus* (Linnaeus, 1758) and leaves of *Salix* sp.-Salicacea from Seydi Stream (Kırka-Eskişehir). Our results have shown that boron concentrations of the Seydi Stream water is higher than the Turkish Environmental Guidelines standard (>1 mg L^{-1}) and in Europe (mean values typically below 0.6 mg L^{-1}).

Keywords Boron · Contamination · Seydi Stream · Kırka

Boron is a non-metallic element that is ubiquitous in the environment, existing naturally in over 80 minerals. It is found in the form of borates in sedimentary rocks, coal, shale, and some soils. It is widely distributed in the nature, with concentrations of about 10 mg kg^{-1} in the Earth's crust (range: 5 mg kg^{-1} in basalts to 100 mg kg^{-1} in shales) and about 4.5 mg L^{-1} in the ocean (WHO 1998a), and it is usually <0.1–0.5 mg B L^{-1} in surface of freshwaters; but its higher concentrations are measured in a few areas. Economic borate deposits are rare, occurring in arid regions of Turkey, the USA, Argentina, Chile, Russia, China, and Peru. Boron exists in the environment mainly through the weathering of rocks, boric acid volatilization from seawater, and volcanic activity. Boron is also released from anthropogenic sources to a lesser extent. Anthropogenic sources include agricultural refuse, and fuel wood burning, power generation using coal and oil, glass products manufacture, use of borates/perborates in the home and industry, borate mining/processing, leaching of treated wood/paper, and sewage/sludge disposal. Many of these sources are difficult to quantify (WHO 1998a). Boron is an essential nutrient for plants, but can be toxic to aquatic and terrestrial organisms above certain concentrations especially when accumulated in high concentrations (Çöl and Çöl 2003). The concentrations of many elements, including boron, are increasing in aquatic ecosystems due to anthropogenic activities. In humans, boron exposure occurs primarily through oral intake of food and drinking water. The natural borate content of groundwater and surface water is usually small. The borate content of surface water can be significantly increased as a result of wastewater discharges, because borate compounds are ingredients of domestic washing agents. Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicate. Concentrations of boron in groundwater throughout the world range widely, from <0.3 to >100 mg L^{-1}. In general, concentrations of boron in Europe were greatest in Southern Europe (Italy, Spain) and the least in Northern Europe (Denmark, France, Germany, the Netherlands, and the United Kingdom). In Italy and Spain, mean boron concentrations ranged from 0.5 to 1.5 mg L^{-1}. Values

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approximately ranged up to 0.6 mg L^{-1} in the Netherlands and the United Kingdom and approximately 90% of the samples in Denmark, France, and Germany were found to contain boron at concentrations below 0.3, 0.3, and 0.1 mg L^{-1}, respectively. Boron concentrations in fresh surface water range from <0.001 to 2 mg L^{-1} in Europe, with mean values typically below 0.6 mg L^{-1}. Similar concentration ranges have been reported for water bodies within Pakistan, Russia, and Turkey, from 0.01 to 7 mg L^{-1}, most of the values were below 0.5 mg L^{-1} (WHO 1998b).

It is well known that metals accumulate in tissues of aquatic and semi-aquatic animals and therefore, the levels measured in tissues of organisms can reflect past exposure and metals in aquatic environments are transferred to humans through food chain. Although there are lots of studies dealing with heavy metal accumulation in different freshwater organisms, little work was done on heavy metal accumulation in benthic invertebrates of Turkey (Duran et al. 2007). Boron accumulation is not often studied for aquatic and semi-aquatic organisms. This paper aims to investigate boron concentration of Seydi Stream water, its sediment and different organisms from surrounding Kırka county of Eskişehir. Biotic and abiotic samples from surroundings of Kırka were collected at different times of the year 2008 for the study (Fig. 1).

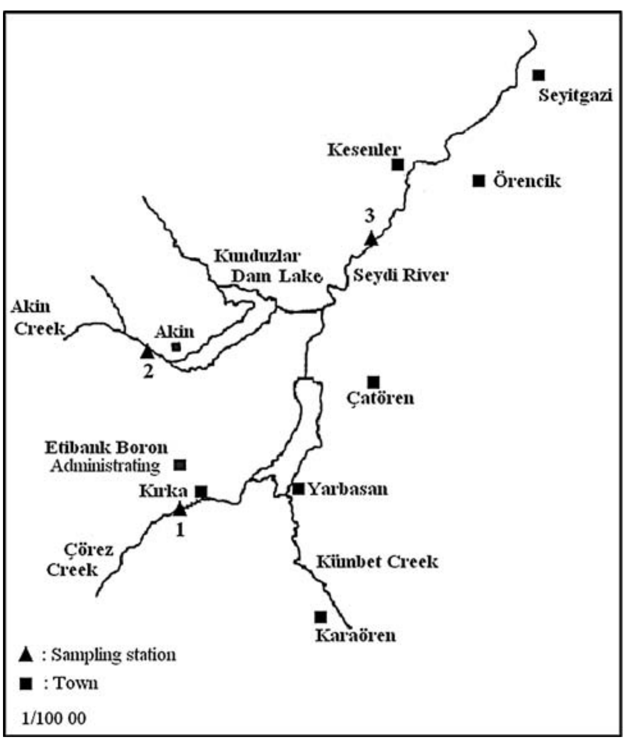

Fig. 1 Study area and sampling sites

Materials and Methods

The last center of borate industry active since 1968 is Kırka, town of Seyitgazi county, Eskişehir. Kırka-Sarıkaya borates line extending over West is the world's largest deposit has ever been discovered. Likewise there are several inactive underground pits. Water, sediment and biotic samples were collected from three stations in order to determine boron concentrations surrounding Kırka. The biotic samples (Gammaridae spp., *Helix* sp., *Donax* sp., *Helobdella* sp., Ephemeroptera nymph, Chrinomidae larvae, Tipulidae larvae, *Rana* sp., *Natrix* sp., *Leiscus cephalus* and leaves of *Salix* sp.) were collected and placed into iceboxes. They were deep frozen at about −20°C and stored until start of analyses. Then, some samples were dissected by stainless-steel (muscle, liver, and gill). All bio-samples were dried for 24 h at 105°C. Bottom sediment samples were dried for 3 h at 105°C for boron analysis. After all samples were passed through a nylon sieve (0.5 mm), 0.5 g of each sample was placed in Pyrex reactors of a CEM Mars 5 microwave digestion unit. $HClO_4$:HNO_3 acids of 1:3 proportions for organisms and sediment were inserted in the reactors respectively. Samples were mineralized at 140°C for 1 h. Afterwards, the samples were filtered in such a way as to make their volumes to 100 ml with 0.1 N HCl. Water samples of one liter in volume were taken at each sampling point and were adjusted to pH 2 by adding 2 ml of HNO_3 into each. Before sampling, sample bottles were cleaned by washing them with detergent and then soaking them in 50% HCl for 24 h. Finally, the bottles were washed with water and then rinsed with distilled water. Bottles were kept in 1% nitric acid before use. Heavy metals were determined by ICP-OES (Varian 720 E) (APHA 1992; EPA METHOD 2001). Detection limit value of boron as (μg L^{-1}) in ICP-OES was to be 0.07 and the absorption wavelength was 249.678 nm.

Statistical analysis of data was carried out using SPSS statistical package software. The correlation and statistical significance of the relationship between the boron concentration of the river water–sediment and biological samples and different tissues of the *Leiscus cephalus* were evaluated using Pearson's correlation coefficient.

Results and Discussion

As we mentioned above, Turkey has the largest natural boron reserves in the world. Borate deposits in the study region were formed by the deposition in Neogene Lake's volcanic ash, mud and exhalation products coming from the faults and containing boric acid, sodium and magnesium. The study region namely Kırka is a small town with an approximate population of 5,000, which has an open pit mine producing colemanite ($Ca_2B6O_{11}\cdot5H_2O$), ulexite ($NaCaB_5O_9\cdot8H_2O$) and borax ($Na_2B_4O_7\cdot10H_2O$).

The average boron concentrations and pH levels in the samples taken from the three stations of the study region are given in Table 1. Boron levels in water were found minimum 1.58 mg L^{-1} and maximum 3.88 mg L^{-1}. Boron levels at all stations are higher than that of the Turkish Environmental Guidelines standard. Water quality regulations in Turkey divide inland waters into four classes. According to the boron concentrations given Table 1, the water of Seydi Stream was included to the fourth class (>1 mg L^{-1}) category which refers to heavily polluted water that should not be used at all.

The boron concentrations found in the upper layer (5 cm) of the sediments of three sampling sites did not vary considerably. In sediment samples, the highest boron concentration was recorded at station 1 (Table 1). Water and sediment samples from the first station which is located at the nearest station to boron production complex (Fig. 1), was determined to have the highest amount of boron content when compared to other two stations (Table 1).

The borate content of surface water can be significantly increased as a result of wastewater discharges, because borate compounds are ingredients of domestic washing agents (ISO 1990). Boron concentrations in fresh surface water range from <0.001 to 2 mg L^{-1} in Europe, with mean values typically below 0.6 mg L^{-1}. Similar concentration ranges have been reported for water bodies within Pakistan, Russia, and Turkey, from 0.01 to 7 mg L^{-1}, with most values below 0.5 mg L^{-1}. Concentrations ranged up to 0.01 mg L^{-1} in Japan and up to 0.3 mg L^{-1} in South African surface waters. The surface water samples of two South American rivers (Rio Arenales, Argentina, and Loa River, Chile) contained boron at concentrations ranging between 4 and 26 mg L^{-1} in areas rich in boron-containing soils. In other areas, the Rio Arenales contained less than 0.3 mg of boron per liter. Concentrations of boron in surface waters of North America (Canada, USA) ranged from 0.02 mg L^{-1} to as much as 360 mg L^{-1}, indicative of boron-rich deposits. However, typical boron concentrations were less than 0.1 mg L^{-1}, with a 90th-percentile boron concentration of approximately 0.4 mg L^{-1} (WHO 1998c). Gemici and Tarcan (2002) indicated that boron concentrations in Turkey are higher than those in Southern and Northern European countries. Our results parallel this data. The average boron concentrations established in biotic samples and different tissue of *Leiscus cephalus* taken from all sampling stations of the study region are given in Tables 2 , 3 and Fig. 2.

Sampling station 1 with the highest boron level both in water and sediment has lower taxa than the other sampling site (Table 2). It is clear that the taxonomic diversity decreased at sampling sites 2 and 3. This situation can explain that boron concentration both in water and sediment had an impact on aquatic organisms especially on benthic invertebrates population.

It is known that the acute lethal dose in animals is estimated to be in the range of 400–900 mg boron equivalents/kg body weight (EGVM 2003). Wide variation existed in boron concentrations between aquatic and semi-aquatic groups (Table 2). *Helix* sp. had the highest boron concentrations, which is followed by *Rana* sp. and *Natrix* sp. The benthic community is a heterogonous group including detrivorous, herbivorous and carnivorous species and they are an important food source for fish. Our results showed that boron concentration was highest in the benthic community *Donax* sp. followed by Ephemeroptera nymph, Gammaridae spp., *Helobdella* sp., Tipulidae (larvae), Chrinomidae (larvae).

Table 2 Boron levels in different organisms in the study region

Samples	Boron (mg kg^{-1})		
	St 1	St 2	St 3
Gammaridae sp.	ns	ns	1.08
Chrinomidae (larvae)	ns	0.44	0.38
Tipulidae (larvae)	ns	0.84	0.63
Ephemeroptera (nymph)	ns	1.98	0.60
Helobdella sp.	ns	1.07	0.92
Donax sp.	ns	ns	14.00
Helix sp. (whole body)	ns	62.00	59.00
Rana sp.(muscle)	56.51	30.00	43.50
Natrix sp. (muscle)	ns	ns	18.36
Salix sp.	83.01	68.46	78.78

St station; *ns* no sample

Table 1 pH value and boron concentrations in water and sediment samples in the study region

Station	Water sample (mg L^{-1})				Sediment sample (mg kg^{-1} dry weight)		
	pH	Min	Max	A.M. ± S.D.	Min	Max	A.M. ± S.D.
1	8.39	3.15	3.88	3.45 ± 0.33	29.4	36.00	32.72 ± 4.63
2	8.28	2.32	2.90	2.51 ± 0.25	17.00	28.50	23.95 ± 4.99
3	8.75	1.19	1.94	1.61 ± 0.24	10.00	27.80	15.67 ± 8.02

Table 3 Boron levels in different tissues of *Leiscus cephalus*

St.	Tissue	B (mg kg^{-1} dry weight)		
		Min	Max	A.M. ± S.D.
1	Muscle	7.05	7.85	7.34 ± 0.44
	Liver	2.56	2.89	2.69 ± 0.17
	Gill	6.58	7.94	7.44 ± 0.74
	Head	52.00	96.00	69.66 ± 23.24
2	Muscle	15.00	100.71	49.24 ± 45.41
	Liver	4.30	14.00	7.92 ± 5.29
	Gill	2.60	7.15	4.18 ± 2.57
	Head	41.36	82.31	60.55 ± 20.58
3	Muscle	29.35	68.32	53.73 ± 21.25
	Liver	13.44	62.31	43.84 ± 26.53
	Gill	6.00	13.20	8.66 ± 3.94
	Head	51.00	82.00	66.00 ± 15.52

St station

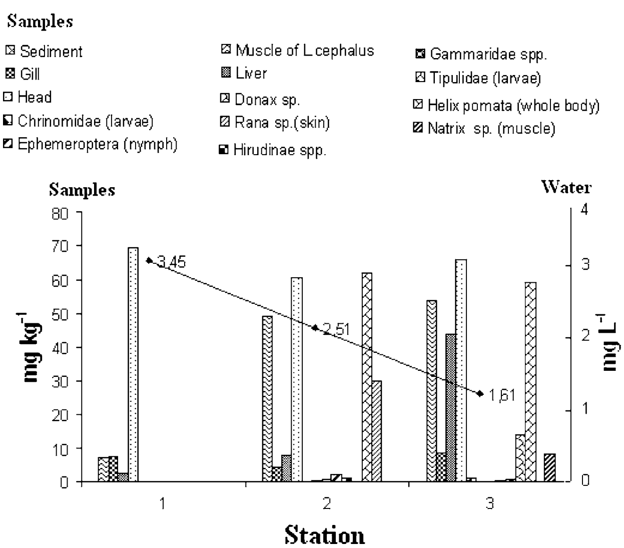

Fig. 2 The average boron concentrations established in biotic and abiotic samples of the study region

Table 4 Statistically significant Pearson Correlation Coefficients between boron concentration of water–sediment and organisms

Relation between	Significance level (r)
B in sediment and in Tipulidae (larvae)	.340(**)
B in sediment and in Chironomidae (larvae)	.419(**)
B in water and in Gammaridae sp.	.322(*)
B in water and in *Helobdella* sp.	.469(**)
B in sediment and in *Helobdella* sp.	.277(*)
B in water and in sediment	.221(*)
B in sediment and in muscle	.299(*)
B in water and in liver	.313(**)

* Significant at $p < 0.05$; ** significant at $p < 0.01$

The comparison of different tissues of *Leiscus cephalus* with respect to the boron levels were given in Table 3. According to average value the highest boron value was found in the head and followed by the muscle (edible part).

There is no information about maximum permissible boron limits in fish tissues in the Turkish standards. Therefore, our results could not have been compared with the levels of Turkish Food Codex Standard.

The relationships between boron level of abiotic and biotic samples were supported by the Pearson Correlation Index (Table 4). It was found that the relation between B level in sediment and in Tipulidae (larvae) ($p < 0.05$, $r = 0.340$), B level in sediment and in Chironomidae (larvae) ($p < 0.05$, $r = 0.419$), B level in water and Gammaridae spp. ($p < 0.05$, $r = 0.469$ and $p < 0.01$, $r = 0.277$, respectively), B level in water also sediment and in *Helobdella* sp. ($p < 0.05$, $r = 0.340$), B in water and in sediment ($p < 0.01$, $r = 0.221$), B in sediment and in muscle, also liver ($p < 0.01$, $r = 0.299$ and $p < 0.05$, $r = 0.313$) were directly proportional.

Our results show that boron levels in Seydi Stream water at all stations (especially at Station 1) are higher than that of the Turkish Environmental Guidelines standard, FAO, WHO and NAS criteria. According to NAS (1980), the recommended maximum level for humans is less than 1.0 mg L^{-1} for drinking water. Aquatic systems' water and their sediments represent an important sink for trace metals in aquatic systems, and sediment-associated metals pose a direct risk to detrital and deposit-feeding benthic organisms, and may also represent long-term sources of contamination to higher tropic levels (Eimers et al. 2001). Fish living in the polluted waters may accumulate trace metals via their food chains. The present study has demonstrated that boron contamination has a strong impact on the benthic invertebrate community and also boron level in edible part of *Leiscus cephalus* was high. Fish from Seydi Stream serve as a source of animal protein and means of livelihood for the population in surroundings of both Seyitgazi and Kırka. Fish is an important source of food for humans. The amount of the toxic elements in fish is dependent on the concentration levels of these elements in the food and the habitats of the fish, and the detoxification rate of the metals. The daily intake of boron for humans may vary widely, depending on the proportions of various food groups in their diet. For example, fresh vegetables, fruit and wine have relatively high boron contents. There may also be a considerable elevation in the daily boron intake from drinking water and mineral water. Data from accidental poisonings indicate that the human acute, lethal dose of boric acid is 2–3 g in infants, 5–6 g in children, and 15–20 g in adults (this would be equivalent to 2.6–3.5 g elemental boron in adults) (EGVM 2003; USEPA-IRIS 2004).

As there are rich natural sources and a boron production complex in Kırka region of Turkey, it is assumed that boron levels in water and sediments of Seydi Stream in this region are higher than the acceptable values and people living in that region are exposed to high boron intake from drinking water and food that are grown in that region and also from fish as an aquatic food. Although, boron was found to be neither genotoxic nor carcinogenic (WHO 1998d), no negative effects of boron on reproductive health were found (Şaylı et al. 2003). One study found that water boron levels in differing locations of the Kütahya Province of Turkey ranged from 2.05 to 29 mg boron L^{-1}, with a mean value of 10.20 ± 4.08 mg boron L^{-1}. Despite such high levels of boron exposure, the authors stated that no remarkable findings of toxicity were observed in the residents. In their discussion, the authors concluded that “chronic boron exposure does not have any important toxic effects because there is no established clear increase in disease among the people living in the region” (Çöl and Çöl 2003). In addition, no difference was found in fertility rates in Turkish villagers living in two regions with boron concentrations of 2.05–29 mg L^{-1} and 0.03–0.4 mg L^{-1} in their drinking water (Şaylı et al. 1998). It is known that, long term consumption of water and food products with increased boron content result in malfunctioning of cardiac-vascular, nervous, alimentary and sexual systems of humans and animals. Not only do they generally work in the borax mines, they also spend their lives in this region. It is clear that they can be exposed to boron intake both through food and water. There is only limited evidence of overt symptoms of reproductive toxicity in humans with industrial exposure (mainly by inhalation). A few studies of Russian male workers exposed for 10 or more years to high levels of vapors and aerosols of boron salts (22–80 mg m^3) involved in borax mining and the production of borates and boric acid suggested low sperm count, reduced sperm motility, changes in seminal fluid composition, and decreased sexual function (Natural Health Products 2007). It is known that boron compounds belong to the second class of toxicological danger (WHO 1998a). We can conclude that Kırka and Seyitgazi consumers are exposed to boron naturally through food, water, air-borne particulate matter, consumer goods and health products. Even though boron is an essential element for plants, the biological function of boron in humans is not clear. Natural Health Products Directorate of Canada (2007) indicated that the Tolerable Dietary Upper Intake Level (DRI UL) for boron is 20 mg/day for adults (≥19 years), 17 mg/day for adolescents (14–18 years), 11, 6 and 3 mg/day for children (9–13, 4–8 and 1–3 years, respectively). Our results showed that average level of boron in edible part of fish is high. However, as we mentioned above there is no information about maximum permissible boron limits in fish tissues (edible part) in the Turkish standards. Therefore, our results could not have been compared with the levels of Turkish Food Codex Standard.

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