




Heavy Metal Accumulation in Wetland Plants and Water-Sediment Relationship in Köprüören-Kütahya

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ABSTRACT

We investigated the concentrations of boron, zinc, arsenic, silver, lead, copper, cadmium and chromium in water, sediment and boron, zinc and arsenic in some wetland plants (*Phragmites australis* (Cav.) Trin. Ex Steud, *Typha latifolia* L., *Nasturdium officinale* L., *Lemna minor* L., *Lythrum salicaria* L., and *Ceratophyllum demersum* L.) of Kocasu Stream and two related ponds in Köprüören, Kütahya. According to our results, among the eight heavy metals investigated in this study, arsenic was found at high concentration in sediment (288.66 mg/kg) whereas boron (903 µg/L) was detected in the highest concentration in water samples. We also determined that zinc, boron and arsenic concentrations in plants varied from 70 to 280, 37.6 to 1682.5, and 0.2 to 34 mg/kg dry weight (DW), respectively. As a result, it was found that *C. demersum*, *L. minor* and *N. officinale* had the highest accumulation capacity of zinc, boron and arsenic.

Keywords: Bioaccumulation, heavy metal, sediment, water, wetland plants

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Köprüören-Kütahya'da Yayılış Gösteren Sulak Alan Bitkileri Tarafından Ağır Metal Akümülayonu ve Su-Sediment İlişkisi

Öz: Köprüören, Kütahya'da bulunan Kocasu Nehri ile bu nehirle bağlantısı bulunan iki göletin kenarlarında yayılış gösteren bazı sulak alan bitkilerindeki (*Phragmites australis* (Cav.) Trin. Ex Steud, *Typha latifolia* L., *Nasturdium officinale* L., *Lemna minor* L., *Lythrum salicaria* ve *Ceratophyllum demersum* L.) bor, çinko ve arsenik miktarları ile su ve sedimentteki bor, çinko, arsenik, gümüş, kurşun, bakır, kadmiyum ve krom konsantrasyonları tarafımızdan araştırılmıştır. Bu çalışmada araştırılan sekiz ağır metal arasından, arsenik sedimentte yüksek konsantrasyonda bulunurken (288,66 mg/kg), su numunelerinde en yüksek konsantrasyonda bor (903 µg/L) tespit edilmiştir. Ayrıca, bitkideki çinko, bor ve arsenik konsantrasyonlarının sırasıyla 70-280, 37,6-1682,5 ve 0,2-34 mg/kg kuru ağırlık arasında değiştiği saptanmıştır. Sonuç olarak, *C. demersum*, *L. minor* ve *N. officinale*'nin en yüksek çinko, bor ve arsenik biriktirme kapasitesine sahip olduğu bulunmuştur.

Anahtar kelimeler: Biyoakümülayon, ağır metal, sediment, su, sulak alan bitkileri

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Introduction

Heavy metal pollution caused by arsenic (As), boron (B), zinc (Zn), lead (Pb), cadmium (Cd) in fresh waters is one of the most important global environmental issue that we are facing.

Untreated discharges of textiles, metal finishing, mining, ceramic and pharmaceutical industries contaminate freshwaters with heavy metals. Along with the increase in concentrations of heavy metals in freshwater ecosystems, bioaccumulation of these heavy metals by plant and animal species also increasing, and so open a way to toxicity in these

living groups (Tchounwou et al. 2012; Priti and Biswajit 2016).

Among heavy metals, Zn and B are essential microelements for plant growth and development (Nable et al. 1997; Broadley et al. 2012). However, when B reaches high levels in the environment (i.e. above 1 mg B/L), it is considered a serious threat to the freshwater resources used for drinking and agriculture purposes (WHO 1998). If boron is deposited at high levels in plant organs, it can cause toxicity symptoms characterized by reduction of shoot-root growth, low chlorophyll content,

leaf deformations, chlorosis, necrosis, inhibition of pollen germination (Howe 1998; Chen et al. 2014; Farag and Zhang 2014; Tripathi et al. 2015).

Zn, enters the environment through industrial wastes, sewage sludge and acid rains, is one of the most common elements on earth (Paschke et al. 2006). Zn is an essential trace element that plays important roles in carbohydrate, lipid and nucleic acid metabolisms along with enzyme activation in plants. Zn is an indispensable micronutrient for plant development, but it can cause toxicity in plants when it reaches high levels in soil and water sources. Although the toxicity threshold of Zn for plants is uncertain, the visible toxicity symptoms such as curling of young leaves, browning leaf tips and chlorosis appear above 300 mg Zn/kg leaf DW (Broadley et al. 2007; Sharma et al. 2013; Tripathi et al. 2015).

Even though biological function of arsenic is not known well, there are studies showing that As is an essential nutrient for rats, hamsters, minipigs, goats and chickens (Uthus 1992). On the other hand, it limits the uptake of Fe and Zn, essential for human health, by plants (Li et al. 2016). Arsenic enters the environment through anthropogenic activities such as mining, metal smelting and burning of fossil fuels. It is toxic in high concentrations and causes decrease in fertility, yield and fruit production in plants (Smedley and Kinniburgh 2002; Finnegan and Chen 2012).

Heavy metals are toxic for plants, but some plants are capable of growing in soils and fresh waters with high concentrations of heavy metals and accomplish their detoxification of these metals by various defense mechanisms (Ali et al. 2013). Heavy metal hyperaccumulating plants such as *Thlaspi caerulescens* L., *Polygonum amphibium* L., *Lemna minor* L., *Eichhornia crassipes* (Mart) Solms., *Pistia stratiotes* L. are used to remove heavy metals from contaminated ecosystems (Arthur et al. 2005; Lone et al. 2008; Rahman and Hasegawa 2011; Moosavi and Seghatoleslami 2013).

There are important metallic mineral and industrial raw material resources mainly boron, chromium, silver, alunite, antimony, copper-lead-zinc, iron, manganese, magnesite, cement raw materials, feldspar, gypsum, fluorite and sand-gravel in Kütahya (Hastorun 2017). In addition, the largest silver deposit of Turkey is located about 7 km south of the Köprüören, Kütahya. Köprüören region fresh waters, on the banks of the Kocasu stream and two ponds, are used by local people for irrigation purposes. On the other hand, Kocasu stream feeds Felent stream as important water potential for Porsuk River (Anonymous 2017). Unfortunately, silver mining activities cause As, Pb, Sb and Zn pollution in soil and surface waters in the area (Arslan and

Çelik 2015). On May 7 of 2011, one of the waste storage reservoir pools of the silver factory in Gümüşköy had collapsed. Right after the collapsing, the investigation in the area by authorities reported the necessity of monitoring the region in terms of environmental and health effects (Türkkan ve Soysal 2011). For this reason, our study determined (1) the heavy metal concentrations in sediment and water of two ponds and Kocasu stream in Köprüören where heavy metals inputs were mainly due to mining, municipal wastewaters and farming, and (2) the ability of some wetland plants to accumulate B, Zn and As, and (3) investigation of the potential of these plants applicable for phytoremediation studies.

Material and Methods

Study site

Köprüören is located in the western part of Kütahya and 21 km away from city center. There are two ponds and one stream called Kocasu in the region. One of the ponds, pond 1, has 63.86 m length and 40.97 m width, and the other one, pond 2, has 17.49 m length and 14.23 m width (Figure 1, Table 1). The ponds are fed with groundwater and water of the each pond falls into Kocasu stream. Pond 1 is surrounded by fences and used as a recreational area by local people. There are no fences around pond 2 and not used as recreational area. Plant species showing distribution along the pond 1, pond 2 and Kocasu stream are: *Lythrum salicaria* L., *Phragmites australis* (Cav.) Trin. Ex Steud, *L. minor* L., *Typha latifolia* L., *Nasturdium officinale* L., and *Ceratophyllum demersum* L.

Sample collection

Samples were collected from pond 1, pond 2 and Kocasu stream in August 2016 in order to determine the B, Zn, As, Ag, Pb, Cu and Cr concentrations in sediment, water and plant species. Sediment, water and plant samples were collected from nine study points. Sediment samples were collected with scoop with low current velocities in depth of 0-5cm. After sampling, sediment samples were sealed in clean polypropylene (PP) containers.

In addition, water samples were collected from each study points and placed in PP bottles. Sediment and water samples were kept in a cooler at 4 °C and transported to the laboratory immediately for further analysis. Plant samples were collected, transported to the laboratory and air-dried at 70°C for 48 h.

Analyses of samples

Heavy metal analyses of all sediments, water and plant samples were performed in Kütahya Dumlupınar University, Advanced Technologies Centre, Kütahya. First, sediment samples were air-dried and removed foreign materials by passing the

dried samples through a 2 mm sieve and then stored in polypropylene bottles (Đozić et al. 2014). Water samples were filtered to remove suspended materials and stored in PP bottles at 4 °C in the refrigerator until heavy metal analysis was performed. Dried plant samples were grounded and 0.1 g plant samples were digested with nitric acid (Merck, Germany) and hydrogen peroxide (Merck, Germany) (Kaçar and

İnal 2008). For heavy metal content determinations, sediment and plant samples were digested and the concentrations of heavy metals (Zn, B, Pb, As, Ag, Cd, Cu and Cr) in sediment, water, and plant were analyzed by Atomic Absorption Spectrometer (AAS, Analytikjena ContraA 300) (Kütahya Dumlupınar Üniversitesi 2018).

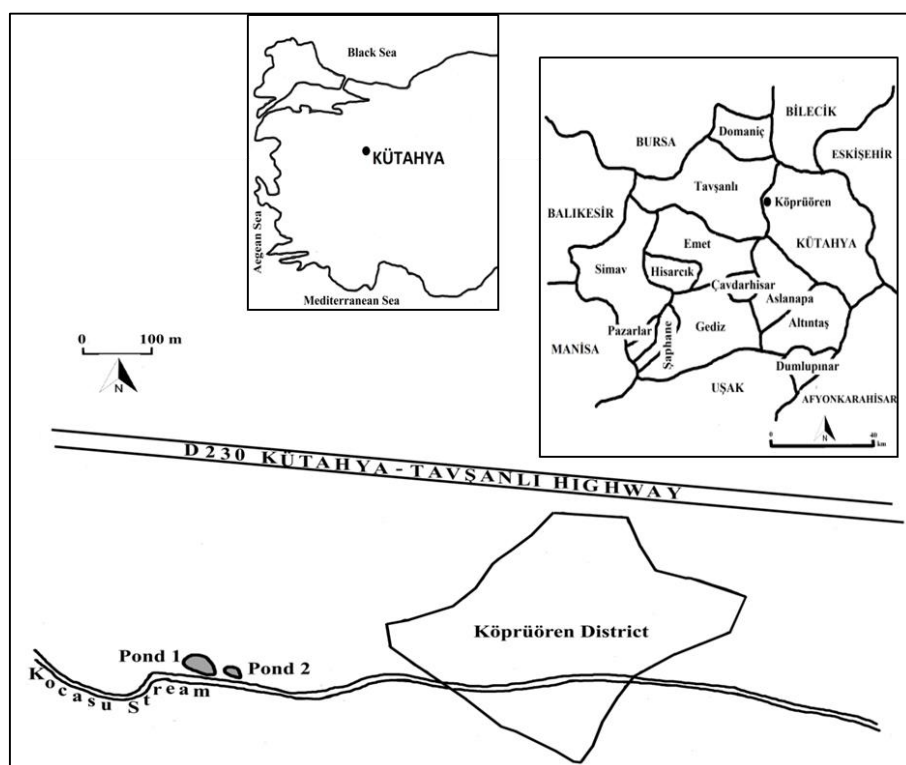


Figure 1. Location of pond 1, pond 2 and Kocasu Stream in Köprüören District.

Table 1. Locations of sampling points.

Study Sites	Sampling Points	Sample Type	Coordinates Latitude	Longitude
Pond 1	1	Water Sediment Plant	39° 30' 27"	29° 44' 59"
	2	Water Sediment Plant	39° 30' 27"	29° 44' 55"
	3	Water Sediment Plant	39° 30' 26"	29° 44' 59"
Pond 2	1	Water Sediment Plant	39° 30' 25"	29° 45' 00"
	2	Water Sediment Plant	39° 30' 26"	29° 45' 01"
	3	Water Sediment Plant	39° 30' 25"	29° 45' 02"
Stream	1	Water Sediment Plant	39° 30' 25"	29° 45' 00"
	2	Water Sediment Plant	39° 30' 26"	29° 45' 01"
	3	Water Sediment Plant	39° 30' 25"	29° 45' 02"

Statistical analysis

All values were expressed as the mean \pm standard deviation of triplicates. Results were evaluated by JMP 6 SAS (JMP SAS 1995) statistical program. F-test was used to determine the differences between the heavy metal accumulation in plants at $p < 0.05$ level. TUKEY-HSD multiple comparison test was used on these applications that statistically different according to F-test.

Results

The results of heavy metal analysis in sediment and water samples were presented in Table 2.

According to AAS results, Ag, Cd, Cu and Cr were detected below detection limit in sediment samples. Zn, B, As and Pb concentrations varied from 133.98 to 215.88, 132.57 to 170.71, 86.49 to 233.44 and 17.19 to 288.66 mg/kg in sediment, respectively. When the distribution of heavy metal concentration were considered, while Pb, As, Ag, Cd, Cu and Cr were under detection limit, Zn and B concentrations varied from 31 to 65 $\mu\text{g/L}$ and from 800 to 903 $\mu\text{g/L}$ in water, respectively. According to the results of our study, it was determined that heavy metals in sediment were higher than water (Table 2).

Table 2. Mean heavy metal concentrations of sediment and water samples in pond 1, pond 2 and Kocasu Stream, Kütahya.

		Zn*	B*	Pb*	As**
Heavy metals in sediment (mg/kg)	Pond 1	150.76 \pm 69.97***	170.71 \pm 27.09	86.49 \pm 63.00	29.72 \pm 17.50
	Pond 2	133.98 \pm 14.01	132.57 \pm 30.31	170.83 \pm 86.43	17.19 \pm 6.54
	Stream	215.88 \pm 90.02	141.66 \pm 66.59	233.44 \pm 107.81	288.66 \pm 162.50
Heavy metals in water ($\mu\text{g/L}$)	Pond 1	65 \pm 98.11	800 \pm 92.31	BDL ¹	BDL ²
	Pond 2	31 \pm 7.5	811 \pm 105.06	BDL ¹	BDL ²
	Stream	36 \pm 20.28	903 \pm 266.47	BDL ¹	BDL ²

* Flame Atomic Absorption Spectrometry, ** Hydride Generation Atomic Absorption Spectrometry

¹ Below Detection Limit (<0.1 mg/L), ² Below Detection Limit (<5 $\mu\text{g/ml}$).

*** Standard error, n=3

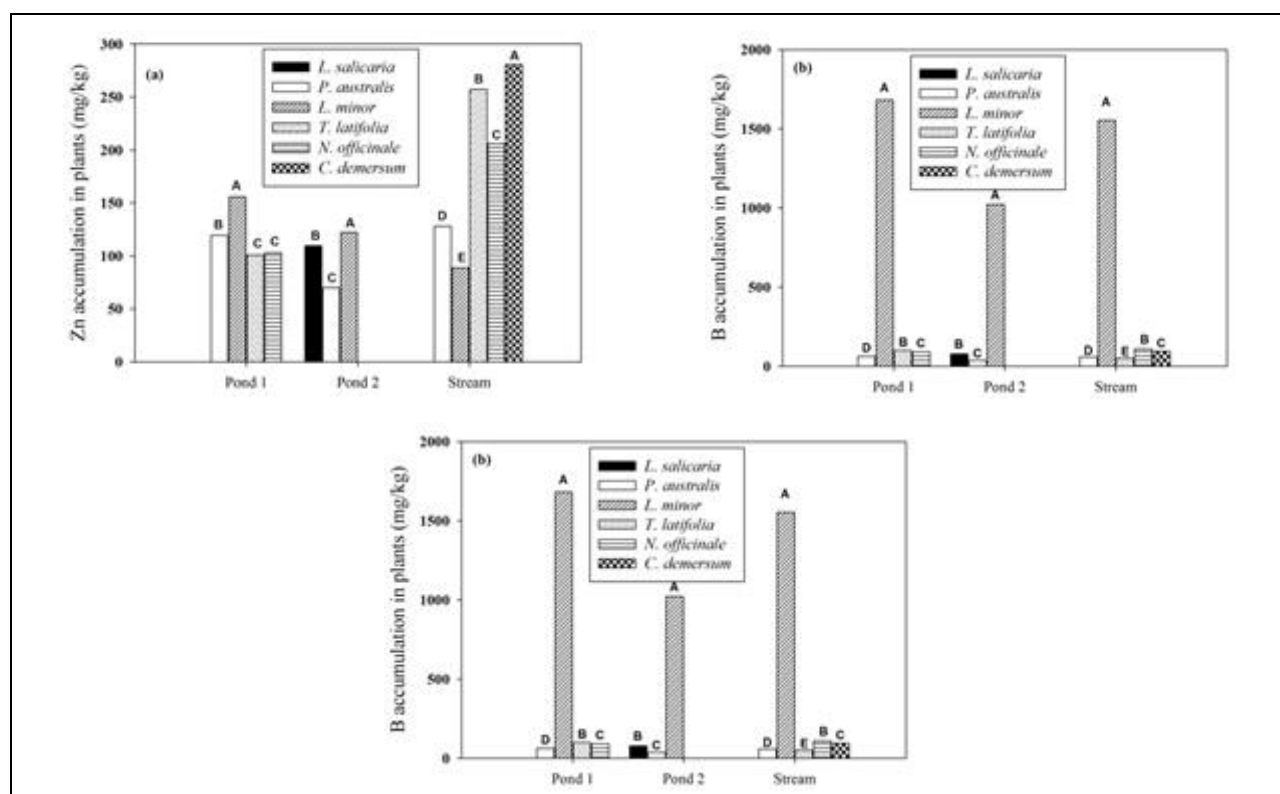


Figure 2. Zinc (a), boron (b) and arsenic (c) accumulation (mg/kg) in *L. salicaria*, *P. australis*, *L. minor*, *T. latifolia*, *N. officinalis*, and *C. demersum* that show distribution along the pond 1, pond 2 and Kocasu stream, Kütahya.

Heavy metal accumulations in plants were presented in Figure 2. While maximum Zn accumulation was obtained in *C. demersum* (280 ± 0.67 mg/kg), minimum Zn accumulation was determined in *P. australis* (70.1 ± 0.58 mg/kg). When

Zn accumulation ability of plants in pond 1 was compared to each other, there were statistically significant differences between mean Zn accumulations of plants. *L. minor* plant (155.8 ± 0.26 mg/kg) zinc accumulation potential is statistically

important than *P. australis* (119.3 ± 0.79 mg/kg), *T. latifolia* (100.6 ± 0.67 mg/kg) and *N. officinale* (103 ± 0.10 mg/kg) in pond 1. In addition, *C. demersum* (280 ± 0.57 mg/kg) in stream and *L. minor* (122.3 ± 0.75 mg/kg) in pond 2 had more accumulation capacity of Zn than others.

Boron concentrations of the plants in pond 1, pond 2 and stream varied from 37.6 ± 0.31 to 1682.5 ± 0.84 mg/kg. The results of statistical analyses showed that the maximum boron accumulation was found in *L. minor* and minimum boron accumulation was found in *P. australis* in all points (Figure 2).

Arsenic concentrations of the plants in pond 1, pond 2 and Kocasu stream varied from 0.2 ± 0.06 to 34 ± 0.53 mg/kg. The maximum arsenic accumulation was found in *N. officinale* (34 ± 0.53 mg/kg) and *C. demersum* (16 ± 0.76 mg/kg) grown in stream. Thus, the arsenic accumulation by *N. officinale* was considerably higher than other aquatic plants. The minimum As accumulation was found in *P. australis* (Figure 2).

Discussion

Among the eight heavy metals investigated in Kocasu stream and two related ponds in Köprüören, arsenic and boron were found at high concentrations in sediment and water samples, respectively. Arslan and Çelik 2015 found that pollution index values were high in stream sediments collected from Köprüören Basin. On the other hand, Çiçek et al. 2013 and Tokatlı et al. 2012 also found that Köprüören village and Felent River were ecologically at risk in term of arsenic heavy metal.

In this study, it was found that the concentrations of Pb and Cr in the water samples collected from Kocasu Stream and related two ponds were below detection limit. However, Yuce et al. 2005 and Kose et al. 2015 have found that concentration of Pb and Cr metals in Porsuk River were over the maximum contamination level. It was thought that the reason for the increase in concentration of these metals is associated with the wastewater contamination from porcelain factories along Porsuk River.

The highest zinc accumulation was observed in *C. demersum* and *T. latifolia* in Kocasu stream. Ghobrial (2000) showed that *C. demersum* could accumulate high concentration of Zn inside its tissues and acts as biological filter for detoxification of domestic effluents. According to research of Kumari and Tripathi (2015), *T. latifolia* plant has the best removal capacity of Zn among Cu, Fe, Ni, Cr, Pb and Cd heavy metals (52.4%). Klink et al. (2013) have stated more zinc was accumulated in root of *T. latifolia* than its stem, so they have identified it as root accumulator plant.

It has been found that *L. minor* accumulate higher concentrations of B than *N. officinale*, *T. latifolia*, *C. demersum*, *L. salicaria*, *P. australis*. Lemna spp., floating aquatic plant, accumulates high concentration of B with its whole plant surface (Del-Campo Marin and Oron 2007; Bökük et al. 2013). Gür et al. (2016) found that *L. minor* accumulated 4007 mg B/kg after a 7-day treatment period. Tatar and Öbek (2014) also determined that B uptake by *L. minor* changes between 140 mg B/g and 274 mg B/g.

N. officinale and *C. demersum* plants were found to accumulate maximum Arsenic in their tissues. *N. officinale* can accumulate high concentration of Arsenic in roots, shoots and leaves under favorable growth conditions (Rahman and Hasegawa 2011; Kisten et al. 2015). According to Ozturk et al. (2010) watercress (*N. officinale*) can accumulate large amounts of Arsenic in its leaves when the plant exposed to 50 M of As. On the other hand, Gounden et al. (2016) determined that watercress plants exposed to over 5 ppm As died after one week of treatment. There are reports about As accumulation presented by a number of authors including Mishra et al. (2013), Srivastava et al. (2014) and Xue et al. (2012), and they all have indicated that *C. demersum* was a potential As accumulator submerged macrophyte plant (76 µg As/g d.w., 489 µg As/g d.w. and 963 µg As/g d.w., respectively).

In recent years, heavy metal pollution due to industrial and agricultural activities has threatened water ecosystems. Especially metal mines and mine processing activities in Kütahya have caused heavy metal pollution in fresh waters. Aquatic plants and macrophytes are one of the main biological component of the fresh water, and able to accumulate high concentrations of heavy metals in their tissues (Matache 2013). In the present study, heavy metal accumulation in some wetlands plants and its relation with sediment and water in Köprüören-Kütahya were investigated. The data showed that while Zn, B, Pb and As was found in the sediments, only Zn and B heavy metals were detected in water samples and B, Zn and As were found in plants. In this study, it was cleared that *C. demersum*, *L. minor* and *N. officinale* have high capacity to accumulate heavy metal in their tissues, and these aquatic plants can be used for phytoremediation.

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