



## Research article

# Monitoring of heavy metals and essential trace elements in aquatic plant *Ranunculus sphaerospermus* Boiss. & Blanche (Ranunculaceae), sediments, and water of volcanic Haydarlar Lake, Türkiye

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Aquatic ecosystems contain communities of organisms that are dependent on each other and on their environment. Monitoring of trace element and heavy metal concentrations is important to understand the possible environmental risks in natural aquatic environments. In the present study, concentrations of some heavy metals and trace elements in aquatic plant *Ranunculus sphaerospermus*, sediments, and water samples of volcanic Haydarlar Lake were analyzed by using ICP-OES. The concentrations were found in the following ranges: 82.11 – 97.38, 9174.50 – 9942.29, and 0.63 – 0.89 for Al; 10.29 – 17.43, 30.60 – 55.60, and 0.81 – 0.98 for B; 1038.44 – 1682.30, 4017.26 – 4503.54, and 1276.61 – 1541.41 for Ca; 120.69 – 178.41, 6894.50 – 8103.47, and 0.51 – 0.69 for Fe; 2503.51 – 2983.38, 1118.50 – 1693.38, and 69.43 – 93.82 for K; 563.38 – 783.22, 885.32 – 1122.47, and 108.55 – 143.36 for Mg in the plant (mg kg<sup>-1</sup>), sediment (mg kg<sup>-1</sup>), and water (mg L<sup>-1</sup>) samples, respectively. The concentrations of Ca, Fe, and K elements in sediments and the content of Ca and K in lake water samples were found as higher than the acceptable limit, while concentrations of all elements in *R. sphaerospermus* were determined to be within acceptable limits. Transfer factors (TF) of the heavy metal and essential elements from sediment to the plant samples were evaluated. The trends of TF for all samples studied were in the following order; K>Mg>B>Ca>Fe>Al. Consequently, the approach used in this study could contribute to pollution monitoring in the future.

**Keywords:** Accumulation; aquatic plants; lava flow area; mineral nutrients; transfer factors; water daisy

**1. Introduction**

*Ranunculus sphaerospermus* Boiss. & Blanche (Ranunculaceae) is submerse type, herbaceous, annual orbiennial aquatic plant. The leaves in the water are filamentous, the roots are in the sediment, and the white flowers are on the surface of the water. Its laminate leaves are absent. Submerged and spreading capillary leaves, numerous and rigid segments, usually do not collapse when removed from the water. Peduncle of fruit is 5-6 cm. Petals of flower are broadly obovate shaped, contiguous throughout anthesis, 9-25 mm; nectar pit elongated, more or less pyriform. Receptacle hairy, somewhat elongated in fruit. Carpels are shorter than 1 mm, somewhat rounded,

glabrous, or slightly hairy around the base of the style. It spreads in shallow and still or fresh waters with low water flow rates, in puddles, swamps, and lake edges. It is native to the Balkans, South and West Asia, Egypt, Himalayas in alt. 0-1730 m. Its flowering time is January-September. *R. sphaerospermus* (water daisy) is known as “su çiçeği”, “su düğünçiçeği” and “su papatyası” and is widely distributed in Türkiye (Cook, 1965; Guner, 2012a; Tas and Topaldemir, 2021).

Like other plants, water daisy needs macroelements (N, Ca, P, K, Na, Cl, Mg, etc.) and trace elements (Fe, Zn, Cu, Mn, Al, B., etc.) for their structure, growth, and metabolic activities in maintaining of proper life. Their uptake from the environment is crucial because these elements cannot be synthesized

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metabolically by the organism itself (Zeiner and Cindrić, 2017; Hocaoglu-Ozyigit and Genc, 2020). For instance, Boron (B) is one of these elements, an essential nutrient for vascular plants, cyanobacteria, algae, fungi and animals and has a largely structural role in development and other metabolic functions in living organisms (Herrera-Rodríguez et al., 2010). Concentration of B ranges between 0.1–0.5 mg/L<sup>-1</sup> in freshwaters and 10–300 mg kg<sup>-1</sup> in soils depending on amount of rainfall, amount of organic matter, soil type and pH (Howe, 1998). In plants, B plays important roles in seed and fruit formation, pollen health, fertilization, protein synthesis, formation and transport of carbohydrates, Calcium (Ca) transportation, and formation of hormones especially auxins in plant metabolism (Jones and Jacobsen, 2012). Deficiency of B causes vegetative and reproductive growth, necrosis, the significant losses in crop quality and yield, reduces the plant fertility, and inhibits the cell expansion in plants (Herrera-Rodríguez et al., 2010; Vatansver et al., 2017). Excess amounts of B leads to significant changes in the structure, physiology, and activity of numerous enzymes and consequently, has negative effects such as altered metabolism, osmotic imbalance, reduced root cell division, increased membrane leakiness in metabolism during the life cycle of plants (Camacho-Cristóbal et al., 2008; Herrera-Rodríguez et al., 2010; Vatansver et al., 2017). Ca serves as an essential element and is taken by the root tips of plants as Ca<sup>+2</sup> ions. Its concentration in the plants varies between 1000 to 20000 ppm (Tewari et al., 2021). Ca plays roles in the development of the end points of plant tissues, the formation of roots and flowers, the structural and physiological stability of plant tissue, as well as cell division, cell wall formation, cell expansion and activation of enzymes (Aydin, 2017). Ca-deficient plants show various symptoms such as blossom-end rot of fruits, necrosis in young leaves, cell breakdown, and loss of membrane integrity (Olle and Bender, 2009). The term heavy metal is generally used for metals such as arsenic, iron, cadmium, nickel, copper, mercury, chromium, manganese, and lead with a density higher than 4-5 g cm<sup>-3</sup> (Caparrós et al., 2022). However, aluminum (Al) with a density of 2.70 g cm<sup>-3</sup> was presented in the heavy metal category due to its contribution to pollution and toxicity according to the results of many research studies (Ghori et al., 2019; Ozyigit et al., 2022; Riyazuddin et al., 2022). In the meantime, although it is not considered as an essential nutrient, low concentrations can sometimes affect plant growth or induce some other necessary metabolic activities. Common effects of Al toxicity include decrease in shoot biomass, total leaf number and size, photosynthetic activity, chlorosis and/or necrosis of leaves, and decrease (Ozyigit et al., 2013; 2019; Dogan et al., 2014). However, slightly higher Al intake is not only very toxic for plants but also is harmful to gill-breathing aquatic animals such as fish, amphibians and some arthropods, causing osmoregulatory failure by destructing the hemolymph ions and plasma (Jaishankar et al., 2014). On the other hand, iron (Fe) is a crucial essential micronutrient for plant growth and development. Its deficiency leads the interveinal chlorosis in plant leaves and reduces crop productivity (Vatansver et al., 2017). In addition, magnesium (Mg) is the most important element for chlorophyll structure, photosynthesis, fat formation, protein synthesis, uptake and transport of phosphorus in the plant body. Mg deficiency can cause reduction in photosynthesis and plant growth (Aydin, 2017). Potassium (K) plays roles in metabolic processes such as photosynthesis, protein synthesis, and carbohydrate translocation. K deficiency can cause

regression in plant resistance mechanism, development, and photosynthesis (Jones and Jacobsen, 2012; Aydin, 2017).

During the last few decades, many studies have focused on trace element analyses and heavy metal accumulation in environment since monitoring of pollution and its effect on plant and animal species in natural habitats is vital (Sungur et al., 2013; Ozturk et al., 2017; Ghori et al., 2019; Ozturk et al., 2019; Karahan et al., 2020; Haq et al., 2021; Ozyigit, 2021; Ozyigit et al., 2022). However, studies on mineral nutrient and heavy metal accumulations in organisms living especially in aquatic ecosystems are very limited (Kaptan and Tekin-Ozan, 2014; Yilmaz et al., 2015; Yilmaz et al., 2021a,b).

The aim of the present work was to determine some heavy metals (Al and Fe) and essential trace element (B, Ca, Mg, and K) concentrations and correlation between levels of their accumulation in sediments, water and plant tissue of *R. sphaerospermus* from the Haydarlar Lake. Also, in this work, the transfer coefficient of the studied elements from sediment to the plant samples was calculated by dividing the concentration. Since transfer factor (TF) is an indicator of heavy metal mobility in soils and quantifies the existing variations in the bioavailability of elements to plants, the knowledge of the optimum TF of heavy metals and trace elements from soil to plant is of crucial importance.

## 2. Materials and methods

### 2.1. Sampling and study area

The present study is based on the content of some trace elements and heavy metals of widely distributed aquatic plant *Ranunculus sphaerospermus*, sediments, and lake water. The plant, sediment and lake water samples used in this study were collected from six different localities of Haydarlar Lake (Hatay province) in the East Mediterranean region of Türkiye during vegetation period in March-April 2021 (Fig. 1).



**Fig. 1.** *Ranunculus sphaerospermus*, (a) Habitus (b-d) General view, (e) flower.

Hatay province, has diverse geographical, topographical, and ecological features that include mountains, plains, rivers, and lakes with a rich biodiversity. A number of ethnobotanical,

ecological, palynological, and genetic diversity studies have been carried out for Hatay province and its vicinity (Altay and Karahan, 2012; Karahan et al., 2012; İlhan et al., 2017; Altay et al., 2018; Alsaadi et al., 2020).

Volcanic Haydarlar Lake is located in the northern part of Hatay Province (36°44' N–36°32' E) near Syria border line and its altitude is 313 m. a.s.l. The surface area of the lake changes from 50 to 75 ha seasonally with a maximum depth of 15 m. in winter seasons (Fig 2). The main habitat type around the lake consists of the lava flow area, which is assumed to have formed throughout the 5 periods between 1.57 million and 26 thousand years ago and is called “Leçelik” in Turkish (Belguzar, 2017). The study area has a climate type close to the oceanic climate, which is semi-humid-semi-arid, medium temperature (Mesothermal) with a mean annual rainfall of about 684.8 mm and an annual temperature of 17.7°C. Annual precipitation is at a maximum level in winter, while it decreases in spring. The mean minimum and maximum temperatures are measured as 6.3 and 28.9°C, respectively in January and July (Aytac and Semenderoglu, 2014; Altay et al., 2016; Topuz et al., 2016). It is used for irrigation and farming by local people.



**Fig. 2.** The study area (up) and localities (down) of the studied aquatic plants *R. sphaerospermus* samples.

For the present study, the plant samples were dried and identified according to related literatures (Cook, 1965; Guner, 2012b). The sampling bottles were immersed about 10 cm below the water surface. Approximately 0.5 L of water for each sampling site were collected. Samples were added 10% HNO<sub>3</sub> and transferred to the laboratory by placing in an ice bath. Sediment samples were also collected using a grab sampler and transported to the laboratory.

## 2.2. Sample preparation

Plant samples of *R. sphaerospermus* were weighted and then dried in an oven at 80°C during 2 days. Samples were ground and passed through 1.5-mm sieve after the drying process. The grinding device was cleansed with 96% ethanol and distilled water after each process. The samples were scaled to 0.2 g and put in Teflon vessels, and 10 ml of 65% HNO<sub>3</sub> for plant samples and 6 ml of 65% HNO<sub>3</sub>, 3 ml of 37% HCl and 2 ml of 48% HF for sediment samples were added into each vessel. Water samples are transferred to a new Falcon tube containing 1% HNO<sub>3</sub> for appropriate dilution. Following this, the plant and sediment samples were digested at 165°C using Mars Microwave and left to cool following the microwaving process. The samples were then transferred into conical 50 ml centrifuge tubes also carefully being washed using distilled water and then filling the tubes up to 50 ml (Karahan et al., 2020).

## 2.3. Determination of Al, B, Ca, Fe, Mg, and K

Ultrapure chemicals of analytical grade were used for this study. Water (Human-Zener Power I) was used as a solvent in dilution procedures in the all experimental steps of the study. For linearity, elemental values of plant, sediment and water samples were measured in triplicate. The EPA 3051A analytical method for ICP-OES was applied using MARS microwave to dissolve the all samples. The B, Al, Fe, Ca, K, and Mg concentrations of the samples were established using ICP-OES (PerkinElmer Optima 7000 DV).

## 2.4. Transfer factors (TF) of the elements from sediment to the plant samples

The transfer coefficient was calculated by dividing the concentration of heavy metal and mineral nutrient elements in plant samples by the total heavy metal concentration in the sediments (Chizoruo et al., 2017).

$$TF = \frac{C_{plant}}{C_{sediment}}$$

Where, C<sub>plant</sub> = element concentration in plant tissue, mg kg<sup>-1</sup> fresh weight and C<sub>sediment</sub> = element concentration in sediment, mg kg<sup>-1</sup> dry weight (mg kg<sup>-1</sup> Dw).

## 3. Results

In this study, trace element (boron, magnesium, phosphorus and potassium) and heavy metals (aluminum and iron) concentrations were determined for *R. sphaerospermus*, as well as for its habitat, from different six sampling localities of Haydarlar Lake sediments and water, and results are presented in Table 1 and Fig. 2.

According to our results, the content of **Al** was found as

**Table 1**Trace element and heavy metal concentrations in *R. sphaerospermus*, sediments and lake water samples and legal concentration limits.

Plant samples (mg kg <sup>-1</sup> ) (mean ± SD)							
LOC. NO	Al	B	Ca	Fe	K	Mg	
<b>P1</b>	86.47 ±1.83	13.56 ±0.20	1275.88 ±19.99	141.22 ±1.23	2741.68 ±30.43	641.11 ±16.45	
<b>P2</b>	82.11 ±2.06	10.29 ±0.23	1038.44 ±14.17	120.69 ±2.92	2503.51 ±34.83	563.38 ±14.49	
<b>P3</b>	91.23 ±1.23	15.79 ±0.16	1389.51 ±11.49	155.02 ±2.87	2833.59 ±22.01	683.41 ±19.38	
<b>P4</b>	83.20 ±1.59	11.23 ±0.14	1163.48 ±18.26	132.51 ±2.38	2673.21 ±68.57	581.20 ±10.95	
<b>P5</b>	88.22 ±1.47	14.01 ±0.26	1493.21 ±26.10	146.63 ±1.31	2796.00 ±43.27	703.23 ±17.25	
<b>P6</b>	97.38 ±1.68	17.43 ±0.27	1682.30 ±13.34	178.41 ±2.26	2983.38 ±74.56	783.22 ±13.00	
<b>Mean</b>	88.10 ±1.64	13.72 ±0.21	1340.47 ±17.23	145.74 ±2.16	2755.23 ±45.61	659.26 ±15.25	
<b>Legal limits<sup>a</sup></b>	15–100	3–90	1000–20000	50–200	3000–10000	100–15000	
Sediment samples (mg kg <sup>-1</sup> ) (mean ± SD)							
LOC. NO	Al	B	Ca	Fe	K	Mg	
<b>S1</b>	9464.03 ±214.76	38.81 ±0.55	4277.08 ±88.84	7552.66 ±131.39	1397.71 ±32.66	974.06 ±15.29	
<b>S2</b>	9174.50 ±196.87	30.60 ±0.75	4017.26 ±98.77	6894.50 ±175.58	1204.50 ±27.68	904.51 ±18.11	
<b>S3</b>	9748.41 ±142.12	44.17 ±0.51	4387.88 ±76.89	7748.21 ±113.44	1247.55 ±15.90	955.32 ±15.79	
<b>S4</b>	9355.69 ±229.64	33.07 ±0.43	4184.31 ±84.32	7409.56 ±127.30	1118.50 ±25.29	885.32 ±19.58	
<b>S5</b>	9641.29 ±189.72	45.84 ±0.56	4421.69 ±51.69	7794.31 ±138.29	1408.41 ±18.55	1043.69 ±22.30	
<b>S6</b>	9942.29 ±225.99	55.60 ±0.69	4503.54 ±70.47	8103.47 ±108.22	1693.38 ±40.52	1122.47 ±21.01	
<b>Mean</b>	9554.37 ±199.85	41.35 ±0.58	4298.63 ±78.50	7583.78 ±132.37	1345.01 ±26.77	980.89 ±18.68	
<b>Legal limits<sup>b</sup></b>	10000–40000	2–100	1440–2867	5–10	200–250	1000–40000	
Water samples (mg L <sup>-1</sup> ) (mean ± SD)							
LOC. NO	Al	B	Ca	Fe	K	Mg	
<b>W1</b>	0.68 ±0.02	0.84 ±0.02	1377.63 ±18.36	0.60 ±0.01	77.88 ±1.71	122.43 ±1.08	
<b>W2</b>	0.63 ±0.01	0.89 ±0.02	1298.50 ±23.59	0.51 ±0.01	69.43 ±1.13	108.55 ±2.27	
<b>W3</b>	0.72 ±0.02	0.81 ±0.01	1421.29 ±20.10	0.57 ±0.01	71.43 ±1.34	131.23 ±1.07	
<b>W4</b>	0.69 ±0.02	0.82 ±0.02	1276.61 ±17.88	0.61 ±0.01	81.36 ±0.90	115.58 ±1.65	
<b>W5</b>	0.77 ±0.01	0.91 ±0.02	1486.56 ±29.93	0.62 ±0.02	85.60 ±1.21	127.78 ±2.66	
<b>W6</b>	0.89 ±0.02	0.98 ±0.02	1541.41 ±14.14	0.69 ±0.02	93.82 ±1.56	143.36 ±2.32	
<b>Mean</b>	0.73 ±0.02	0.87 ±0.02	1400.33 ±20.67	0.60 ±0.01	79.92 ±1.31	124.82 ±1.84	
<b>Legal limits<sup>c</sup></b>	0.3–1	<1	75–800	0.3–5	20–50	50–150	

<sup>a</sup>Karahan et al. (2020), <sup>b</sup>Kabata-Pendias and Mukherjee (2007), <sup>c</sup>United States Environmental Protection Agency (USEPA, 2002) and Water Pollution Control Regulations of Türkiye (WPCRT, 2004).

82.11 – 97.38 (mean 88.10), 9174.50 – 9942.29 (mean 9554.37), and 0.63 – 0.89 (mean 0.73); the content of **B** was found as between 10.29 – 17.43 (mean 13.72), 30.60 – 55.60 (mean 41.35), and 0.81 – 0.98 (mean 0.87); the content of **Ca** ranged between 1038.44 – 1682.30 (mean 1340.47), 4017.26 – 4503.54 (4298.63), and 1276.61 – 1541.41 (mean 1400.33); the content of **Fe** ranged between 120.69 – 178.41 (mean 145.74), 6894.50 – 8103.47 (mean 7583.78), and 0.51 – 0.69 (mean 0.60); the content of **K** ranged between 2503.51 – 2983.38 (mean 2755.23), 1118.50 – 1693.38 (mean 1345.01), and 69.43 – 93.82 (mean 79.92); the content of **Mg** ranged between 563.38 – 783.22 (mean 659.26), 885.32 – 1122.47 (mean 980.89), and

108.55 – 143.36 (mean 124.82) in the plant (mg kg<sup>-1</sup>), sediment (mg kg<sup>-1</sup>), and water (mg L<sup>-1</sup>) samples, respectively (Table 1).

Considering the total accumulation values for all elements (ppm) indicated that Al mean value is the highest as 9554.37 in the sediment and the lowest 0.73 in the water samples; B mean value are highest as 41.35 in the sediment and lowest as 0.87 in the water samples; Ca mean value are the highest as 4298.63 in the sediment and the lowest as 1340.47 in plant samples; Fe mean value are the highest as 7583.35 in the sediment and the lowest as 0.60 in water samples; K mean value are the highest as 2755.23 in the plant samples and the lowest as 79.92 in the water samples; Mg mean value are the highest as 659.26 ppm in

the sediment and the lowest as 124.82 in water samples (Table 1).

When compared to the limit values recommended by the related literatures, concentrations of all elements in *R. sphaerospermus* was determined to be within acceptable limits. The concentrations of Ca, Fe, and K elements in sediments were found as above the acceptable limit, while contents of Al, B and Mg in normal limits for sediments. Moreover, the content of Ca and K in lake water samples were also found as above the acceptable limit, while contents of the other elements remained in normal limits for freshwaters. (USEPA, 2002; WPCRT, 2004; Kabata-Pendias and Mukherjee 2007; Karahan et al. 2020).

The results obtained from our experiment show that TF mean value ranges were: 0.009 for Al, 0.334 for B, 0.310 for Ca, 0.019 for Fe, 2.075 for K, and 0.671 for Mg, respectively and the trend of TF for heavy metal and essential elements in plant samples studied were in order of: K>Mg>B>Ca>Fe>Al. The transfer or mobility of trace elements and heavy metals from soil or sediments to plant body could be influenced by the physicochemical characteristics of sediments and plant samples and is altered by innumerable environmental and anthropogenic factors (Aktaruzzaman et al., 2013). The highest and lowest mean TF values were found as 2.075 for K and 0.009 for Al, respectively.

**Table 2**

Transfer factor (TF) of heavy metal and trace elements from sediments to the plant body.

Samples	Transfer factors (TF)					
	Al	B	Ca	Fe	K	Mg
1	0.009	0.350	0.298	0.019	1.962	0.658
2	0.009	0.336	0.258	0.018	2.078	0.623
3	0.009	0.358	0.317	0.020	2.271	0.715
4	0.009	0.340	0.278	0.018	2.390	0.656
5	0.009	0.306	0.338	0.019	1.985	0.674
6	0.010	0.313	0.374	0.022	1.762	0.698
Mean	0.009	0.334	0.310	0.019	2.075	0.671

#### 4. Discussion

There are some previously performed studies with the aquatic plant species used in this study. In a similar study, some ecological properties of three different aquatic plants and water samples of Gölarmara lake were analyzed and concentrations of P were found between 20 to 40 ppm and K between 18 to 80 ppm in *R. sphaerospermus* and concentrations of Mg were found between 32.11 to 47.54 ppm, K between 10.97 to 11.00 ppm,

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and Ca between 19.23 to 31.87 ppm in lake water. All concentrations were within acceptable limits for both for freshwater and plant samples (Yildiz and Ozdemir, 2005). In another study performed in the Gevaş district of Van (Türkiye), the levels of Al and Fe of the same species (*R. trichophyllus*) were found above the acceptable limits, whereas the levels of K, Ca and Mg were found to be within the normal ranges (Budag and Firat, 2015). When compared with our results, the concentrations of Al, B, Ca, Fe, K and Mg were found to be within the acceptable levels for plants. In another study, soil geography of Hassa district was investigated and it was reported that soil properties of Haydarlar Village had been found as; pH 7.76, K 203, Ca 320, and Mg 28.8 mg kg<sup>-1</sup>. Similarly, the contents of Ca, Fe, and K in the sediment samples were determined as high level according to our findings (Atasoy, 2017). This accumulation is related to the volcanic lands surrounding the lake which occupy a very large area.

K and Mg elements had the highest TF value and TF value of Mg was higher than Ca (Table 2). This is an expected result, because Mg<sup>+2</sup> ions are highly mobile in the phloem unlike Ca (Tang and Luan, 2017). Moreover, Dogan et al. (2014) reported that long term exposure of Al can effect uptake and transport of Ca, Mg and P nutrients. In our results, value of TF for Ca was lower than K and Mg. Hence, the lower value of TF for Ca than K and Mg in our plant samples may be attributable to high level of Al in sediments.

#### 5. Conclusion and recommendations

Haydarlar Lake has been used for land irrigation and farming by local people especially in summer periods. It is also an important location for migratory birds in the wetland ecosystem. Since the contents of Al and Fe in the water samples are within the acceptable limits, it can be regarded as safe for agricultural products and animal health. In this study, the level of pollution and essential nutrients in this aquatic ecosystem were determined for the first time. In addition, due to its interesting geography and the freshwater flowers that cover the lake surface like a blanket, it has a high ecotourism potential.

**Conflict of interest:** The author declares that he has no conflict of interests.

**Informed consent:** The author declares that this manuscript did not involve human or animal participants and informed consent was not collected.

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