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DETERMINATION OF HEAVY METAL CONTENT IN WATER, SEDIMENT AND SOME MACROPHYTE SPECIES, IRON REEDS, BITLIS-TÜRKİYE CASE STUDY

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Abstract

In the context of study, heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, As) content and macronutrients (Mg, Ca) in three aquatic ecosystem plant species (*Juncus gerardii* Loisel. subsp. *gerardii*, *Phragmites australis* (Cav.) Trin. Ex Steud. and *Carex diluta* M. Bleb. subsp. *diluta* and in the surrounding water and sediments were determined in the Iron Reeds, which is one of the most important wetlands in Türkiye within the borders of Bitlis. The concentrations of heavy metals in *Juncus gerardii* Loisel. subsp. *gerardii* and *Carex diluta* M. Bleb. subsp. *diluta* species were reported for the first time in this article. With the results obtained, the aim was to contribute to studies to investigate the uptake of heavy metal pollutants in wetlands and the self-healing effect of the aquatic environment by applying phytoremediation methods in the field. Uncontrolled livestock activities in the region affect the water quality negatively. The silicon and boron contents in the examined waters were above the limit values, as a result of reeds being fed by water sources coming from volcanic areas. There were no problems in terms of trace metals measured in the plants, soil and sediments.

Key words: Iron Reeds, Heavy Metals, Phytoremediation.

Introduction

In recent years, measures taken against environmental pollution have increased in parallel with the European Union harmonization process in our country, and efforts for rehabilitation of contaminated soils have accelerated. Nowadays, environmental treatment technologies require relatively high installation and operating costs in developing countries such as Türkiye. The phytoremediation method is still a developing and promising technology. Studies about this technology using live plants showed that this technology is very advantageous both in terms of application and operating costs, and removal potential. It is known that when plants absorb inorganic substances such as minerals, nitrogen (N) and phosphorus (P) with the help of microorganisms in the soil, they also incorporate heavy metals known to have negative environmental effects in the long term and contribute to the removal of heavy metals from the soil (Ali *et al*., 2013; Wang *et al*., 2012). Phytoremediation, which has become more popular than other treatment systems in recent years and is a more environment friendly treatment system than others, has advantages such as providing on-site treatment, being aesthetically pleasing and low in cost. Accordingly, in the study, heavy metal concentrations that can accumulate in different organs were determined for important plant types in the aquatic ecosystem, such as *Juncus gerardii* Loisel. subsp. *gerardii* (Male head), *Phragmites australis* (Cav.) Trin. exSteud. (Cane) and *Carex diluta* M. Bleb. subsp. *diluta* (Ring Cane), which grow naturally in Iron Reeds, a location in Bitlis. In addition, the trace metal levels in different organs of these plants were compared. In order to determine the hyperaccumulator properties of the plants, heavy metal values of the sediments, surrounding water and the plants were identified.

As a result of industrialization and increasing population, interest in studies conducted about plants resistant to heavy metals is increasing with every passing day. The fact that heavy metals, which could create a toxic effect on many types of plants, do not produce a harmful effect in hyperaccumulator plants has led to the idea of removing the trace metals present in soil by hyperaccumulator plants, and thus the remediation of the soil by using hyperaccumulator plants (Kaya, 2019). Hence, the heavy metal concentrations of three different aquatic plants that are quite important in Iron Reeds, and the sediments surrounding these plants were determined. The Iron Reeds, where the study is carried out, is an area covered with reeds spread over a wide area. The Iron Reeds, with Karasu Stream passing through the middle, is fed by waters descending from the surrounding mountains. However, many hot water and drinking water sources also feed the area (Url 1). As it is located in a volcanic area, this diversifies the water quality of the reed bed, and also the heavy metal species and amounts that pass into the plants. An analysis was carried out to determine the water quality by taking water samples from two different points near the reed bed.

Material and Methods

Research and sampling Area: The Iron Reeds is one of national wetland area in the north of Güroymak district in Bitlis province. The Iron Reeds is west of the Nemrut Crater Lake Ramsar area, and it is approximately 50, 55, 200, 20 and 55 km from the settlements of Bitlis, Muş, Van, Güroymak and Tatvan, respectively.

In the Iron Reeds, many bird species stay and reproduce during migration due to the wetland habitats. The Iron Reeds are considered to be among the ecologically important areas in Eastern Anatolia.

It contains most aquatic ecosystems. Among them, lake areas, wet meadows and reed-swamp areas are important habitats that enable the assessment of the Iron Reeds as a wetland. Among other habitats and land use cases are the Eastern Anatolian mountain steppe habitats, bushes and woodlands, agricultural areas. The lake area consists of large reed areas, wetlands, mountain steppes and agricultural areas. Most of the wetland is covered with *Phragmites australis* communities. The reed area surrounds the wetlands, with the assemblage of *Juncus* *gerardii* subsp. *gerardii* and *Carex diluta* subsp. *diluta.* The study area (Iron Reeds) is shown in (Fig. 1).

Plants used: The aquatic ecosystem plants *Phragmites australis*, *Juncus gerardii* subsp. *gerardii* and *Carex diluta* subsp. *diluta,* (Fig. 2), which naturally grow and dominate the Iron Reeds in the north of Güroymak district in Bitlis province, were collected from this region during the flowering period. Also, sediment and soil samples near these plants were suitably taken from the land. The coordinates of the plant and soil samples at the stations were T1: 38 ° 38′31.4″N42 ° 00′45.0″E, T2: 38 ° 37′17.0″N42° 02′00.9″E, T3: 38° 37′06.2″N42° 00′05.7″E, respectively and they are shown in Figure 3 on a Google Earth map.

Water quality sampling and analysis: The Iron Reeds being located in a volcanic area primarily affects the water quality in the area and the heavy metal types accumulated by plants. Therefore, a sampling analysis study was carried out at the water inlets close to the areas where plants were sampled that feed the reeds. The coordinates of the points where the water samples are taken were W1: 38 ° 39′10.9″N 42 ° 01′07.3″E, and W2: 38 ° 38′ ′38.0″N42 ° 00′46.3″E. The location of the sampled points is shown in (Fig. 3).

Fig. 1. Study area (Iron Reeds).

Fig. 2. a) *Phragmites australis* (common reed), b) *Juncus gerardii* Loisel. subsp. *gerardii* (black rush) c) *Carex diluta* subsp. *diluta* (sedge).

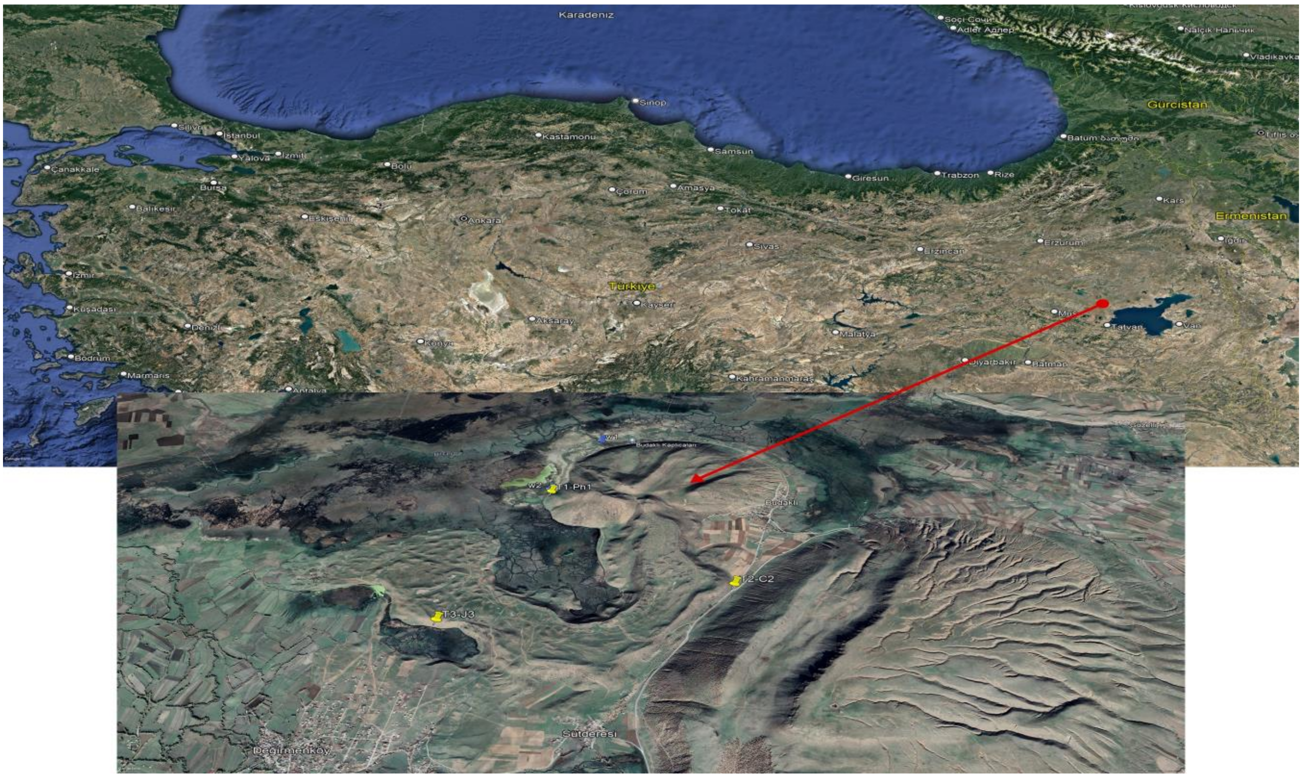

Fig. 3. Google Earth image of the study area.

Samples from the wetland were taken approximately 20 cm below the surface for the study. Temperature, pH, conductivity and dissolved oxygen parameters were determined on site by multimeter. Then, the water samples were brought to the laboratory and total organic carbon (TOC), total nitrogen (TN), NO_3^--N (Nitrate) and turbidity parameters were analyzed without delay in the laboratory. Metal analysis were carried out in Ağrı İbrahim Çeçen University Central Laboratory. Before the analysis step, all water samples were filtered through 0.45 µm pore sized membrane filter, acidified with concentrated nitric acid (HNO_3) and pH adjusted to <2. All of the water quality analysis were conducted according to standard methods. Detailed information about utilized methods and analytical instruments were given in Avşar, 2019 and Avşar *et al*., 2020.

Heavy metal in sediment and plant analysis: During the field studies, two different points at each station that best represent the station were chosen, and plant samples were collected from these points (2 samples from each station). The water samples collected from the stations where macrophyte samples were taken and the water samples collected from control stations via 500 ml polypropylene containers, and 5 ml of nitric acid was injected to the samples in order to reduce pH value. Sediment samples were also derived from the areas where macrophyte samples were taken by means of the Ekman ladle.

These plant species collected from their natural populations were brought to the Bitlis Eren University Environmental Engineering Laboratory for identification. The identification of these species was made using the Flora of Türkiye and the Botanical guide. Parts of these identified species such as leaves, stems, flowers, and roots were reserved for pretreatment. The main purpose was to detect the metal contents accumulated in the underground and above-ground parts of the plant separately and to compare them. Plant samples that were identified in the laboratory were washed with tap water before they were divided into parts such as leaves, stems, flowers, and roots. Plant organs washed with tap water were laid on separate filter papers to be washed and dried with pure water from the ELGA PURELAB-Q DV25 brand pure water device. After drying, each plant piece was left on filter paper at 50°C for 1 day in an MST55 brand oven. The samples collected were crushed in a porcelain mortar to homogenize them (Duman, 2005). The dried plant parts were weighed to approximately 1 gram portions and placed in 50 ml autoclave glass bottles with 10 ml of 65% HNO_3 (nitric acid) added to the samples, they were left at room temperature for 1 day. Later, the samples were heated on a hot plate in a fume cupboard at 120°C until colored steam disappeared, and thus they were completely mineralized. The mineralized plant samples were transferred to 25 ml polypropylene containers and they were completed to 25 ml by adding distilled water (Laing *et al*., 2003). Soil samples were also sampled from the areas where these plants grow naturally. Again, these soil samples were transferred to the Environmental Engineering Laboratory for pretreatment. Soil samples were laid on filter papers to allow ventilation and left for two weeks. Samples were first heated in a Start D and Terminal 260 brand microwave (Time: 00:15:00, T1: 200°C, T2: 110°C, P: 45 bar, Power: Max power. Max power: 1500 W for Ethos and 1200 W for start units.). Then 500 mg of sample was taken and 6 ml of 65% nitric acid (HNO_3) and 2 ml of 30% Hydrogen peroxide (H_2O_2) were added. Burned samples were diluted with 2% HNO_3 50 times (200 µM sample + 9800 µM 2% HNO_3) for reading on the ICP-MS device. For the reading made on the ICP-MS device, peroxide and nitric acid used for dilution in the microwave were also subjected to blank burning. The calculations were made by reading as special blank and by deducting this value from the results of the ICP reading. In 50-time dilutions, the results were transferred to an excel file by calculating on the ICP device. Concentrations of Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, and as and macronutrients (Mg, Ca) which were heavy metals were detected using the ICP-MS device.

Results and Discussion

With the industrial revolution, the pollution observed in aquatic ecosystems started to increase rapidly, and this has become one of the most significant environmental problems of our age (Mason, 1991). In addition, the amount of heavy metals emitted to the environment as a result of industry and agriculture, which have increased without controls in recent years, has reached very high and dangerous levels. Through the phytoremediation method, also known as green rehabilitation (vegetational rehabilitation) (Vanli, 2007), hyperaccumulator plants have the feature of neutralizing heavy metals by accumulating them in high levels in their tissues and passing them through various processes. Thus, they have a very important role in the decontamination of contaminated soil (Aybar *et al*., 2015).

The ability of these plants to accumulate trace metals in various organs was determined and various meaningful results were found by comparing them. As result of the analysis, the following decreasing trends for metal concentrations were observed for *Juncus gerardii* subsp. *gerardii*: in the root Ca> Mg> Fe> Mn> Zn> As> Cu> Cr> Ni> Pb> Cd; in the stem Ca> Mg> Mn> Fe> Zn> Cr> As> Cu> Ni> Pb> Cd; and in the flower Ca> Mg> Mn> Fe> Zn> Cu> Ni> As> Pb> Cr> Cd. *Phragmites australis* species had trends of decreasing heavy metal concentrations of: root Ca> Mg> Fe> Mn> Zn> Cr> Ni> Cu> As> Pb> Cd; stem Ca> Mg> Mn> Fe> Zn> Cr> Cu> Ni> As> Pb> Cd; and leaf Mg> Ca> Mn> Fe> Zn> Cr> Cu> Ni> As> Pb> Cd. Decreasing trends for heavy metal concentrations in *Carex diluta* subsp. *diluta*: root Ca> Mg> Fe> Mn> Zn> Cu> Cr> As> Ni> Pb> Cd; stem Mg> Ca> Fe> Mn> Zn> Ni> Cr> Cu> As> Pb> Cd; leaf Mg> Ca> Fe> Mn> Zn> Cu> Cr> Ni> As> Pb> Cd; and flower Mg> Ca> Fe> Zn> Mn> Cr> Cu> Ni> Pb> As> Cd (Table 1).

When we compared (Kloke *et al*., 1984; Misra & Mani, 1991; Kastori *et al*., 1997; Schulze *et al*., 2005; Kabata-Pendias & Mukherjee, 2007; Kabata-Pendias, 2011; O'Neil, 1993) the data about the heavy metal content (Table 1) of these plants from the aquatic ecosystem with the determined contents given in (Table 2) for acceptable and not acceptable (toxic) contents of metals in investigated plants, metal concentrations were within the acceptable levels. Only As had a toxic value outside these limits.

Table 1. Trace metal levels (mg/kg) in the organs of *Juncus gerardii* subsp. *gerardii, Phragmites australis*, and *Carex diluta* subsp. *Diluta*.

Carex diluta subsp. *diluta*				*Phragmites australis*			*Juncus gerardii* subsp. *gerardii*			Sample
Flower	**Leaf**	**Stem**	**Root**	**Leaf**	**Stem**	**Root**	**Stem**	**Root**	**Flower**	**Organ**
251.3	332.5	165.9	576	107.1	122.1	198	213	246.4	174	Mg
0.182	0.06302	0.1224	0.08806	0.3227	0.2551	0.7712	0.1453	0.1034	0.002526	Cr
2.095	2.091	2.001	2.512	8.925	6.922	8.888	13.75	8.709	13.39	Mn
19.53	25.58	6.136	86.91	7.559	5.281	52.01	8.171	171.4	9.213	Fe
0.08152	0.0369	0.153	0.07308	0.1604	0.09034	0.2537	0.06035	0.08084	0.02836	Ni
0.1028	0.08744	0.04197	0.1081	0.1898	0.2003	0.1572	0.06421	0.1052	0.1032	Cu
2.485	1.534	0.628	2.322	0.7758	1.848	0.9326	1.39	2.951	2.452	Zn
0.000118	0.000153	0.000103	0.000159	0.000042	0.000119	0.000162	0.000129	0.000354	0.000156	Cd
0.01288	0.01116	0.002989	0.03055	0.003967	0.004928	0.01904	0.00678	0.01607	0.005328	Pb
127.1	282.5	79.96	726.9	79.48	728.3	522.2	528.7	513.3	443.2	Ca
0.01285	0.03007	0.006819	0.07974	0.007291	0.01576	0.1165	0.07744	0.2925	0.01318	As

Table 2. Reference values for normal and toxic concentrations of heavy metals in plants.

Metal	Normal Concentration (mg kg^{-1})	Reference	Toxic concentration (mg kg^{-1})	Reference
Copper (Cu)	3 - 15	(1)	20	(2)
Nickel (Ni)	0.1 - 5	(1)	30	(2)
Lead (Pb)	1 - 5	(1)	20	(2)
Mercury (Hg)	<0.1 - 0.5	(1)	5	(2)
Chrome (Cr)	<0.1 - 1	(1)	2	(2)
Manganese (Mn)	15 - 100	(5)	400	(2)
Zinc (Zn)	15 - 150	(1)	200	(2)
Molybdenum (Mo)	0.1 - 0.5	(3)	10 - 50	(3)
Cobalt (Co)	0.05 - 0.5	(5)	30 - 40	(4)
Iron (Fe)	50 - 250	(6)	>500	(6)
Arsenic (As)	10 - 60	(3*)	<2	(3)
Antimony (Sb)	<2 - 29	(4*)	5 - 10	(7)

(1), Kloke *et al*., 1984, (2) Kastori *et al*., 1997, (3) Kabata-Pendias & Mukherjee, 2007, (4) Kabata-Pendias, 2011; (5) Misra & Mani 1991; (6) Schulze *et al*., 2005, (7) Kabata-Pendias & Pendias, 2001, *, µg kg^{-1}

Cadmium (Cd) is a very toxic, non-essential element that affects plant growth, metabolism and water (Divan *et al*., 2009). The lowest Cd range that can cause a decrease in yield for crops is 5 to 30 µg kg^{-1}, and the highest acceptable content in edible plants is as low as 0.001 mg kg^{-1} (O'Neil, 1993). Allen (1989) argued that the Cadmium content in plants in uncontaminated environments is 0.01-0.3 mg kg^{-1}. The Cd limit value accepted by FAO / WHO in plants is 0.5 mg kg^{-1}. Lead is not essential for plants and can be toxic. Pb is quite immobile in soil, tends to accumulate in roots and has sparse translocation towards the above-ground parts (Siedlecka *et al*., 2001). According to Allen (1989), the normal values for lead concentration in aquatic environment sediments are 2-20 mg kg^{-1} and 0.05-3 mg kg^{-1} in plants (Demirezen, 2002). The Pb limit value accepted by FAO/WHO in plants is 2 mg kg^{-1}. Lead and Cadmium are trace metals that are not necessary for flora and fauna; however, these metals can easily produce toxic impacts at low concentrations in humans. Therefore, it is an expected result that Pb and Cd levels are found in very low amounts in the plants used in this study. As concentrations in edible plants are highly variable and mostly differs from 10 to 60 µg kg^{-1}, though the acceptable level for this element in plants is 2 mg kg^{-1} (Kabata-Pendias & Pendias, 2001; Kabata-Pendias & Mukherjee, 2007). Cr concentration in plants has gained great attention recently due to its importance as an important micronutrient in human metabolic processes, as well as its carcinogenic effects. It is not yet known whether Cr is necessary for plant growth. In most plants, it is found at levels ranging from 0.03 to 14 mg kg^{-1} on Cr dry matter basis. Cr level between 5-30 mg kg^{-1} in plants is accepted as toxic for many cultivated plants (Kabata-Pendias & Pendias, 1992). In our analysis results (Table 1), the maximum Cr concentration (0.7712 mg kg^{-1}) was determined in *Phragmites australis,* followed by *Juncus gerardii* subsp. *gerardii* and *Carex diluta* subsp. *diluta*. As for Ni, the maximum concentration in *Juncus gerardii* subsp. *gerardii* was detected in the root part of the plant (0.2537 mg kg^{-1}), followed by the lowest value for the flower part of the same plant (0.02836 mg kg^{-1}) (Table 1). Optimum Ni limit in plants was reported in some studies as 0.02-5 mg kg^{-1} (Kabata- Pendias & Pendias 1992), 0.5-5 mg kg^{-1} (Allen, 1989) and 5 mg kg^{-1} FAO/WHO (2001). As cited in Kabata-Pendias & Pendias, (2001), toxic Nickel levels range from 40 to 246 mg kg^{-1} and vary greatly according to plant species. As a result of our analysis, the highest Ni level was determined in the root of

0.2537 mg kg^{-1} *Phragmites australis*. As a result of our analysis, Cu was found in the highest concentration in the stem of *Phragmites australis* (0.2003 mg kg^{-1}) compared to other plant species and parts. However, this proportion and the Cu concentration detected in other plants are below the critical level (20 mg kg^{-1}) (Kabata-Pendias & Pendias, 1984). The phytotoxic range of Cu concentration in plants is reported to be 25-40 mg kg^{-1}; 2.5-25 mg kg^{-1}; 5 mg kg^{-1}; and 20-100 mg kg^{-1} (Chaney, 1989; Allen, 1989; Khan, 2008). Iron content in plants varies between a few ppm and 500-600 ppm of dry weight, depending on their species, age, organs, and the amount of useful iron in the soil (Güven, 2002). The toxic value for plants in uncontaminated environments is 40-500 mg kg^{-1} (Demirezen, 2002). The limit value of Fe that FAO/WHO accepts in plants is 30 mg kg^{-1}. Our analysis showed that the first three maximum Fe concentrations are as follows: the root of the plant *Juncus gerardii* subsp. *gerardii* (171.4 mg kg^{-1}), the root of the species *Carex diluta* subsp. *diluta* (86.91 mg kg^{-1}), and finally in the root part of *Phragmites australis* (52.01 mg kg^{-1}). Although Mn toxicity varies according to plant species, Mn toxicity starts to be seen in plants containing more than 100 mg kg^{-1} of Mn on a dry matter basis. Manganese toxicity occurs as brown spots on mature leaves in most plants (Kacar & Katkat, 2007). Although the maximum Mn concentration is quite high, especially in *Juncus gerardii* subsp. *gerardii* plants compared to other plants, it was determined to be within the limits of toxic values (Table 1). Zinc (Zn) is an important trace element for plant growth, and at the same time takes an important mission in several cell processes (Hunt, 2003). Zinc concentration in plants is generally between 5 and 100 mg kg^{-1} on a dry matter basis. Zinc toxicity usually starts after 400 mg kg^{-1} in plants (Rout & Das, 2003; Asri & Sönmez, 2006). In this study (Table 1), the highest average Zn concentrations were in the root of *Juncus gerardii* subsp. *gerardii* (2.951 mg kg^{-1}), in the flower of *Carex diluta* subsp. *diluta* (2.485 mg kg^{-1}) and the flower of *Juncus gerardii* subsp. *gerardii* (2.452 mg kg^{-1}). Regarding these heavy metals, it is noteworthy that there are some differences in concentrations depending on the plant species examined, as well as the parts of plants examined (Table 1). Calcium is an immobile element in the plant, and it can respond more quickly than calcium given through the leaf (Locascio *et al*., 1992). *Phragmites australis* is the plant type with the highest Ca concentration among the plant species in the studied area. The amount of Ca in the stem of this plant was determined as 728.3 mg kg^{-1}. The lowest Ca concentration (79.48 mg kg^{-1}) was determined in the leaf of the same plant. In plants, magnesium is found mostly in cell sap, as inorganic salts, as a constituent of the chlorophyll molecule and as compounds in the protoplasm. Mg is mostly found at different amounts than calcium. Although plants contain an average of 0.30% magnesium, 0.77% calcium was found (Güven, 2002). In our study, Mg concentration was higher in the root of *Carex diluta* subsp. *diluta* plant (576 mg kg^{-1}) compared to other organs. The lowest Mg concentration was determined in the leaf of *Phragmites australis* with a value of 107.1 mg kg^{-1}. As a result, although heavy metal concentrations in different organs of these three plant species were found to be within the limit values in the literature, arsenic was detected at a very low value in all three plants and was found to have toxic concentrations.

Average concentrations of Mg, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb and Ca elements in soil samples were detected as follows: 297.58; 3.17; 97.24; 1864.96; 3.80; 1.32; 9.84; 0.08; 2.46; and 32.04 mg kg^{-1}, respectively (Table 3). Trace metal concentrations (excluding Fe) in soil samples taken from three different stations near the plant sample locations, were below the heavy metal limit values for soil given in the Soil Pollution Control Regulation (TKKY, 2005) (Table 4). If the amount of Fe extractable in the soil is below 0.2 mg/kg, it is considered to be low; from 0.2 to 4.5 mg/kg is moderate; and more than 4.5 mg/kg is generally considered to be high and toxic. Considering the analysis of our results, since the amount of Fe detected in the soil was quite high it may have toxic effect.

By combining both minerals in soil and the content of trace metals in plants, the accumulation and adsorption effect of heavy metals in the soil can be examined using bioconcentration factor (BCF) and translocation factor (TF) (Wang 2012a, 2012b). BCF is used to evaluate the capability of plants to accumulate elements or compounds.

$$BCF = CMIP/CMIS$$

CMIP is the heavy metal content in the plant, and CMIS is the heavy metal content in the soil. TF, shows the plants' ability to pass trace metals from roots into stems and leaves. As a result of the analysis, BCF was found for *Phragmites australis* as follows: Mg 0.953, Cr 8.443, Mn 2.986, Fe 0.186, Ni 1.644, Cu 9.682, Zn 13.708, Cd 0.870, Pb 1.043, Ca 463.708, and As 0.168. BCF for the plant *Carex diluta* subsp. *diluta* was as follows; Mg 2.463, Cr 7.345, Mn 0.906, Fe 0.365, Ni 2,561, Cu 7.094, Zn 34.447, Cd 0.049, Pb 5,668, Ca 0.217, and As 0.682. For the plant *Juncus gerardii* subsp. *gerardii*, BCF was found as follows; Mg 61.742, Cr 0.098, Mn 0.887, Fe 0.015, Ni 0.085, Cu 0.297, Zn 1.507, Cd 0.422, Pb 0.003, Ca 0.888, and As 0.389.

$$TF = CMIL/CMIR$$

CMIL is the average heavy metal concentration in the leaf and stem, and CMIR is the heavy metal concentration in the root. As a result of the analysis, TF was found for Phragmites australis plant as follows: Mg 0.157, Cr 0.749, Mn 1.782, Fe 0.246, Ni 0.988, Cu 2.481, Zn 2.813, Cd 0.993, Pb 0.467, Ca 1.546, and As 0.197. In the Carex diluta subsp. diluta plant, TF was found to be; Mg 1.301, Cr 4.172, Mn 2.462, Fe 0.589, Ni 3.764, Cu 3.907, Zn 2.001, Cd 2.352, Pb 0.884, Ca 0.673, and As 0.623. In the Juncus gerardii subsp. gerardii species, TF was found as follows; Mg 1.570, Cr 1.429, Mn 3.116, Fe 0.101, Ni 1.097, Cu 1.591, Zn 1.301, Cd 0.805, Pb 0.753, Ca 1.893, and As 0.309. The higher the BCF value, the stronger the accumulation of heavy metals. The feature of a hyperaccumulator plant is that both BCF and TF are higher than 1 (Wang, 2012a, 2012b). Plants with higher TF are more effective in terms of phytoremediation capability (Fischerova *et al*., 2006).

In the study, the comparison of the results of the analysis of water quality parameters with the Surface Water Quality Regulation (YSKY) published by the Turkish Republic Ministry of Forestry and Water Affairs (MoEF) is given in (Table 5) (YSKY, 2012). In YSKY, water quality is examined in four main classes. The first class represents high-quality water, the second class represents mildly contaminated water, the third class represents contaminated water, and the fourth class represents highly contaminated water. The chemical oxygen demand (COD) equivalent of the total organic carbon (TOC) parameter analysed in the study was obtained by calculation. For this purpose, equation (1) for purified water was used in the literature (Dubber & Gray, 2010).

$$COD = 7.25 + (2.99 \times TOC) \quad (1)$$

Table 4. Heavy metal limit levels (mg/kg) in soil (TKKY, 2005).

Heavy metal	pH 5-6 (mg/kg dry soil)	pH> 6 (mg/kg dry soil)
Lead (Pb)	50	300
Cadmium (Cd)	1	3
Nickel (Ni)	30	75
Chrome (Cr)	100	100
Cobalt (Co)	80	80
Copper (Cu)	50	140
Iron (Fe)	4,5	4,5
Zinc (Zn)	150	300
Mangan (Mn)	70	70

Table 3. Soil sample values (mg/kg) from the study area.

Sample	Mg	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	Ca	As
Sediment (T1)	240.5	0.06843	5.307	68.85	0.1525	0.04029	0.1914	0.000185	0.008524	1.742	0.1364
Sediment (T2)	304.3	0.05002	6.823	140.4	0.1074	0.03273	0.1349	0.007508	0.004768	2253	0.07286
Sediment (T3)	6.268	1.495	30.58	1141	1.036	0.5634	2.548	0.000675	0.3648	1094	0.2324

Table 5. Water quality parameter analysis results and comparison with regulations (YSKY, 2012).

Parameter	Unit	Sample No. 1	Sample No. 2	Quality class (YSKY 2012)
pH	-	7.32	8.39	I (6-9)
Conductivity	µS/cm	330	248	I (<400)
Dissolved oxygen (O_2)	mg/L	5.11	7.48	II (6) - III (3)
Turbidity (0.45 µm filtered)	NTU	6.45	1.54	-
NO_3-N	mg/L	3.3	3.7	II (10)
TOC	mg/L	2.9748	8.2469	-
COD	mg/L	16	32	I (BOD<4; COD25) II (BOD= 8 COD <50

BOD: Biological oxygen demand
NO_3-N: Nitrate nitrogen

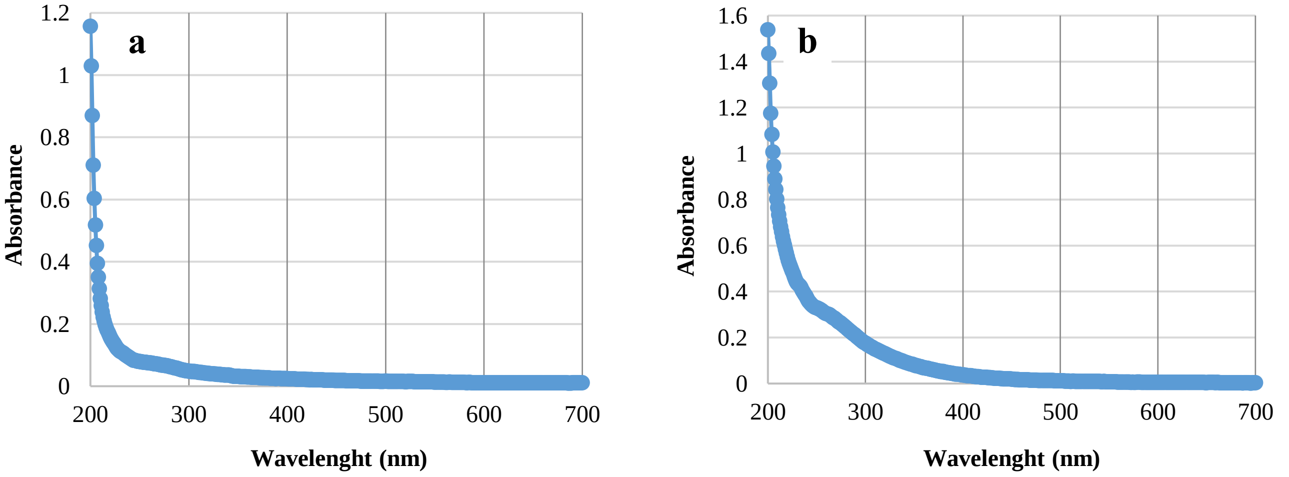

Fig. 4. Wavelength scanning of samples 1 and 2.

Experimental results show that for sample point 1: dissolved O_2 direction indicates Class III (medium); NO_3-N parameter indicates Class II (good); while other parameters indicate Class I (very good). Quality at sample point 2: COD and NO_3-N indicate Class II (good); and dissolved O_2 indicates Class III (medium). Organic matter and nitrogen concentrations are higher at point 2 compared to point 1. To determine the origin of organic pollution in water (natural or industrial), wavelength scanning in the range of 200-700 nm was carried out using a UV visible spectrophotometer. The graphics obtained are given in (Fig. 4).

The absorbance values obtained for both samples decrease exponentially compared to the increase in wavelength. This shows that the organic structures present in the waters are composed of natural aromatic substances and there is no anthropogenic pollution in the water (Avşar, 2013; Avşar *et al.*, 2014; Avşar *et al.*, 2015). However, uncontrolled livestock activities are carried out in the area. Precautions should be taken to prevent this situation from causing organic pollution in the water. For the study, sampling was performed once at both points, and the metal concentrations obtained were compared with the maximum allowable environmental quality standard (MAK-CKS) values given in YSKY in Table 6 (YSKY, 2012).

When the obtained results are compared with the limit values, boron and silicon levels were higher than YSKY standards, while there was no problem in terms of soil and other metals studied in sediment. In the literature, metal concentrations were measured in the Crater Lake in the Nemrut Caldera, a volcanic area, located about 15 km as the crow flies to Iron Reeds. Similar to this study, it was determined that the boron concentration was above the limit value. It is thought that arsenic, sodium, potassium and boron are generally contained in igneous fluids and thus enter water sources (Avşar, 2019).

In the literature, silicon dioxide (SiO_2) was stated to be dominant in rocks that occur naturally with the sudden cooling of volcanoes in the region and different regions (Küçük & Gezer, 2017; Canpolat, 2015). As a result, it is understood that boron and silicon in the water have volcanic origin.

The area where the reeds are located is north of the Van-Tatvan fault line. There are many hot water sources in this area due to volcanic activity. The most important of these is the Germav hot spring, which is 1 km away from the sample area. The water temperature of this source is 38-39°C and pH is around 6.7 (Url 1).

Table 6. Metal content of water samples and comparison with YSKY legal standards.

Metals	Unit	1	2	MAK-CKS Rivers/Lakes (YSKY, 2012)
Beryllium (Be)	ppb	N.D.	N.D.	3.9
Boron (B)		**8067**	**6358**	1472
Sodium (Na)		35040	27850	-
Magnesium (Mg)		110300	86310	-
Aluminum (Al)		2.635	1.245	27
Silicon (Si)		**164800**	**91050**	1830
Potassium (K)		88520	59200	-
Calcium (Ca)		42200	84470	-
Titanium (Ti)		39	19.81	42
Vanadium (V)		5.311	7.573	97
Chrome (Cr)		4.833	5.78	142
Manganese (Mn)		0.324	0.627	-
Iron (Fe)		N.D.	37.58	101
Cobalt (Co)		0.091	0.195	-
Nickel (Ni)		1.285	2.416	34
Copper (Cu)		0.874	1.489	3.1
Zinc (Zn)		2.319	12.16	-
Arsenic (As)		24.33	32.42	53
Selenium (Se)		2.783	2.403	-
Strontium (Sr)		325.6	396.8	-
Molybdenum (Mo)		2.959	2.303	-
Cadmium (Cd)		N.D.	N.D.	<0,45 (Class 1)
Tin (Sn)		N.D.	N.D.	13
Antimony (Sb)		N.D.	0.026	103
Barium (Ba)		14.58	35.57	680
Tungsten (W)		0.108	N.D.	-
Mercury (Hg)		N.D.	N.D.	0.07
Lead (Pb)		N.D.	N.D.	14
Bismuth (Bi)		N.D.	N.D.	-

N.D. Not detected

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