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Seasonal Changes of Metal Accumulation in Water, Sediment and *Phragmites austrialis* (Cav.) Trin. ex Steudel Growing in Lake Kovada (Isparta, Türkiye)

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Abstract: This study was carried out between April 2014 and January 2015, aimed to determine heavy metal concentrations in water, sediment and roots, stems and leaves of the reed (*Phragmites austrialis* (Cav.) Trin. ex Steudel) as seasonally from Lake Kovada. During the study temperature, pH, dissolved oxygen and electrical conductivity of lake water were measured. In water, Cr was below detection limit (<0.0005) in all seasons, Cd (<0.0004) in spring, autumn and winter, Ni (<0.0001) in summer, Pb (<0.003) in spring and summer. Fe has the highest and Cd is the lowest in water as well as sediment among the studies metals. Generally, the metal levels in water increased in winter. Both positive and negative correlations were detected between content in the water and physico-chemical parameters. Results for levels in water were compared with national and international water quality guidelines. All metals were determined in sediment. Metal levels in sediment increased in spring and summer, decreased in autumn generally. High levels of heavy metals were found in root of redd, while low levels in stem and leaf samples depend on metal properties. This results show that a potential danger may occur in the future depending on the agricultural development.

Key Words: Macrophytes, Lake Kovada, *Phragmites austrialis*, Heavy metal, Pollution.

Kovada Gölü (Isparta-Türkiye)'nün Suyunda, Sedimentinde ve Gölde Yetişen *Phragmites austrialis* (Cav.) Trin. ex Steudel Bitkisindeki Metal Birikiminin Mevsimsel Değişimi

Özet: Nisan 2014-Ocak 2015 tarihleri arasında gerçekleştirilen bu çalışmada; Kovada Gölü'nün (Türkiye) suyunda, sedimentinde ve gölde yetişen kamış: *Phragmites austrialis* (Cav.) Trin. ex Steudel'in kök, gövde ve yapraklarındaki ağır metal seviyelerinin mevsimsel değişiminin belirlenmesi amaçlanmıştır. Çalışma süresince göl suyunun sıcaklığı, pH değeri, çözünmüş oksijen miktarı ve elektriksel iletkenlik değeri ölçülmüştür. Suda, Cr (<0.0005) her mevsim, Cd (<0.004) ilkbahar, sonbahar ve kış mevsiminde, Ni (<0.0001) yaz mevsiminde, Pb (<0.003) ilbahar ve yaz mevsiminde analiz limitinin altında kalmıştır. Hem suda hem de sedimenttte en fazla biriken metal Fe, en az biriken metal ise Cd olmuştur. Genel olarak suda metal seviyeleri kış mevsiminde artmıştır. Fiziko-kimyasal parametreler ile metal seviyeleri arasında hem negatif hem de pozitif ilişkiler tespit edilmiştir. Sudaki sonuçlar ulusal ve uluslararası su kalite esasları ile kıyaslanmıştır. Tüm sedimentteki tüm metaller tespit edilmiştir. Sedimentteki metal seviyeleri genel olarak ilkbahar ve yaz mevsimlerinde artmış, sonbaharda azalmıştır. Kamışın kökündeki metal düzeylerinin, metalin özelliğine bağlı olarak gövde ve yaprağa oranla daha yüksek olduğu belirlenmiştir. Bu sonuçlar tarımsal gelişmeye bağlı olarak gelecekte tehlike olabilceğini göstermektedir.

Anahtar Kelimeler: Makrofit, Kovada Gölü, *Phragmites austrialis*, Ağır metal, Kirlilik.

1. Introduction

Our lakes which are ecologically very rich and of vital importance in terms of life and economy, are exposed to some irreversible changes due to conscious or unconscious interventions of today's people. As well as environmental problems that threaten our natural lakes such as the development of technology, the resulting rapid development of economy, the endless needs of mankind and the excessive population growth, non-scientific interventions lead to devastation of the natural habitat as well [1,2]

The most important reason of the inorganic contamination of water is heavy metals. They are the number one chemical pollutants due to the fact that they can emerge from a variety of sources, resist to environmental conditions and easily penetrate to the food chain and accumulate in organisms in high densities [3]. Heavy metals mix in waters through rock fragments carried by erosion, the atmosphere; dust carried by wind, volcanic activities, forest fires, and vegetation and impact the aquatic system [4].

Heavy metals are found in natural waters as free ions, organic or inorganic compounds, and as absorbed by particulate matters [5]. Heavy metals have increased toxic effects if they are found as ions in the aquatic environment. These toxic ions cause damages directly on organisms or on their consumers. After mixing in water, they are firstly carried to sediment and some of them are taken in by organisms [6].

Macrophytes play an important role in the accumulation of heavy metals and are considered as bioindicator of the water quality in ecological studies [7,8]. Aquatic macrophytes take heavy metals from water and sediment and accumulate several times more heavy metals in their tissues compared to their environment [9].

Aquatic macrophytes have numerous characteristics suitable for metal accumulation These are;
a. They are capable of rapid reproduction.
b. Their leaves and other parts constitute large areas for absorption of meal ions.
c. They can absorb metals with their leaves, rhizomes, and roots.
d. They are motionless [10].

The amount of heavy metals in macrophytes varies depending on the physico-chemical properties of the water, the structure of sediment, the type of plant, and seasons [11]. Due to their toxic effects, heavy metals cause deterioration in physiological activities in macrophytes such as transpiration, stoma movements, water intake, photosynthesis, enzyme activity, germination, protein synthesis, membrane stability, hormonal balance [12].

Phragmites australis, belonging to Gramineae family, is one of the most common species in the world [13]. It is a creeping rhizomed, ascendant and perennial plant. The stem can grow up to three meters [14]. Flowers develop mid summer and pollination occurs with wind [15]. Seeds are 1 mm in size and highly variable. They occur throughout autumn and winter and can play an important role in spreading to new areas [16]. In recent years, *Phragmites australis* has been widely used in wetlands established for industrial waste water treatment [17].

Although metal levels of some fish species (*Cyprinus carpio*, *Carassius carassius* and *Sander lucioperca*) living in Lake Kovada were investigated in some previous studies [18-20], there has been no studies on *Phragmites austrialis* growing in the lake. The purpose of this study is to determine seasonal concentrations of some heavy metals (Cd, Cr, Cu, Fe, Mo, Mn, Ni, Pb, Se and Zn) in root, stem and roots of reed (*Phragmites austrialis* (Cav.) Trin.ex Steudel) living in the water and sediment of Lake Kovada, identify the relationship between certain physico-chemical parameters measured in the water and heavy metal levels in the water, and identify relationships between heavy metal quantities in plant root, stem and leaves.

2. Material and Methods

2.1. Study area

Kovada Lake (37º 38´ **N,** 30º 53´ **E)** is located in the southwest of Türkiye lies within Isparta province and south of the Eğirdir Lake (Kovada Channel which is at a distance of 15 km connect Kovada and Eğirdir Lakes) [21] (Figure 1). Kovada Lake has an international importance because of the diversity of habitats, animal and plant species in. Owing to these features, the lake and surrounding area has been declared a natural protected area and national park in 1970 [22]. Its mean width and depth are about 15 km and 6 m. Its area and volume are about 1100 ha and 25.5 hm³, respectively. The lake's geological formation is a tectonic construction [23]. The lake is polluted by industrial waste from agricultural areas though rain wash and fruit juice factories. Agricultural production in the region is dominated by apple and cherry production.

Figure 1. Map of Kovada Lake (Türkiye) (from maps.google.com) and different localities from where the samples were taken.

2.2. Sampling and sample preparation

This study was carried out between April 2014- January 2015 and water, sediment and plant samples were collected at the three sampling stations from Lake Kovada. The temperature, dissolved oxygen, conductivity (EC) and pH values were measured from these different localities in the lake by using YSI multiparameter equipment. Water samples were taken 50 cm below the water surface in 500 ml bottles, filtered through a Whatman 0.45 µm glassfiber filter, transferred 500 ml polypropylene bottle, acidified with 5 ml of concentrated HNO_3 to pH less than 2.0. Then water samples stored at 4 ºC and were analyzed directly.

Sediment samples were taken from the same localities. Sediments were dried in an oven at 50 ºC for 48 h, passed through a 2 mm sieve and homogenized. Plant samples were collected from the same area, and cleaned with fresh water and than distilled water, for the remove foreign particles. Plants were segregated into roots, stems and leaves and dried at 70 ºC for 24-48 h until they reached a constant weight. 0.5 g sediment and other all samples were placed in decomposition beakers and 5 ml HNO_3 added to each, were kept at room temperature for 24 h. Then they were heated at 120 ºC on hot plate for 2 h, until the solution evaporate slowly to near dryness. After cooling, added 1 ml H_2SO_4 and diluted to 25 ml with deionized water, then added 1-2 drop HNO_3.

2.3. Analytical procedures

All samples were analyzed for three times for Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn by using for ICP-AES Vista. Three standard material HISS-1 (National Research Council Canada) were analyzed for each ten elements. The absorption wave length were 228.802 nm for Cd, 267.716 nm for Cr, 324.753 nm for Cu, 238.304 nm for Fe, 257.61 nm for Mn, 202.03 nm for Mo, 231.604 nm for Ni, 220.353 nm for Se, 196.026 nm for Pb and 213.856 nm for Zn, respectively. The analysis limits were 0.4 ug/L for Cd, 0.5 ug/L for Cr, 0.3 ug/L for Cu, 0.35 ug/L for Fe, 0.05 ug/L for Mn, 0.8 ug/L for Mo, 1.3 ug/L for Ni, 3 ug/L for Pb, 5 ug/L for Se and 0.3 ug/L for Zn.

2.4. Statistical procedures

All metal concentrations were determined as milligrams per liter for water and on dry weight basis as milligrams per gram for sediment and plants tissues. But we gave the results as milligrams as per kilogram. Statistical analysis of data was carried out using SPSS 20 statistical package programs. One-Way ANOVA and Duncan's Multiple Comparison Test were used to compare the data among seasons at the level of 0.05. Pearson rank correlation coefficient was used to test for significant associations between heavy metal levels in water and physico-chemical parameters.

3. Results and Discussion

The accuracy and precision were checked by analyzing standard reference materials HISS-1 (Marine Sediment Reference Materials for Trace Metals and Other Constituents) under the same conditions (Table 1). Replicate analysis of these reference materials showed good accuracy, with recovery rates for metals between 83 % and 117% for HISS 1.

Table 1. Concentrations of metals found in certified reference material HISS-1 from the National Research Council, Canada.

Metals	HISS 1 Certified	HISS 1 Observed	Recovery (%)
Cd	0,024±0,009	0,020±0,03	83
Cr	30,0±6,8	27,54±2,25	91
Cu	2,29±0,37	2,03±0,02	88
Mo	-	-	-
Mn	66,1±4,2	58,03±1,12	87
Ni	2,16±0,29	2,54±0,10	117
Pb	3,13±0,40	3,02±0,02	96
Se	0,05±0,007	0,052±0,11	104
Zn	4,94±0,79	4,25±0,02	86

Physico-chemical parameters of water samples by season are given in Table 2. According to the table, water temperature ranged between 8.09 °C (in winter) and 23.39 °C (in summer), respectively. Mean pH varied between 9.57 (in summer) and 6.57 (in winter). Dissolved oxygen was the highest in winter (5.24 mg/lt) and lowest in summer (1.91 mg/lt). EC measurement ranged between 499.90 µs/cm (in summer) and 260.60 µs/cm (in winter).

Table 2. Some physical parameters of Kovada Lake's water

	Temperature(°C)	**pH**	**Disolved Oxygen (mg/L)**	**Electrical Conductivity (µs/cm)**
Spring	20.79-22.13 21.57±0.69	8.75-9.49 9.12±0.37	1.68-5.16 3.24±1.76	257.60-287.00 269.33±15.57
Summer	23.11-23.81 23.39±0.37	9.11-10.10 9.57±0.49	1.46-2.75 1.91±0.72	486.60-507.50 499.90±11.55
Autumn	16.43-16.86 16.62±0.21	7.11-7.75 7.35±0.34	2.57-6.80 4.33±3.00	233.20-241.30 238.23±4.39
Winter	7.85-8.30 8.06±0.22	6.07-7.25 6.57±0.61	3.58-7.70 5.24±2.12	246.80-269.00 260.60±12.04

It was found in studies conducted in Derbent Dam Lake [24], Damsa Dam Lake [25] and Karataş Lake [26] that the pH value of water increased in summer and decreased in winter. The increase in pH value during summer might be related to the increase in the amount of carbonate, bicarbonate and carbon dioxide dissolved in the water due to increased temperature. The level of dissolved oxygen in water is inversely proportional to temperature. As the temperature increases, the solubility of gases in water and water's gas-holding capacity decreases [29]. Accordingly, oxygen-holding capacity of lake water decreases due to increased temperature in summer and the the lowest value was recorded in summer. In winter, the amount of dissolved oxygen in lake water increases due to decreased temperature. The electrical conductivity value was found to be higher during summer compared to other seasons because intensive evaporation in summer increases the concentration of inorganic solid matters in water. In winter, on the other hand, waters coming from sources that feed the lake cause the amount of inorganic solid matters in water and therefore, the electrical conductivity value was found to be decreased.

The heavy metal levels in water were given in Table 3. As seen Table 3, Cr was below detection limit (<0.0005) in all seasons, while Cd (<0.0004) was in spring, autumn and winter, Ni (<0.0001) in summer, Pb (<0.003) in spring and summer. The heavy metals predominantly determined in the water of Kovada Lake were measured as Fe was the highest metal and Cd was the lowest among the analyzed metals. Similar results were reported in Beyler Reservoir [28], Hazar Lake [29], Karataş Lake [26], Kızılırmak River [30], Beyşehir Lake [31]. It was reported that Fe facilities the precipitation of other metals and found at low levels when precipitation occurs [32].

Seasonal variations of heavy metals also can be seen in Table 3. Cu, Mo, Ni, and Zn reached the highest levels in winter, while Mn, Pb and Se were in autumn and Fe in spring. Cu, Fe, Mo and Mn in summer, Ni, Se and Zn in spring, and Pb in winter were the lowest. Fe and Mn levels varied significantly (<0.05) from season to season.

It is believed that fertilizers used around Kovada Lake increase the amount of Cd in summer. The increase in metals during spring may be related to locals' water drawing activities in order to irrigate apple orchards around the lake and therefore, the increase of metal concentration compared to lake volume. The increase in metals during summer and autumn may be related to the increase in water volume due to rain and snow, while the decrease in metals during summer may be related to subsidence of particles containing metal due to the inactivity in summer [26].

Relationships of metal in water with some physico-chemical parameters were measured using the pearson test and given in Table 4. According to the table, there were positive relationships among temperature, pH value (<0.01) and EC (<0.05). Significant negative correlation (<0.05) was determined between temperature and dissolved oxygen. Positive correlations were determined between temperature and Cd, Fe and Mn, the others were negative. When the pH value increased, Cu, Mo, Mn, Ni, Pb, Se and Zn levels decreased. There were positive relationships between oxygen and Fe, Mo, Mn and Ni, the others were negative. EC levels had a negative relationships with all metals except Cd.

Table 3. The concentrations (ppb) of some heavy metals in Kovada Lake's water.

Seasons	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Pb	Se	Zn
Spring	BDL	BDL	6.35-9.46 7.80±0.56[a]	73.54-336.08 206.14±13.29[b]	0.62-0.64 0.63±0.001[a]	10.39-29.96 18.71±1.10[a]	0.020-0.022 0.021±0.001[a]	BDL	7.19-10.63 8.73±1.74[a]	19.49-42.88 31.57±2.71[a]
Summer	0.038-0.04 0.039±0.0001[a]	BDL	3.45-4.61 3.84±0.06[a]	15.65-36.43 24.04±1.94[a]	0.14-0.18 0.16±0.002[a]	3.49-8.15 6.30±0.47[a]	BDL	BDL	6.74-10.58 9.25±2.18[a]	30.70-50.86 42.02±3.30[a]
Autumn	BDL	BDL	6.06-10.70 8.37±1.28[a]	121.88-158.11 137.80±8.50[ab]	0.31-1.98 1.14±0.017[a]	24.02-41.59 33.09±2.80[b]	1.97-3.53 2.75±0.09[a]	0.54-2.43 1.48±0.33[a]	4.08-20.32 12.97±8.23[a]	9.11-69.02 38.64±2.96[a]
Winter	BDL	BDL	3.65-28.70 12.92±3.73[a]	6.41-103.34 44.83±5.48[a]	0.64-1.97 1.16±0.070[a]	4.51-15.84 8.34±1.48[a]	1.93-49.64 19.20±2.44[a]	0.76-0.82 0.79±0.003[a]	2.97-24.63 12.48±11.06[a]	22.08-355.47 139±18.66[a]

* Below Detection Limit

** Means with the same superscript in the same row are not significant different according to Duncan's multiple range test (p<0.05)

The level of heavy metal in water is influenced by physico-chemical properties of water [33]. pH has a significant impact on Cu toxicity. Copper in water may subside when the pH of water is high and loses its toxic effect, but copper dissolves in water when pH is low and its toxicity increases [34]. Our study results suggest that decreased pH during winter leads to an increase in the Cu level. The oxidized form of ferric structure of Fe subsides in alkaline environments and condensate. The ferro structure, on the other hand, turns into ferric form in autumn mix in oxygenated environments [27]. Fe is one of the most common elements on earth. Also, a decrease in the amount of dissolved oxygen is seen in summer due to increased temperature. Accordingly, it is thought that a high amount of Fe is found in water during spring because the transformation of ferro to ferric structure decreases. Cd has one of the highest dissolution rates in water among other heavy metals [35]. The solubility of Cd in water depends on the state it is found in Cd source and pH value [36]. Phosphatic fertilizers usually contain a significant amount of Cd [37]. The increase in water's pH value eventually leads to an increase in the amount of nickel accumulated by water. The amount of chlorophyll in the plant is influenced by the pH value. While the amount of chlorophyll decreases as the acidity of the environment increases, it increases as the pH value gets closer to neutral. In general, metals have high toxic effects in soft and acidic waters, while they have low toxic effects in hard and alkaline waters [38].

Table 4. Pearson correlation matrix showing the relationships of metals in water and some physico-chemical parameters in water.

	Sıcaklık (°C)	pH	Çözünmüş Oksijen (mg/lt)	İletkenlik (µs/cm)	Cd	Cu	Fe	Mo	Mn	Ni	Pb	Se	Zn
Temperature	1	0.923**	- 0.596*	0.605*	0.303	-0.431	0.216	-0.624*	0.055	-0.565	-0.214	-0.232	-0.456
pH		1	-0.430	0.702*	0.329	-0.462	0.105	-0.669*	-0.155	-0.484	-0.456	-0.186	-0.490
Dissolved Oxygen (mg/lt)			1	-0.508	-0.305	-0.052	0.068	0.115	0.350	0.239	-0.197	0.395	-0.096
Conductivity (µs/cm)				1	0.522	-0.316	-0.451	-0.438	-0.518	-0.218	-0.345	-0.152	-0.165
Cd					1	-0.176	-0.268	-0.236	-0.230	-0.117	-0.138	-0.014	-0.108
Cu						1	0.164	0.301	0.050	0.065	0.357	-0.215	0.946**
Fe							1	-0.243	0.646*	-0.261	0.098	-0.117	-0.039
Mo							1		-0.133	0.674*	0.617*	0.436	0.224
Mn									1	-0.274	0.264	0.087	-0.035
Ni										1	-0.058	0.679*	0.035
Pb											1	-0.022	0.298
Se												1	-0.337
Zn													1

* and ** indicate the correlation coefficients were significant at 0.05 and 0.01 probability levels, using two-tailed test.

Table 5. The concentrations (mg kg $^{-1}$)of some heavy metals in Kovada Lake's sediment.

Seasons	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Pb	Se	Zn
Spring	0.04-0.26	4.43-17.75	8.96-33.55	2984.11-11117.25	0.71-6.12	41.87-157.41	10.14-38.39	1.46-8.15	0.34-1.33	17.66-46.29
	0.16±0.01 [a]	13.23±0.62 [a]	22.82±2.59 [a]	7974.53±43.07 [a]	3.30±0.70 [b]	117.20±5.29 [a]	28.68±1.05 [a]	5.60±0.62 [a]	0.97±0.05 [a]	36.57±6.38 [a]
Summer	0.01-0.15	4.97-17.19	7.96-30.07	2744.13-7292.31	0.10-0.90	35.39-91.81	10.81-31.93	2.75-5.73	0.27-1.46	12.39-34.76
	0.08±0.006 [a]	10.99±1.11 [a]	19.02±1.05 [a]	5174.23±22.08 [a]	0.49±0.04 [a]	59.41±9.12 [a]	20.71±1.61 [a]	4.41±1.51 [a]	0.96±0.06 [a]	27.25±2.87 [a]
Autumn	0.03-0.11	6.56-9.50	8.10-11.26	3578.13-4910.10	0.18-0.20	59.65-72.94	13.58-19.08	2.30-3.22	0.27-1.26	16.90-30.74
	0.08±0.004 [a]	8.06±0.46 [a]	9.94±1.64 [a]	4289.17±67.54 [a]	0.19±0.001 [a]	66.57±6.66 [a]	16.22±2.76 [a]	2.62±0.51 [a]	0.92±0.05 [a]	25.27±2.36 [a]
Winter	0.08-0.20	6.33-23.13	9.82-27.61	3678.62-9959.16	0.2-0.4	69.97-137.44	14.25-46.53	3.56-10.25	0.24-1.13	20.44-52.30
	0.12±0.006 [a]	14.37±1.42 [a]	16.70±2.55 [a]	6913.16±144.51 [a]	0.3±0.001 [a]	102.34±3.81 [a]	29.32±6.24 [a]	6.23±1.54 [a]	0.80±0.04 [a]	34.80±6.16 [a]

** Means with the same superscript in the same row are not significant different according to Duncan's multiple range test (*p*<0.05)

The heavy metal concentrations in sediment are summarized (arithmetic mean, minimum, maximum and standart deviation) in Table 5. Fe was the highest and Cd was the lowest in sediment. All analyzed metals were determined in all seasons in Kovada Lake's sediment including some metals such as Cd, Cr, Ni, and Pb which cannot be determined in water in various seasons. Sediment consist of very high metal levels compared with water. Because sediment particles attract the metals and metals accumulate in the sediment over time.

It was determined studies conducted in Beyşehir Lake, Atatürk Dam Lake, Yeniçağa Lake and Taihu Lake that the metals with highest accumulation in sediments were Fe and Mn [31, 39, 40]. It is explained the presence of large amounts of Fe in sediments of lakes, rivers and seas with the fact that Fe is the most abundant metal in the earth crust [41]. In this study, it is believed that the fact that Fe is the most accumulated metal in lake's sediment is related to the geological structure of the lake.

It was found that metal levels increased in spring and summer and decreased in autumn. It was found Pb, Cu and Cd levels to be at their highest in the sediment of Lake Habbaniyah (Iraq) during spring[42]. And it was found that the heavy metal concentration in the sediment of New Calabar River (Nigeria) was higher in summer and winter compared to spring and autumn [43]. In a study[44] conducted in Beyşehir Lake, and found that the amount of metal in sediment decreased in summer and increased in autumn and spring [31]. Using Suğla Lake sediment samples, found that Cu, Fe and Ni levels were at their highest in autumn and Cd, Cr, Mn, Pb and Zn levels were at their highest in winter, while metal levels decreased in spring and summer In a study conducted in Karataş Lake, [26] the amount of metals accumulated in the sediment usually increased in autumn and winter.

In general, the reason that the metal concentration in sediment increases in spring and winter is because spring rains begin to fall and snow begins to melt due to increase in temperatures, while the amount of rainfall is high during winter. Therefore, waters coming from surrounding areas carry pesticides, agricultural fertilizers and heavy metals to the lake and heavy metals mixing in the waters subside and accumulate in the sediment.

The metal composition of different components roots, stems and leaves of *Phragmites austrialis* was analyzed (Table 6). All metals were determined all components. It was determined that among heavy metals analyzed in this study, Cd, Pb and Zn had an accumulation level as root > stem > leaf, while Cr, Cu, Fe, Mo, Mn, Ni and Se had an accumulation level as root > leaf > stem. Heavy metal levels in different macrophytes were studied by [45] in Danube Delta, by [46] in Sultan Reed Bed, by [47] in Beyşehir Lake, by [48] in Sapanca Lake, by Yadav and [49] in India, and by [50] in Varas wetlands and found that the root contained more metals compared to the stem and leaves. [51] reported that *P. australis* was able to accumulate significant amounts of heavy metals in the air spaced cortex parenchyma tissue between its large cells. The fact that a higher metal accumulation is observed in the root compared to the stem and leaves is believed to decrease adverse effects of metals. This higher accumulation in the root is due to perennial nature of *P. australis* and the increase of accumulation over years.

It was determined that the level of metal in the root increased in summer and decreased in spring. The level of metal increases in spring and decreases in summer. The metal concentration in leaves, on the other hand, reaches its peak in autumn and is at its lowest in winter. It is determined that the level of metal in *P. australis* living in Sapanca Lake increased in autumn and winter and decreased in spring [48]. And also it isreported that the level of certain metals in macrophytes increased in autumn and decreased in spring [52]. The fact that the accumulation of metal in the root is high during summer may be related to increased dissolution due to high temperatures and also increased metal intake along with organic and inorganic molecules due to increased photosynthesis and transpiration activities of plants. The increase in the level of metal in the stem during spring may be related to increased interaction of metals with plant stems due to water circulation. On the other hand, the increase in the metal accumulation in leaves may be explained with the accumulation of waste materials and metals on leaves, which are excretory organs, throughout the year.

Table 6. The concentrations of some heavy metals in roots, stems and leaves of *P. australis* from Kovada Lake.

Seasons	Organs	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Pb	Se	Zn
Spring	Root	0.002-0.10 0.041±0.003^{a}	4.49-7.57 5.82±1.11^{a}	16.08±82.04 39.51±2.66^{a}	1472.19-8857.09 4438.29±26.49^{a}	0.29-1.60 0.90±0.45^{a}	238.85-587.12 397.72±13.88^{b}	10.20-18.63 14.52±2.78^{a}	0.9-2.87 1.41±0.05^{a}	2.33-6.24 3.53±0.38^{b}	62.68-114.68 91.03±11.71^{b}
	Stem	0.0001-0.02 0.0077±0.0007^{a}	0.41-0.81 0.54±0.013^{a}	3.62-15.47 8.29±0.21^{a}	36.87-105.01 68.37±2.29^{a}	0.15-1.45 0.79±0.005^{a}	19.88-366.24 142.66±16.75^{a}	0.98-4.87 2,13±0,46^{ab}	0.08-0.10 0.08±0.001^{a}	0.23-1.06 0.49±0.02^{a}	22.38-49.22 33.25±3.01^{a}
	Leaf	0.0005-0.03 0,009±0,001^{a}	0.23-0.57 0.44±0.011^{a}	3.58-15.49 9.92±1.91^{ab}	45.60-96.78 75.25±7.47^{a}	0.69-1.72 1.12±0.39^{a}	38.26-934.00 253.05±35.44^{a}	0.70-5.16 2.57±0.85^{a}	0.03-1.01 0.40±0.05^{ab}	0.21-1.10 0.44±0.03^{a}	15.34-45.84 25.24±1.96^{a}
Summer	Root	0.07-0.98 0.31±0.03^{b}	1.67-14.77 6.38±0.46^{a}	12.71-74.65 31.51±2.13^{a}	3683.51-13581.35 7577.39±35.04^{a}	0.13-3.66 1.23±0.51^{a}	43.43-362.68 213.96±11.71^{a}	8.42-33.75 16.26±2.14^{a}	1.49-6.87 3.78±0.93^{ab}	1.17-2.33 1.80±0.41^{a}	30.57-62.49 42.78±8.85^{a}
	Stem	0.0021-0.0025 0.0023±0.0002^{a}	0.37-2.30 0.84±0.007^{ab}	2.19-4.94 3.79±0.1^{a}	38.15-228.61 94.84±6.05^{a}	0.05-2.13 1.09±0.008^{a}	22.90-106.57 50.24±9.47^{a}	0.10-1.19 0.69±0.05^{a}	0.30-0.50 0.40±0.001^{a}	0.38-0.69 0.60±0.12^{a}	20.57-28.57 25.42±2.75^{a}
	Leaf	0.007-0.011 0.009±0.001^{a}	0.41-1.42 0.78±0.36^{ab}	3.59-36.67 14.95±1.65^{b}	50.09-271.76 146.63±12.71^{ab}	0.98-3.22 1.88±0.91^{ab}	62.05-789.40 265.90±26.54^{a}	0.04-5.08 1.96±0.06^{a}	0.01-0.07 0.040±0.004^{a}	0.61-1.64 1.10±0.04^{b}	9.54-46.57 23.74±3.68^{a}
Autumn	Root	0.01-0.22 0.12±0.009^{ab}	6.00-16.47 9.33±0.39^{a}	24.32-77.18 39.99±1.79^{a}	4355.59-10008.86 6780.72±22.78^{a}	0.73-5.17 2.50±0.87^{a}	75.36-659.24 264.23±20.09^{ab}	13.17-33.93 22.42±1.41^{a}	1.19-6.46 3,55±0,19^{ab}	1.14-3.71 2,29±0,86^{a}	28.77-68.99 45.92±3.81^{a}
	Stem	0.01-0.04 0.0258±0.0025^{a}	0.88-5.43 1.90±0.07^{b}	6.66-51.97 15.13±1.14^{a}	41.60-323.48 102.07±10.13^{a}	0.09-1.21 0.63±0.004^{a}	24.94-103.77 71.03±11.24^{a}	1.10-4.47 2.28±0.41^{b}	0.54-11.58 6,06±1,80^{a}	0.21-1.31 0.59±0.043^{a}	5.48-188.25 42.12±7.88^{a}
	Leaf	0.0076-0.008 0.0078±0.0002^{a}	0.80-4.97 1.82±0.55^{b}	6.00-12.16 9.27±2.19^{ab}	81.21-263.56 163.72±17.13^{b}	1.38-4.07 2.37±0.05^{b}	153,63-731.40 337.19±22.82^{a}	1.40-2.93 2.10±0.063^{a}	0.08-0.75 0.33±0.025^{ab}	0.37-1.75 0.88±0.05^{ab}	9.84-26.88 17.91±2.28^{a}
Winter	Root	0.1-0.55 0.21±0.002^{ab}	1.34-23.20 8.84±0.78^{a}	5.79-312.93 65.86±4.31^{a}	1171.22-13151.68 6625.42±43.21^{a}	0.77-7.59 2.99±0.63^{a}	38.01-153.29 88.96±5.14^{a}	3.74-49.44 22.06±2.37^{a}	0.25-10.41 4.45±1.56^{b}	0.33-3.16 1.52±0.32^{a}	10.56-146.93 61.55±8.35^{ab}
	Stem	0.001-0.08 0.03±0.004^{a}	0.39-1.65 0.82±0.004^{ab}	1.68-5.86 4.06±0.62^{a}	53.33-390.18 128.82±12.31^{a}	0.34-1.45 0.67±0.041^{a}	13.82-127.12 67.89±8.75^{a}	0.10-2.15 1,25±0,90^{ab}	0.03-0.23 0.11±0.009^{a}	0.54-1.88 0.91±0.05^{a}	8.95-57.10 23.90±1.47^{a}
	Leaf	0.001-0.03 0.011±0.001^{a}	0.46-2.31 1.24±0.60^{ab}	2.51-11.13 5.59±0.39^{a}	55.38-206.36 148.44±8.78^{ab}	0.16-3.05 1.47±0.10^{ab}	19.15-147.88 82.89±4.30^{a}	0.43-1.47 1.00±0.042^{a}	0.02-1.16 0.59±0.042^{b}	0.98-1.94 1.40±0.39^{a}	15.81-32.06 21.85±4.33^{a}

** Means with the same superscript in the same row are not significant different according to Duncan's multiple range test (p<0.05)

4. Conclusions

The levels of Zn in all seasons and Cu in winter in the lake water higher than permissible levels given by Republic of Turkey Ministry of Food, Agriculture and Livestock [53]. The levels of analyzed metals were lower than the WHO, EC and EPA [54-57].

Kovada Lake is one of our national parks with many animal and plant species in and around it. There are plenty of farmlands around the lake. The fertilization of these farmlands and fertilizers' high Cd, Pb, Fe and Zn content is a major problem. Fertilized soils are carried to the lake through surface flow. Since the locals earn their livelihoods from agriculture, the use of fertilizers and pesticides must be taken under control and solutions with less polluting factors must be sought.

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