3(2): 87-96 (2017) doi: 10.3153/JAEFR17012

Journal of
Aquaculture Engineering and Fisheries Research

E-ISSN 2149-0236

ORIGINAL ARTICLE/ORİJİNAL ÇALIŞMA

FULL PAPER TAM MAKALE

THE INVESTIGATION OF HEAVY METAL LEVELS IN WATER AND SEDIMENT FROM IŞIKLI LAKE (TURKEY) IN RELATION TO SEASONS AND PHYSICO-CHEMICAL PARAMETERS

Belma Gülcü-Gür, Selda Tekin-Özan

Süleyman Demirel University, Faculty of Science and Art, Department of Biology, Isparta-Turkey

Received: 19.10.2016

Accepted: 25.01.2017

Published online: 24.02.2017

Corresponding author:

Selda TEKİN-ÖZAN, Süleyman Demirel University, Faculty of Science and Art, Department of Biology, Isparta-Turkey

E-mail: seldaozan@sdu.edu.tr

Abstract:

This paper presents data on the concentrations of ten heavy metal levels in water and sediment sampled from Işıklı Lake (Turkey) as seasonally (October-2012, January-2013, April-2013, July-2013) and shows relationships between physico-chemical parameters and levels of heavy metals. Temperature, pH, dissolved oxygen and electrical conductivity were measured. In water, Pb was below detection limit (<0.005) in all seasons, while Cu (<0.0005) was in autumn and winter. Fe had the highest level and Cd had the lowest level among the analyzed metals. Cr, Cu, Fe, Mn, Ni and Se reached the highest levels in summer, while Cd, Mo and Zn were in spring. Cd, Cr, Mo and Zn in autumn, Cu and Se in spring, and Fe, Mn, and Ni in winter were the lowest. Cd, Cu and Mo levels varied significantly (p<0.05) from season to season. There were positive relationships among temperature, pH value (p<0.05) and EC. Significant negative correlation (<0.01) was determined between temperature and dissolved oxygen. Significant (Cr, Cu, Mn and Zn) and non-significant (Cd, Fe, Mo, Ni and Se) positive correlations were detected between content in water and temperature. There were positive correlations between pH and dissolved oxygen, while negative correlation with EC. When the pH value increased, only Mo level decreased. Dissolved oxygen levels had a positive relationship with EC and all studied metals except Cu. There were positive relationships between EC and Cd, Cr, Mn, Mo and Zn, the others were significant negative (<0.01). In sediment, Se was below detection limit in winter, other metals were detected in all seasons. Fe was the highest while Cd was the lowest in sediment. Cd, Cr, Mn, Mo, Ni and Zn reached the highest levels in spring, while Fe in winter, Cu in autumn, Pb in summer. Cr, Mn, Mo, Ni, Pb and Zn in winter, Cd and Se in autumn, Cu in summer and Fe in spring were the lowest. Cd, Cu and Mo levels varied significantly (p<0.05) from season to season.

Keywords: Heavy metal, Pollution, Water, Sediment, Işıklı Lake, Turkey

Introduction

Pollution of the wetlands is one of the world's most serious problems. Different materials like heavy metals, acids, pesticids, fossil fuels, nitrates, sulfates, microorganisms, hot water, radioactive subtances are cause water pollution (Göksu et al., 2003). From these, heavy metals are seem to be one of the most important pollutants of the lakes and these metals may cause a serious hazard to aquatic life because of their long persistence, bioaccumulation, biomagnification and toxicity (Harte et al., 1991; Schüürmann and Markert, 1998; Iqbal and Shah, 2014). Heavy metals are produced from different anthropogenic and natural sources like industrial effluents, mining activities, agricultural runoffs, transport, geological structure, burning of fossil fuels and atmospheric deposition (Adnano, 1986; Dawson and Macklin, 1998; Kalay and Canli, 2000). Low levels of some heavy metals are essential for the development of living organisms, but some of them such as Pb, Hg and Cd are non-essential and very toxic. And also, essential metals may be toxic when they are present above the permissible concentration (Puttaiah and Kiran, 2008).

Heavy metal concentration in the lakes can be verified in aquatic organisms, water and sediment (Förstner and Wittman, 1983). Metals don't subsist in solvable forms in water for a long time, generally exist as suspended colloids or are stable as organic and mineral substances (Kabata-Pendias and Pendias, 2001). Dissolved metal can generate dissolved organic or inorganic complexes, depending on physico-chemical conditions (Petronio et al., 2012). Sediments are important sinks for heavy metals and can be used to detected pollution of heavy metal in aquatic systems (Gangaiya et al., 2004). Some factors such as pH and the property of metal affects the release of heavy metals from sediment into the water (Dean, 2012).

The aim of this study are to determine relationships between the metal levels in water and physico-chemical parameters and to show seasonal variations of heavy metal levels in water and sediment.

Materials and Methods

Işıklı Lake (29º 92´ E, 38º 22´ N), situated on south west of Turkey (Figure 1). Lake water is mainly used for irrigation. The lake is approximately 7 m depth, its area is 9749 ha and fed by Büyük Menderes Stream, Karanlık Stream and Kufi Stream. There are small rush islands in the lake (Aygen and Balık, 2005; Akarsu et al., 2006). During the study period (October-2012, January-2013, April-2013, July-2013) as seasonally water and sediment sampled were collected at the three sampling stations from the Işıklı Lake. Using with YSI multiparameter equipment, the temperature, dissolved oxygen, electrical conductivity (EC) and pH values were measured from these same stations. Surface water samples were taken by using 500 ml polypropylene bottle, added 5 ml of concentrated HNO_3 to keep the pH value less than 2.0. Water samples filtered with a 0.45 µm Whatman glassfiber filter, stored at 4 ºC and were analyzed directly (APHA, 2005).

Figure 1. Map of Işıklı Lake (Turkey) (Taken from googleearth)

The sediment samples were collected by a Ekman grab from a depth of 5-15 cm and were put the oven and the samples dried in it at 50 ºC for 48 h, sieved to obtain the <63 µm fraction (Bryan and Langston, 1992; Buchanan, 1984) and homogenized. 0.5 g sediment was weight, placed in autoclavable bottles and 5 ml HNO_3 (65%) added to each, were kept at room temperature for 24-h. The samples were heated for 2 hours at 120 ºC on hot plate, until the solution evaporate slowly to near dryness. 1 ml H_2SO_4 (30%) added the bottles after cooling, and solvented to 25 ml with deionized water, then 1-2 drop HNO_3 was added (UNEP, 1984).

All samples were analyzed for three times for heavy metals (Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn) by using for ICP-AES Vista. The digestion and analytical procedures were checked by using standard materials DORM-3, DOLT-4 and HISS-1 (National Research Council Canada). The absorption wavelength were 228.802 nm for Cd, 267.716 nm for Cr, 324.754 nm for Cu, 259.940 nm for Fe, 257.61 nm for Mn, 202.03 nm for Mo, 352.454 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 µg/L for Cd, 0.5 µg/L for Cr, 0.3 µg/L for Cu, 0.35 µg/L for Fe, 0.05 µg/L for Mn, 0.8 µg/L for Mo, 1.3 µg/L for Ni, 3 µg/L for Pb, 5 µg/L for Se and 0.3 µg/L for Zn.

SPSS 18 Statistical package programs was used for statistical analysis. To compare the data among seasons at the level of 0.05 and to test for significant associations between heavy metal levels in water and physico-chemical parameters One-Way ANOVA, Duncan's Multiple Comparison Test and Pearson rank correlation coefficient were used (Duncan, 1955; Muller and Bethel, 2002; Gravetter and Wallnau, 2007).

Results and Discussion

The same heavy metals were analyzed under the same conditions from reference materials (DORM-3, DOLT-4, HISS-1) to check the certainty and accuracy (Table 1). Replicate analysis of DORM-3, DOLT-4, HISS-1 showed good precision, with recovery rates for metals between 82% and 115% for DORM 3, 92% and 112% for DOLT 4, 86% and 116% for HISS 1.

Physico-chemical parameters of water samples as seasonally are given in Table 2. According to the table, water temperature varied between 4.17 °C (in winter) and 28.83 °C (in summer), respectively. Mean pH varied between 8.65 (in spring) and 9.13 (in summer). Dissolved oxygen was the highest in spring (9.37 mg/lt) and lowest in summer (4.99 mg/lt). EC measurement ranged between 385.2 µs/cm (in spring) and 262.33 µs/cm (in winter). Important positive relations were found between temperature and pH ($p<0.05$), and dissolved oxygen and EC ($p<0.05$). Negative significant relationships were determined temperature and dissolved oxygen ($p<0.01$). Başyiğit and Tekin-Özan (2013), found that in Karataş Lake, pH and EC values were highest in summer and lowest in winter. Dissolved oxygen decreases in summer and increases in winter. The pH value in water decrease with increasing CO_2. In summer, the pH value increase when CO_2 decrease owing to photosynthesis (Tanyolaç, 2006). Dissolved oxygen was the highest in spring. This can be related to with photosynthesis because there are a lot of macropyhte in the lake and in spring, they produce oxygen via photosynthesis. And the rivers carry too much water with oxygen to the lake. EC level was the highest in summer. In warm seasons, too much water evaporate, so that inorganic substances concentrate increase in water body.

In Table 3, the heavy metal concentrations in water were given. As seen Table 3, Pb was below detection limit (<0.005) in all seasons, while Cu (<0.0005) was in autumn and winter. The heavy metals predominantly determined in the water of Işıklı Lake. Among the analyzed metals, the highest and lowest metals were Fe and Cd. Similar results were reported in Beyler Reservoir (Fındık, 2013), Hazar Lake (Karadede-Akın, 2009), Karataş Lake (Başyiğit and Tekin-Özan, 2013), Kızılırmak River (Akbulut and Akbulut, 2010), Beyşehir Lake (Tekin-Özan, 2008). Ghaffar et al. (2008), reported that Fe facilities the precipitation of other metals and found at low levels when precipitation occurs.

Seasonal variations of heavy metals also can be seen in Table 3. Cr, Cu, Fe, Mn, Ni and Se reached the highest levels in summer, while Cd, Mo and Zn were in spring. Cd, Cr, Mo and Zn in autumn, Cu and Se in spring, and Fe, Mn, and Ni in winter were the lowest. Cd, Cu and Mo levels varied significantly ($p<0.05$) from season to season. Physico-chemical parameters of water like pH, EC, salinity, dissolved oxygen effect the metal levels in water (Wong et al., 2000). The reason of increasing metal levels in summer can be caused by increasing the air temperature and evaporation. The decrease of heavy metals in warm seasons and winter in maybe cause by heavy rain, snow and melting snow. Similar results are also found in Hazar Lake (Karadede-Akın, 2009), Karataş Lake (Başyiğit and Tekin-Özan, 2013), Kızılırmak River Basin (Akbulut and Akbulut, 2010).

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 ($p<0.05$) and EC. Significant negative correlation ($p<0.01$) was determined between temperature and dissolved oxygen. Significant (Cr, Cu, Mn and Zn) and non-significant (Cd, Fe, Mo, Ni and Se) positive correlations were detected between content in water and temperature. There were positive correlations between pH and dissolved oxygen, while negative correlation with EC. When the pH value increased, only Mo level decreased. Dissolved oxygen levels had a positive relationship with EC and all studied metals except Cu. There were positive relationships between EC and Cd, Cr, Mn, Mo and Zn, the others were significant negative ($p<0.01$). Başyiğit and Tekin-Özan (2013) found negative relationships between temperature and Cu and Se, between pH and Se, Zn, between dissolved oxygen and Mn, Mo, Cu, Fe, Cd, Cr, Pb and Zn, between EC and Cd, Cu, Fe, Mn, Pb, Se. Fındık (2013) determined negative correlations between temperature and Fe, Mn, Pb, between dissolved oxygen and Zn, Cu, B, Cr, Ni and Al, between pH and Fe, Al. Witeska and Jezierska (2003) explained that most metals seem to be more toxic in acidic in neutral and alkaline water and showed that an increase in water hardness reduces metal toxicity.

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Table 1. Concentrations of metals found in certificied reference material DORM-3, DOLT-4 and HISS-1 from National Research Council, Canada.

Metals	DORM 3 Certified	DORM 3 Observed	Recovery (%)	DOLT 4 Certified	DOLT 4 Observed	Recovery (%)	HISS 1 Certified	HISS 1 Observed	Recovery (%)
Cd	0.290 ±0.020	0.24 ±0.01	82	24.3 ±0.8	22.45 ±0.12	92	0.024 ±0.009	0.021 ±0.02	87
Cr	1.89 ±0.17	1.72 ±0.11	91	-	-	-	30.0 ±6.8	28.45 ±2.25	94
Cu	15.5 ±0.63	13.21 ±1.69	85	31.2 ±1.1	35.12 ±2.36	112	2.29 ±0.37	1.99 ±0.25	86
Fe	347 ±20	400.78 ±8.25	115	1833 ±75	1698 ±22.1	92	-		-
Mn	-	-	-	-	-	-	66.1 ±4.2	54.95 ±1.45	89
Mo	-	-	-	-	-	-	-		-
Ni	1.28 ±0.24	1.12 ±0.47	87	0.97 ±0.11	0.99 ±0.05	102	2.16 ±0.29	2.45 ±0.15	116
Pb	0.395 ±0.05	0.41 ±0.09	-	8.3 ±1.3	7.97 ±1.12	96	3.13 ±0.40	2.98 ±0.01	95
Se	-	-	105	-	-	-	0.050 ±0.007	0.048 ±0.11	96
Zn	51.3 ±3.1	57.14 ±8.47	111	116 ±6	125.78 ±4.54	108	4.94 ±0.79	5.12 ±1.002	103

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

Season	Temperature (ºC)	pH	Dissolved Oxygen (mg/L)	Electrical Conductivity (µg/cm)
Autumn	11.57-13.12 12.55 ±0.855	7.7-7.83 7.78 ±0.07	4.45-6.04 5.49 ±0.901	265-357 320.33 ±48.75
Winter	3.76-4.63 4.17 ±0.43	7.45-7.57 7.51 ±0.06	7.99-8.41 8.20 ±0.21	247-289 262.33 ±23.18
Spring	16.50-18.98 18.04 ±1.34	7.24-7.29 7.26 ±0.025	8.89-9.95 9.37 ±0.53	355-428 385.2 ±38.17
Summer	27.94-30.05 28.83 ±1.09	9.01-9.35 9.13 ±0.18	4.08-5.81 4.99 ±0.86	300.9-334.5 311.6 ±17.25

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

Season	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Autumn	0.03-0.19 0.11±0.08 [a**]	0.01-1.66 0.77±0.83 [a]	BDL*	56.65-829.44 421.37±388.2 [a]	8.97-47.91 26.53±19.75 [a]	0.44-1.11 0.78±0.47 [a]	1.89-5.33 3.61±2.43 [a]	BDL	4.68-4.70 4.69±0.01 [a]	3.96-6.61 5.02±1.40 [a]
Winter	0.16-0.27 0.21±0.08 [a]	0.72-1.09 0.88±0.19 [a]	BDL	35.19-51.66 43.27±8.24 [a]	4.69-7.63 6.13±1.47 [a]	1.49-1.64 1.57±0.08 [ab]	0.13-0.14 0.135±0.007 [a]	BDL	3.41-5.35 4.4±1.37 [a]	3.68-10.26 5.9±3.79 [a]
Spring	1.60-7.00 3.50±3.04 [b]	2.70-5.80 3.87±1.69 [a]	1.80-6.50 4.67±2.51 [b]	140.00-260.00 210.00±62.45 [a]	27.00-97.0 65.33±35.47 [a]	2.10-4.50 3.27±1.20 [c]	0.57-13.40 6.46±6.48 [a]	BDL	1.40-5.00 2.90±1.87 [a]	340.00-460.00 393.33±61.10 [a]
Summer	2.18-270 2.37±0.28 [ab]	14.69-14.70 14.696±0.002 [a]	9.74-14.31 12.68±2.55 [c]	55.41-8569.09 3206.97±4667.51 [a]	20.97-251.39 116.84±119.98 [a]	2.01-2.44 2.26±0.22 [bc]	10.21-106.33 43.40±54.53 [a]	BDL	2.41-51.39 30.26±25.18 [b]	120.60-373.68 281.63±139.93 [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)

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

	Temperature (ºC)	pH	Dissolved Oxygen (mg/L)	Conductivity (µg/cm)	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Se	Zn
Temperature (ºC)	1	0,755*	-0,644**	0,376	0,493	0,823**	0,884*	0,466	0,600*	0,415	0,517	0,605	0,686*
pH		1	0,161	-0,186	0,051	0,723	0,850	0,486	0,414	-0,057	0,497	0,725	0,174
Dissolved Oxygen (mg/L)			1	0,587*	0,704*	0,465	-0,969**	0,150	0,417	0,777**	0,114	0,107	0,890**
Conductivity (µg/cm)				1	0,676*	0,129	-0,791	-0,079	0,238	0,532	-0,369	-0,236	0,618
Cd					1	0,290	-0,162	0,098	0,426	0,885**	0,074	-0,004	0,679*
Cr						1	0,961*	0,922**	0,916**	0,244	0,966**	0,936**	0,327
Cu							1	0,610	0,488	-0,340	0,638	0,575	-0,540
Fe								1	0,920**	-0,046	0,986**	0,764*	-0,068
Mn									1	0,225	0,911**	0,624	0,202
Mo										1	0,011	-0,094	0,790**
Ni											1	0,807*	-0,111
Se												1	-0,037
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 Işıklı Lake's sediment

Season	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Autumn	0.09-0.11 0.10±0.01^{a**}	9.15-11.92 10.79±1.45 ^{ab}	13.05-16.31 14.43-1.69 ^{a}	2677.23-2891.61 2756.83±117.36 ^{a}	168.10-235.62 200.3±33.87 ^{ab}	0.14-0.17 0.15±0.02 ^{a}	18.37-23.90 21.49±2.83 ^{ab}	1.15-2.46 1.75±0.66 ^{ab}	0.20-1.01 0.66±0.42 ^{ab}	14.87-18.45 16.14±2.002 ^{ab}
Winter	0.10-0.11 0.104±0.01 ^{a}	5.12-7.80 6.40±1.35 ^{a}	10.64-13.22 11.90±1.30 ^{a}	2015.35-2616.19 2297.85±302.02 ^{a}	135.98-150.95 145.03±7.96 ^{a}	0.08-0.19 0.13±0.06 ^{a}	11.55-18.95 15.60±3.75 ^{a}	0.91-1.77 1.32±0.44 ^{a}	BDL*	12.01-13.43 12.85 ±0.74 ^{a}
Spring	0.27-0.30 0.28±0.02 ^{c}	11.75-16.48 13.65±2.50 ^{b}	11.11-14.55 12.74±1.73 ^{a}	5904.89-7700.27 6614.28±955.10 ^{b}	264.03-556.95 361.94±168.88 ^{b}	0.60-0.67 0.63±0.03 ^{c}	25.78-38.93 30.81±7.10 ^{b}	2.13-4.48 3.32±1.18 ^{ab}	0.16-1.92 1.05±0.88 ^{b}	21.70-28.87 24.47±3.85 ^{c}
Summer	0.21-0.27 0.25±0.03 ^{b}	6.74-14.69 11.65±4.29 ^{b}	7.18-16.32 11.62±4.58 ^{a}	4336.97-7567.02 6295.71±1721.26 ^{b}	189.07-332.70 248.83±74.79 ^{ab}	0.46-0.52 0.49±0.03 ^{b}	16.70-34.30 27.68±9.57 ^{ab}	2.52-5.50 3.68±1.60 ^{b}	0.75-1.09 0.94±0.17 ^{ab}	15.49-24.44 20.66±4.63 ^{b}

* 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 metal concentrations in sediment are summarized in Table 5. Se was below detection limit in winter, other metals were determined in all seasons. The total levels of metal concentrations in sediment samples were in order Fe> Mn> Ni> Zn> Cu> Cr> Pb> Se> Mo> Cd. Fe levels were the highest while Cd lowest in Karataş Lake (Başyiğit and Tekin-Özan, 2013), Beyler Reservoir (Fındık and Turan, 2012), Uluabat Lake (Barlas et al., 2005), Hazar Lake (Özmen et al., 2004). Iron is generally the most abundant metal in all of the reservoirs it is one of the most common elements in the Earth's crust (Usero et al., 2014). Pyrite oxidation produced sulphate and the Fe^{2+} ion, which is oxidised to Fe^{3+} by microorganisms such as *Thiobacillus ferrooxidans* (Cabrera et al., 1999). Kerrison et al. (1988), reported that Cd accumulates slowly in the sediment. Cadmium is not found in the organic fraction for low adsorption constant and labile complexion with organic matter (Baron et al., 1990). The Fe, Mn, Zn, Cr, Cu and Cd levels are lower than the values in Beyler Dam Lake (Fındık and Turan, 2012), Kovada Lake (Kır et al., 2007) and Seyhan Dam Lake (Çevik et al., 2009). Cd, Cr, Mn, Mo, Ni and Zn reached the highest levels in spring, while Fe in winter, Cu in autumn, Pb in summer. Cr, Mn, Mo, Ni, Pb and Zn in winter, Cd and Se in autumn, Cu in summer and Fe in spring were the lowest. Cd, Cu and Mo levels varied significantly ($p<0.05$) from season to season. Tekin-Özan (2008) reported that the Cu and Zn levels were highest in spring, while Fe and Mn were in autumn in Beyşehir Lake's sediment. In Beyler reservoir sediment, Fe, Al, Zn, Cu, Mn and B were highest in summer, while Cr, Ni, Cd and Pb were in spring (Fındık and Turan, 2012). In Hazar Lake, heavy metals concentrations were highest in spring and autumn (Karadede-Akın, 2009). Kankılıç et al. (2013) showed Fe, Mn, Cu, As, Pb and Hg levels were highest in summer and lowest in autumn. In aquatic systems, metals are transported either in solution or on the surface of suspended sediments (Dawson and Macklin, 1998). Due to their strong affinity for particles (Luorna, 1990), metals tend to be accumulated by suspended matter or trapped immediately by bottom sediments (Dauvalter, 1998). The heavy metals may be in sediment through indirect discharge or from atmospheric deposition at the power plant (Demirak et al., 2006).

This study showed that Işıklı Lake's sediment contains higher amounts of heavy metals as compared with the quantity of water. Sediments behave as the most important sink or reservoir of metals and other pollutants in the aquatic environment (Abdel-Baki, 2011).

Conclusion

Işıklı Lake is one of the most important water sources of the region because of its use for irrigation and having great potential fisheries activity. In this study, we also compared our results with permissible levels in water for heavy metals given by some different institutes. Based on the heavy metals level, the water of Lake Işıklı was classified as category I according to the standards of Republic of Turkey Ministry of Environment and Forest (Republic of Turkey Ministry of Environment and Forest, 2004). The levels of Zn and Fe in the lake water higher than permissible levels given by Republic of Turkey Ministry of Food, Agriculture and Livestock (Republic of Turkey Ministry of Food, Agriculture and Livestock., 2002). The levels of analyzed metals were lower than the WHO, EC and EPA (WHO, 1998; 2011; EC, 1998; US EPA, 1999).

Acknowledgements

This work is supported by Suleyman Demirel University, SDUBAP 3299-YL1-12 project. I would like to thank Suleyman Demirel University – Scientific Research Project Management for their financial support.

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