ASSESSMENT OF HEAVY METAL CONCENTRATION IN FEATHERS OF ARMENIAN GULL (*LARUS ARMENICUS* BUTURLIN, 1934) AND WATER SAMPLES OF HAZAR LAKE, TURKEY

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Abstract. Accumulation levels of heavy metals in the feathers of birds reflect the abundance of these pollutants in the medium and birds can be useful indicators of this kind of pollution. The aim of the present study was to detected levels of some heavy metals of juvenile and adult Armenian Gull (*Larus armenicus*) and in the surface water of Hazar Lake, Turkey. The feather samples from different parts of the bodies of dead adult and juvenile Armenian Gulls were collected. Water samples were taken from different sampling stations distributed across the lake. Heavy metal concentrations were measured using a Thermo Scientific ICAP 600 Spectrometer. There was no significant statistical difference for bioaccumulation of heavy metals and trace elemets in adult and juvenile gull feathers ($p>0.05$). However, the highest metal concentrations were measured in juveniles. The highest average residue amounts in juvenile cover feathers were 0.02 mg/kg Cd, 0.46 mg/kg Pb, 0.72 mg/kg Cu, 58,31 mg/kg Fe, 0.04 mg/kg Ni, 8.38 mg/kg Zn, 0.07 mg/kg Se, 1.3 mg/kg Mn, 0.005 mg/kg Cr and 0. 01 mg/kg As. Mean values of all metals were within the acceptable limits of normal values for waterbirds, except Pb and Mn. When we evaluated the findings heavy metal concentration of the water were detected decrease in sequence of; Fe>As>Zn>Ni>Cd>Cu>Cr>Pb>Mn>Se. Compared with WHO (World Health Organization) and TSE-266 (Turkish Standarts Institution) standards; Cd, Cu, Zn and Cr concentrations in water were higher than the permissible levels for drinking water. It seems Armenian Gull feathers are useful monitoring tool for assessing heavy metal contamination.
Keywords: *bioindicator, biomonitoring, birds, toxic effect, wetland*

Introduction

Environmental degradation of wetland ecosystems by metals is a worldwide problem because of their toxic effects and long persistence (Mansouri et al., 2012; Klaassen, 2013; Zhang et al., 2018). As the trophic level rises in a food chain, the amount of toxic pollutant build up increases and therefore they involve great threat for all species and ecosystems (Ullah et al., 2014).

Indicator species are used to biomonitor environmental changes and to assess effects of pollution. Birds have been recognized as the useful bioindicators of environmental health (Erwin and Custer, 2000). They can be exposed to heavy metals through intake of food, drinking contaminated water and by physical contact (Becker, 2003; Burger and Gochfeld, 2004; Bostan et al., 2007).

One of the suitable methods of assessing level of the metal pollution in natural habitats is to determine the amount of it in bird feathers. Especially birds of prey species occupying higher trophic levels deemed indicative for bioaccumulation in the whole food chain (Boncompagni et al., 2003; Barbieri et al., 2010). Gulls are top predator species of their food web and they can give information about a large area around sampling site.

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The Armenian Gull (*L. armenicus*) breeds in eastern Turkey, Armenia, southern Georgia and northwestern Iran. It is known that breeding population of species in Turkey has declined rapidly in recent years (Adızel et al., 2010; Nergiz and Durmuş, 2017; Durmuş et al., 2018). There is one known crowded native resident population of Armenian Gull in Hazar Lake in East Anatolia. But studies about Hazar Lake population of the species are scanty.

In this study, we measured levels of Cd, Pb, Cu, Fe, Ni, Zn, Se, Mn, Cr and As in feathers of *L. armenicus* and water samples of its foraging areas at Hazar Lake. The objectives of this study were was to assess relationships between the metal levels in the feather of adult and juvenile Armenian Gulls and to compare the concentration of these metals in feathers of the species and their habitat at Hazar Lake, Turkey. We hope that this study will be a useful reference for the determination of regional contamination and realization of a protection plan for this bioindicator species.

Materials and methods

Feather samples of Armenian Gull were collected during 2015-2016 breeding season from the dead individuals in Hazar Lake. Water samples (n=48) were taken once a month at sampling station distributed across the lake. The details of each sampling station are given in *Figure 1*. Collected specimens were labeled and transported to the laboratory under appropriate conditions.

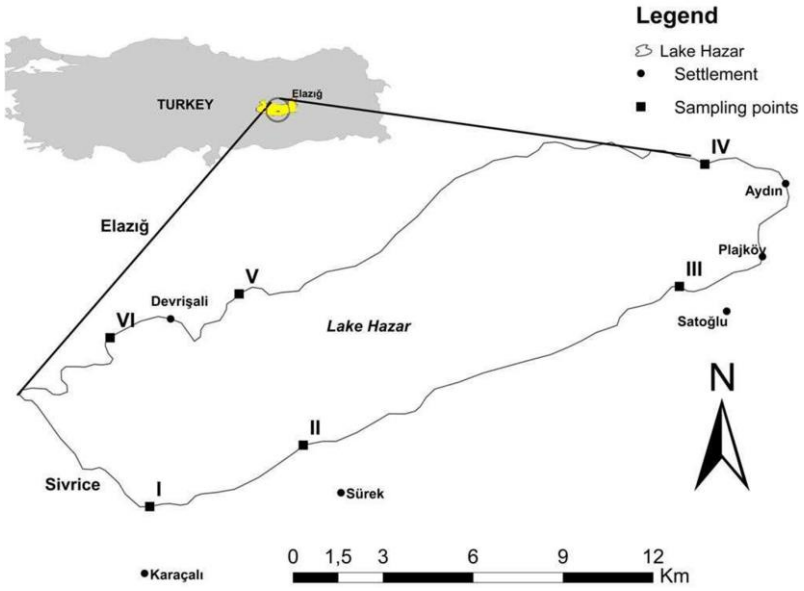

Figure 1. *Location of sampling stations in Lake Hazar*

Surface water samples were taken from 50 cm below the water surface using 100 ml sterile bottles, filtered and acidified with 1 ml of concentrated HNO_3 and then kept in a freezer at 4ºC until measured. Total 40 feather samples from different parts of the bodies of adult and juvenile Armenian Gulls were collected (APF: Adult Primary Wing Feather; ASF: Adult Secondary Wing Feather; ACF: Adult Cover Feather; JCF: Juvenile Cover Feather). Samples of feather transferred to the laboratory were washed with deionized water and rinsed with acetone to wash away the organic materials which

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the water cannot dissolve. All samples were dried at 60ºC for 24 h to remove moisture. The dried feather samples were cut into small pieces with a steel scissors. 0.2 g (dry weight) from each sample were put into glass dissolution vessels and 5 ml HNO_3 (65%) added to each, and stored at room temperature for 24 h. The samples were heated to boiling on a hot plate until the color vapors of the samples vanished slowly and they were completely mineralized. After this, all samples were diluted to 10 ml with deionized water. Each sample was analysed at least three times for Cd, Pb, Cu, Fe, Ni, Zn, Se, Mn, Cr and As using ICP-AAS (Thermo Scientific ICAP 600 series).

Statistical analysis

All metal concentrations were detected as milligrams per liter for water samples and on a dry weight basis as milligrams per gram for feather samples. For this reason, average heavy metal levels were calculated as milligrams per kilogram. Statistical analysis was conducted in order to assess and compare the average values of metals in *L. armenicus*. Data were analyzed with SPSS software (Version 23). The average distribution of metals in *L. armenicus* (adults and juveniles) and water samples were assessed with independent t-test.

Results and discussion

The distribution of heavy metal and trace elements in feathers of *L. armenicus* for adults and juveniles respectively are given in *Table 1*. Results of our work confirm the findings by Burger (1993), Boncompagni et al. (2003) and Malik and Zeb (2009) that heavy metals pile up at different concentrations in feathers of adult and juvenile birds.

Table 1. *Concentrations of heavy metals and trace elements in feathers (mg/kg dry weight) of L. armenicus and in water samples of Hazar Lake (mg/l)*

Metal	Adults Mean ± SD	Juveniles Mean ± SD	Water samples Mean ± SD	p
Cd	0.0207± 0.0185	0.0265±0.0294	0.0091±0.0266	0.56
Pb	0.4491±0.4162	0.4689±0.2592	0.0046±0.01152	0.88
Cu	0.6302±0.1445	0.7295±0.1755	0.0081±0.0418	0.082
Fe	24.0938±19.3146	58.3160±15.0129	0.0697±0.1685	0.06
Ni	0.0063±0.0143	0.0490±0.1321	0.0101±0.03519	0.08
Zn	7.2498±1.7706	8.3848±1.9769	0.0146±0.0432	0.09
Se	0.0598±0.0289	0.0754±0.0238	*BDL	0.09
Mn	0.6212±0.4237	1.3006±0.3392	0.003±0.0055	0.07
Cr	0.0041±0.0125	0.0057±0.0134	0.0077±0.0418	0.18
As	0.0049±0.0037	0.0165±0.0311	0.0175±0.0032	0.25

*BDL: Below Detection Limit, statistically significance was accepted at $p<0.05$

Some studies have been conducted on heavy metals levels in feather of birds. Barbieri et al. (2010) showed that the levels of Cd, Co, Cr, Mn, Ni, Zn, and Pb increased with age. Furthermore, Burger (1996) indicated that the ratio of cadmium and lead in feathers of Franklin's gulls were lower in juveniles. Mansouri et al. (2012) pointed out that metal levels were always higher in adults, because of the age-related bioaccumulation. In the contrast, several studies have reported that there are significant differences in metal contamination in feathers with age related in which chicks had

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significantly higher concentration of metal than adults (Stewart et al., 1997; Dauwe et al., 2000; Burger and Gochfeld, 2009; García-Tarrasón et al., 2013).

Present study provides additional supports for the suggestions by Burger et al. (2008) and Movalli (2000), that there was no significant statistical difference between feather samples taken from adults and juveniles for bioaccumulation of heavy metal and trace elements ($p>0.05$). The average levels of heavy metals detected in juvenile feathers in the present study were as; Cd 0.02 mg/kg, Pb 0.46 mg/kg, Cu 0.72 mg/kg, Fe 58.316 mg/kg, Ni 0.04 mg/kg, Zn 8.38 mg/kg, Se 0.07 mg/kg, Mn 1.3 mg/kg, Cr 0.005 mg/kg and As 0. 01 mg/kg. The chemical profiles of juveniles were as follows: Fe>Zn>Mn>Cu>Pb>Se>Cd>As>Ni>Cr. The highest trace metal concentrations were measured in juveniles. But the differences were smaller (*Figure 2*). This age related differences may be due to diet differences. Juveniles may have foraged in different habitats and fed more often than adults would have higher levels of metals in their feathers. The high levels of heavy metal accumulation in juveniles can be correlated with the egg and their food, which is derived locally.

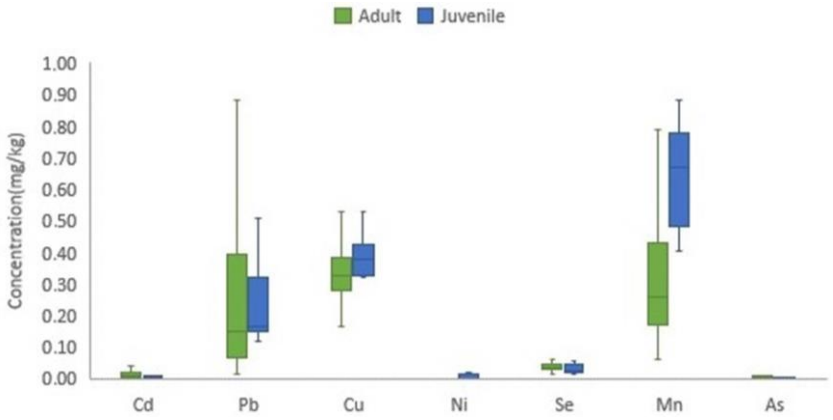

Figure 2. *Comparison of heavy metals in the feather samples taken from adult and juvenile Armenian Gulls*

Pb and Mn levels measured in present study were higher than those reported in previous researches. In the literature, an average of 0.51 ppm Mn and 0.19 ppm Cd was detected for marine birds (Burger, 2002). These values are much lower than that measured in our study. Greater than 2 mg/kg (dw) Cd, 4 mg/kg (dw) Pb, 1200 mg/kg (dw) Zn, 2.8 mg/kg (dw) Cr, 26 mg/kg (dw) Se, 0.96 mg/kg (dw) As concentrations in feathers were considered as abnormal poisoning and indicates increased environmental pollution (Burger, 1993; Heinz, 1996; Burger and Gochfeld, 2000; Taggart et al., 2006; Nighat, 2013). In the present study, mean heavy metal and trace element levels during 2015/2016 were in order of magnitude below known toxic effect levels.

Durmuş et al. (2018) studied metal deposition (Mg, Zn, Cu, Mn, Li, Sn, Co and Se) in feathers of the Armenian Gull from various regions of Van Lake Basin in Turkey. We found the mean concentration of Cr to be lower than their results but Zn, Mn and Se concentrations were slightly higher in our study which might be due to different nutrient density.

The heavy metal levels in water are given in *Table 1*. The mean values revealed that accumulation levels of heavy metals and trace elements in water varied from each other depending on the different sampling site. Pb, Fe, Zn and As were noted in all seasons.

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Among the analyzed metals Fe was the highest and Se was the lowest metal which was below detection limit in all seasons while Cd and Cr were recorded only in autumn and winter, Mn in winter, Cu and Ni in summer, autumn and winter. There were no statistically significant differences in the concentration of metal among seasons ($p>0.05$). The highest levels of Cu, Cr, Fe, Mn, Ni, and Zn were noted during spring, Cd and Pb in summer and autumn (*Table 2*).

The heavy metal and trace elements accumulation in water decreased in the following order; Fe>As>Zn>Ni>Cd >Cu>Cr> Pb>Mn>Se. The highest Fe (1.29 mg/l), As (0.03 mg/l), Zn (0.28 mg/l), Ni (0.18 mg/l) levels were in sites 4 and 5. The highest heavy metal concentrations in the two sampling sites were associated with natural sources and human related activities.

Table 2. *The concentrations (mg/l) of some heavy metals in Hazar Lake*

Season	Cd	Pb	Cu	Fe	Ni	Zn	Se	Mn	Cr	As
Spring	0.01	0.001	0.03	0.11	0.04	0.03	*BDL	0.005	0.03	0.01
Summer	0.02	0.001	*BDL	0.06	*BDL	0.001	*BDL	0.004	0.0002	0.01
Autumn	*BDL	0.01	*BDL	0.1	*BDL	0.006	*BDL	0.002	*BDL	0.01
Winter	*BDL	0.005	*BDL	0.1	*BDL	0.01	*BDL	*BDL	*BDL	0.01

*BDL: Below Detection Limit

We compared the results of heavy metals in water of Hazar Lake with WHO and TSE-266 standards. According to these standards, Cu, Zn and Cr were higher than the permissible levels for drinking water in spring while Cd was in spring and summer.

Özmen et al. (2014) researched level of bioaccumulation of heavy metal and trace elements in water of Hazar Lake and recorded following highest concentrations (in mg/l) 0.43±0.11 Fe, 0.071±0.018 Zn, 0.012±0.002 Ni, 0.025–0.22 Cu. Their results indicated that a general absence of serious pollution caused by heavy metals such as Cd, Pb and As in the lake. Alp et al. (2011) reported that Cr, Pb and Cd levels were below detection limit in all seasons. According to our results the heavy metal concentrations of Hazar Lake' water increased which is presumed to be because of increased anthropological pressures.

Conclusions

Present study, we assessed the concentration of heavy metal and trace elements in feathers of Armenian gull, resident in the eastern Anatolia region of Turkey and breeding on Hazar Lake, for which scarce information existed. The results provide evidence that feathers are efficient metarial to understand heavy metals pollution levels and bioaccumulation along the wetland food chain with higher concentrations found in bird feathers than water. Metal concentrations detected during the study were within the acceptable range of normal concentrations for waterbirds except for Pb and Mn. Furthermore, the heavy metals (Cd, Cu, Zn, Cr) concentrations in water did exceeded WHO and TSE-266 guidelines in spring and summer. Although levels of heavy metals were not high, our results revealed that precautions need to be taken in order to prevent future heavy metal pollution in the lake basin. Consequently, we confirmed that feathers of Armenian Gull can reveal local contamination around the foraging and breeding sites and can be a very useful monitoring instrument for assessing heavy metal contamination.

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