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Research Article

Detection of Heavy Metal Concentrations in Feathers of Armenian Gull (*Larus armenicus* Buturlin, 1934) in Van Lake Basin/TÜRKİYE

Nurgül TAŞKIN, Atilla DURMUŞ*

Van Yuzuncu Yil University, Science Faculty, Biology Department, 65080, Van, Türkiye
Nurgül TAŞKIN, ORCID No: 0009-0008-5155-0754, Atilla DURMUŞ, ORCID No: 0000-0002-5116-9581
*Corresponding author e-mail: atilla@yyu.edu.tr

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Abstract: Birds are the living groups at the top of the food web and most affected by environmental pollutants. The aim of the present study was to detect levels of some heavy metal accumulations in the Armenian Gull (*Larus armenicus*), which uses the Van Lake basin for breeding and feeding purposes. Samples were taken from the body feathers of adult and juvenile gulls and from the waters in their feeding environments, taking into account the feeding rates, in order to determine at what rate the birds at the top of the food web accumulate toxic substances and how they are affected. In the samples taken, Iron (Fe), Cadmium (Cd), Copper (Cu), Lead (Pb) and Arsenic (As) concentrations were measured. Metal concentrations were measured using ICAP 6000 Spectrometer. According to the results of the analysis, Cu (6.43 mg kg^{-1}), Pb (4.02 mg kg^{-1}) and Cd (0.14 mg kg^{-1}) concentrations were highest in juveniles, while Fe concentration (94.32 mg kg^{-1}) was found to be highest in adults. Compared with WHO (World Health Organization) and TSE-266 standart; As, Fe, Cd, Cu and Pb concentrations in water were higher than the permissible levels for drinking water. Concentration differences in Juveniles and adults seem to vary depending on the feeding density.

Van Gölü Havzasındaki Van Gölü Martısı'nın (*Larus armenicus* Buturlin, 1934) Tüylerindeki Ağır Metal Konsantrasyonlarının Tespiti

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Anahtar Kelimeler
Ağır metal,
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Öz: Besin ağının üst basamağında yer alan kuşlar, çevresel kirleticilerden en fazla etkilenen canlı gruplarıdır. Bu çalışmada Van Gölü havzasını üreme ve beslenme amacıyla kullanan Van Gölü Martısındaki (*Larus armenicus*) bazı ağır metal birikimleri araştırıldı. Besin ağının en üst basamağında yer alan kuşların toksik maddeleri hangi oranlarda biriktirdiği ve nasıl etkilendiklerini tespit etmek amacı ile beslenme oranları da dikkate alınarak yetişkin ve yavru martılarının vücut tüylerinden ve beslendiği ortamlardaki sulardan örnekler alındı. Metal konsantrasyonları ICAP 6000 spektrofotometresi ile ölçüldü. Alınan örneklerde; Demir (Fe), Kadmiyum (Cd), Bakır (Cu), Kurşun (Pb) ve Arsenik (As) konsantrasyonlarına bakıldı. Analiz sonuçlarına göre; Cu (6.43 mg kg^{-1}), Pb (4.02 mg kg^{-1}) ve Cd (0.14 mg kg^{-1}) konsantrasyonlarının en fazla yavrularda, Fe konsantrasyonun (94.32 mg kg^{-1}) ise en fazla erginlerde olduğu görüldü. Dünya Sağlık Örgütü (WHO) ve TSE-266 standartlarına göre; Su içerisindeki As, Fe, Cd, Cu ve Pb konsantrasyonlarının içilebilir referans değerinden çok fazla olduğu tespit edildi. Yavru ve yetişkinlerdeki konsantrasyon farklılıklarının beslenme yoğunluğuna bağlı olarak değiştiği görülmektedir.

1. Introduction

There has been a demand in line with the needs that have emerged in parallel with the increase in the human population around the world. In order to meet this increasing demand, nature has been used effectively and as a result of this effective use, a serious problem has arisen both in the consumption of natural resources and in the disposal of waste materials into nature. Wastes of human origin adversely affect other living species in nature. Heavy metals, which are natural components of nature and living things in nature, can be beneficial when they are at a certain limit, but they can be harmful above a certain rate (Zhang et al., 2018; Tepe et al., 2022; Kodat & Tepe, 2023).

Wetland ecosystems are one of the most important ecosystems with the highest biodiversity. Due to its direct and indirect usage characteristics, it has been used by mankind from the past to present. Wetlands have an indispensable importance as a place of nutrition and shelter in the life of many living things, especially fish and waterfowl. Birds, located at the top levels of the food chain, are called the bioindicator group, which is most quickly affected by deteriorating environmental conditions and reacts to this deformation (Burger, 1994). For this reason, one of the most appropriate methods of determining the metal accumulation in bird species in nature is to determine the amount in their feathers. Heavy metals in feathers can accumulate externally by direct contact and internally via the blood path (Movalli, 2000; Ullah et al., 2014). The metals enter the bird's body through feeding and begin to accumulate from the calamus region of the feather, which is connected with blood vessels (Dauwe et al., 2000 and 2003). When we look at the literature, metals with a density higher than 5 g/cm^3 are considered heavy metals i.e., a group of over 60 such as iron, cobalt, copper, mercury and zinc (Burger & Gochfeld, 1995; Järup, 2003; Kahvecioğlu et al., 2003; Durmuş et al., 2018).

In this study, Lake Van, which is an important resting and breeding area for birds, located within the borders of the province of Van, was selected. Lake Van faces the threat of pollution due to domestic and industrial wastes.

The study aims to determine some heavy metal levels in bird feathers and in the water in the area where they live, and investigate the feasibility of using bird feathers in monitoring environmental pollution. For this purpose, the Armenian gull (*Larus armenicus*) was selected as a bioindicator species. The gull is a species in the Near Threatened (NT) status in the IUCN 2022 (International Union for Concervation of Nature) list.

Armenian gull, one of the bird species most affected by environmental pollution, lives in a limited area where Turkey, Israel, Egypt and Iran are located (Durmuş et al., 2018; Nergiz & Şamat, 2019). The species, which is native and distributed only in the East Anatolia religion of Türkiye, feeds on the pearl mullet in summer (*Chalcalburnus tarichi*), which is endemic in Lake Van while it goes down to city centers and feeds from garbage dumps in the winter season (Adızel et al., 2010). Detection of heavy metal accumulations in the body of these species, which are in direct contact with the environment, will be a reference for wildlife conservation studies.

2. Material and Methods

The proposed research project does not need the Animal Research Ethics Committee (Decision number 2016/03).

This study was carried out on the shores and islands of Lake Van, which is located in the east of Turkey and is the largest lake in the country. Situated within the borders of Van and Bitlis provinces, the lake is located at 32.2207 X and 42.75245 Y coordinates (Figure 1).

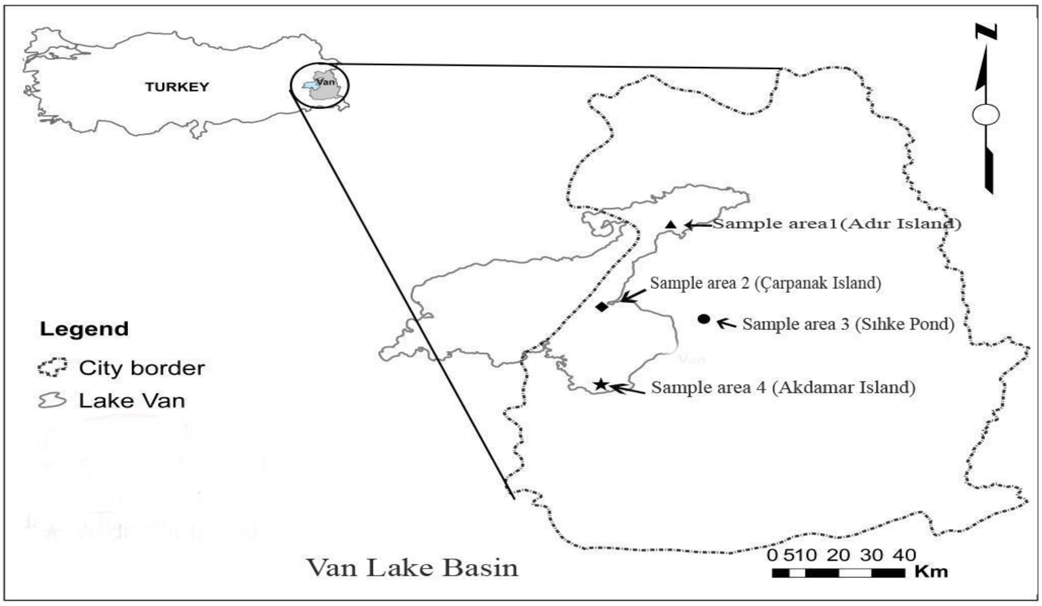

Figure 1. Sample areas in Van province.

Gull feather samples were collected from the islands in Lake Van (Akdamar, Adır, Çarpanak) and from the shores of Lake Van and the Sıhke pond of the city dump, from the adults found dead in July 2017, the post-breeding period, and from dead offsprings around the nests (Figure 1).

These collected feather samples were classified according to their body regions. Samples of primary (APF: adult primary feathers) and secondary flight feathers (ASF: adult secondary feathers) of adult individuals are from 9th and 10th feathers as standard; covert feathers (ACF: adult covert feathers and JCF: juvenile covert feathers) were taken from the thorax of adults and juveniles (Burger & Gochfeld, 1997; Aslan, 2007). During the collection of feather samples, plastic gloves were used to prevent external contamination of the feathers and the feathers were placed in plastic bags.

Plastic bags containing feather samples were labeled according to the individual (adult-pup) from which the samples were taken and feather type then brought to the laboratory. The feather samples brought to the laboratory in closed boxes were kept in closed bags, away from the sun and moisture, until solution preparation and analysis. Feathers can become contaminated because they are in contact with the environment. Therefore, these environmental pollutants are cleaned by washing 3 times with acetone in order not to cause errors in the analysis results (Goede & Bruin, 1986). Feather samples, cleaned from environmental wastes, are kept in glass containers for 24 hours in an oven with a temperature of 70 degrees to dry and samples were cut and weighed at 2 grams of each sample on a precision weigher and placed in a beaker. 8 ml of 65% HNO_3 and 2 ml of H_2O_2 were added and treated with the animal tissue sample program in the microwave incineration unit (E.E.A.M.D.S. Milestone, 230/50 Hz, Italy) (Blust et al., 1988; Janssen et al., 2001). The metal analysis of the samples was conducted using ICP-AAS instrument (Thermo Scientific Icap 6000 Series, ICP Spectrometer).

Among the feather samples taken, Iron (Fe), Cadmium (Cd), Copper (Cu), Lead (Pb) and Arsenic (As) concentrations were measured. The results were calculated as mg kg-1 of dry weight.

Statistical analysis was conducted with IBM SPSS Statistics 21 statistical package program to compare the metal ratios in feathers taken from different body parts of adults, juveniles and water samples.

3. Results

The areas where the gulls (*Larus armenicus*) breed most intensively in Lake Van Basin are the islands within the lake. The seagull, which is native to the region, migrates to 4 islands in the lake as of April and carries out its nesting and breeding activities. They reach an intense breeding activity and high population density in May and June. In June, which is the end of the breeding period, some young and adult individuals in the colony are faced with death due to epidemic disease, competition and nutritional deficiency. In the summer of 2017 after breeding, feather samples were taken from adults and juveniles around Akdamar Island, Çarpanak Island, Adır Islands in Lake Van, and around Sıhke Lake, which is close to the city dump. Some heavy metal amounts detected in feather samples collected from different parts of their bodies are given in Tables 1-3.

Table 1. Metal amounts detected in feather samples of adult Armenian gull (mg kg^{-1} dry weight)

	Sample	n	Median	Mean	Std. dev.	Std.error	Min.	Max.	*p
As	APF	10	.26	.25 b	.15	.05	.08	.56	>.05
	ASF	10	.32	.36 b	.16	.05	.24	.80	
	ACF	10	.38	.72 b	.93	.29	.16	3.28	
Cd	APF	10	.12	.13a	.06	.02	.08	.24	>.05
	ASF	10	.12	.12a	.04	.01	.08	.24	
	ACF	10	.12	.15a	.06	.02	.08	.28	
Cu	APF	10	1.70	1.66ab	.84	.27	.56	3.16	<.001
	ASF	10	2.16	5.45a	7.32	2.32	1.28	21.20	
	ACF	10	2.36	2.37ab	1.04	.33	.64	4.24	
Fe	APF	10	54.80	50.76b	19.55	6.18	21.20	80.00	<.001
	ASF	10	58.00	64.52b	25.48	8.06	29.20	114.80	
	ACF	10	92.40	94.32a	38.34	12.13	39.60	169.20	
Pb	APF	10	1.40	1.51ab	.82	.26	.80	3.60	>.05
	ASF	10	1.56	1.66ab	.81	.26	.80	3.72	
	ACF	10	1.38	1.97ab	1.02	.32	1.00	3.44	

a, b and ab: The difference between groups taking different lowercase letters is significant.
n:Number of samples

When the mean concentration densities between primary, secondary and covert feathers from adult individuals are compared and ranked, it is seen that Fe > Cu > Pb > As > Cd. In the statistical evaluation, while the Iron (Fe) concentration is similar in APF and ASF, there is a significant difference with ACF. When the copper (Cu) concentration is examined, it is seen that there is no significant difference between APF and ACF, but the concentration of ASF is significantly different in these two groups. It is seen that there is a similarity for each hair group in Lead (Pb), Arsenic (As) and Cadmium (Cd) concentrations and there is no statistically significant difference (Table 1).

Table 2. Metal amounts detected in feather samples of juvenile Armenian gull (mg kg^{-1}dry weight)

	Sample	n	Median	Mean	Std. Dev.	Std.error	Min.	Max.	*p
As	JCF	10	.36	.34 b	.10	.03	.16	.52	<.001
Cd	JCF	10	.12	.14a	.04	.01	.08	.20	
Cu	JCF	10	2.00	6.43a	9.41	2.98	1.16	26.00	
Fe	JCF	10	65.00	73.12ab	45.80	14.48	26.40	157.20	
Pb	JCF	10	1.74	4.02a	6.80	2.15	.76	23.20	

a, b and ab: The difference between groups shown with different lowercase letters is significant.

When the average heavy metal concentration densities in the samples taken from the body hair of the pups are listed, it can be seen that it is in the form of Fe > Cu > Pb > As > Cd. It was found that Fe and As concentrations in the covert feathers were statistically different from other metals, but the difference between Cd, Cu and Pb concentrations was not significant (Table 2).

Table 3. Metal amounts detected in the water of Lake Van (mg ml^{-1})

	Sample	n	Median	Mean	Std. dev	Std.error	Min.	Max.	*p
As	Water	10	5.52	5.17 a	4.02	1.27	.40	11.20	
Cd	Water	10	.02	.02b	.02	.01	.00	.08	
Cu	Water	10	.00	.07b	.13	.04	.00	.32	<.001
Fe	Water	10	.66	6.35c	9.83	3.11	.16	26.80	
Pb	Water	10	.00	.02b	.03	.01	.00	.08	

a, b, c: The difference between groups shown in different lowercase letters is significant.

Considering the average concentration densities of the water samples taken from the shores of the sampled islands on the southern shores of Lake Van, the result was found to be Fe > As > Cu > Pb=Cd. The statistical difference between Fe and As concentrations is significant; but this was not the case for the other 3 metals; that is to say, it is seen that there is no statistically significant difference between Cd, Pb and Cu concentrations (Table 3).

When we compared these water results with WHO and TSE-266 standards, all of the concentrations of metals were higher than the permissible levels for drinking water

In addition, Dunn's test for multiple comparisons was used to identify different groups in the obtained data. Spearman's rank correlation coefficient was calculated to determine the relationship between these variables (Figure 2).

		As1	Cd1	Cu1	Fe1	Pb1	As2	Cd2	Cu2	Fe2	Pb2	As3	Cd3	Cu3	Fe3	Pb3	As4	Cd4	Cu4	Fe4	Pb4	As5	Cd5	Cu5	Fe5	Pb5
As1	R	1,000																								
Cd1	R	,199	1,000																							
Cu1	R	-,079	,086	1,000																						
Fe1	R	-,537	-,461	,442	1,000																					
Pb1	R	-,361	,445	-,261	,000	1,000																				
As2	R	-,452	,091	,675*	,452	-,084	1,000																			
Cd2	R	,064	,545	,405	-,060	,240	-,019	1,000																		
Cu2	R	-,232	,030	,401	,535	,405	,090	,488	1,000																	
Fe2	R	-,517	,515	,334	,036	,201	,540	,271	-,162	1,000																
Pb2	R	,459	,396	,517	-,079	-,207	-,071	,744*	,213	,070	1,000															
As3	R	,043	-,633*	,252	,472	-,320	,282	-,364	-,043	-,320	-,234	1,000														
Cd3	R	-,054	-,093	,388	-,146	-,268	,578	-,098	-,080	,038	-,191	,296	1,000													
Cu3	R	,250	,079	-,127	-,055	,274	-,019	-,405	-,304	-,030	-,182	,399	-,165	1,000												
Fe3	R	,287	-,434	,273	,115	-,760*	-,167	-,105	-,055	-,195	,164	,252	-,006	-,261	1,000											
Pb3	R	-,058	-,145	,152	-,207	-,189	,463	-,218	-,162	-,046	-,399	,351	,956**	-,097	-,061	1,000										
As4	R	,388	,487	-,489	-,859**	,283	-,439	,233	-,154	-,192	,038	-,553	,168	-,144	-,389	,249	1,000									
Cd4	R	,229	-,041	,594	,114	-,456	,052	,601	,475	-,171	,652*	-,064	,238	-,695*	,505	,063	-,013	1,000								
Cu4	R	-,356	-,857**	-,110	,695*	-,318	,109	-,543	,070	-,385	-,456	,568	-,064	-,116	,238	,009	-,612	-,070	1,000							
Fe4	R	,122	,066	-,127	-,297	-,334	-,056	,345	-,383	,055	,353	-,141	,089	-,442	-,115	,085	,314	,265	-,043	1,000						
Pb4	R	,134	,046	,515	,030	-,170	-,105	,742*	,584	-,109	,638*	-,178	,146	-,636*	,382	-,012	,107	,922**	-,244	,164	1,000					
As5	R	,070	,396	-,109	-,505	-,256	,295	-,038	-,726*	,457	,052	-,277	,296	-,079	-,261	,290	,333	-,177	-,306	,650*	-,328	1,000				
Cd5	R	,032	,314	,051	-,394	-,405	,344	,055	-,609	,443	,191	-,315	,327	-,299	-,121	,258	,243	,066	-,233	,712*	-,121	,956**	1,000			
Cu5	R	,113	-,202	,246	,097	,165	,000	,138	,381	-,292	-,112	,581	,368	,231	,142	,426	-,015	,155	-,038	-,365	,306	-,561	-,626	1,000		
Fe5	R	,140	,072	,479	,115	,030	,489	,180	,310	-,097	-,018	,546	,674*	,127	-,055	,681*	,019	,240	-,091	-,139	,200	-,116	-,159	,753*	1,000	
Pb5	R	-,100	,063	,649*	,000	-,219	,223	,608	,223	,356	,425	,048	,390	-,403	,403	,253	-,085	,647*	-,326	,150	,751*	-,058	,072	,428	,341	1,000

*:p<0,05 ve **:p<0,01

Figure 2. Concentration changes in feather samples (Spearman's rank correlation).

When the relations of heavy metals with each other in Figure 2 above are examined, it can be seen that the values of (-) and below are negatively related with each other, whereas 0 values are not related with each other, and (+) values are positively related with each other.

4. Discussion and Conclusion

In this study, heavy metal (As, Cd, Cu, Fe, Pb) concentrations were determined in the feathers of the Armenian gull, which uses islands in Lake Van, Turkey's largest lake, and feeds on its shores for breeding and feeding purposes. Within the scope of this study, feather samples were taken from different parts of the bodies of the young and adult seagulls that died on the shore of Lake Sıhke, which is located near the city dump, and from 3 islands in Lake Van. In addition, water samples were taken from the areas where feathers were collected. As a result of the analysis, when the metal concentration densities in the primary, secondary and covert feathers of adults and juvenile individuals were examined, it was seen that they were ranked as Fe > Cu > Pb > As > Cd. However, when the concentration densities in the water samples were examined, it was observed that Fe > As > Cu > Pb=Cd. While iron (Fe) is highest in water and feathers, Arsenic (As) is at the end in feathers, while it is the second and very high in water (Table 3). The reason for this is thought to be due to the geological structure of the region.

When juvenile, adult and water samples were compared with each other, the highest concentrations of Cu (6.43 mg kg^{-1}), Pb (4.02 mg kg^{-1}) and Cd (0.14 mg kg^{-1}) were in juvenile covert feathers. Fe concentration was found to be highest (94.32 mg kg^{-1}) in the adult cover hair and the As concentration (5.17 mg ml^{-1}) in water. The excess of some metals in the juvenile feathers is due to the intense feeding of the offspring by their parents during the post-breeding period. In addition, the fact that the young individuals do not molt during this period causes the accumulation to be more intense.

In studies conducted with waterfowl and herons, it has been observed that heavy metals such as Pb and Cd are higher in the feathers of juveniles than in adults (Burger & Gochfeld, 1995; Spahn & Sherry, 1999). Therefore our study can be considered to be in parallel with the aforementioned studies in literature.

Detection of metal concentrations in all samples taken within the scope of this study shows that birds are affected by pollutants in their environment. When the amounts of heavy metals detected in the water of Lake Van were compared with the acceptable values of heavy metals in aquatic environments given by the World Health Organization (WHO) and Turkish Standards Institution (TSE-266), it was seen that the Fe and As values were considerably higher than the accepted values. Cd, Cu and Pb densities are at least 2 times higher.

The metal ratio seen in the birds at the top of the food web gives an idea about the metal accumulation in the ecosystem and reveals the precautions that can be taken (Zolfaghari et al., 2007; Behrooz et al., 2009). In this study, it was revealed that the heavy metal level is related to diet and habitat characteristics. In Lake Van Basin, heavy metal rates were found to be high in areas where there is agricultural activity or where urban pollution prevailed (Table 1-3).

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