

Karadeniz Fen Bilimleri Dergisi The Black Sea Journal of Sciences ISSN (Online): 2564-7377



Araştırma Makalesi / Research Article

Assessment of Heavy Metal Pollution of Çoruh River (Turkey)

Tamer AKKAN^{1*}, Tanju MUTLU²

Abstract

In this study, the pollution assessment of the water, total suspended solids, and sediment samples collected from the Çoruh River was carried out. For this purpose; aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, and lead were measured in these samples. The water and sediment quality indices were used for the evaluation of the obtained data. When water quality index values were evaluated, it was determined that the river was in the poor water quality class. According to enrichment factor, the Çoruh River sediments in this study are classified as deficiency to minimal enrichment for chromium and nickel, as moderate enrichment for manganese, iron, and cobalt, as significant enrichment for copper and zinc, as very high enrichment for cadmium and lead. Pollution loading index results also showed that the sediment quality deteriorated and it had a high metal load. It suggests that the reason for these pollution factors in the sediment is due to the mining activities in the region. As a result, it was determined that the water and sediment quality of the Çoruh River should be monitored with a regular monitoring program.

Keywords: Metal, Çoruh River, Risk assessment, Water quality, Sediment quality.

Çoruh Nehri'ndeki Ağır Metal Kirliliğinin Değerlendirilmesi

Öz

Bu çalışmada Çoruh Nehri'nden toplanan su, askıda katı madde ve sediment örneklerinin kirlilik değerlendirmesi yapılmıştır. Bu amaç için toplanan numunelerde alüminyum, krom, manganez, demir, kobalt, nikel, bakır, çinko, kadmiyum ve kurşun konsantrasyonları ölçülmüştür. Elde edilen verilerin değerlendirilmesinde su ve sediment kalite indeksleri kullanılmıştır. Su kalitesi indeks değerleri incelendiğinde nehrin kötü su kalitesi sınıfında olduğu belirlendi. Sediment zenginleştirme faktörüne göre krom ve nikel açısından düşük düzeyde zenginleşme, manganez, demir ve kobalt için değiştirilebilir derecede zenginleşme, bakır ve çinko için önemli derecede zenginleşme, kadmiyum ve kurşun için çok yüksek düzey zenginleşmeye tespit edilmiştir. Kirlilik yükleme indeksi sonuçları da sediment kalitesinin bozulduğunu ve yüksek metal yüküne sahip olduğunu göstermiştir. Sedimentteki bu kirlilik faktörlerinin nedeninin bölgedeki madencilik faaliyetlerinden kaynaklandığını düşünülmektedir. Sonuç olarak, Çoruh Nehri'nin su ve sediment kalitesinin düzenli bir izleme programı ile izlenmesi gerektiği belirlenmiştir.

Anahtar Kelimeler: Metal, Çoruh Nehri, Risk değerlendirmesi, Su kalitesi, Sediment kalitesi.

²Recep Tayyip Erdoğan University, Environmental Protection and Control Department, Giresun, Turkey, tanju.mutlu@erdogan.edu.tr

¹<u>https://orcid.org/0000-0002-9866-4475</u> ²<u>https://orcid.org/0000-0001-6514-6914</u>

¹Giresun University, Arts and Science Faculty, Biology Department, Giresun, Turkey, biyoloji@yahoo.com

1. Introduction

Pollution of natural waters is a widespread problem worldwide due to its impact on human health and economic damage besides environmental damages (Marcovecchio et al., 2007). Heavy metals are among the most worrisome of these pollutants due to their environmental persistence, their tendency to accumulate in aquatic organisms and their high toxicity (Benzer et al. 2013; Yancheva et al. 2014; Gedik et al. 2019; Bayır and Mutlu, 2021).

Population, urbanization, industrialization, and agricultural practices can increase heavy metal levels by reaching aquatic ecosystems such as rivers, lakes, and seas (Abdel-Baki et al., 2011; Mutlu et al., 2018). Otherwise heavy metals are found in the natural structure of rocks and can accumulate in sediment because of decomposition of rocks (Wojciechowska et al., 2019; Mutlu et al., 2020).

Sediments, which play an active role in the transport processes of many nutrients and toxic chemicals, are preferred in determining the pollution model in aquatic ecosystems (Akkan et al., 2018). Besides, sediments can increase the level of heavy metals in the benthic organism through direct uptake in water and sediment due to natural or anthropogenic processes (Ho et al., 2010). Metals that are not biodegradable may pose a health risk to people consuming aquatic organisms due to bioaccumulation in the food web (Bahnasawy et al., 2011).

The aim of this study is to determine the origin and possible ecosystem effects of the existing pollutants in the water and sediment structure of the Çoruh River, which flows into the Black Sea from the Çoruh Basin, which is one of the most important basins of the southeastern Black Sea Region, through quality indexes.

2. Materials and Methods

2.1. Sampling Area

This study was carried out in the Çoruh River. Çoruh river is one of Turkey's most important river has a total length of 431 km. Turkey 410 km from the border 21 km to reach the Georgian border and flows into the Black Sea (Birici et al., 2017). Sediment and water samples (0-10 cm) were collected seasonally using grab sampler from four sites in Çoruh River between March 2019 and February 2020, as shown in Fig. 1.



Figure 1. Sampling area (Google maps)

2.2. Analysis

Heavy metal analysis: The water samples were immediately transported to the laboratory and filtered through acid treated Millipore HA filters (0.45 μ m) using a vacuum. These samples were stored in darkness at 4 °C up until analysis (APHA, 1998). Total Suspended Solids (TSS) samples were obtained by filtering (Millipore HA filters, 0.45 μ m) from 1 L of river water. TSS and sediment samples were prepared with a preliminary digesting process via a CEM MARS-5 model microwave instrument. Heavy metal determinations of all the samples were carried out using an ICP-MS-Bruker 820-MS (Alam et al., 2001). The reference materials were used to check the accuracy and reliability of the method. Metal contents were expressed in terms of ppb.

Water quality index: This study water quality index (WQI), which is considered to be a powerful tool that can present a comprehensive picture of river water quality, determined according to Meng et al. (2016). WQI reflects the integrated impact of different water quality (Wang et al., 2013). It is calculated as follows:

$$WQI = \sum \left[\left(Wi \ x \ \left(\frac{Ci}{Si} \right) \right] x \ 100 \tag{1}$$

wi: represents the weight attributed to each parameter *i* and is assigned on the basis of the eigenvalues for each principal component and factor loading for each parameter from the PCA results and represents the relative importance of each individual water quality parameter for drinking purposes.

Ci: is the trace element concentration in water samples, and *Si* is the Chinese Drinking Water Guideline (GB 5749-2006) for each trace element. Five classifications were presented based on the calculated WQI values: $0 \le WQI < 50$ indicates excellent water quality, $50 \le WQI < 100$ indicates good water quality, $100 \le WQI < 200$ indicates poor water quality, $200 \le WQI < 300$ indicates very poor water quality, and WQI >300 represents water that is unsuitable for drinking (Meng et al., 2016).

Enrichment factor (EF) and Pollution Loading Index (PLI): Enrichment factor (EF) and pollution loading index (PLI) are a useful indicator reflecting the status of environmental contamination (Helz et al., 1985; Sinex and Helz, 1981; Trefry and Presley, 1976; Woitke et al., 2003). In calculating the normalized enrichment factors (EF), the original Salomons and Förstner (1984) equation was substituted in the present study by Al. To evaluate a possible anthropogenic origin of the metals, the enrichment factor (EF), and pollution loading index (PLI) were calculated for the metal concentration obtained in surface sediments.(Ozseker et al., 2013). The EF and PLI are calculated based on the following presented equation:

$$EF = M_x X A l_b / M_b X A l_x \tag{2}$$

where M_x and Al_x are the sediment sample contents of the heavy metal and Al. Also, M_b and Al_b are their levels in a suitable background or baseline reference material (Abrahim & Parker, 2008; Salomons & Förstner, 1984).

$$PLI = (CF_1 X CF_2 X CF_3 X \dots X CF_n)^{1/n}$$
(3)

$$CF = C_M / C_B \tag{4}$$

where CM is metal concentration, CB is background concentration of the same metal (Ozseker et al., 2013).

Health Risk Assessment: In human health risk assessment, two methods of carcinogenic and non-carcinogenic can be used to predict health problems that may arise as a result of exposure to chemicals (Kamunda et al., 2016). The target hazard quotient (THQ) equation is used in the risk assessment of non-carcinogenic effects, and if the THQ value is below 1, it means that the adverse effect on human health is negligible. Conversely, if THQ or TTHQ is greater than or equal to 1, there is a potential health risk (Zheng et al., 2007; Mutlu, 2021). THQ was calculated using the equation presented by Chien et al., (2002)

$$THQ = \frac{E_F \times E_D \times W_I \times C}{RfD \times A_{Tn}} \times 10^{-3}$$
(5)

where; THQ is target hazard quotient; EF is the exposure frequency (365 days/year); ED is exposure duration (70 years); WI, water intake is the ratio of water intake to body weight in day (mL/kg/day) according to the EPA's predictions; C is the metal concentration (mg/L); RfD is the oral reference dose for a heavy metal (mg/kg/day), RfD for Cr, Mn, Ni, Zn, Cu, Co, Pb, and Cd are 0.003, 0.14, 0.02, 0.3, 0.005, 0.0003, 0.002, and 0.0005 mg/kg/day, respectively (EPA, 2018); and ATn is the average time for non-carcinogens (assuming 70 years).

Statistical Analysis: Statistical analysis of data was carried out using SPSS statistical package programs. Descriptive statistical analysis including One-way ANOVA was done, with a significance of 0.01 and 0.05. Important differences in the mean values were tested using Tukey's multiple range test. Moreover, relationships among the considered variables were tested using Pearson's correlation. Multivariate analyses of the dam lake data set were performed using Principal component analyses (PCA) and cluster analysis (CA). All of the statistical calculations were performed using SPSS 17.0 for Windows.

3. Findings and Discussion

The range of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the water samples were 56.68-308.70, 0.16-1.89, 20.17-58.69, 316.04-596.99, 1.39-2.40, 33.34-78.99, 2.11-15.68, 12.56-22.98, 0.06-0.50, and 1.35-5.12 μ g/L, respectively (Table 1). The highest metal concentrations were recorded in winter for Al, Fe, Co, and Cd, in fall for Pb, Cr, Mn, Cu, Zn, and Cd, and in spring for Ni and Pb. When the heavy metal values in water are compared with the standards recommended by USEPA and WHO, it has been determined that they are below the level specified for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. Also, when the results are compared with the classification specified by the Turkish standards, Ni is in the 3rd Class water quality class while other metals are in the 1st class. Nickel concentration in water may increase in certain areas as a result of human activities such as mining, fertilizers, pesticides, burning coal and petroleum products (Hussain et al., 2017). Bilgin & Konanç (2016) reported some heavy metals in the Çoruh River water and reported that mining is the most important source of pollution. However, Concentrations of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb were measured in Yağlıdere Stream (Uncumusaoglu et al., 2016) Also, Cr and Cd values were higher than our study, other metals were lower.

Sample	Season	Al	Cr	Mn	Fe	Со	Ni	Cu	Zn	Cd	Pb
	Winter	7587.21	7.36	241.75	12845.22	4.98	4.60	18.19	35.43	0.41	15.26
G 1' /	Spring	9420.45	7.03	338.79	14096.66	5.14	5.31	24.18	36.69	0.61	23.01
Sediment	Summer	5511.21	3.87	277.81	9987.71	4.29	2.24	17.36	45.37	0.46	28.39
	Fall	6300.62	9.87	389.13	13452.69	6.36	3.94	207.53	163.52	1.45	130.16
	Winter	308.70	1.52	49.00	596.99	2.40	65.00	2.11	21.33	0.50	2.48
XX 7 /	Spring	70.18	0.76	20.17	556.67	1.95	78.99	2.18	12.56	0.18	5.12
Water	Summer	56.68	0.16	36.97	316.04	1.39	62.44	2.32	18.21	0.06	4.74
	Fall	155.63	1.89	58.69	496.68	2.35	33.34	15.68	22.98	0.08	1.35
	Winter	29196.25	19.30	822.60	19181.47	7845.53	5128.63	26.17	10729.97	7870.56	16.96
TCC	Spring	12694.56	15.73	35.08	1137.98	0.00	0.00	4153.56	14637.06	1039.76	2779.06
155	Summer	12949.13	18.05	25.99	642.74	0.00	0.00	5023.54	14299.82	5239.38	3641.26
	Fall	5880.10	6893.91	133.84	3180.94	1485.66	0.00	2318.95	5626.96	7203.13	6461.48

Table 1. Metal concentrations of water, sediment and TSS samples collected from Çoruh River. It seems that the highest accumulation is in iron

Heavy Metal Concentration in Sediments: Since sediment contains harmful and toxic substances such as trace elements, it is an important substance that should be monitored in metal studies in the aquatic ecosystem (Balık & Tunca, 2015; Zamani Hargalani et al., 2014). Concentrations of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the sediment samples were varied 5511.21-9420.45, 3.87-9.87, 241.75-389.13, 9987.71-14096.66, 4.29-6.36, 2.24-5.31, 17.36-207.53, 35.43-163.52, 0.41-1.45, and 15.26-130.16 ppb, respectively. Abundance of average metal levels in the sediments is in the order of Fe>Al>Mn>Zn>Cu>Pb >Cr>Co>Ni>Cd. The highest Al, Fe, and Ni concentrations were recorded in spring, while the highest Cr, Mn, Co, Cu, Zn, Cd, and Pb contents were found in fall. Kucuksezgin et al. (2008) reported higher Cr, Mn, Ni and Zn in the sediments of the Gediz River than in our study. Unlike to this, Dundar & Altundag (2007) reported lower Cu, Zn, Cd, and Pb concentrations for Sakarya River than Çoruh River.

Average metal contents of sediment in this study are classified as non-polluted, moderately polluted, and heavily polluted according to the Sediment Quality Guidelines (SQG) declared by USEPA (Gedik et al., 2018; Perin et al., 1997). Based on this assessment, Cu was classified as heavily polluted, Pb was as moderately polluted and the others as non-polluted. It has also been compared with the Interim Canadian Sediment Quality Guidelines (CEQGs) of the Canadian Council of Environment Ministries (CCME), which show the Interim Sediment Quality Targets (ISQG) and the Probable Effect Level (PEL). According to CEQGs; Cr, Cu, Zn, Cd, and Pb contents of sediment samples in this study were lower than PEL values, while Cu, Cd and Pb were higher than ISQG values (Table 2). It is estimated that these high values are caused by the mining activities in the region, since the industrial activities around the sampling station are not much developed.

 Table 2. Comparison of the metal levels in the sediments with CEQGs and SQGs (USEPA) values (mg/kg). Cr, Cu, Zn, Cd, and Pb contents of sediment samples in this study were lower than PEL values, while Cu, Cd and Pb were higher than ISQG values.

	Al	Cr	Mn	Fe	Со	Ni	Cu	Zn	Cd	Pb
This Study	7204.87	7.03	311.87	12595.57	5.19	4.02	66.82	70.25	0.73	49.20
SQGs (USEPA)										
Non-polluted	-	<25	-	-	-	<20	<25	<90	-	<40
Moderately polluted	-	25-75	-	-	-	20-50	25-50	90-200	-	40-60
Heavily polluted	-	>75	-	-	-	>50	>50	>200	>6	>60
CEQGs										
ISQG	-	37.3	-	-	-	-	35.7	123	0.6	35
PEL	-	90	-	-	-	-	197	315	3.5	91.3

SQGs, Sediment Quality Guideline (Perin et al. 1997).

CEQGs: Canadian Sediment Quality Guidelines, ISQG: Interim sediment quality guideline PEL: Probable effect level (CCME, 2001).

Heavy Metal Concentration in Total Suspended Solids (TSS): The range of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the TSS samples were 5880.10-29196.25, 15.73-6893.91, 25.99-822.60, 642.74-19181.47, 0.00-7845.53, 0.00-5128.63, 26.17-5023.54, 5626.96-14637.06, 1039.76-7870.56, and 16.96-6461.48 ppb, respectively. It was statistically recorded that the concentration of many metals (Al, Fe, Cu, Zn, Cd, and Pb) detected in TSS differed significantly compared to water and sediment (p, 0.05). In addition to these, contamination due to Cd, Pb, AL, Cr, Fe, Ni and Zn draws attention in TSS.

Enrichment Factor (EF) and Pollution Loading Index (PLI): EF is used to make comparisons in different periods of different basins or the same basin and to gain information on geochemical trends (Sinex & Helz, 1981). The five contamination categories according to the enrichment factor are expressed as follows; EF<2 is deficiency to minimal enrichment, EF in 2-5 is moderate enrichment, EF in 5-20 is significant enrichment, EF in 20-40 is very high enrichment, EF>40 is extremely high enrichment (Odat, 2013). The mean EF values of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the sediments were 1, 4, 3, 3, 1, 18, 9, 29, and 30, respectively. The sampled sediments in this study are classified as Deficiency to minimal enrichment for Cr and Ni, as moderate enrichment for Mn, Fe, and Co, as significant enrichment for Cu and Zn, as very high enrichment for Cd and Pb. The EF value is between 0-1.5, it indicates that the origin of the sediments is natural, while EF>1.5 indicates that it is caused by anthropogenic activities (Zhang & Liu, 2002). Thus, it can be concluded that all metals detected in sediment samples in this study, except Cr and Ni, are of anthropogenic origin. Similarly, Varol (2011) found the average EF values of the studied metals except Cr and Mn in the Tigris River sediments above 1.5 and drew attention to the anthropogenic effect in the stream. In contrast, in the Geli Stream sediments, the EF value of Cr is reported above 50 and is classified as extremely severe enrichment (Kalender & Cicek Ucar, 2013).

When interpreting the PLI value, the following definition can be taken as the basis: PLI<1 reports perfect sediment quality, PLI=1 only baseline levels of pollutant, and PLI> 1 shows that deterioration of site quality (Wojciechowska et al., 2019). The pollution load index results were determined to be high (PLI>1) in the analysed sediment samples. According to this PLI result, it can be said that the sampling site has deteriorated sediment quality and has a high metal load. Similar to this study, PLI values were found as 1.88 in Tigris River (Varol 2011) and 1.47 in Ulukışla Basin (Lermi & Sunkari, 2020). In contrast, it was reported as 0.47 in Çayeli River (Kırıs and Baltas 2021).

Water Quality Index: WQI values of metals in water samples were calculated and found as 146. According to the evaluation of the WQI values of the Çoruh River over five different classifications, it was observed that it was in the poor water quality class. In a study conducted in Aksu River, it was observed that the water quality of the river was in excellent class according to WQI values and was deteriorated by anthropogenic pollutants (Şener et al., 2017). Also, the WQI value of Emet Stream has been determined over 300 and classified as heavily polluted water quality (Omwene et al., 2019).

Target Hazard Quotient: Target Hazard Quotient (THQ) values calculated for drinking water consumption in Çoruh stream are shown in Table 3. According to the evaluations, it was concluded that the THQ and TTHQ values in Cr, Mn, Ni, Zn, Cu, Pb, Co, and Cd were below 1. This means that it does not pose a health risk concern. Also, the highest TTHQ value was found in <1 age group.

Table 3. Non-carcinogenic risk of heavy metals of different age groups. The THQ and TTHQ values in Cr, Mn, Ni, Zn, Cu, Pb, Co, and Cd were below 1

. ~	WI ¹			THQ						TTHQ
Age Group	(mL/kg- day)	Cr	Mn	Ni	Zn	Cd	Cu	Pb	Co	
<1	29	0.010	0.009	0.087	0.002	0.012	0.032	0.050	0.196	0.397
1 to < 2	13	0.005	0.004	0.039	0.001	0.005	0.014	0.022	0.088	0.178
2 to <3	15	0.005	0.004	0.045	0.001	0.006	0.017	0.026	0.101	0.205
3 to <6	11	0.004	0.003	0.033	0.001	0.004	0.012	0.019	0.074	0.151
6 to <11	10	0.004	0.003	0.030	0.001	0.004	0.011	0.017	0.067	0.137
11 to <16	6	0.002	0.002	0.018	0.000	0.002	0.007	0.010	0.040	0.082
16 to <21	6	0.002	0.002	0.018	0.000	0.002	0.007	0.010	0.040	0.082
21 to <50	11	0.004	0.003	0.033	0.001	0.004	0.012	0.019	0.074	0.151
50+	11	0.004	0.003	0.033	0.001	0.004	0.012	0.019	0.074	0.151
All ages	11	0.004	0.003	0.033	0.001	0.004	0.012	0.019	0.074	0.151

¹EPA Recommended Ratings for Drinking Water Intake Rates by Age (EPA, 2019)

Statistical Analysis: Regardless of water, sediment and TSS, seasonal variation of all detected metals has not been detected (p>0.05), which reveals the presence of metal presence in the study area throughout the year.

Four principal components (PC) were obtained with an eigenvalue of more than 1, explaining greater than 99.24 % of total variance (Table 4). PC 1 grouped metals such as Al, Mn, Fe, Co, and Ni reveal 53.55 % of the total variance. Al, Mn, and Fe had originated from natural sources (Wang et al., 2017). Co and Ni are derived from country of origin. Also, the metals in the PC1 mainly come from industrial and traffic activities. Cu and Zn in PC2 are strongly correlated and clearly separate from the other heavy metals regarding their correlation coefficient analysis and PC 2 explains 24.81 % of the total variance. This separation between them and other heavy metals may suggest that the enrichment of Cu in the suburban soils may be related with the application of agricultural runoff, manure, and Cu-contained agrochemicals. PC3 with a variance loading of 20.88 % was dominated by the loading Cr and Pb (Table 5).

Table 4. Varimax rotated component matrix for trace elements in water and TSS samples. Four principal components (PC) were obtained with an eigenvalue of more than 1, explaining greater than 99.24 % of total variance

Eigenvalues	5.36	2.48	2.09	
Variance (%)	53.55	24.81	20.88	
Cumulative (%)	53.55	78.36	99.24	
Variable	Factor 1	Factor 2	Factor 3	
Al	0.851	0.522	-0.037	
Cr	-0.009	-0.051	0.993	
Mn	0.998	-0.035	-0.014	
Fe	0.999	0.007	0.002	
Со	0.998	-0.022	0.055	
Ni	0.989	-0.025	-0.142	
Cu	-0.233	0.947	0.221	
Zn	0.327	0.940	0.043	
Cd	0.691	0.370	0.581	
Pb	-0.148	0.536	0.831	

"Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Table 5. Correlation matrix of trace elements in Çoruh River. PC3 with a variance loading of 13.94% was dominated by the loading Cr and Pb.

	-0					Water						
		Al	Cr	Mn	Fe	Со	Ni	Cu	Zn	As	Cd	Pb
	Al	1	.688	.591	.648	.777	165	.035	.613	.a	.873	668
	Cr	.231	1	.730	.664	.954*	622	.687	.658	.a	.359	916
	Mn	.062	.632	1	.046	.549	877	.700	.991**	.a	.129	943
Ħ	Fe	.761	.805	.502	1	.852	.168	.015	009	.a	.714	343
me	Со	.064	.961*	.795	.690	1	360	.454	.486	.a	.575	783
Sediı	Ni	.917	.577	.188	.932	.392	1	927	829	.a	.336	.827
	Cu	326	.779	.807	.340	.912	017	1	.610	.a	418	759
	Zn	407	.722	.786	.253	.871	108	.996**	1	.a	.172	901
	As	.895	.184	303	.640	066	.873	468	545	.a	.a	.a
	Cd	229	.782	.884	.407	.923	.048	.989*	$.979^{*}$.a	1	233
	Pb	392	.711	.814	.257	.868	107	.995**	.999**	. ^a	$.985^{*}$	1
					A	All Sample	es					
		Al	Cr	Mn	Fe	Со	Ni	Cu	Zn	As	Cd	Pb
70	Al	1	059	.760**	.624*	.812**	.815**	.273	.692*	.895	.687*	.124
IS	Cr	626	1	090	143	.100	094	.234	.099	.184	.557	.807**
-	Mn	.894	210	1	.922**	.809**	.820**	357	.085	303	.411	277
	Fe	.896	215	1.000^{**}	1	.550	.568	400	082	.640	.179	338

Со	.865	151	.998**	.998**	1	.981**	123	.383	066	.727**	009
Ni	.944	333	.992**	.992**	$.982^{*}$	1	175	.357	.873	.616*	170
Cu	650	170	917	916	936	860	1	$.848^{**}$	468	.431	.762**
Zn	.239	907	220	215	279	094	.557	1	545	.662*	.577*
As	.a	.a	·a	.a	.a	·a	.a	.a	1	430	553
Cd	.318	.405	.618	.608	.656	.549	684	690	.a	1	.637*
Pb	950	.813	727	732	683	806	.435	503	.a	009	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

^a. Cannot be computed because at least one of the variables is constant.

4. Conclusions and Recommendations

Average concentrations of all metals investigated in Çoruh River water were lower than WHO and USEPA standard recommended limits. On the other hand, in terms of Turkish standards, Cr, Mn, Fe, Co, Cu, Zn, Cd, and Pb metals have 1st class water quality, while Ni has 3rd class water quality. On the contrary, when WQI values were evaluated, it was observed that the river was in the poor water quality class.

Since THQ values in water samples are under the limit value of 1, It can be said that the use of the water of the Çoruh River as drinking water will not cause health problems for consumers after the necessary procedures. According to enrichment factor, the Çoruh River sediments in this study are classified as Deficiency to minimal enrichment for Cr and Ni, as moderate enrichment for Mn, Fe, and Co, as significant enrichment for Cu and Zn, as very high enrichment for Cd and Pb. PLI results also showed that the sediment quality deteriorated and it had a high metal load. Moreover, Cu, Cd and Pb content were higher than ISQG values reported by CEQGs. It suggests that the reason for these pollution factors in the sediment is due to the mining activities in the region. Because the sampling area is not well developed in terms of industry and agricultural activities are very low.

Authors' Contributions

All authors contributed equally to the study.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

References

- Abdel-Baki, A. S., Dkhil, M. A., and Al-Quraishy, S. (2011). Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia. *African Journal of Biotechnology*, 10(13), 2541-2547.
- Abrahim, G. M. S., and Parker, R. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental monitoring and assessment*, 136(1), 227-238. https://doi.org/10.1007/s10661-007-9678-2
- Akkan, T., Yazicioglu, O., Yazici, R., and Yilmaz, M. (2018). An Examination of Ecological and Statistical Risk Assessment of Toxic Metals in Sediments at Siddikli Dam Lake: A Case Study in Kirsehir, Turkey. FEB-FRESENIUS ENVIRONMENTAL BULLETIN, 8104.
- Alam, M. G. M., Tanaka, A., Stagnitti, F., Allinson, G., and Maekawa, T. (2001). Observations on the effects of caged carp culture on water and sediment metal concentrations in Lake Kasumigaura, Japan. *Ecotoxicology and Environmental Safety*, 48(1), 107-115. https://doi.org/10.1006/eesa.2000.1989
- APHA. 1998. Standard Method for the Examination of Water and Wastewater. American Public Health Association.19th Ed. Washington D.C. http://www.sciepub.com/reference/205126 (May 18, 2021).
- Bahnasawy, M., Khidr, A. A., and Dheina, N. (2011). Assessment of heavy metal concentrations in water, plankton, and fish of Lake Manzala, Egypt. *Turkish Journal of Zoology*, 35(2), 271-280.
- Balık, İ., and Tunca, E. (2015). A review of sediment contamination assessment methods. *Turkish Journal of Maritime and Marine Sciences*, 1(1), 7-17.
- Bayır, İ., Mutlu, C. (2021). Determination of Some Heavy Metal Levels in Different Tissues of Common Carp (*Cyprinus carpio*, L., 1758) and Pike Barb (*Luciobarbus esocinus*, H., 1843) From Karasu River (Erzincan). Journal of Anatolian Environmental and Animal Sciences, 6(3), 434-440. https://doi.org/10.35229/jaes.964810
- Benzer, S., Arslan, H., Uzel, N., Gul, A., and Yilmaz, M. (2013). Concentrations of Metals in Water, Sediment and Tissues of Cyprinus Carpio L., 1758 from Mogan Lake (Turkey). *Iranian Journal of Fisheries Sciences* 12(1): 45–55.
- Bilgin, A., and Konanç, M. U. (2016). Evaluation of surface water quality and heavy metal pollution of Coruh River Basin (Turkey) by multivariate statistical methods. *Environmental Earth Sciences*, 75(1029). https://doi.org/10.1007/s12665-016-5821-0
- Birici, N., Karakaya, G., Şeker, T., Küçükyılmaz, M., Balcı, M., Özbey, N., and Güneş, M. (2017). Evaluation of Coruh River (Bayburt) Water Quality in Accord with Water Pollution Control Regulation. Int. J. Pure Appl. Sci. 3(1): 54–64.
- Chien, L. C., Hung, T. C., Choang, K. Y., Yeh, C. Y., Meng, P. J., Shieh, M. J., and Han, B. C. (2002). Daily intake of TBT, Cu, Zn, Cd and As for fishermen in Taiwan. *Science of the total environment*, 285(1-3), 177-185. https://doi.org/10.1016/S0048-9697(01)00916-0
- Dundar, M. S., and Altundag, H. (2007). Investigation of heavy metal contaminations in the lower Sakarya river water and sediments. *Environmental monitoring and assessment*, *128*(1), 177-181. https://doi.org/10.1007/s10661-006-9303-9
- Gedik, K., Ozturk, R.C. (2019). Health risk perspectives of metal(loid) exposure via consumption of striped venus clam (Chamelea gallina Linnaeus, 1758), 1176–1188. *Human and Ecological Risk Assessment: An International Journal*, https://doi.org/ 10.1080/10807039.2018.1460802.
- Gedik, K., Terzi, E., and Yeşilçiçek, T. (2018). Biomonitoring of Metal (Oid)s in Mining-Affected Borcka Dam Lake Coupled with Public Health Outcomes. *Human and Ecological Risk Assessment: An International Journal* 24(8): 2247–64. https://doi.org/10.1080/10807039.2018.1443390
- Helz, G. R., Sinex, S. A., Ferri, K. L., and Nichols, M. (1985). Processes controlling Fe, Mn and Zn in sediments of northern Chesapeake Bay. *Estuarine*, *Coastal and Shelf Science*, 21(1), 1-16. https://doi.org/10.1016/0272-7714(85)90002-2

- Ho, H. H., Swennen, R., and Van Damme, A. (2010). Distribution and Contamination Status of Heavy Metals in Estuarine Sediments near Cua Ong Harbor, Ha Long Bay Vietnam. *Geologica Belgica* 13(1–2): 37– 47.
- Hussain, J., Husain, I., Arif, M., and Gupta, N. (2017). Studies on Heavy Metal Contamination in Godavari River Basin. Applied Water Science 7(8): 4539–4548. https://doi.org/10.1007/s13201-017-0607-4
- Kalender, L., and Uçar, S. Ç. (2013). Assessment of Metal Contamination in Sediments in the Tributaries of the Euphrates River, Using Pollution Indices and the Determination of the Pollution Source, Turkey. *Journal of Geochemical Exploration* 134: 73–84. http://dx.doi.org/10.1016/j.gexplo.2013.08.005.
- Kamunda, C., Mathuthu, M., and Madhuku, M. (2016). Health risk assessment of heavy metals in soils from Witwatersrand Gold Mining Basin, South Africa. *International Journal of Environmental Research and Public Health*, 13(7), 663. https://doi.org/10.3390/ijerph13070663
- KIIIS, ., and Baltas H. (2021). Assessing Pollution Levels and Health Effects of Heavy Metals in Sediments around Cayeli Copper Mine Area, Rize, Turkey. Environmental Forensics 22(3-4): 372-384. https://doi.org/10.1080/15275922.2020.1850572.
- Kucuksezgin, F., Uluturhan, E., and Batki, H. (2008). Distribution of Heavy Metals in Water, Particulate Matter and Sediments of Gediz River (Eastern Aegean). Environmental Monitoring and Assessment 141(1–3): 213–225. https://doi.org/10.1007/s10661-007-9889-6
- Lermi, A., and Sunkari, E. D. (2020). Geochemistry, Risk Assessment, and Pb Isotopic Evidence for Sources of Heavy Metals in Stream Sediments around the Ulukışla Basin, Niğde, Southern Turkey. *Turkish Journal of Earth Sciences* 29(7): 1167–88.
- Marcovecchio, J. E., Botté, S. E., and Freije, R. H. (2007). Heavy Metals, Major Metals, Trace Elements. In Handbook of Water Analysis, 2nd Edition. ed. L. M. Nollet. London: CRC Press. https://www.scirp.org/(S(351jmbntvnsjt1aadkposzje))/reference/ReferencesPapers.aspx?ReferenceID= 1076573 (May 18, 2021).
- Meng, Q., Zhang, J., Zhang, Z., and Wu, T. (2016). Geochemistry of Dissolved Trace Elements and Heavy Metals in the Dan River Drainage (China): Distribution, Sources, and Water Quality Assessment. Environmental Science and Pollution Research 23(8): 8091–8103. https://doi.org/10.1007/s11356-016-6074-x
- Mutlu, C., Bayraktar, F., and Verep, B. (2020). Sediment Kalitesi Değerlendirme Çalışmalarına Bir Örnek, Boğacık Deresi (Giresun). *Journal of Anatolian Environmental and Animal Sciences* 5(3): 433–438.
- Mutlu, C., Eraslan Akkan, B., Verep, B. (2018). The heavy metal assessment of Harsit Stream (Giresun, Turkey) using multivariate statistical techniques. *Fresenius Environmental Bulletin*, 27,12B, 9851-9858.
- Mutlu, T. (2021). Heavy metal concentrations in the edible tissues of some commercial fishes caught along the Eastern Black Sea coast of Turkey and the health risk assessment, Spectroscopy Letters, 54:6, 437-445, DOI: 10.1080/00387010.2021.1939386
- Odat, S. (2013). Calculating pollution indices of heavy metal along Irbid/Zarqa highway-Jordan. *Int J Appl Sci Technol*, *3*(8), 72-76.
- Omwene, P. I., Öncel, M. S., Çelen, M., and Kobya, M. (2019). Influence of arsenic and boron on the water quality index in mining stressed catchments of Emet and Orhaneli streams (Turkey). *Environmental monitoring and assessment*, 191(4), 1-16. https://doi.org/10.1007/s10661-019-7337-z
- Ozseker, K., Eruz, C., and Cılız, S. (2013). Determination of copper pollution and associated ecological risk in coastal sediments of Southeastern Black Sea Region, Turkey. *Bulletin of environmental contamination and toxicology*, *91*(6), 661-666. https://doi.org/10.1007/s00128-013-1116-2
- Perin, G., Bonardi, M., Fabris, R., Simoncini, B., Manente, S., Tosi, L., and Scotto, S. (1997). Heavy metal pollution in central Venice Lagoon bottom sediments: evaluation of the metal bioavailability by geochemical speciation procedure. *Environmental Technology*, 18(6), 593-604. https://doi.org/10.1080/09593331808616577
- Salomons, W., and Ulrich, F. 1984. Metals in the Hydrocycle. Berlin, Heidelberg: Springer Berlin Heidelberg. http://link.springer.com/10.1007/978-3-642-69325-0 (March 29, 2021).
- Sinex, S. A., and Helz, G. R. (1981). Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environmental Geology*, 3(6), 315–323. https://doi.org/10.1007/BF02473521
- Şener, Ş., Şener, E., and Davraz, A. (2017). Evaluation of water quality using water quality index (WQI) method and GIS in Aksu River (SW-Turkey). Science of the Total Environment, 584, 131-144. https://doi.org/10.1016/j.scitotenv.2017.01.102
- Trefry, J. H., and Presley, B. J. (1976). Heavy metals in sediments from San Antonio Bay and the northwest Gulf of Mexico. *Environmental Geology*, 1(5), 283–294. https://doi.org/10.1007/BF02676717

- Uncumusaoglu, A. A., Sengul, U., and Akkan, T. (2016). Environmental contamination of heavy metals in the Yaglidere Stream (Giresun), southeastern Black Sea. *Fresenius Environmental Bulletin*, 25(12), 5492-5498.
- Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of hazardous materials*, 195, 355-364. https://doi.org/10.1016/j.jhazmat.2011.08.051
- Wang, J., Liu, G., Liu, H., and Lam, P. K. (2017). Multivariate statistical evaluation of dissolved trace elements and a water quality assessment in the middle reaches of Huaihe River, Anhui, China. Science of the total environment, 583, 421–431. https://doi.org/10.1016/j.scitotenv.2017.01.088
- Wang, Y., Wang, P., Bai, Y., Tian, Z., Li, J., Shao, X., ... & Li, B. L. (2013). Assessment of surface water quality via multivariate statistical techniques: a case study of the Songhua River Harbin region, China. Journal of hydro-environment research, 7(1), 30-40. https://doi.org/10.1016/j.jher.2012.10.003
- Woitke, P., Wellmitz, J., Helm, D., Kube, P., Lepom, P., and Litheraty, P. (2003). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere*, 51(8), 633-642. https://doi.org/10.1016/S0045-6535(03)00217-0
- Wojciechowska, E., Nawrot, N., Walkusz-Miotk, J., Matej-Łukowicz, K., and Pazdro, K. (2019). Heavy metals in sediments of urban streams: Contamination and health risk assessment of influencing factors. *Sustainability*, 11(3):563, 1-14. https://doi.org/10.3390/su11030563
- Yancheva, V., Stoyanova, S., Velcheva, I., Petrova, S., and Georgieva, E. (2014). Metal bioaccumulation in common carp and rudd from the Topolnitsa reservoir, Bulgaria. Arhiv za higijenu rada i toksikologiju, 65(1), 57-65. https://doi.org/10.2478/10004-1254-65-2014-2451
- Zamani Hargalani, F., Karbassi, A., Monavari, S. M., and Abroomand Azar, P. (2014). A novel pollution index based on the bioavailability of elements: a study on Anzali wetland bed sediments. *Environmental monitoring and assessment*, *186*(4), 2329–2348. https://doi.org/10.1007/s10661-013-3541-4
- Zhang, J., and Liu, C. L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. *Estuarine, coastal and shelf science*, 54(6), 1051–1070. https://doi.org/10.1006/ecss.2001.0879
- Zheng, N., Wang, Q., Zhang, X., Zheng, D., Zhang, Z., and Zhang, S. (2007). Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China. Science of the Total Environment, 387(1-3), 96-104. https://doi.org/10.1016/j.scitotenv.2007.07.044