Original Research

Temporal Variation of Metal Concentrations of Creek Sediment Samples

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Abstract

The aim of our study was to investigate the changes of metal concentrations in stream sediments depending on station and sampling period variation. Sediment samples were collected seasonally from six separate stations selected along Kilicozu Creek (Kirsehir, Turkey), and the Pb, Cr, Cu, Ni, Zn, and Cd concentrations were determined. Stations were selected on the basis of pollution gradient. It was observed that the metal concentration means per annum were Zn> Cr> Ni> Cu> Pb> Cd. Seasonal highest values of heavy metals were observed as follows; Pb (14.4 $\mu g \cdot g^{-1}$), Ni (43 $\mu g \cdot g^{-1}$), and Cd (6.2 $\mu g \cdot g^{-1}$) in autumn, Cr (55.7 $\mu g \cdot g^{-1}$) and Zn (71.9 $\mu g \cdot g^{-1}$) in summer, and Cu (42.5 $\mu g \cdot g^{-1}$) in spring. One-way ANOVA results also showed that there were significant metal concentration changes between stations. Potential metal contamination risk was determined for studied sediment samples. It was observed that Cd contamination exceeded the limit values in this stream sediment. According to the reference values, Zn or Pb contamination in the creek sediment has not reached the effective level. The findings of this study may be useful for further biomonitoring studies.

Keywords: contamination, heavy metals, river sediment, biomonitoring, Kirsehir, seasonal variation

Introduction

Heavy metals are among the most highly recognized environmental contaminants. The existence of these pollutants in water and biota indicates that the media has been exposed to natural or anthropogenic contaminants. Metal balance between the sediment and the water of streams changes because of excavation for open new land for agricultural or habitation purposes, and discharging industrial and domestic waste into water. Although metals are vital for some biochemical processes, they are poisonous to both plants and microorganisms above certain concentrations.

Factors such as adsorption capacity of clay, other chemical reactions, and ion exchange affect the retention of heavy metals in sediment. In rainy seasons, heavy metal concentrations in sediment increase significantly because of the organic and inorganic matter that flow into the water. Furthermore, it has been reported in the literature that it becomes much more toxic in the organic complexes through being accumulated by certain organisms [1, 2].

It is known that the chemical contamination of water is strictly related to atmospheric events [3]. Various types of industrial off-gases, as well as urban and intercity traffic, cause air contamination in respect to heavy metals. Stream water is used in several areas, such as for drinking or irrigation water and in aquaculture practices. Thus, monitoring heavy metal contamination in streams is a vital requirement in order to protect water quality and hence human health. In the hydrologic cycle, while less than 1% of contaminants can dissolve in water, 99% of these are accumulated in the sediment, which acts as a basin for the contaminants in the water [4]. Sediment is a final point for heavy metals and, therefore, it is used in determining the metal contamination of aquatic environments.

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Heavy metals are released into the environment as particle-bound; consequently, all suspended materials in water precipitate and join the sediment. The concentration of heavy metals which is accumulated in sediment differs in accordance with the rate and size of the sediment particles, as well as the existence of organic matter in the sediment [5]. Metal adsorption capacity of sediment increases or decreases depending on particle size [6]. It is known that all these reactions are reversible depending on the pH and redox potential, so adsorbed heavy metals can be released back into the body of water [7]. Because heavy metals are excessively accumulated on clay surface, they are easily washed away from the surface and flow into groundwater.

Kilicozu Creek, which flows through Kirsehir Province (Turkey), is running water used for irrigation. Finally, it mixes with the Kizilirmak River, which is the longest river in Turkey. Furthermore, dam lakes have been established on this river for irrigation purposes. In this study, it was aimed to examine the seasonal changes in Pb, Cr, Cu, Ni, Zn, and Cd concentrations and to determine heavy metal pollution of Kilicozu Creek sediment.

Material and Methods

The study was carried out at 6 different stations chosen on the river in the period between July 2009 and April 2010. The first station, located at spring of the creek, was chosen as control station, the 2nd station was near a dam lake, the 3rd station was near a steel-iron factory, the 4th station was in a farming region, the 5th station was very near a city center, and finally the 6th station was the place where the creek mixes with the Kizilirmak (Fig. 1). The samples were taken from the stations in July (summer), October (autumn), January (winter), and April (spring), which were months chosen to represent the seasons.

Before the study, all the materials used were washed with 10% nitric acid and deionized water, and then dried in a drying-oven. The glass materials used in analysis were kept in 10% HNO_3 overnight and washed twice with deionized water. Sediment samples were collected at 1.0 m distance from the riverside and a depth of 15 cm from the surface. The sediment samples were dried by mixing at intervals at room temperature for 7 days and sieved through a 2 mm sieve. The dried samples were fully crushed in a porcelain mortar. Thereafter, 0.5 gr sediment sample weighed and treated with 65% HNO_3 (Merck). Samples were digested in a microwave digestion system with 180ºC temperature and 200 PSI pressure (CEM Mars 5; CEM Corporation Mathews, NC, USA). Inductively coupled plasma optical emission spectroscopy (Varian-Liberty II, ICP-OES) was used for metal analysis. Standard readings were performed after every 10 samples to check the stability of the device. A blind solution was prepared to check the analytical method and possible contamination. The samples were analyzed in triplicate. All chemicals used in this study were analytical reagent grade (Merck. Darmstadt. Germany). The values showed the mean with the standard deviations (n=3). Kolmogrov-Smirnov and Levene's tests were applied to control the normality and homogeneity of data. When heterogeneity was present, logarithmic transformation (ln(x+1)) was applied and homogeneity was again determined. One-way analysis of variance was applied to test the significance of the difference between seasons and between stations. All statistical analyses were carried out by SPSS 15.00 packaged software. Significance degree was accepted as $p<0.05$.

Result and Discussion

The seasonal mean of the metal concentrations of the sediments samples taken from Kilicozu Creek are given in Table 1. Statistically, the highest Pb concentration in Kilicozu River sediment was observed in the autumn (14.4±5.7 $\mu g \cdot g^{-1}$) and the lowest observed in summer

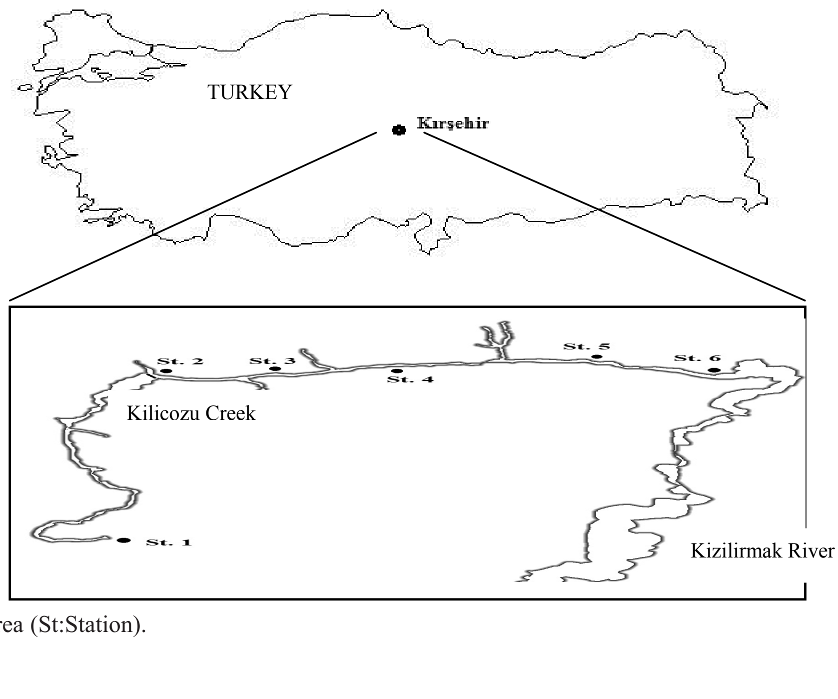

Fig. 1. Map of study area (St:Station).

Table 1. Seasonal variation of the heavy metal concentrations in Kilicozu River Sediment (µg·g^{-1})±SD. (n=3).

	Pb	Cr	Cu	Ni	Zn	Cd
Spring	11±3.8^{A}	41.4±25.2^{A}	42.5±37.7^{B}	37.7±28^{A}	53.1±27.7^{A}	2.8±2.39^{A}
Summer	13.3±4.8^{B}	55.7±32.2^{C}	29.6±6.2^{A}	42±21.8^{B}	71.9±34.7^{B}	3.8±1.6^{B}
Autumn	14.4±5.7^{C}	43.8±16.1A^{B}	29.4±10^{A}	43±24.9^{B}	50.9±30^{A}	6.2±2.6^{C}
Winter	12.3±5.3^{B}	46.3±22.6^{B}	33.2±12.8^{A}	40±22.8A^{B}	51.8±25^{A}	3.3±2.1A^{B}
Total	13±5.1	46.9±24.5	33.2±19.6	41.1±24	56.8±30.4	4.2±2.7

*Different letters in same column indicate significant differences at p< 0.05 (ANOVA). SD – standard deviation.

Table 2. Mean (±SD.) metal concentrations of Kilicozu Creek sediment taken from different stations (n=3).

Station	Pb	Cr	Cu	Ni	Zn	Cd
Cont.	5±0.5^{A}	18±1.4^{A}	16.2±3.8^{A}	20.1±2.2^{A}	34.7±3.4^{A}	1.4±0.5^{A}
2	11.8±1.7^{BC}	49±20^{B}	23.7±4.2^{AB}	29±4.6^{BC}	36.6±4.4^{A}	5.9±1.7^{B}
3	15.5±1.9^{C}	46.8±8.3^{B}	29.3±5.3^{AB}	36.8±4.7^{CD}	44.8±5^{A}	3.9±3.4^{AB}
4	14.25±2.8^{C}	34.4±3.3^{AB}	52.7±36.6^{C}	30.4±6^{BCD}	84.1±15.7^{B}	4.3±1.7^{AB}
5	15±2^{C}	27±8.6^{A}	23.7± 1.5^{AB}	28±5.9^{B}	92.3±39.4^{B}	4.8±2.4^{AB}
6	21.4±5^{D}	46.9±9.8^{B}	35.4±12^{ABC}	39±7.8^{D}	85±22.6^{B}	4.2±3.7^{AB}

*Different letters in same column indicate significant differences at P < 0.05 (ANOVA). SD – standard deviation.

(11±3.87 µg·g^{-1}). There was no statistical difference between winter and summer in terms of Pb concentrations. It was found that the highest Cr concentration in the sediment samples was seen in summer (55.7±32.2 µg·g^{-1}), and the lowest was seen in spring (41.4±25.2 µg·g^{-1}). While the highest Cu accumulation was observed in spring (42.5±37.7 µg·g^{-1}), a statistically significant difference with the other seasons was not found (p>0.05).

Despite the lowest Ni, accumulation was observed in the spring (37.7±28 µg·g^{-1}), but a statistically significant difference with the other seasons was not found. The highest Zn concentration was observed in summer (71.9±34.7 µg·g^{-1}) and there was no statistical difference observed among the other seasons. The lowest Cd concentration in sediment was identified in spring (2.8±2.39 µg·g^{-1}), and the highest was in autumn (6.2±2.6 µg·g^{-1}). Variance analysis results showed that change of station significantly affected the variation of metal concentrations in sediment (Table 2). The lowest metal concentrations were observed in control station. For Pb concentrations, the highest metal accumulation was determined at station 6 (21.4±5 µg·g^{-1}). Apart from the control station, the lowest metal accumulation was detected at station 1. For Cr, there was no statistical difference between station 5 and the control group. The highest Cr accumulation was seen at station 2. The highest Cu accumulation was observed in station 4, and no statistical difference was observed among stations 2, 3, and 5. For Cu accumulation there was no statistical difference among all stations (p>0.05).

The highest Ni accumulation was detected at Station 1 and the lowest at station 5. For Zn, stations 4, 5, and 6 were higher than the other stations but there was no statistical difference among them. No statistical difference was observed in Cd concentrations among the stations.

When the results are examined in terms of seasonal variation, it can be concluded that Cr and Zn levels were higher in summer, Pb and Cd were higher in autumn, and Cu was higher in spring in comparison to other seasons, respectively. A study conducted in the Han River (China) showed that metal accumulation in sediment is higher in wet seasons compared to dry seasons [8]. Our findings support this study in respect to Pb, Cd, and Cu. Contrary to this study, heavy metal concentration in the sediment of the New Calabar River (Nigeria) is higher in summer and winter in comparison to spring and autumn [9]. High metal concentration in wet seasons can be explained by the fact that the final destination of the contaminants carried away by rain and snow water is generally rivers. Besides, metals have a tendency to accumulate in sediment of aquatic systems. Bowman and Harlock [10] determined the range of the heavy metal values allowed to be in the bottom sediment as Pb: 2-80, Cr: 10-100, Cu: 2-100; Ni: 0.5-100, Zn: 10-200, Cd: 0.1-1 µg·g^{-1}. According to the findings of this study, the concentration values of all of the metals, excluding Cd, remained within the limits identified by Bowman and Harlock. When this current study is compared to previous studies, almost all of the metals are higher than the concentrations determined in the other studies (Table 3). The fact that a large portion of the creek that was studied passes through the center of Kirsehir, which is a residential area, is a significant factor in the high concentration found in our study.

Table 3. The heavy metal concentrations in the Kilicozu River Sediment and comparision with different literaute ($\mu g \cdot g^{-1}$).

	Cr	Ni	Zn	Cu	Cd	Pb	Ref.
Asi River	6.5	10.9	1.9	1.03	0.005	0.19	[11]
Tigris River	-	109.14	34.23	38.7	-	-	[12]
Kars River			2.23	1.504	0.11	1.697	[13]
Texoma Lake	30	17	89	38	2	10	[14]
Balaton Lake	5.7-66	4.5-55	13-150	0.7-36	0.1-0.7	2.4-160	[15]
This Study	46.9	41.1	56.8	33.2	4.2	13	

Table 4. The heavy metal concentrations in the Kilicozu River Sediment and comparision with guidelines ($\mu g \cdot g^{-1}$).

	Cr	Ni	Zn	Cu	Cd	Pb	Ref.
LEL (Lovest Effect Level)	26	16	98	16	0.6	31	[19]
TEC (Threshold effect concentration)	41	22.7	123	31.6	0.9	35.8	[19]
PEC (Probable Efect Concentration)	110	46.8	315	110	4.1	128	[19]
SEL (Severe Effect Concentration)	111	75	520	149	10	250	[19]
This study	46.9	41.1	56.8	33.2	4.2	13	

In this study, the heavy metal concentrations accumulated in the stations per annum were found to be Cd<Pb<Cu<Ni<Cr<Zn. In a study reported from Lake Abant, accumulation means per annum as Cd<Cr<Pb<Ni<Zn<Cu<Mn from the stations they designated at Lake Abant [16]. The main reasons for this difference can be explain as heterogeneity of pollutants and their resources. In studied river have heterogeneity of pollutants -like factory area, farming site, domestically uploads-resources too. A list was drawn up of resources that cause high metal contamination in nature [17]. According to this list, industrial and agricultural activities and domestic wastes place a burden on nature in respect to highly concentrated heavy metals of various types. Kaushik et al. [18] determined that the Cd and Ni accumulation in the Yamuna River (India) originates from industrial resources. Similarly, the concentrations in the current study were detected to be high in the stations that were selected near industrial and residential areas.

A list that classifies the potential of contamination into four groups based on the amount of organic and inorganic matters in the sediment has been issued by the National Ocean and Athmospheric Administration [19], headquartered in the United States (Table 4). According to this list, Zn and Pb concentrations are classified as "lowest effect level" (LEL) values, while Ni, Cr, Cu, and Cd are classified as "probable effect concentration" (PEC). According to the reference values, there is no Zn or Pb contamination in the Kizilozu Creek sediment. However, it can be mentioned about pollution in terms of Ni, Cr, Cu, and Cd concentrations. Moreover, Cd concentration will most likely reach "hazardous value concentration" unless precautions are taken against it. The reasons for this contamination can be explained as plastic wastes due to the fact that a large portion of the creek passes through the city center, and agricultural irrigation and domestic sewage is discharged into the creek [1].

In conclusion, it can be said that there is significant contamination in terms of Ni, Cr, Cu, and Cd in the sediment of Kilicozu Creek. It is obvious that the metal concentrations in the sediment will exceed the critical values unless necessary precautions are taken. This study is the first to be conducted to determine metal accumulation in the sediment samples of Kilicozu Creek in spatial and temporal aspects. The results of this study indicate that, in addition to station selection, the sampling period also is important in biomonitoring studies. However, station variable is of greater importance in explaining the variance. In addition, the synergistic effect of these two parameters should be taken into consideration. Several metal types originating from one source can reach aquatic ecosystems. This case is acknowledged as a major handicap for heavy metal removal practices. The findings of this study may be useful for future biomonitoring studies.

References

1. DUMAN F., KAR M. Temporal Variation of Metals in Water, Sediment and Tissues of the European Chup (*Squalius cephalus* L.), B. Environ. Contam. Tox., **89**, 428, **2012**.
2. YILMAZ F., OZDEMIR N., DEMIRAK A., TUNA L. Heavy Metal Levells In Two Fish Species *Leuciscus cephalus* and *Lepomis gibbosus*, Food Chem., **100**, 830, **2007**.

3. KIR I., TEKIN OZAN S., TUNCAY Y. The seasonal variations of some heavy metals in Kovada Lake's water and sediment JFAS., **2**, 155, **2007**.
4. CHA MW., YOUNG L., WONG KM. The Fate of Traditional Extensive (Gei Wai) Shrimp Farming At The Mai Po Marshes Nature Reserve, Hong Kong, Hydrobiologia., **352**, 295, **1997**.
5. SALOMANS W., ROOIJ NM., KERDIJK H., BRIL J. Sediments as a Source for Contaminants, Hydrobiologia., **149,13**, **1987**.
6. JAIM CK. Metal Fractionation Study on Bed Sediments of River Yamuna, India. Water Res., **38**, 569, **2004**.
7. KASHEM MA., SINGH BR. Metal Availability in Contaminated Soils:I. Effects Of Flooding and Organic Matter on Changes İn Eh, Ph And Solubility Of Cd, Ni And Zn. Nutr Cycl Agroecosys., **61**, 247, **2001**.
8. LI S., ZHANG Q. Risk Assessment and Seasonal Variations of Dissolved Trace Elements and Heavy Metals in The Upper Han River, China. J. Hazard. Mater., **18**, 11051, **1987**.
9. ODOKUMA LO., IJEOMAH SO. Seasonal Changes in the Heavy Metal Resistant Bacterial Population of The New Calabar River, Nigeria. Ajol., **9**, 425, **2003**.
10. BOWMAN JJ., HARLOCK S. The Spatial Distribution of Characterised Fly-Ash Particles and Trace Metals in Lake Sediments and Catchment Mosses:Ireland. Water Air Soil Poll., **106**, 263, **1998**.
11. CALISKAN E. Research of Heavy Metal Levels in Water, Sediment and African Catfish (*Clarias gariepinus* BURCHELL, 1822) of the Orontes River. Mustafa Kemal University Graduate School of Natural and Applied Sciences M.Sc. Thesis. pp. 85. **2005**.
12. KARADEDE-AKIN H., UNLU E. Heavy Metal Concentrations in Water, Sediment, Fish and Some Benthic Organisms from Tigris River, Turkey, Environ. Monit. Assess., **131**, 323, **2007**.
13. USLU H. An investigation of concentration levels of some heavy metals in transcaucasian barb (*Capoeta capoeta capoeta* Guldenstaedt, 1772) hunted in Kars Creek and medium sediments, Kafkas University Graduate School of Natural and Applied Sciences M.Sc. Thesis, Kars, pp. 48, **2007**.
14. AN Y-J., KAMPBELL D. H. Total, Dissolved, and Bioavailable Metals At Lake Texoma Marinas. Environ. Pollut., **122**, 253, **2003**.
15. NGUYEN H. L., LEERMAKERS M., OSÁN J., TOROK S., BAEYENS W. Heavy Metals in Lake Balaton: Water Column, Suspended Matter, Sediment and Biota. Sci Total Environ., **340**, 213, **2005**.
16. DUMAN F., OBALI O., AYDIN D. Seasonal variotion some trace element in Abant Lake Sediment. Sakarya University Science and Art Faculty, **8**, 53, **2006**.
17. MARKERT B. Plant as Biomonitors: Indicators for Heavy Metals in The Terrestrial Environment, VCH Weinheim, New York/Basel/Cambridge, **1993**.
18. KAUSHIK A., KANSAL A., SANTOSH., MEENA KUMARI S., KAUSHUIK C. P. Heavy Metal Contamination of River Yamuna, Haryana, India:Assessment by Metal Enrichment Factor of The Sediments. J. Hazard. Mater., **164**, 265, **2009**.
19. NOAA (National Oceanic And Atmospheric Administration), **2009**. SQUIRT, Screening Quick Reference Tables for in Sediment, http://response.restoration.noaa.gov/book_shelf/122_new-Squirts.Pdf