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Monitoring Trace Metal Levels in Yozgat-Turkey: Copper, Iron, Nickel, Cobalt, Lead, Cadmium, Manganese and Chromium Levels in Stream Sediments

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Abstract

In the presented study, the concentrations of some heavy metal ions in bottom sediment samples collected from streams around Yozgat-Turkey in December 1998 and October 1999 were determined by flame atomic absorption spectrometry (FAAS) after leaching with *aqua regia*. Copper, iron, nickel, cobalt, lead, manganese and chromium levels in the sediment samples were found in the range of 10.4-16.7 μg/g, 58.3-113.7 μg/g, 31.9-76.4 μg/g, 8.3-19.2 μg/g, 31.2-60.3 μg/g, 34.3-64.4 μg/g and 26.7-39.6 μg/g, respectively. Cadmium contents of the sediment samples were below 3 μg/g at all stations. These values were below the maximum tolerable limits set by the Water Pollution Control Regulation of the Turkish authorities. Correlations between metal concentrations were evaluated.

Keywords: bottom sediment, trace metals, streams, Yozgat-Turkey, flame atomic absorption spectrometry.

Introduction

Trace heavy metal analysis are an important part of environmental pollution studies [1-5]. Determination of the heavy metal contents of various environmental materials such as soil, natural waters, plants, dusts, etc. [6-8] have been continuously performed by researchers. Also, sediments are an indicator for investigating of heavy metal pollution. Sediments consist of a complex mixture of inorganic and organic components [9-11]. Analysis of the inorganic and organic components of the sediment samples collected from various locations such as river, sea, etc. is very important for investigations of pollution studies [12-15]. Especially trace heavy metal levels of the sediment samples have been widely determined by various researchers. Trace heavy metal contents of sediment samples often include a chemical leach procedure with various leaching agents such as inorganic acids, *aqua regia* etc. before determination by atomic absorption spectrometry [16-18].

Yozgat City is in the central Anatolia region of Turkey. Approximately 250,000 people live in Yozgat City and its surroundings, where agriculture is the main income. The important streams around Yozgat City are Cekerek Cayi, Egriöz Suyu, Karasu, Kanaksuyu and Delice River. Egrioz Suyu is collected in Gelingulu Dam (Figure 1). These streams are generally used for irrigation of the agricultural areas around Yozgat. The trace heavy metal levels of the water samples collected from streams around Yozgat City-Turkey have been performed by our working group [19].

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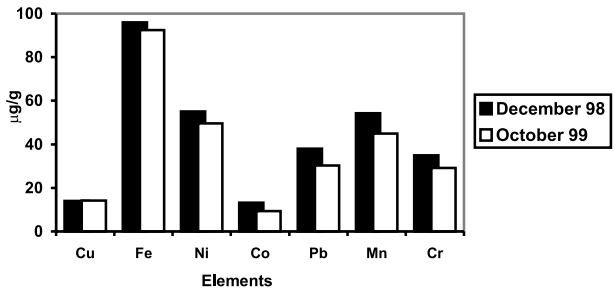

Fig. 1. Mean levels of the investigated metal ions in the sediment samples.

In the present study, the concentration of copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium in the sediment samples taken from the streams around Yozgat City were determined by flame atomic absorption spectrometry (FAAS). The relationships between metal concentrations were calculated.

Experimental

Reagents

All chemicals obtained from commercial sources were of super pure grade unless otherwise stated. All aqueous solutions were prepared using doubly distilled water. Standard solutions of the working elements were prepared by dissolution of pure metals or their salts (Merck Darmstadt, Germany).

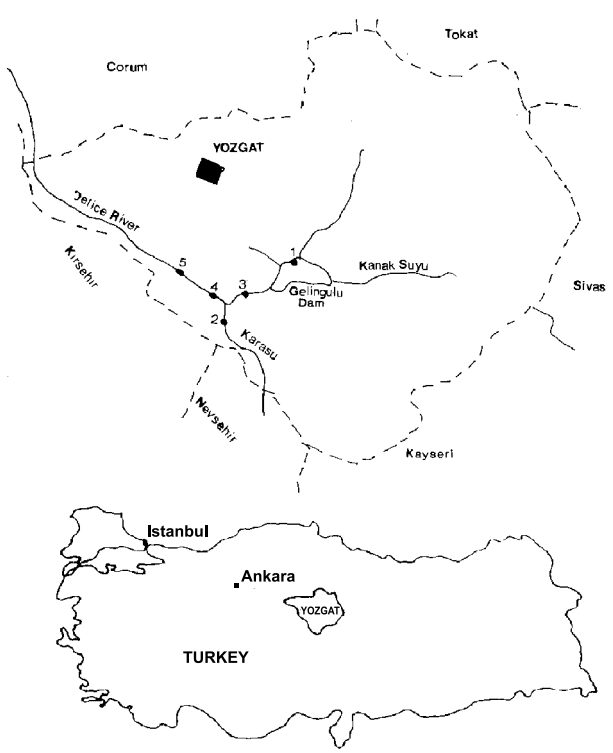

Fig. 2. Map of working area.
Site 1 Gelingulu Dam
Site 2 Karasu
Site 3 Kanak Suyu.
Site 4 Delice River 1
Site 5 Delice River 2

Apparatus

Determinations of the metal ions were performed by a Perkin-Elmer Model 3110 atomic absorption spectrometer. The operating parameters for working elements were set as recommended by the manufacturer. Atomic absorption measurements were carried out in air/acetylene flame without background correction.

Sampling

Sediment samples were collected from five stations: Gelingulu Dam, Karasu, Kanak Suyu and Delice River, in December 1998 and October 1999. A map of the working area is given in Figure 2. Site 1 was in Gelingulu Dam. Site 2 was in Karasu Stream before the mixing point of Karasu and Kanak Suyu near Şefeatli Village. Site 3 was in Kanak Suyu. After mixing Kanak Suyu and Karasu Stream, they were called Delice River and Site 4 was selected at this point. Site 5 was at Delice River. The distance between Site 4 and Site 5 was approximately 5 kilometers.

Leaching Procedure for the Sediment Samples

The sediment samples were digested according to procedure given by Soylak et al. [20] and Narin and Soylak [21]. The samples were dried at 110°C for 3 h and ground to pass through a 200 mesh sieve. 1.0 g of the sample was weighed and transferred to a 100 ml beaker. 10 ml of aqua regia was added. The sample was kept at 90°C for 1 h. After cooling, 5 ml of distilled water was added to the sample and mixed. The residue was filtered through Whatman 41 filter paper. Then the sample was diluted to 25 ml with distilled water. The metal concentrations were determined in the final solutions by flame atomic absorption spectrometry (FAAS).

In order to ascertain the accuracy of the method employed and calibrate for any slight contamination, a reference material was used with every batch (GBW 07309, a stream sediment standard reference material from National Research Centre for Certified Reference Materials (NRCCRM)-China).

Results and Discussion

Copper, iron, nickel, cobalt, lead, cadmium, manganese and chromium concentrations of the sediment samples collected from the five stations at the streams around Yozgat-Turkey were determined by flame atomic absorption spectrometry (FAAS) after leaching with *aqua regia*. Blank leachings were also performed. The results are given for December 1998 and October 1999 in Table 1 and Table 2, respectively. The results are mean of the three replicates. The levels of all investigated ions

Table 1. Trace metal concentrations in sediment samples in December 1998 (N=4).

Site No	Concentration, x ± SD, μg/g						
	Cu	Fe	Ni	Co	Pb	Mn	Cr
1	14.3 ± 10.1	106.6 ± 9.8	31.9 ± 1.2	11.4 ± 1.1	40.6 ± 0.1	63.1 ± 2.6	26.9 ± 0.7
2	15.3 ± 0.2	94.7 ± 9.1	76.4 ± 1.1	19.2 ± 1.0	38.0 ± 0.8	59.1 ± 1.2	37.5 ± 0.1
3	12.8 ± 1.0	102.1 ± 2.2	44.1 ± 1.2	13.3 ± 1.0	45.7 ± 4.4	54.9 ± 4.1	33.3 ± 0.6
4	11.4 ± 0.6	79.1 ± 3.7	57.5 ± 3.1	10.7 ± 0.9	32.9 ± 0.1	42.4 ± 0.1	35.6 ± 0.7
5	16.0 ± 0.6	99.6 ± 5.8	66.9 ± 3.5	11.4 ± 0.8	32.9 ± 0.2	51.9 ± 5.1	39.6 ± 1.6
Mean	14.0 ± 1.9	96.4 ± 10.6	55.4 ± 17.7	13.2 ± 3.5	38.0 ± 5.4	54.3 ± 7.9	34.9 ± 4.9

Table 2. Trace metal concentrations in sediment samples in October 1999 (N=4).

Site No	Concentration, x ± SD, μg/g						
	Cu	Fe	Ni	Co	Pb	Mn	Cr
1	15.6 ± 0.3	110.6 ± 4.8	47.1 ± 4.4	10.7 ± 0.3	60.3 ± 6.9	64.4 ± 0.6	29.3 ± 0.1
2	14.8 ± 0.2	58.3 ± 3.1	48.9 ± 4.0	10.5 ± 0.1	58.9 ± 2.0	35.6 ± 2.2	26.7 ± 0.5
3	16.7 ± 1.3	113.7 ± 4.2	59.1 ± 3.7	8.3 ± 0.2	68.1 ± 5.4	34.3 ± 2.1	29.3 ± 0.2
4	10.4 ± 0.9	94.3 ± 2.7	40.1 ± 3.1	8.4 ± 0.1	31.9 ± 0.9	35.9 ± 2.2	29.6 ± 0.4
5	13.0 ± 0.6	84.9 ± 2.8	39.5 ± 1.3	8.6 ± 0.2	31.2 ± 0.1	54.8 ± 3.1	30.6 ± 1.2
Mean	14.1 ± 2.5	92.4 ± 22.4	49.6 ± 8.0	9.3 ± 1.2	30.2 ± 17.1	45.0 ± 13.8	29.1 ± 1.4

in the sediment samples were found at μg/g levels for seasons.

As can be seen in Tables 1 and 2, copper and iron in the sediment samples were found in the range of 10.4-16.7 μg/g, 58.3-113.7 μg/g, respectively. While in December 1998 the highest level of copper was in Site 5, the highest level of copper at October 1999 was in Site 3. At site 4, the concentration of copper was found at the lowest level. The highest iron concentrations were found in Site 1 in December 1998 and October 1999. The results of the present study for copper and iron were found to be in agreement with earlier works reported in the literature [14, 17, 21].

The concentration of cadmium determined by FAAS in the sediment samples were found below 3 μg/g at all stations. The results found for cadmium were compared with several data for world values. Dong et al. [22] have reported that average sediment cadmium concentrations of samples from the Menomonee River Watershed – USA are in the range 0.11-0.49 μg/g. In another study, river sediment cadmium levels from Izmir-Turkey have been reported as 1.62 μg/g [23].

The concentrations of nickel in December 1998 and October 1999 were 31.9-76.4 μg/g and 39.5-59.1 μg/g, respectively. While in December 1998 the concentration of Ni was lowest in Site 1 and highest in Site 2, the nickel level was lowest at Site 5 and highest in Site 3 in October 1999. Cobalt contents of the sediment samples were found in the range of 8.3-19.2 μg/g. Cobalt levels in December 1998 were higher than the levels of cobalt in October 1999 in the all five stations (Table 1 and Table 2). The nickel concentrations of sediment samples from Menomonee River Watershed – USA have been reported in the range of 2.4-36 μg/g [22]. The mean nickel concentrations of the river sediments from the Izmir by has been reported as 114 μg/g [23].

The lead and manganese levels of the sediment samples from the streams of Yozgat were found in the range of 31.2-60.3 μg/g, 34.3-64.4 μg/g, respectively (Tables 1 and 2.). The concentrations of lead were approximately at the same levels in Sites 4 and 5 at both sampling times. In the other three stations the levels of lead in October 1999 were higher than the results found for the same stations in December 1998. A main source of environmental lead, particularly in urban areas, is the combustion of leaded petrol. In Turkey, unleaded petrol is not in widespread use because of its cost and because of vehicle age [24]. The Pb thus released in the atmosphere is ultimately fixed in soil, sediment, plants [25] and water. The main origin of manganese is from the geological structure of middle Anatolia of Turkey. Those results agree with the results given by Narin in literature [21].

The concentration of chromium in December 1998 and at October 1999 were in the range of 26.9-39.6 μg/g and 26.7-30.6 μg/g, respectively. Approximately, the level of chromium was at the same level in all stations with both sampling times (Tables 1 and 2). The concentration

of chromium found by the present study is lower than the values found by Atgin et al. [22].

The mean level of the investigated metal ions is depicted in Figure 1. The mean level of copper was approximately the same level at both sampling times. The levels of the other metal ions were lower in October 99 than in December 98. Of course, the one year monitoring program is not enough for total characterization of the sediment; longer periods are needed. But the same tendency has been found in analysis of the stream water samples from the same stations [19].

Relationships Between Metal Concentrations

A linear regression correlation test was performed to investigate correlations between metal concentrations. The whole data were subjected to a statistical analysis and correlation matrices were produced to examine the inter-relationships between the investigated metal concentrations. The values of correlation coefficients between metal concentrations are given in Table 3. The sediments vs. sediments system showed strong positive correlations of iron-manganese, nickel-cobalt and nickel-chtromium with corresponding r values of 0.619, 0.570, and 0.678, respectively. Copper has significant positive relationships with nickel (0.552) and lead (0.612). Inverse associations exist between chromium and lead (-0.509). According to the data given (> 0.55) in literature [26-27], these correlations were significant.

Table 3. Correlations between metal concentrations.

	Cu	Fe	Ni	Co	Pb	Mn	Cr
Cu	1.000						
Fe	0.336	0.000					
Ni	0.552	0.008	1.000				
Co	0.220	0.033	0.570	1.000			
Pb	0.612	0.365	0.019	-0.016	1.000		
Mn	0.224	0.619	-0.043	0.492	-0.193	1.000	
Cr	0.050	0.064	0.678	0.378	-0.509	0.178	1.000

In conclusion, the concentrations of copper, iron, nickel, cadmium, cobalt, lead, manganese, and chromium in the sediment samples collected from streams around Yozgat-Turkey were found at μg/g level. The levels of these ions were lower than the level given by Turkish Authorities [28]. Also, the elemental composition of the sediments is not dangerous for the living biota of these streams.

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