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ORIGINAL ARTICLE

Heavy Metal Contents of the Karasu Creek Sediments, Nigde, Turkey

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Abstract Heavy metal contamination in sediments of the Karasu spring was investigated in the presented study. In this respect, sediment samples were collected from contaminant sites along the spring starting from the spring water manifestation site, base of the Akkaya dam to the dam exit site. Heavy metal concentrations were determined by X-ray Fluorescence Spectrometer. Cobalt, copper, arsenic, tin, nickel, zinc, cadmium, lead, aluminum, iron, titan, chromium and manganese contents of the Karasu creek sediments are found as 18.30–69.00, 12.40–595.0 5.50–345.3, 5.80–15.1, 10.9–64.1, 28.90–103,300, 4.1–356.2, 7.70–37,840, 13,460–109,400, 11,740–62,900, 22.18–59.04, 41.70–369 and 12.09–3,480 mg/kg, respectively. Results indicate the presence of a contamination in the Karasu creek. All the metal concentrations were found to be exceeding their acceptable limit values. Eutrophication is developed in the Karasu creek and the Akkaya dam. It is thought that heavy metal accumulation in the creek is originated from discharge from mine quarries, industrial and domestic wastes. Protection zones should be defined and all necessary measures must be taken along the Karasu creek.

Keywords Karasu creek · sediment · heavy metal · geochemistry · Nigde–Turkey

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1 Introduction

The city of Nigde in the central Anatolia of Turkey is an old settlement area and one of the oldest industrial regions of this region. Due to immigration of people from the rural sites and rapid urbanization, density of population in Nigde city has been dramatically increased in recent years. The main industries in Nigde are textile, mine and cement. The household and industrial sewage of the Nigde City is discharged to Karasu creek without any treatment. Mining facilities and small- and moderate-sized industries as well as settlement areas are concentrated along the Karasu creek. Moreover, wastes from the industrial facilities and settlement areas are discharged to the Karasu creek without any refinement. In the Bor basin between Nigde and Bor though which the Karasu creek runs agriculture is widely developed. The agricultural areas around these areas are irrigated with waters from the Karasu creek.

In association with increase of land use, drinking water need has been also increased. In addition, due to improper irrigation, increased use of fertilizers and increasing number of industrial facilities, the impact of pollution has been widened. Metals are very important for humans, plants and environment and some of metals are indispensable for humans and plants while some are toxic (Förstner, 2004; Kara, Pirlak, & Ozdilek, 2004; Mwamburi, 2003; Guéguen, Dominik, Pardos, Benninghoff, & Thomas, 2000; Ghaedi, Fathi, Shokrollahi, & Shajarat, 2006). Over dose of indispensable elements has also a toxic effect on livings. Metals may move with food chain. Therefore, several regulations were described for limiting the concentrations of some of metals in waters and soils. The concentration of trace elements in river sediments is an important indicator of environmental contamination (Narin, Soylak, & Dogan, 1997; Soylak, Narin, Elci, & Dogan, 1999; Alagarsamy, 2006). There is a great number of routine studies on trace element concentration of sediments and soil (Narin & Soylak, 1999; Tuzen, 2003; Dalman, Demirak, & Balci, 2006; Capilla et al., 2006; Arslan & Gizir, 2006; Soylak & Yilmaz, 2006).

The aim of this study is to determine the heavy metal concentrations in sediments of the Karasu creek running through the city of Nigde and discharging to the Akkaya dam. In addition, possible contaminated sites were also defined along the creek. Waters of Karasu creek and the Akkaya dam are utilized in various ways. However, continuous and hygienic use of these waters is only possible if river basin is clean and contamination along the creek has been mitigated as much as possible. Therefore, determination of possible contaminant sites along the creek will provide more healthy use of this water body.

2 Experimental

2.1 Instruments

Coordinates of sample sites were determined with Garmin brand GPS-12CX device. Analyses of Co, Cu, As, Sn, Ni, Zn, Cd, Pb, Al, Fe, Ti, Cr and Mn elements were performed with Spectro-Xepos Benchtop X-ray Fluorescence Spectrometer. Analyses were done on samples of double sided film tablets in 32 mm diameter. Detection System is drift detector with Peltier cooling, energy resolution FWHM<170 eV, measured for the Mn Kα line with an input count vote of 10.000 pulses, Microprocessor controlled detector and electronics. Results are given as mg/kg. Statistical analysis were performed SPSS.

2.2 Sample collection

Sediment sampling was made in November 2005. A total of 26 systematic samples were collected from the base of Karasu creek. Twenty of the samples (K1–K20) were taken from the area towards to the Akkaya dam, five from (K21–K25) the base of Akkaya dam and one (K26) from the exit of the dam. Coordinates of samples were measured with GPS and marked on 1/25.000 scaled topographic map. Samples were collected with hard plastic sample shovel and stored in 1-kg plastic bags for analyses. Before use, bags were washed with 6 mol l^{-1} HNO_3 to avoid from contamination and rinsed with distilled water and then heated at 70 °C. Soil samples were heated at 105 °C for 24 h. Dried samples were sieved through 2 mm plastic sieve to be separated from conglomerates. In the next stage, samples were homogenized with an agate mortar to a grain size of less than 2 mm. The agate mortar was washed with 6 mol l^{-1} HNO_3 and rinsed with distilled water and dried before the each sample process.

The Karasu creek (the Nigde creek) under investigation is in the M33a1, M33a2, L33d3 and L33c4 quadrangles (Figure 1). The Karasu creek issues from the northeast of Nigde (L33c4 and L33d3) and flows through the city (M33a1) and ends at the Akkaya dam southeast of the city (M33a2). Metamorphic rocks of the Paleozoic–Mesozoic Nigde Massive and alluvium material consisting of Neogene–Pliocene sand, clay and silt are exposed in the study area. Metamorphic rocks of Nigde Massive are composed of gneiss, schist, marble and quartzite alternations (Yalcin, 1995).

3 Results and Discussion

Along the Karasu creek and behind the Akkaya dam, waters from the creek and dam are widely used for agriculture. Creek flowing in its natural channel is in close association with the soil. Co, Cu, As, Sn, Ni, Zn, Cd, Pb, Al, Fe, Ti, Cr and Mn contents of samples

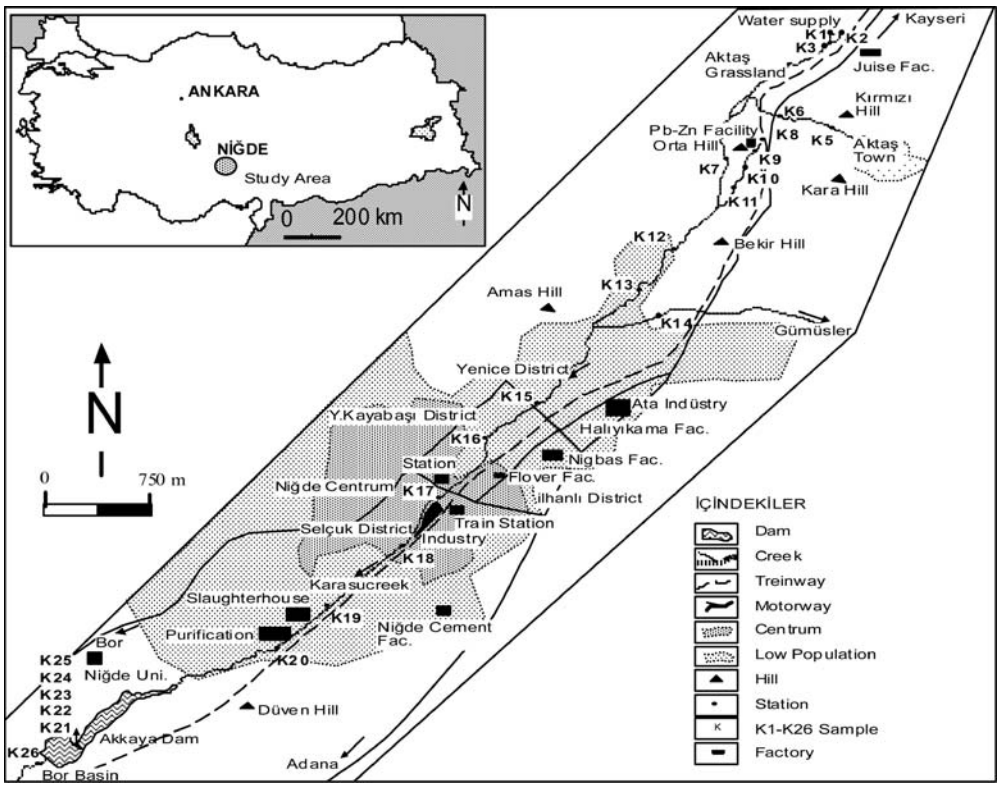


Figure 1 Location of study area and sampling map.

collected along the creek are given in Table I. The minimum and maximum cobalt levels found in our study were 18.3 mg/kg in K16 station and 69.0 mg/kg in K8 station, respectively. Cobalt levels were found at below detection limits in 12 station. Copper levels in samples were range 12.4 to 595.0 mg/kg (lowest in K25 station, highest in K18 station). The minimum and maximum arsenic levels in samples were found 5.5 mg/kg in K5 station and 1367 mg/kg in K9 station, respectively. Tin levels in samples were detected only tree station. The levels in K17, K18 and K18 stations were found 5.8, 7.8 and 15.1 mg/kg, respectively. In other station, tin levels were found below detection limit. Nickel level in the samples were range 10.9 to 64.1 mg/g (highest in K14 station, lowest K13 station). The range of zinc levels detected in the samples analyzed fell between 28.9 mg/kg, for K25 station and 103,300 mg/kg, for K9 station. Cadmium levels in samples were detected only five station (range 4.1 to 356.2 mg/kg). For other 19 station, cadmium levels in sediment samples were found below detection limit. Lead concentration in sediment samples were range 7.7 to 37,840 mg/kg. The minimum chromium level in sediment sample was found 41.7 mg/kg in K10 station and the minimum chromium concentration was found 369.0 mg/kg in K14 station. For the sediment samples, manganese concentration was in the range of 12–3,480 mg/kg. Aluminum, iron and titanium are the most abundant elements in the samples investigated. They are at g/kg levels. Analysis of sediment samples shows that the concentration of aluminum, iron, titanium vary from 13.5 to 109.4; 11.7–60.6 and 1.2–5.9 g/kg, respectively.

Acceptable limits in soil, shale, earth crust and Turkish National Soil Pollution Control Regulation of heavy metals were given Table II. The maximum concentrations of heavy metals in investigated sediment samples were found to be above their acceptable limits. Following its manifestation from the spring, creek water is physically contaminated. The first contamination points are K3 and K4 stations at northeast of Nigde where wastes of fruit juice plant are piled. Following the K3 and K4 stations, depending on Eutrophication, some physical characteristics

Table I The levels of investigated elements in the sediments from the Karasu (mg/kg)

Sample number	Co	Cu	As	Sn	Ni	Zn	Cd	Pb	Cr	Mn	Al*	Fe*	Ti*
K1	32.2	31.6	8.8	BDL	21.9	64.3	BDL	20.6	123.5	831	53.5	40.5	3.5
K2	40.1	36.0	31.9	BDL	42.2	64.4	BDL	21.3	254.0	934	64.7	38.4	3.6
K3	25.3	17.5	12.8	BDL	17.3	49.5	BDL	22.8	109.5	437	55.6	24.4	2.8
K4	37.6	25.3	15.5	BDL	23.1	76.9	BDL	24.8	256.0	525	46.5	29.2	2.3
K5	54.3	26.7	5.5	BDL	32.0	78.3	BDL	7.7	136.0	1,259	56.8	62.9	3.4
K6	52.2	23.8	6.8	BDL	21.9	109.6	BDL	17.1	229.0	12	61.6	60.6	3.4
K7	49.4	31.9	13.5	BDL	31.5	79.9	BDL	21.0	157.0	1,395	53.1	57.9	4.1
K8	69.0	30.5	26.7	BDL	41.7	768.0	BDL	224.0	304.0	969	52.8	54.9	3.3
K9	BDL	12.8	>1,367	BDL	11.0	103,300.0	356.2	37,840.0	BDL	BDL	88.3	44.9	5.0
K10	BDL	47.6	>868	BDL	11.9	53,700.0	213.0	24,180.0	41.7	BDL	109.4	53.8	5.9
K11	BDL	29.0	35.0	BDL	38.3	28,310.0	19.7	743.4	290.0	759	49.4	44.4	2.8
K12	39.0	55.9	75.0	BDL	22.4	76.8	4.1	38.7	58.5	460	65.3	40.2	4.4
K13	31.1	46.2	25.4	BDL	10.9	29.9	4.1	25.6	83.0	314	65.1	37.6	4.3
K14	40.5	57.3	345.3	BDL	64.1	115.1	BDL	58.0	369.0	12	78.1	50.2	5.4
K15	37.8	45.9	33.9	BDL	12.3	32.2	5.0	28.0	58.9	3,480	69.3	39.3	4.1
K16	BDL	44.2	75.1	BDL	41.4	89.4	BDL	30.4	199.0	772	44.5	44.5	BDL
K17	BDL	30.6	62.9	5.8	24.9	70.6	BDL	19.9	74.6	527	36.1	22.8	BDL
K18	BDL	595.0	78.4	7.8	40.2	140.5	BDL	47.4	84.7	565	32.5	23.8	2.3
K19	BDL	32.3	79.7	BDL	31.1	73.7	BDL	20.8	95.3	565	49.8	31.5	BDL
K20	BDL	51.5	133.1	15.1	40.2	144.1	BDL	34.2	189.0	745	55.8	36.1	BDL
K21	22.4	71.8	93.3	BDL	43.9	507.1	BDL	43.6	109.4	424	45.6	32.8	3.2
K22	BDL	102.1	120.0	12.4	44.5	760.0	5.7	50.7	79.1	383	32.9	26.8	2.5
K23	BDL	29.4	53.5	BDL	23.9	156.6	BDL	21.6	82.8	408	25.6	17.1	1.8
K24	BDL	17.5	59.0	BDL	24.8	59.7	BDL	15.6	161.0	601	23.9	20.1	2.0
K25	BDL	12.4	76.0	BDL	20.7	28.9	BDL	9.8	64.4	399	13.5	11.7	1.2
K26	18.3	26.6	79.4	BDL	21.7	155.8	BDL	21.7	72.9	463	23.0	16.3	BDL
Min	18.3	12.4	5.5	5.8	10.9	28.9	4.1	7.7	41.7	12	13.5	11.7	1.2
Max	69.0	595.0	345.3	15.1	64.1	103,300.0	356.2	37,840.0	369.0	3,480	109.4	62.9	5.9
Mean	39.8	76.4	73.0	10.3	29.8	10,441.8	107.6	3,622.7	151.6	797	52.7	37.0	2.8

BDL Below detection limit.

*g/kg.

of the water such as color and odor are significantly changed.

At K5 and K6 stations on tributaries running from the Akta's town, anomalous Fe concentrations were found. The highest Fe concentrations were determined at K5, K6 and K7 stations and they decrease towards the down stream. Iron causes organic decomposition, decrease in oxygen and it transformation to hydroxide and precipitation of iron hydroxide. Similarly, in stagnant ponds of rivers, particularly following the floods, iron rapidly reproduces bacteria which form iron-material accumulation in the pond. High iron concentrations along the river mostly facilitates transformation of microfauna. When iron concentration is higher than 1 mg/l or more, it is harmful to fishes (Topbas, Brohi, & Karaman, 1998). Therefore, iron concentration should be controlled.

Sediment samples collected at K9 and K10 stations in the vicinity of stock site of lead–zinc facility established in the Ortatepe area have high metal concentrations. K14 station on the tributary running from the Gümüsler area shows high heavy metal concentrations due to presence of metal-bearing rocks in this area (Yalcin, 1995). However, concentrations of As, Ni, Ti, Fe and Cr are higher than other metals. Following the K15 and K16 stations, new spring waters join to the creek. Therefore, there is an irregularity in metal concentrations of K15, K16 and K17 stations. Water at the K16 station is clear and has no odor. However, K17 and K18 stations around the

Table II Abundance of heavy elements in the earth crust and their acceptable limits

Elements	Concentration in soil (mg/kg) (Maynard, 1983; Wedepohl, 1969–1978; Connor & Shacklette 1975; Brooks, 1972)	Concentration in shale (mg/kg) (Cagatay, 1993)	Concentration in the earth crust (mg/kg) (Cagatay, 1993)	Acceptable limit in Turkey (mg/kg) (Anonymous, 2005)
Fe	2.1×10^4	4.7×10^4	5.4×10^4	–
Cu	15	50	50	50
Pb	17	20	12.5	50
Zn	36	90	70	150
Cd	0.1–0.5	0.3	0.15	1
Ni	17	80	75	30
Cr	43	100	100	100
Co	10	20	20	20
Mn	320	850	1,000	–
Ti	–	4,500	5,000	–
Sn	10	6	2.5	20
As	7.5	10	1.8	20
Al	14.7	9.2×10^4	8.1×10^4	–

industrial areas in the Nigde city center show Eutrophication signs and are highly polluted. Odor and color of the creek water is completely deteriorated. Similar features are also shown at K19 station.

In addition to this pollution, there is also sewage waste of the city at K20 station lower part of the refinement facility in the Tepebaglari area. The decrease in lead, zinc, aluminum and iron concentrations of sediment samples from this area is attributed to the fact that these metals are found in lesser amounts in domestic wastes by which creek water is diluted. Muddy and bad-smelling creek water is discharged to the Akkaya dam lake. Water of dam lake is also muddy and bad-smelling. Sediment samples collected from the base of dam show similar heavy metal contents with those from the Karasu creek (K21–K26 stations). It is believed that heavy metals are transported with the Karasu water and deposited at the base of the Akkaya dam. Moreover, anomalies similar to other stations are observed at the exit of dam (K26 station).

According to results of analyses for the soil samples, high positive correlations were found for Al–Co, Fe–

Table III Correlations of heavy metals in sediment samples from the Karasu creek

	Co	Cu	As	Sn	Ni	Zn	Cd	Pb	Al	Fe	Ti	Cr	Mn
Co	1												
Cu	−0.183	1											
As	0.032	−0.056	1										
Sn	0.044	0.054	0.303	1									
Ni	0.116	0.250	−0.245	0.187	1								
Zn	0.065	−0.097	0.939**	0.272	−0.339*	1							
Cd	0.078	−0.087	0.973**	0.264	−0.384*	0.977**	1						
Pb	0.080	−0.085	0.975**	0.262	−0.389*	0.969**	0.999**	1					
Al	0.515**	−0.165	0.605**	0.317	−0.154	0.558**	0.595**	0.604**	1				
Fe	0.867**	−0.174	0.204	0.198	0.150	0.235	0.228	0.230	0.699**	1			
Ti	0.508**	−0.028	0.433*	0.117	−0.122	0.413*	0.434*	0.437*	0.742**	0.582**	1		
Cr	0.491*	−0.135	−0.258	0.056	0.652**	−0.234	−0.313	−0.321	0.077	0.404*	0.077	1	
Mn	0.227	−0.029	−0.329	−0.011	−0.102	−0.254	−0.266	−0.271	0.003	0.138	0.018	−0.051	1

*Correlations is significant at the 0.05 level.

**Correlations is significant at the 0.01 level.

Co, Ti–Co, Zn–As, Cd–As, Pb–As, Al–As, Cr–Ni, Cd–Zn, Pb–Zn, Al–Zn, Pb–Cd, Al–Cd, Al–Pb, Fe–Al, Ti–Al and Ti–Fe elements. Moderately positive correlations were obtained for Cr–Co, Ti–As, Ti–Zn, Ti–Cd Ti–Pb and Cr–Fe elements and weak to moderately negative correlations were determined for Zn–Ni, Cd–Ni, Pb–Ni and Cr–Cd elements (Table III). Therefore, it is thought that metals with high positive correlations are the source of pollution.

4 Conclusions

The maximum concentrations of samples collected along the Karasu creek were found to exceed their acceptable limits in soil, shale, earth crust and Turkish National Soil Pollution Control Regulation. High metal concentrations in the study area show a toxic effect. On the basis of correlation table, it was found that heavy metal contents have a similar source. The heavy metal accumulations along the creek and at the base of Akkaya dam are originated from industrial activities, Pb–Zn mine, tributaries and domestic wastes. Eutrophication is developed in the Karasu creek and the Akkaya dam which causes bad smelling around the dam area. Eutrofied Karasu creek is threatened by swamp danger. It is thought that due to high iron concentration, microflora will be significantly changed, no fish will be in life along the creek and even in the Akkaya dam lake. Urgent measures should be taken and protections zones must be defined along the Karasu creek. The absolute (0–300 m), short-distance (300–1,000 m) and moderate-distance (1,000–2,000 m) protections zones should be established until the Akkaya dam. In addition, domestic and industrial wastes have to be collected in a separate site and they should be discharged to the Karasu creek following their refinement.

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