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Assessment of concentration physicochemical parameters and heavy metals in Kızılırmak River, Turkey

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ABSTRACT

Kızılırmak is the longest river of Turkey and the most important one as a resource for various water uses. Therefore Kızılırmak river basin is under pressure from a diverse range of human activities. Six stations were sampled along the Kızılırmak river located in Nevsehir city during 2013–2014 seasonally. The physico-chemical parameters (water temperature, biological oxygen demand (BOD), chemical oxygen demand (COD), pH, dissolved oxygen (DO), conductivity, nitrite (NO_3), ammonium (NH_4), ammonia (NH_3), phosphate (PO_4), sulfate (SO_4) and some metal concentrations (Zn, Cu, B, Cr, Ni, Pb, Hg, As, Se, Sb, Mn, Cd and Al) were measured in the water samples to determine the water quality of the Kızılırmak river. When the water quality classes were examined in terms of the measured physico-chemical parameters, it was detected that the river is IV. class for nitrite, III. class for BOD, phosphate and pH, II. class for NH_4–N. The results showed that the heavy metal concentrations in water of the Kızılırmak river were within the quality class I. limits of the EPA and WPCR.

Keywords: Heavy metals; Physico-chemical parameters; Kızılırmak river; Water quality

1. Introduction

Water is a resource that has many uses, including recreational, transportation, hydroelectric power, agricultural, domestic, industrial and commercial uses. Water also supports all forms of life and affects our health, lifestyle and economic well-being [1].

Runoff, atmospheric deposition, domestic and industrial effluent discharges are the major source of aquatic pollution and physico-chemical characteristics such as PO_4–P and the pH of aquatic ecosystems may determine stream water ecosystem integrity [2]. Surface water has both organic and inorganic based pollution related to uncontrolled agricultural and industrial activities [1].

Agricultural originated nutrients like nitrate, nitrite and phosphate, which comes from various sources, are the main cause of pollution of the rivers in watersheds especially in residential areas (such as: fertilizers, detergents, domestic wastewater etc.) [3–9]. The presence of nutrients in rivers may be attributed to the process of organic mineralization of nitrates and phosphate derived principally from surface runoffs from the immediate vicinity (forests, farms and settlement) and perhaps by in situ mineralization [10].

The quality of water in the river system is seriously affected by pollutants which enter through sources that bring domestic and industrial effluents. These pollutants change the physical and chemical characteristics of water which in turn affects the aquatic life. Heavy metals are among one of the pollutants of freshwater [11,12].

The pollution of water resources due to indiscriminate disposal of pollutant has been causing worldwide

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concern in the recent years [13]. Heavy metal pollution is a quickly growing problem for water systems, such as oceans, lakes, and rivers in the areas with intensive industry. There are several different ways that heavy metal pollution ends up in our oceans, lakes and bays. The four main ways are: burning heavy metal, heavy metal runoff, dumping of heavy metals, and tributary inflow. Roadways and automobiles are also considered to be one of the largest sources of heavy metals. Zinc, copper, and lead are three of the most common heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff. Meanwhile, they are natural components of the Earth's crust [1].

Monitoring of stream water physico-chemical characteristics and heavy metal concentration is necessary to establish the levels of contamination in freshwater. Pearson correlation analysis was adopted to analyze and establish inter-metal relationship and physico-chemical characteristics of the stream water [2].

Kızılırmak River receives substantial loads of nutrients, trace metals and other compounds, resulting from anthropogenic activities within its catchment [14].

Agriculture and domestic pollutants have been discharged to Kızılırmak river a long time. The present study aims to:

1. Investigate the seasonal changes in physicochemical properties of Kızılırmak River.
2. Determine the concentration and distribution of thirteen heavy metals in water and to determine the main sources of heavy metals in the study area.

2. Materials and methods

Kızılırmak River is the most important river in Turkey. It has a catchment area of 78,000 km^2, which covers approximately 11% of Turkish territory. The Kızılırmak River, with a length of 1,355 km, is the longest river in Turkey. It has a precipitation potential of $3.6 \times 1,010$ m^3. River is being used for a variety of agricultural, industrial, drinkable water and recreational activities thus largely contributing to the economy of the region [15].

The study area is located in the Nevsehir city (Fig. 1). Twenty-four water samples were collected from six stations seasonally from August 2013 to May 2014. There are six stations selected among different pollution points (sewage water, agriculture area, detergents etc.) in order to characterize the river.

Water samples were collected by using sample bottles of 500 ml for metals and 1 L for physicochemical parameters. The samples were stored at +4°C until they were analyzed. Samples were analyzed for eleven physicochemical parameters: PO_4, SO_4, NH_4–N, COD, BOD, NO_2, DO, NO_3, Temperature, pH, Conductivity and thirteen metals: Al, Hg, Zn, Pb, As, Se, Cr, Ni, B, Cu, Cd, Sb, Mn.

The water temperature, pH, conductivity and dissolved oxygen were measured with multi parameter analyzer (HQ 40D) in the field. Physico-chemical parameters analyses such as nitrate, nitrite, ammonium, sulfate, phosphate, COD, BOD were carried in accordance with standard methods [16].

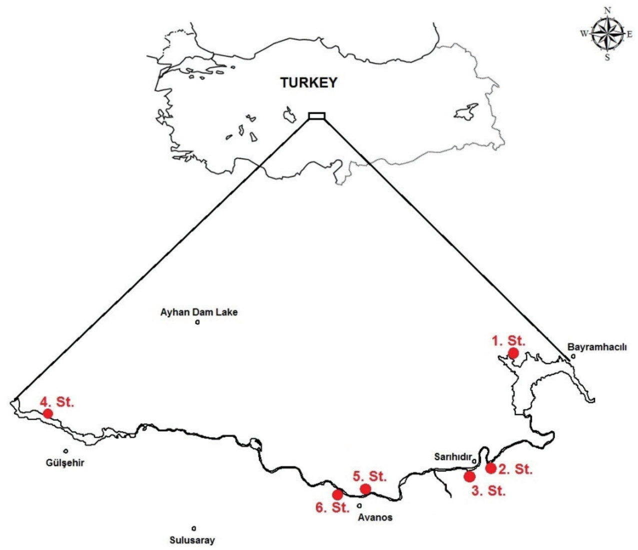

Fig.1. Sampling stations of Kızılırmak River located in Nevsehir.

Heavy metal samples were filtered immediately after transporting them to the laboratory (0.45 µm Millipore filter) and HNO_3 was added to the samples until it becomes pH = 2. All metals were determined by direct aspiration of the sample solution into Perkin Elmer ICP-OES 7000 [17]. Each sample was analyzed in triplicate.

The accuracy of the analytical procedure was checked by analyzing the standard reference materials. Recovery rates ranged from 99% to 100% for all investigated elements.

The mean and standard deviations of the physicochemical parameters and metal concentrations have been calculated in accordance with both stations and seasons. Student *t*-test ($p < 0.05$) was used in order to find whether there is a change between the stations or the seasons. Correlations between physicochemical properties and metal concentrations were made with Pearson correlation coefficients [18,19]. Statistical analysis of the data was carried out using SPSS 19.0.

Results of physico-chemical parameters were compared according to the Turkish Water Pollution Control Regulations while concentrations of heavy metals were compared according to the Turkish Water Pollution Control Regulations [20] and Environmental Protection Agency.

3. Results and discussion

Distributions of physico-chemical parameters by stations are displayed in the Table 1. Differences at the stations for SO_4, NH_4–N, PO_4–P, conductivity and dissolved oxygen were found statistically important ($p < 0.05$). Statistical differences have not been observed for the other physicochemical parameters.

Phosphorus is important to all living organisms. However, excessive phosphorus causes algae blooms, which are harmful to most aquatic organisms. They may cause a decrease in the DO levels of the water, and in

Table 1
Concentrations of the physicochemical parameters in the water according to the stations by mean value, standard deviation and min–max

Station		SO_4	NH_4–N	NO_2	NO_3	PO_4–P	KOI	BOI	Temp	pH	Con	DO
1	Mean ± SD	152.25 ± 33.36	0.223 ± 0.26	0.063 ± 0.03	0.275 ± 0.29	0.069 ± 0.56	14.45 ± 1.5	10.45 ± 2.8	14.98 ± 5.2	8.717 ± 0.5	1,408.5 ± 131	13.597 ± 2.9
	Min	105	0.033	0.026	0.09	0.02	13.2	6.5	9.8	8.07	1,228	10.07
	Max	183	0.602	0.080	0.72	0.15	16.2	13.1	21.3	9.21	1,543	16.9
2	Mean ± SD	200.75 ± 14.43	0.422 ± 0.34	0.130 ± 0.05	0.865 ± 0.816	0.025 ± 0.03	9.71 ± 5.4	13.2 ± 2.6	12.5 ± 3.5	8.435 ± 0.5	1,532 ± 52	8.442 ± 2.0
	Min	187	0.026	0.056	0.335	0.002	4.64	9.8	8.6	7.88	1,459	6.67
	Max	221	0.835	0.174	2.08	0.069	14.7	15.8	16.3	9.08	1,581	10.9
3	Mean ± SD	184.75 ± 7.27	0.387 ± 0.25	0.095 ± 0.029	0.722 ± 0.93	0.035 ± 0.02	5.61 ± 2.4	10.78 ± 1.6	12.13 ± 3.2	8.65 ± 0.5	1,537 ± 21	9.722 ± 1.9
	Min	178	0.122	0.053	0.01	0.015	3.11	8.7	8.5	8.07	1,506	7.63
	Max	192	0.691	0.120	2.100	0.060	8.67	12	15.5	9.12	1,548	11.96
4	Mean ± SD	176.75 ± 5.44	0.237 ± 0.19	0.097 ± 0.045	0.073 ± 0.021	0.037 ± 0.03	11.43 ± 5.5	15.35 ± 9.1	15.42 ± 5.0	8.913 ± 0.6	1,529 ± 29	12.505 ± 3.6
	Min	169	0.063	0.050	0.050	0.02	6.66	9	10	8.21	1,495	9.05
	Max	181	0.463	0.138	0.092	0.078	16.5	28.4	19.89	9.41	1,158	17.49
5	Mean ± SD	191 ± 7.53	0.397 ± 0.27	0.116 ± 0.048	0.926 ± 0.91	0.055 ± 0.02	7.27 ± 2.7	9.9 ± 1.9	12.95 ± 3.3	8.645 ± 0.5	1,545 ± 15	8.905 ± 0.9
	Mmin	182	0.112	0.05	0.425	0.027	4.5	8.2	9.6	8.05	1,528	7.65
	Max	200	0.743	0.160	2.3	2.3	10.3	12.6	17.3	9.3	1,563	9.65
6	Mean ± SD	170 ± 25.65	4.508 ± 4.35	0.121 ± 0.048	0.99 ± 0.87	0.965 ± 1.10	12.85 ± 4.81	18.53 ± 6.1	13.25 ± 3.8	8.537 ± 0.4	1,542 ± 32	9.205 ± 1.1
	Min	142	0.594	0.054	0.45	0.002	7.5	12	8.9	8.01	1,502	7.9
	Max	196	9.93	0.161	2.3	2.3	17.4	25.2	17.1	8.9	1,576	10.45
F		3.289*	3.633*	1.267	1.060	2.766*	2.748	1.95	0.437	0.427	2.985*	3.405*

Table 2
Concentrations of the heavy metals in the water according to the seasons by mean value, standard deviation and min–max

Season		Al	Hg	Zn	Pb	As	Se	Cr	Ni	B	Cu	Cd	Sb	Mn
Summer	Mean ± SD	49.65 ± 49.13	0.00 ± 0.00	0.223 ± 0.26	0.063 ± 0.03	0.275 ± 0.29	0.069 ± 0.56	14.45 ± 1.5	10.45 ± 2.8	14.98 ± 5.2	8.717 ± 0.5	1,408.5 ± 131	13.597 ± 2.9	17.376 ± 4.46
	Min	8.61	0.00	0.033	0.026	0.09	0.02	13.2	6.5	9.8	8.07	1,228	10.07	11.940
	Max	125.76	0.00	0.602	0.080	0.72	0.15	16.2	13.1	21.3	9.21	1,543	16.9	23.359
Autumn	Mean ± SD	19.50 ± 6.32	0.03 ± 0.005	0.422 ± 0.34	0.130 ± 0.05	0.865 ± 0.816	0.025 ± 0.03	9.71 ± 5.4	13.2 ± 2.6	12.5 ± 3.5	8.435 ± 0.5	1,532 ± 52	8.442 ± 2.0	15.77 ± 3.08
	Min	14.28	0.00	0.026	0.056	0.335	0.002	4.64	9.8	8.6	7.88	1,459	6.67	11.940
	Max	29.15	0.01	0.835	0.174	2.08	0.069	14.7	15.8	16.3	9.08	1,581	10.9	20.33
Winter	Mean ± SD	28.71 ± 20.49	0.37 ± 0.19	0.387 ± 0.25	0.095 ± 0.029	0.722 ± 0.93	0.035 ± 0.02	5.61 ± 2.4	10.78 ± 1.6	12.13 ± 3.2	8.65 ± 0.5	1,537 ± 21	9.722 ± 1.9	25.832 ± 6.67
	Min	14.1	0.3	0.122	0.053	0.01	0.015	3.11	8.7	8.5	8.07	1,506	7.63	15.307
	Max	68.81	0.616	0.691	0.120	2.100	0.060	8.67	12	15.5	9.12	1,548	11.96	32.315
Spring	Mean ± SD	3.87 ± 1.34	0.04 ± 0.042	0.237 ± 0.19	0.097 ± 0.045	0.073 ± 0.021	0.037 ± 0.03	11.43 ± 5.5	15.35 ± 9.1	15.42 ± 5.0	8.913 ± 0.6	1,529 ± 29	12.505 ± 3.6	7.032 ± 11.11
	Min	2.39	0.10	0.063	0.050	0.050	0.02	6.66	9	10	8.21	1,495	9.05	1.57
	Max	6.20	0.11	0.463	0.138	0.092	0.078	16.5	28.4	19.89	9.41	1,158	17.49	29.67
F		3.055	19.264**	16.789**	0.086	14.918**	46.601**	47.676**	21.122**	255.759**	8.855**	15.859**	144.911**	7.214*

Table 3
Mean physicochemical parameters* according to seansons and station

Parameters	Mean	WPCR			
		Class			
		I	II	III	IV
Temperature	12.1	25	25	30	>30
pH	8.6 III	6.5–8.5	6.5–8.5	6–	Except 0–9
DO	10.3	8	6	3	>3
Conductivity	1,515.7	–	–	–	–
Phosphate	0.23 III	0.02	0.16	0.65	>0.65
Sulphate	179.2	200	200	400	>400
Ammonium	0.9 II	0.2	1	2	>2
Nitrite	0.1 IV	0.002	0.01	0.05	>0.05
Nitrate	0.61	5	10	20	>20
BOD	13.03 III	4	8	20	>20
COD	10.2	25	50	70	>70

Note: WPCR: Turkish Water Pollution Control Regulations (2012).
*For all physicochemical parameters (except pH, Conductivity and Temperature), the measuring unit is mg/l; for Conductivity µs/cm; for temperature C°.

Table 4
Mean heavy metals* according to seansons and station

Heavy metals		WPCR				
		I	II	III	IV	EPA** (µg/l)
Al	25	300	300	1,000	>1000	–
Hg	0	0.1	0.5	2	>2	2
Zn	0.01	200	500	2,000	>2000	120
Pb	0	10	20	50	>50	65
As	0.014	20	50	100	>100	–
Se	0.001	10	10	20	>20	10
Cr	0.004	20	50	200	>200	16
Ni	0.011	20	50	200	>200	470
B	0.18	1	1	1	1	0.75 (mg/l)
Cu	0.006	0.02	0.05	0,2	0.2	0.013 (mg/l)
Cd	0	3	5	10	>10	4
Sb	0	–	–	–	–	–
Mn	0.015	100	500	3,000	>3,000	

*For all physicochemical parameters (except Al, B and Cu) the measuring unit is µg/l; for the others mg/l.
**Environmental Protection Agency (2001).

Table 5
Pearson correlation between physicochemical parameters and heavy metals

	PO_4–P	SO_4	NH_4–N	COD	NO_2	BOD	NO_3	Al	Hg	Zn	Pb	As	Se	Cr	Ni	B	Cu	Cd	Sb	Mn	Temp	pH	DO
PO_4–P	1																						
SO_4	−0.40	1																					
NH_4–N	0.87**	−0.39	1																				
COD	0.20	−0.35	0.05	1																			
NO_2	0.04	0.43*	−0.02	0.01	1																		
BOD	0.61**	−0.18	0.55**	0.32	−0.08	1																	
NO_3	0.38	0.24	0.20	−0.16	0.49*	0.25	1																
Al	−0.9	−0.64**	−0.06	0.18	−0.44*	−0.30	−0.43*	1															
Hg	−0.14	0.24	−0.09	0.41*	0.49*	−0.18	−0.03	−0.04	1														
Zn	−0.27	0.07	−0.21	0.19	0.45*	−0.38	−0.32	0.00	0.51*	1													
Pb	−0.11	−0.58**	−0.08	0.24	−0.17	−0.09	−0.08	0.73**	0.09	0.04	1												
As	0.20	−0.11	−0.03	0.22	−0.09	0.31	0.56**	0.00	−0.17	−0.55**	0.33	1											
Se	0.23	0.16	0.03	0.17	0.27	0.53**	0.67**	−0.51*	−0.09	−0.32	−0.02	0.78**	1										
Cr	0.32	0.12	0.09	0.21	0.18	0.38	0.77**	−0.28	0.07	−0.48*	0.09	0.89**	0.83**	1									
Ni	0.21	0.12	0.13	−0.19	−0.28	0.30	0.38	−0.12	−0.26	−0.59**	−0.22	0.19	0.12	0.33	1								
B	−0.23	−0.08	−0.03	−0.2	−0.13	−0.47*	−0.73**	0.34	0.26	0.54**	−0.04	−0.85**	−0.88**	−0.84**	−0.33	1							
Cu	−0.18	−0.02	−0.06	−0.23	−0.20	−0.42*	−0.44*	0.33	−0.11	0.31	−0.01	−0.59**	−0.65**	−0.64**	0.06	0.66**	1						
Cd	−0.20	0.26	−0.05	−0.01	0.47*	−0.48*	−0.15	0.02	0.73**	0.78**	0.04	−0.47*	−0.37	−0.30	−0.52**	0.55**	0.16	1					
Sb	0.12	0.12	−0.08	0.23	0.29	0.42*	0.63**	−0.39	0.04	−0.25	0.12	0.82**	0.94**	0.83**	0.03	−0.91**	−0.76**	−0.28	1				
Mn	−0.17	0.08	0.02	0.23	0.03	−0.34	−0.52**	0.07	0.48*	0.59**	−0.13	−0.59**	−0.58**	−0.48*	−0.31	0.63**	0.25	0.62**	−0.47*	1			
Temp	0.20	−0.37	0.13	−0.04	−0.70**	0.40	−0.01	0.34	−0.61**	−0.73**	0.19	0.37	0.05	0.17	0.66**	−0.35	−0.00	−0.80**	0.04	−0.40	1		
pH	−0.10	−0.00	−0.20	0.43*	0.39	0.18	0.25	−0.13	0.47*	0.17	0.26	0.43*	0.57**	0.50*	−0.19	−0.48*	−0.53**	0.10	0.70**	−0.02	−0.21	1	
DO	−0.10	−0.33	−0.18	0.49*	−0.25	0.28	−0.14	0.15	0.12	−0.11	0.32	0.42*	0.31	0.27	−0.04	−0.41*	−0.40	−0.29	0.51*	0.03	0.32	0.64**	1
Cond	0.09	0.44*	0.08	−0.35	0.46*	0.33	0.38	−0.56**	0.00	0.07	−0.41*	−0.22	0.20	0.02	0.33	−0.27	−0.20	−0.02	0.19	−0.06	−0.01	0.16	−0.04

some cases temperature rise. This can result in a fish kill and the death of many organisms [14]. Phosphorus compounds are present in many fertilizers and detergents, industrial and domestic sewage. Presence of phosphorus in large quantities in water bodies will lead to the eutrophication of the waterways by excessive growth of algae [3]. In our study, the lowest average PO_4–P, was measured at the station 2 as 0.025 mg/L, however, the highest PO_4–P was found as 0.965 mg/L at station 6. Discharge of domestic wastewater and untreated sewage of agricultural activities in region, and sizable decrease of water flow rate, are principal reasons of pollution increase [21].

The lowest average NH_4–N, was measured at the station 1 as 0.223 mg/L, however, the highest NH_4–N, was found as 4.508 mg/L at station 6. The major sources of nitrates and nitrites in the water surface are chemical fertilizers, industrial and domestic sewage, leaks from septic tanks and erosion of the natural deposits. Ammonia is produced when nitrogenous organic matter is destroyed by microbiological activity [3]. Station six is located where the wastewater treatment plant of Avanos Municipality is discharged. The highest BOD was measured at station 6 as 18.53 mg/l. Station 6 with high BOD have high nutrient levels in water. Kızılırmak River receives high load of municipal sewage daily.

The values of heavy metal concentrations in water are presented in Table 2. Seasonal differences of concentrations Al and Pb in water were not observed statistically important; however differences of other metals were found statistically important ($p < 0.01$).

It has been observed that the values determined in the study are lower than the average scale values that Bakan et al. had reported. They noticed that metal quality indices both for water and sediment measurements indicate that the river has medium quality of lead pollution which may be caused by automobile exhausts and urban storm runoff. Their research had studied at nine stations that were in downstream of Kızılırmak River. Results showed that increased lead accumulation in the downstream.

The evaluation of the physico-chemical and heavy metal results were made based on WPCR [20–22] and EPA were shown in Table 3 and 4.

While the concentrations of NO_2 was the 4th Grade Quality according to WPCR, concentrations of BOD, phosphate and pH were the 3rd grade. Additionally concentration of NH_4–N was the 2nd grade (Table 3). According to WPCR, water quality of the Kızılırmak river may fall in categories III and IV [23].

The order of concentrations of metals in Kızılırmak river from high to low was: Al > B > Cu > Mn > As > Ni > Zn > Cr > Se > Hg = Pb = Cd = Sb. Akbulut et al. [23] found that heavy metals levels: Si > Fe > Al > Mn > As > Ni > Se > Cd. According to Water Pollution Control Regulations and EPA, mean metal concentrations of water samples were under the limit values (Table 4).

To investigate the correlation between of metals and physicochemical parameters, Pearson correlation analyses were calculated. The results are shown in Table 5. In waters, correlations between PO_4–P and NH_4–N and BOD were significant at the $p < 0.01$. The relationship supports the definition BOD.

4. Conclusions

The obtained results showed that the heavy metal concentrations in water of the Kızılırmak river were within the quality I. class limits of the EPA and WPCR. On the study area, the most significant forms of pollution is agriculture and sewage based. The highest values of pollution observed at Kızılırmak are concentrations of nitrite and phosphate. As a result of this study, it can be said that residential stations pose danger in terms of pollution, based on the data obtained. Therefore, discharge of untreated household waste and sewage from the residential areas in the region must be prevented. In order to track immediate discharges, water quality of the river should be monitored within short intervals.

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