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Integrated Environmental Quality Assessment of Kızılırmak River and its Coastal Environment

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Abstract

Kızılırmak River receives substantial loads of nutrients, trace metals and other compounds, resulting from anthropogenic activities within its catchment. The main aims of this research were to evaluate spatial and seasonal trends in water discharge, nutrients and trace metals and also to compare data with water and sediment quality criteria and with certain quality indices such as water quality index (WQI), sediment quality index (SQI) and trophic state index (TSI), identifying the environmental pressures and assessing the impact of the loads to the coastal environment. Nine stations were sampled within the main stream of Kızılırmak River near to the Black Sea. Field measurements and routine laboratory water analysis were carried on the eight sampling stations seasonally. Wet sediment sample analyses were also performed for EC, pH, organic matter and moisture content within the range of 1.13-1.76 mS; 7.52-8.80; 1.41-4.60%; 18.92-33.65%, respectively. However, trace metal analyses including Cd, Ni and Pb were done by Atomic Absorption Spectroscopy (AAS) both on water and sediment samples with the total digestion methods. Since the analytical cost involved could be a limiting factor for river quality assessments in developing countries, certain quality indices were used in this study. For each type of indices calculations, different approaches from the literature were selected and compared. Calculated NSFWQI, WQI_{new} and $WQI_{min.}$ values are in good agreement and the water quality of the river is considered at medium level. For the Derbent Dam of Kızılırmak River, two different trophic level index calculations have also the same results indicating eutrophic conditions where algal growth and blooms can occur. However, certain 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 run-off.

Keywords: Environmental quality assessment, water quality, sediment quality index, trophic state index, Kızılırmak River.

Kızılırmak Nehri ve Kıyısal Çevresinin Entegre Çevresel Kalite Değerlendirilmesi

Özet

Kızılırmak, havzasındaki insan aktiviteleri nedeniyle yüksek miktarda besin elementleri, iz metaller ve diğer bileşiklerin yüklerini taşımaktadır. Bu araştırmanın ana amaçları; su deşarjları, besin elementleri ve iz metallerinin yersel ve mevsimsel değişimlerini değerlendirme; ayrıca verileri, su ve sediment kalite kriter değerleriyle karşılaştırma ve belli kalite indisleriyle örneğin su kalite indeksi (WQI), sediment kalite indeksi (SQI) ve trofik durum indeksi gibi, çevresel baskıları ve kirlilik yüklerinin kıyısal çevrede neden olduğu etkileri değerlendirmektir. Kızılırmak Nehrinin ana kolunda, Karadeniz'e deşarj ağzına yakın dokuz istasyondan numune alınmıştır. Arazi çalışmaları ve rutin laboratuar su analizleri 8 örnekleme noktasında mevsimsel olarak yürütülmüştür. Islak sediment numune analizlerinde, EC, pH, organik madde ve nem içeriği ölçülmüş ve 1,13-1,76 mS; 7,52-8,80; %1,41-4,60; %18,92-33,65 sıralamasında bulunmuştur. Diğer yandan, iz metal analizleri (Cd, Ni, ve Pb içeren) Atomik Absorpsiyon Spetroskopisi (AAS) cihazıyla hem su, hem de sediment örneklerine toplam sindirim metodu uygulanması sonrası ölçülmüştür. Gelişmekte olan ülkelerde Nehir kalitesi değerlendirmede, yüksek analitik ölçüm maliyeti, çalışmaların yürütülmesinde sınırlayıcı bir faktör olduğu için, bu çalışma da belli kalite indisleri kullanılmıştır. Her tip indis hesabı için, literatürden farklı yaklaşımları seçilmiş ve karşılaştırılmıştır. Hesaplanmış NSFWQI, WQI_n, WQI_{min}, değerleri, birbirleriyle uyumludur ve nehrin su kalitesinin orta seviyede olduğunu belirtmektedir. Kızılırmak üzerinde kurulu Derbent Barajı için iki farklı trofik durum indeks hesaplanması aynı sonuçları vermiştir. Bu durum, barajda ötrofik yapı olduğunu dolayısıyla algal yoğunluktaki artış ve alg patlaması olabileceğini belirtmektedir. Ayrıca, belli metal kalite indisleri hem su hem de sediman ölçümleri için hesaplandığında, nehrin orta kalitede, otomobil ekzosları ve kentsel akışlardan meydana gelebilen kurşun kirliliğine sahip olduğunu belirtmektedir.

Anahtar Kelimeler: Çevresel kalite değerlendirme. su kalite indeksi. sediman kalite indeksi. trofik durum indeksi. Kızılırmak.

Introduction

Rivers are dynamic systems and may change in nature several times during their course because of changes in physical conditions such as slope and bedrock geology. They carry horizontal and continuous one-way flow of a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources. This matter moves downstream and is subject to intensive chemical and biological transformations. The surface water chemistry of a river at any point reflects several major influences, including the lithology of the catchment, atmospheric inputs, climatic conditions and anthropogenic inputs. Identification and quantification of these influences should form an important part of managing land and water resources within a particular river catchment (Bellos and Swaidis, 2005).

The objectives of this research were to evaluate spatial and seasonal trends in water discharge, nutrients and trace metals and also to compare data with water and sediment quality criteria and with certain quality indices such as water quality index (WQI), Sediment quality index (SQI) and Trophic State Index (TSI), identifying the environmental pressures and assessing the impact of the loads to the coastal environment.

Water quality is a major concern all around the world, as water uses are threatened by generalized contamination resulting from human activities. This contamination concerns sediments as well as chemicals and microbiological components coming from industrial, municipal or agricultural point and non-point sources of pollution. Generally, intensification of agriculture in the last decades has been singled out as the most important non-point source of water pollution. This mainly concerns nutrients, nitrogen and phosphorus which are transported from fertilized agricultural lands to surface waters via runoff and erosion and accelerate the eutrophication process. However, this diffuse pollution is also the most difficult to control. This is why disease prevention and environmental protection require intensive monitoring and accurate assessment of water quality in rivers. In environmental management and research, water quality data become imperative to assess the water quality status; to study the controlling processes of water pollution; to define and apply environmental objectives to restore or improve water quality; to assess the effects of best management practices in a watershed and to calibrate hydraulically and water quality models (Quilbe *et al*., 2006).

However, with the growing interest in the rules that govern the fate of pollutants in urban environments, the sediments of urban rivers pose a particularly challenging scientific problem. As in natural environments, urban river sediments have a high potential for storage of trace elements. Unlike natural rivers, however, a large proportion of the trace element load contained in urban sediments is not associated with the original geologic parent material, but with the steady supply of trace elements, both dissolved and in particulate form, carried by treated and untreated urban waters. Changes in the aqueous environment to which urban sediments are exposed, could result in the release of these trace elements that have accumulated over long periods of time (Cheung *et al*., 2003 and Miguel *et al*., 2005).

The study area, Kızılırmak River is the most important river in the Black Sea region of Turkey; it supplies drinkable water and is being used for a variety of agricultural, industrial and recreational activities thus largely contributing to the economy of the region. The Kızılırmak River, with a length of 1,355 km, is the longest river in Turkey. It has a catchment area of 78,000 km^2, which covers approximately 11% of Turkish territory. It has a precipitation potential of $3{,}6\times10^{10}$ m^3. It transports approximately 831 million m^3 water annually to the Black Sea with its average 185 m^3/sec flow. The agricultural lands of Kızılırmak Delta are extensively irrigated from the canals, the river and groundwater. Kızılırmak Delta occupies 50,000 ha and includes 15,000 ha of freshwater marshes and swamps, coastal lakes, and lagoons on both sides of Kızılırmak River. Kızılırmak Delta is the largest and the most significant delta of Turkey, which preserves the natural heritage of the Black Sea Coasts. The ecosystem of the delta wetland area is very rich in biological diversity. The delta, especially with its bird heritage and the dune vegetation is very attractive for fauna and flora (DSI, 1986).

It was reported that the North and Middle Basin areas of Kızılırmak River receive considerably higher pollutant loads, due to the fact that these areas are highly populated and the domestic wastewater, as well as effluents from most of the industries are discharged into the river or its tributaries without any treatment. The presence and operation of high-capacity dams significantly contribute to the natural assimilation capacity of the river since the population density of the area is over the average of Turkey population.

However, the objective of the water and sediment quality assessment is to identify the environmental pressures in the watershed of Kızılırmak River and its coastal environment, and to quantify their effects. Human activity has an enormous influence on the global cycling of nutrients due to extensive use of inorganic fertilizers, and this direct impact is reflected to Kızılırmak River water quality as well. So, environmental quality indicators and indices are a powerful tool for processing, analyzing and conveying raw environmental information to decision-makers and managers.

Water Quality Assessment

The evaluation of water quality in developing countries has become a critical issue in recent years, especially due to the concern that fresh water will be scarce resource in the future. Whereas water monitoring for different purposes is well defined (e.g., aquatic life preservation, contact recreation, drinking water use), the overall water quality is sometimes difficult to evaluate from a large number of samples, each containing concentrations for many parameters. Although any monitored parameter could be analyzed either alone or grouped according to a common feature, such analysis provides partial information on the overall quality. Mathematical-computational modeling of river water quality is possible but requires a previous knowledge of hydraulics and hydrodynamics. Besides, mathematical models require extensive validation (Pesce and Wunderlin, 2000).

The use of water quality indices (WQI) is a simple practice that overcomes many of the above mentioned problems and allows the public and decision makers to receive water quality information. WQI also permits us to assess changes in the water quality and to identify water trends. A quality index is a unit less number that ascribes a quality value to an aggregate set of measured parameters. In general, water quality indices incorporate data from multiple water quality parameters into mathematical equation that rates the health of a stream with a single number. That number is placed on a relative scale that rates the water quality in categories ranging from very bad to excellent.

Meeting water quality expectations for rivers is required to protect drinking water resources, encourage recreational activities, and provide a good environment for fish and wildlife. A general water quality index (WQI) can be used to indicate the overall water quality conditions. It assigns a number to a body of water to indicate its quality. It consists of water quality variables, such as dissolved oxygen (DO), conductivity, turbidity, total phosphorus, and fecal coliform, each of which has specific impacts to uses (Said *et al*., 2004). So, water quality indices are intended to provide a simple and understandable tool for managers and decision makers on the quality and possible uses of a given water body. The first WQI was developed in the United States and applied in Europe since 1970s, initially in the United Kingdom. The WQI approach has many variations in the literature and comparative evaluations have been undertaken (Bordalo, 2001).

There are several water quality indices that have been developed to evaluate water quality in United States and in Canada. All of these indices have eight or more water quality variables. However, most watersheds do not have long-term and continuous data for these variables. The NSF (National sanitation foundation) developed an index, called the NSF Water quality index (NSFWQI), to provide a standardized method for comparing the relative quality of various bodies of water (Table 1). Nine water quality variables are used for the index: DO, fecal coliform, pH, biochemical oxygen demand (BOD), temperature change, total phosphate, nitrate, turbidity, and total solids.

A water quality index with only three parameters, named minimal index (WQI min.) Pesce and Wunderlin (2000) calculated using dissolved oxygen, conductivity and turbidity after normalization (Table 1). The proposed a new WQI index by Said *et al*. (2004) has no need to standardize the variables and the calculations are further simplified through the elimination of sub-indices, keeping the index in a simple equation and a reasonable numerical range (Table 1). However, a general "metal index" (MI) for drinking water (Tamasi and Cini, 2004), which takes into account possible additive effects of heavy metals on the human health that helps to quickly evaluate the overall quality of drinking waters, is also used in this study (Table 2).

Sediment Quality Assessment

In decades, different sediment metal assessment indices applied to marine and freshwater environments have been developed (Careio *et al*., 2005). Each of them aggregates the concentration of metal contaminants and can be classified in three types:

Table 1. Selected water quality index calculations and evaluations

Water Quality Index	Parameters	Evaluation
NSFWQI $WQI = \prod_{i=1}^{n} SI_i^{W_i}$ (Miller *et al*., 1986)	WQI: water quality index, SI_i : subindex i, W_i : weight given to subindex i.	90–100 Excellent quality 70–90 Good quality 50–70 medium quality 25–50 bad quality 0–25 very bad quality.
$WQI_{min.}=(C_{DO} + C_{cond.} + C_{turb.})/3$ (Pesce and Wunderlin, 2000)	C_{DO}: the value due to DO after normalization;$C_{cond.}$: the value due to either conductivity or dissolved solids (TDS) after normalization;C_{turb}: the value due to turbidity after normalization.	A quality percentage, 0-100 scale, with 100 representing the highest quality.
$WQI = \log\left[\frac{(DO)^{1.5}}{(3.8)^{TP}(Turb.)^{0.15}(15)^{FCol/10000} + 0.14(SC)^{0.5}}\right]$ (Said *et al*., 2004)	DO: dissolved oxygen (% oxygen saturation), Turb: Turbidity (NTU), TP: toal phosphates (mg/l), FCol: fecal coliform bacteria (counts/100 ml),SC: specific conductivity in (MS/cm at 25°C).	The maximum or ideal value of this index is 3. From 3 to 2, the water is acceptable,<2 is marginal<1 is marginal and remediation

(i) Contamination indices: which compare the contaminants with clear and/or polluted stations measured in the study area or simply aggregates the metal concentrations;

(ii) background enrichment indices: which compare the results for the contaminants with different baseline or background levels, available in literature, that can be used for any study area; and (iii) ecological risk indices: which compare the results for the contaminants with Sediment Quality Guidelines or Values–SQG (Caeiro *et al*., 2005).

Different sediment quality indices were used in this study representing each category of sediment quality assessment indices (Table 3) such as SEF, sediment metal enrichment index at contamination index class, a new pollution index (PIN) and index of geoaccumulation (NI geo.) at background enrichment index class and finally mean sediment quality quid line quotient, SQG-Q at ecological risk index class.

Trophic State Measurements

Numerous methods have been proposed and used to measure the trophic state (TS) of lakes. These range from single nutrient (phosphorus or nitrogen) or physical (secchi disc) measurements to increasingly more complex approaches such as trophic state indices (TSIs) employing multiparameter measurements, loading models, and dynamic simulation models. Carlson's Trophic State Index (TSI) (Table 4) is a common means for characterizing a lake's trophic state and associating Secchi, Chl-*a* and phosphorus measurements (Carlson, 1977) .

However, the trophic Level Index (TLI) (Table 4) is another indicator of lake water quality (Lambou *et al*., 1983). Four parameters are combined to construct the TLI: total nitrogen, total phosphorus, clarity and Chl-*a*. The parameters reflect the dynamics of the annual lake cycle. Nitrogen and phosphorus are essential plant nutrients. In large quantities, they can encourage the growth of nuisance aquatic plants such as algal blooms. Chl-*a* is the green pigment in plants used for photosynthesis. It is a good indicator of the total quantity of algae in a lake (URL 1).

Materials and Methods

Sample Collection

Sediment and river water samples were collected from the nine sites along Kızılırmak River, the Black Sea coast of Turkey and also reservoir water sample was collected at the Derbent dam of Kızılırmak River. The sampling stations were given in Figure 1. The sampling stations were selected according to the point and non-point pollution load possibilities of the basin mainly from agricultural and minor industrial

Table 2. Different water metal quality index calculations

Metal quality ındex	Parameters	Status
Metal Index $MI = \sum_{i=1}^{N}\left[\frac{Ci}{(MAC)i}\right]$ Tamasi and Cini, 2004	MAC: maximum allowable concentration C: the concentration of each element	The higher the concentration of a metal compared to its respective MAC value, the worse the quality of the water.MI value > 1 is a threshold of warning
Pollution Index $PI = \sqrt{\frac{\left[\frac{Ci}{Si}\right]^2_{max} + \left[\frac{Ci}{Si}\right]^2_{min}}{2}}$ Caerio *et al*., 2005	Ci: concentration of metal in river water Si : national water quality criterion	Class 1 PI <1 no effect Class 2 PI : 1-2 slightly affected Class 3 PI : 2-3 moderately affected Class 4 PI : 3-5 strongly affected Class 5 PI : > 5 seriously affected

Table 3. Two different trophic index calculations

Trophic Index	Parameters	Evaluation
Carlson's Trophic State Index TSI (TSIP)=14.42*[ln(TP average)]+4.15 TSI (TSIC)=9.81*[ln(Chl-*a* average)]+30.6 TSI (TSIS)=60-(14.41*[ln(Secchi average)]) (Carlson, 1977)	Total phosphorus and Chl-*a* are measured in micrograms per liter Secchi disk transparency is measured in meters.	The TSI scale ranges from 0 (ultra-oligotrophic) to 100 hypereutrophic). 40-50 mesotrophy (moderate productivity)>50 eutrophy (high productivity) <40 oligotrophy (low producitivity).
Trophic Level Index TLn=-3.61+3.01 log(TN) TLp=0.218+2.92 log(TP) TLs=5.10+2.27log (1/SD–1/40) TLc=2.22+2.54log(Chl-a) TLI=(TLn+TLp + TLs + TLc)/4 (www.ebop.govt.nz/Water/Lakes/TrophicLevel.asp)	Total nitrogen (TN), Total Phosphorus (TP), Secchi Disc (SD) Chlorophyll–a (Chl-*a*)	The higher the TLI, the lower the water quality.

Table 4. Selected Sediment Quality Index Calculations and Evaluation

Sediment Quality Index	Parameters	Evaluation
Sediment Enrichment Factor $SEF = \frac{C_i - C_0}{C_0}$ (Riba *et al*., 2002)	C_i: the total concentration of each metal i measured in the sediment , C_0: the heavy metal background level established for the ecosystem studied.	< 1 crustal origin > 1 anthropogenic origin
A new pollution index $PIN = \sum_{i=1}^{n} \frac{W^2{}_i C_i}{B_{1i}}$ (Ott, 1978)	Wi: the class of contaminant i considering the degree of contamination (from 1 to n=5), C_i: the concentration of the contaminant i, B_{1i}: the concentration of contaminant i in Class 1 (baseline value-clean sediments).	Class 1 (clean) : [0-7] Class 2 (trace cont.) : [7-95.1] Class 3 (lightly cont.) : [95.1–518.1] Class 4 (contaminated) : [518.1–2548.6] Class5 (highly cont.) : [2548.6-∞]
Index of geoaccumulation $NI_{geo} = \ln \frac{C_n}{1.5xB_n}$ (Ruiz, 2001)	B_n: the concentration of the metal n in unpolluted sediments, C_n : the concentration of the metal.	Unpolluted $NI_{geo.}<1$ Very lightly polluted $1<NI_{geo.}<2$ Lightly polluted $2<NI_{geo.}<3$ Moderately polluted $3<NI_{geo.}<4$ Highly polluted $4<NI_{geo.}<5$ Very highly polluted $NI_{geo.}>5$
Mean sediment quality quideline quotient $SQG-Q = \frac{\sum_{i=1}^{n} PEL-Q_i}{n}$ $PEL-Q = \frac{contaminant}{PEL}$ (Long and MacDonald, 1998)	PEL: the probable effect level PEL–Q : the probable effect level quotient	SQG-Q ≤ 0.1 unimpacted; lowest potential for observing adverse biological effects 0.1< SQG –Q <1 moderate impact potential for observing adverse biological effect SQG-Q ≥1 highly impacted potential for observing adverse biological effects.

activates. The samples collected from each site consisted of 3-4 composite samples. Water was collected in 5 liter plastic bottles. Sediments (top 5-10 cm. of surface) were collected by benthic Ekman-Bridge grab sampler. They were transported to the laboratory immediately. Water samples were stored at 4°C and sediments were freeze-dried before analysis. This sampling program was run through the year (2004-2005) seasonally.

Chemical Analysis

Water samples were collected, preserved and analyzed in accordance with Standards Methods (APHA, AWWA, 1995). Routine field measurements were done by Consort C535 model, such as pH, temperature, salinity, conductivity and redo potential. Routine laboratory analysis such as total phosphate, NO_2^- N, NO_3^-N, kjeldahl-N, BOD, COD, TDS, TSS, turbidity, sulphate, chlorine, Chl-*a*, total and fecal coliform were measured by standard methods (APHA, AWWA, 1995). Water samples, after being filtered by 0.45 µm filter paper and acidified by HNO_3, then total Cd, Ni and Pb were determined by Atomic Absorption Spectroscopy (AAS-ATI-UNICAM 929), atomic absorption spectrophotometry (APHA, AWWA, 1995).

Wet sediment sample analysis was performed for EC, pH, organic matter and water content (%) parameters. Electrical conductivity (EC) and pH were measured on sediment extract obtained by shaking sediment with double distilled water at 1: 2 (w/v) samples: water ratio using a pH meter and conductivity meter, respectively. Homogenized sediment samples were dried at 103°C. The dried sediment samples were sieved from 63 µm sieve size for metal analysis. Total heavy metals including Cd, Cu, Ni and Pb were extracted by HCl (%), HNO_3 (%) -HF (%) total acid digestion method. Finally, extracted sediment heavy metal analyses were performed by AAS.

Results and Discussion

Seasonal average of physicochemical field measurements of Kızılırmak River water (2004-2005) was given at Table 5. It is obvious that the pH was relatively stable among and within the stations during the year. Seasonally, high conductivity levels were observed mainly during the warm period as well as during the wet period with an average of 1.34 (mS/cm). pH variations and DO levels, in turn, regulate the most of the biochemical and chemical reactions affecting water composition. The specific conductance represented the salinity of water which had 0.7 g/L concentration as an average. It is a measure of the ability of water to conduct an electric current. It is highly dependent on the amount of dissolved solids in the water.

Figure 2 shows the results of water parameters of samples collected from different locations such as BOD-COD; NO_3^- -N–kjeldahl-N; T-P, NO_2^- -N and TSS, SO_4^{-3}, Cl concentrations. Seasonal average BOD-COD variations through the sampling stations were presented at Figure 2 (a). The river has Class I quality for BOD, but it has Class II qualification

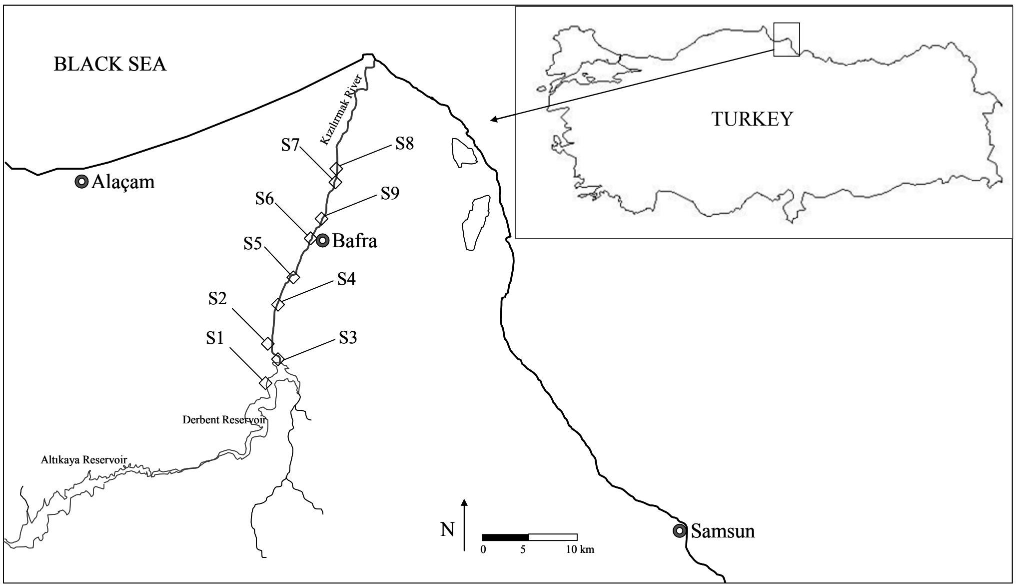


Figure 1. Sampling Stations through the Kızılırmak River (2004–2005)

Table 5. Seasonal average of physicochemical field measurements of Kızılırmak River (2004-2005)

Sampling Stations	pH	Temperature (°C)	Salinity (g/L)	Conductivity (mS/cm)	TDS (mg/L)	Redox Potential
1	8.03	17.87	0.6	1.25	1062	-50
2	7.88	14.97	0.8	1.42	1039	-50
3	7.86	15.32	0.7	1.36	1094	-47
4	7.90	14.37	0.8	1.36	942	-51
5	7.88	15.4	0.7	1.35	908	-49
6	7.80	15.92	0.7	1.36	959	-43
7	8.03	15.8	0.7	1.35	1002	-49
8	8.19	16.3	0.7	1.29	1219	-55
9	7.83	15.2	0.7	1.37	946	-45
Average	7.93	15.68	0.7	1.34	1019	-49

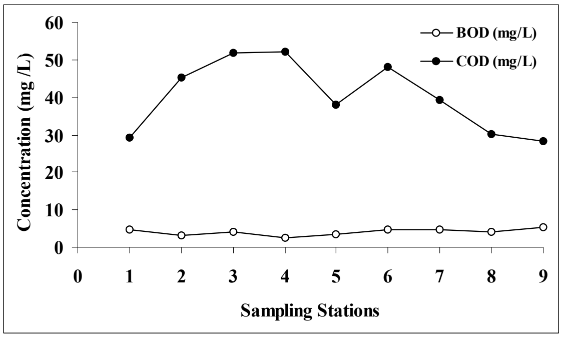
according to the legislations of in-land fresh water quality parameter classification of Turkey.

High values of COD indicate water pollution, which is linked to sewage effluents discharged from town, industrial or agricultural practice. The input of anthropogenic contaminants (from point discharges mixing with urban and agricultural runoff) causes distinct, but variable, COD concentration peaks, responsible for increasing the concentrations in nutrients and organic carbon in the fresh surface waters of the river.

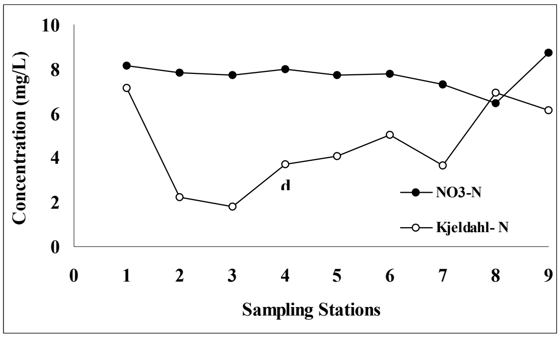
The changes of nitrate-nitrogen and kjeldahl nitrogen results were given at Figure 2 (b) with total average values of 7.74 mg/L for nitrate- N and 4.53 mg/L for kjeldahl–N at Class I. However, the trends of total phosphorus and nitrite-nitrogen parameter measurements were figured out at Figure 2(c) indicating both parameters at Class II.

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 some cases temperature rise. This can result in a fish kill and the death of many organisms. Lastly, the changes of total suspended solids, total sulphate and total chlorine measurements were presented at Figure 2 (d) and there is a possible indication of salt water intrusion of chlorine at the sampling stations near to the Black Sea.

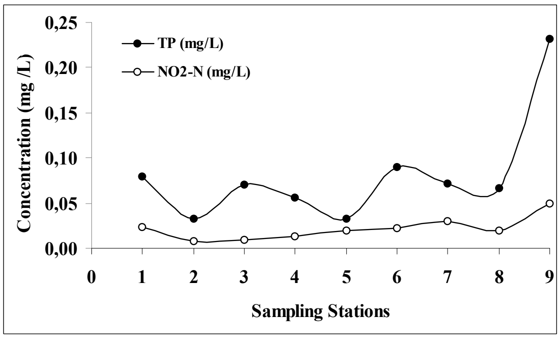
Although water analysis is useful in the assessment of river pollution, sediments can also serve as pollution indicators. The discharge of domestic sewage and industrial effluents seems to cause moderate nutrient and heavy metal pollution in receiving water. The strong binding affinity of heavy metals results in low concentrations in water and high concentration in sediments. Surficial sediments of studied river represent a sink for heavy metals. The accumulation of heavy metals in sediments may be the water pollution source in case of environmental condition change. The contents of heavy metals in sediments are unlikely related to the corresponding contents in the aquatic phase. The accumulation effects are greatly dependent on the sediment composition and structure. So, the variations of sediment organic matter and moisture content were



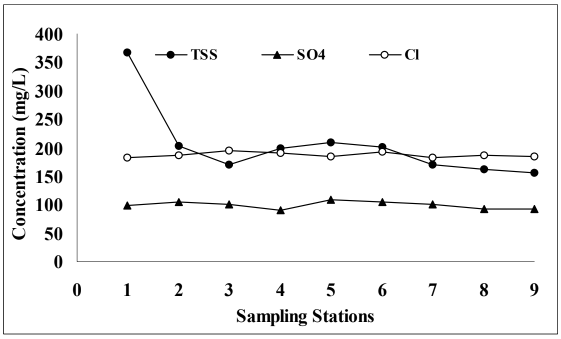
a) BOD–COD Variations



b) NO_3^-N–Kjehl-N variations



c) TP–NO_2^- -N variations



d) TSS – Sulphate – Chlorine Variations

Figure 2. Routine Water Quality Parameters through the Sampling Stations of Kızılırmak River (2004 – 2005).

presented at Figure 3. The moisture content of sediment samples ranged from 18.92% to 33.65%. The moisture content of sediment samples was used to indicate their sensitivity to erosion and resuspension, or perhaps, their suitability as substrate for benthic organisms (Golterman *et al*., 1983). The organic matter of sediment samples ranged from 1.41% to 4.60%. The maximum organic matter was observed at freshwater sediment samples since they were carrying high amount of untreated domestic wastewaters to the Black Sea.

Index Calculations and Evaluations

Looking for a way to evaluate the changes in water quality due to the combined effect of many parameters, we decided to calculate WQI. Since the analytical cost involved could be a limiting factor for water quality assessments in developing countries with scarce budgets for environmental studies, it should be useful to use a WQI which allows the evaluation of spatial and temporal variations measuring only a few simple parameters.

In order to assess the present water quality and the possible uses of Kızılırmak River, different WQI approaches were applied to a data set expressly collected for the present study. Table 6 shows comparison of WQI evaluations for Kızılırmak River. All WQI values are in good agreement. The NSFWQI value is 62.56, which lies on the medium water classification region, so the water is considered at medium quality. To get the NSFWQI, the Q-value should be determined for each variable and also a weighting factor is assigned to each variable (Table 1).

The new WQI gave a value of 2.53 which indicates that the water is acceptable (Table 6). This index can be used to assess water quality for general uses. However, it cannot be used in making regulatory decisions or to indicate water quality for specific uses (Said *et al*., 2004).

However, the other water quality index is WQI_{min} (Table 1) at which three important indicators of water quality are used. Dissolved oxygen is a key factor for aquatic life. Either conductivity or TDS should indicate the presence of salts, mineral acids, or similar contaminants discharged to the river. Turbidity is associated with suspended material and also with bacteriological contamination. Furthermore, these three parameters can be easily evaluated. So far, WQI_{min}. gives reasonable results for trend analysis at a lower cost. WOI_{min}. value is 65.67 indicating medium quality also (Table 6).

Table 7 shows the results of WQI calculations for metal measurements of Kızılırmak River water samples. Two different indexes are used. Pollution index, PI is based on individual metal calculations whereas metal index, MI is based on a total trend evaluation of the present status. According to the PI calculations, Pb metal calculation results at class V, indicating seriously affected medium condition and for Ni at class II, slightly affected whereas Cr has no affect. On the other hand, metal index, MI value for Kızılırmak River was 5.49 (Table 7) clearly indicating

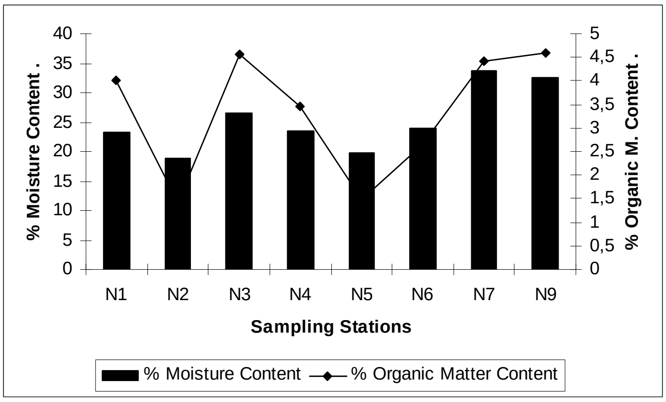


Figure 3. Sediment moisture content and organic matter content variations through the Kızılırmak River.

Table 6. Comparisons of Water Quality Index Evaluations for Kızılırmak River

	Water quality index		
Sampling Stations	WOI_{new}	WOI_{min}	NFSWQI
1	2.55	63	60
2	2.53	63	66
3	2.56	63	66
4	2.57	67	67
5	2.61	67	64
6	2.52	67	62
7	2.51	67	60
8	2.53	67	60
9	2.42	67	58
Average	2.53	65.67	62.56
	(3-2) the water is acceptable	< 100 medium quality	(50-70) medium quality

a "low-quality water" thus a MI value >1 is a threshold of warning; by calculating all metal contaminants into one value.

However, for the Derbent Dam of Kızılırmak River, two different trophic level index calculations were also performed (Table 8). According to those calculations, trophic state index at which only Chl-*a*, T-P and secchi disc parameter were considered (Table 3), the average quality of the reservoir is determined as "eutrophic" with high productivity. However, average trophic level index was 6.01 (Table 8) calculated from the arithmetic mean of four important parameter calculations of TLI (Table 3); such as total N, total P, secchi depth and Chl-***a*.** According to this value (between 5.0-6.0); Derbent Dam is also stated as "supertrophic" at which high algae growth and blooms during calm sunny periods can be expected. In fact, a trophic state index is not the same as water quality index. The term quality implies a subjective judgement that is best kept separate from the concept of trophic state (Carlson, 1977).

According to the calculation of TN to TP ratio at the dam water sample results, the ratio is calculated as greater than 15 and it is concluded that the reservoir is phosphorus limiting and its critical specific load of phosphorus is 759.35 mg/m^3-yr. For OECD approach classification (phosphorus load vs. mean water residence time), it indicates also eutrophic lake conditions (OECD, 1982).

On the other hand, the results of the various sediment quality index calculations for metal measurements of sediment samples were given at Table 9. Different metal assessment indices were used and discussed. Some indices give equivalent information but others give complementary information that can be used for different purposes. Since the computed indices have different aims, their discussion can be divided into two groups: (i) contamination and background enrichments indices, which measure the contamination or enrichment levels and (ii) ecological risk indices, which evaluate the potential for observing adverse biological effects.

However, special care must be taken when comparing the different threshold and index classifications. The contamination index, SEF (sediment enrichment factor) and the background enrichment index, NI_{geo}. (index of geoaccumulation) (Table 4 and Table 9) do not aggregate all contaminants into one value while SEF has no threshold for maximum pollution. On the other hand, the other backgorund index, PIN (pollution index) allows the identification of priority contamination sites for implementation of decontamination action. The PIN index has the advantage of being simple to compute and giving the results to the dredged material classes. This allows comparison with other

Table 7. Water quality index (Nemerrow index) for metal measurements of Kızılırmak River (2004-2005)

Metal	Pollution Index (PI)	Class	Status
Ni	1.82	II	Slightly affected
Pb	7.98	V	Seriously affected
Cr	0.89	I	No effect
Metal Index, MI	5.49	>1	A treshold of warning

Table 8. Average trophic state ındex calculations of derbent dam of Kızılırmak River (2004-2005)

Parameter	TSI	Trophic State	TLI (Trophic Level Index)
Chl-a (mg/m^3)	74	Eutrophic	7.01
T- P (mg/m^3)	67	Eutrophic	5.65
Secchi-Disc (m)	43	Mesotrophic	3.64
Total Nitrogen (mg/m^3)	-	-	7.74
Average	61.3	>50 Eutrophic(high productivity)	6.01 (5.0-6.0) supertrophic

Table 9. Various sediment quality index calculations for metal measurements

SQI	Result	Status
SEF(sediment enrichment factor)	$SEF_{Ni} = 1.34$	Slightly anthropogenic
(contamination index)	$SEF_{Pb} = 13.8$	Moderately anthropogenic
PIN (Pollution ındex)	PIN=35.22	Class II Trace contaminated
(background enrichment index)		
$NI_{geo.}$ (index of geoaccumulation)	$NI_{geo.}$ (Ni)=0.45	< 1 unpolluted
(background enrichment index)	$NI_{geo.}$ (Pb)=2.29	Lightly polluted
SQG – Q (mean sediment quality quideline quotient) (ecological risk index)	2.89>1	Highly impacted potential for observing adverse biological effects.

ecosystems (Caerio *et al*., 2005).

For the other group classification, SQG-Q index (Table 4) is used as an ecological risk index example, it is recent and its predictive ability has been widely tested (e.g., MacDonald *et al*., 1996; Long and MacDonald, 1998; Long *et al*., 2000; Karageorgis *et al*., 2003). In an overall evaluation of indicator criteria performance, SQG-Q evaluates the potential for adverse biological effects more effectively. According to the calculation of SQG-Q for Kızılırmak river sediment metal concentrations, it has a value of 2.89>1; indicating highly impacted potential for observing adverse biological effects whereas infact, this may be the cause of lead pollution at the sediment samples which has higher values at SEF and NI geo. calculations indicating moderately or lightly anthropogenic pollution levels. The automobile exhausts are likely to be a major source of lead and urban storm run-off carries the lead deposits into the river water. The results confirmed that the heavy metal pollution in Kızılırmak River was moderately serious.

Conclusion

Most vital surface water bodies in developing countries are under serious threat of degradation resulting from constant discharge of polluted effluents stemming from industrial, agricultural, mining and domestic /sewage activies. The most affected river systems are those traversing cities and towns in urban areas. This paper reviews the water quality of Kızılırmak River resulting from anthropogenic activities and proposes the framework for the sustainable management of river water quality. Water and sediment qualities are variable in the river; there are some pollution problems at certain location, mainly associated with urban and industrial centers.

The aim of the work on contamination evaluation was to assess the overall contamination of the study area, so the indices were highly appropriate. All WQI values calculated from the measured parameters were in good agreement and the Kızılırmak water was considered at medium quality. However, two different trophic level index calculations were also indicated that the Derbent Dam of Kızılırmak River has eutrophic conditions. Different metal assessment indices were used both for water and sediment samples at which lead pollution was observed at moderately anthropogenic pollution levels.

These preliminary results indicated that river and sediment transported pollutants were likely to be one of the factors for the water quality degradation of Kızılırmak River water. Furthermore, agricultural schemes within Kızılırmak River basin contributed to the deterioration of Kızılırmak River water quality. Major causes of concern are the fertilizers and chemicals. Run-off from agricultural schemes mostly contain chemical residues and fertilizers, which may pollute the water, and depending on loads may result in various hazards to the aquatic life and other lives depending on the river as a habitat and source of water supply. In further study, the concentration of persistent pollutants in various organisms in relation to those in sediments and to trophic level should be conducted to assess the ecological risk.

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