

Physico-Chemical Characteristics and Nutrient Levels of the Eastern Black Sea Rivers

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Abstract

This study was conducted to determine physico-chemical characteristics and nutrient levels on a monthly basis of the rivers of the Eastern Black Sea region with an average flow rate of about 10 m³/sec and above, including Kızılırmak, Yeşilırmak, Melet, Pazarsuyu, Aksu, Harşit, Değirmendere, Solaklı, İyidere, Büyükdere, Fırtına, Çağlayan and Kapistre.

The highest annual average values for electrical conductivity (EC), reactive phosphate (o-PO₄), ammonium (NH₄), nitrite (NO₂), sulphate (SO₄) and hardness were determined as $1.16 \pm 0.29 \text{ mS/cm}$, $0.81\pm0.66 \mu$ M, $11.6\pm10.4 \mu$ M, $2.83\pm3.1 \mu$ M, $333\pm74 \text{ mg/L}$ ve $407\pm47 \text{ mg}$ CaCO₃, respectively, in Kızılırmak (Samsun); the highest turbidity, total suspended solids (TSS) and organic matter (as permanganate index) as 191 ± 99 FTU, $232\pm137 \text{ mg/L}$ and $4.12\pm2.14 \text{ mg}$ O/L respectively in Değirmendere (Trabzon); the highest silicate concentration in Melet (Ordu) as $305\pm47 \mu$ M; the highest nitrate concentration in Íyidere (Rize) as $124\pm79 \mu$ M; and the highest chlorophyll-a levels in Yeşilırmak (Samsun) as $1.98\pm1.70 \mu$ g/L. As a result of cluster analyses, it was established that Kızılırmak river is in a group different from that of other rivers in terms of sulfate, hardness and electrical conductivity and the rivers situated in eastern part of the region is more acidic than those in the west in terms of pH. Data obtained from the study were evaluated according to Water Quality criteria and water quality classes of the rivers were identified by parameters.

Keywords: Eastern Black Sea, river, nutrient levels, physico-chemical levels, land based pollutants.

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Özet

Bu çalışma, Doğu Karadeniz'e dökülen, akarsulardan ortalama debileri yaklaşık 10 m³/sn ve üzerinde olan Kızılırmak, Yeşilırmak, Melet, Pazarsuyu, Aksu, Harşit, Değirmendere, Solaklı, İyidere, Büyükdere, Fırtına, Çağlayan ve Kapistre deresinin fizikokimyasal karakteristikleri ve besin elementi düzeylerinin belirlenmesi amacıyla aylık periyotlarla gerçekleştirilmiştir. Parametrelere ait yıllık ortalama değerler incelendiğinde en yüksek EC, o-PO4, NH4, NO2, SO4 ve sertlik değerleri sırasıyla 1,16 ±0.29 mS/cm, 0,81±0.66 µM, 11,6±10,4 µM, 2,83±3.1 µM, 333±74 mg/L ve 407±47 mg CaCO3 olarak Kızılırmak nehrinde, en yüksek Turbidite, toplam askıda katı madde ve permanganat indeksi değerlerinin 191±99 FTU, 232±137 mg/L ve 4,12±2,14 mg O/L olarak Değirmendere deresinde, en yüksek silikat (Si) değerlerinin 305±47 µM olarak Melet ırmağında, en yüksek nitrat derişimlerinin 124±79 µM olarak İyidere deresinde ve en yüksek klorofil-a değerleri ise 1,98±1,70 µg/L olarak Yeşilırmak nehrinde belirlenmiştir. Sınıflandırma analizleri sonucunda, sülfat, sertlik ve elektriksel iletkenlik yönünden Kızılırmak nehrinin diğer akarsulardan farklı bir sınıfta yer aldığı, pH yönüyle ise bölgenin doğusundaki akarsuların batıdakilere gore daha asidik özellik taşıdığı belirlenmiştir Çalışmada elde edilen veriler Su Kalite kriterlerine göre değerlendirilmiş ve parametrelere göre akarsulardaki su kalite sınıfları belirlenmiştir.

Anahtar Kelimeler: Doğu Karadeniz, akarsu, besin değeri, fiziko-kimyasal seviye, kara kökenli kirleticiler.

Introduction

Water is vital for the welfare of human societies. 95.96% of the total water on earth is in seas and oceans, 2.97% in glaciers and 1% in groundwater, 0.009% in lakes and 0.0001% in rivers (Graham and Farmer, 2007). Rivers are surface water which have multi-purpose usage areas such as drinking, irrigation, aquaculture and energy production (Kumar *et al.*, 2011). Water quality of a river is a reflection of several major effects, including basin lithology, atmospheric and anthropogenic inputs and climate

© Published by Central Fisheries Research Institute (CFRI) Trabzon, Turkey in cooperation with Japan International Cooperation Agency (JICA), Japan conditions. Due to anthropogenic activities such as urban, industrial and agricultural activities as well as natural events, including precipitation, erosion and climate change, potential use of water decreases day by day (Bakan *et al.*, 2010, Kumar *et al.*, 2011). Therefore, damage to the internal water resources is one of the last century's most important environmental problems (Tanriverdi *et al.*, 2010).

Water quality is determined by physical, chemical and microbiological properties of water. Anthropogenic effects result in significant reduction in the quality of the surface water of the aquatic systems in the basin. Surface water and sewage discharges are the two most important factors which carry nutrients into rivers and cause water pollution (Kumar *et al.*, 2011).

Nitrogen pollution is a global problem (Hadjikakou et al., 2011). Nitrogen and phosphorus concentrations play a key role in determining the ecological status of aquatic systems. Essential for biochemical cycle, these elements enter the water usually with anthropogenic activities such as domestic, industrial, wastewater and unknown source of discharges. Excessive nitrogen and phosphorus are often thought to be the major causes of eutrophication. Eutrophication is one of the most serious environmental hazards to the aquatic ecosystems. As a result of eutrophication, many problems arise such as algal blooms, oxygen depletion, odour and taste problems, fish death and loss of biodiversity. Therefore, understanding the dynamics of nutrients carried by rivers is critical for and resource management prevention of eutrophication (Luo et al., 2011).

Due to the growing problems of water quality and quantity in Europe, the Water Framework Directive (WFD; EU/2000/60/EC-WFD, 2000) has been established. One of the most important objectives of the Directive is to protect the current status of water bodies and make all water bodies in the European Union reach a 'good ecological status' by 2015 by applying an integrated approach to water management (Sanchez-Montoya Mdel *et al.*, 2012).

With a quite large drainage area and a special ecosystem on earth, the Black Sea takes vertical mixtures and inorganic nutrients with diffusions from the land, atmosphere and its own intermediate layer waters. River-based nutrient increase started in the Black Sea on the northwest coast before 1970s. 80% of the nutrients transported to the sea between 1970 and 1980 were carried through the Danube river and these nutrients are known to be from different sources such as agriculture, industry and urban settlement. Dissolved inorganic nitrogene (DIN) and ortho phosphate (o-PO₄) emission from the river Danube has been reported to decrease by 50% in recent years. The rest of the nutrient transportation is known to be from the rivers of Ukraine on the northwest coast (Dniepr, Dniester, Bug) and of Turkey on the southern coast. When total discharges were analyzed,

phosphate-based pollutants were reported to be discharged more from Turkish rivers. It was discovered that nitrogen and phosphorus emissions increased from the 1950s to 1990s and decreased in parallel with the reduction in fertilizer use due to the economic crisis in the 1990s. However, in the assessments between 2000 and 2005, nitrogen and phosphorus emissions were reported to be approximately 1.5 times higher than the amounts of 1950s (Oguz *et al.*, 2008).

While the amount of silicate (Si) reaching to the Mediterranean and the Black Sea decreases due to the construction of dams on rivers, the incidence of nitrate and phosphate is reported to increase due to increasing anthropogenic inputs (Oguz *et al.*, 2008). Although there is information available on nitrate and phosphate levels in European rivers in the European Environmental Agency (EEA, 2007) databases, there are deficiencies for African countries and Turkey in this respect (Ludwig *et al.*, 2009).

The rivers flowing into the Black sea contain untreated domestic and industrial waste (Bat *et al.* 2009). In the literature, there are reports of studies carried out at various periods on the rivers of the Black sea, including the Fırtına (Karaçam *et al.*, 1994, Aksungur *et al.*, 2007, Gedik *et al.*, 2010), the İyidere (Verep *et al.*, 2005), the Solaklı (Boran and Sivri 2001, Gültekin *et al.*, 2012), the Değirmendere, the Yeşilırmak (Akbal *et al.*, 2010, Hadjikakou *et al.*, 2011) and the Kızılırmak.

This study aims to concurrently establish the physicochemical properties of the high-flow rate rivers flowing into the Eastern Black sea and determine monthly, seasonal and river-related changes in terms of nutrient transport. This study will contribute greatly to foreseeing future effects of increasing number of dams and hydroelectric power plants (HEPP) on nutrient levels conveyed to the Black Sea.

Materials and Methods

This study was conducted on a monthly basis in the rivers with an average flow rate of about 10 m³/sec and above in the Eastern Black Sea in 2012 (Figure 1). Nomenclatures for the rivers were as follows: SB (Kızılırmak), SC (Yesilırmak), OM (Melet), GB (Pazarsuyu), GM (Aksu), GT (Harşit), TM (Değirmendere), TO (Solaklı), Rİ (İvidere), RC (Büyükdere), RA (Fırtına), RF (Çağlayan) and AA (Kapistre). The temperature, pH and electrical conductivity were measured in situ by YSI 556 MPI and dissolved oxygen by Hach 40Q at the stations located near river mouths. Water samples collected for analyzing dissolved nutrients were filtered through membrane filters of 0.45 micrometer pore size at the time of sampling before being taken to the laboratory using a car type refrigerator/freezer.

Of the nutrient components, ammonia nitrogen (modified $4500-NO_3^-$ F), (nitrate+nitrite) nitrogen



Figure 1. Sampling stations of the Eastern Black Sea rivers.

(modified 4500-NO₃⁻ Nitrate) and total nitrogen (after digestion with persulfate), ortho-phosphate (4500-P Phosphorus) and total phosphate (after digestion with persulfate) and silicate (4500-SiO₂) were tested by a Seal CFA chemical auto analyzer (APHA 2011).

Total suspended solids were determined gravimetrically by SM 2540 D method, chlorophyll-a spectrofotometrically according to SM 10200 H method after acetone extraction, sulphate by DR 2000 spectrophotometer using a kit, and permanganate index (SM 4500-OB) and total hardness (SM 2340 C) were measured titrimetrically (APHA 2011).

Statical evaluation of the data (ANOVA, Principle Component Analysis and Factor Analysis) was conducted using Statistica version 10.

Results and Discussion

Standard deviations and mean values of seasonal variations of temperature, DO, pH, EC, turbidity, total suspended solid, hardness, permanganate index, chlorophyll-a, sulphate, nitrate, nitrite, ammonium, phosphate and silicate parameters measured in SB (Kızılırmak), SÇ (Yeşilırmak), OM (Melet), GB (Pazarsuyu), GM (Aksu), GT (Harşit), TM (Değirmendere), TO (Solaklı), Rİ (İyidere), RÇ (Büyükdere), RA (Fırtına), RF (Çağlayan) and AA (Kapistre) rivers are shown in Figure 2-6.

Temperature of surface water is associated with seasons, time of measurement during the day, weather conditions, size of water mass and coordinates of the water (latitude and longitude). Water temperature is important because it increases rate of chemical reactions and reduces solubility of especially O_2 as well as CO_2 , N_2 , NH_4 and other gases. When all the rivers were evaluated together, the average temperature was determined as $13.25\pm 5.64^{\circ}C$. Minimum temperature was $3.2^{\circ}C$ in Pazarsuyu river

in February and maximum temperature was 24.7° C in the Yeşilırmak both in August and in September. Average, minimum and maximum temperatures by seasons were as follows: $6.8\pm2.1^{\circ}$ C, $(3.2-11.4^{\circ}$ C) in winter, $10.7\pm2.7^{\circ}$ C, $(6.3-16.2^{\circ}$ C) in spring, $19.5\pm2.0^{\circ}$ C, $(16.0-24.8^{\circ}$ C) in summer and $16.0\pm4.1^{\circ}$ C, $(8.8-24.8^{\circ}$ C) in autumn (Figure 2).

Oxygen is an important factor for aquatic life and the chemical characteristics of the environment. Average DO concentrations in the rivers were measured as 11.7 ± 2.0 mg/L in winter, 11.8 ± 0.7 mg/L in spring, 8.3 ± 0.8 mg/L in summer and 8.4 ± 1.1 mg/L in autumn. DO concentrations in summer and autumn are lower than those in winter and spring. Although GM generally has higher DO values compared to other rivers, the difference between rivers in terms of temperature, dissolved oxygen and chlorophyll-a concentrations was statistically insignificant, P<0.05 level (Figure 2).

pH, which is another basic quality parameter of water, influences many chemical and biological processes so it is practically used for evaluations related to water quality. The lowest average pH of the rivers was measured as 7.85 ± 0.46 in spring, and other average pH values were 8.15 ± 0.38 , 8.03 ± 041 and 8.09 ± 055 in winter, summer and autumn, respectively (Figure 2).

Kızılırmak has the highest average electrical conductivity, while the Değirmendere river has the highest average turbidity every season. In terms of total suspended solid (TSS), the Değirmendere river is statistically different from all the rivers and the Büyükdere river is different from all the rivers except for Solaklı river at P<0.05 level. The Degirmendere and Buyukdere rivers are notable with persistently high TSS and turbidity values. As for TSS parameters, the Değirmendere river is different from all the other rivers in terms of turbidity at P<0.05

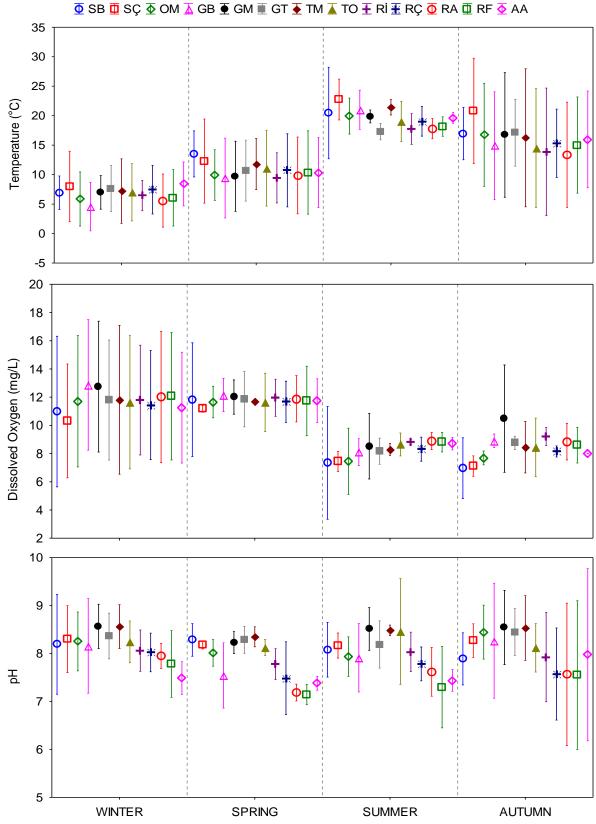


Figure 2. Seasonal changes of temperature, dissolved oxygen and pH in the Eastern Black Sea rivers.

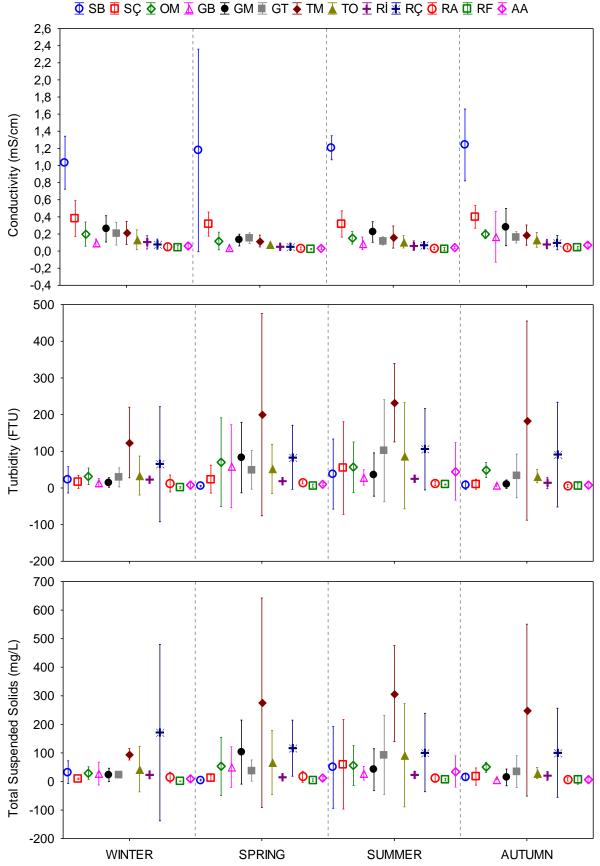


Figure 3. Seasonal changes of conductivity, turbidity and total suspended solids in the Eastern Black Sea rivers.

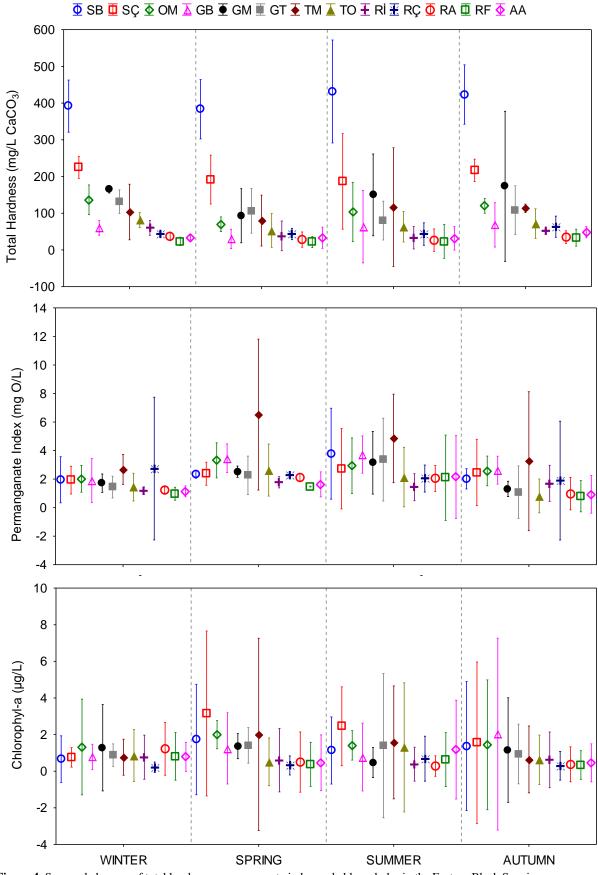


Figure 4. Seasonal changes of total hardness, permanganate index and chlorophyl-a in the Eastern Black Sea rivers.

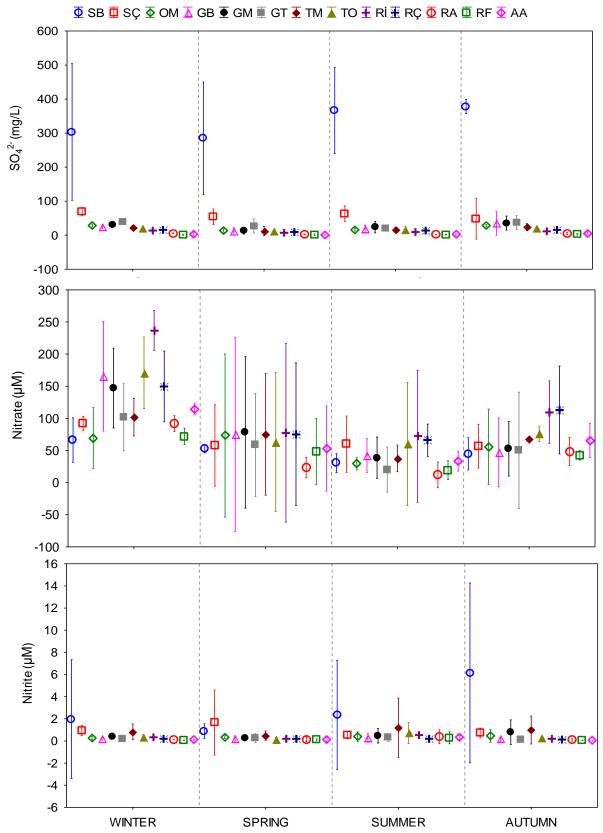


Figure 5. Seasonal changes of sulphate, nitrate and nitrite in the Eastern Black Sea rivers.

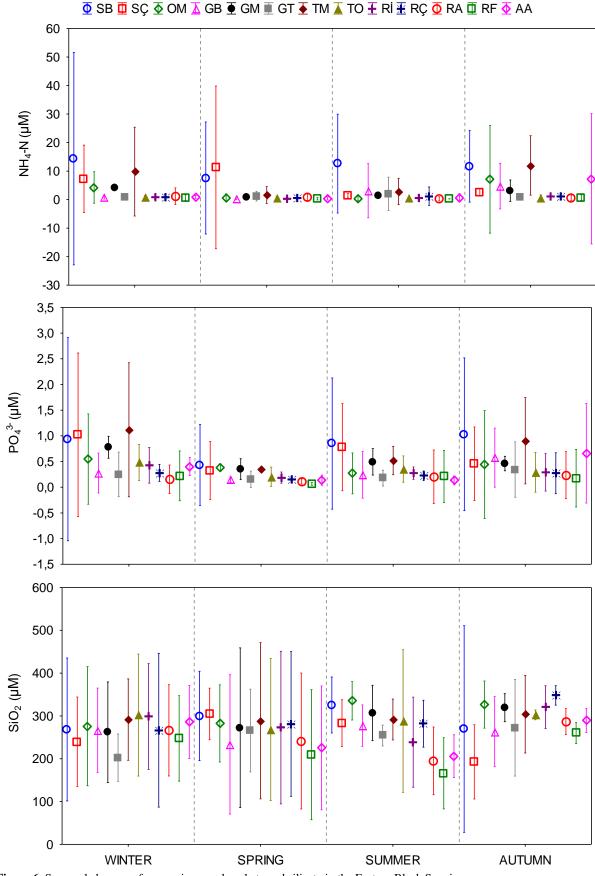


Figure 6. Seasonal changes of ammonium, o-phosphate and silicate in the Eastern Black Sea rivers.

level. The Büyükdere river is statistically different from all the other rivers except for Solaklı and Melet rivers at P<0.05 level. Considering these high parameters, river rehabilitation and road construction works on these rivers are thought to be important factors (Figure 3).

The hardness of natural waters depends mainly on the presence of dissolved calcium and magnesium salts. Hardness usually decreases from western to eastern parts of the region and Kızılırmak is the river with the highest hardness in every term. The source of difference between the rivers in terms of permanganate index is the Değirmendere river (Figure 4). Although the Degirmendere river is similar to the Kızılırmak, the Melet and the Pazarsuyu rivers, it has a higher permanganate index value (P<0.05). Although sulfate naturally exists in surface water in a concentration range of 2 to 80 mg/L, its concentration significantly increases up to levels above 1000 mg/L in dry regions containing sulfate minerals as a result of decomposition of minerals such as gysum and pyrite in rocks and industrial discharges (Chapman, 1996). As for the sulphate, the Kızılırmak is statistically different from all the other rivers and the Yesilırmak is statistically different from all the rivers except for the Harşit (P<0.05). The sulphate concentration measured in the Kızırmak and the Yesilırmak was higher than all the other rivers (Figure 5).

Inorganic nitrogen is present in water in the form of nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺) and molecular nitrogen (N₂) depending on its oxidation step and such nitrogen forms play an important role in nitrogen cycle in nature. In this study, the largest differences between the rivers in terms of nitrate were found in winter. Nitrate concentrations of lyidere and Solaklı rivers situated in neighboring valleys during winter were higher than those of other rivers (Figure 5). The lyidere river has higher concentration of nitrate than Kızılırmak, Melet, Harşit, Fırtına and Cağlayan rivers and it is statistically different at P<0.05 level. The difference between rivers in terms of nitrite concentration is statistically significant and the nitrite concentration measured in the Kızılırmak was higher than that of the other rivers. The difference between the other rivers in terms of nitrite concentration was statistically insignificant (P<0.05) (Figure 5).

The difference between rivers in terms of ammonium nitrogen is statistically significant and it is due to the Kızılırmak river. The difference between the Kızılırmak and the Değirmendere and the Yesilırmak in terms of the concentration of ammonium nitrogen is statistically insignificant, whereas the difference between the Kızılırmak and the other rivers is statistically significant (Figure 6).

Presence of silicate in aquatic enviroment is very important for growth of diatom (Egge and Aksnes, 1992). Because of the diatom contain considerable amounts of silica in the frustule (Wang and Li, 1969) decreasing silicate concentrations could influence the course of the spring succession of plankton diatom species in arctic or temperate coastal waters (Paasche 1975). Silicate concentrations of rivers situated in eastern part of the region were lower especially in summer (Figure 6).The difference between rivers in terms of silicate concentration is due to the rivers Melet and Cağlayan. There was no difference between the other rivers in terms of Si concentration (P<0.05).

As a result of PCA analysis, Kızılırmak river was characterized by high values for hardness, conductivity, sulphate, nitrite, ammonium, and phosphate parameters, which can be associated with the length and geological structure of Kızılırmak river. It is thought that high nitrite and ammonium concentrations are in line with low flow rate and low oxygen content with respect to urban wastewater and agricultural activities. Yeşilırmak river was characterized by higher chlorophyll-a concentration compared to other rivers.

The diagrams of the similarities between rivers in terms of pH and EC are given in Figure 7. In general terms, the rivers are grouped according to

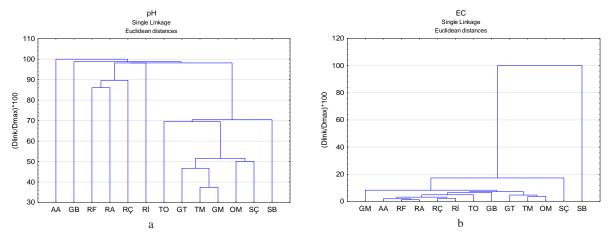


Figure 7. Similarity dendogram for pH (a) and EC (b) in Eastern Black Sea rivers.

their location in the Central and Eastern Black Sea regions in terms of pH in line with the geographic location. Although all the rivers had statistical differences from at least one river in terms of pH, the Pazarsuyu river was found similar to all the other rivers.

The difference between the rivers in terms of electrical conductivity is statistically significant (P<0.05). The K1211rmak and the Yesi11rmak have significantly different EC values both from each other and from the others. The K1211rmak has the highest EC value, which is about 3 times higher than that of the Yesi11rmak. Caglayan and F1rt111 rivers have the lowest EC values.

The Kızılırmak and the Yesilırmak are different from each other as well as from the other rivers in terms of hardness at P<0.05 level and have a higher hardness level than the others. The water of the Kızılırmak is about twice as hard as that of the Yesilırmak.

The phosphate concentration of the Kızılırmak was found to be higher than that of Pazarsuyu and Harsit rivers and the Solaklı, İyidere, Buyukdere, Fırtına, Caglayan and Kapistre streams in the east of Trabzon. The highest phosphate concentrations were measured in the Yesilırmak and Degirmendere rivers, following the Kızılırmak. The similarity diagram between rivers in terms of hardness and phosphate concentration is given in Figure 8.

When the results of the analysis were evaluated according to the Regulation of water pollution of Surface water quality management, the Kızılırmak river was observed to have the worst quality among all the rivers in the Eastern Black Sea region in general terms and by nutrient parameters. All the rivers were found to have Class I water quality for nitrate and temperature and Class I water quality for EC, except for the Kızılırmak and the Yesilırmak, whereas all the rivers are out of Class I quality for nitrite (Table 1).

When the rivers were evaluated in terms of trout aquaculture, total suspended solids were found to be the main limiting parameter, and average TSS values in all the rivers except for the lyidere, Firtina, Caglayan and Kapistre rivers were over the limit values specified in the circular.

The values showing the correlation of the parameters are given in Table 2. In view of the table,

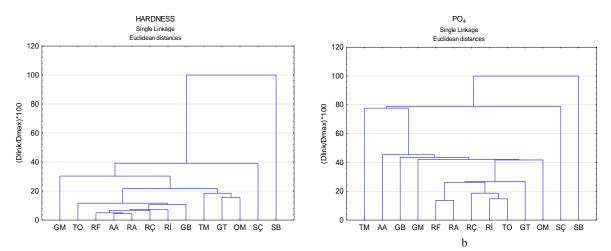


Figure 8. Similarity dendogram for hardness (a) and phosphate (b) in Eastern Black Sea rivers.

River Name	River Code	Temp	рН	EC	DO	NO ₃	NO ₂	NH ₄	PO ₄
Kızılırmak	SB	Ι	II	III	III	Ι	IV	Π	II
Yeşilırmak	SÇ	Ι	II	II	II	Ι	III	II	II
Melet	OM	Ι	II	Ι	II	Ι	III	II	II
Pazarsuyu	GB	Ι	II	Ι	II	Ι	II	Ι	Ι
Aksu	GM	Ι	II	Ι	II	Ι	III	Ι	Ι
Harşit	GT	Ι	II	Ι	II	Ι	II	Ι	Ι
Değirmendere	TM	Ι	II	Ι	II	Ι	III	II	II
Solaklı	TO	Ι	II	Ι	II	Ι	III	Ι	Ι
İyidere	Rİ	Ι	Ι	Ι	Ι	Ι	II	Ι	Ι
Büyükdere	RÇ	Ι	Ι	Ι	Ι	Ι	II	Ι	Ι
Fırtına	RÁ	Ι	Ι	Ι	Ι	Ι	II	Ι	Ι
Çağlayan	RF	Ι	Ι	Ι	Ι	Ι	II	Ι	Ι
Kapistre	AA	Ι	II	Ι	Ι	Ι	II	Ι	II

Table 1. Water quality classes of Eastern Black Sea rivers

it is seen that temperature has a significant level of negative correlation with dissolved oxygen (-0.83)and electrical conductivity has a significant level of positive correlation with total hardness (0.94), sulfate (0.97) and nitrite (0.77). Turbidity has a significant with TSS positive correlation (0.85)and permanganate index (0.64). Sulphate has a significant positive correlation with electrical conductivity (0.97) and total hardness (0.87). Nitrite has significant positive correlation with electrical conductivity (0.77), hardness (0.69) and sulphate (0.76), which can be related to this parameter being prominent in the Kızılırmak and the Yesilırmak rivers. Similarly, ammonium has a significant positive correlation with total hardness (0.62) and nitrite (0.60). Total nitrogen has positive correlation with nitrate (0.79) and Si (0.65), while total phosphorus has significant positive correlations with turbidity (0.52) and total suspended solids (0.53).

In the study conducted in the Degirmendere river by Gultekin *et al.* (2012) representing the rainy periods, the following results were found: turbidity 66, hardness 80.6 mg CaCO₃, nitrite 0.060 mg/L, nitrate 1.32 mg/L, ammonium 1.10 mg/L, phosphate 0.92 mg/L and sulphate 25.4 mg/L. In our study, the average values determined in the same river were as follows: turbidity 191±99, hardness 103±44 mg CaCO₃, nitrite 0.037±0.034 mg/L, nitrate 3.85±2.24 mg/L, ammonium 0.118±0.112 mg/L, phosphate 0.068±0.044 mg/L and sulphate 18.5±6.5 mg/L. Although the majority of the parameters measured in the two studies were similar, ammonium and phosphate concentrations found in our study were quite low but the nitrate concentrations were higher.

Boran and Sivri (2001) and Gultekin *et al.* (2012) carried out some studies in the Solaklı river. The mean values determined in our study were as follows: turbidity 51.6 ± 42.9 , hardness 67.5 ± 19.7 mg CaCO₃, nitrite 0.017 ± 0.014 mg/L, nitrate 5.74 ± 3.59 mg/L, ammonium 0.012 ± 0.006 mg/L, phosphate 0.031 ± 0.016 mg/L and sulphate 16.8 ± 5.0 mg/L. The nitrate concentrations detected were higher than the previous two studies but phosphate concentrations were lower.

Verep et al. (2005) measured water quality criteria at four different stations in the lyidere river. The mean values determined for the lyidere river in our study were as follows: turbidity 20.1±6,1, hardness 45.8±16.1 mg CaCO₃, nitrite 0.013±0.007 mg/L, nitrate 7.69 ± 4.94 mg/L, ammonium 0.014±0.007 mg/L, phosphate 0.028±0.014 mg/L and sulphate 10.2±2.9 mg/L. Our values are similar to those found by Verep et al., 2005 except for the ammonium concentration, which is considerably lower in our study than the value reported by Verep et. al (2005).

The mean values determined in the Kızılırmak in this study were as follows: turbidity 18.3 ± 1.0 , hardness 407 ± 47 mg CaCO₃, nitrite 0.130 ± 0.143 mg/L, nitrate 3.00 ± 1.03 mg/L, ammonium

 0.208 ± 0.187 mg/L, phosphate 0.077 ± 0.063 mg/L and sulphate 333 ± 74 mg/L. Some water quality parameters were studied in the K1z11rmak by Bakan *et al.* (2010) and Akbal *et al.* (2011). The nitrate concentrations detected in our study were in agreement with the results reported by Akbal *et al.* (2011) but were considerably lower than the values reported by Bakan *et al.* (2010), whereas nitrite concentrations were similar to those reported by Bakan *et al.* (2011) but were higher than the values reported by Akbal *et al.* (2011).

The mean values determined in the Yeşilırmak in our study are as follows: turbidity 26.3 ± 33.5 , hardness 205 ± 37 mg CaCO₃, nitrite 0.044 ± 0.036 mg/L, nitrate 4.23 ± 1.47 mg/L, ammonium 0.102 ± 0.139 mg/L, phosphate 0.061 ± 0.049 mg/L and sulphate 58.9 ± 17.0 mg/L. These values are similar to those determined by Akbal *et al.* (2011).

There was no report of silicate measurements in the studies previously conducted on the Eastern Black Sea rivers. However, silicate contents of rivers and lakes are in the range of 1-30 mg/L (Chapman 1996). In this study, Si concentrations (mg/L) for the Kızılırmak, Yesilırmak, Melet, Pazarsuyu, Aksu, Harşit, Degirmendere, Solaklı, Iyidere, Buyukdere, Firtina, Caglayan and Kapistre rivers were 8.15±2.02, 7.29±1.35, 7.14±1.57, 8.55 ± 1.32 , 8.13±1.55, 6.97±1.25, 8.23±1.38, 8.13±1.69, 7.91±1.72, 8.25±1.77, 6.93±1.60, 6.18±1.61 and 7.05±1.51, respectively.

In order to determine the factors affecting physico-chemical water quality of the rivers, the Principle Component Analysis and Factor Analysis were applied to the data. Factor analysis revealed four factors effective in explaining the variations in the water quality of the rivers in the Eastern Black Sea and these factors explained 75% of the total variance (Table 3). Factor 1 explains 29.4% of total variance and is associated with strong loadings of EC, hardness, SO₄, NO₂ and NH₄. Water hardness is usually related to the geological structure that the water is in contact with and EC and SO₄ increase indicates the soil washing in the river domain. Factor 2 explains 23.3% of total variance and is associated with turbidity, hardness and strong loading values of permanganate index. It is considered to be associated with both natural erosion as a result of rainfall and particulate transport due to riverbed activities. Factor 3 explains 11.7% of total variance and has positive relationship with temperature but high negative relationship with dissolved oxygen and nitrate. Therefore, factor 3 indicates seasonal effects. Factor 4 explains 10.8% of total variance and is associated with chlorophyll-a. It is thought to be associated with the amount of organic load.

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Table 2. Correlation matrix for Eastern Black Sea river waters

	Temp	pН	EC	DO	Turb.	TSS	Hard.	PI	Chl-a	SO ₄	NO ₃	NO ₂	NH ₄	PO ₄	Si	TP	TN
Temp	1.000																
pH	-0.065	1.000															
EC	0.362	0.287	1.000														
DO	-0.832	0.235	-0.253	1.000													
Turbidty	-0.052	0.189	-0.163	0.093	1.000												
TSS	-0.119	0.191	-0.138	0.146	0.854	1.000											
Hardness	0.322	0.446	0.936	-0.210	-0.123	-0.124	1.000										
P. Index	-0.111	0.281	0.040	0.227	0.642	0.747	0.057	1.000									
Chl-a	-0.172	0.375	0.097	0.433	0.478	0.372	0.123	0.494	1.000								
SO_4	0.243	0.214	0.968	-0.192	-0.170	-0.134	0.873	0.023	0.049	1.000							
NO ₃	-0.518	0.237	-0.214	0.418	0.280	0.273	-0.151	0.202	0.147	-0.189	1.000						
NO_2	0.308	0.051	0.772	-0.359	-0088	-0.085	0.693	0.014	-0.006	0.762	-0.150	1.000					
NH_4	0.185	0.211	0.534	-0.272	-0.088	-0.130	0.621	0.052	-0.086	0.497	-0.119	0.604	1.000				
PO_4	0.246	0.218	0.560	-0.437	-0.131	-0.116	0.582	0.001	-0.177	0.510	-0.052	0.641	0.554	1.000			
Si	-0.124	0.006	-0.107	-0.040	0.376	0.203	0.015	0.077	0.225	-0.100	0.424	-0.056	0.206	0.017	1.000		
TP	-0.018	0.221	0.058	-0.122	0.516	0.533	0.130	0.334	0.154	0.022	0.238	0.016	0.341	0.296	0.388	1.000	
TN	-0.392	0.193	-0.028	0.235	0.275	0.207	0.075	0.151	0.168	-0.040	0.788	0.022	0.229	0.084	0.648	0.417	1.000

 Table 3. Rotated factor loadings in the Eastern Black Sea river waters

Factor Loadings (Varimax normalized) Extraction: Principal components (Marked loadings are >.700000)							
Parameter	Factor 1	Factor 2	Factor 3	Factor 4			
Temperature	0.081305	0.156091	0.913314	0.108776			
pH	0.237493	0.339081	-0.098810	0.517636			
Conductivity	0.926667	-0.059360	0.114361	0.228622			
Dissolved Oxygen	-0.192700	-0.064224	-0.857116	0.311026			
Turbidity	-0.102514	0.919291	0.032010	0.047924			
TSS	-0.086878	0.922642	-0.000886	0.064265			
Hardness	0.923682	0.001278	0.053993	0.221574			
Permanganate index	0.116568	0.785725	0.112357	0.221739			
Chlorophyl-a	0.040916	0.285475	0.079776	0.714450			
SO ₄	0.871721	-0.105493	0.069757	0.269471			
NO ₃	-0.047789	0.119193	-0.819420	-0.193152			
NO ₂	0.781040	0.028471	0.150191	-0.178216			
NH4	0.742212	0.090307	0.023599	-0.351412			
PO ₄	0.661518	0.154579	0.020940	-0.459079			
Si	0.210752	0.408633	-0.142220	-0.447416			
Expl.Var	4.250471	2.767390	2.334655	1.720022			
Prp.Totl	0.283365	0.184493	0.155644	0.114668			

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