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ARAŞTIRMA MAKALESİ

RESEARCH PAPER

Determination of Heavy Metal Pollution in River of Artvin, Rize and Trabzon Provinces, Turkey^[*]

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*Corresponding author: Hazel BAYTAŞOĞLU Recep Tayyip Erdogan University, Faculty of Fisheries and Aquatic Sciences, 53100 Rize, Turkey. ⊠: gokbuluthazel@gmail.com **Abstract:** The aim of this study was to evaluate the stations selected from the provinces in the Eastern Black Sea region (Artvin, Rize, Trabzon), Turkey in terms of some physicochemical parameters and heavy metals. A total of 27 stations were selected from these rivers and their tributaries feeding the Black Sea, and sampling was carried out in 2019-2020 depending on the land conditions. Temperature, dissolved oxygen, pH, electrical conductivity, and total dissolved solids parameters were measured with a HQ 40 D brand water measuring device. For heavy metal analysis, services were purchased from the Sinop University Central Research Laboratory (SUBİTAM). As a result of the analyses made, it was determined that all stations had a very high concentration in terms of Al and some stations in terms of Cd. Furthermore, it was observed that almost all of the stations showed high quality water characteristics in terms of Mn, Zn, Pb, Ni, Fe, Cu. It has been determined that physicochemical parameters varied depending on factors such as seasonal temperatures, land structure, slope, precipitation rate, and parameters, except pH showed 1st class water characteristics according to the limits determined in the legislation. This study suggests that the pollution in this region is not at a high level and that it has suitable water conditions for life in terms of the parameters examined.

Keywords: Eastern black sea, heavy metals, pollution, river

Artvin, Rize ve Trabzon İlleri Akarsularının Ağır Metal Kirliliğinin Belirlenmesi

Öz: Bu çalışmanın amacı, Doğu Karadeniz bölgesinde bulunan illerden (Artvin, Rize, Trabzon) seçilen istasyonların bazı fizikokimyasal parametreler ve ağır metaller bakımından değerlendirilmesini sağlamaktır. Karadeniz'i besleyen bu akarsular ve kollarından toplamda 27 istasyon seçilmiş ve 2019-2020 yıllarında arazi şartlarına bağlı olarak örnekleme yapılmıştır. Sıcaklık, çözünmüş oksijen, pH, elektriksel iletkenlik, toplam çözünmüş katı madde parametreleri HQ 40 D marka su ölçüm cihazı ile ölçülmüştür. Ağır metal analizleri için SUBİTAM'dan hizmet alımı yapılmıştır. Yapılan analizler sonucu, Al bakımından tüm istasyonların, Cd bakımından ise bazı istasyonların oldukça yüksek konsantrasyona sahip olduğu tespit edilmiştir. Mn, Zn, Pb, Ni, Fe, Cu bakımından istasyonların hemen hemen hepsinin yüksek kaliteli su özelliği gösterdiği görülmüştür. Fizikokimyasal parametrelerin mevsim sıcaklıkları, arazi yapısı, eğim, yağış oranı gibi faktörlere bağlı olarak değiştiği, pH dışındaki ölçümlerin mevzuatta belirlenen sınırlara göre 1. Sınıf su özelliği gösterdiği tespit edilmiştir. Çalışma sonuçları bu bölgede kirliliğin yüksek seviyede olmadığını, incelenen parametreler açısından canlı yaşamı için uygun su özelliğin sahip olduğunu göstermiştir.

Anahtar kelimeler: Ağır metaller, akarsu, doğu karadeniz, kirlilik.

[*] This study was produced from the master thesis.

*Sorumlu yazar:

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INTRODUCTION

The Eastern Black Sea Basin is one of the richest basins in terms of water resources and receives the most precipitation in Turkey. Almost all of the basin's streams get their sources from the peaks of the mountains that run parallel to the coast. Because of their geological structure, they have a high slope and precipitation rate and their flows are continuous. But for the same reasons, they drag large amounts of sand and gravel and accumulate in the areas where they spill into the sea (DOKAP, 2013). It is known that the physicochemical or ecological conditions of the rivers carrying water to the seas (fertilizers, pesticides affecting the seas, hormones, wastes from industrial establishments and houses, wastewater, erosion) affect the seas significantly (Verep et al., 2020). Previous studies have emphasized that the discharge of domestic and industrial wastes into the seas via rivers is the main cause of Black Sea pollution (Bozcaarmutlu et al., 2009; Alkan et al., 2008). Although some metals and heavy metals are necessary for the life of living things, they are considered important pollutants due to their high concentrations in aquatic environments, their accumulation properties, and their toxicity. Heavy metals in surface waters increase due to atmospheric transport, terrestrial inputs, hydrothermal activities, rocks and anthropogenic inputs resulting from human activities (Metin Dereli et al., 2017). In the literature, there are water quality studies conducted at different time intervals in different rivers in this basin (Bakan & Büyükgüngör, 2000; Boran & Sivri, 2001; Altın et al., 2009; Bayram & Önsoy, 2011; Gültekin et al., 2012; Satilmis & Bayram, 2014; Nacar & Satilmis, 2017; Nacar et al., 2018). However a limited number of stations and different pollution parameters were used in these studies. The aim of this study was to determine some physicochemical parameters and heavy metal (Al, Mn, Fe, Ni, Cu, Zn, Cd, Pb) concentrations in streams flowing from Artvin, Rize and Trabzon, Turkey to the Black Sea.

MATERIAL AND METHOD

Artvin, Rize and Trabzon provinces of Turkey selected as the study area are surrounded by the Black Sea in the north, Ardahan in the east, Giresun in the west, Erzurum, Gümüşhane and Bayburt in the south. There are many large and small river systems in the study area. Samples were taken from a total of 27 stations between 2019 and 2020. For the determination of physico-chemical parameters, temperature, dissolved oxygen, pH and electrical conductivity (EC), total dissolved solids (TDS) parameters were measured in the field with the HQ 40 D brand water measuring device. Water samples were taken from a depth of approximately 0.5 m, depending on the depth of the stream, using 2-liter polypropylene bottles. For heavy metal analysis, water samples were filtered with 0.45 micron mesh filter papers. The pH was brought to the range of 1.5 - 2.0 by adding concentrated nitric acid solution to. Before the analysis, filtration with filter paper was repeated and an ICP-MS device was used to make the measurements. For this process, services were purchased from the Sinop University Central Research Laboratory (SUBITAM). The map of the sampling area is given in Figure 1. Ethics committee approval is not required for this study.

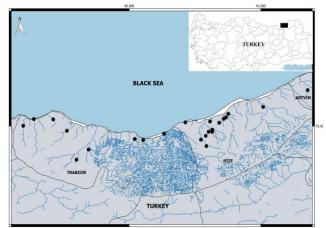


Figure 1. The map of sampling stations.

RESULTS

The descriptions of selected sampling stations from the rivers of Artvin, Trabzon and Rize provinces in the Eastern Black Sea basin are given in Table 1.

Some physicochemical parameters measured in the field during the fieldwork are given in Table 2. The temperature parameter was measured between 4.7-21.8 °C. When evaluated according to the sampling periods, the temperature parameter was found to be suitable for seasonal temperature values. The dissolved oxygen parameter was measured between 8.7 and 11.9 mg/L. Considering that the slope and precipitation rate of the study area are high, it is normal for these values to be relatively high (Table 2). The pH is expected to be in the range of 6.5-8.5 in clean waters (Sağlam, 2003). In this study, the pH ranged from 4.74-6.5. It is thought that this situation mav have resulted from short-term contamination. Conductivity is the capacity of water to conduct electric current or the resistance of the solution to conduct electric current. Since conductivity is accepted as an indicator of dissolved substances in water, it is a monitoring parameter in streams. The charge and concentration of dissolved substances in water affect conductivity (Anonim, 2011). EC and TDS values are in parallel with each other. The EC and TDS parameters was measured between $30.1-198.2 \,\mu$ s/cm and $22.7-154.3 \,m$ g/L, respectively. When the physicochemical parameters measured in the field were compared with the limits specified in the legislation (Table 3). it was seen that the parameters other than pH showed high quality water characteristics (Table 2).

Table 1. Descriptions of sampling stations.

Station Number	Stations Names	Sampling Dates	Province	Coordinates
St-1	Stream Arhavi	3.11.2020	Artvin	41.2537 N
31-1	(A tributary of Stream Orçi)	5.11.2020	Aitvin	41.3565 E
St-2	Stream Potomya	12.7.2020	Rize	40.9747N
	Sucan rotomya	12.7.2020		40.6313E
St-3	Stream Alakoz 2	17.7.2020	Rize	40.9604N
	birduin million 2	11112020	iune	40.6041E
St-4	Stream Firtina 2	5.11.2019	Rize	41.1358N
				41.0181E
St-5	Stream Derepazarı	30.6.2020	Rize	41.0270 N
	Suban Dereputar	50.0.2020	Tune	40.4272 E
St-6	Stream Andon	5.8.2020	Rize	40.8595N
31-0	birduin / Indon	5.0.2020	iune	40.5868E
St-7	Stream Alakoz	17.7.2020	Rize	40.9317N
51-7				40.5818E
St-8	Stream Yeşildere	5.8.2020	Rize	40.9052N
DI O	Sucuri reșndere			40.5457E
St-9	Stream Sabuncular	6.8.2020	Rize	41.0619N
	birdun birdinedita	0.0.2020		40.7356E
St-10	Stream Azsu	30.6.2020	Rize	41.0518N
51-10	Sucan Azsu	50.0.2020		40.7181E
St-11	Stream Büyükköy	6.8.2020	Rize	41.0243N
	Stream Duyukkoy	6.8.2020	KIZE	40.6844E
St-12	Stream Veliköy	5.8.2020	Rize	41.0329N
	Sucan venkoy	5.6.2020		40.6144E
St-13	Stream Seldere	12 7 2020	Rize	40.9607N
	Stream Seidere	12.7.2020	Rize	40.6310E
St-14	Stream Manahoz	2.9.2020	Trabzon	40.9018N
	Sucall Wallanoz			40.1064E
St-15	Stream Manahoz 2	12.9.2020	Trabzon	40.8015N
				40.1423E
St-16	Stream Çataklıhoca	6.8.2020	Trabzon	41.0865N
				40.7536E
St-17	Stream İskefiye	3.9.2020	Trabzon	41.0483N
				39.4232E
St-18	Stream Karadere 2	2.9.2020	Trabzon	40.9092N
				40.0426E
St-19	Stream Kalyan	1.9.2020	Trabzon	40.8353N
	Stream Karyan			39.6916E
St-20	Stream Cataklı 2	1.9.2020	Trabzon	40.7253N
31-20	Sireani Çataklı 2	1.9.2020	1140200	40.2335E
St-21	Stream Ağasar	3.9.2020	Trabzon	41.0028N
	Su calli Agasai			39.1950E
St-22	Stream Yeniköy (Hayrat)	1.9.2020	Trabzon	41.0453N
	(my,m)			39.5076E
St-23	Stream Söğütlü (Hayrat)	1.9.2020	Trabzon	40.9676N
				39.5270E
St-24	Stream Çataklı	22.1.2020	Trabzon	40. 8020N
	Sucalli Çalaklı	22.1.2020	Tranzon	40.2466E
St-25	Stream Altıntaş	28.10.2019	Trabzon	40.7635 N
	Su cam Atuntaş	20.10.2017	11402.01	39.5998 E
St-26	Stream Fol	22.1.2020	Trabzon	41.0502 N
	Sucall POI	22.1.2020	1140200	39.2758 E
St-27	Stream Cumapazarı	28.11.2010	Trabzon	40.9462 N
		28.11.2019	maozofi	40.2646 E

Table 2. Some water quality parameters measured in the field.

Stations	Temperature	Temperature Dissolved Oxygen		Total Dissolved Solids	Electrical Conductivity
	(°C)	(mg/L)	pН	(mg/L)	(µs/cm)
St-1	11.4	11.8	5.40	25.8	39.4
St-2	16	9.58	4.81	25.9	45.1
St-3	17.7	9.33	5.60	55.2	30.1
St-4	14.4	10.73	5.45	38.5	61.7
St-5	15.0	10.39	5.39	80.1	135.7
St-6	14.2	9.49	5.04	24.1	40.5
St-7	17.7	9.33	5.60	55.2	30.1
St-8	18.2	9.29	4.80	36.7	67.8
St-9	18.2	9.15	5.27	27.7	50.9
St-10	21.8	10.02	5.57	54.1	107.5
St-11	18.5	9.34	5.63	61.0	112.3
St-12	18.6	9.29	5.11	56.7	104.1
St-13	16.4	9.53	4.74	22.7	40.2
St-14	19.0	9.54	5.66	32.9	61.9
St-15	21.1	9.38	5.29	35.8	70.4
St-16	21.2	8.86	5.24	47.6	93.2
St-17	20.9	9.42	5.76	83.5	154.2
St-18	20.7	8.70	5.93	27.7	53.5
St-19	17.6	8.7	5.9	39.8	111.2
St-20	18.3	9.25	5.48	37.0	68.2
St-21	16.3	9.29	5.33	19.54	34.5
St-22	18.1	9.33	6.2	55.3	124.1
St-23	18.2	8.18	6.5	58.4	136.2
St-24	6.5	11.4	6.2	77.4	104.5
St-25	7.8	9.11	6.5	94	153.2
St-26	4.7	11.9	6.5	154.3	198.2
St-27	15.1	9.82	5.77	56.4	119.4

Parameters -	Classes					
rarameters —	Ι	II	III	IV		
Temperature (°C)	25	25	30	>30		
pH	6.5-8.5	6.5-8.5	6-9	Outside of 6-9		
Dissolved Oxygen (mg/L)	8	6	3	<3		
TDS	500	1500	5000	>5000		
Al (mg/L)	0.3	0.3	1	>1		
Mn (µg/L)	100	500	3000	>3000		
Fe (µg/L)	300	1000	5000	>5000		
Ni (µg/L)	20	50	200	>200		
Cu (µg/L)	20	50	200	>200		
Zn (μg/L)	200	500	2000	>2000		
Cd (µg/L)	3	5	10	>10		
Pb (µg/L)	10	20	50	>50		

According to the results obtained from the sampling stations, the highest Al value (358.8 ppb) was obtained from St-24 and St-4 stations. and the lowest Al value (4.6 ppb) was obtained from St-2 and St-13 stations (Figure 2). Al is the most abundant and common element in the Earth's crust. It enters water resources through both natural and anthropogenic sources (Lantz & MacKenzie, 1979). Its common source in freshwater systems is due to heavy rains and melting snow. and aluminum particles from rock and soil (Bjerknes et al., 2003). When the Al values measured in this study were evaluated according to the surface water quality classes, it was determined that all stations showed 4th class water characteristics and the concentrations were quite high.

Mn values were found to be higher (41.9 ppb) at St-24 and St-1 stations, compared to other stations and lower (0.3 ppb) at St-13 and St-4 stations (Figure 2). In the study conducted by Sönmez 2012 on the Karasu River (Black Sea), it was emphasized that some stations showed polluted water characteristics. Although the concentration determined at the St-2 station in the Mn measurements made in this study was relatively high, all stations were included in the 1st class water quality class.

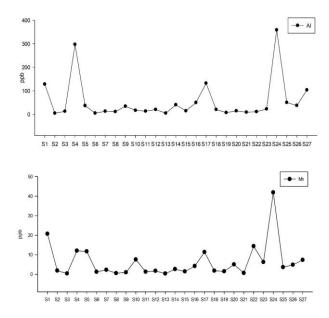
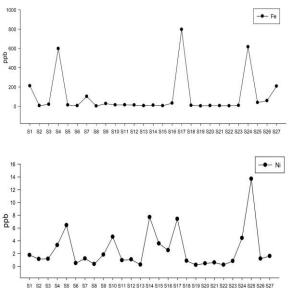


Figure 2. Al and Mn concentrations in the sampling stations.

The highest Fe values (796.9 ppb) were found at St-17 and St-24 stations and the lowest Fe values (3.1 ppb) were found at St-8 and St-19 stations (Figure 3). It is noted that Fe, which is one of the most abundant elements in the soil and the Earth's crust, is an important problem in spring waters (Gray, 1996; Türkmen, 2003). Although it acts as a catalyst in many chemical reactions it has a toxic effect when the amount of Fe oxide in the water exceeds 5 ppm (Kiracı, 2014). In previous studies, it was noted that the Fe concentration was quite high in Aksu Stream (Toroğlu et al., 2006) and increased in places in some river systems on the Central Black Sea coast (Arıman et al., 2007). When the measurement results were evaluated according to the inorganic parameter values of the surface water quality standards, it was seen that 3 stations selected in this study showed 2nd class water characteristics and 3 different stations, although in 1st Class water quality class were measured higher compared to other stations (Table 3).



51 52 53 54 55 56 57 58 59 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 Figure 3. Fe and Ni concentrations in the sampling stations.

The highest Ni values (13.7 ppb) were found at St-25 and St-14 stations and the lowest Ni values (0.2 ppb) were found at St-19, St-22 and St-13 stations (Figure 3). Ni is mostly found in the wastewater of ceramics, coins, batteries, magnets machine parts, motor vehicle and aircraft industries. Substances such as selenium, nickel, titanium, uranium and aluminum that cause water pollution have a lethal effect for living things if their concentrations exceed the limit value.

The highest Cu values (20 ppb) were found at St-17 and St-15 stations and the lowest Cu values (0.8 ppb) were found at St-8 and St-9 stations (Figure 4). Previous study concluded that the concentration was low in copper measurements made during different studies from the Middle Black Sea Yeşilırmak, Abdal Çayı, Kızılırmak, Kürtün, Aksu streams and its branches (Arıman et al., 2007). In this study, it was determined that 1 station showed 2nd class water characteristics and 1 station had a relatively high concentration compared to other stations (Table 3). The highest Cd values (85.2 ppb) were found at St-13 and St-7 stations and the lowest Cd values (1.5 ppb) were found at St-6 and St-22 stations (Figure 4). Cd metal is used extensively in industry as a sub-product in the production of metals such as copper, zinc, lead, and in phosphate fertilizers. With this use in industry, it is considered to be an important ecotoxicological metal (Kiracı, 2014). In the sampling studies conducted along the Gediz river, Cd concentrations varied between 1st and 4th class water quality (Kayar & Çelik, 2003). The Cd value was measured quite low in the stations selected from the Central Black Sea region (Arıman et al., 2007). In the measurements made in this study, it was determined that 4 stations showed 4th class water features and 3 stations showed 2nd class water features.

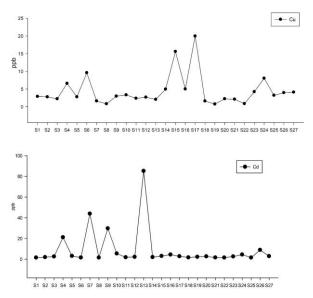
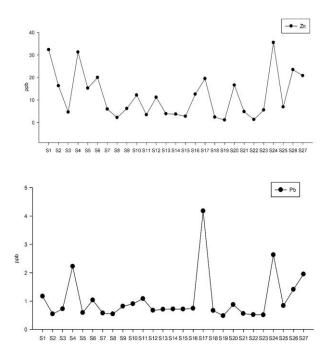


Figure 4. Cu and Cd concentrations in the sampling stations.

The highest Zn values (35.5 ppb) were found at St-24 and St-1 stations and the lowest Zn values (1.1 ppb) were found at St-19 and St-22 stations (Figure 5). Sönmez et al. (2012) and Kayar & Çelik (2003) found that the zinc values were in the polluted water criterion sampled from the Karasu and Gediz rivers, respectively. Toroglu et al., (2006) measured the amount of zinc in Aksu Stream and determined that the stations showed 1st and 2nd class water characteristics. According to the data obtained in this study, the Zn value in the rivers of Artvin, Rize and Trabzon provinces were measured very low at all stations. When the surface waters were evaluated according to quality standards, it was determined that it showed 1st class water feature in terms of Zn.

The highest Pb values (2.6 ppb) were found at St-24 and St-17 stations and the lowest Pb values (0.5 ppb) were found at St-8 and St-2 stations (Figure 5). Pb, which is frequently used in daily routines through materials such as cosmetic products, ceramics and gasoline, increases its toxicity depending on factors such as pH of the environment, presence of organic substances, hardness of water (Kiracı, 2014). In the Pb, measurements made from the rivers flowing into the Black Sea from the Eastern Black Sea provinces, it was observed that the concentration in all stations was quite low. When the surface waters were evaluated according to quality standards, it was determined that it showed a 1st class water feature in terms of Pb.





CONCLUSION

In conclusion, some physicochemical properties and heavy metal measurements of the streams flowing into the Black Sea from the borders of Artvin Rize and Trabzon provinces varied. In terms of temperature, oxygen, tds parameters, the stations showed 1st class water characteristics. It showed second and third class properties in terms of pH. In terms of Mn, Zn, Pb, Ni, and Fe, it was determined that almost all stations showed high quality water characteristics. However, Cd in some stations found to be very high concentration and other stations had high quality water characteristics. This study suggests that the pollution in this region is not at a high level, and that it has suitable water conditions for life in terms of the parameters examined.

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