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Determination of phytoplankton density, and study of the variation of nutrients and heavy metals in the surface water of Riva Stream; one of the water sources of Istanbul, Turkey

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ABSTRACT

In this study, the water quality and heavy metal pollution status of Riva Stream which is related to Ömerli Dam Lake, one of the water resources of Istanbul (Turkey), was determined. For this purpose, some physicochemical parameters, phytoplankton compositions, some nutrient, and heavy metal concentrations in the surface water of Riva Stream were investigated. Samples were collected at six sampling sites in the course of the stream in February 2012 and May 2012. A total of 19 taxa, belonging to five divisions, were identified. The phytoplankton density varied from 47 to 264 ind./cm^3; chlorophyll-*a* contents varied between 1.52 and 1.83 mg/m^3. Measured concentrations of heavy metals and nutrients showed difference related to sampling points. As a result of measurements, the lowest and highest heavy metal and mineral nutrient concentrations of measured water samples were as follows: Al (617.40–1094.16 μg/L), B (1010.40–5736.00 μg/L), Ca (1015.80–1925.40 mg/L), Cd (1.45–5.22 μg/L), Cr (61.26–164.16 μg/L), Cu (35.04–372.66 μg/L), Fe (28.50–369.06 μg/L), K (179.10–1314.60 mg/L), Mg (202.68–1755.60 mg/L), Na (669.00–1553.40 mg/L), Ni (40.62–269.70 μg/L), Pb (6.48–76.86 μg/L), and Zn (429.18–990.60 μg/L). It was observed that Riva Stream is highly polluted by some heavy metals, and a number of heavy metal resistant/tolerant phytoplankton species are present in the stream. Pearson's correlation and Spearman rank correlation analyses were applied to examine the relationship between Al, B, Ca, Cd, Cu, Cr, Fe, K, Mg, Na, Ni, Pb, Zn, pH, chlorophyll-*a*, salinity, and conductivity. The physicochemical characteristics of Riva Stream as a high concentration of nutrients make it a similar eutrophic. It is required that, Riva Stream should be taken under protection as soon as possible for improving its water quality by relevant authorities.

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Keywords: Phytoplankton; Trace elements; Nutrients; Physicochemical parameters; Chlorophyll-*a*; Istanbul

1. Introduction

Rapid population growth, excessive urbanization, industrialization, and increasing use of natural resources led to environmental problems in Turkey, as well as the rest of the world [1,2]. Heavy metal pollution is one of the primary problems which must be resolved in both terrestrial and aquatic environments. The main heavy metals are Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn [3]. A certain amount of these elements are necessary for biotope in nature. However, some of them are toxic to living organisms, such as As, Cd, Cr, Hg, and Pb, even at quite low concentrations, while others like Cu, Fe, Se, and Zn are biologically essential and natural constituents and only become toxic at very high concentrations [4–7].

Heavy metals cause pollution in the aquatic systems by atmospheric deposition, erosion of geological matrix and anthropogenic activities such as industrial effluents, domestic sewage, and mining wastes [8–10]. Rivers, which feed lakes and seas, are very important water suppliers in freshwater systems. One of the effective natural sources for transportation of heavy metals in aquatic environments is the transportation of heavy metals by rivers to coastal regions as a result of erosion [11].

Determination of heavy metal concentrations has a huge importance in aquatic ecosystems. Phytoplankton are known to be the primary producers in aquatic environments and are represented at the bottom level of the food chain. Also, they are able to adsorb and assimilate metals from their aqueous environment [6]. Thus, the amount and diversity of phytoplankton in a water body reflects the average ecological condition and therefore, may be used as an indicator of water quality. Nowadays, they are being widely used in biological monitoring and assessment of safe environmental levels of heavy metals [12,13]. The objective of this study is to evaluate the pollution level of Riva Stream by determining the accumulation of some heavy metals, some nutrients, and some phytoplankton composition.

2. Materials and methods

2.1. Study area

Riva Stream is located in Marmara Region, on the Asian side of Istanbul, about 40 km northeast from the city center. It originates from Kocaeli province and pours to the Black Sea at Cayagzi (Riva) village, after running 65 km from its origin. The source of the stream is Ömerli Dam and it flows northwest, through the Riva village, to the Black Sea (Fig. 1). The length of a slow-running part of the stream, having silent water characteristics in some parts, is 33 km long. There are some settlements, agricultural lands, and stock farms around the river. Also, the stream bank is used as a recreation area [14,15].

2.2. Phytoplankton composition and density

The study was carried out in February 2012 and May 2012 at six different sampling stations (Fig. 1, and Table 1). Samples were taken from the surface to Nansen bottles and were fixed with Lugol's iodine. Phytoplankton were counted with an Nikon TMS made inverted microscope at a magnification of 400, according to Lund et al. [16]. Phytoplanktonic organisms were identified in reference to the literature, including several comprehensive reviews on the subject.

2.3. Analysis of samples

Chlorophyll-*a* measurements of the phytoplankton were estimated according to Parsons and Strickland

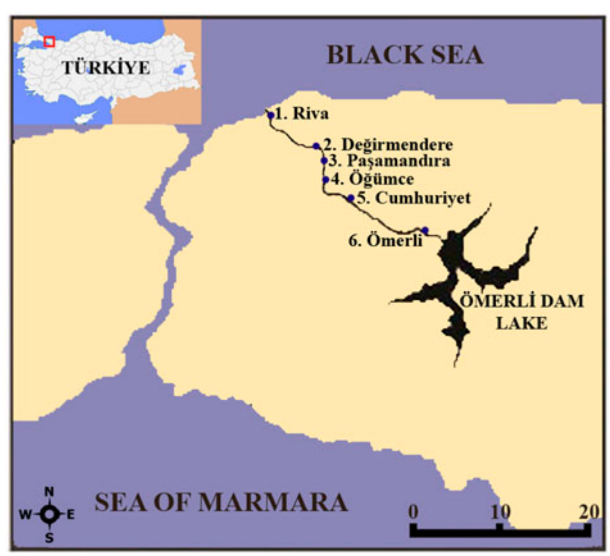

Fig. 1. The map of Riva Stream and sampling stations.

Table 1
Locations of sampling stations

St. 1: Riva	41° 13´19.63´´N	29° 12´58.07´´E
St. 2: Değirmendere	41° 11´05.05´´N	29° 16´02.67´´E
St. 3: Paşamandıra	41° 10´26.86´´N	29° 16´08.43´´E
St. 4: Öğümce	41° 09´37.10´´N	29° 16´14.17´´E
St. 5: Cumhuriyet	41° 07´44.91´´N	29° 16´58.64´´E
St. 6: Ömerli dam input	41° 03´51.49´´N	29° 20´48.59´´E

[17]. Salinity, conductivity, and pH values were measured with the WTW Multi 340i/set made multiparameter in the field. Standard procedures were applied and heavy metal and mineral nutrient amounts were measured by using ICP-OES. Samples were filtered with 1–2 μm pore size filter paper and placed into 50 mL sterile falcon tubes. Because of the predicted high concentration values of the mineral elements and high salinity content, filtered samples were diluted to 1:30. In order to analyze Al, B, Cd, Cr, Cu, Fe, Ni, Pb, and Zn concentrations in the samples with ICP-OES, a blank solution distilled deionized water and 10-25-50-100-250 ppb multi-element standard solutions were prepared and to analyze the concentrations of Ca, K, Mg, and Na elements 50-100-250-500-1000 ppb multi-element solutions were prepared in separate sterile falcon tubes.

2.4. Correlation analysis

In this study, the Pearson's correlation [18] and Spearman rank correlation [19] analyses were applied to examine the relationship between Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Zn, pH, chlorophyll-*a*, salinity, and conductivity by using the SPPS 20.0-database program.

3. Results

In this study, a total of 19 taxa were identified belonging to five divisions: Bacillariophyta (10), Chlorophyta (3), Cryptophyta (1), Cyanophyta (2), and Euglenophyta (3). Distribution of phytoplankton groups is given in Fig. 2 and the list of recorded taxa is given in Table 2. The Bacillariophyta division was found to be dominant in terms of species number. *Microcystis aeruginosa* of blue-green algae, which is also known to be a toxin-producing organism, was found as dominant species in terms of density (59.57%). The phytoplankton density varied between 47 and 264 ind./cm^3. The minimum phytoplankton density was recorded at station 6 and the maximum was recorded at station 4 in February 2012.

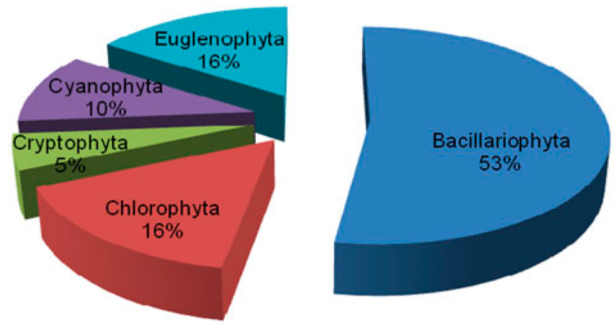

Fig. 2. Percentage distribution of phytoplankton groups in Riva Stream.

3.1. Phytoplankton composition of station 1

A total of 12 taxa were identified belonging to five divisions: Bacillariophyta (7), Chlorophyta (1), Cyanophyta (2), Cryptophyta (1), and Euglenophyta (1). Phytoplankton density changed from 120 ind./cm^3 (February 2012) to 262 ind./cm^3 (May 2012). *M. aeruginosa* was found as dominant species in both February 2012 (70 ind./cm^3) and May 2012 (159 ind./cm^3). *Ulnaria acus* and *Gomphonema olivaceum* were found only at station 1. *U. acus* usually occurs in shallow, enriched turbid waters including rivers and has a tolerance for flushing, it is sensitive to nutrient depletion [20,21].

3.2. Phytoplankton composition of station 2

A total of eight taxa were identified belonging to five divisions: Bacillariophyta (2), Chlorophyta (1), Cyanophyta (1), Cryptophyta (1), and Euglenophyta (3). Phytoplankton density varied from 81 ind./cm^3 (May 2012) to 112 ind./cm^3 (February 2012). *M. aeruginosa* was recorded as dominant species in both February 2012 (73 ind./cm^3) and May 2012 (47 ind./cm^3). *Cosmarium depressum* of Chlorophyta, *Phacus orbicularis* and *Euglena gracilis* of *Euglenophyta* were recorded only at station 2 in low numbers. Usually, Chlorophyta members were found widely and abundantly from mesotrophic to eutrophic lakes [22]. It is known that *C. depressum* indicates mesotrophic waters. Members of Euglenophyta were more abundant in contaminated waters and developed well in environments with high organic matter input [23]. *E. gracilis* and *P. orbicularis* are characteristic species for small organic ponds [20,21].

3.3. Phytoplankton composition of station 3

A total of 11 taxa were identified belonging to five divisions: Bacillariophyta (7), Chlorophyta (1),

Table 2
Recorded taxa at sampling stations in Riva Stream

	St. 1	St. 2	St. 3	St. 4	St. 5	St. 6
Divisio: Bacillariophyta						
Cyclotella atomus Husted	+	+	+	+	+	+
Cyclotella ocellata Pantocsek	+	+	+	+	+	+
Nitzschia acicularis (Kütz.) Wm. Smith	+	–	+	–	–	–
Ulnaria ulna (Nitzsch) P. Compere	+	–	+	+	–	–
Ulnaria acus (Kütz.) M. Aboal	+	–	–	–	–	–
Gomphonema olivaceum (Hornemann) Brebisson	+	–	–	–	–	–
Melosira varians Agardh	+	–	–	+	–	–
Pinnularia sp.	–	–	+	–	–	–
Cocconeis placentula Ehrenberg	–	–	+	–	–	–
Navicula cuspidata (Kütz.) Kütz.	–	–	+	+	–	–
Divisio: Chlorophyta						
Oocystis borgei J. Snow	+	–	+	–	–	+
Monaraphidium falcatus (Corda) Ralfs	–	–	–	–	–	+
Cosmarium depressum (Naeg.) P. Lundell	–	+	–	–	–	–
Divisio: Cyanophyta						
Microcystis aeruginosa (Kütz.) Kütz.	+	+	+	+	+	+
Oscillatoria tenuis Agardh	+	–	–	+	–	–
Divisio: Cryptophyta						
Cryptomonas erosa Ehrenberg	+	+	+	+	+	+
Divisio: Euglenophyta						
Phacus orbicularis Hübner	–	+	–	–	–	–
Trachelomonas hispida (Perty) Stein	+	+	+	–	–	–
Euglena gracilis Klebs	–	+	–	–	–	–

Cyanophyta (1), Cryptophyta (1), and Euglenophyta (1). Phytoplankton density changed from 118 ind./cm^3 (May 2012) to 212 ind./cm^3 (February 2012). *M. aeruginosa* was found as dominant species in both February 2012 (161 ind./cm^3) and May 2012 (35 ind./cm^3). *Cocconeis placentula* and *Pinnularia* sp. of Bacillariophyta were found only at station 3. Minimum concentration of chlorophyll-*a* was recorded as 1.52 mg/m^3 at sampling station 3.

3.4. Phytoplankton composition of station 4

A total of nine taxa were identified belonging to three divisions: Bacillariophyta (5), Cyanophyta (3), and Cryptophyta (1). Chlorophyta and Euglenophyta members were not recorded at station 4. Phytoplankton density varied between 120 ind./cm^3 (May 2012) and 264 ind./cm^3 (February 2012). Maximum density was recorded as 264 ind./cm^3 at sampling station 4 in February 2012. *M. aeruginosa* was found as dominant species in both February 2012 (207 ind./cm^3) and May 2012 (74 ind./cm^3).

3.5. Phytoplankton composition of station 5

A total of four taxa were identified belonging to three divisions: Bacillariophyta (2), Cyanophyta (1), and Cryptophyta (1). Chlorophyta and Euglenophyta members were not recorded at station 5. Phytoplankton density changed from 118 ind./cm^3 (May 2012) to 121 ind./cm^3 (February 2012). *M. aeruginosa* was found as dominant species in February 2012 (93 ind./cm^3) while *Cyclotella atomus* was dominant in May 2012 (38 ind./cm^3). Maximum content of chlorophyll-*a* was recorded as 1.83 mg/m^3 at sampling station 5.

3.6. Phytoplankton composition of station 6

A total of six taxa were identified belonging to four divisions: Bacillariophyta (2), Chlorophyta (2), Cyanophyta (1), and Cryptophyta (1). Euglenophyta members were not recorded at station 6. Phytoplankton density changed from 47 ind./cm^3 (February 2012) to 95 ind./cm^3 (May 2012). *M. aeruginosa* was found as dominant species in February 2012 (22 ind./cm^3) while *C. atomus* was dominant in May 2012 (36 ind./cm^3). Minimum content of chlorophyll-*a* was recorded as 1.52 mg/m^3 at sampling station 6.

During the study period, measured chlorophyll-*a* contents varied between 1.52 mg/m^3 and 1.83 mg/m^3, salinity varied from 0.1 to 5.3‰, conductivity changed between 686 μS/cm and 9,470 μS/cm, and pH ranged from 7.15 to 8.38 (Table 3). Electrical conductivity was measured higher than normal values. Na and Ca values were higher than the standards of United States Environmental Protection Agency (EPA) [24]. It was determined that salinity and conductivity decreased towards the entrance of Ömerli Dam Lake. Additionally, Na values measured with ICP-OES also supported these results. The maximum value of salinity, Na, and conductivity was measured in station 1 which is located at the entrance of Black Sea. According to the measured pH values, water of Riva Stream is slightly alkaline (close to neutral values pH 7) and within normal limits (Tables 3 and 4).

As a result of ICP-OES measurements, the lowest and highest heavy metal and mineral nutrient concentrations of water samples shown in Table 4. are as follows: Al (617.40–1,094.16 μg/L), B (1,010.40–5,736.00 μg/L), Ca (1,015.80–1,925.40 mg/L), Cd (1.45–5.22 μg/L), Cr (61.26–164.16 μg/L), Cu (35.04–372.66 μg/L), Fe (28.50–369.06 μg/L), K (179.10–1,314.60 mg/L), Mg (202.68–1,755.60 mg/L), Na (669.00–1,553.40 mg/L), Ni (40.62–269.70 μg/L), Pb (6.48–76.86 μg/L), and Zn (429.18–990.60 μg/L).

Water samples of this study were collected both in winter (February) and spring (May) periods of 2012. When heavy metal and mineral nutrient values of different seasons were compared, it was observed that Al, Ca, Cu, and Mg values were higher in winter, while B, Cd, Cr, Fe, K, Na, Ni, Pb, and Zn values were higher in spring. The highest B, Ca, K, Mg, Na, and Zn was measured in St. 1. Fe in St. 2, Cd in St. 4, Ni in St. 5, and Cr, Cu ,and Pb in St. 6, while the lowest Cr, Cu, and Ni was in St. 1, Al, Pb, and Zn in St. 2, B, Pb, and Zn in St. 4, Fe, Mg, and Na in St. 5 and Cd was in St. 6. A slight increase was observed in Al, Cr, Ni, and Pb from St. 1 to St. 6, while a slight decrease was observed in B, Ca, Mg, Na, and K. Zn and Cu values were closer to each other in all the stations. However, Fe was only higher in St. 2 and Cd was lower in both St. 5 and 6 when stations were compared.

In the presented study, Pearson's correlation and Spearman rank correlation analyses were applied to examine the relationship between Al, B, Ca, Cd, Cu, Cr, Fe, K, Mg, Na, Ni, Pb, Zn, pH, chlorophyll-*a*, salinity, and conductivity. In Annexure 1, the Pearson's correlation coefficients are presented for the data-set and the statistically significant correlations are flagged. As shown in Annexure 2, significant positive correlations between Al and Cu; B and Ca, K, Na, salinity, and conductivity; Ca and Mg; Cr and Ni; K and Na, salinity and conductivity; Ni and Pb; pH and Pb and Cr were found. Moreover, there is a strong positive correlation between salinity, K, Na, and conductivity.

Significant negative correlations between B and Cu; Ca and Ni and Pb; Cd and Al; K and Cu; Mg and Pb and Ni; Na and Cu; Ni and Mg; Pb and Ca and Mg; Zn and Cu are detected. A negative correlation between Chlorophyll-*a* and Ca and Mg is determined.

The results of the Spearman rank correlation analysis are presented in Annexure 2. As shown in the Annexure 2, the results show significant positive correlation between Al and Cu; B and Ca, K, Na, salinity, and conductivity; Ca and Mg; Cr and Ni; K and Na, salinity and conductivity; Ni and Pb; similar to Pearson's correlation analysis. Furthermore, a strong positive correlation between salinity, K, Na, and conductivity is present. Additionally, significant positive correlation between pH and Na and Fe; Na and Fe is spotted.

Similar to Pearson's correlation analysis, significant negative correlations between B and Cu; Ca and Ni and Pb; K and Cu; Mg and Pb and Ni; Na and Cu; Ni and Mg; Pb and Ca; were observed. A negative correlation between Chlorophyll-*a* and Fe is determined thereunto.

4. Discussion and conclusion

In this study, it was determined that *C. atomus* and *Cyclotella ocellata* of Bacillariophyta, *M. aeruginosa* of Cyanophyta, *Cryptomonas erosa* of Cryptophyta were recorded in all sampling stations, when compositions of phytoplankton were examined in sites. Centric diatoms *C. atomus* and *C. ocellata* were accepted as one of the typical components of both oligotrophic lakes

Table 3
Chlorophyll-*a*, salinity, conductivity and pH values of sampling stations in Riva Stream

Parameters	Cl-*a* (mg/cm^3)		Salinity (‰)		Conductivity (μS/cm)		pH	
Stations	Feb. 12	May 12	Feb. 12	May 12	Feb. 12	May 12	Feb. 12	May 12
St. 1	1.59	1.54	2.5	5.3	4,730	9,470	7.23	7.29
St. 2	1.54	1.53	0.5	1.7	1,462	3,380	7.21	7.22
St. 3	1.54	1.52	0.5	1.3	1,332	2,810	7.17	7.19
St. 4	1.54	1.54	0.1	0.6	686	1,648	7.20	7.15
St. 5	1.66	1.83	0.1	0.1	694	793	7.17	7.16
St. 6	1.55	1.52	0.1	0.1	704	783	7.15	8.38

Table 4
Heavy metal and mineral nutrient values in six different stations of Riva Stream

		St. 1	St. 2	St. 3	St. 4	St. 5	St. 6
Al μg/L	February	852.00 ± 20.11	810.00 ± 19.52	957.00 ± 15.98	949.80 ± 13.49	810.00 ± 14.99	1,094.16 ± 17.29
	May	702.60 ± 18.76	617.40 ± 19.02	670.80 ± 13.22	700.80 ± 12.47	672.00 ± 13.10	784.20 ± 10.82
B μg/L	February	4,692.60 ± 49.74	2,006.40 ± 31.50	1,861.80 ± 33.14	1,010.40 ± 19.10	1,163.40 ± 14.78	1,257.00 ± 19.86
	May	5,736.00 ± 81.45	3,501.60 ± 45.87	3,195.00 ± 48.56	2,100.00 ± 27.93	1,633.20 ± 30.38	1,706.40 ± 28.84
Ca mg/L	February	1,925.40 ± 2.31	1,769.40 ± 7.26	1,658.40 ± 1.33	1,424.40 ± 4.42	1,185.00 ± 2.49	1,201.80 ± 0.96
	May	1,837.80 ± 2.94	1,505.40 ± 1.05	1,503.60 ± 2.41	1,285.80 ± 5.40	1,015.80 ± 1.83	1,120.20 ± 0.34
Cd μg/L	February	4.08 ± 0.19	3.89 ± 0.14	3.92 ± 0.19	4.26 ± 0.11	2.97 ± 0.15	1.45 ± 0.03
	May	5.04 ± 0.21	4.69 ± 0.12	4.09 ± 0.13	5.22 ± 0.22	3.65 ± 0.21	3.67 ± 0.18
Cr μg/L	February	61.26 ± 2.16	94.08 ± 4.70	98.34 ± 2.60	63.54 ± 2.01	81.72 ± 3.40	87.72 ± 2.70
	May	116.76 ± 5.10	129.48 ± 2.78	129.90 ± 3.61	87.00 ± 2.97	157.02 ± 4.19	164.16 ± 6.17
Cu μg/L	February	140.88 ± 2.20	367.92 ± 3.60	343.38 ± 5.36	346.80 ± 6.35	371.94 ± 7.74	372.66 ± 8.98
	May	35.04 ± 0.76	132.00 ± 0.88	74.88 ± 2.13	216.72 ± 3.36	147.42 ± 3.11	178.92 ± 2.79
Fe μg/L	February	105.72 ± 3.33	281.46 ± 11.88	99.30 ± 3.45	74.46 ± 3.29	28.50 ± 0.90	72.90 ± 1.60
	May	140.70 ± 3.46	369.06 ± 13.55	124.32 ± 4.97	130.32 ± 4.94	90.84 ± 2.91	156.18 ± 3.97
K mg/L	February	1,092.00 ± 3.82	362.28 ± 2.46	227.16 ± 1.34	167.70 ± 0.54	179.10 ± 0.84	197.22 ± 0.28
	May	1,314.60 ± 8.15	863.40 ± 5.27	559.80 ± 4.31	518.70 ± 3.32	279.42 ± 2.29	304.50 ± 0.79
Mg mg/L	February	1,755.60 ± 13.17	1,712.46 ± 11.30	1,092.12 ± 2.51	832.40 ± 7.07	234.54 ± 1.43	225.42 ± 0.97
	May	1,281.60 ± 7.18	1,312.20 ± 9.45	1,082.40 ± 1.73	571.44 ± 5.26	202.68 ± 0.65	216.06 ± 1.19
Na mg/L	February	1,317.61 ± 2.11	1,135.80 ± 3.64	955.20 ± 6.40	781.80 ± 2.42	669.00 ± 2.61	861.60 ± 5.26
	May	1,553.40 ± 7.92	1,351.20 ± 5.95	1,192.80 ± 8.47	1,050.60 ± 3.47	889.80 ± 4.27	1,119.60 ± 6.16
Ni μg/L	February	40.62 ± 1.41	103.98 ± 1.62	134.22 ± 3.15	113.70 ± 2.02	127.62 ± 1.90	161.88 ± 3.22
	May	72.66 ± 3.14	141.90 ± 3.05	199.98 ± 2.90	225.36 ± 3.43	269.70 ± 3.80	263.16 ± 5.66
Pb μg/L	February	11.40 ± 0.18	6.48 ± 0.11	28.80 ± 0.50	25.80 ± 0.50	25.98 ± 0.43	69.84 ± 1.20
	May	16.62 ± 0.21	10.92 ± 0.22	34.74 ± 0.65	27.30 ± 0.26	47.46 ± 0.79	76.86 ± 1.08
Zn μg/L	February	909.60 ± 4.37	429.18 ± 0.64	686.40 ± 3.91	784.80 ± 2.04	505.02 ± 4.14	810.00 ± 3.97
	May	990.60 ± 3.27	720.00 ± 5.61	834.00 ± 7.84	897.60 ± 5.92	799.20 ± 4.72	918.00 ± 7.07

Note: Values expressed in mean ± SD of three replicates.

and reservoirs by many investigators, whereas *Cyclotella* species indicates mesotrophic small- and medium-sized lakes with species sensitive to the onset of stratification [22,25]. The species *M. aeruginosa* was observed as the dominant species at nearly all stations. The maximum density of *M. aeruginosa* was found in February 2012 at sampling station 4. *M. aeruginosa,* which usually inhabits eutrophic waters, is a well-known *Cyanobacterium* that is responsible for the formation of toxic water blooms all over the world. Shallow, warm, and eutrophic reservoirs provide the most favorable conditions for *M. aeruginosa* development [20,21,26]. The species *C. erosa*, which is usually found in small, enriched lakes with low light tolerance, was found in low numbers. This species reflects the low grazing pressure in almost all lentic ecosystems [20,21]. *Ulnaria ulna*, is known to be a characteristic inhabitant of eutrophic lakes and refers frequently stirred up, inorganically turbid shallow lakes [25,27]. *U. ulna* was recorded at stations 1, 3, and 4 in this study. *Trachelomonas hispida* of Euglenophyta is typically found in shallow mesotrophic lakes [20,21]. It was recorded in low numbers at stations 1–3 in May 2012.

It is known that, the EPA has announced a water quality trading policy, which aims at cutting industrial, municipal, and agricultural discharges into US waterways. EPA standardized the water quality in four different classes and mentioned the acceptable element values for each class. The ministries of agriculture and environment of different countries made few variations in values according to needs of their country (Table 5).

In this study, Al, B, Ca, Cd, Cr, Cu, K, Mg, Na, and Ni exceeded normal limits with average highest values. Only average highest values of Fe and Zn (Class I) are within normal limits. However, average lowest values of Al, B, Cd, Cu, Ni, and Pb are within normal limits (Between Class II and III) (Table 5). Sakcali et al. [9], have reported anomalies in metal concentrations and have related this to sources such as landfill leaching and municipal and industrial discharges in Meric, Arda, Tunca, and Ergene Rivers in Turkey. The same sources could be the reason of this high level of heavy metal pollution in Riva Stream.

In St. 1, where the highest B, Ca, K, Mg, and Na values were measured, *C. atomus*, *C. ocellata*, *Nitzschia*

Table 5
Trace element based freshwater classification

	I	II	III	IV
Al μg/L	300	300	1,000	>1,000
B μg/L	1,000	1,000	1,000	>1,000
Ca mg/L	75	200	800	–
Cd μg/L	3	5	10	>10
Cr μg/L	20	50	200	>200
Cu μg/L	20	50	200	>200
Fe μg/L	300	1,000	5,000	>5,000
K mg/L	20	50	–	–
Mg mg/L	50	150	–	–
Na mg/L	125	125	250	>250
Ni μg/L	20	50	200	>200
Pb μg/L	10	20	50	>50
Zn μg/L	200	500	2,000	>2,000

Sources: United States EPA (2002) [24] and Water Pollution Control Regulations of Turkey (2004) [28].

acicularis, U. ulna, U. acus, G. olivaceum, Melosira varians, Oocystis borgei, M. aeruginosa, Oscillatoria tenuis, C. erosa, and *T. hispida* were observed. *C. atomus, C. ocellata, U. ulna, M. varians, Navicula cuspidata, M. aeruginosa, O. tenuis*, and *C. erosa* were also observed in high Cd measured station (St. 4). In station 5, where the highest Ni was measured, *C. atomus*, *C. ocellata*, *M. aeruginosa*, and *C. erosa* were observed. Additionally, in St. 6, where the highest Cr, Cu, and Pb were measured, *C. atomus*, *C. ocellata*, *O. borgei*, *Monaraphidium falcatus*, *M. aeruginosa*, and *C. erosa* were observed.

Chlorophyll-*a* distribution is an important indicator of pollution and primary production in surface waters. It was known that chlorophyll-*a* was used for determining the algal biomass in many investigations [29]. In the present study, chlorophyll-*a* concentrations were estimated between 1.52 mg/m^3 and 1.83 mg/m^3. Although there were some differences between phytoplankton densities in different stations, this result did not reflect to chlorophyll-*a* concentrations, since the phytoplankton density was calculated as $organism/cm^3$ instead of biomass. A negative correlation between Chlorophyll-*a* and fresh water abundant elements, Ca and Mg is observed. While Ca is more abundant in natural waters, Mg has a special importance for being an important constituent of the chlorophyll molecule.

In Riva Stream, electrical conductivity values were higher than the standard limits (150–500 μS/cm) of the protocols assigned for protection of surface water sources against pollution [29], and an increase was observed from Ömerli Dam Lake to the Black Sea coasts. The main reason of this situation is the effect of salty sea water.

According to Pearson's correlation and Spearman rank correlation analysis, an important positive correlation between Al and Cu; B and Ca, K, Na, salinity, and conductivity; Ca and Mg; K and Na, salinity, and conductivity; Ni and Pb were observed. Moreover, while there was a significant positive correlation between salinity, K, Na, and conductivity, negative correlation between B and Cu; Ca and Ni and Pb; K and Cu; Mg and Pb and Ni; Na and Cu; Ni and Mg; Pb and Ca were also observed.

Contamination degree of streams can be defined by observing the numbers and groups of existing relative organisms. For this purpose, blue-green algae, diatoms, and green algae are used as available taxonomic groups for measurement of biological conditions of streams [20,30]. Phytoplankton of Riva Stream consists of diatoms, blue-green algae, *M. aeruginosa,* and green algae members. The algal flora of Riva Stream did not show rich species variation as a result of inflows causing very low numbers of phytoplankton taxa and biomass in running waters [31]. Additionally, high heavy metal levels could be one of the reasons for this situation, especially lack of some non-resistant/tolerant phytoplankton species. Recent studies showed that, some species of phytoplankton, known to be sensitive to metals, dramatically decreased in abundance while other more tolerant species subsequently increased [32,33].

Riva Stream is getting polluted by industrial and domestic pollutants in present day. There are settlements, agricultural lands, and stock farms around it. Moreover, the stream bank is used as a picnic area during summer [34]. Previous studies pointed out the pollution problem at the stream [14,15,34].

The physicochemical characteristics of Riva Stream as a high concentration of nutrients make it a similar eutrophic. It is required that, Riva Stream should be taken under protection as soon as possible to improve its water quality by relevant authorities. Therefore detailed studies on phytoplankton including physicochemical parameters, heavy metal, and nutrient concentrations, have to be carried out for controlling the water quality in Riva Stream.

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Annexure 1

Pearson's correlation coefficients of Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Zn, pH, chlorophyll-*a*, salinity, and conductivity

Pearson correlation coeff.	Distance m	Al µg/L	B µg/L	Ca mg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe µg/L	K mg/L	Mg mg/L	Na mg/L	Ni µg/L	Pb µg/L	Zn µg/L	pH	Chlorophyll-*a* mg/cm^3	Salinity ‰	Conductivity µS/cm
Distance m	1	0.383**	−0.704**	−0.820**	−0.701**	0.320**	0.378**	−0.307**	−0.692**	−0.844**	−0.575**	0.654**	0.923**	0.013	0.492**	0.115	−0.621**	−0.662**
Al µg/L	0.383**	1	−0.428**	0.021	−0.650**	−0.547**	0.734**	−0.464**	−0.456**	−0.143	−0.487**	−0.283**	0.317**	−0.128	−0.072	−0.188	−0.483**	−0.355**
B µg/L	−0.704**	−0.428**	1	0.713**	0.530**	0.044	−0.768**	0.299**	0.983**	0.652**	0.913**	−0.490**	−0.476**	0.482**	−0.068	−0.212*	0.858**	0.952**
Ca mg/L	−0.820**	0.021	0.713**	1	0.432**	−0.404**	−0.199*	0.315**	0.665**	0.944**	0.658**	−0.812**	−0.722**	0.018	−0.260**	−0.454**	0.554**	0.665**
Cd µg/L	−0.701**	−0.650**	0.530**	0.432**	1	0.082	−0.551**	0.397**	0.564**	0.487**	0.581**	−0.101	−0.594**	0.296**	−0.019	−0.224*	0.521**	0.503**
Cr µg/L	0.320**	−0.547**	0.044	−0.404**	0.082	1	−0.521**	0.299**	0.005	−0.316**	0.252**	0.705**	0.464**	0.229*	0.539**	0.237*	0.114	0.008
Cu µg/L	0.378**	0.734**	−0.768**	−0.199*	−0.551**	−0.521**	1	−0.240*	−0.756**	−0.231*	−0.760**	−0.123	0.094	−0.674**	−0.180	−0.036	−0.656**	−0.686**
Fe µg/L	−0.307**	−0.464**	0.299**	0.315**	0.397**	0.299**	−0.240*	1	0.347**	0.525**	0.578**	−0.071	−0.386**	−0.202*	0.101	−0.347**	0.553**	0.196*
K mg/L	−0.692**	−0.456**	0.983**	0.665**	0.564**	0.005	−0.756**	0.347**	1	0.622**	0.904**	−0.484**	−0.498**	0.496**	−0.069	−0.205*	0.886**	0.935**
Mg mg/L	−0.844**	−0.143	0.652**	0.944**	0.487**	−0.316**	−0.231*	0.525**	0.622**	1	0.662**	−0.716**	−0.790**	−0.101	−0.275**	−0.410**	0.556**	0.548**
Na mg/L	−0.575**	−0.487**	0.913**	0.658**	0.581**	0.252**	−0.760**	0.578**	0.904**	0.662**	1	−0.299**	−0.366**	0.459**	0.148	−0.381**	0.831**	0.837**
Ni µg/L	0.654**	−0.283**	−0.490**	−0.812**	−0.101	0.705**	−0.123	−0.071	−0.484**	−0.716**	−0.299**	1	0.693**	0.182	0.396**	0.308**	−0.451**	−0.526**
Pb µg/L	0.923**	0.317**	−0.476**	−0.722**	−0.594**	0.464**	0.094	−0.386**	−0.498**	−0.790**	−0.366**	0.693**	1	0.326**	0.566**	0.119	−0.510**	−0.449**
Zn µg/L	0.013	−0.128	0.482**	0.018	0.296**	0.229*	−0.674**	−0.202*	0.496**	−0.101	0.459**	0.182	0.326**	1	0.294**	−0.122	0.313**	0.471**
pH	0.492**	−0.072	−0.068	−0.260**	−0.019	0.539**	−0.180	0.101	−0.069	−0.275**	0.148	0.396**	0.566**	0.294**	1	−0.232*	−0.113	−0.093
Chlorophyll−*a* mg/cm^3	0.115	−0.188	−0.212*	−0.454**	−0.224*	0.237*	−0.036	−0.347**	−0.205*	−0.410**	−0.381**	0.308**	0.119	−0.122	−0.232*	1	−0.250**	−0.209*
Salinity ‰	−0.621**	−0.483**	0.858**	0.554**	0.521**	0.114	−0.656**	0.553**	0.886**	0.556**	0.831**	−0.451**	−0.510**	0.313**	−0.113	−0.250**	1	0.848**
Conductivity µS/cm	−0.662**	−0.355**	0.952**	0.665**	0.503**	0.008	−0.686**	0.196*	0.935**	0.548**	0.837**	−0.526**	−0.449**	0.471**	−0.093	−0.209*	0.848**	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

Annexure 2

Spearman rank correlation coefficients of Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Zn, pH, Chlorophyll-*a*, Salinity, and Conductivity

Spearman correlation coeff.	Distance m	Al µg/L	B µg/L	Ca mg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe µg/L	K mg/L	Mg mg/L	Na mg/L	Ni µg/L	Pb µg/L	Zn µg/L	pH	Chlorophyll-*a* mg/cm^3	Salinity ‰	Conductivity µS/cm
Distance m	1,000	0.167*	−0.616**	−0.782**	−0.476**	0.120	0.350**	−0.360**	−0.551**	−0.792**	−0.575**	0.559**	0.573**	−0.021	−0.479**	0.032	−0.738**	−0.667**
Al µg/L	0.167*	1,000	−0.266**	0.128	−0.175**	−0.322**	0.543**	−0.261**	−0.322**	0.054	−0.224**	−0.099	0.163*	0.016	−0.139*	0.084	−0.364**	−0.383**
B µg/L	−0.616**	−0.266**	1,000	0.526**	0.565**	0.216**	−0.414**	0.560**	0.939**	0.511**	0.851**	−0.117	−0.171**	0.368**	0.345**	−0.058	0.836**	0.933**
Ca mg/L	−0.782**	0.128	0.526**	1,000	0.345**	−0.125	−0.077	0.302**	0.471**	0.869**	0.503**	−0.560**	−0.418**	0.059	0.350**	−0.064	0.560**	0.441**
Cd µg/L	−0.476**	−0.175**	0.565**	0.345**	1,000	0.015	−0.344**	0.424**	0.509**	0.361**	0.519**	−0.075	−0.235**	0.301**	0.236**	−0.157*	0.598**	0.507**
Cr µg/L	0.120	−0.322**	0.216**	−0.125	0.015	1,000	−0.168*	0.389**	0.267**	−0.109	0.291**	0.521**	0.396**	0.162*	0.132	−0.314**	0.061	0.118
Cu µg/L	0.350**	0.543**	−0.414**	−0.077	−0.344**	−0.168*	1,000	−0.296**	−0.470**	−0.060	−0.493**	0.006	0.126	−0.346**	−0.295**	0.151*	−0.546**	−0.537**
Fe µg/L	−0.360**	−0.261**	0.560**	0.302**	0.424**	0.389**	−0.296**	1,000	0.560**	0.393**	0.682**	0.113	−0.185**	0.261**	0.408**	−0.402**	0.485**	0.475**
K mg/L	−0.551**	−0.322**	0.939**	0.471**	0.509**	0.267**	−0.470**	0.560**	1,000	0.455**	0.851**	−0.062	−0.110	0.429**	0.346**	−0.059	0.774**	0.874**
Mg mg/L	−0.792**	0.054	0.511**	0.869**	0.361**	−0.109	−0.060	0.393**	0.455**	1,000	0.488**	−0.494**	−0.518**	0.010	0.371**	−0.133*	0.585**	0.425**
Na mg/L	−0.575**	−0.224**	0.851**	0.503**	0.519**	0.291**	−0.493**	0.682**	0.851**	0.488**	1,000	−0.094	−0.148*	0.405**	0.445**	−0.210**	0.756**	0.778**
Ni µg/L	0.559**	−0.099	−0.117	−0.560**	−0.075	0.521**	0.006	0.113	−0.062	−0.494**	−0.094	1,000	0.630**	0.254**	−0.350**	−0.179**	−0.292**	−0.183**
Pb µg/L	0.573**	0.163*	−0.171**	−0.418**	−0.235**	0.396**	0.126	−0.185**	−0.110	−0.518**	−0.148*	0.630**	1,000	0.285**	−0.294**	−0.043	−0.418**	−0.279**
Zn µg/L	−0.021	0.016	0.368**	0.059	0.301**	0.162*	−0.346**	0.261**	0.429**	0.010	0.405**	0.254**	0.285**	1,000	0.156*	−0.045	0.222**	0.281**
pH	−0.479**	−0.139*	0.345**	0.350**	0.236**	0.132	−0.295**	0.408**	0.346**	0.371**	0.445**	−0.350**	−0.294**	0.156*	1,000	−0.339**	0.329**	0.328**
Chlorophyll−*a* mg/cm^3	0.032	0.084	−0.058	−0.064	−0.157*	−0.314**	0.151*	−0.402**	−0.059	−0.133*	−0.210**	−0.179**	−0.043	−0.045	−0.339**	1,000	−0.101	−0.030
Salinity ‰	−0.738**	−0.364**	0.836**	0.560**	0.598**	0.061	−0.546**	0.485**	0.774**	0.585**	0.756**	−0.292**	−0.418**	0.222**	0.329**	−0.101	1,000	0.871**
Conductivity µS/cm	−0.667**	−0.383**	0.933**	0.441**	0.507**	0.118	−0.537**	0.475**	0.874**	0.425**	0.778**	−0.183**	−0.279**	0.281**	0.328**	−0.030	0.871**	1,000

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).