Sigma J Eng & Nat Sci 38 (1), 2020, 383-392

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

TRACE AND TOXIC ELEMENTS IN THE WATERS OF A CONTAMINATED WATERSHED IN TURKEY

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Received: 20.06.2019 Revised: 19.08.2019 Accepted: 31.12.2019

ABSTRACT

Ergene River Basin is the main fluvial habitat of Thrace Part of Marmara region and known as one of the most polluted river ecosystems of Turkey. The aim of this study was to evaluate the water quality of Ergene River Basin components (Meriç and Ergene Rivers and 10 most significant tributaries of the basin) by investigating 25 trace and toxic element concentrations (Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sb, Ba, Tl and Pb). Water samples were collected in rainy season (spring) of 2018 from 21 stations and element levels were investigated by using an ICP-MS. Cluster Analysis (CA) was used to classify the investigated trace and toxic elements in terms of accumulation levels in the waters of Ergene River Basin and to classify the investigated stations in terms of contamination levels. According to the results of element analysis, Ergene River has Class II and Çorlu Stream has Class III water quality in terms of nickel and chromium parameters. Almost all the investigated watershed elements have Class III and Ergene River and Çorlu Stream have Class IV water quality in terms of selenium parameter. According to the results of elemental CA, 4 statistically significant clusters were formed, which were named as "Most intense elements", "Second most intense elements", "Moderate intense elements" and "Rarest elements". According to the results of locational CA, 3 statistically significant clusters were formed, which were named as "Less contaminated regions", "Moderate contaminated regions" and "Most contaminated regions".
Keywords: Ergene river basin, trace and toxic elements, water quality, cluster analysis.

1. INTRODUCTION

Toxic elements are the significant contaminants for the aquatic ecosystems. They can be strongly accumulated and biomagnified along water, sediment and aquatic food chain and have hazardous effects on the ecological balance of the environment. Although they are extremely dangerous, significant quantities of toxic elements are being discharged to the aquatic habitats continuously (Massoudieh et al., 2010; Yu et al., 2011; Çiçek et al., 2019).

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Meriç River is the lo ngest fluvial ecosystem of Balkans and it is known that the water quality of the Meriç River has decreased significantly after merging with the Ergene River and this situation has a negative impact on biota (Elipek et al., 2010; Güher et al., 2011; Tokatlı and Baştatlı, 2016). Meriç River Basin constitutes one of the most productive agricultural areas of Turkey and the main usage area of the system is irrigation water supply. 95% of the basin (over a million hectares) is suitable for agriculture, the rest is suitable for irrigation technically and economically (TZOB, 2003; Anonymous, 2005). Rice, sugar beet, sunflower, corn, and some kinds of vegetable and fruit are the main product varieties in the basin (Kibaroglu, 2008). Ergene River, which is one the most important tributaries of Meriç River, is known to be exposed to serious pollution due to rapid urbanization and industrialization on its watershed. Ergene River is also the most important irrigation water source of the Thrace Region. It was reported that the main sources of contamination in Ergene River Basin are wastes of domestic and organized industrial sites and agricultural derange waters and there are numbers of industrial enterprises in Çorlu, Çerkezköy, Muratlı and Lüleburgaz districts located in the Ergene River drainage area (Hallı et al., 2014; Tokatlı and Baştatlı, 2016; Tokatlı 2017; 2018; 2019; Kahraman and Özkul, 2018). In two recent studies performed in Ergene River Basin, sediment qualities of lotic and artificial lentic habitats of the watershed were evaluated by using bio – ecological risk assessment indices. According to the results of these researches, chromium and cadmium, which are known as agricultural and industrial origin elements, were determined as the riskiest elements for the fluvial ecosystems of the basin and cadmium, lead and arsenic were found to be the highest ecological risk factors for the reservoirs of the basin (Tokatlı, 2019a; 2019b). In another recent investigation conducted in the same watershed, it was reported that the organic contamination grade in water and toxic element accumulations in sediment of the Meriç River Basin have reached to critical levels and the system is under effect of agricultural and industrial pressure (Tokatlı, 2019c).

The aim of this study was to determine the trace and toxic element concentrations in water of Ergene River Basin components and evaluate the water quality in terms of ecosystem and human health.

2. MATERIALS AND METHODS

2.1. Study area and collection of samples

After a preliminary field study, 21 stations were selected on the Ergene River Basin considering the main tributaries and pollution sources. 9 of the selected stations are located on the Ergene River and 2 of the selected stations are located on the Meriç River (one is located before the merge and the other after the merge). The stations were selected in order to determine the effects of Ergene River on Meriç River. The last 10 of the selected stations were located on the main tributaries of Ergene River (T1: Safaalan Creek, T2: Çorlu Stream, T3: Ahmetbey Creek, T4: Köprüaltı Creek, T5: Ana Creek, T6: Hayrabolu Stream, T7: Büyükdere Creek, T8: Kuleli Stream, T9: Ana Stream, T10: Irrigation Canal). The map of study area is given in Figure 1. Water samples were collected from the middle of the rivers (over the bridges on the streams) in rainy (spring) season of 2018, when the precipitation and surface runoff have increased significantly in the region. Water samples were collected 0.5 m below the water surface in 1 L pre-cleaned glass bottles and kept at 4 ^{0}C until the chemical analysis are conducted.

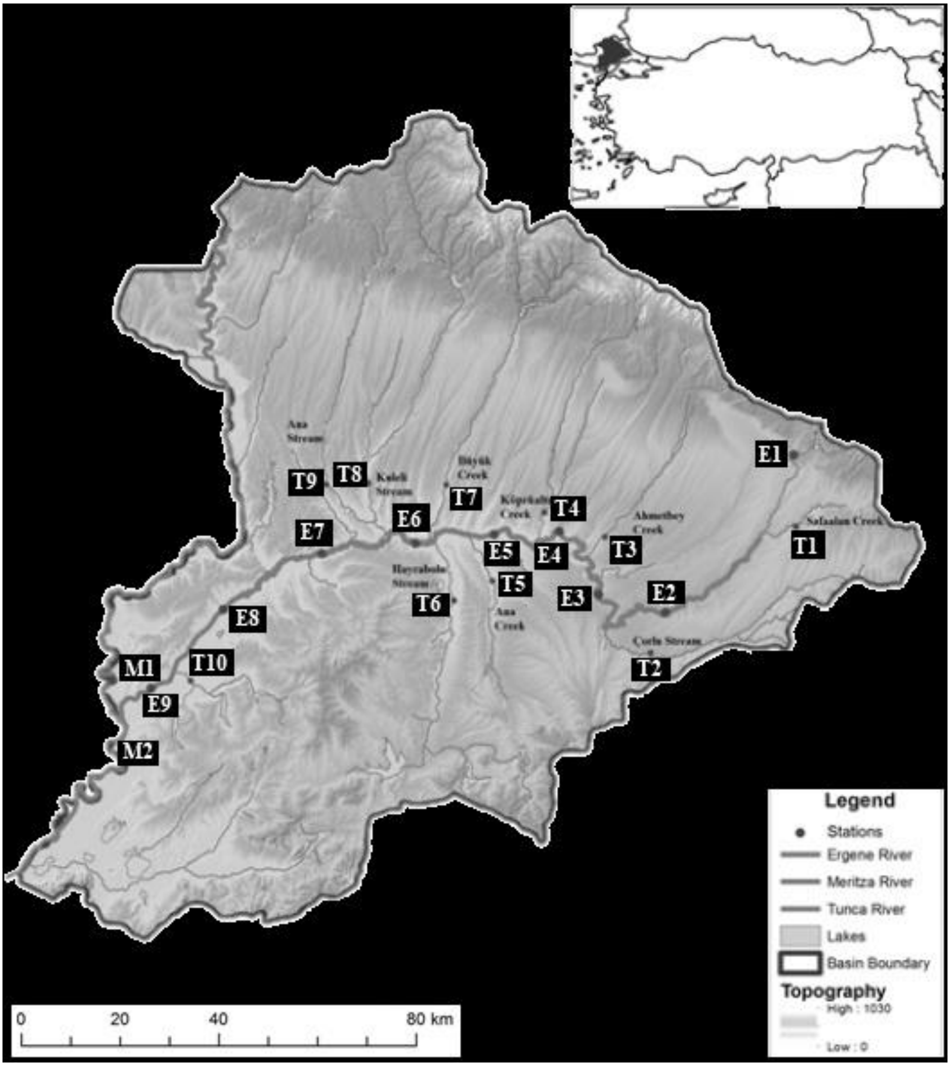

Figure 1. Topographic map of Ergene River Basin and selected stations

2.2. Chemical analysis

For determination of element concentrations in water, water samples of one liter were adjusted to pH 2 by adding 2 mL of HNO_3. Afterwards, all the samples were filtered (cellulose nitrate, 0.45 µm) in such a way as to make their volumes to 50 mL with ultra-pure water. The element levels in water samples were determined by using the "Agilent 7700 xx" branded Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) device in Trakya University Technology Research and Development Application and Research Center (TÜTAGEM). The center has an international accreditation certificate within the scope of TS EN / ISO IEC 17025 issued by TÜRKAK (representative of the World Accreditation Authority in Turkey). The elemental analyses were recorded as means of triplicate measurements (APHA, 1992; EPA, 2001). Cluster Analysis was applied to the results by using the "PAST" package statistical program.

2.3. Statistical analysis

Cluster Analysis (CA) is an important group of multivariate statistical methods and is being used to classify the objects. The primary purpose of CA is to classify the objects into clusters based on their similar characteristics. The hierarchical agglomerative clustering that is one of the most common approaches in CA provides intuitive similarity relationships between any one sample and the entire data set (Tabachnick and Fidell, 1996; Shrestha and Kazama, 2007). In the present study, CA according to Bray Curtis was applied to measured data by using the "PAST" statistical package program.

3. RESULTS AND DISCUSSION

Cluster Analysis (CA) is one of the most widely used multivariate statistical technique to evaluate the water quality (Köse et al., 2014; Belkhiri and Narany, 2015; Tiri et al., 2017). In this study, CA was used to determine the similar groups among the investigated trace and toxic elements according to accumulation levels in water samples and to determine the similar groups among the investigated locations according to contamination levels. The diagram of elemental CA is given in Figure 2 and the diagram of locational CA is given in Figure 3.

According to the results of elemental CA, 4 statistically significant clusters were formed, which were named as "Most intense elements (C1)", "Second most intense elements (C2)", "Moderate intense elements (C3)" and "Rarest elements (C4)". In a study performed in the same river basin, CA was used in order to classify the micro and macro elements in sediments of Meriç – Ergene River Basin. In another study performed in Meriç River Delta, CA was used in order to classify the essential and toxic elements in tissues of some fish species. According to the results of these 2 studies, 5 statistically significant clusters were formed and as similar to the present study, they were named as "most intense elements", "second most intense elements", "moderate intense elements", "second rarest elements" and "rarest elements" (Tokatlı and Baştatlı 2016, Tokatlı 2018).

According to the results of locational CA, 3 statistically significant clusters were formed. The cluster of C1 was named as "Less contaminated regions" and formed by the station of T1, where was located on the Safaalan Creek (upstream region of the basin); stations of M1 and M2, where were located on the Meriç River; and station of E1, where was located on the source region of Ergene River. The cluster of C2 was named as "Moderate contaminated regions" and was formed by the stations of T3, T4, T5, T6, T7, T8, T9, where were located on the main tributaries of Ergene River; and stations of E8 and E9, where were located on the downstream of Ergene River after diluting by main tributaries. The cluster of C3 was named as "High contaminated regions" and was formed by the station of T2, where was located on the Çorlu Stream (exposed to intensive industrial pollution); and stations of E2, E3, E4, E5, E6 and E7, where were located on the middlestream of Ergene River after mixing Çorlu Stream.

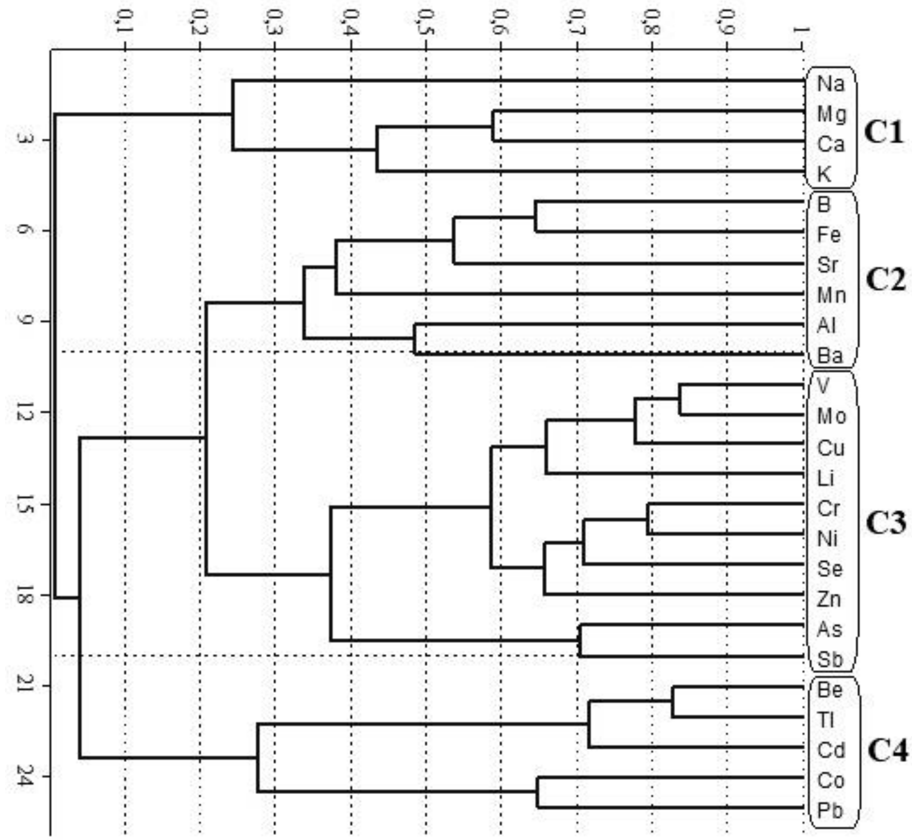

Figure 2. Elemental CA diagram

The element concentration diagrams of the grouped components by means of the results of elemental CA are given in Figure 4. Mean values recorded in water of Meriç and Ergene Rivers and investigated main tributaries and water quality classes of the investigated fluvial ecosystems are also given in Table 1.

The toxic element concentrations of water in Ergene River Basin were evaluated in accordance with Turkish Regulations (SKKY, 2015). Water quality regulations in Turkey separate inland waters into four classes. Class I includes high-quality water that has a high potential to be used for drinking water, recreational purposes, and the production of trout. Class II refers to less contaminated water that can be used as surface water is to become potential for drinking water outside of trout production and for all uses other than Class I. Class III includes polluted water, which can only be used as industrial water after treatment. Class IV refers to heavily polluted water that should not be used at all (SKKY, 2015).

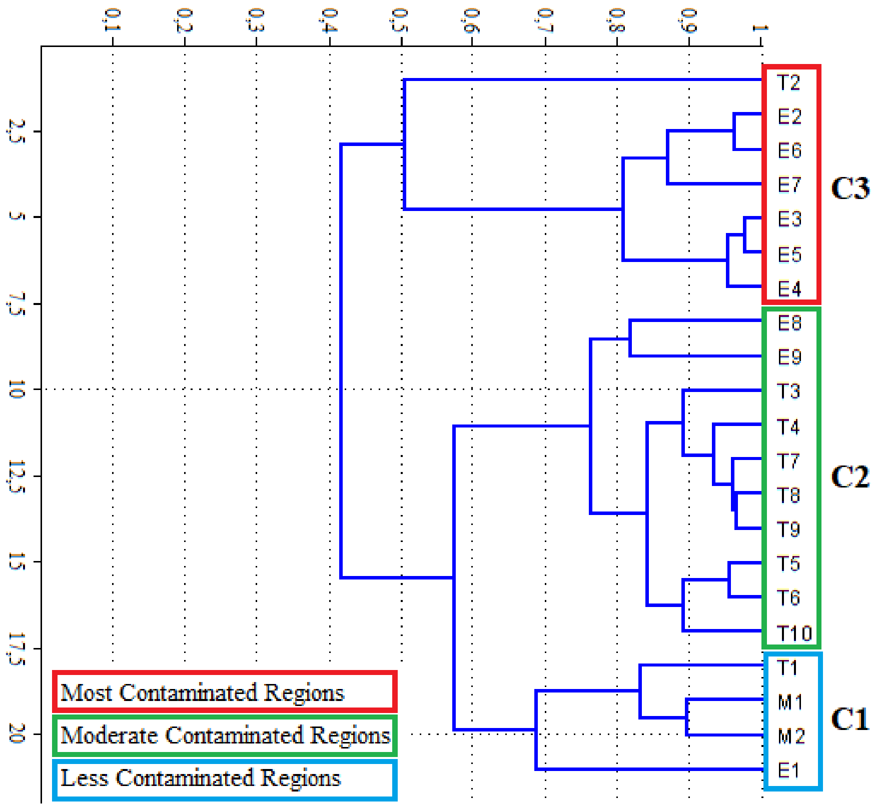

Figure 3. Locational CA diagram

According to the Water Pollution Control Regulation criteria in Turkey (SKKY, 2015), Ergene River has Class II and Çorlu Stream has Class III water quality in terms of nickel and chromium parameters. Nickel and chromium occur naturally in the Earth's crust and they may enter to the environment a result of natural processes and mainly by human activities. The most significant anthropogenic point sources of nickel and chromium in aquatic habitats are the wastewater from electroplating operations, leather tanning industries and textile manufacturing, which are all located on Ergene River Basin (ATSDR, 2005; ATSDR, 2012). Although the nickel and chromium levels detected in waters of watershed elements are not very high, these toxic metals were detected in quite high levels in water of Ergene River and especially Çorlu Stream. These results reflect that Ergene River and Çorlu Stream are being significantly affected by industrial contamination.

The selenium levels detected in water of the basin were between values of 9.29 (Ahmetbey Creek) – 63.78 (Çorlu Stream) mg/L. The measured selenium concentrations in almost all the investigated tributaries and Meriç – Ergene Rivers exceeded the limit of 10 mg/L specified by Turkish Regulations and the Ergene River Basin has Class III – IV water quality in terms of selenium parameter, in general (SKKY, 2015). It is known that selenium is released to the water via sewage effluent, agricultural runoff and industrial waste water (ATSDR, 2003). The detected quite high selenium contents even in the investigated stations known to be not exposed to industrial contamination, suggests that the main source of selenium accumulation in water of the Ergene River Basin may due to sewage wastes and agricultural activities.

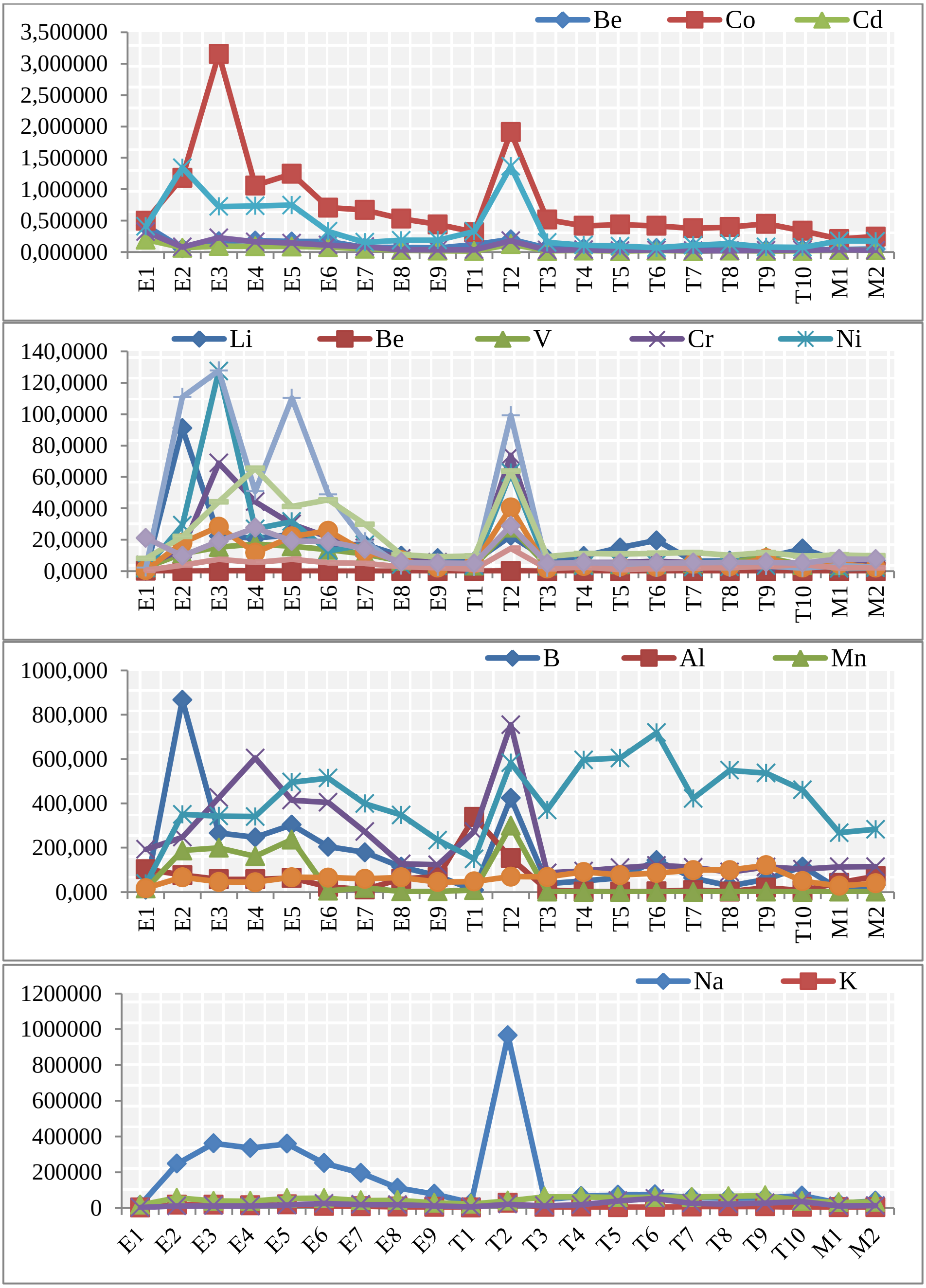

Figure 4. Element levels in waters of basin components according to CA (X axis: stations; Y axis: element concentrations – mg/L)

Elements (mg/L)	ªWater Quality Classes				Ergene River Basin Components*(mean)											
	I (clean)	II (slightly polluted)	III (polluted)	IV (highly polluted)	Meriç River (M)	Ergene River (E)	Safaalan Creek (T1)	Çorlu Stream (T2)	Ahmetbey Creek (T3)	Köprüaltı Creek (T4)	Ana Creek (T5)	Hayrabolu Stream (T6)	Büyükdere Creek (T7)	Kaleli Stream (T8)	Ana Stream (T9)	Irrigation Canal (T10)
As	20	50	100	> 100	2.110 Class I	4.527 Class I	1.260 Class I	14.622 Class I	1.598 Class I	2.615 Class I	1.036 Class I	1.586 Class I	2.040 Class I	2.449 Class I	3.095 Class I	4.155 Class I
Cu	20	50	200	> 200	3.590 Class I	14.307 Class I	4.910 Class I	40.610 **Class III**	1.815 Class I	3.277 Class I	3.196 Class I	2.794 Class I	4.719 Class I	3.236 Class I	8.379 Class I	2.352 Class I
B	1000	1000	1000	> 1000	21.405 Class I	251.496 Class I	8.678 Class I	425.184 Class I	37.082 Class I	50.794 Class I	63.974 Class I	143.855 Class I	63.033 Class I	28.023 Class I	56.780 Class I	114.305 Class I
Zn	200	500	2000	> 2000	3.135 Class I	52.898 Class I	2.756 Class I	99.281 Class I	2.181 Class I	4.086 Class I	2.045 Class I	2.175 Class I	2.159 Class I	2.160 Class I	3.275 Class I	2.084 Class I
Cd	2	5	7	> 7	0.034 Class I	0.082 Class I	0.018 Class I	0.126 Class I	0.021 Class I	0.024 Class I	0.015 Class I	0.024 Class I	0.015 Class I	0.025 Class I	0.018 Class I	0.020 Class I
Cr	20	50	200	> 200	4.313 Class I	23.496 **Class II**	4.100 Class I	73.860 **Class III**	4.817 Class I	5.526 Class I	5.697 Class I	6.378 Class I	5.403 Class I	5.168 Class I	5.443 Class I	5.217 Class I
Pb	10	20	50	> 50	0.175 Class I	0.536 Class I	0.330 Class I	1.364 Class I	0.155 Class I	0.113 Class I	0.096 Class I	0.071 Class I	0.110 Class I	0.137 Class I	0.083 Class I	0.078 Class I
Ni	20	50	200	> 200	1.895 Class I	28.280 **Class II**	3.630 Class I	62.845 **Class III**	3.429 Class I	3.321 Class I	4.596 Class I	4.303 Class I	2.473 Class I	2.686 Class I	3.484 Class I	4.947 Class I
Se	10	10	20	> 20	10.144 **Class III**	30.704 **Class IV**	9.693 Class I	63.789 **Class IV**	9.296 Class I	11.332 **Class III**	10.997 **Class III**	11.441 **Class III**	11.957 **Class III**	10.128 **Class III**	11.861 **Class III**	9.637 Class I

ªTurkish Regulations, 2015; *Class II – III – IV water qualities are given in bold

Table 1. Water Quality Criteria and water qualities of the basin components

4. CONCLUSIONS

In this study, contamination status of the Ergene River Basin that is the most significant aquatic ecosystems of Thrace Region was evaluated. In this context, trace and toxic element concentrations in water of Meriç and Ergene Rivers and 10 significant tributaries of Ergene River Basin were investigated and detected data were evaluated by using Cluster Analysis (CA).

Elemental CA grouped 25 macro and micro elements into 4 clusters of similar characteristics in surface water of the basin; "Most intense elements", "Second most intense elements", "Moderate intense elements" and "Rarest elements". Locational CA was grouped 21 stations into 3 clusters of similar water quality characteristics in surface water of the basin; “Less contaminated regions”, “Moderate contaminated regions” and “High contaminated regions”.

According to detected data, the pressure of Çorlu Stream on the system was clearly presented and it was recorded as the main pollutant factor on the Ergene River Basin among the investigated tributaries of the watershed. It was determined that Ergene River and Çorlu Stream were significantly affected by the industrial activities conducted around the Çorlu and Çerkezköy Regions. It was also determined that almost all the investigated basin components were significantly affected by the agricultural activities conducted almost all around the basin.

In conclusion, as a result of this research and as many researchers indicated, Ergene River has Class III – IV water quality in terms of many parameters and it is the most polluted river ecosystem of Thrace Region and one of the most polluted river ecosystems in Turkey. The measured data reveals that agricultural runoff caused from especially paddy fields around the basin and the industrial discharges caused from especially Çorlu Stream are the main contamination factors for the basin.

Acknowledgement

The author would like to thank for the financial and technical supports supplied by Trakya University, Turkey. This investigation has been supported by the project numbered as 2017/211 accepted by Trakya University, Commission of Scientific Research Projects.

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