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Original Research

Trace and Toxic Element Levels in River Sediments

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Abstract

The Meriç River is the longest river of the Balkans and it can be declared as most important aquatic ecosystem in the Thrace Region of Turkey. The Tunca and Ergene rivers are the most important branches of the Meriç and they are known to be exposed to important organic and inorganic pollution from agriculture and industry in their basins. We evaluated the sediment quality of the three rivers by determining a total of 25 trace and toxic element accumulations, including lithium (Li), boron (B), sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), arsenic (As), selenium (Se), strontium (Sr), silver (Ag), cadmium (Cd), antimony (Sb), barium (Ba), titanium (Ti), and lead (Pb). Also, one-way ANOVA testing was used to determine the statistical differences of element accumulations among the stations, and cluster analysis (CA) was used to classify the rivers according to sediment qualities and to classify the elements according to accumulation levels. As a result of the study, statistically significant differences were identified among the investigated rivers in terms of almost all the trace and toxic elements and the contamination levels of investigated aquatic ecosystems as follows: Ergene River > Meriç River > Tunca River in general. According to the results of elemental CA, five statistically significant clusters were formed: "most intense elements," "second most intense elements," "moderately intense elements," "second rarest elements," and "rarest elements." According to the results of locational CA, two statistically significant clusters were formed: "highly contaminated locations" and "moderately contaminated locations."

Keywords: Meriç River, Tunca River, Ergene River, sediment quality, trace and toxic elements

Introduction

Environmental pollution has become a matter of global concern over the last few decades as a result of anthropogenic activities and applications. And it is clearly known that aquatic habitats are the most affected ecosystems. Toxic metals that can be strongly accumulated and biomagnified along water, sediments, and the aquatic food chain are one of the most dangerous inorganic contaminant groups discharged to aquatic ecosystems [1-5]. Sediments that may act as a sink for various contaminants that are contaminated with toxic metals pose a direct risk to detritus and deposit-feeding benthic organisms and may also represent a long-term source of contamination in the form of higher trophic levels [6-8].

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Table 1. Location properties of selected stations.

Station	Location	Coordinates		Explanation
		North	South	
Tunca River	Edirne Province	41.66850	26.55413	Downstream of Tunca River
Ergene River	Uzunköprü District	41.28291	26.69906	Downstream of Ergene River
Meriç River	İpsala District	40.94654	26.36079	Downstream of Meriç River

The Tunca and Ergene are the most important branches of the Meriç, which is the longest river of the Balkans. It flows through Turkish territory on both banks and forms the border between Greece on the west bank and Turkey on the east bank to the Aegean Sea. The Meriç Delta that is formed across some 45,000 ha at the mouth of Meriç is listed as a Class A International Wetland. This significant aquatic ecosystem is being exposed to intensive organic and inorganic pollution by means of agricultural applications – especially paddy agriculture conducted around the Meriç (about 25% of total rice production of Turkey is being supplied from this basin) and industrial activities conducted around the Ergene, which is known as a dramatically contaminated ecosystem and one of the most polluted lotic habitats of Turkey [9-11].

The aim of this study was to determine the trace and toxic element concentrations in sediments of the Meriç, Ergene, and Tunca, and evaluate the sediment quality of the system using cluster analysis.

Materials and Methods

Study Area and Collection of Samples

Sediment samples were collected in autumn 2015 from three stations (one of them downstream of the Meriç, one downstream of the Tunca, and one downstream of the Ergene) by using an Ekman grab to take small portions from the center of the dipper and grab with a polyethylene spoon to avoid contamination by metallic parts of the grab. Coordinates, explanations, and the locations of selected stations are given in Table 1 and Fig. 1.

Chemical and Statistical Analysis

Sediment samples were dried for 3 h at 105ºC for element analyses. Then all sediment samples were placed (0.25 g of each sample) in Pyrex reactors of a CEM Mars Xpress 5 microwave digestion unit. $HClO_4$:HNO_3 acids of 1:3 proportions were inserted into the reactors. Samples were mineralized at 200ºC for 30 minutes. Afterward the samples were filtered in such a way as to make their volumes 100 ml with ultra-pure distilled water.

Element levels were determined by Inductively Coupled Plasma-Optic Emission Spectrophotometric (Varian 720 ES) method in the TUTAGEM laboratory of Trakya University. The element analyses were recorded as means triplicate measurements [12, 13].

Cluster Analysis (CA) according to Bray Curtis was applied to the results using the PAST package program, and one-way ANOVA was applied to the results using the SPSS 17 package program.

Results and Discussion

The averages of trace and toxic element levels observed in sediment samples in the Meriç, Ergene, and Tunca with minimum, maximum, and SD values and the results of one-way ANOVA are given in Table 2.

According to the results of one-way ANOVA, statistically significant differences were identified among the investigated stationsm and sediment contamination levels detected in the Ergene were significantly higher than the other investigated rivers in terms of almost all the toxic element levels, including Li, V, Cr, Mn, Co, Ni, Cu, Ga, As, Sr, Ag, Ba, Ti, and Pb (p<0.05). The most significant anthropogenic point sources of chromium and nickel in surface waters and sediments are the wastewater

Fig. 1. Downstream basin of the Meriç River and selected stations.

Table 2. Element accumulation levels and the results of one-way ANOVA testing.

Elements (ppb)	Tunca River				Meriç River				Ergene River			
	min	max	**mean***	SD	min	max	**mean***	SD	min	max	**mean***	SD
Li	154.26	180.87	**169.27^{a}**	11.05	347.68	356.28	**351.61^{b}**	2.38	704.90	781.16	**734.97^{c}**	30.21
B	458.20	771.18	**582.38^{ab}**	112.39	423.69	523.48	**479.67^{a}**	36.30	617.22	855.42	**728.08^{b}**	80.59
Na	401.67	545.98	**483.14^{a}**	47.20	236.79	309.08	**280.65^{b}**	22.56	14.51	65.46	**37.72^{c}**	16.72
Mg	2,461.47	3,023.34	**2,760.51^{a}**	196.60	3,345.55	3,897.68	**3,654.13^{b}**	164.54	3,662.70	4,496.52	**3,939.98^{b}**	253.50
Al	13,517.13	17,106.77	**15,355^{a}**	1,124.10	13,523.77	15,866.48	**14,786^{a}**	690.72	14,705.44	17,326.06	**15,581^{a}**	823.29
K	46,199.91	53,161.99	**50,021^{a}**	2,697.94	95,557.63	109,467.50	**98,525^{a}**	4,227.28	198,558.99	232,139.83	**218,805^{b}**	13,012.80
Ca	269,710.96	309,322.99	**293,856^{a}**	17,356.92	210,498.62	223,751.82	**217,547^{a}**	3,742.57	520,444.35	624,621.84	**584,527^{b}**	44,435.58
V	595.75	700.88	**658.28^{a}**	43.13	1715.19	1,788.74	**1,749.88^{b}**	22.93	2,950.58	3,459.61	**3,243.47^{c}**	183.13
Cr	1,132.03	1,311.49	**1,248.56^{a}**	77.79	2,311.02	2,778.81	**2,599.98^{b}**	191.57	3,107.22	3,648.47	**3,409.38^{c}**	192.74
Mn	13,661.19	15,919.44	**14,992^{a}**	920.00	27,187.00	28,582.15	**27,776^{b}**	427.24	33,337.74	37,739.17	**36,055^{c}**	1,715.39
Fe	8,252.77	10,233.81	**9252^{a}**	665.55	12,319.90	14,364.54	**13,505^{b}**	621.00	11,194.27	13,369.57	**11,976^{c}**	602.78
Co	172.04	196.06	**185.57^{a}**	9.77	323.90	336.03	**330.52^{b}**	4.42	460.97	540.32	**510.92^{c}**	35.88
Ni	488.33	555.38	**530.07^{a}**	30.11	848.17	915.33	**888.01^{b}**	24.28	1,336.59	1,826.92	**1,616.42^{c}**	206.42
Cu	211.05	240.22	**228.54^{a}**	12.50	616.22	656.79	**639.98^{b}**	14.27	1,424.88	1,684.34	**1,587.62^{c}**	116.46
Zn	840.78	960.69	**916.48^{a}**	53.32	3,280.67	3,414.51	**3,349.22^{b}**	45.93	3,499.03	4,097.44	**3,849.66^{b}**	254.44
Ga	164.38	203.30	**184.91^{a}**	15.99	448.79	467.29	**456.88^{b}**	5.91	824.53	993.78	**922.87^{c}**	73.07
As	92.68	118.51	**105.84^{a}**	9.89	241.62	253.71	**249.37^{b}**	4.40	306.13	360.68	**336.71^{c}**	22.31
Se	395.05	424.28	**413.41^{a}**	8.77	429.75	468.23	**452.79^{a}**	11.71	463.15	566.14	**528.48^{b}**	43.22
Sr	1,104.91	1,304.20	**1,240.26^{a}**	77.35	2,431.76	2,609.17	**2,518.36^{b}**	62.38	3,774.32	4,280.26	**4,066.92^{c}**	193.68
Ag	35.03	54.60	**47.97^{a}**	6.18	71.72	87.65	**76.61^{b}**	5.53	273.48	322.65	**305.71^{c}**	16.24
Cd	3.16	3.97	**3.61^{a}**	0.29	23.65	24.27	**24.00^{b}**	0.22	19.17	22.74	**21.12^{c}**	1.11
Sb	9.68	13.00	**11.60^{a}**	1.19	2.58	5.58	**3.82^{b}**	0.92	0.08	3.81	**1.01^{c}**	1.31
Ba	1,512.43	1,765.30	**1,670.70^{a}**	105.70	4,321.58	4,453.36	**4,384.43^{b}**	47.75	9,463.19	10,225.74	**9808.58^{c}**	235.84
Ti	3.94	4.55	**4.25^{a}**	0.22	10.90	11.86	**11.41^{b}**	0.30	17.05	19.22	**17.97^{c}**	0.67
Pb	218.73	250.79	**239.00^{a}**	14.61	1,021.76	1,043.52	**1,034.46^{b}**	8.04	1,994.02	2,095.69	**2044.25^{c}**	34.43

*Values marked with different letters in the same line are statistically different ($p<0.05$). min: minimum; max: maximum; SD: standard deviation

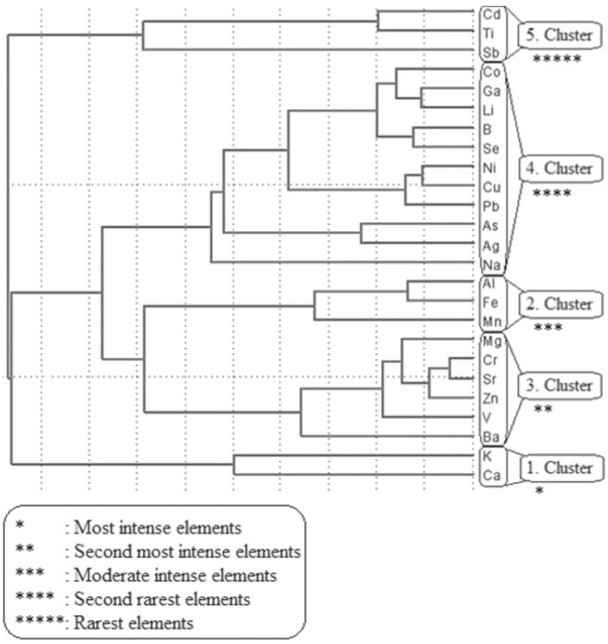

Fig. 2. Cluster analysis diagram of elements.

from electroplating operations, leather tanning industries, and textile manufacturing, which are all located in the Ergene basin [5, 14-15]. It is also known that industrial manufacturing and wastewater from industries may contain much higher levels of copper, lead, and silver [16-20]. However, Cd accumulations detected in sediments of the Meriç were significantly higher than for the Ergene and Tunca ($p<0.05$). Cadmium is an agricultural origin toxic metal and can easily be emitted to soil and water and accumulate in aquatic organisms and agricultural crops by applying phosphate fertilizers that are known to be intensively used around the Meriç [21].

MacDonald et al. [22] reported a sediment quality guideline (SQG) for toxic elements in freshwater sediments. Results of the present study were compared with the lowest effect level (LEL) reported in the SQG, which means that sediments are considered to be clean to marginally polluted and no effects on the majority of sediment-dwelling organisms are expected below this concentration. Although toxic metal accumulations detected in sediment samples of especially the Ergene were at quite high levels, the recorded As, Cd, Cr, Cu, Pb, Ni, and Zn levels in sediments of investigated stations were lower than the limit values of LEL (As: 6 ppm; Cd: 0.6 ppm; Cr: 26 ppm; Cu: 16 ppm; Pb: 31 ppm; Ni:16 ppm; and Zn: 120 ppm) according to SQG.

Cluster analysis (CA) is an important group of multivariate statistical techniques. Its primary purpose is assembling objects based on their characteristics. Hierarchical agglomerative clustering, which is one of the most common approaches in CA, provides intuitive similarity relationships between any one sample and the entire data set. In order to provide visual summaries of the clustering processes, it is also typically illustrated by a dendrogram [23-26].

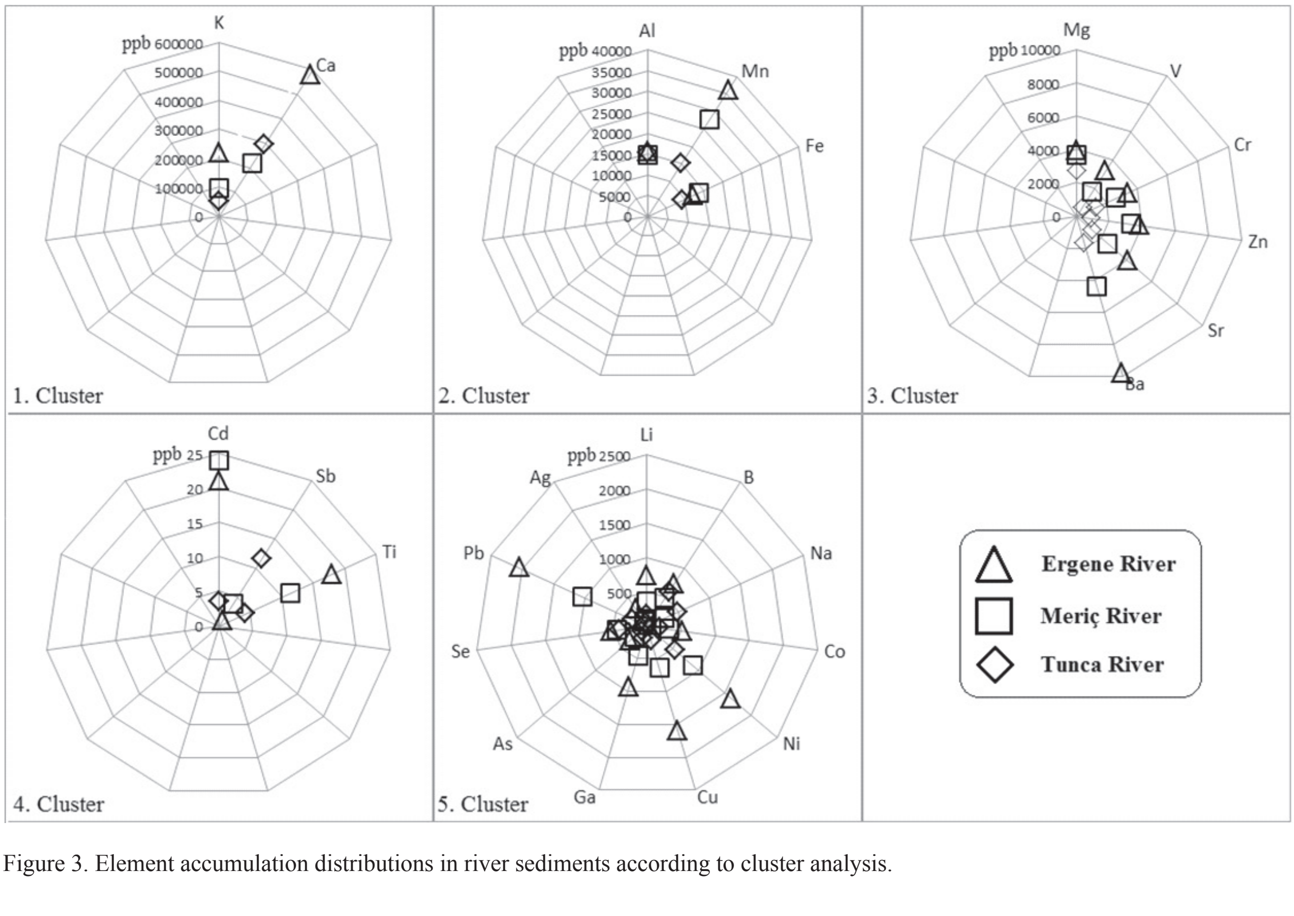

Figure 3. Element accumulation distributions in river sediments according to cluster analysis.

In the present study CA was used to determine the similar groups among the investigated elements according to concentration levels in sediment samples. The diagram of elemental CA is given in Fig. 2. According to the results of elemental CA, five statistically significant clusters were formed and the accumulation diagrams of the grouped elements are given in Fig. 3.

Cluster 1 corresponded to Ca and K, which were the most intense elements on the system with the lowest toxicities; Cluster 2 corresponded to Al, Mn, and Fe, which were the second most intense elements on the system with low toxicities; Cluster 3 corresponded to Ba, V, Zn, Sr, Cr, and Mg, which were the moderate intense elements on the system with moderate toxicities in general; Cluster 4 corresponded to Pb, Cu, Ni, Li, Ga, Co, Se, B, As, Ag, and Na, which were the second rarest elements in the system, with high toxicities in general; and Cluster 5 corresponded to Sb, Ti, and Cd, which were the rarest elements in the system, with high toxicities in general.

CA was also used to classify the investigated rivers according to sediment qualities. The diagram of locational CA is given in Fig. 4. According to the results of locational CA, two statistically significant clusters were formed: Cluster 1 corresponded to the location on the Ergene that was highly contaminated by inorganic pollutants; Cluster 2 corresponded to the locations on the Tunca and Meriç that were moderately contaminated by inorganic pollutants.

Although metals like cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), selenium (Se), and zinc (Zn) are known as essential nutrients required for various biochemical and physiological functions, the other metals like aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), gallium (Ga), lead (Pb), lithium (Li), nickel (Ni), silver (Ag), strontium (Sr), titanium (Ti), and vanadium (V) have no established biological functions and are considered as non-essential toxic metals [27-28].

Toxic metals occur naturally in the Earth's crust and they may enter the environment as a result of natural processes, but mostly as a result of human activities. Most environmental contamination and human exposure results from anthropogenic activities caused by mining and smelting operations, industrial production, domestic and agricultural use of these metals, and use of metal-containing compounds [29-30].

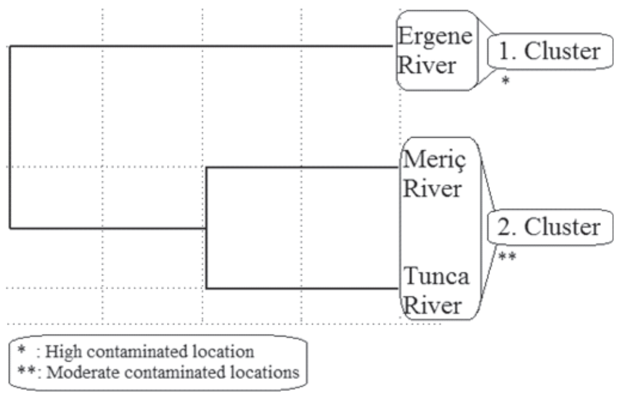

Fig. 4. Cluster analysis diagram of locations.

The Ergene is one of the most important river basins located in the Thrace region of Turkey, and about 1,000 industrial companies are located in its basin. Also, pollution in the Ergene River basin caused by industrial activity (especially near urban areas like Lüleburgaz, Çorlu, and Saray) is one of the major problems of water and sediment qualities in the region [11, 31-32].

Conclusion

The present study investigated some trace and toxic element accumulations in sediments of the Meriç, Tunca, and Ergene rivers. According to data observed, the contamination levels among the investigated most significant lotic ecosystems in the Thrace Region are generally: Ergene River > Meriç River > Tunca River.

Results of the present study reflect that the investigated trace and toxic element accumulation levels are rising significantly after discharge from the Ergene to the system in general, and this adverse situation causes a significant decrease of sediment quality for the Meriç. The Tunca does not constitute a significant risk for the Meriç basin in terms of investigated trace and toxic element accumulations, and it was also determined that it helps to dilute the toxic element levels and increase the sediment quality of the Meriç.

Briefly, all the inorganic data obtained and used in the multistatistical technique show that the Meriç basin is exposed to intensive inorganic pollution and is under the effect of industrial applications sourced from the Ergene basin.

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