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Research Article

Trace metal-induced ecological risk analysis of Sarıçay River sediments, Çanakkale, NW Turkey

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Abstract

Metals have come to the fore among the pollutants monitored in aquatic ecosystems in recent years. Fresh waters especially constitute a "hot spot" due to their limited reserves. In order to analyze the sources of metal-induced pollution, ecological risk level and pollutants of the Sarıçay River passing through the city of Çanakkale, sediment samples were collected from 26 stations and element analyses were carried out in ICP-MS. Anthropogenic effects and the risks they cause were determined by calculating the enrichment factor, geoaccumulation index, and potential ecological risk from the obtained data. Anthropogenic enrichment was detected for Cr, Ni, Pb, Au, Ag and Ba, Bi, Tl, Na, Zn, Mg, K, As, Sb, and Mn with the largest amount being Cd. The level of enrichment varies from moderate to very high. According to the results of risk analysis, a moderate risk for Cd was determined and a very high risk for Ni and Pb. Agricultural activities, atmospheric deposition and mineral deposits in the basin were identified as the major sources from the multivariate statistical analysis performed to determine the main sources of metal inflows.

Keywords: Trace metal, Pollution, Ecological risk, Sarıçay Stream, Çanakkale, Turkey.

Introduction

Coastal plains, in particular river deltas, have been amongst the most preferred areas for establishing cities since early times. Due to the increasing need for water in cities arising from population growth along with the development of agriculture and industry, water and sediment pollution in nearby rivers now poses an environmental threat (Esetlili et al., 2018; Algan et al., 2002; Tchounwou et al. 2012). The serious increase of contaminants is substantially caused by the input of trace metals due to use of fertilizers (N, P, K, Cu, Fe, As and Cd), sewage (As, Cr, Cu, Mn and Ni), and industrial waste (Cd, Ni, Pb, Se, As and Hg), leading to physicochemical and biological changes in various elements of sensitive ecosystems, such as plants (Hawkes, 1997; Nagajyoti et al., 2010), soils (Wei et al., 2016), people (Duruibe et al., 2007), and microorganisms living in water (Förstner and Prosi, 1979). The local inhabitants are especially exposed to trace metal pollution as these toxic matters retained in soft tissues cannot be removed by the body (Jarup, 2003; Xu et al., 2018). For example, at high levels, arsenic has a carcinogenic effect (Tchounwou et al., 2003), cadmium, lead and mercury can cause kidney disease (Xu et al., 2018) and chromium can damage the cardiovascular system.

In recent years, there has been considerable interest in the impacts of human-induced trace metal pollution in the water and sediment quality of the largest rivers in the world (Benet, 2019; Zhou et al., 2020) such as the Amazon (Telxeira et al., 2018), Brahmaputra (Saikia et al., 2016), Yamuna (Pandey et al., 2011), Ganga (Paul, 2017), Lerna (Mendoza et al., 2018), Niger (Izah et al., 2017), Nile (Lasheen and Ammar, 2009; El Bouraie et al., 2010; Satar et al., 2017), Danube (Rusina et al., 2019; Belis et al., 2019; Abonyi et al., 2019) and Po (Farkas et al., 2007). In Turkey, densely populated cities have also been established along the 8333 km-long coastline, especially alongside rivers and on delta plains where overpopulation leads to the same environmental risks (Gazioğlu, 2018).

Among the most polluted urban areas, those in the Marmara Region where industrialization is at its highest level are under risk of ecological degradation. On the southern coast of Istanbul, the Strait of Istanbul (Bosphorus) and river mouths in its vicinity are seriously affected by ecological risk due to metal enrichment in sediments (Sur et al., 2004; Gazioğlu et al., 2002; Ünlü and Alpar, 2015; Haciyakupoglu et al., 2015; Salr and Gazioğlu, 2021). Domestic wastes as well as industrial inputs lead to heavy pollution in Izmit Bay to the east of the Marmara Sea (Pekey et al., 2004). On the Black Sea coast of Turkey where cities are aligned alongside the coast due to the mountains behind, trace metal pollution in stream waters and sediments as well as fish tissues are caused mostly by anthropogenic sources and mining activities (Gedik and Boran, 2013; Ozseker et al., 2013, 2014, 2016; Polat et al., 2015; Engin et al., 2016; Ustaoglu and Tepe, 2019). The industrial, agricultural and domestic waste discharges into Büyükmenderes and Gediz rivers flowing into the Aegean Sea to the west result in a substantial level of pollution (Akcay et al., 2003; Esen et al., 2010; Akinci et al., 2013). Even in the southeastern Anatolia region of Turkey where industry is not so developed, pollution occurs at significant levels in rivers, as in the Tigris river (Gümgüm et al., 1994; Varol, 2011).

This study aims to analyze the ecological risk factors caused by metal pollution from sediments in the Sarıçay River, which flows through the city of Çanakkale into the Çanakkale Straits (Dardanelles), using different indices such as the enrichment factor, contamination factor, geoaccumulation index, pollution load index and potential ecological risk..

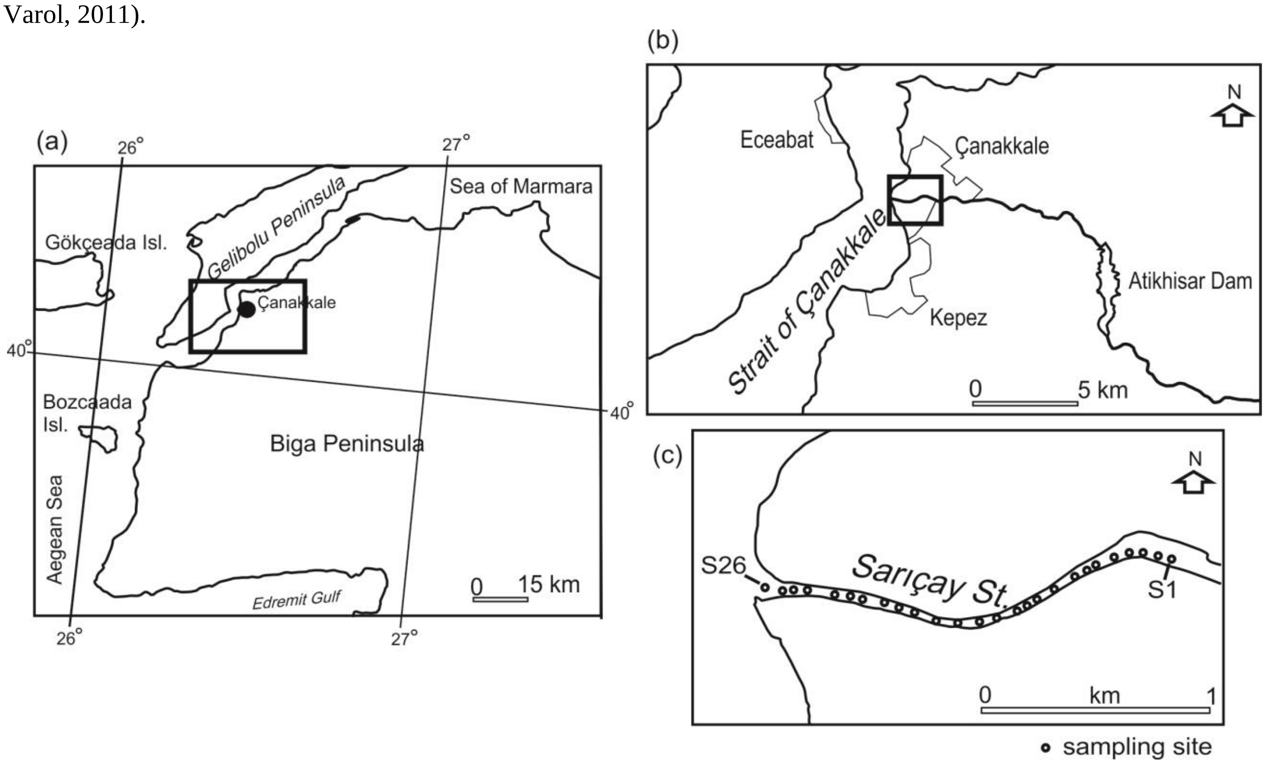

Fig.1. Location map of study area.

Material and Methods

Study area

Sarıcay Stream is one of the most important streams in the Biga Peninsula, NW Turkey, which flows into the Çanakkale Straits, an international waterway connecting the Mediterranean with the Sea of Marmara (Fig. 1a,b). It has a drainage catchment area of 393.78 km^2 (Öztürk and Erginal, 2001) and is exposed to serious flood potential, as understood from the 2010, 2012 and 2013 floods (Tiryaki, and Karaca, 2018). Unlike the other streams in Biga Peninsula, Sarıçay is the only stream where city developments exist. According to Çanakkale's climatic data from the Turkish State Meteorological Service between 1975 and 2018, the annual average temperature is 15.9^{o}C, annual total open surface evaporation is 1387.4 mm, and the annual average precipitation is 613.73 mm

The main inputs caused by agriculture, forestry, grazing, raw sewage, and industrial discharges may pose an ecological risk to the Sarıçay ecosystem. Along the Sarıcay Stream are many industrial plants such as food, leather, mining (lead, zinc and gold) and timber processing (Aksoy et al., 1997; Kocum and Dursun, 2007; Alkan, 2020). Additionally, on the sides of Saricay Stream, there are gas stations and an airport. All told, the increasing population, heavy traffic in Çanakkale city, busy Dardanelles shipping, fishing and boat maintenance, and thermal power plants in the Biga Peninsula also contribute substantially to increased discharges.

Sampling and analyses

In this study, surface sediments were collected using a Van Veen grab sediment sampler from 26 different sites (stations) on the stream's channel alongside the urban development area (Fig. 1c). Additionally, 5 rock samples were collected to calculate the background values of the river basin. The trace metal concentrations (Mn, Ba, Ag, Zn, Sr, Hg, Pb, Cu, V, Cr, Ni, As, Au, Co, Fe, Ca, Al, U, Sb, Na, Mg, Cd, Bi, Tl, K, P, Ti) in the samples were measured by using inductively coupled plasma mass spectrometry (ICP-MS) at the ACME (Bureau Veritas Commodities, Canada) laboratory. Based on ***multi-element ICP-MS data***, the enrichment factor (EF), contamination factor (CF), potential ecological risk (PER), geoaccumulation index (Igeo) and pollution load index (PLI) values were calculated. Principal Component Analysis was applied to the data set to determine the possible sources and transport processes of the elements. Spearman's correlation analysis was applied to determine the meaningful relationships between metals and cluster analysis was used to group the variables according to their similarities.

Enrichment factor (EF). Enrichment Factor (EF) analysis is used to measure whether the metal accumulation in the sediment comes from anthropogenic or natural sources. EF is obtained by dividing the current metal/reference element ratio by the successive metal/reference element ratio. For the reference element, conservative elements abundant in rocks such as Fe, Al, Ca, Ti and Mn are generally used. In this study, Al was used as the reference element. According to Sutherland (2000), EF values are assessed as enrichment values, such as deficiency to minimal (EF<2), moderate (EF=2–5), significant (EF=5–20), very high (EF=20–40) and extremely high (EF>40). In addition, in the literature we accept the limit of 1.5 for EF; in cases where the EF value is below 1.5, the enrichment of metals occurs by natural sources and processes. In cases where the EF value is greater than 1.5, enrichment in metals is considered to occur as a result of anthropogenic effects (Bergamaschi et al., 2002).

Geo-accumulation index (Igeo). Geoaccumulation index (Igeo) analysis is another method used to determine anthropogenic effects on metal concentration in the sediment. Igeo is calculated using the formula below:

$$\mathrm{Igeo} = \log_2 \frac{C_m}{1{,}5 * B_m}$$

In the formula, C_m is the measured concentration of the metal and B_m is the background value of the metal. According to Müller (1969), Igeo values are considered as unpolluted (Igeo < 0), unpolluted to moderately (0 <Igeo < 1), moderately (1 <Igeo < 2), moderately to strongly (2 <Igeo <3), strongly (3 <Igeo <4), strong to extremely (4 <Igeo <5) and extremely polluted (Igeo> 5).

Potential ecological risk index (PER). The Potential ecological risk index (PER) developed by Hakanson (1980) is used to predict the potentially toxic effects of metals deposited in the sediments of an ecosystem. The modified risk factor calculated separately for each metal (Eri) and the integrated risk factor (PER) include all metals to be evaluated (Hakanson, 1980; Zhang et al., 2017). The formula used for the PER of a single trace metal was:

$$\mathrm{Eri} = E_f^i \times T_f^i$$

where E_f^i is the enrichment factor, and T_f^i is the response coefficient for toxicity of a single trace metal. Response coefficients used for the metals were as follows: Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, Zn=1, Mn=.1 Co=5, Tl=10 and V=2 (Hakanson, 1980; Rodriguez-Espinosa et al., 2018; Li et al., 2018). The following classification was used to assess the risk factor (Hakanson, 1980): low potential ecological risk (Eri <40), moderate potential ecological risk (40 ≤ Eri <80), considerable potential ecological risk (80 ≤ Eri <160), high potential ecological risk (160 ≤ Eri <320), and very high potential ecological risk (Eri ≥ 320).

Integrated PER values were calculated as follows:

$$\mathrm{PER} = \sum E_f^i$$

PER values are considered as having low ecological risk (PER <150), moderate ecological risk (150 ≤ PER <300), considerable ecological risk (300 ≤ PER <600), or very high ecological risk (PER ≥ 600).

Results and Discussion

Trace Metal Content

Descriptive statistics of the metals are given in Table 1. While the smallest values according to the element averages of the stations were measured at stations 18, 14 and 16; the highest values were measured at stations 4, 2 and 5. The determined ranges of metals are as follows; Mn 331-1151 ppm, Ba 91.3-612.4 ppm, Ag 111-407 ppb, Zn 90.2-251.3 ppm, Sr 66.1-116.4 ppm, Hg 19-99 ppb, Pb 29.25-83.03 ppm, Cu 33.62-82.5 ppm, V 43-87 ppm, Cr 27.8-113.9 ppm, Ni 25.5-73.3 ppm, As 13.7-28.2 ppm, Au 5-68.6 ppb, Co 9.8-14.7 ppm, Fe 2.06-3.14%, Ca 1.32-2.63%, Al 1.35-2.74%, U 1.3-2.2 ppm, Sb 0.66-1.42 ppm, Na 0.07-2.43%, Mg 0.53-0.98%, Cd 0.30-1 ppm, Bi 0.27-0.56 ppm, Tl 0.24-0.41 ppm, K 0.18-0.42%, P 0.06-0.34% and Ti 0.01-0.04%.

When metal concentrations of the surface sediment samples are compared with background values, it is seen that concentrations of the elements Mn, Ba, Ag, Zn, Pb, Cr, Ni, As, Au, Co, Ca, Al, U, Sb, Mg, Cd, Bi, K and P are above the background values. On the other hand, the concentrations of elements Sr, Hg, Cu, V, Fe, Al, Na and Ti are below the background values. Sr concentrations were below the background value at stations 13 and 14, while Hg concentrations remained below the background value in all stations except 11, 15, 17, 25 and 26. Cu concentrations are below the background value in all sampled stations. Concentrations of V are below the background value in all stations except 2 and 6. Fe concentrations were below the background value at station 21, while Na concentrations were determined below the background value in many stations, such as 1, 2, 3, 4, 5, 7, 8, 9 and 13. Ti concentrations remained below the background value in all stations, as with Cu. While element concentrations above background values are indicative of metal input from natural or human resources, values below background values are related to the easy removal of these elements from the medium.

Ecological risks and possible sources

Metals studied in Saricay River show a decreasing order in terms of the average enrichment factor as follows; Cd> Cr> Ni> Pb> Au> Ag> Ba> Bi> Tl> Na> Zn> Mg> K> As> Sb> Mn> P> U> Ca> Co> Al> S> Fe> Hg> V> Cu> Ti (Fig. 2). Considering the average enrichment values, we determined very high enrichment for Cd, significant enrichment for Cr, Ni, Pb, Au, Ag and Ba, and moderate enrichment for Bi, Tl, Na, Zn, Mg, K, As, Sb, and Mn. There is deficiency of minimal enrichment for Co, Al, Sr, Fe, Hg, V, Cu, P, U, Ca and Ti metals. In terms of distribution by station, the stations with the highest enrichment are 20, 21, and 19, respectively, while the stations with the lowest enrichment are 10, 12, and 5, respectively.

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Table 1. Descriptive statistics of 27 variables in Saricay.

	Cu ppm	Pb ppm	Zn ppm	Ag ppb	Ni ppm	Co ppm	Mn ppm	Fe %	As ppm	U ppm	Au ppb	Sr ppm	Cd ppm
Mean	55.46	56.14	186.66	225.46	38.27	13.00	657.04	2.63	18.40	1.59	16.05	102.15	0.72
Min	33.62	29.25	90.20	111.00	25.50	9.80	331.00	2.06	13.70	1.30	5.00	66.10	0.30
Max	82.50	83.03	251.30	407.00	73.30	14.70	1151.00	3.14	28.20	2.20	68.60	116.40	1.00
Std.deviation	12.12	12.80	38.07	65.42	10.08	1.22	229.78	0.30	3.67	0.23	12.61	11.65	0.17
Background value	90.11	4.28	36.58	24.40	2.98	6.14	221.80	2.10	6.02	0.68	1.42	73.12	0.02

	Sb ppm	Bi ppm	V ppm	Ca %	P %	Cr ppm	Mg %	Ba ppm	Ti %	Al %	Na %	K %	Tl ppm	Hg ppb
Mean	0.91	0.45	55.27	1.98	0.15	44.73	0.74	366.30	0.02	1.96	0.83	0.28	0.31	63.69
Min	0.66	0.27	43.00	1.32	0.06	27.80	0.53	91.30	0.01	1.35	0.07	0.18	0.24	19.00
Max	1.42	0.56	87.00	2.63	0.34	133.90	0.98	612.40	0.04	2.74	2.43	0.42	0.41	99.00
Std.deviation	0.18	0.06	11.03	0.32	0.06	26.66	0.13	150.99	0.01	0.38	0.86	0.08	0.04	18.59
Background value	0.31	0.07	80.60	0.88	0.06	3.38	0.17	51.80	0.10	1.33	0.17	0.09	0.05	79.30

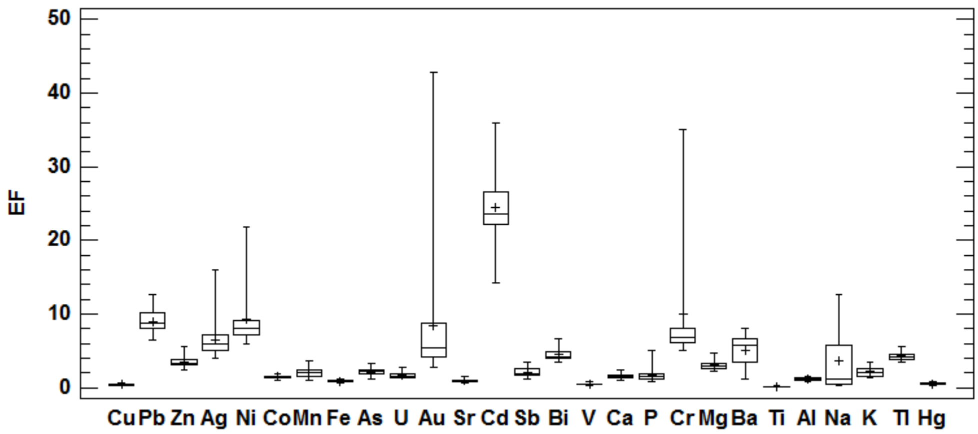

Fig.2. EF values of elements.

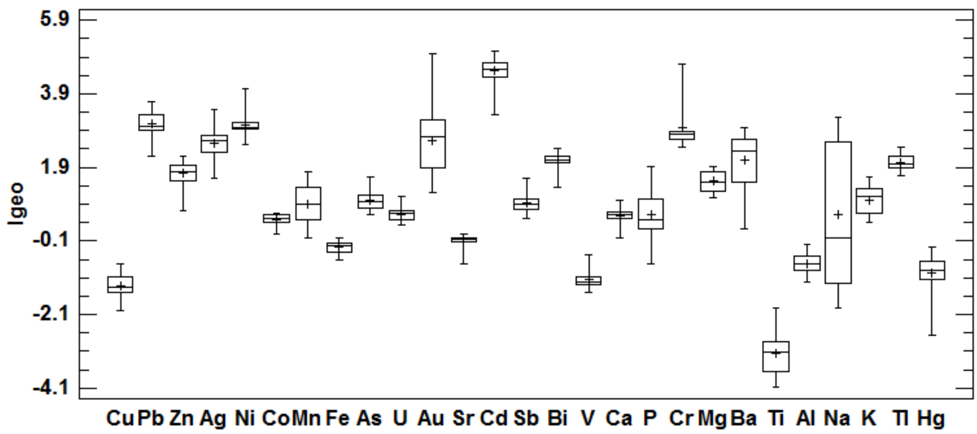

Fig.3. I geo values of elements.

The average geoaccumulation values of heavy metals studied in Sarıçay River in descending order are as follows: Cd> Pb> Ni> Cr> Au> Ag> Ba> Bi> Tl> Zn> Mg> K> As> Sb> Mn> U> P> Na> Ca> Co> Sr> Fe> Al> Hg> Cu> Ti (Fig. 3) Averages of the geoaccumulation values are strong to extremely contaminated for Cd, strongly contaminated for Pb and Ni, moderately to strongly contaminated for Cr, Au, Ag, Ba, Bi and Tl, moderately contaminated for Zn and Mg, uncontaminated to moderately contaminated for Sb, Mn, U, P, Na, Ca, Co, K and As, and uncontaminated for Sr, Fe, Al, Hg, V, Cu and Ti.

According to the sampling stations, those with the highest geoaccumulation values are respectively 20, 26 and 24, while stations with the lowest geoaccumulation values are 18, 13 and 6, respectively.

The Saricay basin is surrounded by extensive agricultural lands. Cd, Pb Zn, Ni and As enrichment may be associated with fertilizers and pesticides used in farming (Cai et al., 2015; Köleli and Kantar, 2005). In addition, the mining map of Çanakkale province displays Pb-Zn deposits in the basin that can be considered as sources of enrichment (https://www.mta.gov.tr/v3.0/sayfalar/hizmetler/maden-haritalari/canakkale.pdf) and also shows the presence of barite, magnesite and gold deposits and silver works in the Saricay Basin. The raw materials of cement are also extracted from the region and Na, K, Ca, Fe and Al are found in these raw materials (Kapkaç, 2007). Cement factories are also found in the basin. Tl accumulates in the atmosphere both from coal burning and cement production processes and is subsequently transported into the sediment (Karbowska, 2016). Cement factories in the region may also have contributed to As and Cr enrichment (Berg and Steinnes, 2005). Although bismuth is not harmful to the environment due to its low toxicity, it is used in industrial areas for pigments, pharmaceuticals and cosmetics (Yang and Sun, 2011) and may therefore cause various domestic wastes, depending on their usage. Ni can be released by burning fuels such as coal, diesel, and fuel oil (Cempel and Nikel, 2006). The enrichment levels for As and Sb were determined at the limit of "non-contamination-moderate contamination". Although these elements have predominantly natural sources, an atmospheric anthropogenic contribution is also possible: Sb from automotive fumes and As from coal combustion (Dousova et al., 2020). Similarly, Cr may be caused by vehicle fuels (Mishra and Bharagava, 2016).

The average mEri values of the heavy metals studied in Sarıçay River are listed in decreasing order as follows: Cd> Ni> Pb> Hg> As> Cr> Co> Zn> Cu> Mn> Tl> V. Considering the average mEri values: the potential ecological risk is very high for Cd and moderate for Ni and Pb. Metals with low ecological risks are Hg, As, Cr, Co, Zn, Cu, Mn, Tl and V (Fig. 4).

There is a very high ecological risk (PERI) at 25 of the 26 stations sampled in Saricay River (PER≥600). On a station-to-station basis, those with the highest PERI values are 20, 21, and 19, respectively (Fig. 5). The stations with the lowest PERI values are 18, 2, and 5, respectively. The average PERI value of all 26 stations is 904.77. The maximum value is 1390.56 (station 20) and the minimum value is 559.85 (station 18).

Statistical analyses

Principal component analysis (PCA) was applied to the data set to identify possible sources of the metals. Seven components (PCs) with eigenvalues> 1 were determined. The striking point in PCA is the coexistence of anthropogenic and lithogenic elements in its components, indicating that the elements come from their own sources and were redistributed by the same hydrogeochemical processes (Karthikeyan et al., 2018).

PC1 accounts for 34.59% of the total variance, consisting of Cu, Pb Zn, Ag, Cd, Bi, Mg and Hg (Table 2). This component mostly refers to basin-based elements that reach the river through flows. Cu, Pb, Zn, Ag and Mg are the elements with deposits in the Sarıçay basin. Hg has a low value of EF, coming from lithogenic sources. Cd arises from agricultural activities and Bi comes from waste water.

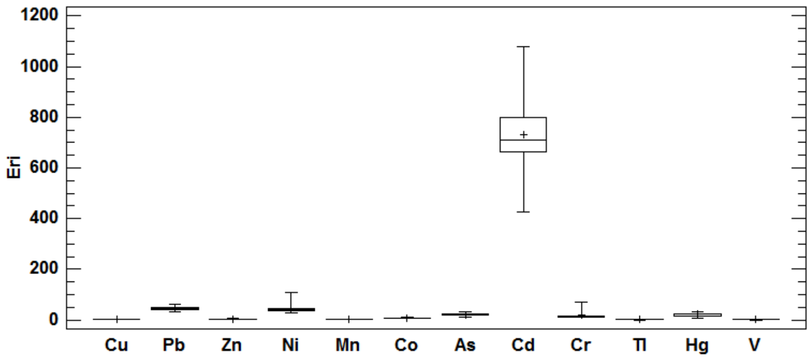

Fig.4. mEri values of trace element

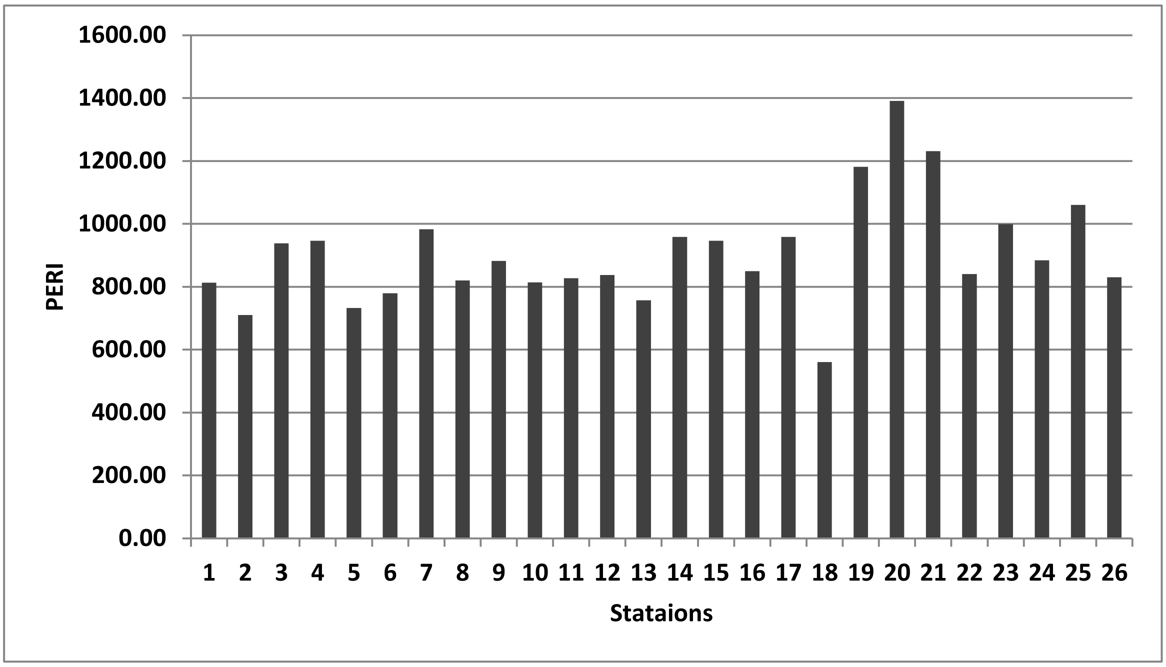

Fig.5. PERI values of stations.

The second component is responsible for 17.76% of the total variance and represents mainly atmospheric inputs. It consists of Ni, Au, P and Cr moving in the same direction and Pb and Tl moving in the opposite direction. Pb is an element whose weight is close to each other in the first two components, revealing that it has multiple sources. The source in the first component is considered lithogenic, and the second is atmospheric. Au within the component comes from mining activities. Cr and Ni may be due to the use of automotive fuel. It is thought that Tl may have been released from coal burning and mixed into the river.

The third component represents 13.79% of the variance and includes Co, Mn, As, Sr and Ba, revealing them to be of lithogenic origin due to weathering in the basin. Co and Sr arise entirely from natural sources. As and Mn are on the border of uncontaminated-moderate enrichment. Only Ba has a markedly high enrichment rate and the presence of barite deposits in the basin explains this enrichment. Co binds strongly to manganese and can be found in many minerals with As (Sigg and Behra, 2005). PC4 accounts for 6.87% of the total change and consists of Sb, Na, K and Tl. This component represents industrial cement works; Na and K are extracted from the basin and used as cement raw materials. During the production of Tl cement, it oxidizes at high temperature and then concentrates as ash particles at low temperatures (Karbowska, 2016). PC5, PC6 and PC7 represent elements of completely natural origin transported into the sediment. It consists, in PC-5 of U and Ti, in PC6 of Fe, V, and Ti, and in PC7 of Al, Ca, Sr and Sb. Sr and Sb are also highly represented in other components as they have mixed sources.

Conclusions

Çanakkale city is under heavy pollution pressure from urbanization, industrialization and agricultural activities. In this study, an element-based ecological risk assessment of Sarıçay River, which divides Çanakkale into two parts, was made. In the analysis of sediment samples taken along the river, anthropogenic enrichment was determined for Cd, Cr, Ni, Pb, Au, Ag and Ba, Bi, Tl, Na, Zn, Mg, K, As, Sb and Mn. The level of this enrichment varies from moderate to very high. According to the results of the risk analysis, a moderate risk for Cd was determined but it was very high for Ni and Pb. Agricultural activities, atmospheric deposition and mineral deposits in the basin were identified as the main source of metal inflows. In Sarıçay River, which is one of the important water resources of the region, regular comprehensive basin-based assessments should be made by local government in order to control contaminant inputs and careful attention should be paid to the management of waste-generating resources, especially the use of fertilizers and pesticides on agricultural lands.

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