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Research Article

GIS Analysis of spatial-temporal variation of the ecological risk caused by element and organic pollutants in Lake Marmara TURKIYE

Şakir Fural

Kırşehir Ahi Evran University, Faculty of Arts and Science, Department of Geography, Kırşehir, TURKIYE

* E-mail: furalsakir@gmail.com

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Abstract

Located in western Anatolia (Türkiye), Lake Marmara is a wetland with high ecological value. Lake Marmara, which was exposed to intense anthropogenic effects after 1940, is experiencing ecological deterioration in recent years. This study aimed to analyze the ecological risk level of the lake by using Enrichment Factor (EF), Toxic Risk Index (TRI), Modified Potential Ecological Risk Index (mER) etc. The research hypothesized that the discharge of water from the Gediz River and Kum Stream to the lake after 1940 triggered ecological risk problems. Moderate toxic risk, low potential ecological risk, moderate element contamination were detected throughout the lake. It was determined that Mo, P and Hg of anthropogenic origin and As, Ni, Cr, Cu of lithological origin created ecological risk at a regional scale. Domestic-industrial wastes and agriculture in the Gediz River basin and around the lake were identified as the dominant anthropogenic activity. The temporal variation of the ecological risk indices based on the elements did not reflect the anthropogenic traces of water discharge into the lake from the Gediz River basin. However, the temporal variation of TOC, N, P and CDP showed the effects of anthropogenic interventions in the lake. According to the threshold values; P is highly contaminated and N is close to the severely contaminated limit. The findings, while confirming the research hypothesis, showed that the dominant ecological risk factor in Lake Marmara is not elemental contamination, but organic pollutants, nitrogen and phosphate.

Keywords: Wetland ecology, Limnology, Ecological risk, Organic pollution

Introduction

Anthropogenic activities increased rapidly after the industrial revolution and the post-1784 era was defined as the Anthropocene (Crutzen, 2006; Ertek, 2017). Elemental and organic pollutants triggered ecological risk issues as natural biomes transformed into anthropogenic biomes in the Anthropocene (Vitousek et al., 1997; Cürebal et al., 2015; Nawab et al., 2018; Chen et al., 2021). Ecological deterioration occurred in wetlands such as marine ecosystem (Bat et al., 2017; Özkan et al., 2022), dams (Fural et al., 2022; Cüce et al., 2022), rivers (Yüksel et al., 2022; Ustaoğlu et al., 2022), and lakes (Kükrer et al., 2015; Kaya et al., 2017). The most striking example of the diffuse effect of the elements in wetlands is the detection of Hg pollution at a depth of 10 km in the Pacific Ocean (Sanei et al., 2021). Elements entering the aquatic environment are stored in the sediment, increasing the toxic level and are not cleaned with standard treatment systems (Wang et al., 2015). Interaction related to culture and natural environment between wetlands and people is quite extensive. Therefore, potential pollution problems in wetlands can cause serious health problems in humans (Rovira et al., 2011). Wetlands should be protected from highly contaminated element and organic matter discharges in order to prevent the cited risks.

Lake Marmara (Western Anatolia, Türkiye) is a wetland with high natural resource value where ecological risk problems are observed (Figure 1). There are commercial fishing activities in the lake for fish species such as Cyprinus carpio, Sander lucioperca, Mugu cephalus etc. (İlhan and Sarı 2015). 34 species of waterfowl use the lake as a breeding ground such as Microcarbo pygmeus, Pelecanus crispus, Ixobrychus minutus, Tadorna ferruginea, Tadorna ferruginea, Chlidonias hybridus and Vanellus spinosus (Gül et al., 2013). The basin, which has been a settlement since the Bronze Age, has received increased and continuous human influence in the Anthropocene and the natural environment has been gradually destroyed (Tağıl, 2007; Gülersoy, 2013; Vardar 2018; Kılıç et al., 2023). After 1940, water started to be discharged from the Kum Stream and Gediz River, which drain the Gediz basin to Lake Marmara with the help of irrigation regulators (İnandık, 1965; Girgin, 2011; Derinöz, 2022). So, Lake Marmara, which drains a small closed basin of 1780 km^2, to the anthropogenic effects of the Upper Gediz Basin of 17500 km^2, where approximately one million people live.

Ecological deterioration in Lake Marmara started with eutrophication and the trophic level increased rapidly (Ustaoğlu 1993; Kocataş 2002; Yıldız et al., 2005). The sediment sampling study conducted in the summer of 2019 determined that the hypertrophic level progressed towards the last stage. It was observed that most of the lake surface was covered with aquatic plants and swampy areas were formed. The lake dried up completely in the summer of 2020. Due to heavy rains, water began to be retained in some parts of the lake in January 2022. However, in the meantime, the wetland ecosystem has experienced an ecological destruction that is difficult to transform.

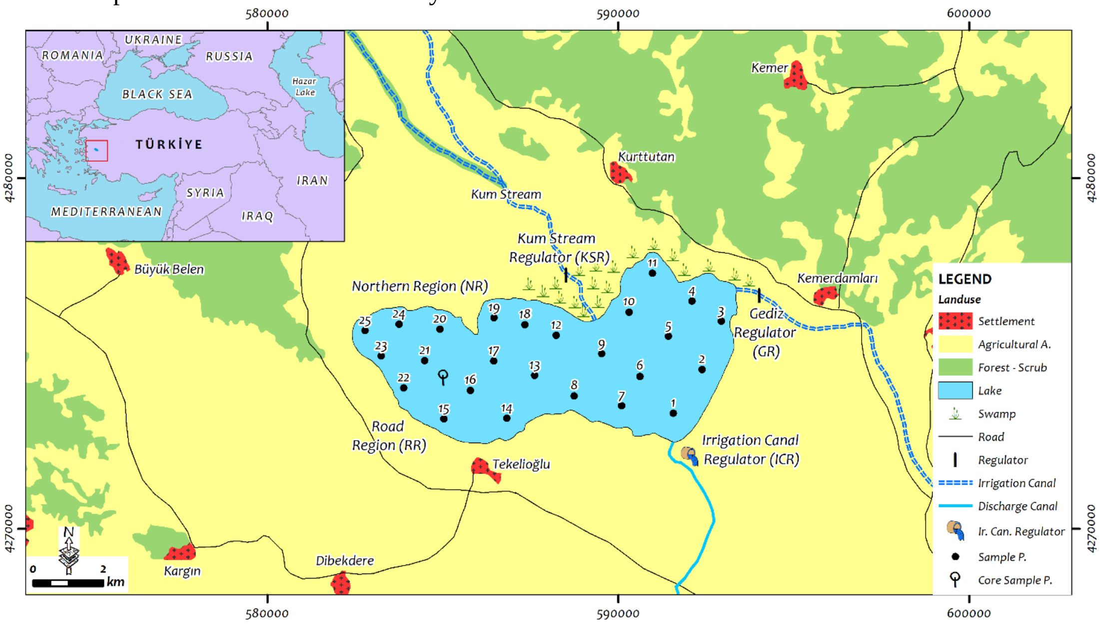

Fig. 1. Location and sampling point map.

This study analyzed the spatial and temporal variation of the ecological risk originating from element and organic pollutants in Lake Marmara, undergoing the process of drying out. The research statement was defined as follows: Lake Marmara is experiencing ecological degradation problems. The research hypothesized that the discharge of water from Gediz River and Kum Stream to Lake Marmara triggered ecological deterioration in the lake. A holistic evaluation was conducted with ecological risk indices, multivariate statistical analyzes and spatial analyzes to offer solutions to the research problem and test the validity of the hypothesis.

Material and Method

Elements stored in sediment remain stable for a long time (Wang et al. 2015). For this reason, sediment samples were used in the study. Surface sediment samples were taken from 25 sampling points in the summer of 2019 by using the Van Veen Grab. A 70 cm core was taken from the deepest point of the lake (4.5 m) with a Kajak sediment sampler. Sediments contained the last ecological records before the lake completely dried out.

Prepared sample is digested with a modified Aqua Regia solution of equal parts concentrated HCI, HNO_3, and DIH_2O for about one hour in a heating block. Sample was made up to volume with dilute HCI. Within the scope of the study; Calcium (Ca), Iron (Fe), Aluminum (Al), Magnesium (Mg), Potassium (K), Phosphate (P), Manganese (Mn), Nickel (Ni), Chromium (Cr), Zinc (Zn), Arsenic (As), Copper (Cu), Lead (Pb), Molybdenum (Mo), Cadmium (Cd) and Mercury (Hg) elemental analyzes were performed by ICP-MS in the Bareu Veritas laboratory (Canada). Hg concentration measurement was made with the closed system of ICP – MS.

Quality control was performed with standard reference material. Recovery was determined between 95% and 106%. Carbonate (CO_3^{-2}) concentration was found with Scheibler Calcimeter (Schlichting and Blume 1966), and Chlorophyll Degradation Products (CDP) analysis was performed by spectrophotometric method with acetone extraction (Lorenzen, 1971). Total Organic Carbon (TOC) was analyzed by Walkley-Black Titration method (Gaudette et al., 1974). Nitrogen (N) analysis was carried out at Kastamonu University Central Laboratory Application and Research Center using the CHL analyzer.

The enrichment factor (EF) was used to determine the natural and anthropogenic sources of the elements (Formula 1).

$$EF=\frac{(C_x/C_n)_{Environment}}{(B_x/B_n)_{backgorund}} \qquad \text{(Eq.1)}$$

In the formula; C_x represents element concentration and C_n represents the element (Al) concentration used in geochemical normalization. B_X is the background value of the element and B_n is the background value of Al selected for normalization (Sutherland 2000; Bo et al., 2015; Kükrer et al., 2021). The minimum element concentrations in the core slices after geochemical normalization were used as background values. Toxic Risk Index (TRI) was used for toxic risk analysis (Formula 2). (Zhang et al., 2016).

$$TRI_i = \sqrt{\frac{(C_x/TEL)^2+(C_x/PEL)^2}{2}} \qquad \text{(Eq.2)}$$

In the formula; TRI_i represents individual toxic risk, C_x represents element concentration, TEL represents “Threshold Effect Level” and PEL represents “Probable Effect Level” (MacDonald et al., 2000). Integrated toxic risk was calculated with TRI (Formula 3).

$$TRI = \sum_{i=1}^{n} TRI_i \qquad \text{(Eq.3)}$$

The Modified Ecological Risk Index (mER) was used to determine the ecological risk level. (Formula 4). (Hakanson 1980).

$${}_{m}ER = T_{RF} \text{ x } EF \qquad \text{(Eq.4)}$$

In the formula; T_{RF} represents the toxic risk coefficient and EF represents the enrichment factor (Hakanson 1980; Brady et al., 2015). Toxic risk coefficients are as follows: Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, Zn=1, Mn=1 (Hakanson 1980). The modified potential ecological risk index (${}_{m}$PER) was used to determine the integrated ecological risk (Formula 5). (Hakanson 1980; Brady et al. 2015).

$$mPER=\sum {}_{m}ER = (T_{RF} \text{ x } EF) \qquad \text{(Eq.5)}$$

Unlike the above indices, the Modified Hazard Quotient (mHQ) was calculated by comparing the "threshold effect level" (TEL), "probable effect level" (PEL) and "severe effect level" (SEL) of the element concentrations (Formula 6). (MacDonald et al., 2000; Benson et al., 2018).

$$mHQ = \left[C_x \left(\frac{1}{TEL} + \frac{1}{PEL} + \frac{1}{SEL}\right)\right]^{1/2} \qquad \text{(Eq.6)}$$

In the formula; C_x represents element concentration and TEL, PEL and SEL represent threshold levels. ECI performs ecological risk assessment in an integrated manner using mHQ data and principal component analysis/factor analysis data (Benson et al. 2018). B_n is the inverse of the eigenvalue obtained from principal component analysis in ECI (Formula 7).

$$ECI = B_n \sum_{i=1}^{n} mHQ_i \qquad \text{(Eq.7)}$$

Contamination level was determined by Contamination Severity Index (CSI) (Pejman et al., 2015). CSI was calculated based on ERL (*effect range low*) and ERM (*effect range median*) data (Formula 8). (Long et al., 1998).

$$CSI = \sum_{i=1}^{n} W_i \left[\left(\frac{Cx}{ERL_i}\right)^{1/2} + \left(\frac{Cx}{ERM_i}\right)^{2}\right] \qquad \text{(Eq.8)}$$

In the formula; W_i is the contamination weight, C_x is the element concentration, and n is the number of elements used in the analysis. CSI was calculated with statistical data (Formula 9). Index findings were evaluated according to Table 1.

$$W_i = \frac{(loading\ value_i x\ eigen\ value)}{\sum_i^n (loading\ value_i x\ eigen\ value)} \qquad \text{(Eq.9)}$$

Spatial analyzes were performed with the kriging interpolation device in the Arc – Map 10.7 interface. Multivariate statistical analyzes were performed with Statgraphics 19 software.

Results and Discussion

The lake floor was divided into five regions for spatial analysis. (1) Gediz Regulator (GR), the area where water is discharged from the Gediz River. (2) Kum Stream Regulator (KSR), the area where water is discharged from the Kum Stream, (3) Irrigation Canal Regulator (ICR), irrigation canal outlet, (4) Road Region (RR), the highway to the south and (5) Northern Region (NR), the north of the lake.

Mean element concentration is as follows: (mg/kg): Ca (69800) > Fe (36300) > Al (32500) > Mg (19400) > K (8900) > P (600) > Mn (832.72) > Ni (121.02) > Cr (93.20) > Zn (64.92) > As (43.06) > Cu (35.30) > Pb (20.80) > Mo (1.01) > Cd (0.18) > Hg (0.078). Elemental concentrations in the GR and KSR region were generally minimal (excluding Mo, P, and Hg). There are two possible reasons for this situation: (1) Deceleration of the sedimentation rate due to the driving force of the stream and (2) decreased element uptake due to the increase in the grain size of the sediment. Mo, Hg and P were not affected by the two conditions mentioned above. Mo and Hg reached the highest concentration in the GR region, and P in the KSR region (Figure 2). The probable reason for this is the discharge of Mo, P and Hg into the lake in very high concentrations, which precipitate at the water discharge points despite the unfavorable settling conditions. Generally, stable spatial distributions were observed in regions other than GR and KSR. Figure 2 presents the detailed spatial distribution of the elements. Except for Cr, Fe, Mn, all elemental concentrations tend to decrease from the core to the surface (Figure 3). The temporal variation of element concentrations does not adequately reflect the effects of the connection between Lake Marmara and Gediz basin.

Total organic carbon (TOC) is at its maximum in the KSR region, which consists of reed and marshy areas. Carbonate (CO_3^{-2}) concentration is high in the ICR and KSR region. The spatial distribution of CO_3^{-2} is compatible with the distribution of limestone formations around the lake (MTA, 2022). The concentration of chlorophyll degradation products (CDP) is high in the KSR region. TOC, CO_3^{-2} and CDP concentrations decrease in the GR region due to unfavorable settling conditions (Figure 2). The regions where TOC and CDP reach high concentrations are the areas where eutrophication, aquatic plant distribution and swamp environment occur.

Annual precipitation rate in Marmara Lake was calculated as 0.06 cm (Bulkan et al. 2018). The data show that each slice of the core, divided into 5 cm sections, was deposited in about 83 years. In this case, the first slice of the core (0 – 5 cm) represents a temporal change of approximately 83 years (1935 – present). A 65 cm core from Marmara Lake, close to this core, was dated 778 years ago (Kılıç et al., 2023).

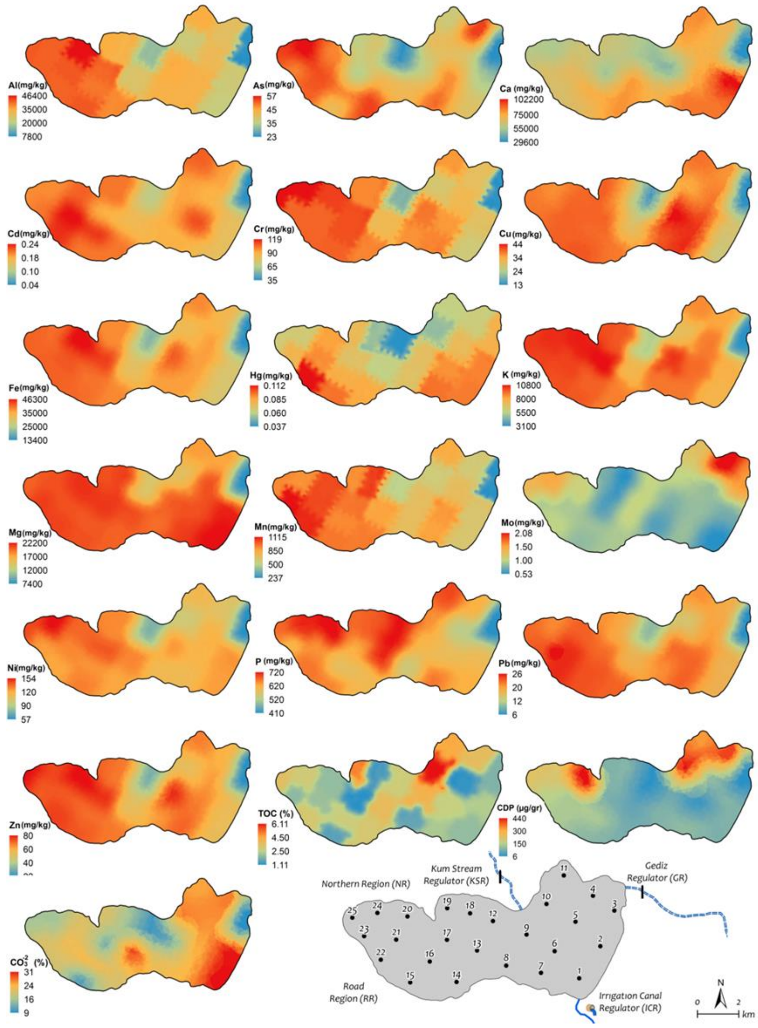

Fig. 2: Spatial analysis of element, TOC, CDP and CO3-2concentration

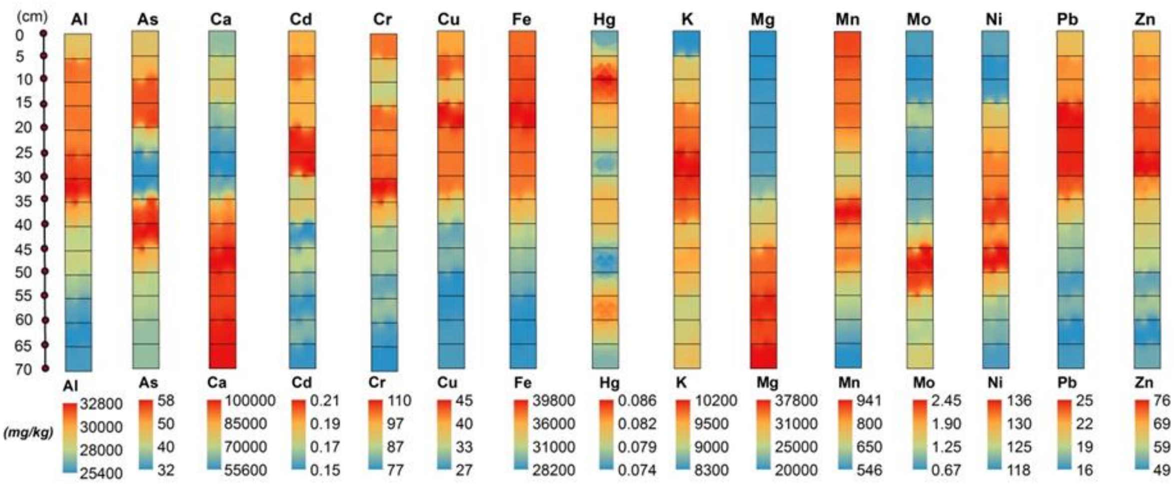

Fig3: Time variation of element concentrations

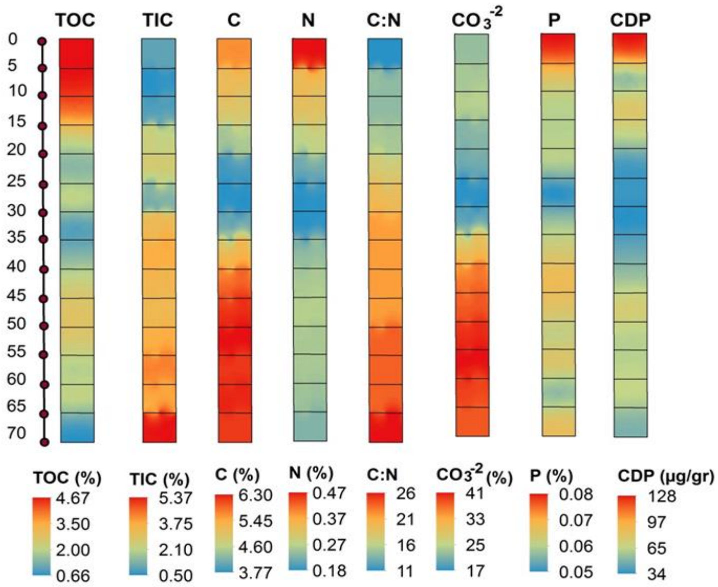

Fig. 4: Time variation of TOC, TIC, C, N, C:N, CO3-2, P and CDP concentrations

Table 1: Ecological risk indices evaluation scale

Table 1a: Enrichment Factor	
EF	(Sutherland 2000)
<2	Deficiency to minimal enrichment
2 – 5	Moderate enrichment
5 - 20	Significant enrichment
20 – 40	Very high enrichment
> 40	Extremely high enrichment
Table 1b: Toxic Risk Index	
TRI	(Zhang et al. 2016).
TRI ≤ 5	No toxic risk
5 < TRI ≤ 10	Low toxic risk
10 < TRI ≤ 15	Moderate toxic risk
15 < TRI ≤ 20	Considerable toxic risk
TRI > 20	Very high toxic risk
Table 1c: Modfy Ecological Risk Index	
mER	(Hakanson 1980).
< 40	Low ecological risk
40 ≤ mER < 80	Moderate ecological risk
80 ≤ mER < 160	Significant ecological risk
160 ≤ mER < 320	High ecological risk
≥ 320	Very high ecological risk
Table 1d: Modfy Potantial Ecological Risk Index	
mPER	(Hakanson 1980)
< 150	Low potential ecological risk
150 ≤ mPER < 300	Moderate potential ecological risk
300 ≤ mPER < 600	Significant potential ecological risk
mPER ≥ 600	Very high potential ecological risk

Table 1e: Modified Hazard Quotient	
mHQ	(Benson et al. 2018)
< 0.5	Nil to low severity
0.5 ≤ 1	Very low severity
1 ≤ 1.5	Low severity
1.5 ≤ 2	Moderate severity
2 ≤ 2.5	Considerable severity
2.5 ≤ 3	High severity
3 ≤ 3.5	Very high severity
> 3.5	Extreme severity
Table 1f: Ecological Contamination Index	
ECI	(Benson et al. 2018)
< 2	Uncontaminated
2 ≤ 3	Uncontaminated to slightly contaminated
3 ≤ 4	Slightly to moderately contaminated
4 ≤ 5	Moderately to considerably contaminated
5 ≤ 6	Considerably to highly contaminated
6 ≤ 7	Highly contaminated
> 7	Extremely contaminated
Table 1g: Contamination Severity Index	
CSI	(Long et al. 1998).
< 0.5	Uncontaminated
0.5 ≤ CSI < 1	Very low severity of contamination
1 ≤ CSI < 1.5	Low severity of contamination
1.5 ≤ CSI < 2	Low to moderate severity of contamination
2 ≤ CSI < 2.5	Moderate severity of contamination
2.5 ≤ CSI < 3	Moderate to high severity of contamination
3 ≤ CSI < 4	High severity of contamination
4 ≤ CSI < 5	Very high severity of contamination
CSI ≥ 5	Ultra high severity of contamination

According to this data, the annual precipitation rate in the lake is 0.08 cm. The dating data support each other. The first slice of the core covers approximately the period when the lake was opened to the anthropogenic influence of the Gediz River. The 15th cm of the core represents approximately BP 187 - 249, that is, a period close to the beginning of the Anthropocene (1769). The concentration of TOC, carbon (C), nitrogen (N), and phosphate (P) is at maximum at the core surface. The total inorganic carbon (TIC) concentration tends to decrease at the surface of the core. The N concentration is 0.18% at the core base and 0.47% at the surface slice. The N concentration which is highly effective at the trophic level (Adams et al., 2018) increased more than 2.5 times from the core bottom to the surface.

The C:N ratio is a good indicator for detecting the TOC source. If the C:N ratio is < 15, the source of TOC is planktonic organisms. If this ratio is > 15, terrestrial plants become dominant (Sampei and Matsumoto 2001). The C:N ratio in the core is between 11 and 26. The C:N ratio, which was found to be > 15 until the 15th cm, started to decrease towards the surface and decreased to 1. TOC source in the lake is terrestrial plants up to 15 cm and planktonic organisms from 15 cm to the surface. These data indicate that the TOC source changed after the onset of the Anthropocene. It is noteworthy that the P concentration is at maximum in the surface slice of the core (BP 83). P eutrophication is effective on algae and aquatic plant growth (Correll 1998; Sönmez et al. 2008; Hasançavuşoğlu and Gündoğdu 2021).

According to the sediment quality guide prepared by the Canadian Ministry of Environment and Energy, the pollution classes are as follows; N ≤ 0.05% uncontaminated, N > 0.48% heavily contaminated. P ≤ 0.06% uncontaminated, P > 0.2% severely contaminated (Yang et al. 2017; Dan et al. 2020; Dan, et al. 2021). The increase in N pollution, which started at the 15th cm of the core, approached a serious level in the surface slice. Pollution P exceeded the severely contaminated level (0.2%) in the surface slice by four times.

The CO_3^{-2} concentration is between 17% and 41%. The CO_3^{-2} concentration, which was 25% - 41% until the middle slices of the core, decreased up to 15 cm and tended to increase again. CDP concentration increased significantly on the core surface (Figure 4). The 5th and 15th cm of the core are the breaking points where TOC, N, P and CDP have a significant upward trend. According to the models made according to the sedimentation rate; 5th cm of the core corresponds to (BP 83) and the 15th cm corresponds to (BP 187 - 249). These dates correspond to the beginning of the discharge of water from the Gediz River to the lake (1940-1950) and the beginning of the Anthropocene (1784), respectively.

Mean EF value of surface sediments are as follows: Mo (1.45) > P (1.10) > As (1.08) > Ca (1.07) > Cu (1.00) > Zn (0.99) = Fe (0.99) > Pb (0.98) > Mn (0.97) > Hg (0.93) > K (0.87) > Cd (0.86) > Ni (0.85)> Cr(0.84)> Mg (0.79). Spatial analyzes showed that the GR and KSR regions, the water discharge points of the lake, are enrichment points (Figure 5). As, Hg, Ca and P were moderately enriched and Mo was significantly enriched in the GR region. Mo and P were moderately enriched in the KSR region. Hg moderately enriched in the ICR region Spatial analyzes showed that the maximum EF values of the non-enriched elements were concentrated in the GR and KSR regions (Gediz Basin water discharge points). The high ecological risk in the Gediz River has been proven by scientific studies (Akçay et al., 2003; Küçüksezgin et al., 2008; Delibacak et al., 2007). Existing literature and spatial analyzes showed that Gediz River and Kum Stream increased the anthropogenic element load of the lake. The sources of moderately enriched As, Hg, Ca, and P are complex, but their transport processes are similar. According to statistical analysis, As is closely related to elements of lithological origin (Fe, Al, Mn). There are two possible reasons for this situation: (1) As, affected by anthropogenic sources, was discharged into the lake (stream) by similar transport processes with elements of lithogenic origin and (2) The lithological erosion processes in the volcanic rocks in the Gediz Basin (Küçüksezgin et al., 2008) cause enrichment by increasing the As concentration in the lake. Anthropogenic sources of Hg are domestic - industrial wastes and solid fuel use (Pacyna et al., 2003). The source of the Hg enrichment in the lake is most likely the anthropogenic activities carried out in the Gediz River basin (Küçüksezgin et al., 2008). The probable reason why Hg is closely related to lithophile rocks in statistical analyzes is that it is discharged into the lake with the same transport mechanism. Ca is an important macronutrient used in agriculture (Tewari et al. 2004). Therefore, the possible source of Ca was estimated to be the agricultural activities carried out in the Gediz River basin and around the lake. However, Ca and CO_3^{-2} are closely related in statistical and spatial analyses. Therefore, Ca has been identified as having lithophile origin. Anthropogenic sources of P are domestic and industrial waste and manure (Correll 1998; Sönmez et al., 2008). The probable source of P, which has a strong relationship with Hg in statistical analyzes, is agriculture and domestic-industrial wastes in the Gediz Basin and around the lake. The anthropogenic sources of Mo are industrial - domestic wastes and solid fuel consumption (Chappaz et al., 2008). The probable source of Mo, which is closely related to P in statistical analyses, is the anthropogenic activities around the lake and in the Gediz Basin. No element enrichment was detected in the core according to the average data based on the examination of the temporal variation of EF. The enrichment tendency of Cu, Pb, Zn, Mn, Fe, As, Cd, Cr, Ni and P on the core surface is remarkable (Figure 6). Cu, Zn, Mn, Fe, Cd, P are important macronutrients used in plant nutrition (Cymerman and Kempers, 2001). Therefore, the possible source of the increase in the mentioned macronutrient enrichment is the agricultural activity carried out around the lake and in the Gediz Basin.

The mean mER values in the surface sediments are Hg (37.17) > Cd (25.86) > As (10.83) > Cu (5.02) > Pb (4.88) > Ni (4.25) > Cr (1.69) > Zn (0.99) > Mn (0.97).

According to the average values, none of the elements creates an ecological risk. Spatial analyzes point to GR as the most risky region in terms of ecological risk (Figure 7). In the GR region, Hg caused significant ecological risk, while Cd caused moderate ecological risk. These two toxic elements are responsible for 68% of the ecological risk in the lake. According to the spatial analysis of the elements that do not pose an ecological risk; GR and KSR regions are the areas where the maximum values are concentrated. This supports the hypothesis that the water discharged from the Gediz Basin increases the ecological risk hazard. According to the temporal change of ecological risk, the risk level of Hg, which creates a moderate ecological risk in the core, tends to decrease today. Cd is the second risky element after Hg, with an ecological risk level approaching the medium level. The ecological risk level of Cd, Cr, Cu, Mn tends to increase, while the ecological risk level of other elements tends to decrease (Figure 8).

The mean mHQ value of the surface deposits is as follows: Ni (3.41) > As (3.32) > Cr (2.08) > Cu (1.21) > Pb (0.94) > Zn (0.90) > Hg (0.80) > Cd (0.61). According to the average values, Ni and As cause pollution at very high severity level, and Cr causes pollution at considerable severity level. GR and KSR, which are risky regions according to EF, mER, and PER, are defined as risk-free regions in other indexes (mHQ, ECI, CSI and TRI). There are two possible reasons for this: (1) Increased grain size of the sediment and decreased element uptake by the discharge of water from the GR and KSR regions to the lake and (2) Contamination analysis without particle size normalization in mHQ , ECI, CSI and TRI indices.

According to spatial analysis element contamination is concentrated in the NR, RR and ICR region (Figure 9). These areas have no water discharge. Marmara Lake is located near the Kula – Adala Volcanic Geopark (Westavay et al., 2004; Ulusoy et al., 2019). Lithophile elements such as Cr, Fe, Mn may create ecological risks in streams in volcanic areas (Mariyanto et al., 2019). Previous studies in the field confirm that Cr, Ni and As, which are closely related in statistical analyzes, are of lithophilic origin (Küçüksezgin et al., 2008). Mean mHQ value in core is as follows: Ni (3.50) > As (3.40) > Cr (2.08) > Cu (1.22) > Pb (0.95) > Zn (0.89) > Hg (0.82) > Cd (0.60). As and Ni are contaminated at very high severity, Cr at considerably severity, Cu at low severity level. A general decreasing trend has been observed in the mHQ level from past to present (Figure 10).

According to the average mPER data (91.67), there is no potential ecological risk problem in the lake. According to spatial analysis, the potential ecological risk in the GR and ICR regions is moderate (Figure 11). Hg and Cd, of anthropogenic origin, discharged from the Gediz River are responsible for the potential ecological risk in these regions. None of the elements in the core posed potential ecological risk. However, the ecological risk level tends to increase after the 25th cm of the core (Figure 12). Moderate toxic risk was detected according to mean TRI (11.11).

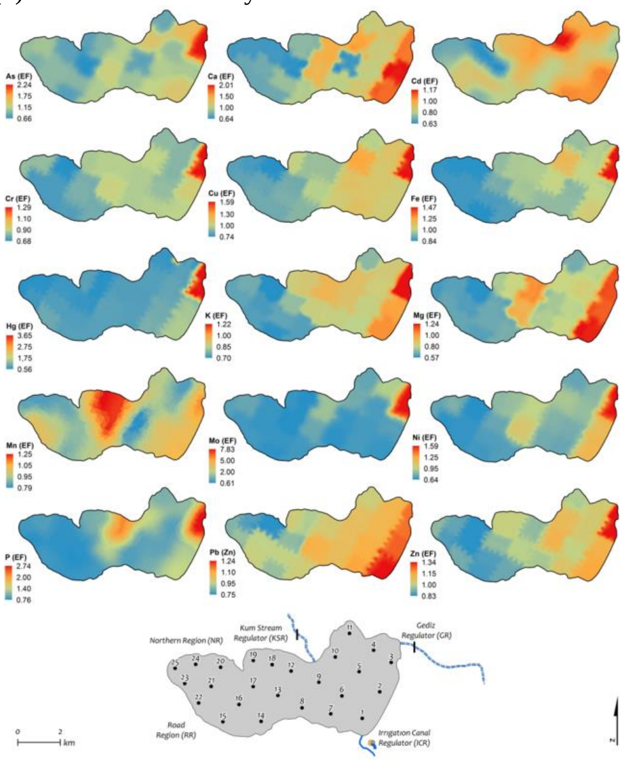

Fig. 5: Spatial analysis of EF

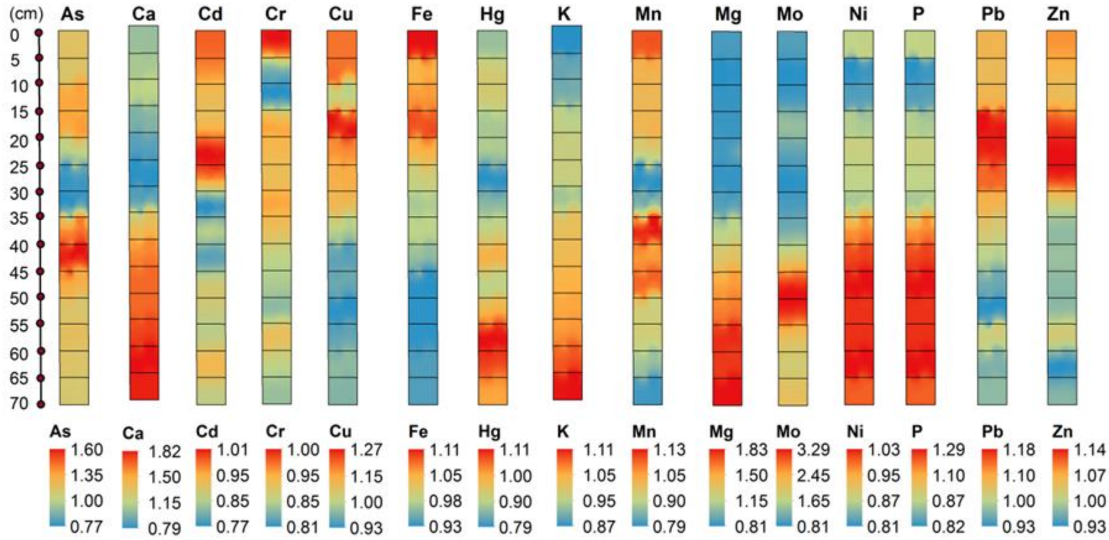

Fig. 6: Temporal variation of enrichment factor

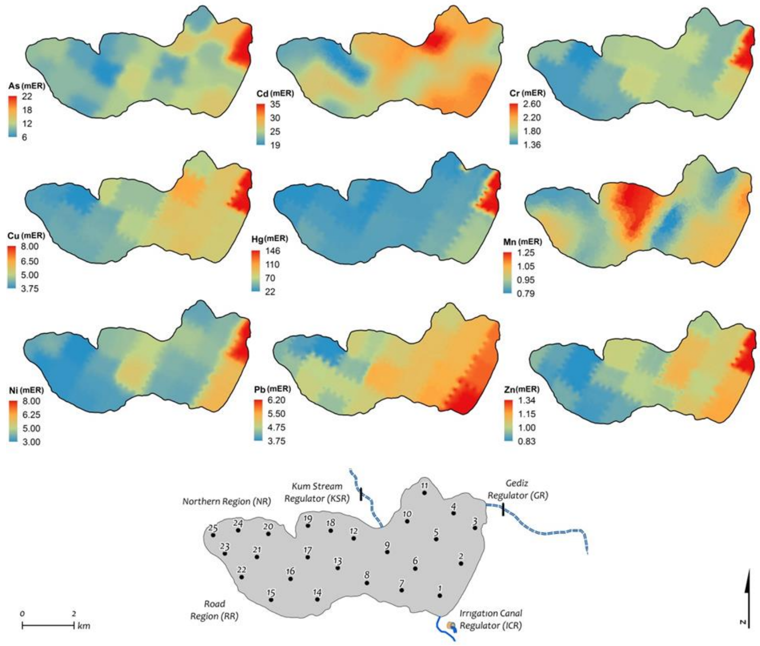

Fig. 7: Spatial analysis of mER

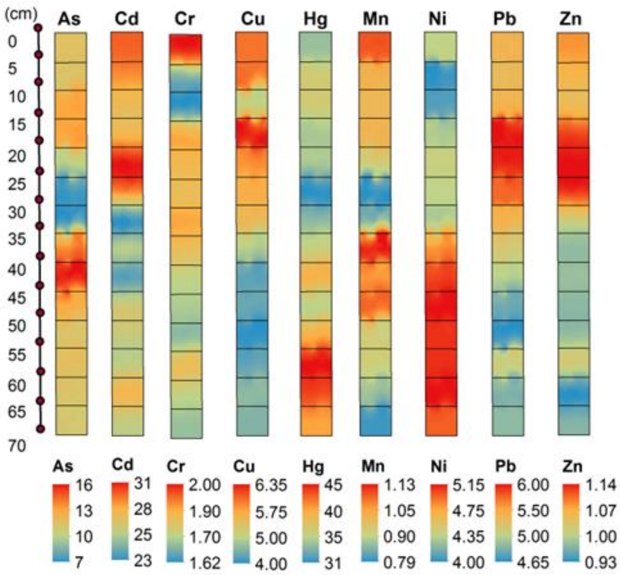

Fig. 8: Temporal variation of mER

Table 2: Factor Analysis

	Factor 1	Factor 2	Factor 3	Factor 4
Mo	-0.235	-0.230	**0.862**	-0.015
Cu	**0.880**	0.151	0.081	-0.080
Pb	**0.954**	0.189	-0.023	-0.150
Zn	**0.980**	0.018	0.014	0.002
Ni	**0.864**	0.144	-0.147	0.097
Mn	**0.899**	0.009	-0.128	0.067
Fe	**0.977**	-0.006	0.040	0.028
As	**0.685**	0.228	0.479	-0.178
Cd	**0.877**	0.301	0.123	0.078
Ca	0.159	**0.949**	-0.040	-0.027
P	0.435	0.087	0.050	**0.760**
Cr	**0.979**	-0.066	0.020	0.032
Mg	**0.797**	0.418	-0.345	0.029
Al	**0.974**	-0.103	0.071	-0.029
K	**0.976**	0.029	-0.078	0.046
Hg	**0.325**	0.262	-0.123	-0.749
CO_3^{-2}	-0.024	**0.962**	0.085	-0.002
TOC	-0.091	0.237	0.513	**0.526**
CDP	0.232	0.171	**0.764**	0.303

According to spatial analysis, the most problematic areas of the lake in terms of toxic risk are RR and NR. According to mean ECI (2.23), the risk level is between uncontaminated to slightly contaminated. Regions at risk for ECI are NR > RR > ICR, respectively. The risk level according to mean CSI (1.68) is low to moderate severity of contamination. The most risky region for CSI is NR. The highway in RR and settlements in NR are possible sources of high TRI, ECI and CSI values. Mean data according to temporal variation indicate risk at ECI (uncontaminated to slightly contaminated), CSI (very low severity of contamination) and TRI (moderate). TRI, ECI and CSI tend to move very similarly in core. For TRI, ECI and CSI, the increase after the 50^{th} cm of the core and the decreasing trend after the 15^{th} cm are the striking breaking points.

Factor analysis consists of 4 classes that explain 86.50% of the total variance. Factor 1 explains 55.67% of the variance. In factor 1, lithophile is included together with elements of anthropogenic origin and elements that create ecological risk. Factor 2 explains 12.53% of the variance and consists of lithophilic CO_3^{-2} and Ca. Factor 3, which explains 11.64% of the variance, includes Mo and CDP of anthropogenic origin. Factor 4 explains 6.65% of the variance and consists of P (of anthropogenic origin) and TOC. Factor analysis shows common transport processes rather than common sources of elements (Table 2).

According to Spearman Rank Correlations Analysis data, there is a strong negative correlation between Mo and Mg of lithological origin. This supported the view that Mo was of anthropogenic origin. The positive correlation between Mo and As and P was remarkable. P of anthropogenic origin had the strongest correlation with Mo. Hg of anthropogenic origin and Mg and Pb of lithological origin showed a positive correlation. This situation revealed the possibility that lithological factors in the Gediz basin may have a share in the Hg enrichment (Table 3). The view that Ni, As and Cr, which are moderately to highly contaminated according to mHQ, are of lithological origin was supported by the findings of statistical analyses. Hg, P and Mo of anthropogenic origin were clearly separated from other elements in the cluster analysis (Figure 13). In the cluster analysis, moderately enriched As was in the same cluster with the lithophile elements and Ca was included in a cluster close to it. This supported the possibility that As and Ca were enriched by the effect of lithological sedimentation processes. TOC and CDP were in the same cluster, but CO_3^{-2} was in different cluster. This showed that the source of TOC and CDP was in the lake, while the source of CO_3^{-2} was carried by rivers.

Conclusion

This study was based on the hypothesis that "water discharged from the Gediz River Basin causes ecological deterioration in Marmara Lake". Within the scope of the research, the validity of the hypothesis was tested by using ecological risk indices, spatial analyzes and multivariate statistical analyzes. Research findings showed that the areas with the highest level of ecological risk based on anthropogenic effects in Marmara Lake are the points where water is discharged into the lake (GR and KSR regions). Hg, P and Mo were defined as risky elements based on the EF, ER and PER data, which are sensitive to the grain size of the sediment and calculated with regional background values. According to MHQ, which works according to the threshold effect level, As, Ni, Cr, Cu were identified as contaminated elements. Research findings demonstrated that anthropogenic and lithophile elements have a combined effect on the level of contamination and ecological risk.

The temporal variation of the ecological risk analyzes based on the elements did not present ecological traces of water discharge into the lake from the Gediz River and Kum Stream. However, a regional ecological risk problem was detected in the areas where water was discharged from two rivers. The temporal variation of TOC, N, P and CDP clearly reflected the negative ecological effects of water discharge into the lake from the Gediz River and Kum Stream. The mentioned variables reached their maximum value in the surface slice of the core. This situation accelerated ecological degradation and expanded the distribution area of aquatic plants. Aquatic plants accelerated the drying of the lake by consuming water. According to the findings, it was determined that organic pollutants, nitrogen and

Table 3: Spearman's rank correlation

	Mo	**Cu**	**Pb**	**Zn**	**Ni**	**Mn**	**Fe**	**As**	**Cd**	**Ca**	**P**	**Cr**	**Mg**	**Al**	**K**	**Hg**	**CO_3^{-2}**	**TOC**
Mo																		
Cu	-0.333																	
Pb	-0.072	**0.719**																
Zn	-0.051	**0.639**	**0.789**															
Ni	-0.165	0.167	0.367	**0.647**														
Mn	-0.138	0.413	**0.777**	**0.729**	**0.613**													
Fe	-0.043	**0.594**	**0.801**	**0.929**	**0.607**	**0.792**												
As	**0.381**	0.208	**0.592**	0.426	0.201	0.428	0.381											
Cd	0.063	**0.583**	**0.816**	**0.604**	0.237	**0.708**	**0.646**	**0.524**										
Ca	-0.169	-0.008	0.005	-0.352	-0.229	-0.148	-0.349	0.172	0.119									
P	**0.315**	-0.081	0.003	0.23	0.375	0.242	0.185	0.115	0.247	-0.193								
Cr	0.015	**0.532**	**0.794**	**0.925**	**0.735**	**0.776**	**0.899**	**0.521**	**0.633**	-0.316	0.237							
Mg	**-0.507**	0.166	0.302	0.359	**0.514**	0.488	0.278	0.028	0.163	0.253	0.112	0.259						
Al	0.061	**0.587**	**0.871**	**0.912**	**0.658**	**0.829**	**0.932**	**0.535**	**0.728**	-0.244	0.239	**0.945**	0.268					
K	-0.165	**0.605**	**0.696**	**0.949**	**0.706**	**0.733**	**0.916**	0.337	**0.521**	-0.451	0.197	**0.905**	0.375	**0.868**				
Hg	-0.306	0.401	**0.549**	0.272	0.118	0.299	0.177	0.161	0.334	0.331	-0.304	0.175	**0.558**	0.291	0.151			
CO_3^{-2}	-0.09	-0.142	-0.206	-0.413	-0.181	-0.266	-0.387	0.118	-0.036	**0.852**	-0.143	-0.406	0.225	-0.354	-0.424	0.106		
TOC	0.426	-0.018	-0.141	-0.064	-0.105	-0.257	-0.103	0.146	0.118	0.129	0.332	-0.096	-0.423	-0.083	-0.169	-0.303	0.218	
CDP	0.409	0.065	0.312	0.332	0.146	0.262	0.361	**0.542**	**0.549**	0.145	0.284	0.391	-0.017	0.424	0.274	-0.117	0.256	0.223

phosphate pollution, were responsible for the ecological deterioration in Marmara Lake rather than elements. The findings proved the validity of the research hypothesis. The recommendations are presented below to solve the ecological risk problems in the lake:

- National and international protection status of Lake Marmara should be increased.
- The decision to discharge water from the Gediz River basin to the lake should be reviewed. Projects should be developed to analyze the water resources near the lake and to discharge water from a clean source.
- All anthropogenic activities in the Gediz River basin should be inspected.
- Agricultural activities in the closed basin of Lake Marmara should be supervised and organic farming practices should be encouraged.
- The cultivation of plants with low water needs in the basin should be encouraged to reduce agricultural irrigation from the lake.
- Infrastructure projects should be developed to provide more income from fisheries and ecotourism besides agriculture from Lake Marmara

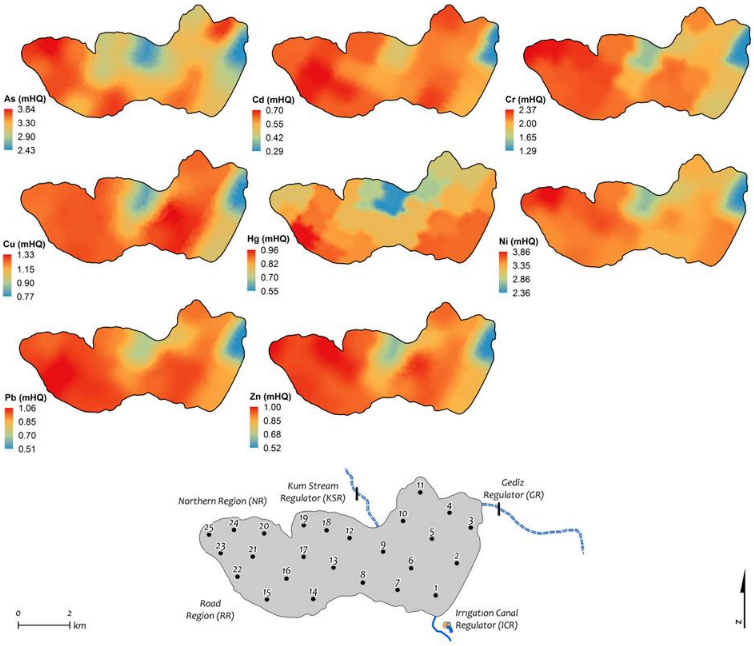

Fig. 9: Spatial analysis of MHQ

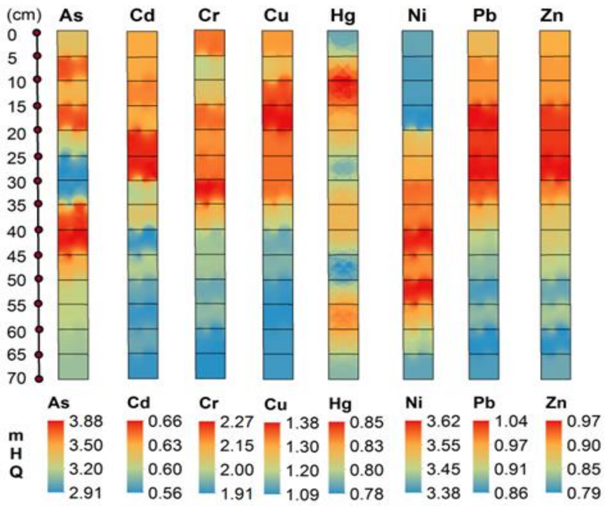

Fig. 10: Temporal variation of mHQ

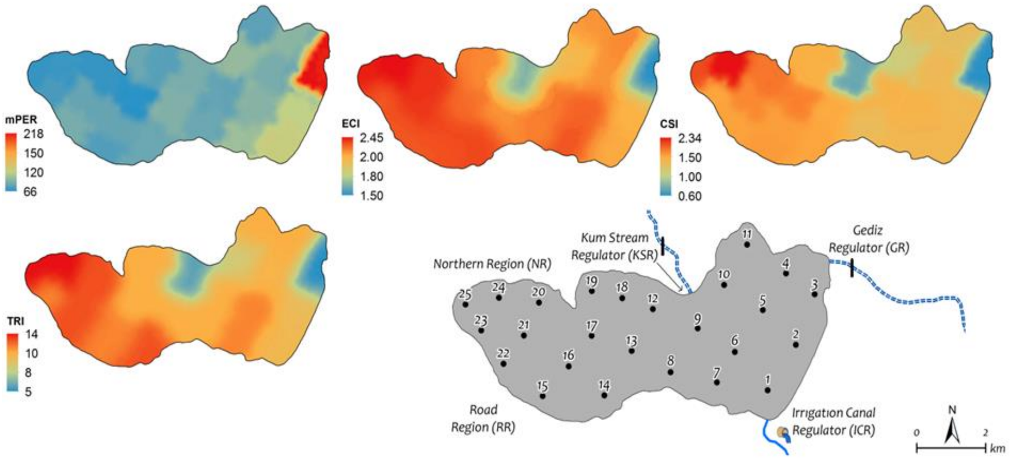

Fig. 11: Spatial analysis of mPER, ECI, CSI and TRI

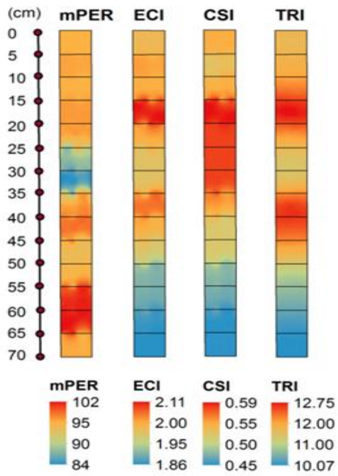

Fig12: Temporal variation of mPER, ECI, CSI and TRI

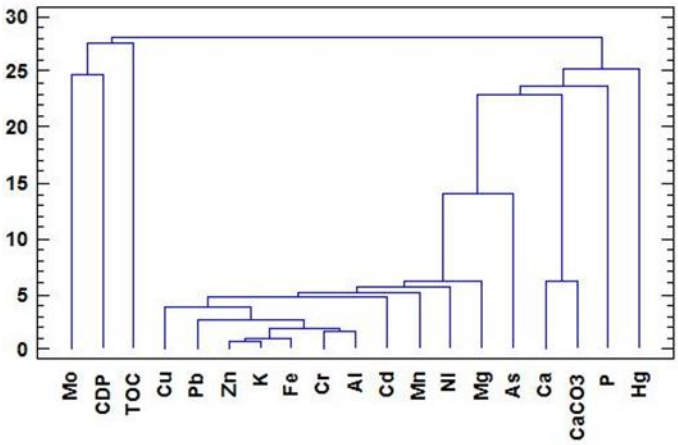

Fig. 13: Cluster analysis

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