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A comparative study on ecological risk assessment of some potentially toxic elements accumulation in surface sediment of stagnant and running water ecosystems in Meriç delta wetland, Turkish Thrace

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Abstract: This study determined arsenic, chromium, cadmium, copper, zinc, nickel and lead concentrations in the sediment of the lake and river and evaluated their ecological risk profile and compared the ecological risk profile of some potentially toxic elements accumulated in surface sediment of stagnant and running water ecosystems in the Meriç Delta Wetland, Turkish Thrace which is located in the European part of Turkey and have two important river systems, Meriç and Ergene, which provide freshwater resources for the region. Sediment samples were taken seasonally from three stations (one station from the river and two stations from the lake) in 2020. Ecological and biological risk analyses were calculated using the potential ecological risk index (*RI*), biological risk index ($mERM\text{-}Q_i$), contamination factor (*CF*), contamination degree (*CD*) and pollution load index (*PLI*). As a result, although *RI* stated that Cd was determined as the riskiest element and $mERM\text{-}Q_i$ stated that Zn was determined as the riskiest element, indicated that there were no high ecological risks besides the investigated elements in the area. Although it is expected that the sediment quality of running water systems is better than that of stagnant water systems, the results of risk indices in the present study showed that the station selected for running water was the riskiest station in terms of potentially toxic elements.

Keywords: ecological risk indices; toxic elements assessment; lagoon lake; Meriç River Delta.

INTRODUCTION

Increasing toxic element (TEs) pollution has become a global ecological concern for water, air, and soil ecosystems.[1] Supply to industry and agriculture due to the growth of the population increases the accumulation of TEs, especially

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in aquatic ecosystems.[2] Toxic pollution, which is discharged into aquatic ecosystems by precipitation and waste channels, accumulates in the sediment. The sediment plays a significant role in water quality and the health of aquatic organisms and the intense accumulation in the sediment causes the complicated biogeochemical exchanges.[3,4] Therefore, periodic investigation and monitoring of the sediment quality are essential for sustainability of the aquatic ecosystem.[3,5] Some indices that were developed for determining the ecological risk profile of potentially TEs in sediments are used and recommended for this purpose.[1,4,6–12] In the present study, the indices; potential ecological risk index (*PERI*), biological risk index (*BRI*), contamination factor (*CF*), contamination degree (*CD*) and pollution load index (*PLI*) were used because of their widely intended application. However, they also have some disadvantages and in despite of their disadvantages, they are very useful for saving and protecting a wetland.[11]

The Turkish Thrace Region is located in the European part of Turkey and have two important river systems, Meriç and Ergene. The rivers and their tributearies provide freshwater resources for the region. Due to the availability of arable lands and freshwater resources, the region is under intensive agricultural applications and pollution load.[2] The Meriç Delta located in Turkish Thrace Region lies in Turkey lands on about 35,000 ha area (about 10,000 ha part of the delta lies in Greece lands) and it is in A Class Wetland category.[13] The delta have different water bodies and the Dalyan Lagoon Lake is one of them. The Dalyan Lagoon Lake is located in the area where the Meriç River empties into the Aegean Sea, in Edirne province. The lagoon lake is formed by alluvial flows from the Meriç River. Due to its rich aquatic biodiversity, the lagoon lake is an important wetland for fish and especially for waterfowl.[14] The Enez District centre is located just north-east of the Dalyan Lagoon Lake and the lake is surrounded by agricultural lands. This situation causes significant urban and agricultural pressures on the lagoon lake.[14] There are many studies showing that wetlands in the Meriç Delta is exposed to pollution (Gala Lake, Sığırcı Lake, Ergene River, Meriç River and dam lakes).[2,4,13,15–17] In the present study, As, Cr, Cd, Cu, Zn, Ni, and Pb concentrations in the sediment of the Dalyan Lagoon Lake and the Meriç River connected with the Dalyan Lagoon Lake were determined seasonally and were detected by spectrometric method. According to the element concentration results, the ecological risk profile was evaluated and compared by using the indices; *PERI*, *BRI*, *CF*, *CD* and *PLI*. Although, there are many studies about sediment quality of the wetlands in the Meriç Delta,[2,3,13,15,16] the Dalyan Lagoon Lake and the Meriç River segment connected with the Dalyan Lagoon Lake were investigated for the first time in the present study. Thus, data about the sediment quality and ecological risk profile of the area were obtained. In additional, with this study, sediment structures and deposition of stagnant and running water ecosystems were compared in terms of flow dynamics.

EXPERIMENTAL

Study area and sediment sampling

Details about the study area are given in the Supplementary material to this paper

Sediment sampling was conducted seasonally (spring, summer, autumn and winter) between May 2020 and December 2020 from 3 stations. Two stations (St.1 and St. 2) were selected from the Dalyan Lagoon Lake and one station (St. 3) were selected from the Meriç River (Fig. S-1 of the Supplementary material). Sediment samples were taken using Ekman Grab (sampling 15×15 cm^2 area) from the lake and the river. The upper to 5 cm sediment portion was collected with sampler in sterile glass bottles. Sediment sample belonging to each station was obtained by mixing sediments randomly collected three times.

Chemical analysis

To determinate the elements (As, Cr, Cu, Cd, Zn, Ni, Pb) in sediment samples, obtained material was dried for 3 h at 105 °C. One gram each of dry samples were dissolved in 3 mL of distilled water. The solution obtained by adding an acid mixture HNO_3, HCl, $HClO_4$, at the volume ratio of 5:2:1, was passed through filter paper and taken into polyethylene bottles.[18] The element concentrations in the sediment samples were detected using the "Agilent 7700 xx" branded inductively coupled plasma-mass spectrometer (ICP-MS) device at the Trakya University Technology Research and Development Application and Research Center (TÜTAGEM).[19] Concentration values (given in mg/L) of all examined elements (As, Cr, Cu, Pb, Zn, Cd, Ni) are presented in Fig. S-1.

Risk indices

*Potential ecological risk index (*RI*)*. *RI* is used to evaluate the ecological contamination risk and based on the sensitivity of the aquatic ecosystems productivity. The index is calculated by the following formula:[6]

$$RI = \sum E^i_{\rm r} \quad (1)$$

$$E^i_{\rm r} = T^i_{\rm r} C^i_{\rm f} \quad (2)$$

$$C^i_{\rm f} = C^i_0 / C^i_{\rm n} \quad (3)$$

where $E^i_{\rm r}$ = potential ecological risk index of an each element. The scale of $E^i_{\rm r}$ is given in Table I; $T^i_{\rm r}$ = toxic response factor;[6] $C^i_{\rm f}$ = The contamination factor; C^i_0 = The concentration of elements in the sediment; $C^i_{\rm n}$ = The preindustrial reference value for elements.[6]

*Biological risk index (*mERM-Q*)*. Biological risk index is used to evaluate the assessing the potential effects of multiple element contamination in sediment. The index is calculated by the following formula:[20]

$$mERM\text{-}Q = (\sum n_i = ERM\text{-}Q_i)/n \quad (4)$$

$$ERM\text{-}Q_i = C_i / ERM_i \quad (5)$$

where *mERM-Q* = the effect range median quotient of multiple element contaminations. The scale of *mERM-Q* is given in Table I; C_i = the concentration of an element in the sediment from the sampling stations; *ERMi* = the *ERM* value of a determined element;[6] n = the number of selected elements.

*Contamination factor (*CF*)*. This method is used to account for the contamination of single elements and is calculated by the following formula.[6] The scale of *CF* is given in Table II:

$$CF = C_{\rm sample} / C_{\rm background} \quad (6)$$

where C_{sample} = the concentration of an element in the sediment from the sampling stations; $C_{background}$ = the reference value for elements.[6,7]

*Contamination degree (*CD*)*. This method is defined sum of all *CF*s for given lake.[6] The scale of *CD* is given in Table II:

$$CD = \sum CF \tag{7}$$

*Pollution load index (*PLI*)*. This index is used to evaluate sediment contamination and is defined as the n^{th} root of the product of the *nCF*. The following formula is used to calculate the index.[21] The scale of *PLI* is given in Table II:

$$PLI = (CF1 \times CF2 \times CF3 \times \cdots \times CFn)/n \tag{8}$$

TABLE I. The scale for E^i_r, *RI*, $ERM\text{-}Q_i$ and *mERM-Q*[20]

Potential ecological risk assessment				Biological risk assessment	
E^i_r	Monomial factor	*RI*	Multinomial factors	$ERM\text{-}Q_i$ and *mERM-Q*	Monomial and multinomial factors
<40	Low ecological risk	<95	Low ecological risk	<0.1	Low priority side
40–80	Moderate ecological risk	95–190	Moderate ecological risk	0.1–0.5	Medium-low priority side
80–160	Considerable ecological risk	190–380	Considerable ecological risk	0.5–1.5	High-medium priority side
160–320	High ecological risk	>380	Very high ecological risk	>1.5	High priority side
>320	Very high ecological risk				

TABLE II. The scale for *CF*, CD and *PLI*;[6,21] *CF* – contamination factor; *CD* – contamination degree; *PLI* – pollution load index

CF	Contamination	*CD*	Contamination	*PLI*	Pollution state
< 1	Low	< 8	Low	< 1	Unpolluted
$1 \leq CF \leq 3$	Moderate	$8 \leq CD < 16$	Moderate	> 1	Polluted
$3 \leq CF \leq 6$	Considerable	$16 \leq CD < 32$	Considerable		
≥ 6	Very high	≥ 32	Very high		

RESULTS AND DISCUSSION

The results of measured element levels in the sediment are presented in Fig. S-1. According to this, for As concentration values vary between 0.11 and 1.56 mg/L; for Cr between 0.06 and 0.52 mg/L; for Cu between 0.23 and 3.57 mg/L; for Pb between 0.3 and 5.02 mg/L; for between Zn 0.33 and 39.9 mg/L; for Cd between 0.001 and 0.043 mg/L; for Ni between 0.001 and 6.3 mg/L. The results of E^i_r, multinomial *RI*, monomial $ERM\text{-}Q_i$ and multinomial *mERM–Q* for each station and season were identified and given in Table S-I of the Supplementary material. In addition, the results belonging to the *CF*, *CD* and *PLI* were identified and given in Table III.

TABLE III. The toxic element risk index values (*CF*, *CD* and *PLI*) in sediments of the Dalyan Lagoon Lake (Ave: Average; St: Station)

St	CF							CD	PLI
	As	Cr	Cu	Pb	Zn	Cd	Ni		
				Spring					
1	0.008	0.002	0.012	0.006	0.005	0.025	0.005	0.063	0
2	0.01	0.001	0.006	0.004	0.007	0.003	0.005	0.037	0
3	0.104	0.004	0.071	0.03	0.038	0.01	0.084	0.342	0
Ave	0.041	0.002	0.03	0.013	0.017	0.013	0.032		
				Summer					
1	0.009	0.001	0.005	0.006	0.002	0.001	0.002	0.025	0
2	0.011	0.001	0.006	0.005	0.002	0.002	0.002	0.028	0
3	0.069	0.001	0.016	0.007	0.005	0.004	0.005	0.107	0
Ave	0.03	0.001	0.009	0.006	0.003	0.002	0.003		
				Autumn					
1	0.017	0.003	0.022	0.028	0.228	0.01	0.011	0.319	0
2	0.046	0.004	0.028	0.048	0.032	0.02	0.008	0.186	0
3	0.03	0.004	0.028	0.072	0.119	0.01	0.012	0.275	0
Ave	0.031	0.003	0.026	0.049	0.127	0.013	0.01		
				Winter					
1	0.007	0.002	0.008	0.007	0.008	0.014	0.00001	0.046	0
2	0.021	0.002	0.012	0.005	0.009	0.012	0.00001	0.061	0
3	0.033	0.006	0.019	0.025	0.012	0.043	0.00004	0.138	0
Ave	0.021	0.003	0.013	0.012	0.01	0.023	0.00003		
Average	0.03	0.002	0.02	0.05	0.04	0.01	0.01		

According to *PERI*, the results of monomial factor E^i_r and multinomial factor *RI* all the investigated stations and seasons exhibited "low ecological risk". The monomial factor E^i_r belonging to *PERI*s indicated that the density of the investigated TEs can be followed as Cd > Pb > As > Cu > Zn > Ni > Cr (Fig. 2). The multinomial factor *RI* belonging to *PERI*s showed that the ecological risks of the investigated stations can be sorted as St. 3 (2.597) > St.1 (1.287) > St. 2 (1.165), Table S-I.

According to *BRI*, although the results of monomial factor $ERxM\text{-}Q_i$ posed "low priority side" at all the investigated stations and seasons, nickel at St. 3 in spring season and zinc at St. 1 in autumn season posed "medium-low priority side". The results of multinomial factors (*mERM–Q*) posed "low priority side" at all the investigated stations and seasons and the toxicity of the investigated elements can be sorted as Zn > Ni > Pb > As > Cu > Cr > Cd (Fig. 3). The multinomial factor *mERM-Q* of *BRI*s indicated that the biologically risk of contamination to sediments of the investigated stations can be sorted as St. 3 (0.015) > St. 1 (0.008) > St. 2 (0.004), Table S-I.

As a results of C*F* values for all the investigated elements showed "low contamination" and the risks of the investigated TEs in terms of *CF* can be sorted as Pb > Zn > As > Cu > Cd = Ni > Cr (Table IV). As a results of *CD* values for all the investigated elements showed "low degree of contamination" and total contamination degree followed the order of stations St. 3 (0.21) > St. 1 (0.11) > St. 2 (0.08). Also, The *PLI*s indicated that all stations were unpolluted (Table III).

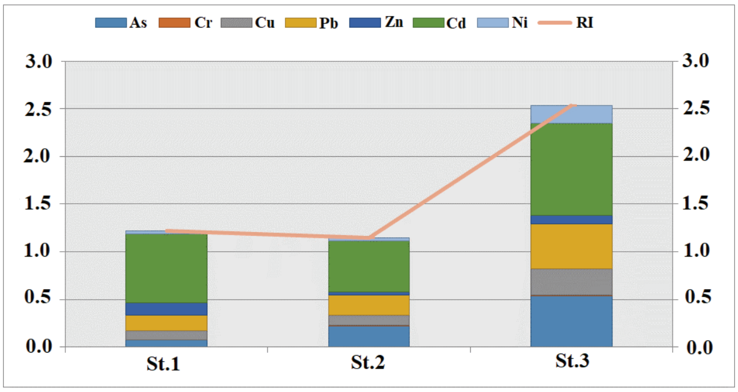

Fig. 2. Values of potential ecological risk index (*PERI*).

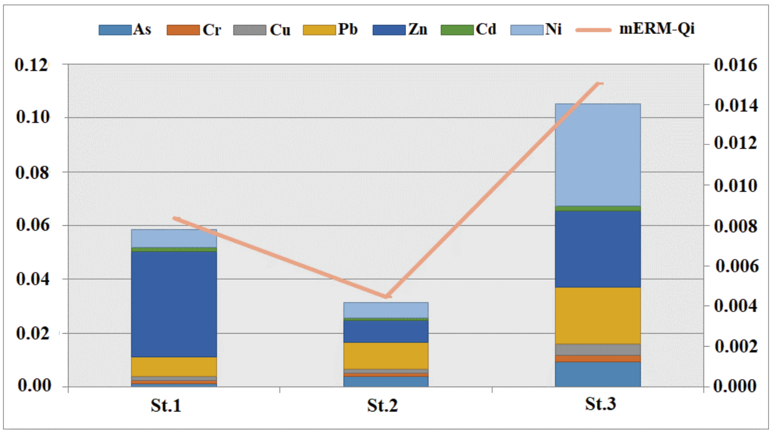

Fig. 3. Values of Biological Risk Index (*BRI*).

The present study was carried out to determine and compare the existence and risk profile of some potentially TEs in stagnant and running water ecosystems at Meriç Delta Wetland. According to result of $mERM\text{-}Q_i$, Zn was determined as the riskiest element, and as a result of *RI*, Cd was determined as the riskiest element for the sediments of the Dalyan Lagoon Lake. In previous studies performed in Meriç Delta, Cd was reported as the riskiest toxic element.[4,15] In the studies carried out in dam lakes in the Meriç Delta[4] and Gala Lake,[15] it was reported that cadmium was found to be the highest risk factor in terms of potential *RI*.[4,15] Cadmium is a toxic element in agriculture and it can be easily spread to water by using phosphate fertilizers.[4,15] According to the study,[22] cadmium residues in fertilizers taken from different fertilizer factories were investigated and the results showed that the vales were over the limit values notified for fertilizers.[22] Because of intensive agricultural applications in Meriç-Ergene River Basin (especially rice production), excessive use of fertilizer can cause Cd accumulation.

Zinc is exceedingly related to organic matter.[23] Aquatic systems are inclined to have a higher deposition rate of organic matter.[24] So, the accumulation of Zn is widespread in sediment. In the present study, Zn was determined as the riskiest element and the monomial factor ($ERM\text{-}Q_i$) for Zn posed a "medium-low priority side" at St. 1 in the autumn season.

Nickel occurs naturally in the Earth's crust and enters natural resources, usually through anthropogenic activities.[9] In the study carried out in Gala Lake;[15] Ni was the riskiest element according to *BRI*.[15] In the present study, the results of the monomial factor ($ERM\text{-}Q_i$) for Ni posed a "medium-low priority side" at St. 3 in the spring season.

Since the water of the lake is connected with the water of the Meriç river, two stations were selected from the lake (St. 1 and 2) and one from the Meriç river (St. 3). The results of used risk indices in the present study indicated that St. 3 (selected from Meriç River) was the riskiest station in terms of investigated TEs. In the studies conducted on other water bodies in the Meriç Delta, there is a significant accumulation of TEs due to intensive agricultural and industrial applications.[2,4,15] For this reason, it is an expected result that the station (St. 3) selected from the Meriç River in this study is the riskiest. In addition, there are many studies investigating ecological risk analyzes in sediment in lagoon lakes in Turkey.[25–27] According to studies,[25,27] there were no pollution and no moderate or high ecological risk for Köyceğiz (Muğla) Lagoon System. According to the results of ecological risk assessment study of Çardak Lagoon Lake (Çanakkale), the toxic risk index ranged from 5.21 to 11.00, with a low mean value of 7.98.[26]

CONCLUSION

As a result of the study, it was concluded that toxic element pollution in the sediments of selected stations at the present study (Dalyan Lagoon Lake and Meriç River) is less than in other water bodies in the Meriç River Delta (Gala Lake, Sığırcı Lake, Ergene River, Meriç River and dam lakes in the Meriç River Delta). The presence of sea currents and channels in lagoon lakes is important in maintaining water quality and thus sediment quality. Although there is agricultural and industrial pollution in other water bodies in the delta, it can be said that Dalyan Lagoon Lake has improved the water and sediment quality by the sea connections. However, other biological and physicochemical studies that support these results are needed in the region. Water and sediment quality of stagnant and running water ecosystems are different from each other due to their flow dynamics. It is expected that the sediment quality of running water systems is better than that of stagnant water systems. In this study, despite the flow dynamics of the Meriç River, there is a higher risk of TEs compared to the Dalyan Lagoon Lake due to intensive agricultural applications and the industrial pollution load of the Ergene River. Because, the Meriç River arises in Bulgaria and unites with the Arda River in Edirne. Then merging the Tunca River south of Edirne, it joins the Ergene River and flows into the Aegean Sea (Saros Gulf). So, the Ergene River increases the pollution load of the Meric River. The studies performed in the Ergene and Meriç rivers showed that agricultural and industrial pollution load were intensive. It is recommended that such studies must be carried out periodically and kept under control for the sustainability of the lagoon lake where fishing is carried out intensively.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12778, or from the corresponding author on request.

ИЗВОД

КОМПАРАТИВНА СТУДИЈА О ПРОЦЕНИ ЕКОЛОШКОГ РИЗИКА ОД АКУМУЛАЦИЈЕ НЕКИХ ПОТЕНЦИЈАЛНО ТОКСИЧНИХ ЕЛЕМЕНАТА У ПОВРШИНСКОМ СЕДИМЕНТУ ЕКОСИСТЕМА СТАЈАЋИХ И ТЕКУЋИХ ВОДА У МОЧВАРНОМ ПОДРУЧЈУ ДЕЛТЕ РЕКЕ МЕРИЧ, ТУРСКА ТРАКИЈА

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Овом студијом утврђене су концентрације арсена, хрома, кадмијума, бакра, цинка, никла и олова у седименту језера и реке, процењен је профил њиховог еколошког ризика и упоређен профил ризика неких потенцијално токсичних елемената акумулираних у површинском седименту екосистема стајаћих и текућих вода у Мочварном подручју делте Мерича, Турска Тракија. Ова делта налази се у европском делу Турске и има два важна речна система, Мерич и Ергене, који обезбеђују слатководне ресурсе за регион. Узорци седимента су узимани сезонски са три станице (једна станица са реке и две станице са језера) у 2020. години. Анализа еколошког и биолошког ризика израчуната је коришћењем индекса потенцијалног еколошког ризика (*RI*), индекса биолошког ризика (*mERM-Q*$_i$), фактора контаминације (*CF*), степена контаминације (*CD*) и индекса оптерећења загађењем (*PLI*). Као резултат тога, иако је *RI* показао да је Cd најризичнији елемент, а *mERM-Q*$_i$ је указао на Zn као најризичнији елемент, ова студија показује да нема високих еколошких ризика у овој области. Иако се очекује да је квалитет седимента у системима за текућу воду бољи него у системима са стајаћим водама, резултати индекса ризика у овој студији су показали да је станица одабрана за текућу воду била најризичнија станица у погледу истраживања потенцијално токсичних елемената.

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