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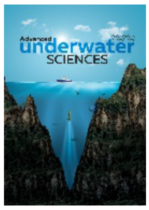

Metal Pollution Status of Surface Sediments in the Two Coastal Regions of the Mersin Bay, Northeastern Mediterranean Sea

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Keywords
Metal pollution assessment,
Sediment,
River systems,
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ABSTRACT
The objective of this study is to determine metal pollution status of surface sediments in the two coastal regions of Mersin Bay under the influence of Seyhan and Göksu River inflows for the 2005-2009 period. The average metal concentrations orders were found to be Al > Cr > Cu > Zn > Cd for the Station Mersin affected by Seyhan River inflows and Al > Zn > Cr > Cu > Cd for the Station Taşucu under the influence of Göksu River. According to classification of metal pollution of surface sediments, though there was no Cd pollution, the sediments are highly polluted by heavy metals Cr, Cu and Zn in the Seyhan River influenced coastal region due to agricultural and industrial wastewater discharges.

1. INTRODUCTION

It was well known that some metals are essential for living organisms while several heavy metals such as cadmium and lead are nonessential for life and can be highly toxic (Yim and Tam, 1999; Okay et al., 2008; Tan and Aslan, 2020). These toxic heavy metals have critical importance for the aquatic ecosystems since they are non-biodegradable and persistent (Diagomanolin et al., 2004; Buccolieri et al., 2006; El-Sorogy et al., 2016). Toxic metals entering the food chain via bio-accumulation are, therefore, hazardous for the ecosystem functioning (Yu et al., 2012).

The shelf region of Mersin Bay, located in the North-Eastern Mediterranean Sea, is 43 km wide in the east off the Seyhan River Delta and narrows down to 8.4 km near the Göksu River Delta in the west (Okyar et al., 2013). The coastal region the Mersin Bay has been affected by regional rivers that are Ceyhan, Seyhan, Berdan, Lamas and Göksu Rivers (Tugrul et al., 2009). In the Seyhan River basin, there are many rural and urban areas and in these areas agricultural and industrial activities are carried out intensively. The Seyhan River is highly affected by these socio-economic activities, and therefore, among the regional rivers flowing into Mersin Bay, Seyhan River has the maximum volume fluxes with the higher organic and inorganic matter inputs (Tugrul et al., 2009; Kocak et al., 2010). Therefore, the Seyhan River is the largest river flowing to the shelf region of the Mersin Bay. Based on the study performed by Kocak et al. (2010), annual discharge rate of Göksu River is almost 4-fold lower than annual volume fluxes of Seyhan River. The inorganic matter inputs (nutrients) from the Göksu River to the coastal site are also from 3 to 20 fold less than calculated for the Seyhan River (Akcay et al., 2021).

In the marine ecosystems, metals can be transported by natural and terrestrial inputs (Saher and Siddiqui, 2016). The sources of anthropogenic metal pollution in the coastal regions are generally rivers, estuaries, wastewater discharges, vehicle emissions, and

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agricultural runoff (Ip et al., 2007; Saher and Siddiqui, 2016; Tan and Aslan, 2020). In the present study, metal pollution status of surface sediments was determined in the two coastal sites affected by Seyhan and Göksu Rivers flowing into the coastal region of the Mersin Bay. Four different pollution assessment tools were used for the four selected metals measured in the surface sediments by the study of Tugrul et al. (2009).

2. METHODOLOGY

In the present study, the sediment data were retrieved by Tugrul et al. (2009). In authors' study, the concentrations and spatial distributions of the Chromium (Cr), Cupper (Cu), Zinc (Zn), Cadmium (Cd) and Aluminum (Al) in surface sediments were reported (Tugrul et al., 2009). In this study, however, the ecological risk assessment of metal pollution in the surface sediments of two coastal regions were determined in the Mersin Bay affected by Seyhan and Göksu Rivers having different discharge rates. The sampling strategy and measurements methods were presented in the study of Tugrul et al. (2009). The stations were annually visited between 2005 and 2009. The total depths of visited stations were nearly 30 m for the Station Mersin and 20 m for the Station Taşucu affected by Seyhan and Göksu River inflows, respectively.

The assessment of metal pollution was performed using the mean metal concentration of each parameter for the 2005-2009 period. Metal pollution status of surface sediments were assessed using four different classification tools that are presented in Table 1. Enrichment Factor (EF) (Sakan et al., 2009), Geoaccumulation index (Igeo) (Müller, 1981) and contamination factor (CF) (Hakanson, 1980) were used for the degree of metal pollution. Pollution Load Index (PLI) (Tomlinson et al., 1980) was used for the assessment of overall metal pollution in sediments of the two coastal regions of Mersin Bay.

Table 1. Assessment of metal pollution in sediments

Pollution Index	Classification	Formula
Enrichment factor (EF)	< 2 Depletion to mineral enrichment 2 ≤ EF < 5 Moderate enrichment 5 ≤ EF < 20 Significant enrichment 20 ≤ EF < 40 Very high enrichment EF > 40 Extremely high enrichment	$EF=\frac{(M_{xs}/M_{Al})_{SAMPLE}}{(M_{xb}/M_{Al})_{BACKGROUND}}$

Enrichment factor (EF) is used to determine heavy metal pollution that increases as a result of anthropogenic activities accumulated in the sediment (Rani et al., 2021):

where $(M_{xs}/M_{Al})_{Sample}$ is the ratio of trace elements and aluminum concentrations in the sediment sample, and $(M_{xb}/M_{Al})_{Background}$ is the ratio of trace elements and aluminum concentrations in the background sample.

Pollution Index	Classification	Formula
Geoaccumulation index (Igeo)	Igeo ≤ 0 Unpolluted 0 ≤ Igeo ≤ 1 Unpolluted to moderately polluted 1 ≤ Igeo ≤ 2 Moderately polluted 2 ≤ Igeo ≤ 3 Moderately to strongly polluted 3 ≤ Igeo ≤ 4 Strongly polluted 4 ≤ Igeo ≤ 5 Strongly to extremely polluted Igeo > 5 Extremely polluted	$Igeo=\log_2\left(\frac{M_{xs}}{1.5 \times M_{xb}}\right)$

It was developed to determine the level of toxic metal pollution in the metal sediment and shows the pre-industrial and current status of the metal level in the sediment (Martínez-Guijarro et al., 2019; Rani et al., 2021)

where M_{xs} is the measured concentration of the element x in the sediment, M_{xb} is the geochemical background concentration or reference value of the element x.

Pollution Index	Classification	Formula
Contamination factor (CF)	CF < 1 low 1 ≤ CF < 3 Moderately 3≤ CF <6 considerable contamination factors CF ≥ 6 very high contamination factor	$CF=\frac{M_{xs}}{M_{xb}}$

The CF index is used for metal pollution assessment in the sampling region (Martínez-Guijarro et al., 2019):

The CF index is the ratio between element concentration at the sampling site (M_{xs}) and the concentration of the same element at reference level (M_{xb}).

Pollution Index	Classification	Formula
Pollution load index (PLI)	≤ 1 Unpolluted > 1 Polluted	$PLI=(CF_1 x CF_2 x CF_3 \text{ x} \ldots \text{ x } CF_n)^{1/n}$

Pollution load index (PLI) is used for the overall quality of sediment (Rani et al., 2021):

Background/reference values were taken from Krauskopf (1979).

Figure 1. Mersin and Taşucu stations in the study of Tugrul et al. (2009).

3. RESULTS and DISCUSSION

The mean values of metal concentrations of the surface sediments for the 2005-2009 period were presented in Table 2. The spatial variability of surface sediment concentrations of Cr, Cu, Zn and Al was more pronounced between 2005 and 2009 with the maximum concentrations recorded in the Station Mersin. The average metal levels of the surface sediments are in the following order: Al > Cr > Cu > Zn > Cd for the Station Mersin affected by Seyhan River inflows and Al > Zn > Cr > Cu > Cd for the Station Taşucu under the influence of Göksu River.

Table 2. The mean values of metal concentrations for the 2005-2009 period (data were retrieved from Tugrul et al. (2009).

Station	Cr (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Al (mg/kg)
Mersin	173	137	0.25	124	25251
Taşucu	66.3	33.8	0.25	94.0	19007

The sources of anthropogenic metal pollution in the coastal regions are generally rivers, estuaries, wastewater discharges, vehicle emissions, and agricultural runoff (Ip et al., 2007; Saher and Siddiqui, 2016; Tan and Aslan, 2020). Based on the calculated metal pollution assessment tools, the sediment in the Seyhan River influenced region was highly contaminated by metals (Figure 2-5). The surface sediments were highly enriched by Cr, Cu and Zn in the region affected by Seyhan River inflows having greater volume fluxes and suspended matter concentrations (Tuğrul et al., 2009; Koçak et al., 2010). On the other hand, level of metal contamination in surface sediments of the Göksu River-influenced region was low (Figure 2-5). However, the calculated metal pollution indices showed that surface sediments in the Göksu River influenced region is contaminated by Zn (Figure 2-5).

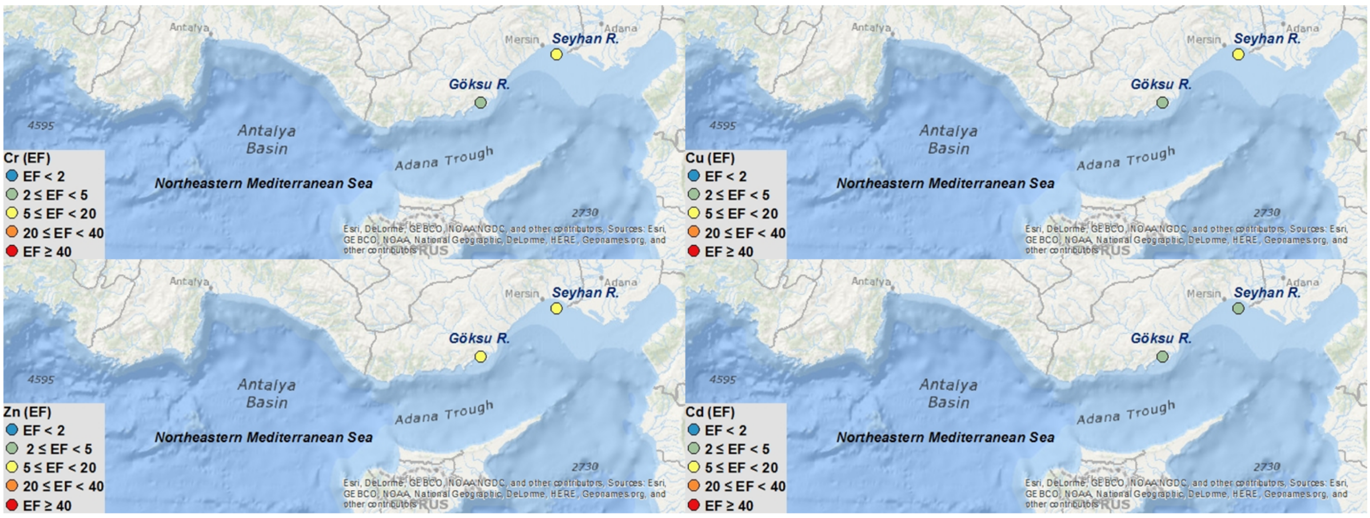

Figure 2. Assessment of metal pollution based on Enrichment Factor (Index values were calculated from the data obtained by Tugrul et al. (2009).

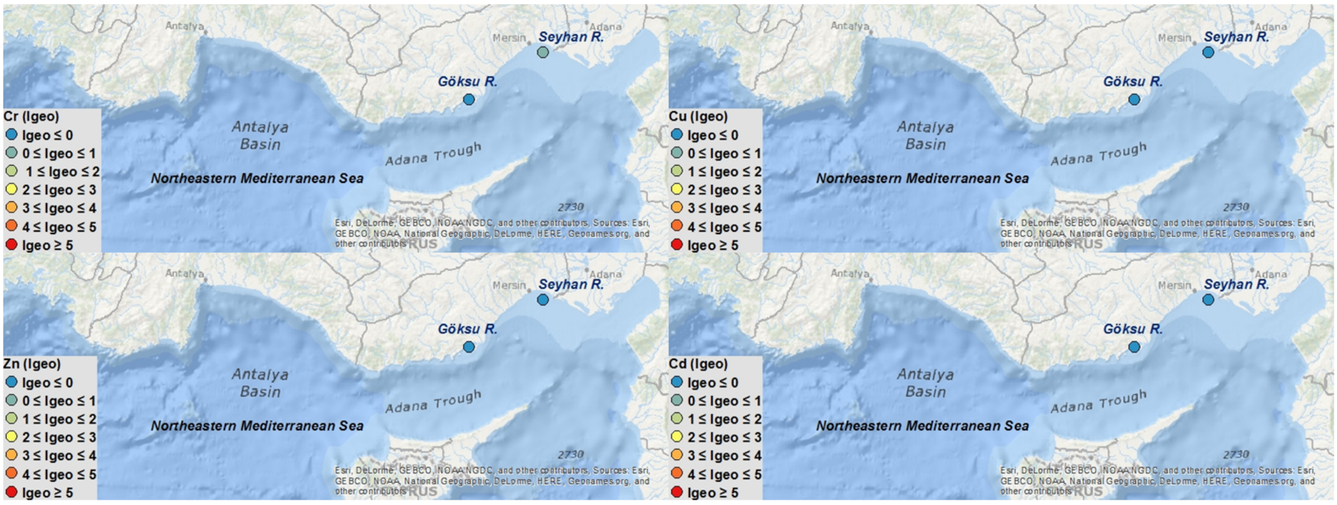

Figure 3. Assessment of metal pollution based on Geo-accumulation Index (Index values were calculated from the data obtained by Tugrul et al. (2009).

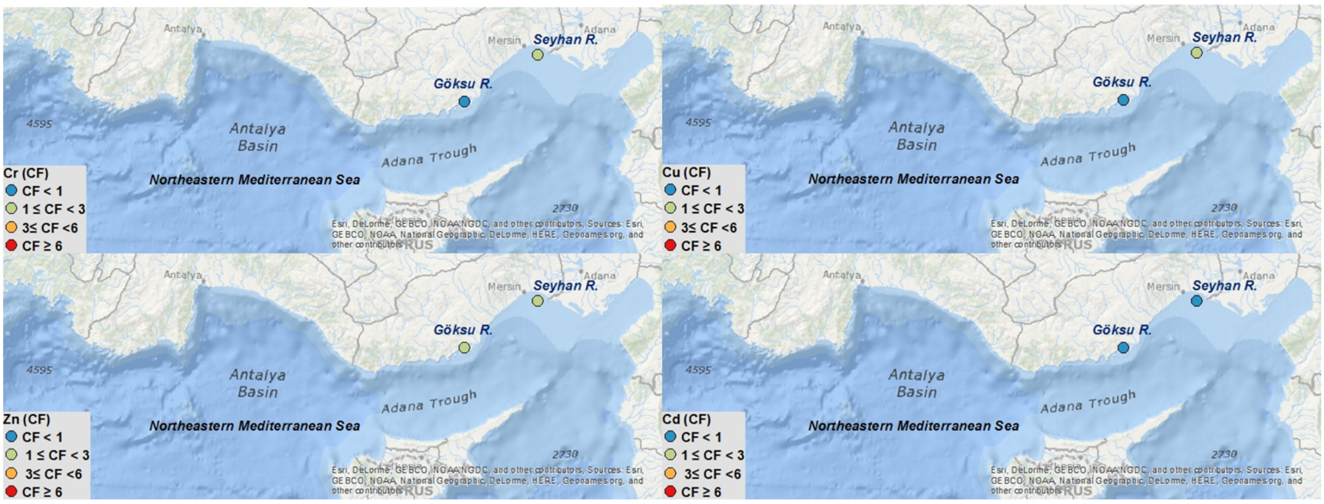

Figure 4. Assessment of metal pollution based on Contamination Factor (Index values were calculated from the data obtained by Tugrul et al. (2009).

Comparison of metal pollution status in sediments of different coastal regions of the Mediterranean Sea showed heavy metal pollution due to anthropogenic pressures (Table 3). Sediments of the coastal regions, affected by contaminated rivers and wastewaters, were polluted by different metals (Table 3). It was shown that there was an apparent sediment Cd pollution in the Southeastern Mediterranean Sea whilst surface sediments were not contaminated in the Mersin Bay, NE Mediterranean Sea. However, surface sediments were highly polluted by Zn in the study sites in the Mersin Bay compared to other regions in the Mediterranean Sea. According to the sediment Cr and Cu pollution assessment, this study showed that in the Seyhan River-influenced coastal regions, surface sediments were highly contaminated by Cr and Cu compared to the different regions of the NE Mediterranean, Western and Southeastern Mediterranean Sea (Table 3).

The PLI values, showing the overall metal pollution status of sediments, indicated Cr, Cu, Zn pollution in the coastal site influenced by Seyhan, Ceyhan and Berdan River inflows. In the Göksu River-influenced region, however, surface sediments were contaminated by only Zn (Fig. 5). Furthermore, the calculated PLI values showed that there was no apparent Cd pollution in the surface sediments of the studied sites.

The study findings indicated that organic and inorganic matter (metals) inputs from the Seyhan River have increased the enrichment of metals accumulated in the sediments of coastal region of the Mersin Bay. The study of Cevik et al. (2009) showed Cd and Cr pollution in the Seyhan Dam from the seasonally obtained sediment samples in 2004-2005 period. Though there was no Cd pollution in the studied sites, the Cr, Cu and Zn pollution was determined in surface sediments of the coastal region in the eastern Mersin Bay due probably to metal pollution of Seyhan and other rivers originated from agricultural activities and discharges of Chrome mines (Cevik et al., 2009; Ozbay et al., 2013).

Table 3. Comparison between metal pollution indices in sediments of the studied region and other regions in Mediterranean Sea (see Table 1 for the classification)

Station	EF				Lgeo				CF			
	Cr	Cu	Zn	Cd	Cr	Cu	Zn	Cd	Cr	Cu	Zn	Cd
Mersin[1],Turkey	6.3	9.9	5.0	3.1	0.2	-0.1	-0.2	-9.2	1.7	2.7	1.3	0.9
Taşucu[1],Turkey	3.2	3.3	5.1	4.1	-1.2	-2.2	-0.7	-9.2	0.7	0.7	1.0	0.8
Rosetta, Egypt[2]	0.001	0.26	0.79	51.57	-5.96	-1.61	0.72	4.84	0.002	0.52	1.84	96.27
Cyprus[3]	0.69	8.61	3.27	-	0.40	2.87	1.55	-	0.82	1.21	0.98	-
Sabratha,Libya[4]	-	12.80	8.56	81.48	-	1.01	-0.61	0.59	-	0.38	0.28	2.78
Muğla[5], Turkey	8.1	3.81	5.28	-	-	-	-	-	-	-	-	-
Thermaikos Gulf, Greece[6]	0.6	2.2	2.4	-	-2.1	0.0	0.3	-	0.5	1.8	1.9	-

[1] Pollution assessment indices were calculated from the data obtained by Tugrul et al. (2009)
[2] El-Sorogy et al. (2016)
[3] Abbasi et al. (2021)
[4] Nour and El-Sorogy (2017)
[5] Tuncel et al. (2007)
[6] Christophoridis et al. (2009)

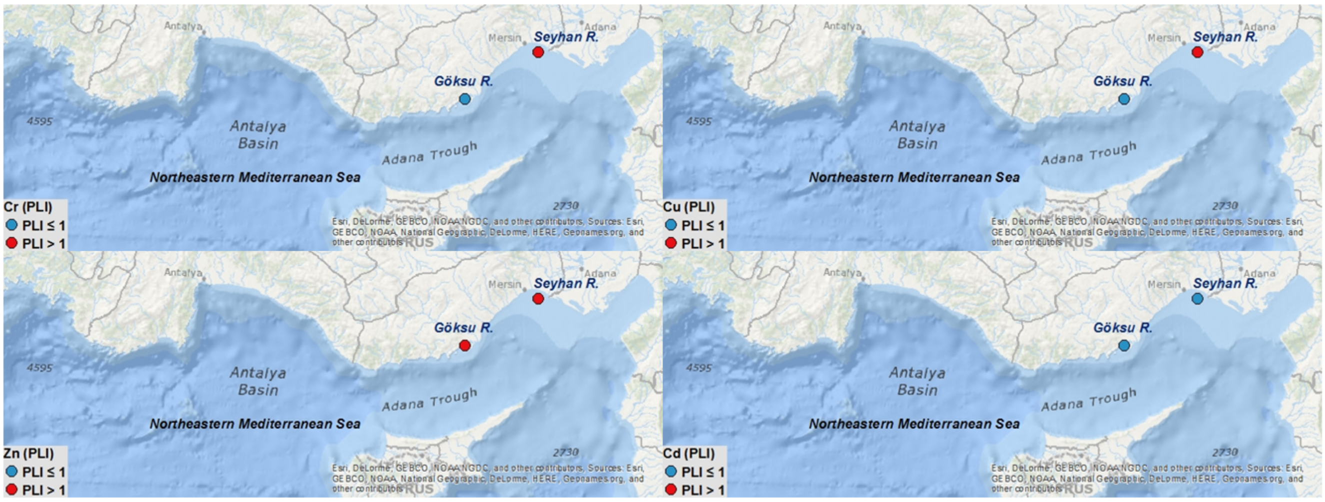

Figure 5. Assessment of metal pollution based on Pollution Load Index (Index values were calculated from the data obtained by Tugrul et al. (2009).

4. CONCLUSIONS

Metal pollution status of surface sediments in the two coastal regions of Mersin Bay (Northeastern Mediterranean Sea) was determined using four different assessment tools. The study findings showed that there was no Cd pollution in surface sediments of the Mersin Bay. However, the sediments are highly polluted by heavy metals Cr, Cu and Zn in the eastern Mersin inner bay due to metal pollution of Seyhan and other regional rivers flowing to coastal region of the bay originated from discharges by anthropogenic activities and Chrome mines. In order to prevent further metal pollution of Mersin inner bay, it is important to increase the efficiency of wastewater treatment plants.

Author contributions

The authors contributed equally.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Statement of Research and Publication Ethics

For this type of study formal consent is not required.

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