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# An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses

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**Abstract** The aim of this study was to determine if high concentrations of any heavy metals exist in the sediment of Seyhan Dam reservoir to be considered toxic to the aquatic environment. Surface sediment samples from five stations in the Seyhan dam were collected quarterly from 2004 to 2005 and examined for metal content (Cr, Zn Cu, Mn, Cd, Fe, Ca, K, and Na), organic matter, and grain size. Correlation analyses showed that metal content of Seyhan dam sediment was affected by organic matter and grain size. The results have been compared with values given in the literature. The evaluation of the metal pollution status of the dam was carried out by using the enrichment factor and the geoaccumulation index. A comparison with sediment quality guideline values has also been made. Based on the enrichment factor, dam sediments were treated as a moderately severe enrichment with Cd and minor enrichment with Cr and Mn. The results of geoaccumulation index reveal that sediments of Seyhan Dam were strongly polluted in stations 1, 2, 4, and 5, and were moderately polluted in station 3 with Cd. Moreover, Cd and Cr concentrations in the sediments were above TECs except ERL for Cd.

**Keywords** Metal · Sediment · Enrichment factor · Geoaccumulation index · Seyhan dam

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## Introduction

Population growth and distribution, use of chemicals and land use are affecting the environment. Sediments play a major role in the determining pollution pattern of aquatic systems (Casas et al. 2003), they act as both carriers and sinks for contaminants, reflecting the history of pollution (Singh et al. 2005), and providing a record of catchment inputs into aquatic ecosystems (Mwamburi 2003).

Metals are a group of pollutants of high ecological significance. They are not removed from water by self-purification, but accumulate in suspended particulates and sediment, and then enter the food web via passing to higher consumer (Ghrefat and Yusuf 2006; Khaled et al. 2006). They always present in aquatic ecosystems and redistribute only among different components (Linnik and Zubenko 2000).

Sources of metals in aquatic sediments are natural or anthropogenic sources (Singh et al. 2005; Khaled et al. 2006; Ghrefat and Yusuf 2006; Demirak et al. 2006). Main natural sources are weathering of soils and rocks and atmospheric deposition. Dischargings agricultural, municipal, residential or industrial waste products into water bodies are anthropogenic sources (Demirak et al. 2006).

In the sediments, metals accumulate through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds. Several physico-chemical parameters, such as pH, oxidative–reductive potential, dissolved oxygen, organic and inorganic carbon content, and the presence in water phase of some anions and cations influence the adsorption process (Ghrefat and Yusuf 2006).

Studying the distribution of metals in sediments adjacent to settlement and agricultural areas can provide researchers with evidence of the anthropogenic impact on ecosystems and, therefore, aid in assessing the risks associated with discharged human waste.

The aim of this study was to determine if high concentrations of any heavy metals exist in the reservoir to be considered toxic to the aquatic environment. Heavy metals of concern were Cr, Zn Cu, Mn, Cd and Fe. A few so called "light" metals such as Ca, K, and Na were also studied. Four aspects are considered: (1) seasonal and regional distribution of the metals in the sediment, (2) comparing metal concentrations in other lakes sediment recorded in the literature and the standart sediment quality, (3) determining if there is any evidence of metals from Körkün Creek, the rivers Çakıt and Seyhan, and (4) determining enrichment factor and geoaccumulation index of the metals.

## Material and methods

### Study area

Seyhan dam, one of the most important reservoirs in the Mediterranean Region in Turkey, was built for floods, irrigation and energy production. It was chosen in this study as it is a major recreation area serving Adana city. A typical Mediterranean climate prevails in the study area. Major land use in the common watershed of lake is agriculture and settling area. Also, there are many chrome ores in the Seyhan river basin (Göksu et al. 1997).

The dam has been operating since 1956 and was built across the river Seyhan. The lake, with an average width of 4 km and average length of 23 km, reaches its maximum depth of 45 m in spring. It covers a maximum of 9,200 ha. The average height from the sea is 67 m. The river Seyhan, Çakıt river and Körkün creek flow into the lake and the lakewater flows into the Mediterranean Sea. The Seyhan dam is classified as a mesotrophic lake (Çevik et al. 2007).

### Sampling and sample preparation

Seasonal sediment samples (October, February, April, July) were taken in 2004–2005 at five sampling stations (stations 1, 2, 3, 4, and 5; Fig. 1) using an Ekman bottom grab (Hydrobios, 20×20×20 cm) device from the top 20 cm layer of the bottom. Samples which were put in the acid-rinsed polyethylene containers were immediately taken to the laboratory. Then stones and plant fragments were removed by passing the dried sample through a 2 mm sieve.

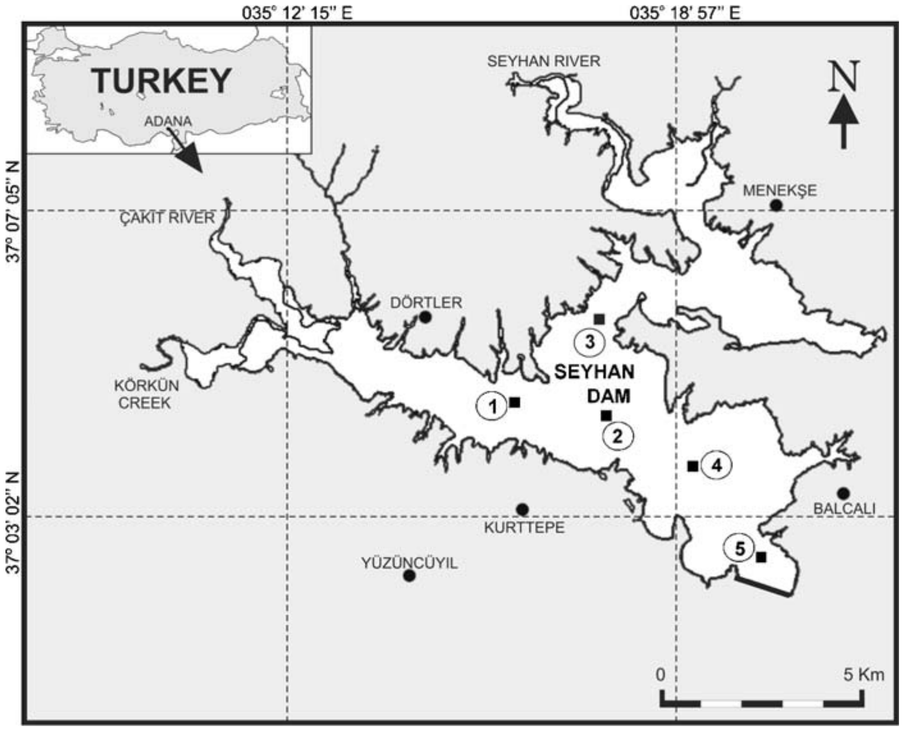
All chemicals used were of the highest purity available (Merck) and all glassware and the laboratory equipment used were carefully cleaned with HCl to minimize potential contamination.

The sediment samples for heavy metal determination were oven-dried at 80°C on glass dishes until the constant weight, homogenized with a pestle and mortar, and each of the weighed samples (approximately 500 mg) were transferred into Teflon vessels, digested with 10 ml $HNO_3$ in a microwave oven (Milestone MLS-1200 Mega). The digestates were left to cool at room temperature and then filtered through a 0.45 μm nitrocellulose membrane filter. The filtered digestates were diluted with distilled deionised water to 25 ml in a volumetric flask (USEPA 1994).

The concentrations of the metals Fe, Zn, Cu ve Mn were determined by using atomic absorption spectroscopy (Varian Model 1100). Metals such as Cr and Cd were determined by ICP-AES (Jobin Yvon-Ultrace 138). Flame photometer 2380 was used for the measurements of Na, K and Ca. All analyses were taken in duplicate and mean values were calculated.

The organic material (OM) was evaluated by revised Walkley–Black titration method. Dried sediment was weighted (2 g) and treated with potassium dichromate solution followed by rapid addition of concentrated sulphuric acid containing 0.5 g silver sulphate. After samples were allowed to cool for 30 min, the mixture was diluted by distilled water, and orthophosphoric acid is added. Finally, the excess dichromate was back-titrated with 0.5 N iron (II) sulphate solution using barium diphenylamine sulphonate as an indicator. OC in sediment was determined as % (Leong and Tanner 1999).

**Fig. 1** Map of Seyhan dam and selected stations (1–5)




The pipette method was used for grain size analyses. This method is based on the difference in sedimentation speed between small and large particles. The pipetted suspension is condensed and dried and weighing determines the mass ratio of the pipetted fraction (USEPA 2003).

## Statistical analyses

All data were checked for the assumption of normal distributions. One-way ANOVA was carried out to test for significant variations in metal concentrations with respect to seasons and stations. Duncan's new multiple range test was used for the comparisons among means for mean effects. Also, Pearson multiple correlation analysis was applied to all results. Statistical analyses of data were performed using SPSS statistical software package (Version 10).

# Results and discussion

## Sediment characteristics

The grain size distributions of the study area are given in Fig. 2. The grain size distribution showed that silt (2–63 µm) and clay (>2 µm) percentages appear to be the principal sediment type throughout the investigated stations, while station 3 was more sandy (0.063–2 mm) and with low clay substrates. Silt was the main component of all sediment samples. Station 1, located at the vicinity of the mouths of Çakıt river and Körkün Creek, had the highest silt contents, whereas station 3, located at the vicinity of the mouths of Seyhan River, had the lowest clay and the highest sand.

The organic matter in the sediment of Seyhan dam ranged between 3.05% and 8.53% and the differences found to be significant among the stations ($p<0.01$;

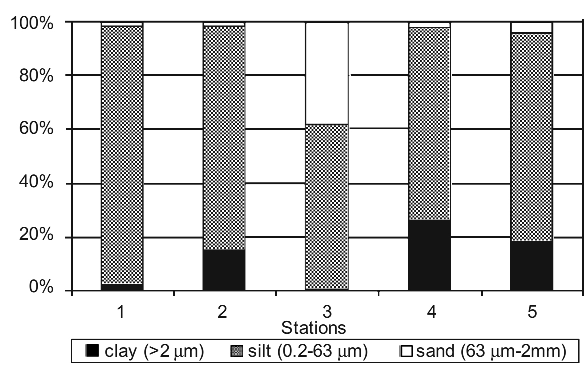



**Fig. 2** Grain size composition of surface sediments in Seyhan dam

Table 1). But, the organic matter showed no significant seasonal variations. Organic matter concentrations were the highest in Station 4 and the lowest in station 3, which had the highest sand. Because of their smaller spesific surface area, sands are usually low in organic material (Hart 1982).

As shown in Table 2, presence of metals in sediments is affected by the grain size and organic matter. All metals have a positive relationship with clay and Cr, Fe, and K are significant at $p<0.05$ probability level. The relationship between metals and sand is negative and Cr, Mn, Fe, and K are significant ($p<0.05$). Except Na and Ca, correlations of metals with organic matter are strongly positive ($p<0.01$; Table 2).

Particle size and density play important roles in determining the chemistry and ecology of sediments. The clay/silt fraction (<63 µm) has a high specific surface area per unit quantity of material and, because of surface coatings of iron and Mn oxides and natural organics, it is more likely to adsorb organic and trace metal contaminants (Hart 1982; Maher et al. 1999) and, it is most likely to be involved in the physico-chemical sorption reactions (Hart 1982). Most anthropogenic contaminants are associated with the clay and silt fractions.

Major and heavy metal levels

According to the results of one-way ANOVA test, the acid-soluble concentrations of all metals in the <2.00 mm fractions of the sediment samples showed no significant seasonal variations, whereas all metals were found to be significantly differences among the stations ($p<0.01$; Table 1).

In general, the lowest value of all metals were found at Station 3, except at Station 2 for Na and at Station 4 for Ca. The highest value of Cd, Cr, Mn, Cu, Fe and K were observed at Station 4, while Station 1 revealed higher concentrations of Zn and Ca, and Station 5 revealed higher concentrations of Na.

The mean concentration of metals in sediments of Seyhan dam represented the next decreasing order Ca>Fe>K>Mn>Na>Cr>Zn>Cu>Cd. The average concentrations of Cr and Cd in the sediment were higher than the average shale values (Mwamburi 2003). In other studies of the Seyhan dam; Göksu et al. (2003) also found high concentrations of Cd in the edible parts of *Cyprinus carpio* and *Stizostedion lucioperca*. Cr concentrations of Çakıt river were found at critical levels because of chromite plant, and in Seyhan dam water. Cr concentration were at a normal level according to the Fisheries Regulation of the Fisheries law no 1380. The Cr concentration of the waste of the Chromite plant was found to be 4.6 mg $L^{-1}$ (Göksu et al. 1997).

The comparison between the present concentrations and those in the literature concluded that the concentrations observed in the Seyhan dam were lower or higher than those recorded (Table 3). The average concentrations of Cd obtained in this study

**Table 1** Duncan's Multiple Range Test results for the mean metal (µg $g^{-1}$) and organic matter (%) concentrations of sediments in stations

| Metals | Stations | | | | | *F* |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | |
| Cd | 2.31$^{bc}$ | 2.13$^{b}$ | 1.55$^{a}$ | 2.44$^{c}$ | 2.31$^{bc}$ | 19.79** |
| Cr | 125.73$^{bc}$ | 115.49$^{b}$ | 84.92$^{a}$ | 135.51$^{c}$ | 133.10$^{c}$ | 24.24** |
| Mn | 872.10$^{c}$ | 764.88$^{b}$ | 595.10$^{a}$ | 904.77$^{c}$ | 881.31$^{c}$ | 22.50** |
| Zn | 43.34$^{b}$ | 38.63$^{ab}$ | 32.88$^{a}$ | 42.09$^{b}$ | 38.53$^{ab}$ | 4.14** |
| Cu | 21.90$^{c}$ | 17.99$^{b}$ | 12.42$^{a}$ | 23.83$^{d}$ | 22.84$^{cd}$ | 54.87** |
| Fe | 42190.63$^{b}$ | 39391.38$^{b}$ | 30640.25$^{a}$ | 43204.50$^{b}$ | 41323.25$^{b}$ | 15.30** |
| Na | 375.43$^{b}$ | 323.17$^{a}$ | 338.85$^{ab}$ | 428.34$^{c}$ | 439.27$^{c}$ | 12.07** |
| K | 4353.00$^{bc}$ | 3806.00$^{b}$ | 2164.50$^{a}$ | 4704.12$^{bc}$ | 3966.75$^{c}$ | 15.45** |
| Ca | 80326.00$^{b}$ | 59918.75$^{a}$ | 56809.13$^{a}$ | 56368.00$^{a}$ | 58179.50$^{a}$ | 2.67** |
| Org. mat. | 7.32$^{b}$ | 6.56$^{b}$ | 4.02$^{a}$ | 7.09$^{b}$ | 6.75$^{b}$ | 18.27** |

The means labelled with different letters within columns are significantly ($p<0.01$) differ by Duncan's New Multiple range test

**$p$<00.1

**Table 2** Correlation of grain size and organic matter with metals in Seyhan dam sediment

| Composition | Cd | Cr | Mn | Zn | Cu | Fe | Na | K | Ca |
|---|---|---|---|---|---|---|---|---|---|
| Sand | −0.28 | −0.91* | −0.89* | −0.86 | −0.86 | −0.96* | −0.41 | −0.94* | −0.32 |
| Silt | 0.044 | −0.06 | 0.00 | 0.16 | −0.52 | 0.02 | −0.29 | −0.05 | 0.82 |
| Clay | 0.26 | 0.91* | 0.87 | 0.79 | 0.86 | 0.93* | 0.50 | 0.93* | 0.03 |
| Organic matter | 0.80** | 0.70** | 0.79** | 0.59** | 0.79** | 0.78** | 0.26 | 0.77** | 0.26 |

*$p<0.05$

**$p<0.01$

was much higher than sediments of Balaton lake (Nguyen et al. 2005), Uluabat lake (Barlas et al. 2005), and Dipsiz stream (Demirak et al. 2006) and similar to Lake Texoma (An and Kampbell 2003). Cr and Mn were also higher than the sediments of other regions. While average concentrations of Zn were lower than Atatürk dam (Karadede and Ünlü 2000) and Lake Texoma (An and Kampbell 2003), Cu concentrations were lower than the sediment of Lake Texoma (An and Kampbell 2003). The average concentration of Fe was only higher than Wadi Al-Arab dam (Ghrefat and Yusuf 2006).

## Enrichment factor and geoaccumulation index

For the estimation of anthropogenic inputs, some of the most often used indicators in the sediment are enrichment factor and geoaccumulation index (Covelli and

**Table 3** Comparative trace metal concentrations (dw) in the sediment from different regions of the world and sediment quality guidelines

| | | Metals | | | | | |
|---|---|---|---|---|---|---|---|
| | | Cd | Cr | Mn | Zn | Cu | Fe |
| This study (μg $g^{-1}$) | | 2.15±0.38 | 118.95±21.7 | 803.63±137 | 39.09±6.50 | 19.80±4.57 | 39,350±5,754 |
| Wadi Al-Arab Dam (mg $g^{-1}$)[a] | | 0.007–0.013 | – | 0.21–0.81 | 0.17–0.96 | 0.02–0.19 | 7.78–15.75 |
| Uluabat Lake (μg $g^{-1}$)[b] | | 0.078±0.1 | 2.95±1.04 | – | 3.89±0.25 | 0.75±0.09 | – |
| Dipsiz stream (μg $g^{-1}$)[c] | | 0.80±0.60 | 19.70±15.60 | – | 37.00±26.00 | 13.00±9.00 | – |
| Atatürk Dam (ppm)[d] | | ND | | 73.600–514.07 | 60.79–59.14 | 14.57–22.70 | 12,587–19,265 |
| Lake Texoma (mg $kg^{-1}$dw)[e] | | 2±3 | 30±13 | 377±161 | 89±53 | 38±34 | 19,393±7,835 |
| Balaton lake (μg $g^{-1}$)[f] | | 0.1–0.7 | 5.7–66 | 160–760 | 13–150 | 0.7–36 | – |
| St. Lucie Estuary (mg $kg^{-1}$)g | | 4.9–23 | 5.2–91 | 23–223 | 3.4–127 | 3.1–72 | 1.6–37 |
| Threshold effect concentrations | TEL | 0.596 | 37.3 | – | 123 | 35.7 | – |
| | LEL | 0.6 | 26 | – | 120 | 16 | – |
| | MET | 0.9 | 55 | – | 150 | 28 | – |
| | ERL | 5 | 80 | – | 120 | 70 | – |
| Probable effect concentrations | PEL | 3.53 | 90 | – | 315 | 197 | – |
| | SEL | 10 | 110 | – | 820 | 110 | – |
| | TET | 3 | 100 | – | 540 | 86 | – |
| | ERM | 9 | 145 | – | 270 | 390 | – |

[a] Ghrefat and Yusuf (2006)

[b] Barlas et al. (2005)

[c] Demirak et al. (2006)

[d] Karadede and Ünlü (2000)

[e] An and Kampbell (2003)

[f] Nguyen et al. (2005)

[g] Zhang et al. (2003)

*TEL* Threshold effect level, *LEL* lowest effect level, *MET* minimal effect threshold, *ERL* effect range low, *PEL* probable effect level, *SEL* severe effect level, *TET* toxic effect threshold, *ERM* effect range median

Fontolan 1997; Ghrefat and Yusuf 2006; Gonzáles-Macías et al. 2006; Chen et al. 2007). According to this technique, metal concentrations were normalized to metal concentrations of average shale (Mwamburi 2003; Ghrefat and Yusuf 2006) or average crust (Gonzáles-Macías et al. 2006). Widely used elements for normalization are Al (Chen et al. 2007) and Fe (Ghrefat and Yusuf 2006). In this study, iron has also been used as a conservative tracer to differentiate natural from anthropogenic components and we prefer to express the metal contamination with respect to the average shale to quantify the extent and degree of metal pollution. The values of the average shale used in this work are from Mwamburi( 2003). These values are: Fe 46,700, Cr 90, Cu 45, Cd 0.3, Mn 850 and Zn 95 μg $g^{-1}$. The metal enrichment factor (EF) is defined as follows:

$$EF = \frac{\left(\frac{M_{\text{sample}}}{Fe_{\text{sample}}}\right)}{\left(\frac{M_{\text{average shale}}}{Fe_{\text{average shale}}}\right)}$$

Where:

| | |
|---|---|
| $M_{\text{sample}}$ | concentration of the examined metal in the examined sediment |
| $Fe_{\text{sample}}$ | concentration of the reference metal in the examined sediment |
| $M_{\text{average shale}}$ | concentration of the examined metal in the average shale |
| $Fe_{\text{average shale}}$ | concentration of the reference metal in the average shale |

According to Chen et al. (2007), EF<1 indicates no enrichment, EF<3 is minor enrichment, EF=3–5 is moderate enrichment, EF=5–10 is moderately severe enrichment, EF=10–25 is severe enrichment, EF=25–50 is very severe enrichment, and EF>50 is extremely severe enrichment.

The calculation of enrichment factors showed that Cd, Cr and Mn were enriched in sediments of Seyhan dam. Cd had the highest EF values among the five metals studied and it has a moderately severe enrichment (average value 8.45). Cr and Mn had minor enrichment (average value 1.57 and 1.12, respectively). Cu and Zn exhibited the lowest EF values among metals studied (average value 0.52 and 0.49, respectively) and had no enrichment (Fig. 3).

The geoaccumulation index ($I_{\text{geo}}$) was also used to assess metal pollution in sediments of Seyhan dam. Geoaccumulation index is expressed as follows:

$$I_{\text{geo}} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

where, $C_n$ is the measured concentration of the heavy metal ($n$) in the sediments, $B_n$ is the geochemical background value in the average shale of element $n$, and 1.5 is the background matrix correction factor due to lithogenic effects (Loska et al. 1997; Ghrefat and Yusuf 2006; Gonzáles-Macías et al. 2006; Chen et al. 2007).

According to Loska et al. (1997) and Gonzáles-Macías et al. (2006), the contamination level may be classified in a scale ranging from 1 to 6 ($I_{\text{geo}}\leq0$= unpolluted, $I_{\text{geo}}<1$=unpolluted to moderately polluted, $I_{\text{geo}}<2$=moderately polluted, $I_{\text{geo}}<3$=moderately to strongly, $I_{\text{geo}}<4$=Strongly polluted, $I_{\text{geo}}<5$= strongly to very strongly polluted, $I_{\text{geo}}>5$=very strongly polluted).

The results of geoaccumulation index reveal that sediments of the Seyhan dam are moderately to strongly polluted at stations 1 (2.36), 2 (2.24), 4 (2.43), and 5 (2.35), and are moderately polluted at station 3 (1.74) with Cd. The results show that the sediments are unpolluted with Cr, Mn, Zn, Fe, and Cu (Fig. 4). Pollution of Cd is due to anthropogenic sources including fertilizers and pesticides used in agricultural activities. Agricultural land in the Mediterranean region of Turkey makes up 20.8% of the total agricultural land of the country. The largest amount of pesticides is used in this region. It reached 4.8 kg $ha^{-1}$ in 1998. The amount of fertilizers is also higher in the region than the national average. The

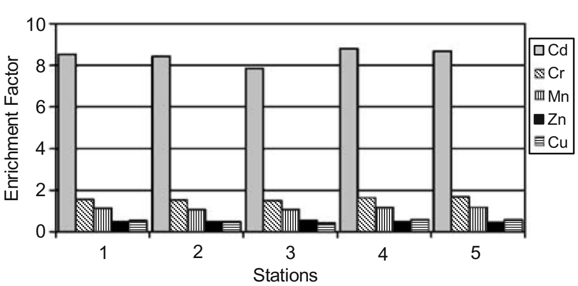



**Fig. 3** Enrichment factors (EF) in surface sediments of Seyhan dam

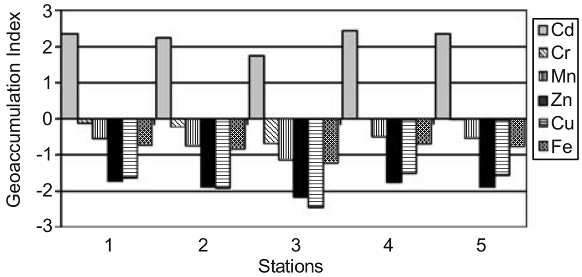



**Fig. 4** Geoaccumulation Index ($I_{geo}$) in surface sediments of Seyhan dam

amount of chemical fertilizer use is 128 kg $ha^{-1}$ (Tanrivermis 2003).

Sediment quality guidelines

Sediment Quality Guidelines (SQGs) are very important for protection of benthic organisms in freshwater ecosystems and can be used to assess sediment ecosystem health. The threshold effect concentrations (TECs) and the probable effect concentrations (PECs) for sediment levels were reported by MacDonald et al. (2000). The TECs were intended to identify contaminant concentrations below which harmful effects on benthic organisms were not expected. The PECs were intended to identify contaminant concentrations above which harmful effects on benthic organisms were expected to occur frequently (MacDonald et al. 2000).

In this study, metal concentrations in the Seyhan dam sediments are compared with threshold effect levels (TELs), effect range low values (ERLs), lowest effect levels (LELs), minimal effect thresholds (METs), which are included TECs, and probable effect levels (PELs), effect range median values (ERMs); severe effect levels (SELs), and toxic effect thresholds (TETs), which are included PECs. Table 3 indicates that Cd and Cr concentrations in the Seyhan dam are above TECs (except ERL for Cd). Cu is above LEL. Cd, Cu, and Zn concentrations are less than the PECs but Cr is more than the PECs (except ERM).

Correlation analyses

To investigate the common characteristics (behaviour, origin, etc.) of metals in Seyhan dam, correlation analyses between metals were calculated. In sediments, correlations between metals Cd, Cr, Mn, Zn, Cu, Fe and K (except with Na) were significant at the $p<0.01$ probability level as shown in Table 4. While Ca is only correlated with Zn, Na is correlated with Cr, Mn and Cu. These correlations between metal concentrations suggest either a common or a similar geochemical behaviour or origin.

Factors including source rock or soil types, weathering processes, surface adsorption phenomena, and characteristics of depositional environment affect to the distribution of metals in sediments. Therefore, metal/metal relationships may vary significantly (NAVFAC 2003).

According to Zabetoglou et al. (2002), Fe and Mn oxides/hydroxides have a high affinity with most trace metals and Fe often correlate with concentrations of other metals in aquatic environments. In this study, the high correlation between Fe and Mn suggests the presence of Fe/Mn compounds.

**Table 4** The coefficients of correlation of heavy metal concentrations in Seyhan dam

| | Cd | Cr | Mn | Zn | Cu | Fe | Na | K | Ca |
|---|---|---|---|---|---|---|---|---|---|
| Cd | 1.00 | 0.86** | 0.97** | 0.74** | 0.91** | 0.99** | 0.31 | 0.73** | 0.13 |
| Cr | | 1.00 | 0.84** | 0.45** | 0.91** | 0.82** | 0.56** | 0.70** | −0.18 |
| Mn | | | 1.00 | 0.80** | 0.94** | 0.95** | 0.41** | 0.70** | 0.24 |
| Zn | | | | 1.00 | 0.64** | 0.75** | 0.06 | 0.59** | 0.56** |
| Cu | | | | | 1.00 | 0.87** | 0.59** | 0.76** | 0.05 |
| Fe | | | | | | 1.00 | 0.27 | 0.69** | 0.13 |
| Na | | | | | | | 1.00 | 0.25 | −0.24 |
| K | | | | | | | | 1.00 | 0.12 |
| Ca | | | | | | | | | 1.00 |

*$p<0.05$

**$p<0.01$

## Conclusion

The results indicate that Cd and Cr in the sediments of Seyhan dam are higher than average shale values. The mechanism of accumulation and distribution of metals is controlled by grain size and organic matter content. Seasonal variation of metals, organic matter and grain size are not significant statistically. A positive relationship was found between the concentrations of metals and clay and organic matter content. Agricultural activities and chrome mines are likely to be the main sources of increased concentrations for Cd and Cr elements observed in recent sediments of Seyhan dam.

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