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Research Article

Assessment of Metal Pollution in Water and Surface Sediments of the Seyhan River, Turkey, Using Different Indexes

The aim of this study was to assess the level of heavy metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) contamination and enrichment in the surface sediments of the Seyhan River, which is the receiving water body of both treated and untreated municipal and industrial effluents as well as agricultural drainage waters generated within Adana, Turkey. Sediment and water samples were taken from six previously determined stations covering the downstream of the Seyhan dam during both wet and dry seasons and the samples were then analyzed for the heavy metals of concern. When both dry and wet seasons were considered, metal concentrations varied significantly within a broad range with Al, 7210–33 967 mg kg^{-1} dw; Cr, 46–122 mg kg^{-1} dw; Cu, 6–57 mg kg^{-1} dw; Fe, 10 294–26 556 mg kg^{-1} dw; Mn, 144–638 mg kg^{-1} dw; Ni, 82–215 mg kg^{-1} dw; Pb, 11–75 mg kg^{-1} dw; Zn, 34–146 mg kg^{-1} dw in the sediments while Cd was at non-detectable levels for all stations. For both seasons combined, the enrichment factor (EF) and the geo-accumulation index (I_{geo}) for the sediments in terms of the specified metals ranged from 0.56 to 10.36 and −2.92 to 1.56, respectively, throughout the lower Seyhan River. The sediment quality guidelines (SQG) of US-EPA suggested the sediments of the Seyhan River demonstrated ''unpolluted to moderate pollution'' of Cu, Pb, and Zn, ''moderate to very strong pollution'' of Cr and Ni. The water quality data, on the other hand, indicated very low levels of these metals suggesting that the metal content in the surface sediments were most probably originating from fine sediments transported along the river route instead of water/wastewater discharges with high metal content.

Keywords: Enrichment factor, Geo-accumulation index, Metals, River pollution, Sediments

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1 Introduction

Accelerated by the industrial development, urbanization, and population increase in the last decades, many rivers are now carrying ecologically destructive levels of pollutants including heavy metals [1]. Heavy metals are deemed as severe inorganic pollutants due to their high enrichment factor (EF), slow removal rate, potential toxicity to aquatic life, persistent, and bio-accumulative nature, [2, 3]. Heavy metals may enter into river systems via weathering and erosion of the earth or anthropogenic activities such as mining, industrial processing, agriculture (run-off), and sewage disposal [4, 5]. Sediments in riverbeds act as sinks for pollutants and, therefore, they play a significant role in the remobilization of heavy metals in aquatic systems [6]. While the heavy metals may be transferred from water to sediments through settling of particles, their remobilization may be carried out via the aquatic biota [7].

The concentration and speciation of the total metals in sediments can be used to explain mobility, bioavailability, and toxicity of metals and ultimately to assess the potential environmental impacts [8]. After various modifications proposed by Tessier et al. [9], Calmano and Forstner [10], Qiao et al. [11] and long-time application, sequential extraction has become a significant speciation tool in determining ecotoxicological risk to biota based on the metals. However, as a consequence of some disadvantages such as low reproducibility especially with large particles and encapsulated pollutants [12], the error propagations [13], strong influence of operative conditions [14], non-selectivity of the extracting reagents [15], and possible redistribution among phases during extraction [16]. These sequential extraction procedures require additional experimental investigation and solid matrix characterization to identify the actual form of metals in soils [17]. On the other hand, enrichment factor – EF [18], geo-accumulation index – I_{geo} [21], individual and global contamination factors-ICF/GCF [19], and sediment quality guidelines – SQG (USEPA) [20] can be used to assess the degree of potential risk of metals to flora and fauna in any river.

The focus of this research, the Seyhan River, flows through the lower Seyhan plain and has a catchment area of 20 731 km^2. There are intense agricultural activities and population with a great economic contribution both industrially and agriculturally activities in Turkey. There have been several studies reported in the

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literature about the Seyhan River including natural radioactivity [21], the impact of climate change [22], potential use of the river as a sink for heat pump [23], estimation of spatial distribution of soil loss [24], developing management strategies for pollution control on the Seyhan River basin [25]. However, there is very limited information on the heavy metal content and their distribution in the surface sediments [26, 27]. The overall objectives of this investigation were (1) to identify concentrations of heavy metals in surface sediments in order to provide preliminary baseline data for pollution control in the Seyhan River, (2) to assess their anthropogenic discharge, and (3) to evaluate the data on metal levels in the context of similar data reported from other countries.

2 Materials and methods

2.1 Study area

The Seyhan River is the receiving water body of municipal and industrial effluents and agricultural drainage waters of so-called "Cukurova region" in Turkey. Although miscellaneous large industries located in the area subject their wastewaters to treatment processes, small industries are suspected to discharge their wastewaters directly into the river without any treatment. The Seyhan River divides the Cukurova plain into two sub-plains, Tarsus and Yuregir plains. The lower Seyhan River refers to the part about 94 km in length after the Seyhan Dam, flows through the city of Adana with about 1 300 000 inhabitants and flows to the Mediterranean Sea. There are subsequent dams on the Seyhan River built for the purposes of irrigation and energy production. These dams lead to change the water quality and quantity of the river. The climate of the region is moderate subtropical type and the annual average temperature is 18°C with a mean rainfall of 110.2 mm. The soil type of the basin is alluvion consisting of clay, silt, fine-to-coarse sand and pebbles. The sampling stations selected for this study are shown in Fig. 1.

The sampling stations, except first and final stations, were selected considering the effects of point and non-point pollution sources discharging into the river. Furthermore, the stations were strategically chosen at zones where the hydraulic conditions of the river changed dramatically (see Fig. 1). S-1 was located downstream of the second regulator bridge, which controls the hydraulic conditions for irrigation and over-flow. S-2 and S-4 were chosen near different citrus gardens to demonstrate the possible effects of non-point agricultural drainage waters received by the river. S-3 was at a point where the hydraulic conditions of the river changed dramatically due to meanders. The illegal use of the area around this station as sand/gravel supply for building materials lead to changes in the composition of the bed sediments. S-5 was located nearby a settlement called Tabaklar. The final station, S-6, was located in the downstream of the main agricultural drainage collector channel discharge point. The domestic wastewaters of the settlements surrounding the channel and the effluents of miscellaneous industries located in the lower Seyhan River basin are carried by the collector channel as well as the drainage waters from the main drainage collector of western plain. Fig. 2

2.2 Sediment sample collection and preservation

The sampling was carried out in October 2009 and June 2010 representing wet and dry seasons, respectively. The water samples taken

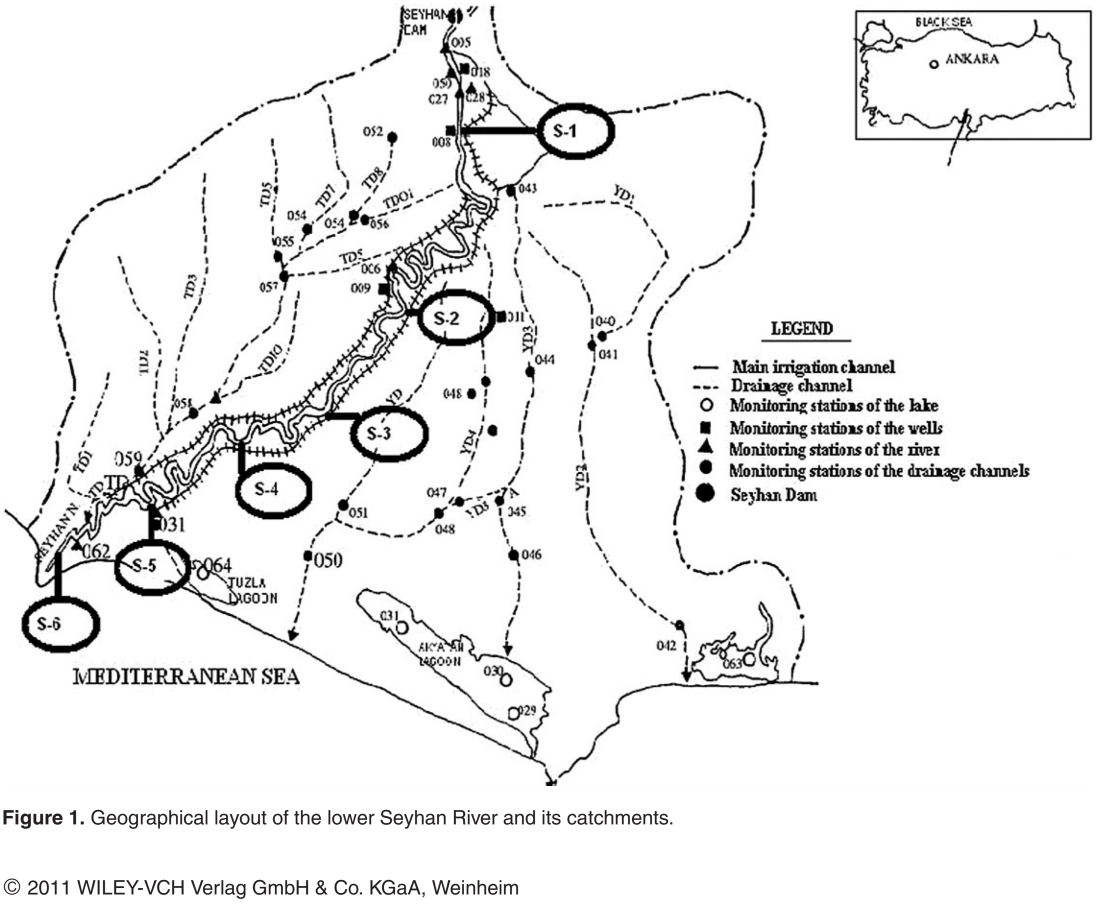

Figure 1. Geographical layout of the lower Seyhan River and its catchments.

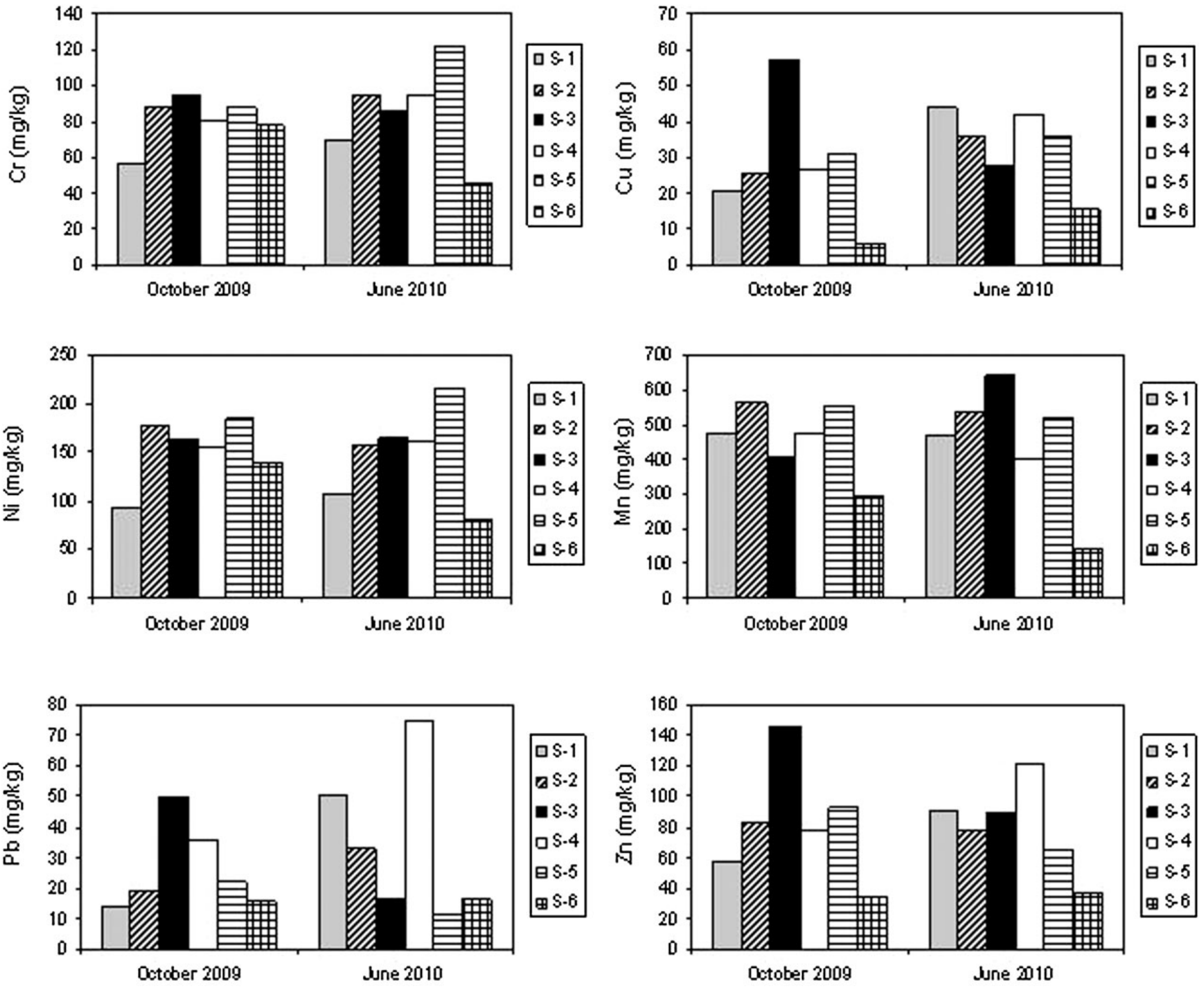

Figure 2. Seasonal variation of metals in surface sediments of the lower Seyhan River.

from the specified stations located along the river were collected in sterile capped containers as described by standard methods [28]. To avoid contamination between samples and from other sampling means, disposable gloves were washed with 10% HNO_3 solution v/v and rinsed with de-ionized water before sampling on-site. The water samples were acidified with concentrated nitric acid to $pH < 2$ and stored in polythene bottles. The sample bottles were kept in large plastic ice-cold air-tight containers at 4°C and were transported to laboratory within 6 h after collection for further processing and analyses.

The surface sediment samples, on the other hand, were collected using an Ekman^{TM} grab sampler from the specified sampling stations. At each sampling station and exactly where the water samples were taken, three samples of upper sediments were collected from the shallow area near the river bank. Immediately after measuring the samples for redox potential (ORP) and pH on site, the samples were kept in air-sealed plastic bags placed in a portable cooler at 4°C, transported to the laboratory, and stored in the freezer at -20°C until further analyses. The frozen sediment samples were defrosted and air-dried at 40 ± 2°C and then ground with a pestle and mortar for homogenization. Each sample was sieved through a stainless steel mesh to remove any particle larger than 63 μm in size since there is a strong association of metals with fine-grained sediments [29]. The moisture content of the samples was determined by heating the sediment samples at 105 ± 2°C in glass plates until constant weight. All data reported in this paper were calculated on dry weight basis.

2.3 Reagents and Apparatus

Double distilled water (DDW) was used for extraction, solution preparation, and rinsing during experimental studies. For analyses, calibrations, and solution preparation, analytical-grade quality reagents and stock solutions were used (Merck, Darmstadt, Germany). In order to assess the precision of the analytical studies carried out within the scope of the work, standard reference materials (BCR 701) were also analyzed and the results were compared with the certified values (see Tab. 1). After repeating the analyses four times for BCR-701, the recovery rates were found to be 87% for Cd, 94% for Cr, 100% for Cu, 86% for Ni, 93% for Pb, and 87% for Zn indicating strong precision rates. Glass, plastics, and other laboratory ware were cleaned through soaking in 10% HNO_3 solution (by volume) overnight and then rinsing with de-ionized water.

Table 1. Results of analysis of standard reference material (BCR 701-Lake sediment) in comparison with certified values (mg/kg as dry weight)

SRM (BCR 701-Lake sediment)	Analyzed SRM value	Certified SRM value	% Recovery
	Total digestion ($n = 4$)		
Cd	10.2 ± 0.07	11.7 ± 1.0 [a]	87
Cr	255.9 ± 14.9	272 ± 20 [a]	94
Cu	273.8 ± 6.04	275 ± 13 [a]	100
Ni	88.3 ± 2.12	103 ± 4 [a]	86
Pb	132.8 ± 6.52	143 ± 6 [a]	93
Zn	396.1 ± 17.3	454 ± 19 [a]	87

[a] Indicative values.
Mean and standard deviation of four replications for BCR®-701 were shown.

A microwave unit (Berghof MWS-2, Germany) was used for the digestion of sediment samples with acid. An ICP instrument (Perkin-Elmer, ICP OES Optima 2100 DV, USA) was used for the determination of all specified metals in the acid-digested samples. The operational conditions for the ICP were adjusted in accordance with the manufacturer's guidelines to obtain optimal determination.

2.4 Microwave-assisted acid digestion procedure

The metal content of the sediment samples were determined after digestion of 0.5 g of air-dried sediment sample with 5 mL conc. HNO_3 and 15 mL conc. HCl in an advanced polytetrafluoroethylene (PTFE) vessel. The digested samples were then filtered through filter paper (0.45 μm pore size) and diluted to 100 mL with DDW in a volumetric flask.

2.5 Enrichment factor (EF) and geo-accumulation index (I_{geo}) analysis

The sediment quality and metal contamination in the Seyhan River were further discussed when other approaches for environmental assessment were also considered such as the EF, geo-accumulation index, and the sediment quality criteria. Through EF, anomalous metal concentrations can be identified using geochemical normalization of the heavy metal data to a conservative element, which is either Al or Fe [18]. In this study, the metal EF determined based on Fe was used as an index to evaluate the anthropogenic impact on the sediment quality. Mathematically, EF is expressed as follows [18]:

$$\mathrm{EF} = \frac{(\mathrm{Me}/\mathrm{Fe})_{\mathrm{sample}}}{(\mathrm{Me}/\mathrm{Fe})_{\mathrm{background}}} \tag{1}$$

where $(\mathrm{Me/Fe})_{\mathrm{sample}}$ is the metal to Fe ratio in the samples of interest; $(\mathrm{Me/Fe})_{\mathrm{background}}$ is the natural background value of the metal to Fe ratio in the earth's crust. The background values utilized were 56 300 mg/kg for Fe, 0.2 mg/kg for Cd, 100 mg/kg for Cr, 55 mg/kg for Cu, 950 mg/kg for Mn, 75 mg/kg for Ni, 12.5 mg/kg for Pb, and 70 mg/kg for Zn, respectively [30].

This approach has found wide application in observing trace metals in aquatic environments including rivers [31, 32]. Based on the assessment criterion by Zhang and Liu [31], EF values between 0.5 and 1.5 suggest that the trace metals may be entirely from crustal materials or natural weathering processes while EF values greater than 1.5 suggests that a significant portion of trace metal is delivered from non-crustal materials. On the other hand, Han et al. [32] divided the contamination into different categories based on EF values. EF ≤ 2 suggests deficiency to minimal metal enrichment and EF greater than 2 suggests various degrees of metal enrichment.

Another commonly used criterion to evaluate the heavy metal pollution in sediments is the geo-accumulation index (I_{geo}) originally introduced by Müller [33] in order to determine and to define metal contamination in sediments by comparing current concentrations with pre-industrial levels. The geo-accumulation index (I_{geo}) is defined by the following equation:

$$I_{\mathrm{geo}} = \frac{\log(2) C_{\mathrm{n}}}{1.5\, B_{\mathrm{n}}} \tag{2}$$

where C_n is the measured concentration of the examined metal (n) in the sediment and B_n is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithogenic effects. The background values of the metals of interest are the same as those used in the aforementioned EF calculation. Similar to the metal enrichment factor, the geo-accumulation index can be used as a reference to estimate the extent of metal pollution. Müller [33] has distinguished seven geo-accumulation index classes from class 0 ($I_{geo} \leq 0$) to class 6 ($I_{geo} > 5$). The highest class (class 6) reflects at least a 100-fold enrichment above the background values.

3 Results and discussion

Based on the average metal contents of the two seasonal observations, overall metal concentrations in the lower Seyhan River sediments were in the order of Al > Fe > Mn > Ni > Cr > Zn > Cu > Pb. Concentration of these metals in the river water was either very low or below the detection limit of 0.0005 mg/L with wet season having slightly higher metal concentrations. This may be due to higher temperature resulting in biological degradation of the organic matter in the surface sediments and release of the metals bound to organic matter. The metals in the lower Seyhan River water varied between 0.002 and 0.477 mg/L for Al, 0.0 and 0.064 mg/L for Cd, 0.001 and 0.004 mg/L for Cr, 0.001 and 0.074 mg/L for Cu, 0.0 and 0.006 mg/L for Fe, 0.001 and 0.009 mg/L for Mn, 0.0 and 0.002 mg/L for Ni, 0.001 and 0.152 mg/L for Pb, and 0.003 and 0.331 mg/L for Zn. The river serves as a water resource for irrigation during dry season and there is less water released from the Seyhan Dam resulting in lower water flow. Since there are no background levels of the metals of concern available for the Seyhan River sediments, it is impossible to cf. the change in the metal contents over a long time period. The water quality data were certainly important for the objectives of the study and especially to understand the origin of the metals in the sediments. The metal concentrations in the river water were very low, and therefore, it was understood that the metal content in the surface sediments were most probably originating from fine sediments transported along the river route instead of water/wastewater discharges with high metal content. From this point forward, the water quality data were not discussed further and the results and discussion based on sediment quality only were provided below. The Seyhan River sediment quality and metal contamination were further assessed based on the EF and geo-accumulation index (I_{geo}) as well as the SQG.

3.1 Cadmium

Cadmium concentration in the sediments was found to be at a non-detectable level at all sampling stations. It should be kept in mind that the analytical method used for Cd detection in the study had a lowest detection limit of 0.0005 mg/kg. Since there is no data available for the Cd content of the aquatic plants, we are unable to comment on whether there is a tendency of bio-accumulation of the heavy metal by the aquatic plants despite the fact that Cd is a non-essential element. However, some phytoplanktons and hydrophytes can store up to 2 mg/kg of Cd despite the reports for the toxicity of Cd on plants above 1 ppm [34].

3.2 Chromium

Chromium levels in the sediments varied from 56.77 to 95.17 mg/kg with a mean concentration of 81.03 mg/kg in wet season and 46.30 to 121.90 mg/kg with a mean concentration of 85.55 mg/kg in dry season (see Tab. 2). Despite the fact that there was a larger range of Cr content in the surface sediments during dry season, the overall average Cr levels were similar indicating little or no mobilization between seasons. Chromium is a specific pollutant indicating industrial pollution [7]. However, there are no chromium related industries located around the downstream Seyhan River such as metal processing, mining facilities, textile industry, petroleum refineries, tanneries, chemical industry, and all sorts of dyeing and paint facilities. On the other hand, this leaves the chromium mines around the source of the Seyhan River as a reasonable cause for the Cr in the surface sediments. It should also be kept in mind that the riverbed surface area gradually increases from S-1 until S-6 (from north to south) and there are relatively miniscule discharges from the drainage channels around the downstream of the Seyhan River and high flow discharges from the drainage channel of Tarsus irrigation district as shown in Fig. 1. When the present Cr concentrations were compared with the average Cr concentrations in uncontaminated soils with 1 to 2.5 mg Cr/kg content [2], the concentrations in the surface sediments of the Seyhan were highly contaminated.

Six heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) were classified in Tab. 3 and assessed based on the SQG [20], and the sediments at four out of six sampling stations can be classified as heavily polluted in terms of Cr concentrations ranging from 87.8 to 104.6 mg/kg while the remaining stations fall into the moderately polluted category with 62.2 and 63.3 mg Cr/kg.

The observed values in October 2009 and June 2010 indicated Cr EFs varying from 1.61 to 2.71 in the sampling sites with S-1 and S-2 showing relatively higher Cr enrichment factor of 2.54 and 2.71, respectively, with only S-4 and S-6 <2 (see Fig. 4). The average enrichment factor (wet and dry seasons combined) for Cr (2.19 ± 0.39) was found to be >2 suggesting that the contamination of this metal is present in the Seyhan River surface sediments (SRSS) due to anthropological reasons based on the assessment criteria of Han et al. [32]. Based on the criteria by Zhang and Liu [31], the metal enrichment >1.5 might be from non-crustal materials or in other words anthropological. In fact, moderate to significant enrichment of this metal was found in all sites (Fig. 3). It is difficult to correlate the contamination of Cr to local point or non-point sources, which could directly affect by the discharge of the Seyhan River.

As shown in Fig. 5, the results of the calculated I_{geo} values from this study ranged between -0.52 and -1.27 for Cr indicating insignificant Cr contamination in the SRSS according to the scale of Müller

Table 2. Statistical evaluation of total metal concentrations in the Seyhan River sediments

Parameter	Unit	Min	Mean	Max	Median	SD	CV
Wet season (October 2009)							
Al	mg/kg	7209.69	18 899.37	25 198.67	19 260.78	6427.56	0.34
Cr	mg/kg	56.77	81.03	95.17	84.09	13.29	0.16
Cu	mg/kg	6.12	27.90	57.22	26.10	16.76	0.60
Fe	mg/kg	14 148.47	19 745.48	26 555.84	19 090.70	4302.33	0.22
Mn	mg/kg	291.10	461.03	563.30	474.44	101.17	0.22
Ni	mg/kg	93.09	152.11	183.93	159.29	33.23	0.22
Pb	mg/kg	14.09	26.09	49.87	20.72	13.95	0.53
Zn	mg/kg	34.21	81.78	146.04	80.05	37.78	0.46
Dry season (June 2010)							
Al	mg/kg	16 061.08	25 154.17	33 966.92	25 455.98	5863.08	0.23
Cr	mg/kg	46.3	85.55	121.9	90.2	25.60	0.30
Cu	mg/kg	15.63	33.48	43.67	35.97	10.44	0.31
Fe	mg/kg	10 293.95	18 479.83	26 087.89	18 947.18	5283.00	0.29
Mn	mg/kg	143.92	449.82	638.32	492.19	169.35	0.38
Ni	mg/kg	82.21	147.83	214.90	158.47	46.85	0.32
Pb	mg/kg	11.34	33.70	74.72	24.81	24.80	0.74
Zn	mg/kg	36.95	80.46	121.10	84.27	28.27	0.35
Overall							
Al	mg/kg	7209.69	22 026.77	33 966.92	23 468.48	6713.72	0.30
Cr	mg/kg	46.28	83.29	121.93	86.68	19.59	0.24
Cu	mg/kg	6.12	30.69	57.22	29.37	13.63	0.44
Fe	mg/kg	10 293.95	19 112.65	26 555.84	19 090.70	4640.79	0.24
Mn	mg/kg	143.92	455.43	638.32	474.44	133.13	0.29
Ni	mg/kg	82.21	149.97	214.90	158.47	38.79	0.26
Pb	mg/kg	11.34	29.90	74.72	20.72	19.59	0.66
Zn	mg/kg	34.21	81.12	146.04	80.97	31.82	0.39

SD: Standard deviation
CV: Coefficient of variation.

Table 3. Spatial sediment quality evaluation of heavy metal concentrations in the Seyhan River (mg/kg dw)

Element	Stations						Sediment Quality Guidelines[a]		
	S-1	S-2	S-3	S-4	S-5	S-6	Non-polluted	Moderately polluted	Heavily polluted
Cd	Nd	Nd	Nd	Nd	Nd	Nd	–	–	>6
Cr	63.3	91.2	90.6	87.8	104.6	62.2	<25	25–75	>75
Cu	32.2	30.8	42.4	34.3	33.6	10.9	<25	25–50	>50
Ni	100.3	167.6	164.7	157.4	199.4	110.4	<20	20–50	>50
Pb	32.3	26.3	33.2	55.2	16.6	15.8	<40	40–60	>60
Zn	74.4	81.0	117.9	99.1	78.9	35.6	<90	90–200	>200

[a] Long et al., 1995 [20]

[19]. The spatial variations in Cr contamination in the SRSS can be attributed to hydrodynamic factors more than local point and non-point sources especially irrigational return. The average geo-accumulation index of Cr was -0.88 ± 0.28 suggesting that the SRSS have not been polluted overall by this metal in general. This constitutes a conflict to the assessment by the criteria of Zhang and Liu [31] and Han et al. [32].

3.3 Copper

Copper levels in the sediments varied from 6.12 to 57.22 mg/kg with a mean concentration of 27.90 mg/kg in wet season and 15.63 to 43.67 mg/kg with a mean concentration of 33.48 mg/kg in dry season (see Tab. 2). Unlike Cr, there is a shorter range of Cu content in the surface sediments during dry season and the average seasonal Cu levels demonstrate significant differences indicating some mobilization of Cu between seasons.

According to the SQG summarized in Tab. 3, the sediments at five out of six sampling stations can be classified as moderately polluted in terms of Cu concentrations ranging from 30.8 to 42.4 mg/kg (S-1 through S-5) while the remaining station (S-6) fall into the non-polluted category with 10.9 mg Cu/kg.

When both seasons were considered, the overall Cu data indicated an enrichment factor varying from 0.56 to 2.34 for the sampling sites

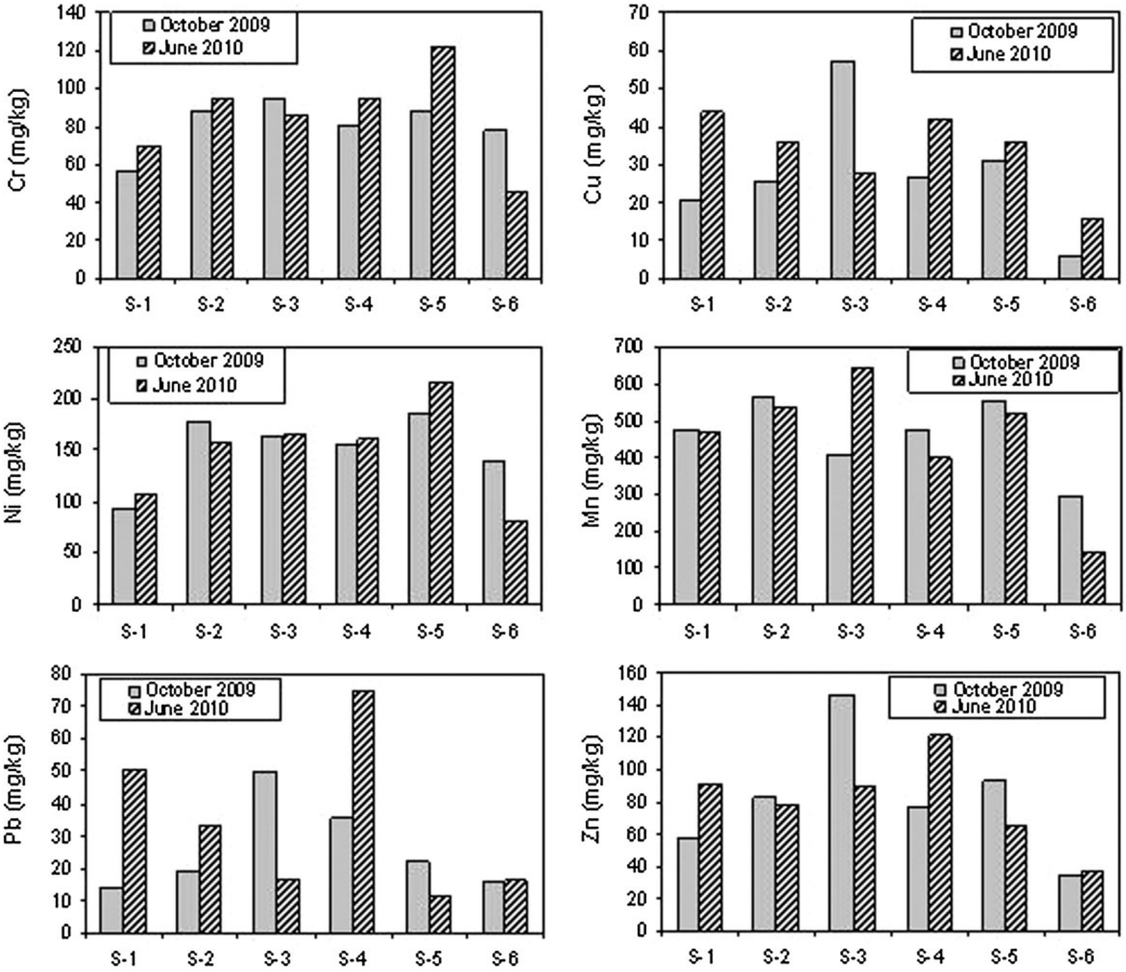

Figure 3. Spatial variation of metals along the lower Seyhan River.

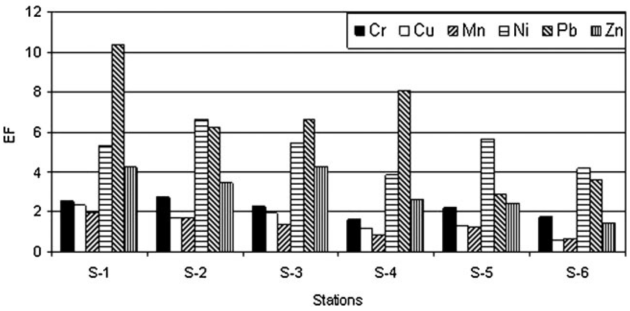

Figure 4. Variation of enrichment factor for metals between sampling stations.

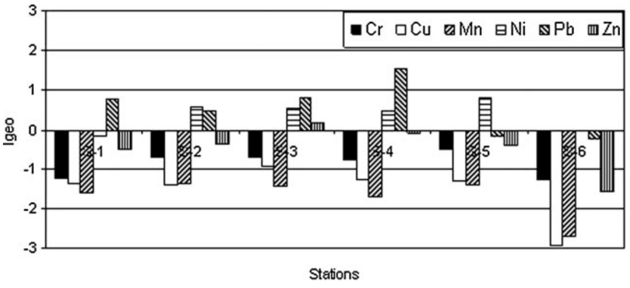

Figure 5. Variation of geo-accumulation index for metals between stations.

with S-1 and S-3 showing relatively higher Cu enrichment factors of 2.34 and 1.93 mg/kg, respectively, with only S-1 <2 mg Cu/kg level (see Fig. 4). The average Cu enrichment factor for both seasons combined was 1.49 ± 0.57 and generally <2 suggesting that the only crustal existence of this metal is present in the SRSS.

The calculated I_{geo} values for Cu, as shown in Fig. 5, varied between -0.52 and -1.27 for Cu with an average of -1.54 ± 0.64. Similar to the assessment of enrichment factor, these values suggest that the SRSS have not been polluted overall by this metal in general.

3.4 Nickel

Nickel levels in the sediments varied from 93.09 to 183.93 mg/kg with a mean concentration of 152.11 mg/kg in wet season and 82.21 to 214.90 mg/kg with a mean concentration of 147.83 mg/kg in dry season (see Tab. 2). Similar to Cr, there is a wider range of Ni content in the surface sediments during dry season as compared to the wet season and the average seasonal Ni levels do not demonstrate significant differences indicating deficiency of or no mobilization of Ni between seasons. According to the classification of heavy metals and the SQG summarized in Tab. 3, the sediments at all six sampling stations can be classified as heavily polluted in terms of Ni concentrations ranging from 100.3 to 199.4 mg/kg.

To further back this inference, the Seyhan River sediment quality and metal contamination were further assessed based on as the enrichment factor (EF) and geo-accumulation index as well as the sediment quality criteria. The observed values in October 2009 and June 2010 indicated an Ni enrichment factor varying from 3.86 to 6.64 in the sampling sites with S-2 showing the highest Ni enrichment with a factor of 6.64, with S-4 and S-6 at 3.86 and 4.16, respectively (see Figure 4). The average overall enrichment factor for Ni was 5.20 ± 0.94 and all stations ≫2 suggesting that high Ni contamination are present in the SRSS. In fact, a moderate to significant enrichment of this metal was found in all sites.

The I_{geo} values for Ni ranged between -0.17 and 0.83 for Ni indicating minimal pollution of Ni in the SRSS (Fig. 5). The average geo-accumulation index of Ni was 0.37 ± 0.35 suggesting that the SRSS have been slightly polluted by this metal in general. There is no direct evidence as to what the major cause of the high Ni content in the sediments. The spatial variations in Ni contamination in the SRSS might be caused by local point sources. However, there are neither nickel related industries located around the downstream Seyhan River nor nickel mines upstream of the Seyhan River as a reasonable cause. Furthermore, there is no nickel containing geological formation around the river.

3.5 Lead

Lead levels in the sediments varied from 14.09 to 49.87 mg/kg with a mean concentration of 26.09 mg/kg in wet season and 11.34 to 74.72 mg/kg with a mean concentration of 33.70 mg/kg in dry season (see Tab. 2). The range of Pb content in the surface sediments was wider during dry season and the average seasonal Pb concentrations demonstrate slight difference between seasons indicating some enrichment.

According to the SQG, the sediments at all sampling stations except S-4 can be classified as non-polluted in terms of Pb concentrations ranging from 15.8 to 33.2 mg/kg. The surface sediments from S-4, on the other hand, fall into the upper limit of the moderately polluted category.

Lead enrichment factor varied between 2.85 and 10.36 for the sampling stations with S-1 and S-4 providing the highest Pb concentration with 10.36 and 8.12, respectively, whereas S-5 and S-6 provided the lowest with 2.85 and 3.57, respectively (see Fig. 4). The average overall enrichment factor was 6.30 ± 2.56 with all stations >>2 suggesting high lead enrichment in the SRSS. In fact, significant Pb enrichment was found at all sites.

As shown in Fig. 5, the I_{geo} values for Pb ranged between -0.25 and 1.56 with an average geo-accumulation index of 0.54 ± 0.62. This suggests that the SRSS have been enriched by this metal at various degrees (mostly low) in general. The spatial variations in Pb contamination in the SRSS can be attributed to changes in the riverbed surface area as well as the river velocity and hence the mobilization and accumulation of the surface sediments around low flow areas.

3.6 Zinc

Zinc levels in the sediments varied from 34.21 to 146.04 mg/kg with a mean concentration of 81.78 mg/kg in wet season and 36.95 to 121.20 mg/kg with a mean concentration of 80.46 mg/kg in dry season (see Tab. 2). There is no significant difference in the Zn content between seasons unlike the other metals.

The sediments at all sampling stations except S-3 and S-4 can be classified as moderately polluted in terms of Zn concentrations with 117.9 and 99.1 mg/kg, respectively, according to the SQG as seen in Tab. 3. The surface sediments from other stations fall into the non-polluted category with most of them near the upper limit of the non-polluted category. Geo-accumulation index for Zn, as shown in Fig. 5, ranged between -1.56 and 0.17 with an average of -0.46 ± 0.54 indicating that there was insignificant Zn enrichment in the SRSS of the stations observed according to the categorization by Müller [19]. While the concentrations, SQG, and the geo-accumulation index point out that the SRSS have been polluted little or not by this metal in general, the enrichment factor indicates otherwise.

The enrichment factor (EF) for Zn in the surface sediments varied between 1.44 and 4.26 with S-1 and S-3 providing the highest Zn enrichment factor with 4.26 and 4.21, respectively, whereas S-6 provided the lowest with 1.44 (see Fig. 4). The average Zn enrichment factor for both seasons combined was 3.06 ± 1.01 and all stations but one >>2 suggesting that moderate to high Zn enrichment was present in the SRSS.

3.7 Correlation between concentrations of metals

To further examine the extent of metal contamination in the study area, Spearman correlation matrix was formed for the concentration of the metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn). The correlation matrices of the metals for wet and dry seasons were summarized in Tab. 4. A swift comparison between the matrices for the average metal content of October 2009 and June 2010 indicated that, for wet season, there were more correlation pairs among Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the Seyhan River sediments over 60% level than those for dry season. The correlation between the metals during the wet and dry season varied in a wide range and was 0.09−0.94 and 0.03−0.94, respectively. The only negative correlation was between Fe and Mn during wet season with −0.09, whereas, during dry season, multiple negative correlation was obtained between Al and Pb (−0.09), Cr and Pb (−0.03), Cu and Mn (−0.09), Fe and Pb (−0.14), Mn and Pb (−0.14), Ni and Pb (−0.26). While Fe and Mn provided weak correlations with the other metals during wet season between 0.09 and 0.49, Mn alone provided no strong correlation with the other metals with values between 0.09 and 0.49. Significantly high correlation was observed for Al—Zn, Cr—Zn, Cu—Pb, Cu—Zn with values between 0.89 and 0.94 for wet season. For dry season on the other hand, the highest correlation was observed for Al—Fe, Cr—Fe, C—Ni, Pb—Zn with a range of 0.83−0.94. Overall, 14 out of 28 possible metal pairs were correlated with each other showing a good positive association over 0.60 in wet season and 9 out of 28 metal pairs provided correlation values higher than 0.60 in dry season.

The combined correlation matrices for average values of the metals observed during wet and dry seasons again showed positive strong correlations with values above 0.77 and as high as 0.95, whereas the remaining demonstrated correlation mostly well below 0.49. Negative correlation was observed for Mn and Ni with Pb with −0.03 and −0.14, respectively. A highly significant correlation between these metals generally indicates their common origin. Better correlation of Cr and Ni with Fe (0.77 and 0.83, respectively), a majority of clay minerals, indicate a natural origin of the two metals. In contrast, a weak or lack of correlation with Fe, such as for Al, Cu, Mn, Pb, and Zn (0.49, 0.37, 0.43, 0.09, and 0.43, respectively), reflects an anthropogenic contribution due to urban development around the catchments of the lower Seyhan River.

3.8 Comparison with total metal contents in sediments of other rivers

The metal concentrations obtained in the study for the SRSS were further compared to those of other rivers around the world such as India, China, Hong Kong, Italy, Spain, Greece as well as average shell values.

Apart from Cd and Mn, the highest concentration level of all metals studied herein were mostly higher than the average shell values with Ni 3-fold, Pb 6-fold, and Zn 2-fold, approximately,

Table 4. Correlation analysis for metals in the Seyhan River sediments

	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Wet season (October 2009)								
Al	1							
Cr	**0.66**	1						
Cu	**0.77**	**0.77**	1					
Fe	0.09	0.09	0.20	1				
Mn	0.49	0.31	0.26	−0.09	1			
Ni	**0.77**	**0.77**	**0.66**	0.43	**0.66**	1		
Pb	0.43	**0.77**	**0.89**	0.31	0.09	0.54	1	
Zn	**0.89**	**0.89**	**0.94**	0.09	0.37	**0.77**	**0.77**	1
Dry season (June 2010)								
Al	1							
Cr	**0.71**	1						
Cu	0.54	0.37	1					
Fe	**0.83**	**0.94**	0.26	1				
Mn	0.37	0.31	−0.09	0.49	1			
Ni	0.49	**0.83**	0.14	**0.77**	**0.60**	1		
Pb	0.09	−0.03	**0.60**	−0.14	−0.14	−0.26	1	
Zn	0.03	0.20	**0.71**	0.03	0.09	0.14	**0.89**	1
Average								
Al	1							
Cr	**0.89**	1						
Cu	0.49	0.37	1					
Fe	0.49	**0.77**	0.37	1				
Mn	**0.83**	**0.89**	0.14	0.43	1			
Ni	**0.77**	**0.95**	0.26	**0.83**	**0.77**	1		
Pb	0.03	0.03	**0.77**	0.09	−0.03	−0.14	1	
Zn	0.43	0.49	**0.83**	0.43	0.37	0.43	**0.77**	1

The data are correlation coefficients with $p < 0.05$. The bold data represent a relatively better correlation.

Table 5. Comparison of total metal contents in river sediments around the world

Study on	Concentrations (mg/kg dw)						
	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Seyhan River, Turkey	ND	46.3–121.9	6.12–57.22	143.92–638.32	82.21–214.90	11.34–74.72	34.21–146.04
Gomti River, India [35]	0.34–8.38	2.22–19.13	1.38–35.03	82.57–263.1	6.53–29.76	6.27–75.33	3.06–101.73
Yangtze River, China [18]	0.12−0.75	–	6.87–49.7	413–1112	17.7–48.0	18.3–44.1	47.6–154
Danube River, Germany [36]	ND–25.6	34.9 ± 4.0	31.3–662.9	442–1379	24.6–142.8	14.7–107.6	83–622
Shing Mun River, Hong Kong [37]	22.0–47.0	17–66	207–1660	–	–	126–354	32–2200
Le An River, China [38]	5.31–9.39	–	124–2852	–	21.2–43.5	54.0–230.3	59.9–869
Po River, Italy [39]	0.203−1.448	148–414	44–102	713–1189	83–283	14.3–63.8	139–398
Louro River, Spain [40]	0.371−1.40	80.9–139	30.5–55.9	–	32.5–60.7	43.6–91.1	–
Axios River, Greece [41]	1–11	39–180	14–93	–	19–188	11–140	42–271
Hindon River, India [42]	1.3–3.28	43.0–249.6	35.6–194.7	61.3–201	–	5.17–59	4.11–84.7
Average shell values	0.2[a]	100[a]	55.0[a]	950[a]	75[a]	12.5[a]	70.0[a]

[a] Taylor, 1964 [30]

whereas maximum observed Ni (215 mg/kg) and Pb (75 mg/kg) were slightly higher than those of the earth's crust with 75 and 12.5 mg/kg, respectively. When the average metal concentrations were considered, these levels confirm the increase of concentrations of Ni, Pb, and Zn in the surface sediments of the SRSS. This may be due to anthropogenic activities around the lower Seyhan. The metal concentrations in the surface sediments of the river reported herein were then compared with those published by other researchers on some important rivers of the world (see Tab. 5). For this purpose, information on the Gomti River (India) [35], Yangtze River (China) [18], River Danube (Germany) [36], Shing Mun River (Hong Kong) [37], Le An River (China) [38], River Po (Italy) [39], Louro River (Spain) [40], Axios River (Greece) [41], and Hindon River (India) [42] was provided in the Table. The SRSS were among the least contaminated rivers based on Cu, Mn, Pb, and Zn compared to those in the Table. On the other hand, Cr and Ni contents of the Seyhan River were among the highest.

4 Conclusions

This study indicated that there was a considerable increase of some metals in the surface sediments of the lower Seyhan River. Based on the average seasonal (wet and dry) metal contents of the sediments, there is no significant difference in metal concentrations for the stations monitored between dry and wet seasons. However, the metal concentrations observed during wet season were slightly higher than those of dry season possibly due to temperature change and biodegradation of the organic matter in the sediments. When the spatial distributions of the heavy metal contents were considered, it was observed that the concentrations were higher at the more remote stations from the canal and the drainage discharges. When the metal contents only are of concern, the lower part of the river suspected to receive metals from most possibly anthropological sources. If mobilized and accumulated through the food chain, these metals in the surface sediments of the river may ultimately pose a threat to the biological diversity, valuable fish species, wildlife resources, and human beings. Therefore, intense monitoring of the discharges to the river – the drainage channels and the non-point sources from the agricultural land around the catchments of the river – should be planned and carried out. The data obtained in this study will constitute a background on the lower SRSS for future studies since there was no background information for the metals of concern. As a future study, the monitoring of the sediments and water quality should be continued, and hence, the change in the metal contents over a long time period can be observed and compared.

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