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Monitoring of Seasonal Variation of Heavy Metal Concentrations in Bed Sediments of Lower Seyhan River, Turkey

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In this study, variation of total heavy metal concentrations in the bed sediments against the flow rate of the lower Seyhan river has been evaluated. Sediment samples were collected at 6 representative sampling stations along the lower Seyhan river, Turkey under low and high flow conditions during four seasons. Concentrations of Cd, Cu, Fe, Mn, Ni, Pb and Zn decreased by increasing river flow rate. Sediment quality assessment according to the "U.S.EPA Sediment Quality Guidelines (SQG)" revealed that there was heavy metal pollution with respect to especially Ni, Cd and Zn. However, mean Cu and Pb levels in the river indicated that the river was non-contaminated. There were several mechanisms suggested for heavy metal distribution in the river such as immobilization by sedimentation, remobilization by pH decrease due to microbial degradation of organic matter and resuspension due to increased river flow rate.

Key Words: Trace metals, Seasonal distribution, Sediment quality, Immobilization.

INTRODUCTION

The distribution and bioavailability of heavy metals in the aquatic environment have become a significant research topic due to their toxicity. There are already numerous studies on the distribution and variation of heavy metals in the aquatic environment especially the rivers as a major means of transportation of materials such as soluble, suspended and residual matter.

Heavy metals are essential trace elements for the organisms. However, these elements such as iron, manganese, zinc, lead, copper and nickel pose toxic effects when accumulated at high concentrations in the living cells[1,2]. When establishing and observing the environmental regulations and legislation, the bioavailability, bioaccumulation and persistence to biological activities of the heavy metals are to be significantly considered[3-5]. Therefore, heavy metals fall into the priority pollutants list of water quality classifications for a large number of developed countries[6].

Heavy metals can enter river systems through natural sources (erosion, forest fires and volcanic eruptions) and anthropogenic activities such as discharge of wastewaters with heavy metals content, which can be generated through industrial and agricultural activities and domestic use. However, agricultural activities come up as a major source for heavy metal pollution in rivers. Heavy metals contained in fertilizers and pesticides enter water bodies through settling of airborne soil particles after agricultural cultivation and drainage waters[7-10].

Heavy metals follow different pathways based on the conditions of the aquatic environment and can be distributed as water-soluble species, colloids, suspended matter and sediments[11]. Sediments have high affinity to store heavy metals as well as many other pollutants and may contain heavy metals at higher concentrations compared to those of water bodies[12]. As a fact, heavy metals stabilized within the contents and structure of the sediments are no longer a significant threat to water organisms[13-16]. On the other hand, sediments can act as a carrier for heavy metals when these sediments are resuspended in water bodies through changes in the hydrological conditions of the rivers, anthropogenic activities on river beds and biological activities such as bioturbation and bioirrigation[17]. Moreover, changes in the environmental conditions of the rivers affect the sediment chemistry (pH, redox potential) and contents resulting in the release of metals bound in different forms in the sediment[18-20]. Thus, heavy metals accumulated within the sediments over a long period of time are carried over to the overlying water column and act as a secondary pollution source while increasing the bioavailability[21,22].

The concentration of heavy metals in the sediments is a significant environmental quality criterion that illuminates the past pollution levels of importance. The environmental regulations limiting the heavy metals concentration in water bodies are only limited to short-term infringement while sediment quality provides vital long-term information about heavy metal contamination in rivers. Therefore some countries have accepted guideline values for sediment quality assessment[23]. There are many discussions and conflicts present on whether the guideline values for heavy metals obtained through sediment quality assessments using various methodologies can be universal. However, for every water body, environmental assessment can be done by comparing the sediment concentrations of heavy metals with the guideline values[24,25].

Seyhan river, as a research focus, flows through lower Seyhan plain with a catchment area of 20,731 km^2 and dense agricultural activities and population with a great economic contribution with 15 % of the industrial and 35 % of the agricultural activities in Turkey. In the literature, despite the several studies on the effect of agricultural activities on Seyhan river water quality, there are no studies reported on the heavy metal content and distribution in the sediments. Nevertheless, high metal concentrations were observed in the sediments of a drainage channel in the region (merges with the main collector drainage channel and then the river) to where some industrial facilities discharge their wastewaters[26]. In this study, the extent of heavy metal contamination in the sediments of Seyhan river was determined. The impact of seasonal flow variations of the river on the sediment quality was also evaluated based on total heavy metals content.

EXPERIMENTAL

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 treat their wastewaters, small industries are suspected to discharge their wastewaters directly into the river without any treatment. Seyhan river divides Cukurova plain into two parts, which are Tarsus and Yüregir plains. Lower Seyhan river refers to the part of the river system (about 94 km in length) after Seyhan dam and flows through the city of Adana (with about 1,300,000 inhabitants) and merges with Mediterranean sea. There are subsequent dams on Seyhan river built for the purposes of irrigation and hydroelectric 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 average temperature is 18 °C with a mean annual rainfall of about 110.2 mm. The soil type of the basin is alluvion consisting of clay, silt, fine-to-coarse sand and pebbles.

TABLE-1
SUMMARIZED CHARACTERISTICS FOR EACH SAMPLING STATION

Sampling stations	Location (km)	Characteristics of the sampling stations
SS1	0	Downstream of regulator bridge and initial point of study
SS2	18	Easy to reach and near a citrus farm to characterize agricultural non-point discharges to the river
SS3	33	Change in hydraulic conditions depending on river expansion and meandering and hauling of river sand as construction material
SS4	41	Away from settlements, high underground water level, intense farming
SS5	54	Near largest settlement, Tabaklar village, around the river
SS6	63	After TD0 discharge point and end of river

Major land use in the region is agriculture, generally irrigated by the river water in the network of artificial irrigation channels. Crops such as cereals, fruits (especially citrus), cotton and peanut are grown in the river-shed area where the use of fertilizers is common practice. Most of the area is drained through an extensive network of drainage channels called Tarsus Drainage Channels and the drainage water collected in the main collector is discharged into the river about 3 km before flowing into Mediterranean sea.

The sampling stations, except first and final stations, were selected in order to take into account the effects of point and non-point pollution sources discharging to the river. The characteristics of each sampling stations is summarized in Table-1. Furthermore, the sampling stations (SS) were chosen at strategic zones where the hydraulic conditions of the river changed dramatically. SS-1 was at the beginning point of the study area located in the downstream of Seyhan river after the second regulator bridge. SS-2 was located at a citrus garden to assist present the effects of agricultural drainage waters received by the river. SS-3 was located at the meandering point of the river which caused changes in the hydraulic conditions. The area around this station was also used illegally as sand supply for building materials and led to change the composition of the bed sediments. SS-4 was located at a point due to similar reasons for SS-2. SS-5 was located at the village of Tabaklar, which is located next to the river. The final station, SS-6, was located in the downstream of the main agricultural drainage collector channel inlet (TD0), which carries the domestic wastewaters of settlements surrounding the channel and the effluents of miscellaneous industries located in the lower Seyhan basin.

The bed sediment samples were collected using an Ekman™ Grab Sampler from six sampling stations mentioned above at lower Seyhan river in four separate seasons. The sampler takes samples at the top portion of the river bed up to 2-5 cm depending on the sediment size and river bed morphology. The samples were arbitrarily collected from 3 different points at each sampling station to obtain a composite sediment sample and the sediment samples were stored in clean polyethylene bottles, which were prewashed with 10 % nitric acid and kept at 4 ºC prior the sampling[27].

Method 3050B (Hot plate digestion technique) and Method 6010B (inductively coupled plasma, atomic emission spectrometry, ICP/AES) by US EPA[28,29] were used, respectively, to digest and analyze cadmium, copper, iron, manganese, nickel, lead and zinc concentrations. The analyses of heavy metals were carried out using Perkin-Elmer™ OES 3100 ICP instrument.

RESULTS AND DISCUSSION

The results of heavy metals analyses of the sediment samples were summarized in Table-2. The results indicate that the change in Cd, Cu and Pb concentrations between sampling stations was negligible. The heavy metals concentrations for SS-1 downstream to the regulator bridge were the lowest compared to those of the other sampling points. This may be due to that the river bed is composed of coarse materials and the water released from the regulator bridge flushes away the materials in the river bed since river beds with finer sediments have higher affinity to absorb heavy metals due to their large surface areas[30].

TABLE-2
AVERAGE HEAVY METALS CONCENTRATIONS MEASURED IN THE SEDIMENT OF THE STATIONS

Sampling Stations	Concentrations (mg/kg dry weight)*			
	Cd	Cu	Fe[a]	Mn
SS1	4.85 ± 1.63	11.63 ± 4.82	14.0 ± 2.73	507.3 ± 122.0
SS2	7.33 ± 1.88	11.14 ± 3.88	18.9 ± 3.76	722.0 ± 100.4
SS3	6.31 ± 1.32	19.35 ± 9.85	22.5 ± 8.13	887.5 ± 227.3
SS4	6.68 ± 1.10	11.51 ± 5.77	30.6 ± 3.80	740.5 ± 231.4
SS5	7.28 ± 2.42	12.92 ± 8.26	26.2 ± 5.08	737.0 ± 246.9
SS6	4.97 ± 1.86	19.64 ± 10.64	19.9 ± 3.14	483.0 ± 107.5
	Ni	Pb	Zn	
SS1	167 ± 18.3	3.11 ± 1.58	194.7 ± 193.6	
SS2	193 ± 46.5	5.65 ± 3.89	366.3 ± 244.0	
SS3	220 ± 51.7	10.58 ± 4.86	324.6 ± 215.1	
SS4	267 ± 51.7	8.86 ± 4.18	520.7 ± 459.2	
SS5	243 ± 49.2	4.74 ± 3.77	334.7 ± 193.6	
SS6	223 ± 52.3	2.88 ± 1.27	346.0 ± 306.4	

[a] $\times 10^3$; *Statistical mean ± standard deviation

At SS-2, the concentrations of heavy metals except Cu were observed to increase. The sediment samples from this station are dark-coloured and heavily-odoured especially during seasons when the river flow is low. These characteristics indicate the existence of intense organic materials and anoxic conditions. The increase in the metal concentrations can be explained as Lin and Gen[31] described in their study with a positive correlation between the organic content of the river sediments and heavy metal concentrations. Slight decrease of pH by microbial degradation of organic matters, however, results in metal mobilization bound to Fe and Mn oxides as indicated by Bourg[32].

At SS-3, heavy metals concentrations increased. The river meanders and expands especially around this sampling station. The decrease in river water at this point results in the accumulation of suspended materials and thus heavy metals to be absorbed within the sediment around this sampling station[33]. At SS-4, most of the heavy metals reached their peak concentrations. The level of groundwater was observed high and there were water pools around the river bank where other pollutants were accumulated. These water pools are in interaction with the river proportional to water elevation levels and thus the river flow rate.

The heavy metal content of the river sediments from SS-5 did not differ significantly from those of SS-4. SS-6 was the final sampling point after which the river flowed into the sea. At this point, all metal concentrations except for Cu decreased possibly due to dilutions with advancing seawater at this station. On the other hand, Turner and Millward[34] concluded from their study that the heavy metal concentrations decreased in the sediments of a mixing zone where the river water and seawater mixed. This resulted in the introduction of chloride ions readily found in seawater and, as Bourg[32] and Hatje *et al.*[35] pointed out. Chloride ions efficiently forms inorganic complexes through solubilizing heavy metals especially at Cl^- concentrations typically greater than 0.01 M. However, the level of heavy metal solubilization depends on metal speciation.

The flow rate of Seyhan river changed between 25 and 250 m^3/s as a consequence of sequential constructed dams. The flow rate of the river decreased dramatically especially during the summer months when some of the river flow was diverted to the irrigation channels. In these months, heavy metal concentrations measured in the sediments were observed to reach maximal concentration levels. During the study period, it was observed that the heavy metals concentrations decreased in the sediments with increased river flow as shown in Fig. 1. The drastic change in the river flow, as observed, resulted in the deterioration of the sediments followed by their resuspension and oxidation. This change consequently impacted the behaviour of the heavy metals bound as various components in the sediments. The aeration of resuspended anoxic sediments depending on the river flow rate causes the microbial activity to increase and thus the pH to decrease. Low pH levels promote the release of the metals from the sedimental components they are bound[14,36]. The chemical changes in the sediment-metal complexes result in the heavy metals to mobilize as sulphide-bound complexes (FeS/MnS) and transport within the river[21]. It can be deducted that the concentrations of Fe and Mn within the sediment complex are high enough to cause remobilization of the heavy metals in the resuspended sediments.

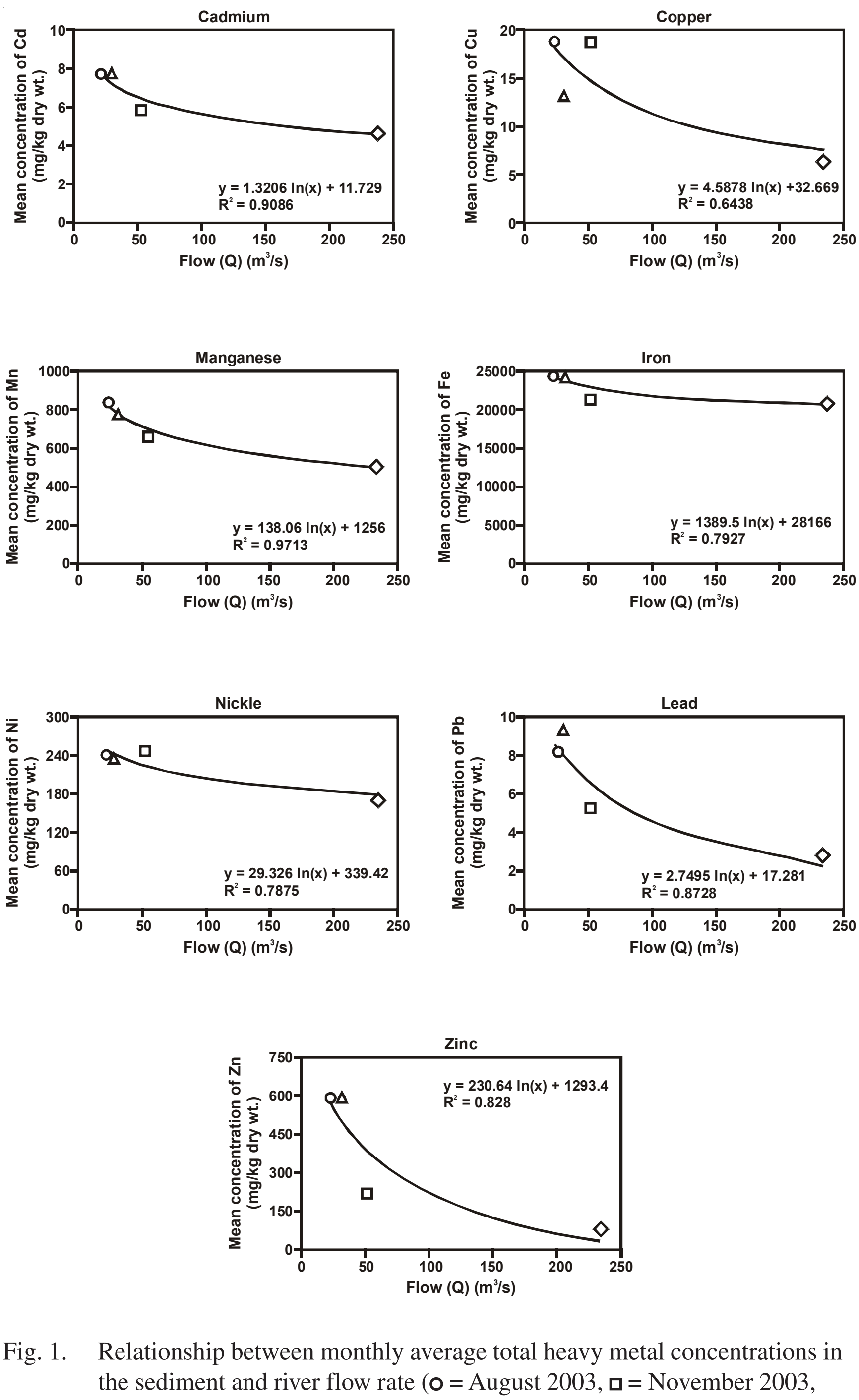

Fig. 1. Relationship between monthly average total heavy metal concentrations in the sediment and river flow rate (○ = August 2003, □ = November 2003, ◇ = October 2004, △ = May 2004)

TABLE-3
SEDIMENT QUALITY ASSESSMENT BY NOAA

Elements	ER-L (mg/kg dry wt.)	ER-M (mg/kg dry wt.)	Mean values of measured metal concentrations along the river (mg/kg dry wt.)	Sediment Characterization
Cd	1.2	9.6	6.36	Contaminated
Cu	34.0	270.0	14.24	Not contaminated
Fe	–	–	22507.00	Not available
Mn	–	–	696.30	Not available
Ni	20.9	51.6	221.00	Heavily contaminated
Pb	46.7	218.0	6.10	Not contaminated
Zn	150.0	410.0	354.00	Contaminated

In order to determine the relationship between the flow rate and the levels of sedimental heavy metals, Jain and Sharma[37] conducted a study on Hindon river and reported decreasing heavy metal levels as a result of increasing river flow attributed to monsoon precipitation. Similarly, a study by Davide *et al.*[38] carried out on river Po indicated that the concentrations of heavy metals and nutrients decreased with the flushing effect of the river under high flow conditions.

There are several sediment quality guidelines (SQG) used in the effects of pollutants in aquatic ecosystems. However, assessment methods such as laboratory toxicity assays, bioaccumulation studies may be inadequate to fully reflect and characterize the study area and the effects of heavy metals. Therefore, SQG values should be used as a proof of observation or the quantity of toxic materials[39].

In this study, the sediment quality assessment for heavy metals was done using "Effect Range-Low" (ERL) and "Effect Range-Medium" (ER-M) values suggested by National Oceanic and Atmospheric Administration (NOAA). If the heavy metals are over ER-L values but lower than ER-M, then it means that the heavy metal pollution has reached a state of concern and that the pollution is classified as medium-contamination level. If the concentrations of heavy metals are above ER-M values, then it is categorized as heavily contaminated level[40].

The river sediments are included in the heavily contaminated level based on Ni. Similar levels were reported by Zaimoglu *et al.*[26]. This suggests that the high Ni concentrations in the river are caused by the geo-morphological characteristics of the basin. Based on mean Cd and Zn concentrations measured along the river, the river sediments fall into the contaminated category. However, these values represent total heavy metal concentrations and therefore further experimental studies such as sequential extraction procedure should be applied to find out the metal fractions and infer on the mobility and toxicity of the heavy metals content within the sediments.

Conclusion

This study may further lead to other studies about heavy metal pollution in the sediments of Seyhan River used for water supply, hydroelectricity production and agricultural irrigation purposes. The heavy metal content of the sediments is affected by environmental factors that may lead to heavy metal mobilization expressed by many researchers such as change in the hydrological conditions of the river, organic matter content, pH and redox potential. Further studies are also needed (1) to identify heavy metals sources by enrichment factor (EF), (2) to determine the distribution coefficient (K_D) to evaluate the solid/solutions relationship and (3) to obtain the metal specification by sequential digestion technique to evaluate toxicity.

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