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Variation of Lead, Cadmium, Copper, and Zinc in Aquatic Macrophytes from the Seyhan River, Adana, Turkey

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The Seyhan River is situated in the Cukurova region which is a Turkish river flowing south southwest into the Mediterranean (Figure 1). It runs from Central Anatolia to the Mediterranean Sea. The Seyhan River is an important water supply for agricultural lands of Cukurova. The region comprises an area that is rapidly expanding in population, agriculture and industry. It has a subtropical climate and receives rainfall mainly during autumn and winter months. The Seyhan River recieves large quantites of untreated industrial, chemical pollutants and domestic sewage due to heavy agricultural and industrial activities (Kargin, 1998).

Metals are naturally occurring in the nature. In receiving water bodies, metals can originate both from natural and anthropogenic sources (Novotny, 1995). Zn, Cu, Pb and Cd are common pollutants, which are widely distributed in aquatic environments. Their sources are mainly from weathering of minerals and soils (Merian, 1991); atmospheric deposition (Merian, 1991); industrial effluents (Prater, 1975) and domestic effluents (Dean et al., 1972). Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous and are included on the US Environmental Protection Agency's (EPA) list of priority pollutants (Cameron, 1992).

Aquatic macrophytes are known to have great importance, forming a substantial component of the primary production in many aquatic habitats (Pip, 1990). Vascular aquatic macrophytes may accumulate considerable amounts of heavy metals in their tissues (Kovacks et al., 1984). In the recent past, several of the submerged, emergent and free-floating aquatic macrophytes are reported to bioconcentrate heavy metals in natural waters as well as after exposure to wastewaters (Greger, 1999). Some aquatic or semi aquatic plants such as *Eichornia crassipes* (Dierberg et al., 1987), *Lemna minor* (Mo et al., 1989), *Spirogyra fluviatilis* (Saygideger, 1998), *Veronica anagallis-aquatica* and *Ranunculus aquatilis* (Saygideger, 2000) can take up heavy metals from contaminated solutions.

This study was undertaken to investigate the current heavy metal levels in sediment and macrophytes from the Seyhan River.

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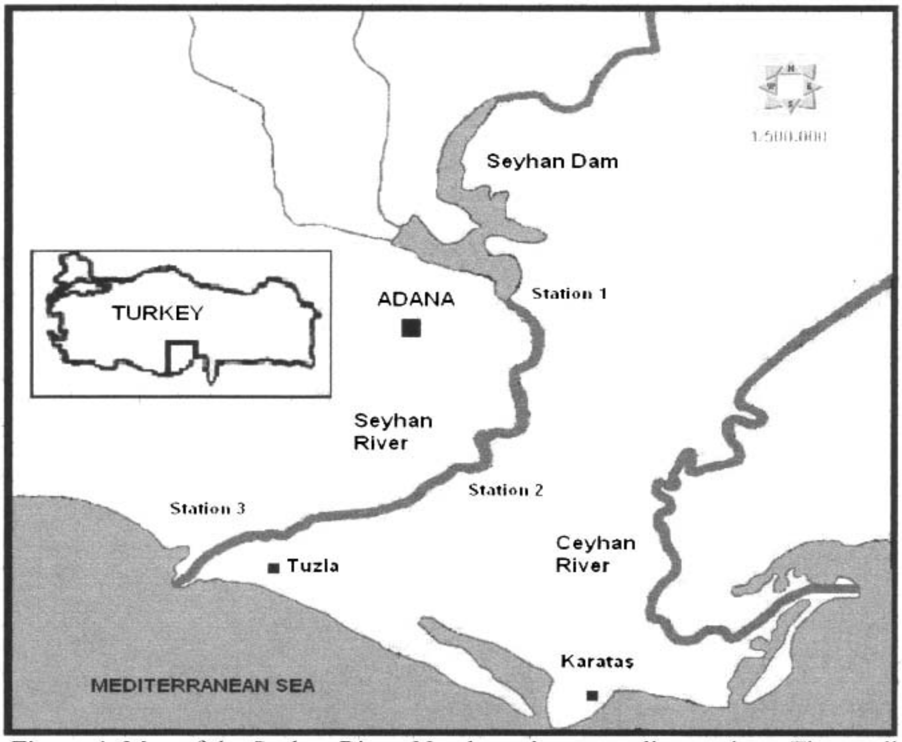

Figure 1. Map of the Seyhan River. Numbers show sampling stations. The small map shows Turkey and the study area.

MATERIALS AND METHODS

Three sampling sites were selected as illustrated in Figure 1. Pertinent details of three sampling sites are as follows: Station 1 (The exit of Seyhan Dam) where there are no agricultural or industrial activites, but has light traffic. Station 2 which is in an agricultural area also featuring intensive industrial establishments. Station 3 near the Mediterranean. Near this station agricultultural activites are widespread and pollution is at maximum levels.

At each site sediment samples and aquatic macrophytes were collected in triplicate in May 2002 and transported daily to laboratuary in clean plastic bags. Bottom sediments were sampled at an average depth of 10 cm. Sediment samples were stored in acid cleaned (3 M HNO_3) dark plastic bottles at 4 °C refrigerator until analysis. Water pH was immeditealy measured at the places where samples were collected (HANNA HI 9025).

Emergent macrophytes *Typha latifolia* and *Phragmites australis* and submerged macrophytes *Potamogeton crispus*, *Potamogeton pectinatus* and *Myriophyllum spicatum* were carefully washed using freshwater followed by deionised water for the quantitative removal of soil and other foreign objects. They were dried to constant weight at 70 °C in electric furnace, and pulverized. 0.5-1.0 G. of dried samples were mineralized in 14 M HNO_3 (Merck) and, residues desolved in 1 M HCl (Merck) (Saygideger, 1998). The sediment samples were then dried at 80 °C in an electric furnace and homogenised. The total concentrations Pb, Cd, Cu and Zn in the sediment samples were determined by digestion with a mixture of concentrated HNO_3:HCl (1:1) for 90 min at 90 °C (Mudroch and Capobianco, 1979). The metals in both samples were determined by atomic absorption spectrophotometer using air-acetylene flame (HITACHI 180-80 Polarized Zeeman Spectrophotometer). Measurements of Pb, Cd, Cu and Zn were carried out at wavelengths 283.3, 228.8, 324.8 and 213.9 nm, respectively. All analyses were done in duplicate. All results for macrophytes and sediments were calculated on dry weight basis.

Differences between mean concentrations of heavy metals in macrophytes and sediments samples were evaluated with a multiple range test (LSD; Least Significant Difference). All statistical calculations were carried out using SPSS 11.0 package programme.

RESULTS AND DISCUSSION

The pH ranges of water in examined sites during sampling periods in station 1, station 2 and station 3 were measured as 6.98–7.23, 7.41-7.65 and 7.89-8.11, respectively. According to these, pH levels of the river water were changed from station to station and were near neutral or slightly alkaline.

Heavy metal concentrations in sediments investigated in station 1 (unpolluted site) were lower than other two sampling stations (Table 1). The least contaminated part of the river system was found to be the exit of Seyhan Dam (station 1), which does not receive significant levels of effluents from industrial, agricultural and domestic sources in Adana when compared to the other stations. Among the three stations investigated, station 3 was the most heavy metal contaminated area. Heavy metal concentrations in station 2 and 3 sediments were significantly high with respect to station 1 ($P<0.01$). The maximum concentrations of Pb, Cd, Cu and Zn in the sediments were determined as 13.4, 0.80, 36.1 and 408.0 $\mu g\ g^{-1}$, respectively.

Heavy metal concentrations of the macrophytes collected from different stations of the Seyhan River are given in Table 2. Heavy metal concentrations in the macrophytes tended to vary significantly among stations. Among the four heavy metals analysed, Zn was the most abundant metal in all the macrophytes studied. The minimum metal concentrations were determined in the station 1. In all collected macrophytes Pb, Cd, Cu and Zn concentrations were higher in station 2 and 3 than in station 1 ($P<0.01$). The heavy metal concentrations of aquatic macrophytes obtained from literature, normal composition of these elements in a plant and results of present study are given in Table 3. Comparison of concentrations of the heavy metals in the examinated aquatic macrophytes with

Table 1. Heavy metal concentrations in sediments ($\mu g\ g^{-1}$ d.w.) at different stations from Seyhan River in May 2002.

Material	Station	Metal ($\mu g\ g^{-1}$ d.w.)			
		Pb	Cd	Cu	Zn
Sediment	1	0.13±0.04 a	0.05±0.03 a	2.6±0.7 a	35.5±7.3 a
	2	4.6±1.2 b	0.53±0.08 bc	21.0±6.3 bc	288.9±76.9 bc
	3	13.4±3.6 c	0.80±0.16 c	36.1±6.6 c	408.0±57.8 c

Values expressed as mean ± standard deviation. Means with different letters are significantly different one another according to LSD test (P<0.01).

Table 2. Heavy metal concentrations of aquatic macrophytes at different stations from Seyhan River in May 2002.

Macropyhte	Stat.	Metal ($\mu g\ g^{-1}$ d.w.)			
		Pb	Cd	Cu	Zn
T. latifolia	1	2.4±1.1 a	0.07±0.03 a	2.4±1.8 a	38.1±12.4 a
	2	4.7±2.2 ab	0.32±0.07 ab	16.3±4.2 ab	157.8±42.8 bc
	3	9.3±2.5 b	0.71±0.31 b	23.6±8.1 b	198.1±25.7 c
P. australis	1	1.8±0.8 a	0.03±0.01 a	3.9±1.2 a	51.2±.9.7 a
	2	6.1±1.8 b	0.19±0.04 b	15.8±3.8 b	160.2±31.6 b
P. crispus	1	3.5±1.6 a	0.12±0.04 a	4.7±2.1 a	168.7±21.6 a
	2	4.3±1.9 a	0.31±0.13 a	14.3±5.1 a	391.3±66.8 b
P. pectinatus	1	5.7±2.6 a	0.11±0.07 a	7.3±3.4 a	125.1±38.3 a
	3	16.8±6.3 a	0.76±0.23 b	19.7±5.3 b	423.0±75.3 b
M. spicatum	1	5.3±2.1 a	0.18±0.06 a	9.6±3.7 a	175.0±18.6 a
	2	18.9±6.4 ab	0.58±0.21 a	25.7±6.3 ab	452.3±63.1 ab
	3	33.5±10.1 b	1.64±0.56 b	28.7±6.7 a	526.4±164.3 b

Values expressed as mean ± standard deviation. Means with different letters are significantly different one another according to LSD test (P<0.01).

mean values established for background concentrations in plants showed that Pb, Cd, Cu and Zn concentrations higher than background values (according to Markert, 1994) in stations 2 and 3. The ranges of mean metal concentrations ($\mu g\ g^{-1}$ d.w.) in the macrophytes tissues were as follows: the range of Pb concentration was 1.8-33.5, that of Cd was 0.03-1.64, that of Cu was 2.4-28.7 and that of Zn was 38.1-526.4. According to the literature, an increase in the concentration of metals is observed in the tissues of macrophytes growing in polluted areas. This is also confirmed by the results of our study.

As the accumulation of trace metals in organisms depends upon the concentration of pollutants in water as well as the length of time the organisms have been exposed, the tissue analysis of aquatic macrophytes may provide a cumulative evaluation of exposure (Wells et al., 1980; Oertel, 1991). Submerged species accumulate relatively high heavy metal concentrations when compared with emergent species in the same area as reported by Yurukova and Kochev (1994)

Table 3. Pb, Cd, Cu and Zn concentrations of aquatic macrophytes obtained from literature (1-7), normal composition of these element in a plant (8) and results of present study (*).

	Metal (µg g^{-1} d.w.)			
Literature	**Pb**	**Cd**	**Cu**	**Zn**
1	2-33	0.2-3.4	5-37	12-92
2	0.1-0.9	1	5-20	15-180
3	1.0- 18.9	0.3-5.4	3.6-21.5	10.2-145.0
4	1.2-9.8	<0.002-5.2	1.9-29.1	25.2-814
5	31.7-60.2	0.0-2.5	1.0-5.3	18.0-132.0
6	0.2-431.5	0.00-16.1	4.0-431.0	13.0-4296.1
7	12.3-99.2	0.2-5.1	3-37	24-770
8	1.0	0.05	10	50
*	1.8-33.5	0.03-1.64	2.4-28.7	38.1-526.4

1, Mudroch and Capobianco 1979; 2, Kabata-Pendias and Pendias 1993; 3, Sawidis et al. 1995; 4, Samecka-Cymerman and Kempers 1996; 5, Stankovic et al. 2000; 6, Cardwell et al. 2002; 7, Samecka-Cymerman and Kempers 2003; 8, Markert, 1994; *, results of present study.

and Rai et al. (1995). In the present investigation, the considerable differences in heavy metal concentrations among the macrophytes were determined according to ecological needs. High heavy metal concentrations in tissues of the submerged macrophytes *P. crispus*, *P. pectinatus* and *M. spicatum* highlighted their ability to take up and accumulate high concentrations of metals compared with emergent macrophytes *T. latifolia* and *P. australis*. According to research of Greger and Kautsky (1993) *M. spicatum* accumulated much higher amounts of Pb, Cd and Zn in its tissues than other submerged macrophytes (*P. perfoliatus* and *P. pectinatus*). This was also confirmed by our results.

Rapid urbanization, industrialization and pesticide usage in our region have resulted in heavy metal pollution of the Seyhan River. The heavy metal concentrations in the sediments and macrophytes investigated were high in polluted stations. The macrophytes analyzed also reflected the heavy metal pollution status of their growing environment.

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