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TRACE METAL LEVELS IN SURFICIAL SEDIMENTS OF LAKE MANYAS, TURKEY AND ITS TRIBUTARY RIVERS

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ABSTRACT

Some trace element contents of surficial sediment samples from sampling stations in Lake Manyas (Bird Lake) in Turkey and its tributary rivers have been analyzed by flame atomic absorption spectroscopy. The mean levels ($\mu g g^{-1}$ dry weight) of Mn, Fe, Cu, Pb, Ni, and Zn for five sampling stations in the first season (March 1996) and for eight sampling stations in the second season (May 1996) have been listed. The results have been compared with the values given in the literature. A comparison with the available benchmark sediment quality criteria and toxicity guideline values has also been made. The results in the light of those comparisons suggest that a pollution problem especially with respect to Cu, Pb, Zn and Ni exists at several stations which are effected by municipal and industrial effluents and at the middle of the lake.

1. INTRODUCTION

Currently, environmental pollution as a result of urbanization and industrial development is a major concern. In this respect the amount and speciation of trace metals in natural water systems which may signal pollution has gained further importance. It has been established that heavy metals such as cadmium, mercury and lead are biologically non-essential and demonstrably toxic even at relatively low concentrations and some elements i.e. iron, iodine, copper, manganese, zinc, cobalt, molybdenum, selenium, chromium, tin, vanadium, fluorine, silicon and nickel are essential for normal body function. Even then, such an element may be highly toxic when present at higher concentrations since for all the trace elements that are considered to be essential there exists a fairly narrow "concentration window" between the essential and toxic levels.[1] Perhaps one of the most distinguishing features of metals from other toxic pollutants is that they are not biodegradable. Many metals added to a body of natural water are eventually incorporated into the sediment and accumulate to high levels in bottom sediments. Furthermore the sediment bound metals are later released to the water column when the physico chemical conditions become favorable for such remobilization. It has been stated that specific local sources such as discharges from smelters (Cu, Pb, Ni), metal based industries (e.g. Zn, Cr and Cd from electroplating) paint and dye formulators (Cd, Cr, Cu, Pb, Hg, Se and Zn) petroleum refineries (As, Pb) as well as effluents from Chemical Manufacturing Plants may lead to metal accumulation in sediments.[2] The amounts of trace metals in the sediments of the aquatic system vary depending upon the source, the season and the industrial processes carried out in the vicinity.

The area of Manyas Lake (Bird Lake) in Turkey is known as the Bird Paradise and is one of the most important hosting areas for the migrant birds where they can feed themselves and shelter and hatch out their chicks on their journeys between the continents of Europe and Africa. Fishing is also largely practised in this area. So far, to the authors' knowledge the amounts of trace metals in the sediments of this lake have not been determined. In this study the amounts of Mn, Fe, Cu, Pb, Ni, Zn, in the sediments of Lake Manyas, and their seasonal and locational variations have been determined. The purpose of this study has not only been to investigate the present implications of those results but also to establish background data for much needed future monitoring of this area for any anthropogenic activity.

2. EXPERIMENTAL

2.1. Description of the study site

The Manyas Lake (Bird Lake) (Fig. 1) is one of the most profitable lakes of Anatolia which is situated in the Southern Marmara Zone at a distance of 22 km. from the Marmara Sea and 18 km. from the Bandırma

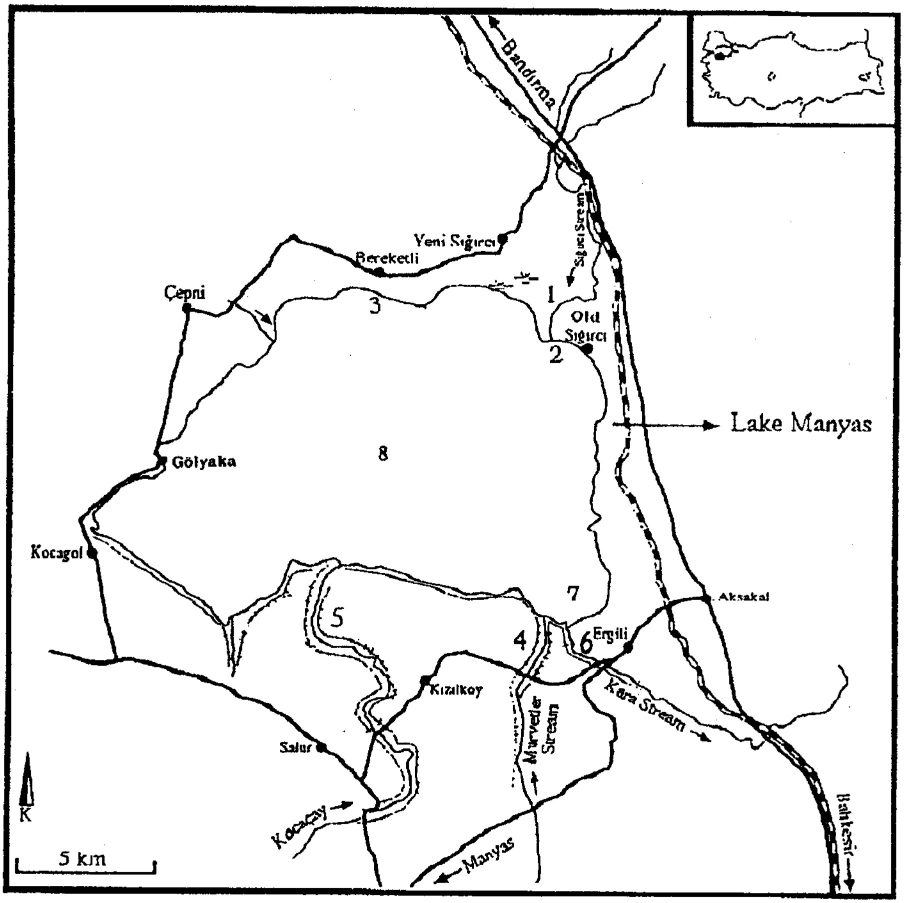

Figure 1. Map of Lake Manyas. 1. Sığırcı stream 2. Sığırcı stream-Lake junction 3. Off the beach at Bereketli 4. Mürvetler stream 5. Kocaçay 6. Kara stream 7. Kara stream-Lake junction 8. Center of the lake.

District. The lake is at a height of 15 m. from the sea level and has a shallow character. According to Balık[3] the maximum depth during one year is 3.40 m. and the surface area varies around 150-160 km^2. The rivers Kocaçay, Akıntı stream, Dutlu stream, and Sığırcı stream flow into the lake and the lakewater flows into the Marmara Sea near the Gemlik Bay through the rivers Kara stream first and then the Susurluk River. Because of those drainages, in some seasons, an apparent circulation movement can be observed at the southern portions of the lake. The Bird Paradise National Park which covers a 64 hectare forest area is situated at the north-east region of the lake where the river Sığırcı stream joins the lake. Although this National Park and the Manyas Lake (Bird Lake) had a balanced ecosystem character previously, it has been stated that it has been suffering from various pollutions during the recent years.[3]

The first set of sediment samples have been collected from five different stations in March 1st. 1996 (1st. season); Three more stations have been added to those stations during the collection of the second set of samples in June 23rd. 1996 (2nd. season).

The stations are the following:

1. Sığırcı stream
2. Sığırcı stream- Lake junction
3. Off the beach at Bereketli
4. Mürvetler stream
5. Kocaçay
6. Kara stream
7. Kara stream-Lake junction
8. Center of the lake

2.2. Trace Metal Analysis

A grab was used for sampling at the stations. The samples represented ca. the top 5-15 cm. of the sediment. Samples were taken from the center of each grab sample by an acid cleaned stainless steel scoop and transferred to precleaned polyethylene containers and stored at 4°C until the drying process followed by laboratory analysis.

Sediment samples were dried at 105–110°C for 24 hr. Large material was picked out by hand and discarded. Samples were ground, sieved through a 20 mesh sieve and mixed to give a stock sample, and stored at room temperature in plastic bottles.

The nitric acid-hydrogen peroxide digestion procedure[4] was used as the preparative step for the determination of Mn, Fe, Cu, Pb, Ni, Zn by flame atomic absorption spectroscopy. This is a procedure in which the reagent loading and unnecessary additional contamination is believed to be kept minimized and organic matter can be easily oxidized. It has already been used previously for the determination of trace metals in soil and sediment samples.[5-7]

All glassware were soaked in 20% HNO_3 for 12 hr. and rinsed with distilled deionised water before use. Reagents used were: conc. Nitric acid reagent grade (Merck), Hydrogen Peroxide 30% (Merck), distilled deionised water. The standards used for the trace element measurements were: $MnCl_2.4H_2O$, $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $PbNO_3$, $Ni(NO_3)_2.6H_2O$, Zn(metal) (all from Merck).

0.5 g. of sample was weighed and transferred to a 150 ml. beaker. It was then slurried with 0.5 ml. distilled deionised water in order to minimize sample splash and rapid reaction with the acid. 10 ml. conc. HNO_3 was added to the slurry. The beaker covered with a watch glass was put on a hot plate and the contents were digested at 100°C for 2 hr. After a 15 mm. cooling; 3 ml. of 30 % H_2O_2 was added to the mixture and heating was continued for another hour with intermittent stirring by gentle swirling of the beaker flask. The digestate was left to cool at room temperature and then vacuum filtered through a medium porosity sintered glass funnel into a 50 ml. Erlenmeyer flask. The filtered digestate was diluted with distilled deionised water to 50 ml. in a volumetric flask and used as a stock solution. For the determinations of Cu, Ni, Pb the stock solution was used directly, for Mn and Zn a tenfold diluted solution, for Fe a hundredfold diluted solution was used.

A Perkin Elmer Flame Atomic Absorption Spectrophotometer 2380 was used for the measurements.

3. RESULTS AND DISCUSSION

The amounts of Mn, Fe, Cu, Pb, Ni, Zn ($\mu g g^{-1}$) in the first set of samples collected from stations (1-5) in March 1996 (1st. season) and the second set of samples collected from stations (1-8) in May 1996 (2nd.

season) are listed in Table I. The values are the means of six experiments in $\mu g g^{-1}$ of dry sample. The values are also shown comparatively in Figures (2-7). Each metal is discussed separately below.

Table I. Trace Metal Levels ($\mu g g^{-1}$ dry weight) in sediments of sampling stations 1-8. The values are the means of 6 experiments.

Stations	Seasons	Mn		Fe		Cu		Pb		Ni		Zn	
		mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.	mean	std. dev.
1	March-96	993.1	33.1	10342	854	59.8	2.2	9.4	0.7	61.4	1.8	96.8	3.2
	May-96	639.1	16.7	32652	963	50.4	1.8	13.0	0.5	62.1	2.1	93.2	3.8
2	March-96	760.7	32.7	23419	7054	33.6	2.7	119.1	4.7	29.6	1.4	224.7	9.0
	May-96	879.8	29.2	32980	1528	51.2	1.7	124.0	4.3	49.4	1.1	246.6	12.3
3	March-96	606.5	28.0	10745	1150	14.5	0.6	81.4	3.8	20.9	0.8	114.7	4.6
	May-96	834.9	9.0	27832	1001	48.2	1.4	215.1	6.7	36.7	0.9	252.9	28.9
4	March-96	762.3	49.7	17880	3859	24.2	1.1	32.4	1.5	22.0	0.8	49.7	2.8
	May-96	326.1	14.5	16663	459	16.8	0.5	15.7	0.5	23.2	1.1	39.1	1.6
5	March-96	377.9	30.2	17383	4666	20.6	1.2	86.5	4.1	11.2	3.0	221.4	6.6
	May-96	515.4	13.0	16902	474	28.2	0.8	120.3	3.9	16.4	3.3	316.9	10.1
6	March-96												
	May-96	503.2	18.3	14277	409	24.9	0.9	64.1	2.6	18.4	0.6	71.1	1.6
7	March-96												
	May-96	347.3	18.0	13482	435	17.2	0.3	70.6	2.5	11.3	0.3	241.3	9.0
8	March-96												
	May-96	1042.5	28.2	32816	1122	50.0	1.8	217.4	7.9	43.8	2.0	253.8	11.6

Manganese

As can be seen from Figure 2 and Table I, the values of March 1996 with respect to the stations follow the order $1 > 4 \cong 2 > 3 > 5$.

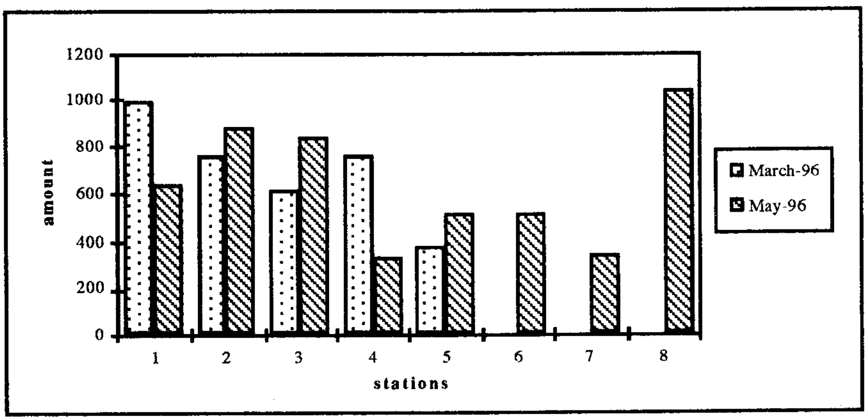

Figure 2. Amount ($\mu g g^{-1}$) of Mn vs. stations

The highest value being at Sığırcı stream followed by Sığırcı stream Lake junction and Mürvetler. The order of May 1996 (Figure 2, Table I) is 8 > 2 > 3 > 1 > 5 > 6 > 7 > 4. These values show that the middle of the lake has the highest value followed by the Sığırcı stream-lake junction. These values are higher than the values found for Lake Eğridir sediments.[7] The lowest value is found at Kara stream which flows out of the lake. The value of 1042.5 μgg^{-1} at station 8 i.e. the middle of the lake is higher than the mean sediment value of 770 μg/g.[8] These results may implicate that there is an anthropogenic input of this metal through the rivers flowing into the lake and mainly by Sığırcı stream.

Iron

The values of March 1996 with respect to stations follow the order 2 > 4 > 5 > 3 > 1 (Figure 3, Table I). Although a high value is not observed at Sığırcı stream, the highest value corresponds to Sığırcı stream-Lake junction which may implicate that there is deposition at this point. The results of May 1996 follow the order 8 > 2 > 1 > 3 > 5 > 4 > 6 > 7 > 8 (Figure 3, Table I). Here again we observe that the middle of the lake has the highest value, and Kara stream which flows out of the lake has the lowest value. The values are higher than the values of Lake Eğridir sediments (Alemdaroğlu et al., in press). Although these values are lower than the mean sediment value 2.3 %,[8] the results suggest

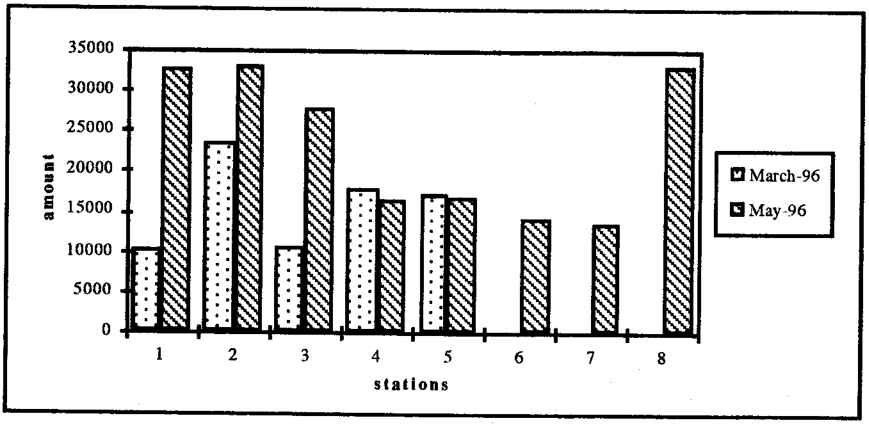

Figure 3. Amount (μgg^{-1}) of Fe vs. stations

that there is input through the rivers flowing into the lake and mainly by Sığırcı stream.

Copper

In March 1996, the values with respect to the stations follow the order 1 > 2 > 4 > 5 > 3 Figure 4, Table I). Sığırcı stream followed by

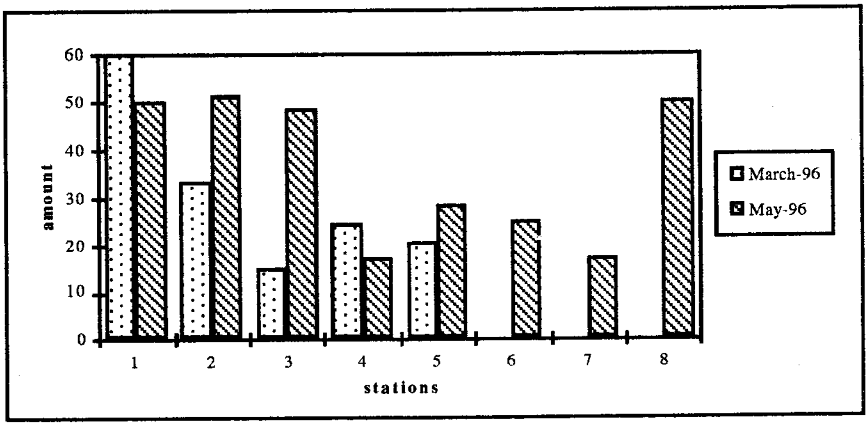

Figure 4. Amount (μgg^{-1}) of Cu vs. stations

the Sığırcı stream-Lake junction have the highest values. In May 1996 the trend is 2 > 1 > 8 > 3 > 5 > 6 > 7 > 4 (Figure 4, Table I). Here again we observe that the Sığırcı stream-Lake junction followed by the middle of the lake has the highest value of 51.2 μgg^{-1} This value is greater than the mean sediment value of 33 μg/g[8] and exceeds the EPA criteria for heavily polluted sediments > 50 μg/g[9] which suggests that there is input through mainly Sığırcı stream. The fact that the amount of Cu at those stations are also higher than that of Lake Eğridir sediments[7] which is considered to be unpolluted, except at Karadere flowing out of the lake, supports the above idea.

Lead

In March 1996, the values with respect to the stations follow the order 2 > 5 > 3 > 4 > 1 Figure 5, Table I). Sığırcı stream-Lake junction and Kocaçay have the highest values. In May 1996 the trend is 8 > 3 >

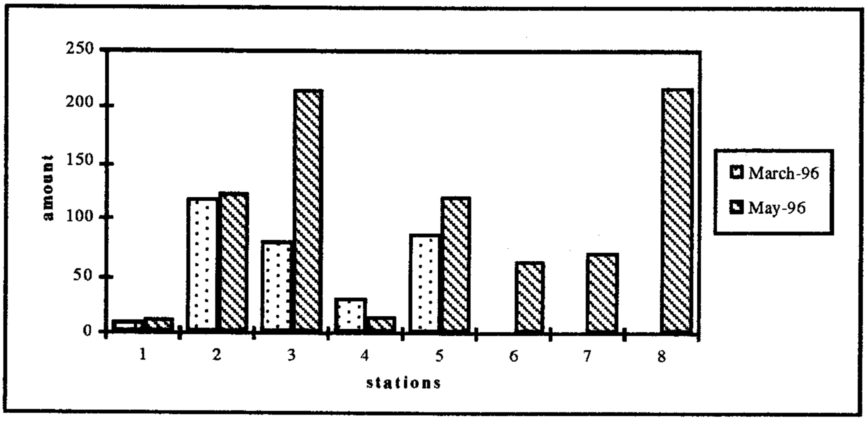

Figure 5. Amount (μgg^{-1}) of Pb vs. stations

2 > 5 > 7 > 6 > 4 > 1 Figure 5, Table I). The middle of the lake appears to have the highest level with 217.4 μgg^{-1} This value together with the values of other stations are much higher than those found in Lake Eğridir sediments,[7] they are also much higher than the mean sediment value 19 μg/g[8] and the EPA criteria for heavily polluted sediments >60 μg/g.[9] This implicates that this metal is carried by the streams flowing into the lake mainly by Sığırcı stream and Kocaçay and deposited to high levels in the lake.

Nickel

The level of nickel with respect to the stations in March 1996 is 1 > 2 > 4 > 3 > 5 (Figure 6, Table I). Sığırcı stream and Sığırcı stream-Lake junction appear to have the highest levels. In May 1996 the order is 1 > 2 > 8 > 3 > 4 > 6 > 5 > 7 (Figure 6, Table I). At some stations the amounts are of the order of Lake Eğridir sediments, at others they exceed those of lake Eğridir sediments.[7] Again we observe that the Sığırcı stream, Sığırcı stream-Lake junction followed by the middle of the lake have the highest values. EPA criteria for heavily polluted sediments for Ni is >50 μg/g.[9] It appears that this value has been exceeded at Sığırcı stream and has been approached at Sığırcı stream-Lake junction and the middle of the lake. This suggests that this metal is transported mainly by Sığırcı stream to the lake.

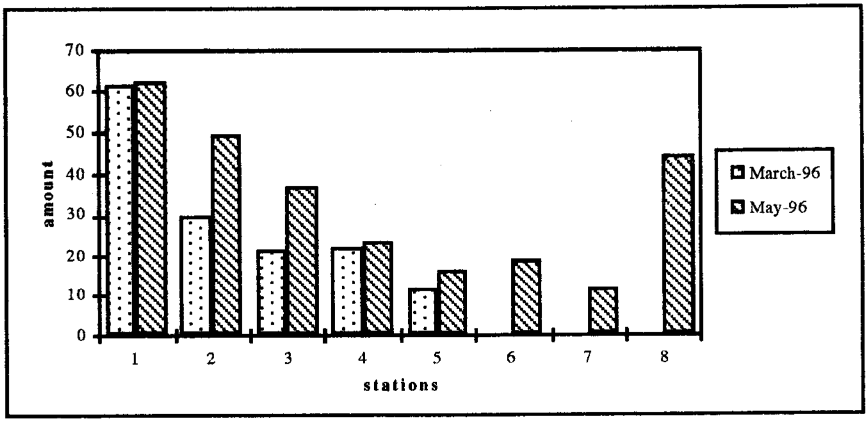

Figure 6. Amount (μgg^{-1}) of Ni vs. stations

Zinc

In March 1996 the amount of zinc with respect to the stations follow the order 2 > 5 > 3 > 1 > 4 (Figure 7, Table I). Sığırcı stream and Kocaçay appear to have the highest values. In May 1996 the order is 5 > 8 > 3 > 2 > 7> 1 > 6 > 4 (Figure 7, Table I). It appears that Kocaçay and Sığırcı stream transport this metal to the lake and it is mainly deposited at the middle of the lake and off the beach at Bereketli. The amounts of zinc at all the stations are much higher than those of the

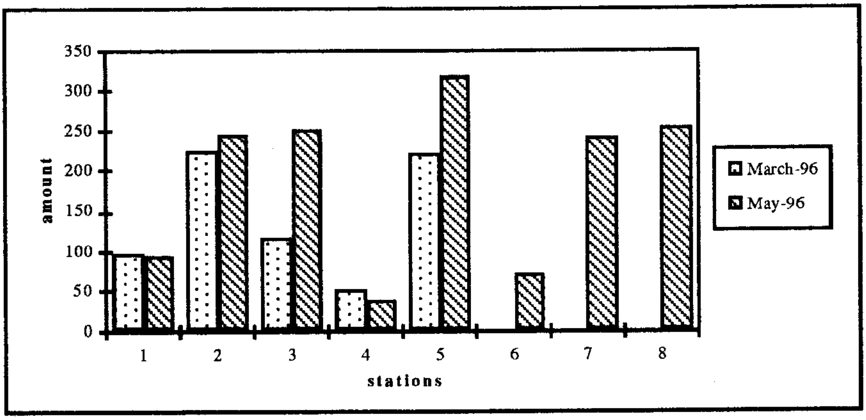

Figure 7. Amount (μgg^{-1}) of Zn vs. stations

Lake Eğridir sediments[7] except at Mürvetler stream. The highest value of zinc of 316.9 μgg^{-1} at Kocaçay is higher than the mean sediment level and is higher than the EPA criteria >200 μg/g[9] for heavily polluted sediments, which suggests that there is anthropogenic input of this metal to the lake.

When we compare the values of stations (1-5) (Figures 2-7) of the first season March 1996) with the values of the second season (May 1996) we observe that there is an increase in the amounts of Mn, Cu, Pb, Ni, Zn at stations 2, 3, 5 and there is a decrease in the amounts of Mn, Cu, Pb, Zn at stations 1, 4 in the second season. For Ni the amounts of stations 1,4 in the second season remain approximately the same. Whereas for Fe an increase in the second season is observed at stations 1, 2, 3 and a decrease in the second season is observed at stations 4, 5. These fluctuations may be due to variations in input or rainfall depending upon the season.

In addition to the mean sediment value, EPA criteria and Lake Eğridir sediments in Turkey; a general comparison of our results with those of the literature was made. Our values for Pb, Cu, Zn, Fe when compared to the values given for the surficial sediments from the Kishon river[10] were lower than some stations and higher than some other stations. It should be noted that this study had been performed at a different depth (0.5m.). The values of Pb and Zn in our study were generally higher than those of several lakes surrounding a coal fired electric generating facility at southwest Houston.[11] The value of Pb in our study was much higher than those of Laguna Lake values[12] although the other metals were lower. These comparisons also signal a pollution problem with respect to Pb and Zn.

In a study of Bonnevie et al.[2] it has been stated that it is useful to assess sediment quality conditions through comparisons to as many different sediment quality approaches as possible, and hazard indices have been calculated by dividing the mean concentrations found in each waterway by various sediment quality criteria and guideline values. A ratio of 1.0 or greater was assumed to indicate a sediment metal concentration with the potential to pose an adverse effect on benthic biota. In this study the same approach was followed i.e. the mean concentrations of Cu, Pb, Ni and Zn for each sampling station was divided by various sediment quality criteria and guideline values as given by Bonnevie et al.[2] and the results are presented in Table II and Table III. Nearly at all the stations Cu, Pb, Ni and Zn exceeded the Canadian Lowest Effect Levels. Pb and Zn exceeded at most stations the NOAA ER-L and California Bivalve AET values.

Table II. Ratio of the mean Ni, Zn amounts ($\mu g g^{-1}$ dry weight) in surficial sediments of Lake Manyas, Turkey and its tributary rivers to benchmark sediment quality criteria and guidelines and NOAA toxic effects values.

		NOAA*	WADOE*		Ontario Canada*		California*		
		ER-L	ER-M		lowest effect level	severe effect level	amphipod AET	Bivalve AET	Benthic AET
Nickel		30	50	n/a	16	75	>170	>170	>170
1	March-96	2.1	1.2		3.8	0.8	0.4	0.4	0.4
	May-96	2.1	1.2		3.9	0.8	0.4	0.4	0.4
2	March-96	1.0	0.6		1.9	0.4	0.2	0.2	0.2
	May-96	1.7	1.0		3.1	0.7	0.3	0.3	0.3
3	March-96	0.7	0.4		1.3	0.3	0.1	0.1	0.1
	May-96	1.2	0.7		2.3	0.5	0.2	0.2	0.2
4	March-96	0.7	0.4		1.4	0.3	0.1	0.1	0.1
	May-96	0.8	0.5		1.5	0.3	0.1	0.1	0.1
5	March-96	0.4	0.2		0.7	0.2	0.1	0.1	0.1
	May-96	0.6	0.3		1.0	0.2	0.1	0.1	0.1
6	May-96	0.6	0.4		1.2	0.3	0.1	0.1	0.1
7	May-96	0.4	0.2		0.7	0.2	0.1	0.1	0.1
8	May-96	1.5	0.9		2.7	0.6	0.3	0.3	0.3
Zinc		120	270	410	120	820	870	150	340
1	March-96	0.8	0.4	0.2	0.8	0.1	0.1	0.7	0.3
	May-96	0.8	0.3	0.2	0.8	0.1	0.1	0.7	0.3
2	March-96	1.9	0.8	0.5	1.9	0.3	0.3	1.5	0.7
	May-96	2.1	0.9	0.6	2.1	0.3	0.3	1.6	0.7
3	March-96	1.0	0.4	0.3	1.0	0.1	0.1	0.8	0.3
	May-96	2.1	0.9	0.6	2.1	0.3	0.3	1.7	0.7
4	March-96	0.4	0.2	0.1	0.4	0.1	0.1	0.3	0.2
	May-96	0.3	0.1	0.1	0.3	0.1	0.1	0.3	0.1
5	March-96	1.8	0.8	0.5	1.8	0.3	0.3	1.5	0.7
	May-96	2.6	1.2	0.8	2.6	0.4	0.4	2.1	0.9
6	May-96	0.6	0.3	0.2	0.6	0.1	0.1	0.5	0.2
7	May-96	2.0	0.9	0.6	2.0	0.3	0.3	1.6	0.7
8	May-96	2.1	0.9	0.6	2.1	0.3	0.3	1.7	0.8

* Bonnevie (1994)

Table III. Ratio of the mean Cu, Pb amounts ($\mu g g^{-1}$ dry weight) in surficial sediments of Lake Manyas, Turkey and its tributary rivers to benchmark sediment quality criteria and guidelines and NOAA toxic effects values.

		NOAA*		WADOE*	Ontario Canada*		California*		
		ER-L	ER-M		lowest effect level	severe effect level	amphipod AET	Bivalve AET	Benthic AET
Copper		70	390	390	16	110	>690	66	310
1	March-96	0.9	0.2	0.2	3.7	0.5	0.1	0.9	0.2
	May-96	0.7	0.1	0.1	3.2	0.5	0.1	0.8	0.2
2	March-96	0.5	0.1	0.1	2.1	0.3	0.1	0.5	0.1
	May-96	0.7	0.1	0.1	3.2	0.5	0.1	0.8	0.2
3	March-96	0.2	0.0	0.0	0.9	0.1	0.0	0.2	0.1
	May-96	0.7	0.1	0.1	3.0	0.4	0.1	0.7	0.2
4	March-96	0.4	0.1	0.1	1.5	0.2	0.0	0.4	0.1
	May-96	0.2	0.0	0.0	1.1	0.2	0.0	0.3	0.1
5	March-96	0.3	0.1	0.1	1.3	0.2	0.0	0.3	0.1
	May-96	0.4	0.1	0.1	1.8	0.3	0.0	0.4	0.1
6	May-96	0.3	0.0	0.0	1.1	0.2	0.0	0.3	0.1
7	May-96	0.3	0.0	0.0	1.1	0.2	0.0	0.3	0.1
8	May-96	0.7	0.1	0.1	3.1	0.5	0.1	0.8	0.2
Lead		35	110	450	31	250	>340	71	150
1	March-96	0.3	0.1	0.0	0.3	0.0	0.0	0.1	0.1
	May-96	0.3	0.1	0.0	0.4	0.1	0.0	0.2	0.1
2	March-96	3.4	1.1	0.3	3.8	0.5	0.4	1.7	0.8
	May-96	3.5	1.1	0.3	4.0	0.5	0.4	1.8	0.8
3	March-96	1.2	0.7	0.2	2.6	0.3	0.2	1.1	0.5
	May-96	6.1	2.0	0.5	6.9	0.9	0.6	3.0	1.4
4	March-96	0.9	0.3	0.1	1.0	0.1	0.1	0.5	0.2
	May-96	0.5	0.1	0.0	0.5	0.1	0.1	0.2	0.1
5	March-96	1.2	0.8	0.2	2.8	0.4	0.3	1.2	0.6
	May-96	3.4	1.1	0.3	3.9	0.5	0.4	1.7	0.8
6	May-96	1.8	0.6	0.1	2.1	0.3	0.2	0.9	0.4
7	May-96	2.0	0.6	0.2	2.3	0.3	0.2	1.0	0.5
8	May-96	6.2	2.0	0.5	7.0	0.9	0.6	3.1	1.5

* Bonnevie (1994)

There are industrial plants along the costs of Sığırcı stream and Kocaçay. These plants are continuously discharging industrial effluents to these two rivers which are then carried to the lake. Besides, municipal and agricultural wastes are additionally discharged to these rivers. These may be the possible causes of the high Cu, Pb, Ni and Zn amounts mainly at Sığırcı stream and Kocaçay sediments. The high levels observed at the center of the lake suggest that there is deposition in the lake.

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