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Full Length Research Paper

Heavy metals burden of Keenjhar Lake, District Thatta, Sindh, Pakistan

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Detection of heavy metals (HMs) content from Keenjhar Lake water was carried out monthly from January to December, 2003. Zinc, chromium, copper, iron, manganese, nickel and cadmium were analyzed by dual mode of analytical methods flame atomic absorption spectrometry and electrothermal atomic absorption spectrometry (FAAS and ETAAS) by multi element standard solution. The concentrations of zinc, chromium, copper, iron, manganese Nickel and cadmium were 1.4 to 104.3 µgL^{-1}, 1.28 to 4.9 µgL^{-1}, 0.6 to 7.3 µgL^{-1}, 2 to 45.6 µgL^{-1}, 0.2 to 6.7 µgL^{-1}, 3.54 to 39.5 µgL^{-1} and 1.0 to 4.3 µgL^{-1}, respectively. Zn^{2+}, Cr^{+}, Cu^{2+}, Fe^{2+} and Mn^{2+} concentrations were recorded lower than those of permissible limits, whereas Ni^{+} and Cd^{+} were higher than those of permissible limits recommended by WHO (2004).

Key words: Heavy metals, Keenjhar Lake, toxicity.

INTRODUCTION

Over the past several years, many fresh water reservoirs have been degraded and lost their significant importance due to unsustainable exploitation, increased levels of the urban's domestic effluents discharge and accelerated anthropogenic activities into aquatic environment along with the draught condition (Pourang et al., 2005). Pollutants derived from a growing number of diverse sources (industrial waste, urban run-off, sewage treatment plants, boating activities, agricultural fungicides, domestic garbage, dumps, anthropogenic activities and mining operations) have increasingly affected aquatic ecosystems (Garrett, 2000; Macfarlane and Burchett, 2001; Youn and Donald, 2003). Hydrographic conditions of aquatic ecosystem and seasonal variation of physico-chemical properties affect the abundance and distribution of trace and toxic metals in water column (Ansari et al., 2004; Arain et al., 2008; Assunta et al., 2001; Ghazanfar et al., 2000; Javed and Hayat, 1999; Kamran et al., 2003).

Environmental pollution mainly of aquatic ecosystems has become public interest (Gibbs, 1972; Niemi et al., 1990). It is not only undeveloped countries that have been suffered by environmental issues, besides developed nations are also suffering from the effective adverse impact of aquatic pollution as well (Listori and World Wide Bank, 1990) due to disordered economic growth associated with the exploration of virgin natural resources (Assunta et al., 2001). Heavy metals (HMs) in aquatic ecosystem have attracted considerable attention owing to their toxicity and accumulation in aquatic biota (Mason, 1998).

Keenjhar Lake is an exclusive source of fisheries potential, irrigation, picnic spot and wild life sanctuary. The contaminations are accelerated by anthropogenic, imprudent activity of visitors and fisher folks, and oil seepage from boating activities, thus, it is necessary to operate against such activities, to prevent Keenjhar Lake from further degradation. HMs have acute harmful effects on consumers; there are number of villages existing in the vicinity of Keenjhar Lake (Korai et al., 2008; Lashari, 2009).

In recent years, due to awareness regarding aquatic pollution, programs have been initiated in province Sindh for monitoring and for the abatement of lake pollution, including HMs pollution in Keenjhar Lake. In the wake of

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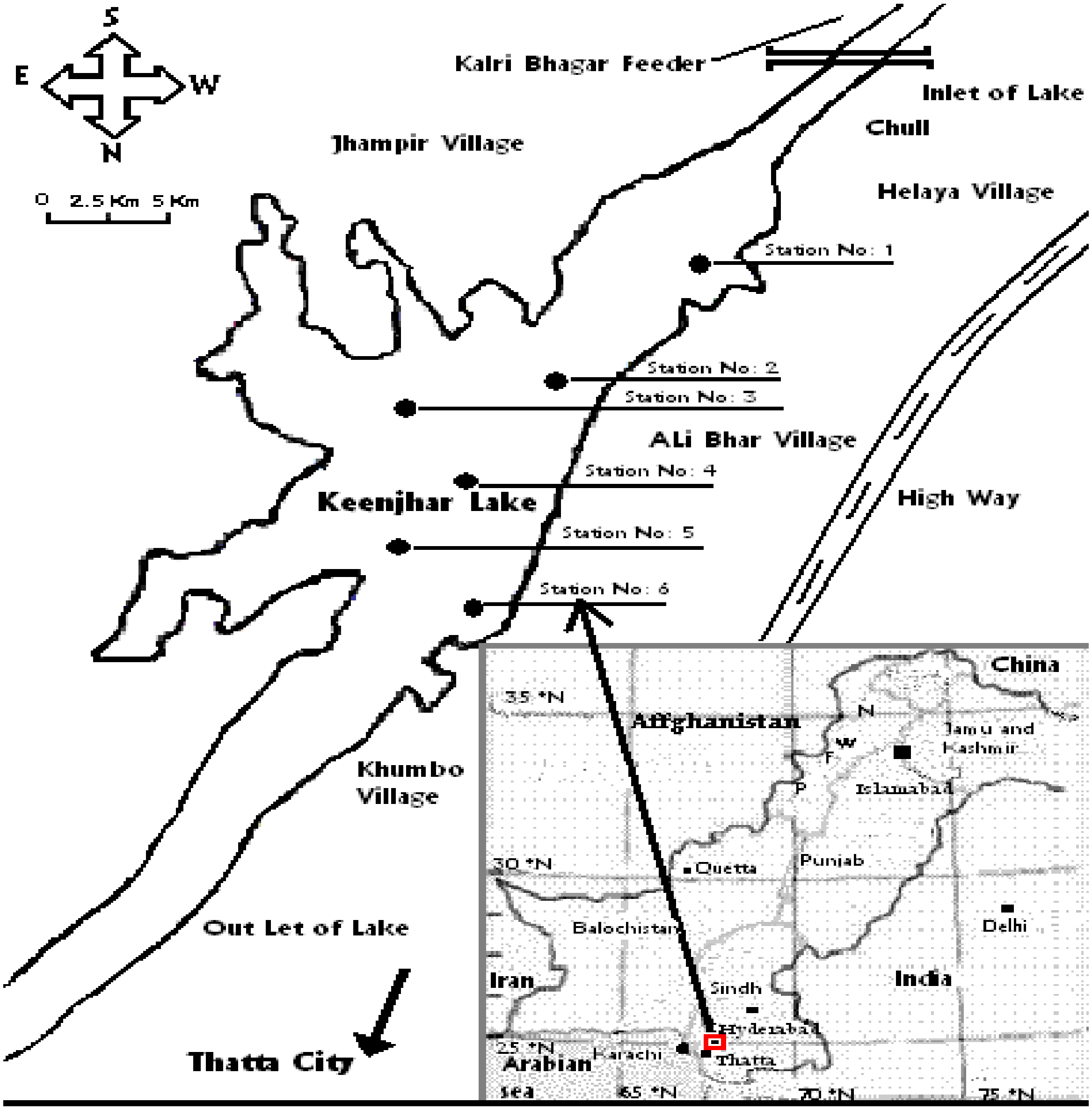

Station no: 1 corresponds to SUNHERI
Station no: 2 corresponds to HELAYA
Station no: 3 corresponds to NOORI
Station no: 4 corresponds to BOATING
Station no: 5 corresponds to RESTING
Station no: 6 corresponds to KHUMBO

Figure 1. Sampling stations of Keenjhar Lake during the studies.

rapid industrialization, large amount of HMs and toxic compounds are continuously released into Keenjhar Lake, hence, the aim of current study was to investigate the HMs content from Keenjhar Lake water.

MATERIALS AND METHODS

Water samples were collected for each month from six sampling stations of Keenjhar Lake. In order to cover the maximum area of the Lake, the sampling network was designed at key stations, such as inlet (Station 1, Sunheri), middle of Lake (Station 2, Helaya), centre of Lake (Station 3, Noori), the main boat basin (Station 4, Boating), surrounding of Lake, (Station 5, Resting), and outlet (Station 6, Khumbo) as shown in Figure 1, from January to December, 2003. Water samples were collected at the depth of ~1 to 1.2 m from surface water with the Van Dorn plastic bottles, from 2 to 3 spots of each station randomly and were reserved in well Stoppard polythene plastic bottles, formerly soaked in 10% nitric

Table 1. Analytical parameters of Electro Thermal Atomic Absorption (ETAAS).

Parameter	Cadmium	Chromium	Nickel	Manganese
Wave length (nm)	224.8	354.9	229.0	281
Slit-width (nm)	1.4	1.3	0.2	0.6
Lamp current (mA)	7.6	7.6	9	7.4
Dry	80 – 120 / 15[a]	80 – 120 / 15[a]	80 – 120 / 15[a]	80 – 120 / 15
Atomization	1500 – 1800 / 5[a]	2600 – 2700 / 5[a]	2500 – 2600 / 5[a]	2400 – 2500 / 5
Cleaning	1800 – 2000 / 2[a]	2700 – 2900 / 2[a]	2600 – 2800 / 2[a]	2500 – 2800 / 2
Ash	300 – 600 / 15[a]	300 – 700 / 15[a]	500 – 700 / 15[a]	400 – 500 / 15
Cuvette	Cup	Tube	Cup	Tube
Chemical modifier $(NO_3)_2$	Mg $(NO_3)_2$+Pd $(NO_3)_2$	Mg $(NO_3)_2$	Mg $(NO_3)_2$	Mg $(NO_3)_2$

Carrier gas was 200 mL/min and sample volume was (10 +10) µL modifier in each case.

Table 2. Analytical parameters of Flame Atomic Absorption (FAAS).

Element	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Burner light	Fuel (acetylene kgcm $^{-2}$)
Copper[b]	325.0	1.3	8.0	7.5	0.20
Zinc[b]	214.0	1.3	7.5	7.5	0.20
Iron [b]	247.4	0.2	9.8	7.4	0.30

D_2, Lamp used for background correction; [a]temperature range °C/time (s); [b]air as a oxidant = 1.6 kgcm^{-2}.

acid for 24 h and rinsed with ultrapure water obtained from ELGA laboratory water system. The water samples were collected following the standard procedure described by America Public Health Association (1998) and Department of Water Affairs and Forestry (DWAF) (1992).

Water samples were stored in an insulated cooler containing ice and delivered to the laboratory. All samples were kept at 4°C prior advance procedure and analysis. Water samples from the same station were mixed into a washed plastic container to make a composite sample, and were filtered through 0.45 µm filter paper (Whatman No. 1).

The filtrate was acidified with HNO_3 for heavy metal analysis. Polytetrafluoroethylene (PTFE) tubes bearing the volume of 50 mL were used for evaporation of water samples. Atomic absorption spectrophotometer (Hitachi Ltd., Model 180-50, S. N. 5721-2, Tokyo, Japan) with a deuterium lamp back corrector equipped with a 10 cm burner head and graphite furnace (GA-03 Hitachi Model 056 recorder) was used for recording the analytical data of HMs. Hitachi hollow cathode lamps were used as radiation sources. Analytical parameters are shown in Tables 1 and 2.

Reagents

Ultrapure water obtained from ELGA laboratory water system (ELGA Laboratory water Division, VWS (UK) Ltd., Bucks, UK) was used for all the samples. Nitric acid and hydrogen peroxide were of analytical grade (KGaA 64271, Merck, and Darmstadt, Germany) and were checked for possible trace metal contamination. Standard solutions of detected HMs were arranged by dilution of certified standard solution (1,000 ppm; Fluka Kanica, Bhchs SG and Switzerland) of corresponding metal ions. Standard Reference Materials (SRM) 1643e (Water) were purchased from National Institute of Standard and Technology (NIST) (Gaithersburg, Maryland, USA). Argon gas with 99.99% purity was used as sheath gas for the atomizer and for internal cleanse. Glassware was kept overnight in 5 M HNO_3 rinsed with deionized water prior to use.

Analytical procedure

Lake water analysis

Sampling was usually done in the morning time (7:00 to 9:00 am PST). The analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples. 10% or more of the acid-treated composite water samples were duplicated as a quality assurance requirement. The sample solutions were concentrated five times by evaporating the water at 90°C on an electric hot plate, filtered and kept at 4°C till further analysis.

Data treatment by statistical method

The variations of the HMs of lake water were evaluated by using the correlation matrix, Spearman non-parametric correlation coefficient (Spearman *R*) by using SPSS V.13.0.

Quality control

Analytical blanks and certified samples with known concentrations of elements were prepared and analyzed using the same procedures and reagents. For the accuracy of the determination procedure, it was assessed by triplicate analysis of certified reference materials of water (SRM 1643e). Their certified values and observed values are shown in Table 3. The limits of quantification (LOQ) and limit of detection (LOD) for elements were calculated as under LOQ = 10 s/m and LOD = 3 s/m, where “s” is the standard deviation of 10 measurements of the blank and “m” is the slope of the calibration graph obtained for each case (Table 4).

RESULTS AND DISCUSSION

Maximum zinc concentration in water was 104.3 µgL^{-1} in

Table 3. Analytical results of certified reference material.

Water element	SRM 1643e	
	Certified value (µg L^{-1})	Our value (µg L^{-1})
Cd	6.568 ± 0.073	6.64 ± 0.4
Cr	20.40 ± 0.24	18.5 ± 0.52
Ni	62.41 ± 0.69	60.79 ± 0.92
Mn	38.97 ± 0.45	36.8 ± 1.68
Zn	78.5 ± 2.2	78.1 ± 3.5
Cu	27.06 ± 0.32	25.08 ± 0.78
Fe	98.1 ± 1.4	96.7 ± 4.2

Table 4. Limits of quantification (LOQ) and limit of detection (LOD) for elements.

Limit	Cd	Cr	Cu	Fe	Ni	Mn	Zn
LOQ (µg.l^{-1})	1.12	15.2	57.5	232.4	22.6	58.9	33.9
LOD (µg.l^{-1})	0.331	4.5	17.1	64.8	6.71	17.5	10.6

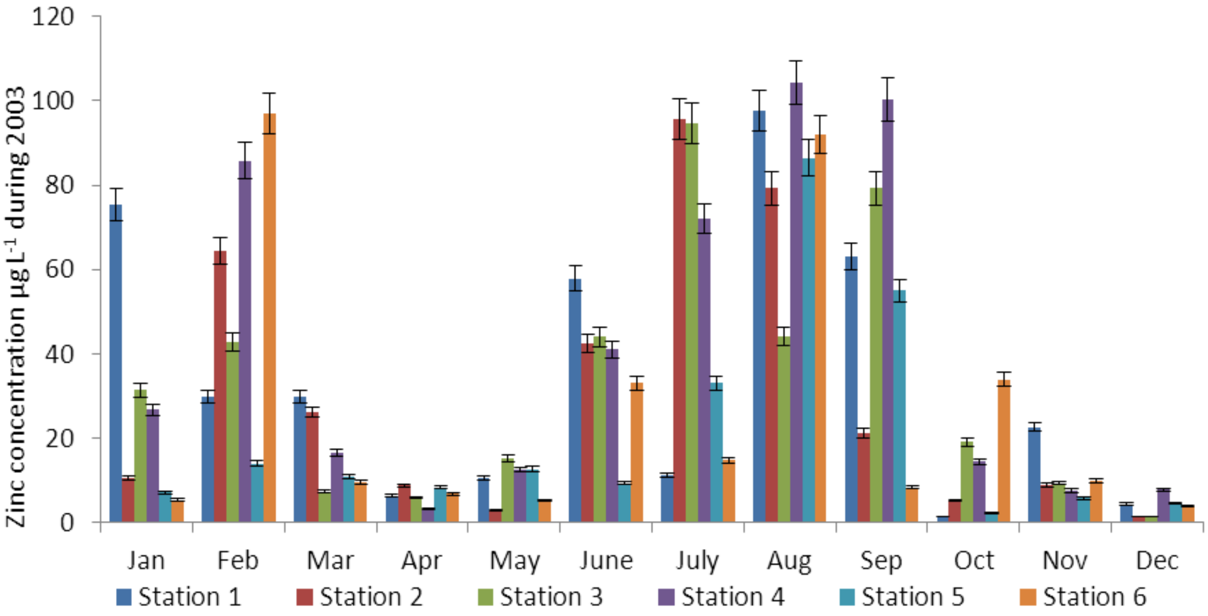

Figure 2. Zinc concentrations (µg/L) at different sampling stations in Keenjhar Lake from January-December, 2003.

the month of August at Station 4 and was minimum (1.4 µgL^{-1}) in the month of October and December at Stations 1, 2 and 3 (Figure 2 and Table 5). Similar observations were documented by Javed and Mahmood (2000) from river Ravi (Moore and Ramamoorthy, 1984).

Chromium is airborne and the element originates from industrial sources, particularly ferrochrome production during refining (Casarett and Doull's, 2001), chemical and refectory processing, the manufacture of cement and combustion of fossil fuels; chromium precipitated and that fall out are deposited on ground level and water; land fall out is eventually carried to water by run off, where it is deposited in sediment and accumulated by aquatic organism especially bottom dwellers (Arain et al., 2008; Lashari, 2009; Korai et al., 2010). Chromium content in Keenjhar Lake water was 4.9 µgL^{-1} in the month of August at Station 1 and 1.28 µgL^{-1} in the month of April at Stations 3, 4 and 6 (Figure 3 and Table 5). Chromium level was below that of WHO (2004).

Our results are in agreement with the results of Ansari et al. (2004), Boyd (1990) and Anazawa et al. (2004). Maximum nickel concentration in water was 39.5 µgL^{-1} in

Table 5. Heavy metals range during January to December, 2003.

Heavy metal (HM's)	Maximum (µg/L)	Minimum (µg/L)
Zinc	August 104.3	October and December 1.4
Chromium	August 4.9	April 1.28
Copper	February 7.3	October, November and December 0.6
Iron	December 45.6	June 2
Manganese	September 6.7	August 0.2
Nickel	June 39.5	January March and November 3.54
Cadmium	April 4.3	August 1.0

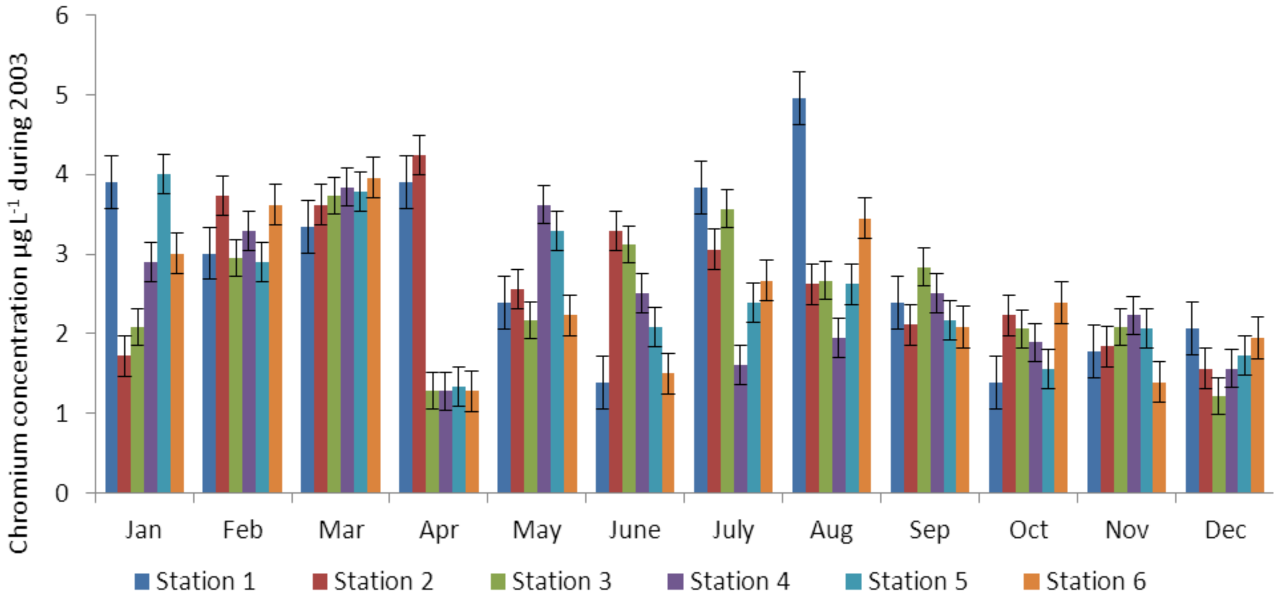

Figure 3. Chromium concentrations (µg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

the month of June at Station 2 and the minimum (3.54 µgL^{-1}) was recorded in the month of June, March and November at Stations 2 and 6 (Figure 4 and Table 5). Nickel concentration in water samples at Station 2 was high compared with the rest stations. Station 1, inlet from the Indus via Kalri Baghar feeder and Station 2, the main boat basin, carries pollution into the lake, which contains fine particles of HMs; later on those particles settles at the bottom of the lake (Korai 2010; Korai et al., 2010) due to low water current.

Concentration of cadmium in water ranged between 4.3 µgL^{-1} at Station 1 in the month of April and 1.0 µgL^{-1} at Station 6 in the month of August (Figure 5 and Table 5). Cadmium concentrations were higher than that of WHO

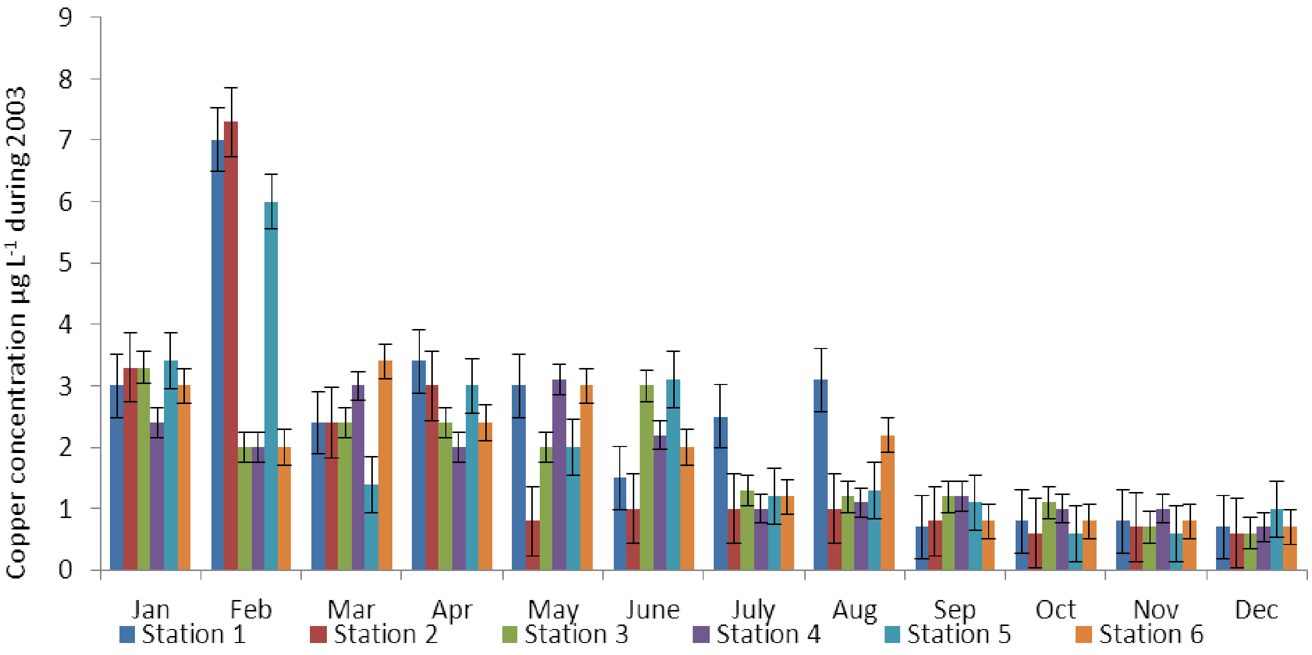

Figure 4. Copper concentrations (µg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

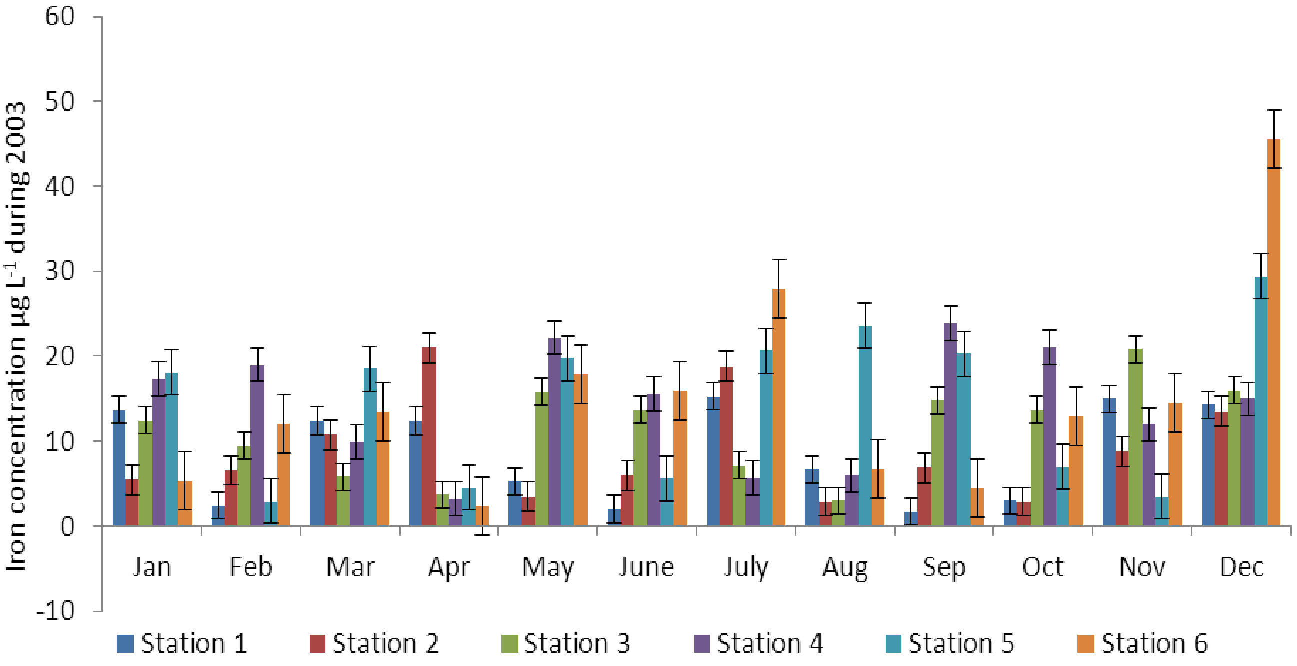

Figure 5. Iron concentrations (µg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

(2004). Cadmium showed increase in lethality in water and sediment pollution, and had profound adverse effect on aquatic ecosystem due to discharges of metal bearing effluent into lake (Korai et al., 2010; Lashari, 2009).

Manganese occurs in collaboration with carbonates and silicates. Manganese is an undesirable element in domestic water and supplies deposits that are unpleasant in food utensils during cooking (Lashari, 2009). Manganese concentration in Keenjhar Lake water ranged between 6.7 µgL^{-1} in the month of September at Station 3 and 0.2 µgL^{-1} at Station 4 in the month of August (Figure 6 and Table 5). Manganese concentrations were lower

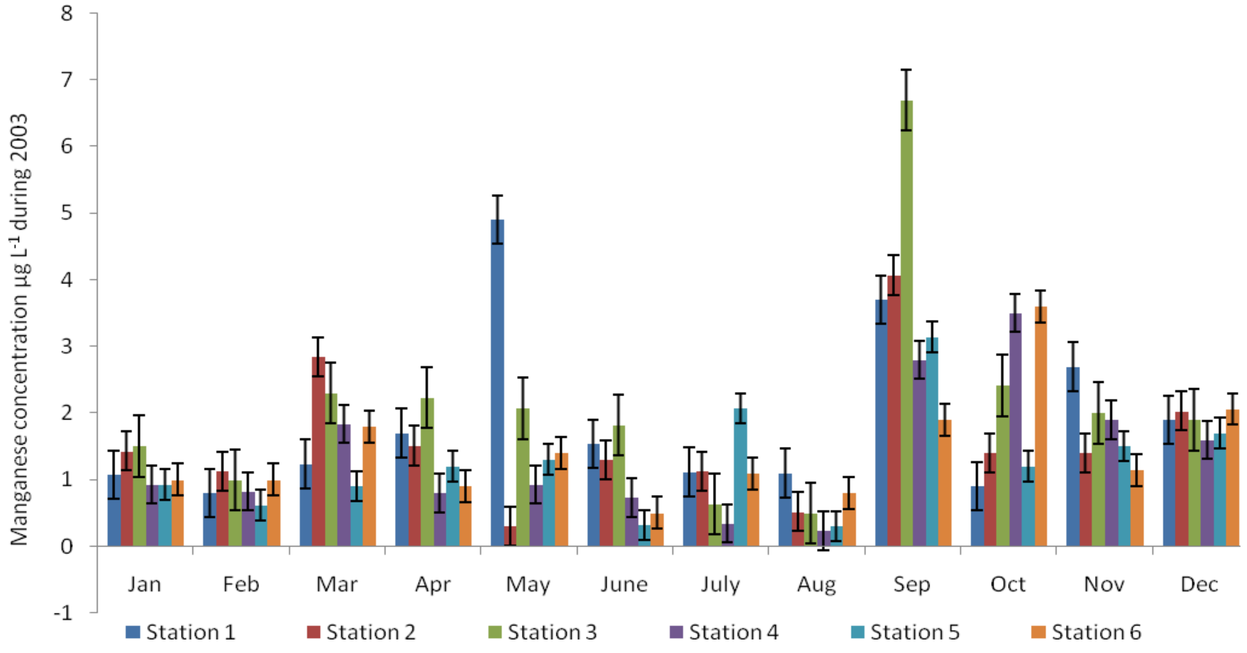

Figure 6. Manganese concentrations (μg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

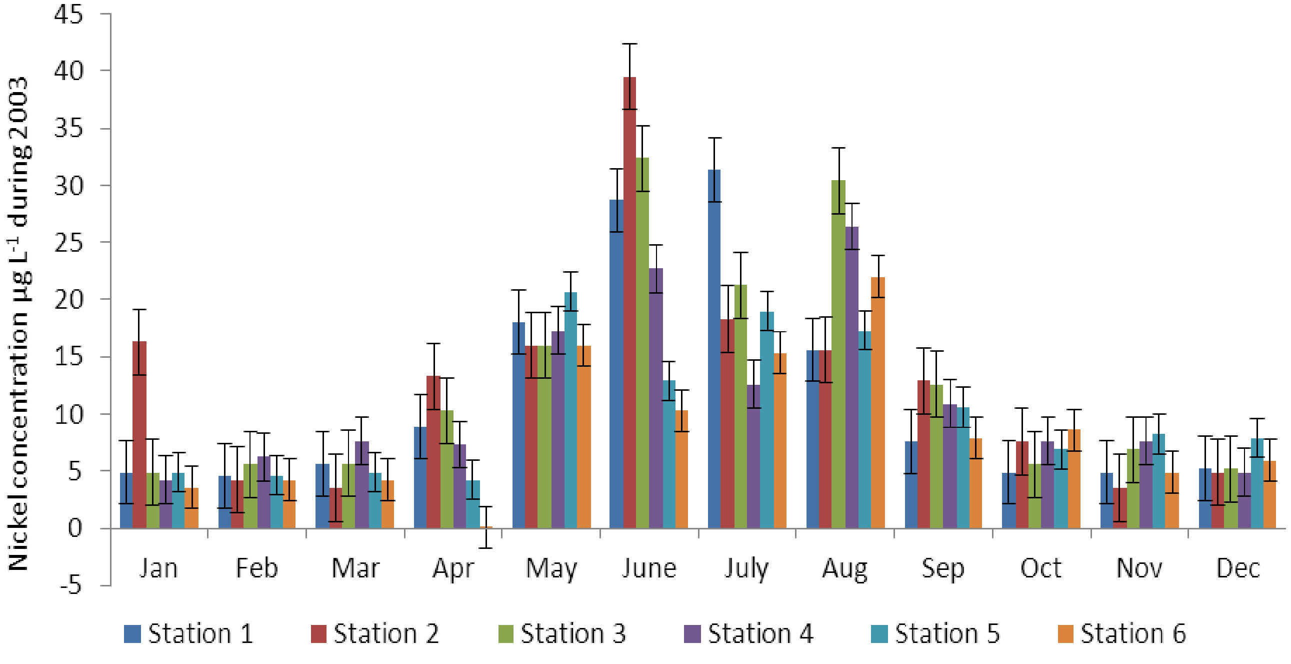

Figure 7. Nickel concentrations (μg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

than that of WHO (2004). Our results are in agreement with those of Allan (1997), Arain et al., (2008), Garrett (2000), Javed and Hayatt (1996).

Copper is reported in the aquatic environment as associated with the anthropogenic input such as mining, smelting, electroplating, tanning, fertilizers and many other industrial sources (Lashari, 2009). The concentration of copper in lake water during the current study varied between 7.3 µgL^{-1} in the month of February at Station 1 and 0.6 µgL^{-1} in the month of October, November and December at Stations 2, 3 and 5 (Figure 7 and Table 5). Our results are in agreement with that of

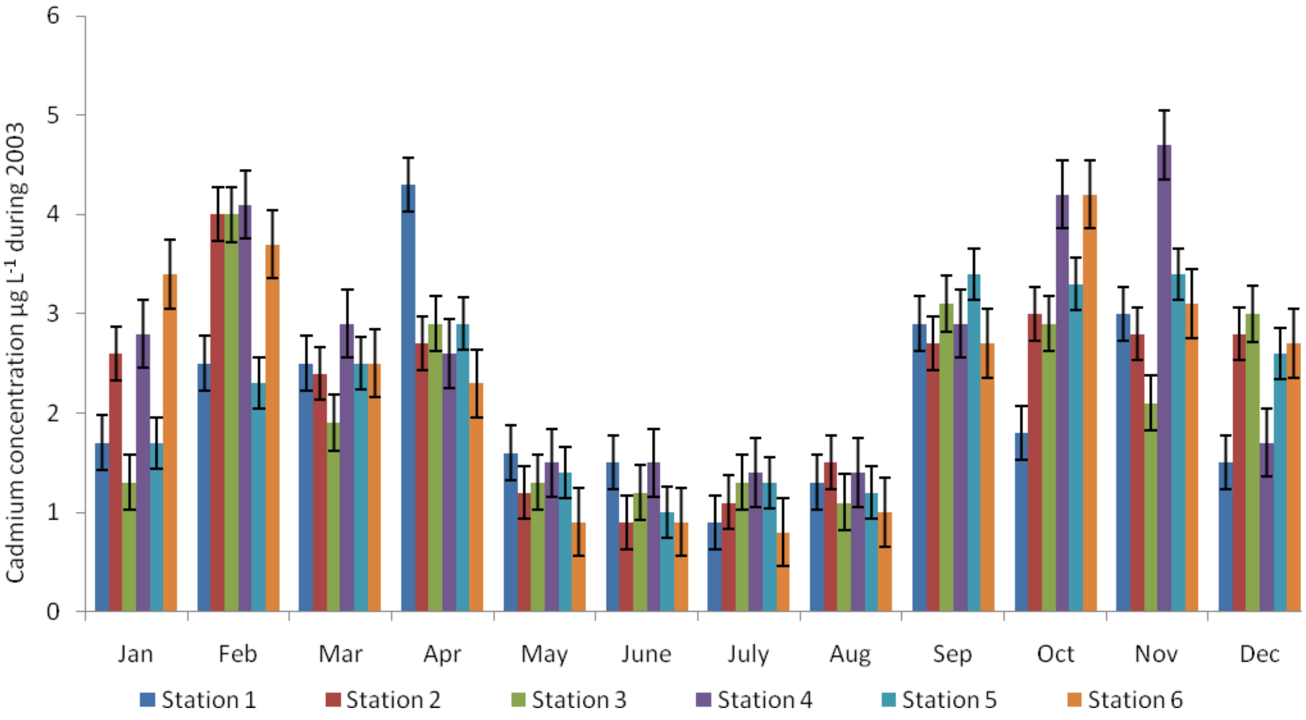

Figure 8. Cadmium concentrations (µg/L) at different sampling stations in Keenjhar Lake from January to December, 2003.

Moiseenko (2001), Rizo et al., (1993), Stauenwhite and Wangersky (1991) and Youn-Joo and Donald (2003).

Iron is a common element in the earth crusts and it is found as major as well as minor constituent of minerals (Clark and Hawley, 1966). In most minerals formed near the surface of earth, it is combined with oxygen as the ferric oxide. Ferro-bacillus or thio-bacillus, iron oxidizing bacteria may cause serious problem of stream and river pollution and metal corrosion because of the acidic ferric ion containing solution they produce. They can cause serious problem in public water supplies by their growth and obstruction of iron pipes and conduits (Wagner and Boman, 2003). The concentration of iron in lake water during this study ranged between 45.6 µgL^{-1} at Station 6 in the month of December and 2 µgL^{-1} at Station 1 in the month of June (Figure 8 and Table 5). These concentrations were well lower than that of WHO (2004). Our results are in agreement with that of Arian et al. (2008), Korai et al., (2010) and Lashari (2009).

Conclusion

Our results specify that levels of zinc, chromium, copper, iron and manganese were well lower than the recommended permissible limits by WHO (2004), whereas nickel and cadmium were higher. The result of analyses provides base line structure of metal toxicity. The accumulation of such toxic metals in aquatic food chain, will cause possible risk to human health due to water and food consumption offered by lake. On the basis of our finding, it is possible to recommend various steps for better systematic management of Keenjhar Lake in terms of its productivity and undesirable discharge in the Keenjhar Lake by the local population and boating activity of visitors, which is hazardous to the entire aquatic ecosystem and to the end consumers.

It is recommended that domestic waste containing trace metals should not be discharged directly or indirectly into aquatic environment to minimize metal toxicity at the end.

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