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Assessment of heavy metals in seasonal lakes near balloki head works and comparison of their water quality

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Abstract

Five seasonal lakes situated near Balloki Head Works near River Ravi in Qasur district, Punjab, Pakistan were studied for the comparison of their water quality and heavy metals contamination in water, sediments and hydrophytes of the lakes. In the assessment of water quality physicochemical parameters i.e. pH, Electrical Conductivity, Dissolved Oxygen, Salinity, Total Dissolved Solids, Temperature, Nitrates, Phosphates, Sulphates and Chlorides were selected to be determined. Presence of Pathogenic bacteria (Total Choliforms) was equally determined using most probable counting number method. These all marked parameters were found within the permissible range for the propagation of aquatic life established by USEPA and Punjab Environmental Quality Standards (PEQS). The process of assessment of heavy metals in the lakes was started with collection of samples on fortnightly bases for two months and 4 time sampling was done. Samples of water, sediments and hydrophytes were collected, these samples were acid digested and analyzed using Atomic Absorption Spectrophotometer for heavy metals. Three heavy metals i.e. Zinc, Copper and Chromium were assessed in water, sediments and two types of aquatic plants namely *Typha angustifolia* and *Persicaria amphibian* and their concentration was high in samples of sediments, less in Hydrophytes and little in samples of water. In this wake land encroaching for agriculture, restaurants and other purposes should be checked strictly to reduce the inlet of heavy metals into these lakes.

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Introduction

The seasonal lakes along with other wetlands play significant role in supporting variety of ecosystems and equally facilitate dumping of sewerage and industrial wastewaters into them which is threatening the ecosystem at a significant level. Heavy metals are polluting the water and posing a serious threat to public health in Pakistan (Azizullah *et al.,* 2011). Observance of any heavy metal in water, sediments, plants and fish plays a pivotal role in pointing out means of heavy metal flux in aquatic systems (Javed and Mahmood, 2001).Heavy metals are prime among the list of alarming pollutants for the environment owing to their toxic and bioaccumulative characteristics (Feng *et al.,* 2012).

Mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As) account for the environmental pollution after their accumulation surpasses defined limits (Kennish., 1992). Like other developing countries, state of Pakistan is also running short of water due to palpable pollution level. The country has lost its considerable resources of water (PCRWR., 2005). It poses symbol of imminent water stress which can inflict water scarcity in the time to come (Hashmi *et al.,* 2009).

Although a lot of work has been carried out in Distrcit Qasoor to raise the concern about potential impacts of water pollution caused by tanneries, no any significant work pointing out the pollutions of the seasonal lakes of the area has been carried out. These seasonal lakes are supporting a variety of marine ecosystem but the damage being caused to them through pollution is not getting attention. The aim of this study is to highlight the water pollution of seasonal lakes at Balloki Headwork which is lacking any eloquent study still. Contamination of Marine ecosystem including sediments by heavy metals can phase out aquatic systems (Charkhabi *et al.,* 2005). Polluted Sediments can serve as the source of heavy metals releasing them into the aquatic ecosystems and engrossing the pollution (Mohammed and Markert, 2006).

Lakes, namely Spur no.1, Spur no. 2, Spur no. 3, Spur no.4, Spur no.5, under study depend upon river Ravi for their hydrology getting water by seepage from the river. Seasonal rains also play part in their Hydrological demands. These five Lakes are being used for fish cultivation and agricultural purposes. Meadows linked with these lakes provide fodder for cattle and sheep and nearby community also uses their aquatic vegetation for multiple purposes i.e. for fuel, weaving of mats and baskets and for the construction of their lodges. These selected lakes are also supporting biodiversity in the area.

Among important inlets of pollution in the river Ravi, from Lahore Siphon to Balloki head works, are waste water from urban areas, agricultural and industrial locations, mainly from electroplating workshops, steel factories, paper and pulp industries, medicine and scientific laboratories, surface runoff and municipal sewage (Rauf *et al.,* 2009). The objectives of study include estimation of heavy metal contamination, evaluation of the potential of aquatic plants recycling heavy metals load and the comparison of water quality in water and sediments of seasonal lakes of river Ravi near head Balloki.

Materials and methods

Study Area:

Study was conducted on five seasonal lakes, Spur no.1, Spur no.2, Spur no.3, Spur no.4, spur no.5, of river Ravi near Balloki head works in district Qasur. Samples of water, sediments and hydrophytes were collected on fortnightly basis for 2 months started from March 2013 to April 2013. In this duration 4 times sampling was performed.

Collection of samples

Water sampling: Random samples of water were taken by filling it into the bottles directly from different places in each lake. Two pipette drops of concentrated HNO_3 were poured in each bottle of water samples which baffles growth of microbes, controls flocculation and lessens adsorption on surfaces of the containers. The water samples were brought in the laboratory for further preparation and analysis.

Sediment sampling: Two sediment samples were collected randomly in pre cleaned polythene zipper bags from each lake. Sediments were collected with the help of augar, shifted to the laboratory keeping them in ice boxes during the time of shifting and stored at 4^0C in the laboratory before further process.

Sampling of Aquatic Plants: Dominated species of aquatic plants were collected in polythene bags from each lake. Plants were taken with all parts i.e. roots, shoots, leaves and flowers/fruits if available. These were taken to the laboratory, identified and stored at 4^0C before further process.

Documentation of Sampling: Samples were labeled at the site during sampling. Samples from Lake Spur no.5 were labeled as lake 1, Lake Spur no.4 as Lake 2, Lake spur no.3 as Lake 3, Lake spur no.1 as Lake 4 and Lake spur no.2 as Lake 5. Some of the parameters like DO, EC, pH, Salinity and TDS were measured and noted on site during sampling.

Surface water quality analysis: Physical, chemical, inorganic, metals and microbiological parameters, to check quality of surface water, were tested in accordance with procedures described in Standard Methods (APHA 1998).

Physical analysis: In order to analyze physical traits of water Turbidity, Temperature and Total Dissolved Solids were observed. Turbidity meter (HI93703 Microprocessor) for turbidity and digital thermometer was used for temperature. TDS were determined using filtration method in which Oven dried beaker were first weighed then filtered samples were placed in them and evaporated at 105°C, then beakers were again weighed to determine the amount of Total Dissolved Solids in the samples.

Chemical analysis: The evaluation of chemical characteristics of surface water was done by measuring pH, Electrical Conductivity, Dissolved Oxygen on site during sampling. The pH, Electrical conductivity and Dissolved Oxygen were measured using pH meter (pH100 YSI), EC meter (EC300 YSI) and DO meter (DO200 YSI) respectively.

Inorganic analysis: A number of previous studies have confirmed the serious contamination of river sediments by heavy metals and persistent organic pollutants (POPs) in urban areas (Feipeng *et al.,* 2012). To analyze inorganic concentration of the water of marked lakes, concentration of Sulphates, Phosphates, Nitrates and Chlorides was measured. Concentration of phosphate in water was evaluated by 4500-P-E-Ascorbic Acid Method. Ammonium molybdate and potassium antimony tartarate reacted, under acidic condition, with orthophosphate present in collected samples of water to prepare phosphomolybdic acid and by getting ascorbic acid reacted in it intense blue color was appeared in 20 minutes. The intensity of light absorbed by this solution was afterwards recorded using VIS721 spectrophotometer at wavelength of 890 nm. Sulphates in water were estimated by 4500-SO_4^{2-}-E Turbid metric Method. In this 100 ml of water sample was taken in beaker 5 ml conditioning reagent and 5 ml of $BaCl_2$ was added in the sample. To get suspension of Barium sulphates, $BaCl_2$ was used to make Sulphate ions precipitated in water. VIS 721-spectrophotometer at wavelength of 420nm was used to record the light absorbance of this suspension.

Nitrate concentration test: Presence of Nitrates in samples of water was observed using 4500-NO_{3-} Chloimetric method while light absorbance was recorded at wavelength of 410nm. In this method 10 ml of water sample was taken in test tube 2 ml NaCl solution and 10 ml of H_2SO_4 (4:1) was added in the test tube. The addition of acid raised the temperature, 0.5 ml of Brucine Sulphanilic Acid was added when this mixture attained the room temperature. This mixture was placed in hot water bath at 90°C for 20 mints and absorbance was checked when the mixture attained the room temperature. Chlorides in water were calculated with the help of 4500Cl-Silver nitrate Titration method in which Potassium chromate, as an indicator, was dropped into water samples and finally was titrated against silver nitrate solution until reddish brown color appears so that all chlorides could be precipitated as silver chloride.

Microbiological Testing of Water: Microbiological test of water was done by estimation of total coliforms which were assessed using 9221-C Most Probable Number Count Method where Lauryl tryptose broth was utilized in this test. Having incubated samples at 37°C for 24 hours, growth was noticed because presence of gas in inverted tube gives symptoms of presence of coliforms.

Heavy Metals analysis: Samples of water, sediments and hydrophytes were acid digested then heavy metals were determined by Polarized Zeeman Atomic Absorption Spectrophotometer (Hitachi Z-5000). Samples were digested in the following way;

Water: in wake of the prospective low concentrations of the metals in the natural water samples and less sensitive instruments, pre-concentration test of the water samples was done by evaporating 100 ml of the water to 4 ml on a hot plate. The water samples were then got digested by pouring 5 ml of concentrated Nitric acid and heating it on the hot plate for 30 min. Some 10 ml of concentrated HCl was dropped so that digestion may continue until the solution appear light brown or colorless. The distilled water was added to bring the volume of solution at 25ml. (Ochieng *et al.,* 2007).

Sediments: In lakes**,** Sediments mostly work as a reservoir for discharged pollutants which either keep adhered to the particles of sediments or get dissolved in pure water (Chon *et al.*, 2012). Approximately 1 g of sediment sample was placed in a 250-mL volumetric flask and 10 ml of concentrated HNO_3 was added into it and was boiled to make it dry. Once cooled, 5 mL of concentrated HClO4 was added and the mixture was boiled gradually until dense white fumes appeared. After getting it cooled, 20 mL of distilled water was added and the mixture was boiled further to make it fume free. The solution was cooled, transferred quantitatively to a glass tube and diluted to 25 ml with distilled water (Feng *et al.,* 2012).

Hydrophytes: The hydrophyte samples were washed thoroughly with tap water as well as rinsed twice with distilled water and then dried at 70°C for 24 hours. The deride samples were ground using mortar and pestle. The 1.0 g of sample powders were weighed into 100mL Pyrex beakers, and treated with 10mL concentrated HNO3 (ultrapure 65%). The beakers were covered with watch glass, and the suspensions were heated to 130°C for 1hour. A total of 4mL 20% H_2O_2 was added in four aliquots of 1mL each. After cooling to the room temperature, the liquid carrying suspensions was filtered so that filtrates could be collected using 50mL flasks. The collected filtrates were diluted, afterwards, by adding distilled water to 50 ml (Zhang *et al.,* 2009).

Water Quality Analysis: The quality of water was analysed to evaluate its physical, microbial and chemical characteristics including various parameter (i.e) pH, EC, DO, TDS, Chloride, nitrates, phosphates, sulphates and total coliforms etc.

Results and discussions

Comparison of Physicochemical analysis of water of selected lakes:

The pysico-chemical parameters for quality of any lake water , according to WHO, includes turbidity, total dissolved solids (TDS), pH, Electrical conductivity (EC), dissolved oxygen (DO). The results of these parameters for the five lakes are shown in table 1.

Bioaccumulation of heavy metals depends mainly upon myriads of biotic and abiotic factors such as temperature, pH and dissolved ions in water (Aksoy *et al.*, 2005). The results of pH in Water quality analysis were found in the range of 6.5-9.0 which are not exceeding the level of pH recommended by WHO for surface water quality. There was a minor variation in pH of the selected lakes. There is no significant variation in pH in all of the selected lakes and pH value is falling in the range recommended by WHO. The variation of pH in the selected lakes has been shown in figure 1.

Dissolved oxygen is also in range of WHO recommended range for the propagation of aquatic life.

It is found that dissolved oxygen is more than the 9 mg/l in 4 of the selected lakes and the one lake i.e lake number 4 has the average value of dissolved oxygen 8.63 mg/l.

Table 1. Comparison of average physicochemical & pathogenic characteristics of the selected 5 lakes.

	pH	D.O mg/l	E.C µS/cm	Salinity Ppt	TDS mg/l	Temp ºC	Nitrates mg/l	Sulphates Mg/l	Phosphates mg/l	Chlorides mg/l	Total Coliforms MPN/100ml
PEQS*	6-9	-	-	-	3500	40	40	600	-	1000	-
USEPA	6.5-9.0	5.5-9.5			1000		=90	<500	=0.82	250	=126
Lake1	8.55	11.12	349.8	0.225	213.5	24.63	4.17	8.88	0.029	30.84	30
Lake2	7.66	10.64	543.75	0.25	341.25	26.42	1.43	6.27	0.026	35.13	500
Lake3	8.13	11.23	552	0.33	322.75	29.38	1.95	85.05	0.04	55.66	16
Lake4	7.79	8.63	551.1	0.3	325.7	27.125	4.025	57.26	0.027	46.16	62
Lake5	7.93	9.78	580.5	0.35	341.75	28.15	2.2	6.41	0.0393	42.79	41

Table 2. Coefficient of Correlation of Zn between water, sediments and hydrophytes.

Zn		Water	Sediment	Typha	Persicaria
Correlation	Water	1	-0.09650	0.16073	-0.67246
Correlation	Sediment	-	1	-	-0.5973
Correlation	Typha	0.16073	-0.14423	1	0.23528
Correlation	Persicaria	-	-0.59730	0.23528	1

This quantity is also favorable for aquatic life i.e. it is not a less amount than the requirement of aquatic life. The variation of dissolved in the 5 selected lakes have been shown in figure 2. Electrical conductivity does work as an important parameter in evaluation of lake water because it helps directly in calculating the level of dissolved salts present and indirectly points out the quantity of inorganic pollutants in that water.

Electrical conductivity has shown variation from lake to lake. Electrical conductivity varied from 349-580 µS/cm. Lake5 has the maximum average value of EC because it supports large amount of flora and fauna. Hydrophytes are rich with nutrients and organic and inorganic salts due to which EC of the water increases in which they live, die and decay.

Table 3. Correlation of Cu between water, sediments and hydrophytes.

Cu		Water	Sediment	Typha	Persicaria
Correlation	Water	1	0.01655	-	0.81974
Correlation	Sediment	0.01655	1	-	0.15501
Correlation	Typha	0.03728	-0.38972	1	0.20101
Correlation	Persicaria	0.81974	0.15501	0.20101	1

The variation of electrical conductivity has been shown in the figure 3. Salinity of the water of all the lakes was measured using salinity meter. Average salinity of the lakes ranges from 0.022 to 0.35 ppt. The comparison of average salinity of the lakes has been shown in figure 4.

The amount of total dissolved solids was recorded in the water of lakes. All of the selected lakes have an average amount of TDS within the range. TDS have variation from 213-341mg/l in the water of selected lakes. The variation of TDS in the water of selected have been shown in the figure 5.

Table 4. Concentration of Zinc, Copper and Chromium in Sediments and water.

Sediments	Zn	Cu	Cr
	Ppm	Ppm	Ppm
Lake1	0.76	0.21	0.9
Lake2	0.68	0.27	1.96
Lake3	0.58	0.28	1.19
Lake4	0.78	0.25	2.24
Lake5	0.95	0.36	1.76
Water	Zn	Cu	Cr
	Ppm	Ppm	Ppm
PEQS*	5.0057	1.00114	1.00114
Lake1	0.12	0.06	0
Lake2	0.095	0.065	0
Lake3	0.06	0.235	0
Lake4	0.105	0.055	0
Lake5	0.055	0.05	0

Table 5. Concentration of Zinc, Copper and Chromium in *Typha angustifolia*.

Typha	Zn	Cu	Cr
	Ppm	Ppm	Ppm
Lake1	0.2	0.08	0
Lake2	0.14	0.1	0
Lake3	0.18	0.08	0
Lake4	0.15	0.08	0
Lake5	0.16	0.07	0

Temperature of the lakes was also noted on site with the help of digital thermometer. Temperature of all of the 5 lakes was moderate. Lake 3 showed the comparatively high temperature because it is a shallow lake, and its area to depth ratio is large. So it is receiving more sun rays which were the cause of its relatively increased temperature.

The comparison of temperature between the lakes has been shown in the figure 6.

Nitrates were also found within acceptable limits of USEPA for the propagation of aquatic life i.e. =90 mg/l. Nitrates are ranging from 1.43 to 4.17 mg/l in the lakes under study. In lake 1 the average value of nitrate was 4.17 mg/l it is the maximum concentration of nitrates as compared to other lakes.

Table 6. Average Concentration of Zinc, Copper and Chromium in Persicaria amphibian**.**

Persicaria	Zn	Cu	Cr
Lake1	0.18	0.09	0
Lake2	0.2	0.1	0
Lake3	0.38	0.12	0
Lake4	0.19	0.07	0
Lake5	0.22	0.09	0

This high concentration in this lake may be due to the reason that the nearby area is cultivated area; use of fertilizers increases the amount of nitrates.

The relatively minimum concentration of nitrates was found in lake2 i.e. 1.43 mg/l, because this lake is situated in the low lying area and it is surrounded by dense growth of vegetation.

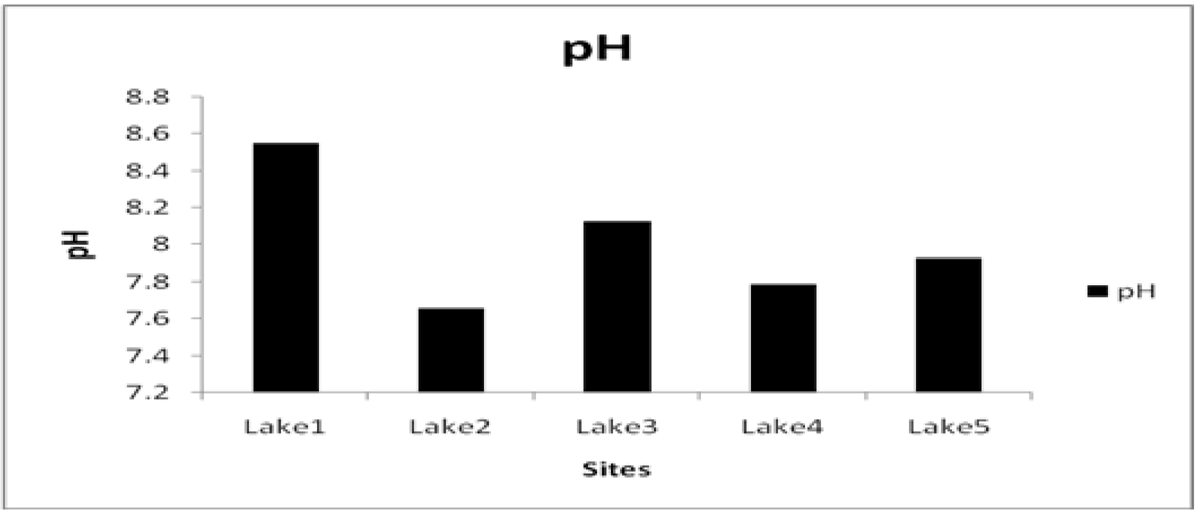

Fig. 1. Comparison of average pH in the 5 lakes.

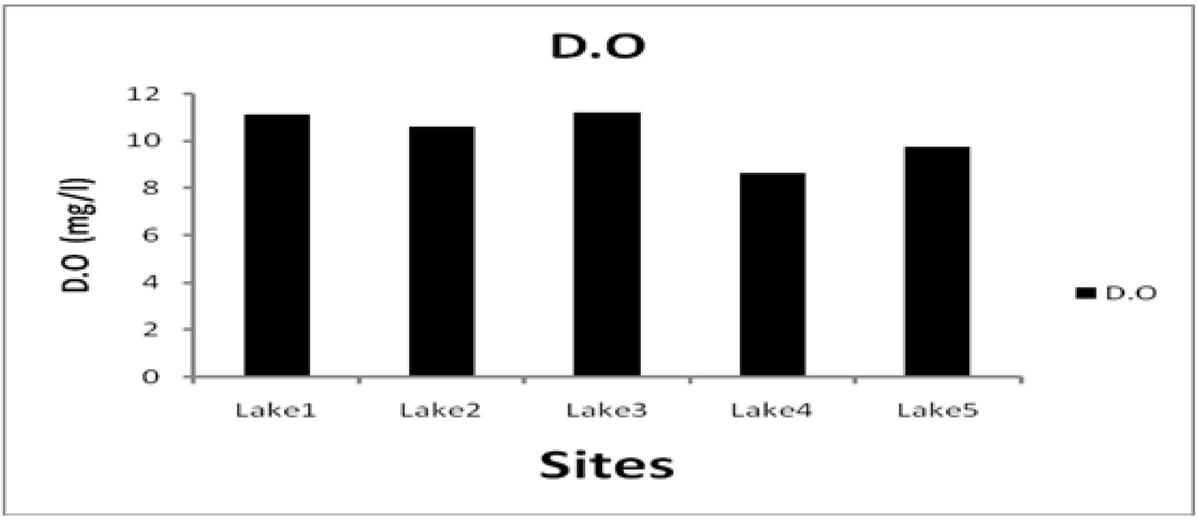

Fig. 2. Comparison of average Dissolved Oxygen in the 5 lakes.

This vegetation protects the lake from anthropogenic effects and the run off get filtered by the vegetation before entering the lake. The comparison of phosphates has been shown in figure 7.

Maximum allowable range of sulphates in surface is 500 mg/l. The phosphate determined in all examined lakes was found within acceptable range. In these lakes concentration of sulphates was determined from 6.27 to 85.05mg/l.

Lake3 contains the maximum concentration of sulphates as compared to other lakes, the reason is that it is in the range of anthropogenic effects and the other are relatively less affected by anthropogenic effects. The comparison of presence of sulphates has been shown in figure 8.

Concentration of phosphate was very low in all the lakes ranging from 0.026-0.4 mg/l. Phosphates determined in lake 1, 2, 4 and 5 were 0.029, 0.026, 0.027 and 0.0393 mg/l respectively.

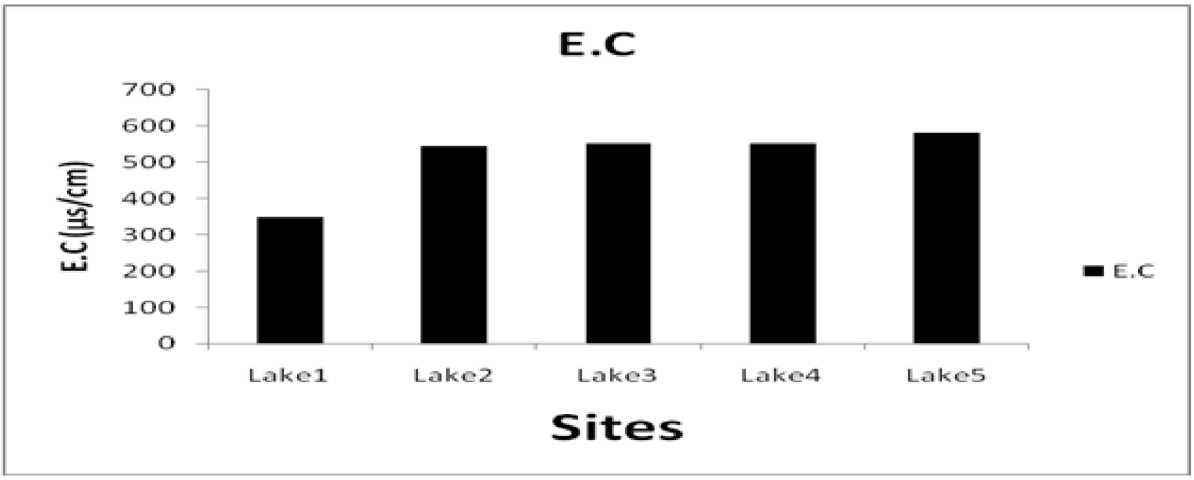

Fig. 3. Comparison of average Electrical Conductivity of 5 lakes.

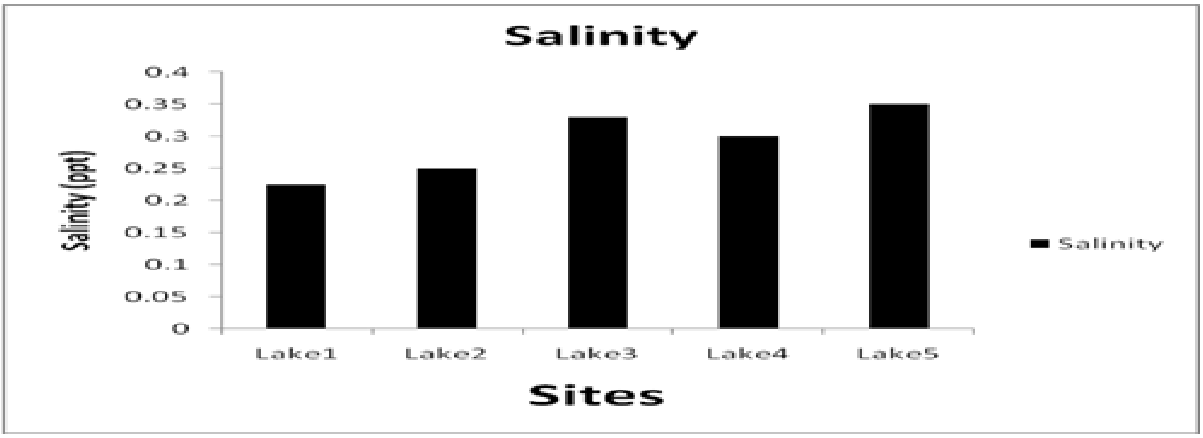

Fig. 4. Comparison of average salinity of 5 lakes.

Lake 3 contains the relatively higher concentration of phosphates i.e. 0.04 mg/l, this is because there are a number of small restaurants on one bank of this lake which are a source of pollution to this lake. In myriads of studies, observed concentration of phosphorus was found too low to cause any adverse health impact. The variation of phosphates has been shown in figure 9.

Chlorides were also found within allowable limits of USEPA guidelines for the propagation of aquatic life in the lakes. Chlorides are ranging from 30.84 to 55.66 mg/l in the lakes under study. Again the maximum concentration of chlorides was found in Lake 3 due to anthropogenic effects. The comparison of average concentration has been shown in figure 10.Number of total colifroms was also determined using the most probable number counting method (MPN).

All of the lakes showed coliforms in allowable range except the lake 2 in which there is high number of coliforms. It shows that its water highly contaminated with coliforms. The reason of contamination of water of this lake seems to be cattle. Cattles are using this for grazing upon its vegetation, drinking its water and bathing in it. Feces of cattle are the source of contamination. The comparison of average coliforms has been shown in figure 11.

Heavy metals: The presence of heavy metals exceeding prescribed limits can cause disturbance in survival of species and stability of the ecosystem (Seralathan *et al.*, 2008). Heavy metals were analyzed in the water, sediments and hydrophytes of the selected lakes. Three metals were assessed in the samples i.e. Zinc, Copper and Chromium. Pearson Coefficient of Correlation was applied on the results.

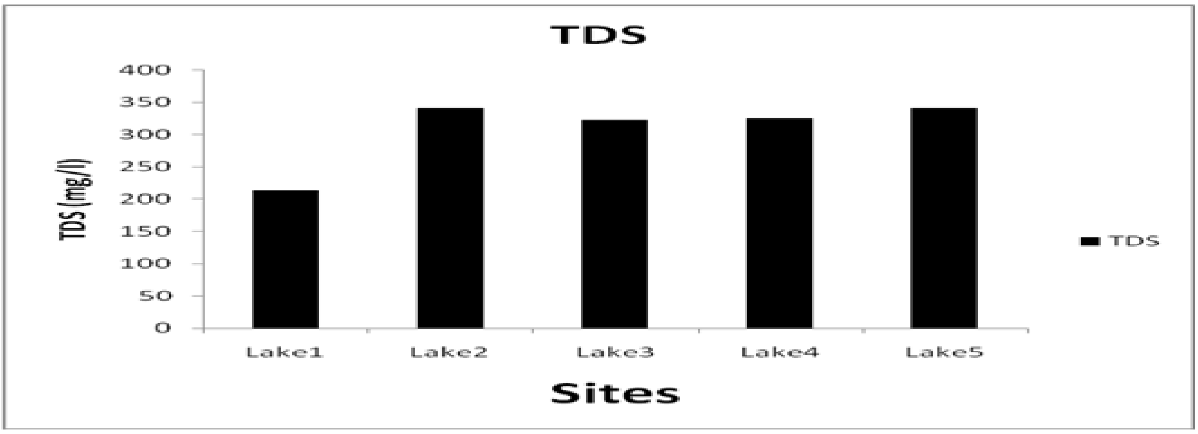

Fig. 5. Comparison of total dissolved solids in 5 lakes.

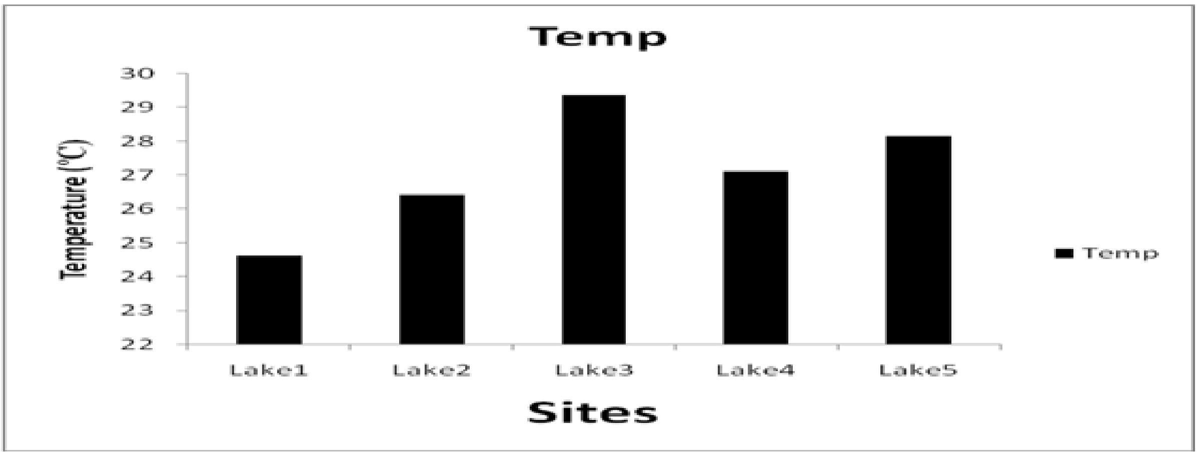

Fig. 6. Comparison of average Temperature of 5 lakes.

Coefficient of Correlation showed by water, sediments and plants for these three metals is shown in following paragraphs.

Zinc: In case of Zinc if coefficient of correlation (r) for water is 1 then r value for sediments is -0.0965 the negative shows the inverse relationship between water and sediments for retaining the Zn i.e. if there is increased concentration of Zn in water, then the concentration of Zn will be decreased in the sediments and vice versa.

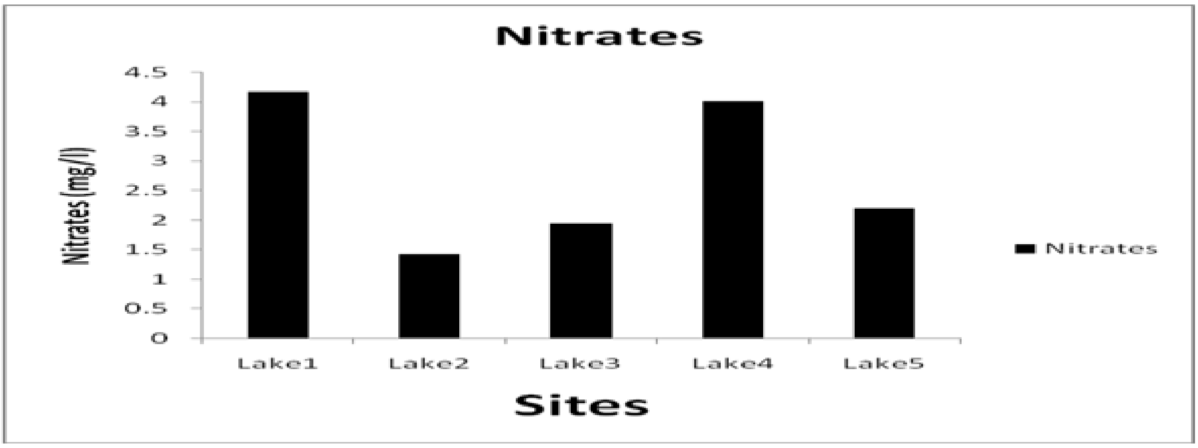

Fig. 7. Comparison of Nitrates of 5 lakes.

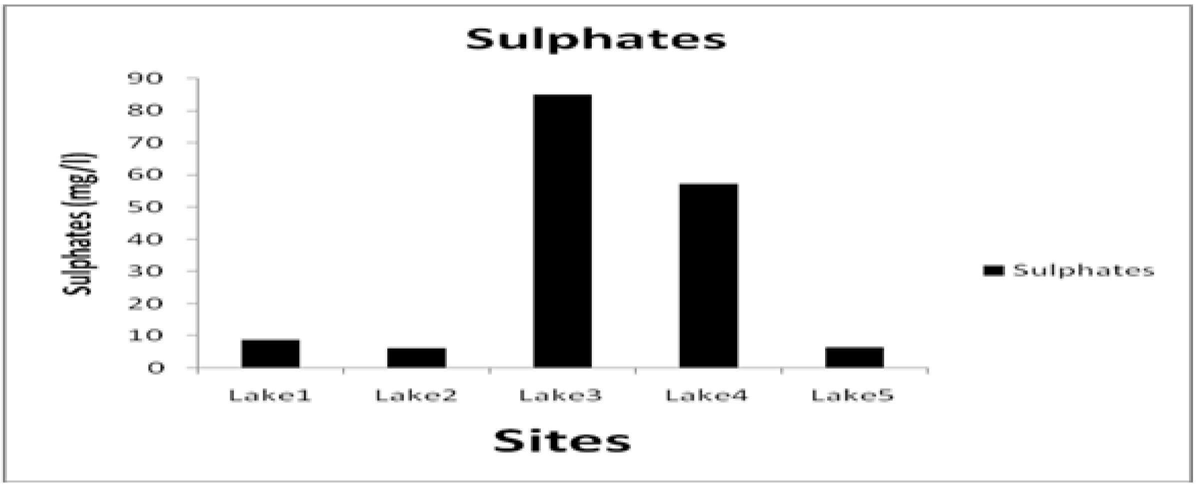

Fig. 8. Comparison of Sulphates in 5 lakes.

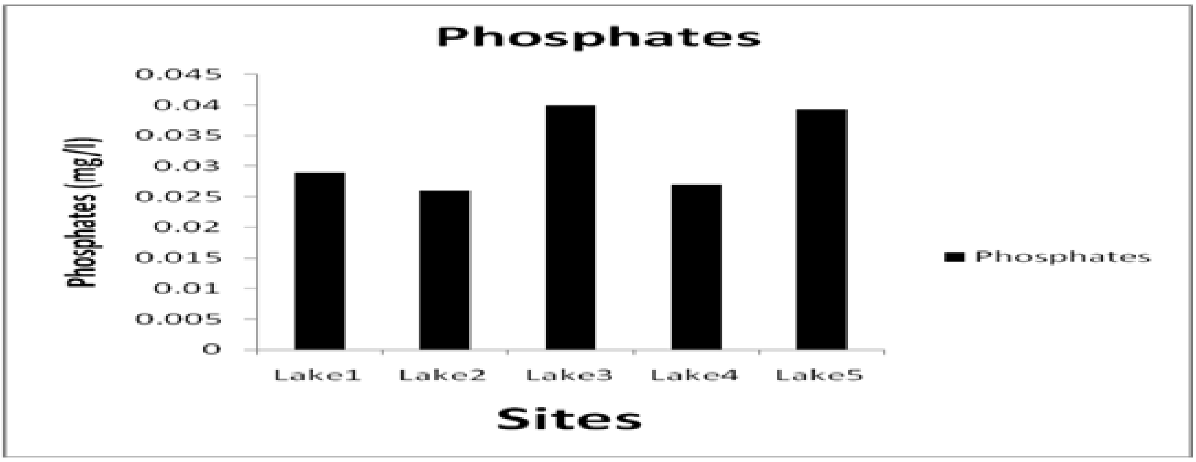

Fig. 9. Comparison of Phosphates in 5 lakes.

In our samples sediments have showed the greater concentration of Zn in them as compared to samples of water and hydrophytes. But during some geomorpholigical changes sediments may release Zn to the water, hence increasing the concentration of Zn in water and there will be decrease in the concentration of Zn in sediments. *Persicaria amphibia* has also showed the negative correlation of up taking of Zn from water. There is a positive relationship of Zn up taking in *Typha* and water which means an increase in the concentration of Zn in water will increases the up taking of Zn in Typha and vice versa. The aquatic macrophytes work effectively to remove the different metals from the environment (Lilit and Baban 2006). They lessen the impact of alarming concentration of heavy metals.

W.A Maher *et al.* 1992 determined Zn concentration in water, sediments and aquatic vegetation in Lake Burley Griffen, they found that sediments contained the most concentration of Zn than the water or aquatic plants samples. Coefficient correlation is shown in Table 2.

Copper: In case of Copper the Correlation of water with sediments and Persicaria is positive i.e. if there is an increase of copper concentration in water the relative storing or up taking capacity of sediments and persicaria will be increased. *Typha* has shown the negative value of r in the case of copper. It can be explained in the way that if there is less concentration of copper in water in the presence of *Typha* then we can conclude that there will be relatively more concentration of copper in typha than in water.

In study of the removal of heavy metals from industrial wastewater in constructed wetlands, it was concluded that hydrophytes contained the highest concentration of Cu in heavy metals contaminated aquatic ecosystem, and the *Typha* is one of the most effective accumulator of Cu as compared to the other hydrophytes under study (S. Khan *et al.*,2009). Coefficient correlation is shown in Table 3.

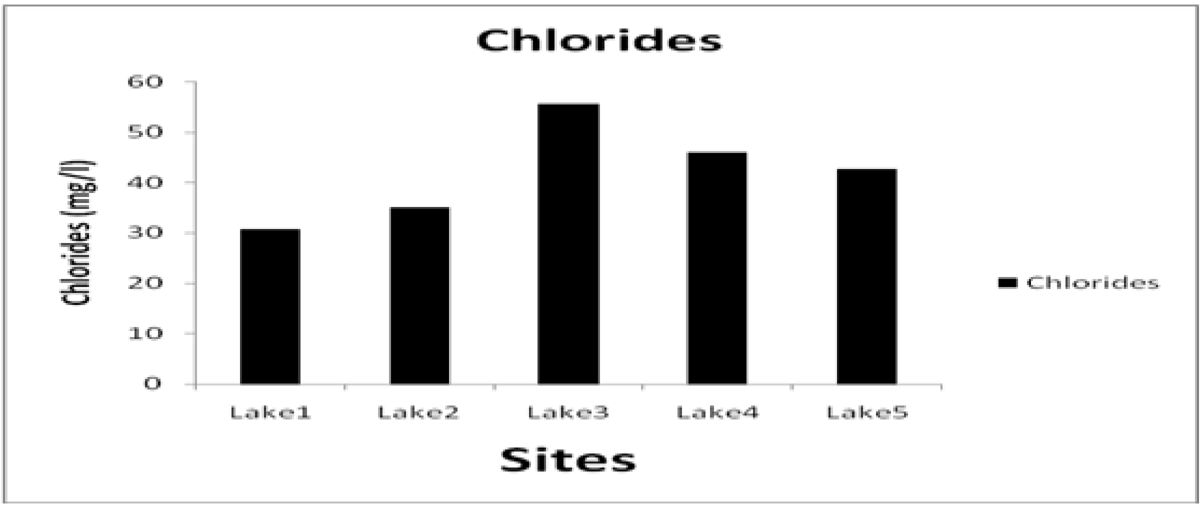

Fig. 10. Comparison of Chlorides in 5 lakes.

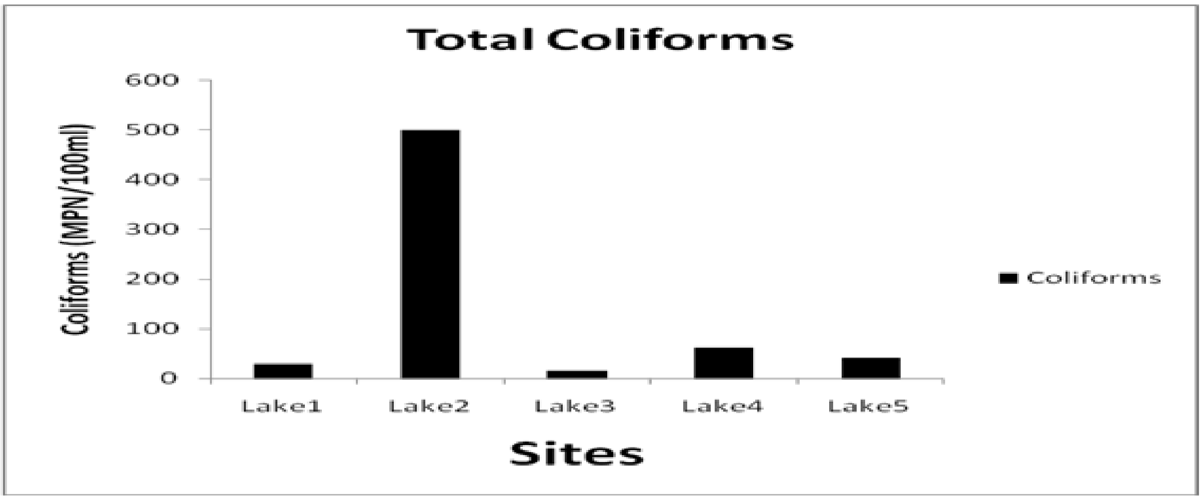

Fig. 11. Comparison of Total Coliforms in 5 lakes.

Chromium was detected on in sediments. Concentration of chromium in water and hydrophytes was below detectable range of instrument. So there is no correlation of sediments with water and hydrophytes because instrument has shown the 0.0 ppm concentration of chromium in water and hydrophytes so their correlation with sediments is also zero. Coefficient correlation is shown in Table 4.

Conclusion

Water quality of all the lakes under study was found within the permissible range for the propagation of aquatic life established by USEPA. Concentrations of heavy metals i.e. Zinc, Copper and chromium were found most in sediments, less in hydrophytes and least in water samples. This shows that sediments are the main storage of heavy metals in aquatic ecosystems.

Coefficient of Correlation also showed sediments as the main storage sites for heavy metals in these aquatic ecosystems. Hydrophytes should be protected around and within the lakes these hydrophytes are buffering the lakes against anthropogenic effects. Land encroachment for agricultural and other purposes should be checked. Restaurants and other buildings should be established to a reasonable distance from the lakes that users and the buildings do not disturb the ecosystem. Water harvesting from the lakes for agricultural and other purposes should be within prescribed limits of National Environmental Quality standards.

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