▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol. 18, No. 2, April 2007, pp. 61-68 ISSN 1021-1012

STUDIES ON RELATIONSHIP BETWEEN SEASON AND INORGANIC ELEMENTS OF KALLAR KAHARLAKE (CHAKWAL), PAKISTAN

Nadeem Raza, Shahida B. Niazi*, M. Sajid
Department of Chemistry, Bahauddin Zakariya University, Multan 60800, Pakistan.
Farhan Iqbal, Muhammad Ali
Institute of Pure and Applied Biology, Bahauddin Zakariya University,Multan.

Abstract

The present study is designed to demonstrate the seasonal variations in inorganic elements of Kallar Kahar Lake, for a period of one year from December 2001 to November 2002. Water samples were collected on monthly basis. Ten metals sodium, potassium, magnesium, iron, nickel, cobalt, copper, cadmium, lead and zinc were analyzed in lake water using atomic Absorption Spectrometry and relationship was developed with reference to season. The concentration ranges found in lake water for Na, K, Mg, Fe, Ni, Co, Cu, Cd, Pb and Zn are 250.10 - 650.14, 20.27 - 33.88, 51.48 - 249.12, 0.20 - 5.46, 0.04 - 0.25, 0.01 - 0.16, 0.01 - 1.20, 0.01 - 0.05, 0.01 - 0.30 and 0.44 - 2.82 ppm respectively. The average values of all the metals were significantly different through out the season. The overall levels of inorganic elemental concentrations in water were not within the safe limits during the study period and use of this lake water for domestic and agricultural purposes could be a threat for life.

Keywords: Atomic absorption spectrometry, inorganic elements, Kalar Kahar Lake, water samples.

INTRODUCTION

Kallar Kahar Lake is one of the famous wetland areas in Pakistan. It is 25 Km in north from Chakwal. Kallar Kahar Lake is famous site for migratory birds during winter season. Rain and mountain brooks are the major water source of the lake. The lake water is brackish and is not used for domestic and drinking purpose but for recreation as to some extent for agricultural purposes in the area. At present, Lake is contaminated by sewage water and a Government project for the cleanliness and betterment of lake is in progress.

Metals are natural constituents of the fresh water environment. Some metals are essential for life, some are merely beneficial and many are highly toxic. The concentrations at which metals may be considered important is variable, as some are essential at low concentration levels yet toxic at others. Human activity has increased the levels of metals in many of the natural water systems and it has raised concerns regarding the metal bioaccumulation and human health hazards. With increasing public awareness of environmental contamination, there is a growing need to monitor, evaluate, manage and remediate ecological damage [Kushlan 1993].

* author for correspondence

The concentration of metals in surface water depends on several factors: airborne contribution from long-range transport; local point sources; natural presence in bedrock and soils and airborne contribution from soil dust [Frank and Cross 1974]. In addition, conditions in the catchments and in the lake are important for the mobility and availability of metals in the water. As rivers and lakes are exposed to atmospheric depositions of anthropogenically derived trace elements, such elements can create harmful effects on environmental and human health due to their toxicity and bioaccumulation in various environmental compartments [Leonard 1971, Boyd and Tucker 1998]

During recent years, the study of inorganic metal concentration in fresh water bodies to evaluate the contamination level is becoming popular both in Pakistan and world wide. A number of physico-chemical studies in various water bodies have been carried by many researchers [Chaudhary *et al.* 1999, Vazquez *et al.* 2000, Salam *et al.* 2002, Farkas *et al.* 2003, Bangash and Alam 2004, Iqbal *et al.* 2004, Samina *et al.* 2004] but still a lot of work needs to be done.

The objective of the present study was to estimate the concentration of inorganic elements in the Kallar Kahar Lake waters and to observe the effect of monthly variations on them. This is a preliminary work as no data regarding elemental concentration is available for this lake.

MATERIALS AND METHODS

REAGENTS

Deionized water used throughout the work was obtained from Pak Arab Fertilizer Ltd. Multan. All the chemicals used for preservation and preparation of calibration standards were of Merck Anal. R. grade. Nitric acid, used was 65% with sp.g. 1.40. Standard stock solutions (1000 ppm) of Na, K, Mg, Fe, Ni, Co, Cu, Cd, Pb, and Zn were prepared by dissolving appropriate amounts of their respective salts in 5% nitric acid. These solutions were diluted with 1% nitric acid to obtain working standard solutions of appropriate concentration for flame atomic absorption spectrometric (FAAS)Measurements.

SAMPLE COLLECTION

Triplicate water samples were collected on monthly basis from the subsurface in pre-washed and dried polythene bottles having a capacity of 1.5 liter. The sampling period ran during December 2001 to November 2002. For transportation towards laboratory, no stabilizers or buffer solutions were added; however, 1% nitric acid was used for dilution purposes. These samples were immediately used for metal analysis.

METAL ANALYSIS

Metals were analyzed using FAAS technique. A Hitachi model A-1800 atomic absorption spectrometer equipped with standard burner and air acetylene flame was used. Standard hollow cathode lamps were used as a radiation source for sodium, potassium, magnesium, zinc, iron, copper, nickel, cadmium, lead and cobalt. To calculate the absorbance data, atomic absorption (concentration) measurement mode with integration of absorbance signals, was used. The optimum instrumental conditions for each element are given in Table 1. Various parameters calculated statistically for different metals have been listed in Tables 2 and 3.

Table 1: Instrumental parameters for the Determination of Elements by FAAS.

Elements	Wave length (nm)	Lamp current (mA)	Slit (nm)	Air flow Kg cm^{-2}	Acetylene flow Kg cm^{-2}	Burner height (mm)
Ni	232	10	0.2	1.6	25	10
Fe	248.3	10.5	0.2	1.6	30	7.5
Co	240.7	10	0.2	1.6	35	10
Cu	324.8	7.5	1.3	1.6	30	7.5
Cd	228.8	7.5	1.3	1.6	25	7.5
Pb	283.3	7.5	1.3	1.6	30	7.5
Mg	285.2	7.5	2.6	1.6	20	7.5
K	766.5	10	2.6	1.6	30	7.5
Na	589	10	0.4	1.6	25	7.5
Zn	213.8	10	1.3	1.6	20	7.5

Table 2: Statistical Parameters for the Distribution of Macronutrients and Essential Elements.

	Na	Mg	K	Zn	Fe	Cu
Minimum	250.10	51.48	20.27	0.44	0.2	0.01
Maximum	650.14	247.12	33.88	1.94	5.46	1.20
Mean	396.97	114.50	28.19	1.41	1.45	0.26
Median	344.51	92.66	29.23	1.20	0.80	0.10
Standard Deviation	134.95	63.20	4.43	1.17	1.56	0.44
Sample variance	18221.60	3994.70	19.62	1.377	2.42	0.19

Table 3: Statistical Parameters for the Distribution of Macronutrients and Essential Elements.

	Ni	Mg	K	Zn
Minimum	0.04	0.01	0.01	0.01
Maximum	0.25	0.05	0.3	0.16
Mean	0.12	0.028	0.16	0.062
Median	0.10	0.030	0.14	0.060
Standard Deviation	0.06	0.01	0.11	0.047
Sample variance	0.004	0.000	0.012	0.002

Computation work was done using the developed methods [Ansari and Iqbal 1993, Chaudhary *et al.* 1999, Salam *et al.* 2002]. Seasonal variation in elemental concentration was evaluated using computer packages Mini Tab and Excel.

RESULTS AND DISCUSSION

The statistical parameters on the distribution of macronutrients (Na, K and Mg), essential elements (Fe, Zn and Cu) and non essential elements (Ni, Co, Cd and Pb) in Kallar Kahar lake water samples are given in Tables 2 and 3. All metals showed seasonal variations through out the study period (Fig. 1) and average values of all the inorganic metals were significantly different in all the months during present study. To find the accuracy and precision of data on the distribution of metals in Kallar Kahar lake water, analysis of variance was carried out and it was found that the concentration of metals varied significantly during summer and winter months as given in Table 4. The analytical data of seasonal variation of metal contents is given in Table 5. Variations in metal contents in water may be due to the fact that in summer season fresh water from mountains dilutes the concentration of some metals and at the same time concentration of other metals increases because of rainy water full of salts from mountains and rocks. In winter season water level in lake is very low that concentrates the metals thus increasing the levels of various metals and non metals. Dissolved metallic ions creating turbidity and discoloration, can precipitate down to form the bottom sludge. Limits on individual metals are usually based on toxicity levels. Various metals including the essential micronutrient are toxic to organisms at their higher concentrations. Normally the free form of the element is potentially toxic to aquatic biota; complexation with organic ligands significantly reduces the concentration and adverse effects. Other factors such as pH and hardness also effect the concentration of free metal ions and thus regulate toxicity. However, several regulatory agencies have specified limits on total metals to provide a sufficient safeguard against possible synergistic effects. These limiting stream concentrations are generally set at 1.00 g ml^{-1} of total heavy metals [Frank and Cross 1974].

Table 4: ANOVA table showing the comparison between elemental concentrations in Kallar Kahar Lake waters.

Element	Df	SS	MS	F	P
Nickel	11,99	0.291	0.026	53.05	0.000
Iron	11,99	79.98	7.27	7767.43	0.000
Cobalt	11,99	0.071	0.006	72.83	0.000
Copper	11,99	6.248	0.568	375.93	0.000
Cadmium	11,99	0.0068	0.000061	8.02	0.000
Lead	11,99	0.422	0.03	44.20	0.000
Sodium	11,99	1279160	116287	1.7E +05	0.000
Magnesium	11,99	174946.20	15904.20	1.9E +04	0.000
Potassium	11,99	4530.48	411.862	494.23	0.000
Zinc	11,99	28.266	2.569	7.7 E + 04	0.000

*Df stands for degree of freedom, SS for sum of squares, MS mean of squares, F test, and P degree of leaveness, E for power of 10.

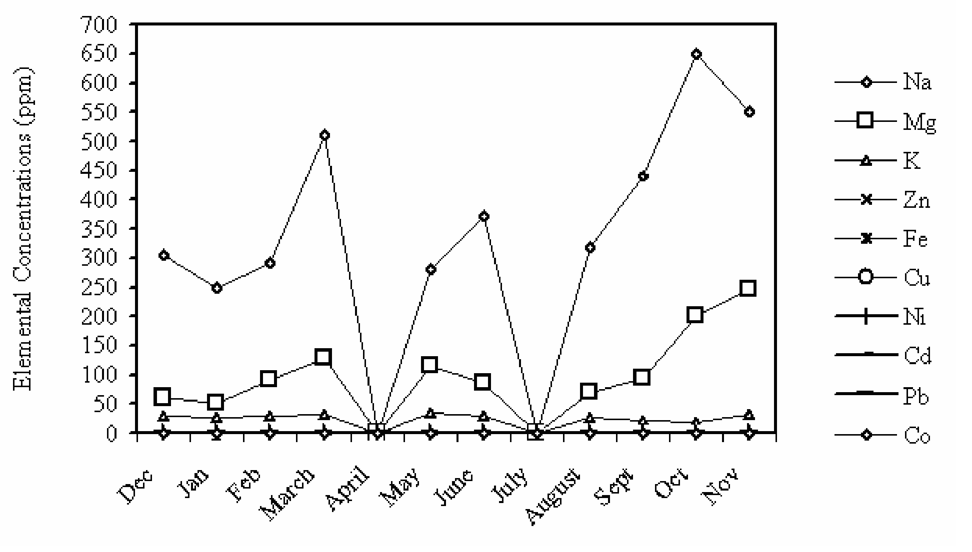

Fig. 1: Seasonal Variation of Metal concentration in Kallar Kahar Lake water.

Table 5: Analytical Data on the Seasonal Variations of Metal Contents (ppm) in Kallar Kahar Lake Waters.

Month	Ni	Fe	Co	Cu	Cd	Pb	Na	Mg	K	Zn
Dec. 2001	0.04±0.02	2.64±0.08	0.01± 0.03	0.15±0.02	0.01±0.01	0.28± 0.06	304.23± 0.12	60.34± 0.20	29.48± 0.30	1.94± 0.21
Jan. 2002	0.25 ±0.01	2.36±0.13	*	0.13±0.01	0.02±0.01	*	250.10± 0.23	51.48± 0.31	28.00± 0.20	*
Feb.	0.13 ±0.01	0.87±0.03	*	1.17±0.01	0.03±0.01	*	292.38± 0.10	91.30± 0.08	28.98± 0.10	0.45± 0.11
March	0.08 ±0.01	1.23±0.06	*	1.20±0.01	*	0.17± 0.04	510.91± 0.21	128.10± 0.02	31.31± 0.23	2.82± 0.08
April	0.06 ±0.06	5.46±0.08	0.05± 0.04	0.10±0.01	*	0.09± 0.01	*	*	*	*
May	0.08±0.06	0.48±0.01	0.06± 0.02	0.10±0.01	0.02±0.01	0.11± 0.06	281.97± 0.23	115.25± 0.01	33.88± 0.38	*
June	0.12±0.03	0.23±0.03	0.16± 0.06	0.06±0.01	0.03±0.01	0.30± 0.11	371.51± 0.51	86.02± 0.03	30.50± 0.39	*
July	0.21±0.01	0.34±0.07	*	0.10±0.01	0.05±0.02	*	*	*	*	0.44± 0.06
Aug.	0.10±0.02	0.20±0.01	*	0.04±0.01	0.02±0.01	*	317.51± 0.08	70.11 ± 0.01	27.26± 0.04	*
Sept.	0.13±0.02	0.72±0.08	0.03± 0.02	0.01±0.01	0.01±0.01	*	440.20± 0.13	94.01± 0.04	20.88± 0.38	*
Oct.	0.11±0.01	0.42±0.03	0.06± 0.03	0.01±0.01	0.03±0.01	*	650.14± 0.26	201.3± 0.03	20.27± 0.38	*
Nov. 2002	0.10±0.04	2.52±0.03	0.06± 0.04	0.03±0.01	0.03±0.01	0.01± 0.10	550.79± 0.35	249.12± 0.04	31.33± 0.47	*
Mean	0.12±0.02	1.46±0.05	0.04± 0.06	0.26±0.01	0.03±0.01	0.08± 0.06	397.97± 0.02	115.71± 0.02	28.29± 0.029	0.47± 0.02
Range	0.04-0.25	0.20-5.46	0.01- 0.16	0.01-1.20	0.01-0.05	0.01- 0.30	250.10- 650.14	51.48- 249.12	20.27- 33.88	0.44- 2.82

* meant for no observations

It has been observed that sodium concentration increases in winter season when the lake water level is low and decreases in summer season when water flow in lake is high. The sodium concentration ranged between 250.10 to 650.14 ppm during the study period. The maximum concentration (650.14 ± 0.26 ppm) was observed in October and the minimum (250.10 ± 0.23 ppm) in January with an average of 397.97 ppm. The concentration of sodium ions becomes remarkably high in saline and brackish waters. The higher concentration of sodium limits the biological diversity due to osmotic stress. If sodium contents in the form of chloride and sulphates are very high, it makes the water salty and unfit for human consumption, as in the case of present study. High sodium content in irrigation water brings about puddling of soil. As a result the water intake of soils gets reduced and it becomes hard in which the germination of seeds become difficult.

Potassium plays the same role in water as the sodium. Although it is present in small amounts, yet it plays an important role in the metabolism of freshwater environments and is regarded as an important macronutrient. The potassium concentration ranged between 20.27 to 33.88 ppm during the study period. The maximum concentration (33.88 ± 0.38 ppm) was observed in May and the minimum (20.27 ± 0.38 ppm) in October with an average of 28.29 ppm.

Magnesium occurs in all natural waters. It has been an essential constituent of chlorophyll without which no ecosystem could work. The maximum concentration (249.12 ± 0.04ppm) of magnesium was observed in November and the minimum (51.48 ± 0.31 ppm) in January with an average of 115.71 ppm during the study period. High magnesium concentration in water gives an unpleasant taste and make it unfit for drinking purpose and reduces its utility for domestic use.

Of the essential metals (Fe, Zn and Cu), iron is regarded to be quantitatively the most important trace metal for autotrophs due to its indispensability for many enzymes and redox processes. Iron concentration up to 0.10 ppm is acceptable while 1.0 ppm or more in fresh water could be harmful for life. The average level of iron in present studies is 1.46 ppm that is above the safe limits [WHO 1990, EPA Quality Criteria 2003].

Zinc was not detected in January, April to June and from August to November but it showed seasonal variation in other months of study period. Zinc concentration was the maximum in March (2.82 ± 0.08 ppm) and the minimum in July (0.44 ± 0.06 ppm) with an average of 0.47 ppm during the study period.

The maximum concentration (1.20 ± 0.01 ppm) of copper was found in March and the minimum (0.01 ± 0.00 ppm) in September – October with an average of 0.258 ppm.

The maximum concentration (0.25 ± 0.01 ppm) of nickel was in January and the minimum (0.04 ± 0.02 ppm) in December with an average of 0.12 ppm during the study period. It may be anticipated that Ni in these waters could have its origin in the relevant rock structure, perhaps as nickel oxides, halides or other nickel contaminated compounds occurring naturally.

The cobalt concentration ranged between 0.01 to 0.16 ppm during the study period. Its levels were below the limit of detection during January - March and July - August.

Cadmium remained non detectable in March – April, however, it showed seasonal variation in other months of study period. The maximum cadmium concentration (0.05 ± 0.01 ppm) was observed in July and the minimum (0.01 ± 0.01 ppm) in December.

Lead was not detected in January-February and July - October. The maximum lead concentration (0.3 ± 0.11 ppm) was observed in June and the minimum (0.01 ± 0.10 ppm) in November with an average of 0.08 ppm during the study period. The origin of lead may be traced in ground rock sources, atmospheric fallout from vehicular emissions or in industrial effluents.

The presence of these metals in Kallar Kahar lake water may have its origin from calcareous and argillaceous matter containing non continuous rock structure in contact with water bed. Moreover, the source of water for this lake is mainly rainy water from the neighboring mountains. Waste water from local areas and industrial effluents is also contributing much in increasing the levels of macronutrients, essential and non essential elements.

A comparison of mean, median and other statistical parameters of the metals (Na, K, Mg, Fe and Zn) indicates that they do not follow normal distribution, thereby indicating some sources other than natural sources, responsible for their higher levels in lake water. Large standard deviation observed for Na, K, Mg, Fe and Zn reveals that their distribution in lake water is random, a fact that supports the above observation in terms of variable sources of contamination.

CONCLUSIONS AND RECOMMENDATIONS

From the present study it is concluded that overall concentrations levels of the inorganic elemental are not within the safe limit [WHO 1990, EPA Qualtiy Criteria 2003] throughout the period of study and water of Kallar Kahar Lake is not suitable for drinking, farming and for aquaculture.

Many chemical substances introduced into the environment from anthropogenic sources pose a threat to the functioning of aquatic ecosystems and the use of water for various purposes. Strengthened measures to prevent and control the release of these substances into the aquatic environment should be adopted.

- The precautionary principle should be applied when selecting water quality parameters and establishing the criteria to protect and maintain individual uses of waters.
- In setting water quality criteria, particular attention should be paid to safeguarding sources of drinking-water supply. In addition, the aim should be to protect the integrity of aquatic ecosystems and to incorporate specific requirements for sensitive and specially protected waters and their associated environments, such as wetland areas.
- Water-management authorities in consultation with industries, municipalities, farmers associations, the general public and others should agree on the water uses in a catchments area.
- Water-management authorities should be required to take appropriate advice from health authorities in order to ensure that water quality standards are appropriate for protecting human health.
- In setting water quality objectives for given water body, water quality requirements for its specific uses as well as downstream uses, should be taken into account.
- Water quality objectives for multipurpose use of water should be set at a level that provides the protection of the most sensitive use of a water body.
- Established water quality objectives should be considered as the ultimate goal or target value indicating a negligible risk of adverse effects.
- The public should be kept informed about water quality objectives that have been established and the measures taken to achieve them.

References

Ansari, T.M. and Iqbal, M.A. (**1993**) "Computer programme for comprehensive treatment of data in Flame Atomic Absorption Spectroscopy", *J. Anal. Environ. Chem*., **2**, 84-89.

Bangash F.K. and Alam, S. (**2004**) "Extent of pollutants in the effluents of Hyatabad industrial estate, Peshawar", *J. Chem. Soc. Pak.* **26**(3), 271-278.

Boyd, C.E. and Tucker, C.S. (**1998**) "Pond Aquaculture Water Quality Management", Kluwer Academics Publishers, London.

Chaudhary, A., Salam, A., Ansari, T.M. and Nadeem, S. (**1999**) "Studies on the effect of seasonal variations on physical and chemical characteristics of Indus River Water", *J. Pure and Appl. Sci.,* **17**, 26-33.

Farkas, A., Salanki, J. and Varanka, I. (**2003**) "Crustaceans as biological indicators of heavy metal pollution in lake Balaton (Hungary)", *Hydrobiologia*, 506-509.

Frank, L. and Cross, P.E. (**1974**) "Management Primer on Water Pollution Control" Technomic Publishing Co, Inc. West Port, 23-27.

Iqbal, F., Ali, M.Salam, A. and Khohkar, Y. (**2004**) "Studies on relationship between season and inorganic elements of river Soan at Dhoak Pathan Bridge (Chakwal), Pakistan", *P.J.B.S.* **7**(1), 93-95.

Kushlan, J.A. (**1993**) "Colonial water birds as bio- indicators of environmental change", *Col. Water Birds*, 223-251.

Leonard, L.C. (**1971**) "Water and Water Pollution", Marcel Dekker Inc., New York, p. 1.

EPA (**2003**) "Quality Criteria for Water", EPA-816-F-03-016, United States Environmental Protection Agency, Washington, D.C.

Salam, A., Ansari, T.M., Tariq, N. and Akhtar, Q.A. (**2002**) "Effect of body size on metal concentration in farmed Cirrhinus mirgala", *Asian Fish. Sci.,* **15**, 329-334.

Samina, J., Jaffar, M. and Shah, M.H. (**2004**) "Physico-chemical profiling of ground water along Hazara strip, Pakistan", *J. Chem. Soc. Pak.* **26**(3), 288-292.

Vazquez, M.D., Fernandez, J.A., Lopez, J. and Carballeira, A. (**2000**) "Effects of water acidity and metal concentration on accumulation and within plant distribution of metals in the aquatic bryophyte", *Fontinalis antipyretica. Wat. Air Soi. Pollu.* **120**, 1-19.

WHO (**1990**) "International Standards for Drinking Water", 3rd ed., Geneva, p. 34.