Comparative Statistical Approach for the Assessment of Pollution of Heavy Metals in Rawal Lake Water and Main Streams Entering Rawal Lake

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This study was conducted to assess the distribution of heavy metals (Cr, Co, Cd, Zn, Ni, Cu, Mn and K) in water and liquid waste samples at different stations of Rawal Lake and main streams entering Rawal Lake (Pakistan). The samples were analyzed by flame atomic absorption spectrophotometer. The results were discussed in view of quality standards set by Environmental Protection Agency. At most sites of Rawal Lake, concentration of Ni was relatively high and exceeded the permitted levels. Statistical methods of relevance to the trace metal data have been applied such as standard deviation, average concentration and correlation coefficients for investigating the distribution pattern of metals in water and liquid waste system.

Key words: Water pollution, Heavy metals, Statistical analysis, Rawal Lake.

Introduction

The problem of water quality control has received special attention in the wake of fast urbanization and industrialization whereby both underground and surface water resources face a greater threat of chemical befoulment. Fresh water resources are threatened by deterioration of water quality. The seriousness of the situation has been recognized in developing countries too where agricultural and industrial activities have started causing an undeliberated exposure of the water resources to potentially harmful chemicals fed directly or indirectly to water masses either through seepage or surface run-off (Peter and Douben 1989).

In line with the objective to establish a base for water quality control, attempt has been made in the present investigation to examine Rawal Lake water and liquid wastes entering from main streams with respect to their quality through the evaluation of heavy metal concentrations. The toxic properties of numerous inorganic compounds especially those of the heavier metallic elements have been known for years. The detection of these metallic substances in water at concentrations approaching toxic level has created a great amount of global interest (Scottg and Domngo 1996).

Determination of trace metals in water samples is difficult because the concentrations of these metals are minute. These trace metals occur in diverse forms. Large concentrations of

interfering matrix also increase the difficulty of determination (Hellmann 1987).

Many different methods have been used to analyze water and waste water samples, Including Inductively Coupled Plasma Emission Spectrometry (ICP-AES), Neutron Activation Analysis (NAA), Cathodic Stripping Voltammetry (CSV) and Atomic Absorption Spectrometry (AAS) etc; each method has its particular advantages (Jagner 1993).

Recent emphasis on heavy metal research in the environment has shifted from the study of total metal concentrations. General analysis of water quality was included to provide some information on the status of pollution (if any) on the Rawal Lake and waste water streams entering it. Lakes and reservoirs are traditionally valued resources to human society. They provide a multitude of uses and are prime regions for human settlement and habitation. Uses include drinking and municipal water supply, industrial and cooling water supply, power generation, navigation, commercial and recreational fisheries, body contact recreation, boating and other aesthetic recreation. In addition, lake water is used for agricultural irrigation, canalization and for waste disposal. It has been commonly believed that lakes have an infinite ability to absorb or dilute industrial and municipal waste (Changzhou 1996).

Water is a natural resource that cannot be replaced, but can be regenerated. Good water quality in lakes is essential in maintaining recreation and fisheries and in the provision of

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municipal drinking water. These uses are clearly in conflict with the degradation of water induced by agricultural use and by industrial and municipal waste disposal practices. The management of lake water quality is usually directed to the resolution of these conflicts (Loizidou and Kapetanios 1993).

This paper describes water-quality problems associated with water and waste water streams entering Rawal Lake.

Materials and Methods

Study area and sampling stations. In the present study water and liquid wastes samples for chemical analysis were collected from Rawal Lake and main streams entering Rawal Lake. Fourteen sampling sites were selected for lake water sample collection. Six sampling sites were selected for the collection of waste water samples from three major streams, namely Bariimam, Banigala and Malpure drainage streams. Details of sample collection were compiled at the time of sampling. Each sample container was labelled so that its contents could be unequivocally identified as shown in Fig I.

Sample preparation . Water samples were stabilized at pH 2 with 5% nitric acid prior to filtration through Whatman filter paper No 40. These samples were directly aspirated for trace metal analysis by atomic absorption spectrophotometer (Jaleel *et al* 1996).

A wide variety of wet digestion and dry ashing procedures are available for the digestion of liquid waste samples. In the present investigation, a nitric acid based digestion method was followed (Boris and Gerta 1989). Special precautions were taken to avoid trace metal contamination during the process. The acid base digestion procedure involved addition of an accurately weighed quantity of 50 ml of the liquid waste samples to 25 ml of nitric acid, which was heated on hot plate (Model BHS-2) at 140 ± 1^0C, until one third of the sample is left behind. At this point, the digested samples were filtered with additional washing. Each sample was transferred to a 100 ml volumetric flask and diluted to a fixed volume of 100 ml with deionized water.

Atomic absorption measurements of trace metal concentrations. Before estimating trace metal concentrations, optimum measuring conditions were determined as a function of acetylene flow rate, air flow rate, burner height and lamp current for all trace metals. The instrumental response was recorded at a high S/N ratio in each case using contine ously variable response control. The Shimadzu Atomic Absorption Spectrophotometer (AA-670) equipped with automatic background correction capability, was used for measuring the concentrations of trace metals in water and liquid wastes samples. Total concentrations of Cr, Co, Cu, Cd, K, Mn, Zn, and Ni

Rawal lake water sample
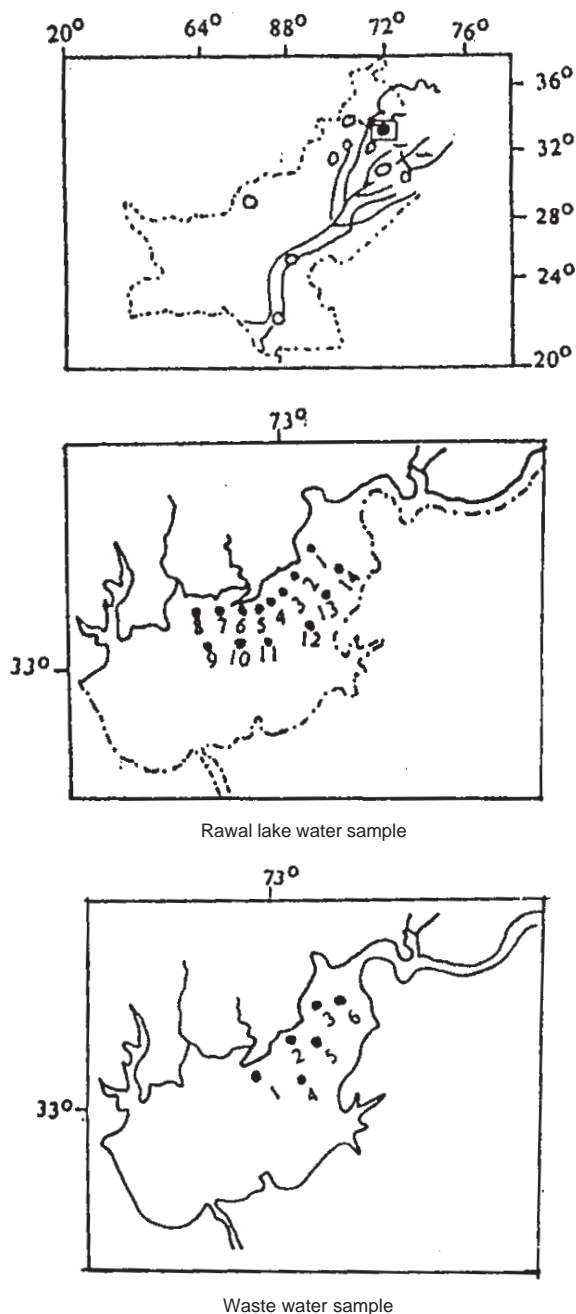
Waste water sample

Fig 1. Study area showing sampling sites: for Rawal Lake water (RW1-RW14), waste water samples entering Rawal Lake (DW1-DW8).

metals were measured by flame atomic absorption spectrophotometer under optimum operating conditions.

Standard solutions. Research grade chemicals were used for the preparation of standards. Normally, Merck chemicals were used to prepare aqueous standard solutions for each trace metal by dissolving an accurately weighed quantity of the relevant salt in doubly distilled water to yield a metal ion concentration of 100 mg l^{-1}. Appropriate aliquots were taken from these standards for subsequent dilution
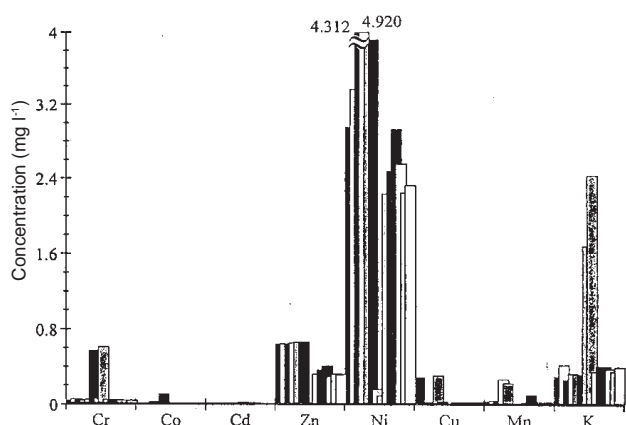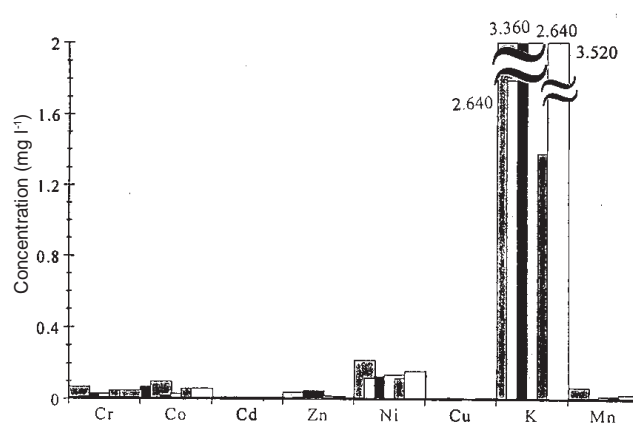
Fig 2. Levels of trace metals (mg l⁻¹) in water samples of Rawal Lake from RW1 through RW14 (left to right).

Fig 3. Levels of trace metals (Mg l⁻¹) in liquid wastes samples entering in Rawal Lake from DW1 through DW6 (left to right).

to the desired concentration level. Each time fresh standards were prepared and calibrated against the previous standards in order to check any probable discrepancy in the finished concentration.

Results and Discussion

The average concentrations of estimated trace metals, Cr, Co, Cd, Zn, Ni, Cu, K and Mn, in water and wastes water samples are given in Tables 1 and 2 and Fig 2 and 3. The reported values are averaged for triplicate subsamples of water and waste water (Dittrich *et al* 1995). The precision of triplicate measurements were found within ±2%, while inter laboratory checks between ± 1.5 - 2.0 % (USEPA 1992).

An analysis of the data in Table 1, indicated that in water samples, Ni had maximum concentration (4.920 mg l⁻¹) in RW4, while Co has lowest concentration below detection limit in RW2 as compared to other metal concentrations. However, maximum permissible level for Ni is 1.00 mg l⁻¹ and is quite serious. Almost all the water samples show Ni concentration above the maximum permissible limit. This high concentration may be attributed to surface run off and / or different streams entering Rawal Lake. People of these areas use hydrogenated oil, therefore, main streams entering Rawal Lake carrying high concentration of Ni (Jaffer *et al* 1985).

The examination of data in Table 2 showed that in waste water samples K was found to have maximum concentration (3.520 mg l⁻¹) in DW6.

Table 1
Concentration* (mg l⁻¹) of selected metals in various Rawal Lake water samples

Code/metal	Cr	Co	Cd	Zn	Ni	Cu	Mn	K
RW1	0.040	0.003	0.002	0.645	2.956	0.290	0.031	0.300
RW2	0.057	0.000	0.002	0.647	3.370	0.027	0.041	0.421
RW3	0.050	0.004	0.002	0.640	4.310	0.026	0.032	0.262
RW4	0.043	0.030	0.002	0.657	4.920	0.026	0.270	0.332
RW5	0.052	0.012	0.002	0.665	3.920	0.310	0.230	0.321
RW6	0.570	0.110	0.002	0.666	3.340	0.033	0.013	0.320
RW7	0.059	0.016	0.003	0.022	0.161	0.002	0.011	1.687
RW8	0.610	0.015	0.021	0.005	0.095	0.001	0.009	2.440
RW9	0.048	0.002	0.011	0.325	2.240	0.030	0.028	0.350
RW10	0.045	0.002	0.020	0.368	2.480	0.030	0.103	0.410
RW11	0.048	0.003	0.012	0.410	2.936	0.028	0.025	0.410
RW12	0.043	0.002	0.013	0.305	2.560	0.013	0.030	0.380
RW13	0.045	0.003	0.011	0.325	2.250	0.030	0.023	0.350
RW14	0.040	0.002	0.012	0.320	2.330	0.029	0.030	0.400

* ± SD values given in Table 3; RW, Rawal Lake water samples.

Table 2

Concentration* (mg l⁻¹) of selected metals in liquid wastes for various samples entering Rawal Lake

Code/Metal	Cr	Co	Cd	Zn	Ni	Cu	K	Mn
DW1	0.070	0.070	0.010	0.040	0.220	0.000	2.640	0.070
DW2	0.010	0.100	0.000	0.010	0.120	0.000	1.790	N.D
DW3	0.030	0.020	0.010	0.050	0.130	0.010	3.360	0.010
DW4	0.030	0.030	0.010	0.010	0.140	0.000	2.640	0.020
DW5	0.050	0.060	0.010	0.020	0.120	0.000	1.380	0.010
DW6	0.050	0.060	0.010	0.010	0.160	0.010	3.520	0.030

*, ± SD values given in Table 3; RW, waste water samples; N.D, Not detected.

Table 3

Statistical parameters of selected metals in various water samples (n = 14) and liquid wastes samples (n= 6) from Rawal Lake

Metal	Rawal Lake water			Liquid wastes samples		
	Range (mg l⁻¹)	$\overline{X}$	± SD	Range (mg l⁻¹)	$\overline{X}$	± SD
Cr	0.040 - 0.610	0.125	0.197	0.010 - 0.070	0.040	0.021
Co	0.000 - 0.110	0.015	0.029	0.020 - 0.100	0.057	0.029
Cd	0.002 - 0.021	0.008	0.007	0.000 - 0.010	0.008	0.004
Zn	0.005 - 0.666	0.429	0.232	0.010 - 0.050	0.023	0.018
Ni	0.095 - 4.920	2.705	1.354	0.120 - 0.220	0.148	0.035
Cu	0.001 - 0.310	0.062	0.101	0.000 - 0.010	0.003	0.005
Mn	0.009 - 0.270	0.063	0.083	0.000 - 0.070	0.023	0.025
K	0.262 - 2.440	0.599	0.640	1.380 - 3.520	2.555	0.844

Table 4

Statistical multiple correlations between paired water and liquid wastes samples from Rawal Lake and main streams entering Rawal Lake

Metal	Cr	Co	Cd	Zn	Ni	Mn	Cu	K
Water samples								
Cr	-							
Co	0.681	-						
Cd	0.201	-0.313	-					
Zn	-0.195	0.269	-0.657	-				
Ni	-0.333	0.149	-0.541	0.926	-			
Mn	-0.266	0.019	-0.266	0.457	0.592	-		
Cu	-0.196	-0.085	-0.392	0.480	0.303	0.384	-	
K	0.552	-0.009	0.366	-0.764	-0.806	-0.272	-0.277	-
Liquid wastes samples								
Cr	-							
Co	-0.066	-						
Cd	0.701	-0.738	-					
Zn	0.327	-0.410	0.373	-				
Ni	0.774	0.103	0.364	0.339	-			
Mn	0.838	0.046	0.457	0.35	0.991	-		
Cu	0.000	-0.449	0.316	0.295	-0.068	-0.103	-	
K	0.164	-0.532	0.444	0.311	0.353	0.312	0.812	-

Table 3 provides information about ranges of metal concentrations, average concentrations and standard deviation values for lake water samples. An analysis of the tabulated data for water samples, indicated that concentration of Cr mg l^{-1} is in the range (0.040-0.610), Co (0.000-0.110), Cd (0.002-0.021), Zn (0.005-0.666), Ni (0.095-4.920), Cu (0.001-0.310), Mn (0.009-0.270) and K (0.262-2.440). In waste water samples Table 3, Cr is in the range (0.010-0.070), Co (0.020-0.100), Cd (0.000-0.010), Zn (0.010-0.050), Ni (0.120-0.220), Cu (0.000-0.010), Mn (0.000-0.070) and K (1.380-3.520) mg l^{-1}. Of all these metals studied in lake water samples, the largest average concentrations (2.705 mg l^{-1}) and standard deviation values ($\pm$ 1.354 mg l^{-1}) were recorded for Ni, while Cd has lowest average concentration and standard deviation values (0.008 mg l^{-1} and $\pm$0.007 mg l^{-1} respectively). In liquid waste samples, the K contents has maximum average concentration and standard deviation values (2.555 mg l^{-1} and $\pm$0.844 mg l^{-1} respectively) and minimum value of average concentration was found for Cu (0.003 mg l^{1}) and minimum standard deviation values was found for Cd ($\pm$0.004 mg l^{-1}).

The linear correlation analysis of the data in Table 4 augments various distinct patterns observed between concentrations of metals in water samples. In water samples a strong positive correlation was found for Ni-Zn at r = 0.926. In liquid waste samples, strong positive correlation was found between Mn-Ni, Mn-Cr and K-Cu at r = 0.991, 0.838 and 0.812, respectively.

Conclusion

The proposed implementation plan focuses on the identification of water quality throughout the Lake. Central themes are the need to develop and maintain and to focus on a system analysis approach to identify the cause and effect relationships that must be understood if the problems are to be solved.

In particular, domestic sewage and industrial waste water containing large quantities of chemical substances, are being drained into rivers without treatment, causing serious water pollution.

Lastly, the current water-resources management system should be reformed and the management of surface water and ground water, water quality, supply development and protection must be co-ordinated.

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