

M. W. Mumtaz<sup>1,2</sup>, A. Adnan<sup>2</sup>, H. Mukhtar<sup>2</sup>, M. Danish<sup>1</sup>,  
M.A. Raza<sup>1</sup>

**DETERMINATION OF TOXIC METALS IN WATER  
OF LAHORE CANAL  
BY ATOMIC ABSORPTION SPECTROSCOPY**

<sup>1</sup> Department of Chemistry, Hafiz Hayat Campus,  
University of Gujrat, Pakistan;

<sup>2</sup> Department of Chemistry, GC University Lahore, Pakistan  
asamgcu@yahoo.com

*Present study describes the atomic absorption spectro-photometric determination of metals (Ni, Cr, Zn, Fe, As and Cu) in the surface water of Lahore canal passing through the center of Lahore (city) Pakistan. Analysis showed that month wise average Ni, Zn and As concentrations lies within the National Environmental Quality Standards limits for these metals as designed by Environmental Protection Agency Pakistan, while Cr, Fe and Cu showed marked rise in their month wise average concentrations from their limiting values.*

**Key words:** Lahore canal, water quality, toxic metals, atomic absorption spectrophotometric

### Introduction

Water is one of the essentials that supports all forms of plant and animal life [1] and it is generally obtained from two principal natural sources. Surface water such as fresh water lakes, rivers, streams, etc. and Ground water such as borehole water and well water [2, 3]. Water has unique chemical properties due to its polarity and hydrogen bonds which means it is able to dissolve, absorb, adsorb or suspend many different compounds [4], thus, in nature, water is not pure as it acquires contaminants from its surrounding and those arising from humans and animals as well as other biological activities [3]. One of the most important environmental issues today is ground water contamination [5] and between the wide diversity of contaminants affecting water resources, heavy metals receive particular concern considering their strong toxicity

© M. W. Mumtaz, A. Adnan, H. Mukhtar, M. Danish, M. A. Raza, 2015

even at low concentrations [6]. Water and land are being increasingly stressed various activities of man leading to environmental pollution [7]. Water may be temporarily or permanently impaired in quality as a result of these actions. The Lahore Canal (study area) flows through the center of the Lahore (Pakistan) city receives raw sewage, untreated industrial discharges from small scale industries. Resultantly, the water in the canal is virtually highly polluted by a variety of the pollutants varied in quality and quantity. The use of this water is directly or indirectly playing havoc with the health of a large number of the people living in the thickly populated residential areas along the canal.

Heavy metals are stable and persistent environmental contaminants of coastal waters and sediments. The extent of metals like Zn, Cu, Fe and Mn, which are required for metabolic activity in organisms, lies in the narrow "window" between their essentiality and toxicity. Others heavy metals like Cd, Hg, Cr and Pb, may exhibit extreme toxicity even at low concentration under certain conditions, thus necessitating regular monitoring of sensitive aquatic environments [8]. Our research group is engaged in monitoring and assessments of water quality and this work is continuity of our previous work [9, 10].

### **Experimental**

For heavy metals analysis, thoroughly cleaned, acid rinsed sample containers were used in this study for sampling from nine (09) sampling stations of Lahore Canal (a stretch of almost 45 km from Bambavali-Ravi-Bedian Canal (BRB) canal to "Ammar Textiles Pvt. Ltd"). Samples were preserved immediately after sampling by acidifying with concentrated nitric acid at pH below 2 and filtered for dissolved metals before preservation. After acidifying, samples were stored in a refrigerator at approximately 4°C. Under these conditions, samples with metal concentrations several milligram per liter remain stable for up to six months [11 – 14]. To reduce interference by organic matter and to convert metal associated with particulates usually to form the free metal that can be determined by atomic absorption spectroscopy using one of the digestion techniques. Least rigorous digestion method was used to provide complete and consistent recovery compatible with the analytical method and the metal being analyzed. Nitric acid – hydrochloric acid digestion method was used [15]. Nitric acid digest most samples adequately, nitrate is an acceptable matrix for both flame and electrothermal atomic absorption. The digested samples were filtered through Whatman's papers (0,45 µm membrane). To ensure precision in results, filters were preconditioned by rinsing it with 50 ml of de-ionized

water. The filtrate was then subjected to Atomic Absorption Spectrometer (AAS) (Model Solaar 969) for determination of metal concentration.

### Results and Discussion

Analysis of metal (Ni, Cr, Zn, Fe, As and Cu) in water samples from Lahore canal was conducted during the study period from May 2007 to September 2007 in Apex Environmental Research Laboratory Lahore and research labs of Department of Chemistry, Industrial Biotechnology and Zoology, Government College University Lahore, Pakistan. Statistical analysis was carried out using statistical package for the social sciences (SPSS) and results are compared with the National Environmental Quality Standards (NEQS) as Designed by Environmental Protection Agency (EPA) Pakistan.

Arsenic is a highly poisonous metallic element registered with the Chemical Poisoning and Environmental Toxicity Centers. Arsenic is a carcinogen, and those with high levels of arsenic within their tissues are at a high risk for skin, scrotal, liver, lymphatic, and lung cancer. Other symptoms of arsenic poisoning are: headaches, confusion, drowsiness, changes in fingernail pigmentation, vomiting, diarrhea, bloody urine, muscle cramps, gastrointestinal upsets, coma, death etc [16]. Table 1 shows monthly average of As (ppm) concentration at nine sampling stations for the study period and it is clear from the table that month wise average As concentration of the Lahore canal shows an irregular trend at different sampling stations and that the As concentration lies within the NEQS limiting value i.e. 1,0 ppm on the average basis at all sampling stations.

Although nickel is important in low quantity for deoxyribonucleic acid and ribonucleic acid stabilization and activation of certain enzymes but in excess amounts it is considered carcinogenic [17]. Table 2 shows monthly average of Ni concentration at nine sampling stations for the study period and it is clear from the table that month wise average Ni concentration of the Lahore canal lies almost within NEQS limiting value i.e.1,0 ppm. Iron in water can cause staining of laundry and porcelain. Some ground waters and acid surface drainage may contain considerably more iron. A bittersweet astringent taste is detectable by some persons at levels above 1 mg/L. In water samples iron may occur in true solution, in a colloidal state that may be peptized by organic matter, in inorganic or organic iron complexes, or in relatively coarse suspended particles [16]. Table 3 shows monthly average of Fe concentration at nine sampling stations for the study period and it is clear from the table that month wise average Fe concentration of the Lahore canal shows an irregular trend at

different sampling stations and that the Fe concentration exceeds the NEQS limiting value i.e. 2,0 ppm on the r from month wise average Zn concentration of the Lahore canal shows an irregular trend at different sampling stations.

*Table 1. Month wise variation of Cu and As (ppm) in canal water at different sampling stations*

Metal	Sample points	May	June	July	August	September	Average	SD ( $\pm$ )
Cu	1	0,62	0,96	1,03	0,74	0,43	0,74	0,26
	2	1,00	0,80	1,43	0,96	1,35	1,11	0,27
	3	0,58	1,23	1,37	0,86	1,09	1,03	0,31
	4	1,06	1,55	1,00	0,94	1,12	1,13	0,24
	5	1,11	0,73	1,23	0,76	1,25	1,02	0,24
	6	1,20	1,03	0,93	1,05	1,02	1,05	0,10
	7	0,88	0,96	1,07	0,86	1,09	0,97	0,10
	8	1,46	1,66	0,90	1,04	1,32	1,27	0,30
	9	1,41	0,95	1,55	1,16	1,03	1,22	0,25
As	1	0,05	0,18	0,22	0,05	0,10	0,12	0,08
	2	0,15	0,06	0,14	0,15	0,09	0,12	0,04
	3	0,03	0,08	0,20	1,13	0,12	0,31	0,46
	4	0,06	1,25	0,14	0,06	1,15	0,53	0,61
	5	0,15	0,09	1,00	0,15	0,08	0,29	0,40
	6	1,43	0,06	1,25	0,43	1,15	0,86	0,59
	7	1,06	0,07	2,09	0,06	1,09	0,87	0,84
	8	1,08	0,02	0,35	0,08	1,10	0,53	0,53
	9	1,12	0,02	1,04	0,12	1,06	0,67	0,55

Chromium salts are used extensively in industrial processes and may enter into water supply through the discharge of wastes. Chromate compounds frequently are added to cooling water for corrosion control [17]. Table 2 shows monthly average of Cr concentration at nine sampling stations for the study period and it is clear from the results that month wise average Cr concentration of the Lahore canal shows an increasing trend from sampling station 0 toward sampling station 9, Cr concentration exceeds the NEQS limiting value i.e.1,0 ppm at sampling stations from 1 to 8.

Zinc is an essential and beneficial element in human growth and most commonly enters the domestic water supply from deterioration of galvanized

iron and dezincification of brass. Zinc in water also may result from industrial waste pollution [17]. Table 3 shows monthly average of Zn concentration at nine sampling stations for the study period and it is clear from the table that month wise average Zn concentration of the Lahore canal shows an irregular trend at different sampling stations.

*Table 2. Month wise variation of Cr and Ni (ppm) in canal water at different sampling stations*

Metal	Sample points	May	June	July	August	September	Average	SD ( $\pm$ )
Cr	1	0,94	1,00	0,85	0,54	1,01	0,87	0,19
	2	1,22	1,32	1,02	0,98	1,21	1,15	0,144
	3	1,15	1,56	0,98	1,25	1,56	1,30	0,26
	4	1,35	1,89	1,05	1,34	1,68	1,46	0,33
	5	1,44	1,45	1,56	1,56	1,24	1,45	0,13
	6	1,64	1,57	1,48	1,82	1,65	1,63	0,12
	7	1,66	2,00	2,00	1,63	2,30	1,92	0,28
	8	1,79	1,56	2,15	2,00	1,98	1,90	0,23
	9	1,90	2,24	1,89	2,15	1,75	1,99	0,20
Ni	1	0,09	0,21	0,55	1,02	0,46	0,47	0,36
	2	0,69	0,85	0,46	1,01	0,98	0,80	0,23
	3	0,94	1,02	0,57	1,05	0,87	0,89	0,19
	4	1,00	0,65	0,68	1,07	1,04	0,89	0,20
	5	0,52	0,89	0,70	0,69	0,95	0,75	0,17
	6	0,61	0,24	0,35	0,86	0,48	0,51	0,24
	7	0,95	0,30	0,45	1,02	0,75	0,69	0,31
	8	1,02	1,12	0,83	1,05	0,83	0,97	0,13
	9	0,69	1,01	0,27	0,65	0,88	0,70	0,28

Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes. Corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into water. Medical conditions associated with copper toxicity include: biliary obstruction (inability to excrete excess copper), liver disease, renal dysfunction, muscle and joint pain, depression, chronic fatigue symptoms, irritability, tremors, anemia, learning disabilities, behavioral disorders, leukemia and high blood pressure [17].

Table 1 monthly average of Cu concentration at nine sampling stations for the study period and it is clear from result that month wise average Cu concentration of the Lahore canal shows an irregular trend at different sampling stations and that the Cu concentration exceed the NEQS limiting value i.e.1,0 ppm on the average basis at all sampling stations except 0.

We observed month wise three values at each sampling station and then calculated average value. The above Table 2 shows average heavy and toxic metals concentrations along with standard deviation of their month wise averages for nine sampling stations during the study period. The observed average Ni concentrations along with their standard deviation during the study period of five months i.e. from May 2007 to September 2007 as shown in Table 2 were 0,72; 0,70; 0,54; 0,94 and 0,80 respectively, while the observed average Cr concentrations along with their standard deviation during the study period were 1,45; 1,62; 1,44; 1,47 and 1,60 ppm respectively.

*Table 3. Month wise variation of Zn and Fe (ppm) in canal water at different sampling stations*

Metal	Sample points	May	June	July	August	September	Average	SD ( $\pm$ )
Zn	1	0,81	0,56	0,93	0,68	0,62	0,72	0,15
	2	1,70	0,85	1,02	0,85	0,76	1,04	0,38
	3	0,69	1,02	1,21	0,76	1,00	0,94	0,21
	4	0,85	0,75	1,00	1,04	1,24	0,98	0,19
	5	1,27	0,84	0,78	0,52	0,85	0,85	0,27
	6	1,36	0,56	0,56	0,76	0,76	0,80	0,33
	7	1,43	0,43	1,06	1,17	0,26	0,87	0,50
	8	0,89	0,79	0,67	0,95	0,45	0,75	0,20
	9	2,30	1,04	0,36	0,49	0,84	1,01	0,77
Fe	1	2,89	3,65	2,22	2,68	4,02	3,09	0,73
	2	3,61	4,95	4,15	5,01	3,35	4,21	0,76
	3	6,82	4,67	5,68	4,71	5,27	5,43	0,88
	4	3,62	5,75	4,35	5,24	4,87	4,77	0,82
	5	4,34	2,68	5,63	3,69	4,02	4,07	1,07
	6	5,01	3,68	4,02	4,52	3,98	4,24	0,52
	7	4,22	2,68	3,68	4,65	3,67	3,78	0,74
	8	3,14	4,51	6,56	5,00	4,56	4,75	1,22
	9	5,28	3,86	3,95	5,28	3,61	4,40	0,82

The observed average Zn concentrations along with their standard deviation during the study period of five months as shown in Table 3 were 1,26; 0,76; 0,84; 0,80 and 0,75 ppm respectively, while the observed average Fe concentrations along with their standard deviation during the study period were 4,33; 4,05; 4,47; 4,53 and 4,15 ppm respectively. The observed average As concentrations were 0,57; 0,20; 0,71; 0,25; 0,66 ppm respectively, while the observed average Cu concentrations along with their standard deviation during the study period of five months from May 2007 to September 2007 were 1,02; 1,10; 1,17; 0,93; 1,08 ppm as shown in Table 1.

Analysis of variance (ANOVA) test was applied on the observed data to test the significant difference between nine sampling stations during the study period (May 2007 to September 2007). The P-values for heavy metals Ni, Cr, Zn, Fe, As and Cu are 0,033; 0,000; 0,891; 0,012; 0,170 and 0,07 respectively and on the basis of collected data, the P-values for Ni, Cr and Fe are  $< 0,05$ , while the P-values for Zn, As and Cu are  $>$  than 0,05.

Multiple comparison test least significant difference is applied for pair wise comparison of nine sampling stations for the heavy metals (Ni, Cr and Fe) for which the P-values of ANOVA were  $< 0,05$ . For Ni, P-values of Pairs (0,1), (0,2), (0,3), (0,7), (2,5), (3,5) and (5,7) are  $< 0,05$ , that means there is 95% probability of confidence that the average Ni concentration for these pairs differ significantly for the whole study period. For Cr, P-values of Pairs (0,1), (0,2), (0,3), (0,4), (0,5), (0,6), (0,7), (0,8), (1,3), (1,4), (1,5), (1,6), (1,7), (1,8), (2,5), (2,6), (2,7), (2,8), (3,6), (3,7), (3,8), (4,6), (4,7), (4,8), (5,6) and (5,8) are  $< 0,05$ , that means there is 95% probability of confidence that the average Ni concentration for these pairs differ significantly for the whole study period. For Fe, P-values of Pairs (0,1), (0,2), (0,3), (0,5), (0,7), (0,8), (1,2), (2,4), (2,5) and (2,6) are  $< 0,05$ , that means there is 95% probability of confidence that the average Ni concentration for these pairs differ significantly for the whole study period.

## Conclusions

It was concluded that concentrations of Ni, Zn and As were lies within the range as formulated by National Environmental Quality Standards and the values of Cr, Fe and Cu are some what high as NEQS limits. So before, any practical corrective measures are adopted; it is of utmost importance that metals in the canal should be quantified along with identification of their sources.

## References

- [1] *Vanloon G. W., Duffy S. J.* // Environmental Chemistry: A Global Perspective. – New York: Oxford University Press, 2005. – P. 197–211.
- [2] *McMurry J., Fay R.C.* // McMurry Fay Chemistry. K.P. Hamann (Ed.). – New Jersey: Pearson Education, 2004. – P. 575–599.
- [3] *Mendie U.* // The Theory and Practice of Clean Water Production for Domestic and Industrial Use. – Lagos: Lacto-Medals Publishers, 2005. – P. 1–21.
- [4] *WHO.* Quality Assurance of Pharmaceuticals: A Compendium of Guidelines and Related Materials. – Geneva: World Health Organisation, 2007. – 2. – P. 170–187.
- [5] *Vodela J. K., Renden J. A. Lenz S.D. Mchel-Henney W.H., Kemppainen B.W.* // Pollut. Sci., 1997. – 76 – P. 1474–1492.
- [6] *Marcovecchio J.E., Botte S.E., Freije R.H.* // Handbook of Water Analysis /Ed. L.M. Nollet. – London: CRC Press, 2007. – P. 275–311.
- [7] *Ibe K. M., Sowa A. H. O., Osondu O. C.* // Niger. J. Min. Geol. – 1992. – 28. – P. 87–91.
- [8] *Derde M. P., Massart D. L.* // Anal. Chim. Acta. – 1973. – 45. – P. 2251.
- [9] *Mumtaz M. W., Ahmad A., Hamid M., Khalid N. Ahtisham R., Zahoor A.* // Environ. Monit. Assess. – 2011. – 17. – P. 581–587.
- [10] *Mumtaz M. W., Muhammad H., Hamid M., Zahoor A., Sumaira U.* // Ibid. – 2010. – 167. – P. 437–446.
- [11] *Feldman C.* // Anal. Chem. – 1974. – 46. – P. 99–102.
- [12] *Batley G. E., Gardner D.* // Water Res. – 1977. – 11. – P. 745.
- [13] *Subramanian K.S., Chakrabarti C.L.* // Anal. Chem. – 1978. – 50. – P. 444.
- [14] *Greenberg E., Clesceri L.S., Eaton A.D.* Standard Method for Examination of Water and Waste Water. – 18<sup>th</sup> Ed. – Washington: Amer. Public Health Assoc., 1992.
- [15] *Duffus J. H.* // Pure Appl. Chem. – 2002. – 74, N5. – P. 793–807.
- [16] *Kuhn Karl F., Koupelis T.* In Quest of the Universe. – 4<sup>th</sup> Ed. – Toronto: Jones and Bartlett Publ, 2004.
- [17] *Andrew D., Eaton A. W. W. A.* Standard Methods for Examination of Water and Wastewater. – 19<sup>th</sup> Ed. – Washington: Amer. Public Health Assoc., 2005.

Received 06.03.2012