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Monitoring of anthropogenic influences on underground and surface water quality of Indus River at district Mianwali-Pakistan

[Pakistan-Mianwali'deki Indus Nehri'nin yeraltı ve yüzey suyu kalitesi üzerine antropojenik etkilerin izlenmesi]*

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ABSTRACT

Aim: Quality of underground and Indus river surface water at Kalabagh, Pakistan was monitored to investigate the anthropogenic activities in the region because people of the Mianwali district often suffer from rusty spot on their teeth and clothes.

Material and Methods: Fully flush sampling method was used for underground water samples. Surface water samples were collected from the main river flow. Conductivity, total dissolved solid (TDS), pH, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were measured using the standard procedures. Heavy metals were determined by plasma atomic emission spectrophotometry.

Results: The obtained results were compared with the set limits of National Environmental Quality Standards (NEQs) and World Health Organization (WHO). In river water samples, the average levels for BOD, COD, TDS, conductivity, pH and heavy metals were exceeding the limits of NEQs and WHO. In underground water samples of Kamer village, levels for COD, BOD, TDS and heavy metals such as cadmium and chromium were below their maximum contamination limits (MCL). However, the levels for pH, conductivity, iron and manganese were above the limits of MCL. In underground water samples from Mianwali city, the parameters including BOD, COD, TDS and heavy metals, including cadmium and chromium were below their MCL, while the conductivity, pH, and heavy metals were also observed higher than their MCL.

Conclusion: The investigated parameters for river water like dissolved oxygen (DO), BOD, COD, TDS, iron, manganese, lead, cadmium were reported above MCL. In underground drinking water of Kamer village and river water samples of Mianwali city areas, the concentration levels for lead, iron and manganese were also found higher than their MCL. This may be one of cause for rusty spot on teeth and clothes of the residents. The statistical linear correlation study indicates that metals might have their origin from anthropogenic activities and natural influences.

Keywords: River water, underground water, heavy metals, anthropogenic influences

Conflict of interest: Authors have no conflict of interest

ÖZET

Amaç: Mianwali halkı dişlerindeki ve giysilerindeki paslı noktadan sık sık muzdarip olduğundan, bu bölgedeki antropojenik aktiviteleri araştırmak için Kalabagh'daki (Pakistan) yeraltı ve Indus nehrinin yüzey suyu kalitesi izlenmiştir.

Yöntem: Yeraltı su örnekleri için "fully flush" örnekleme yöntemi kullanılmıştır.

Yüzey suyu örnekleri ana nehir akışından toplanmıştır. İletkenlik, toplam çözünmüş katı (TÇK), pH, kimyasal oksijen ihtiyacı (KOİ) ve biyokimyasal oksijen ihtiyacı (BOİ) standart yöntemler kullanılarak ölçülmüştür. Ağır metaller plazma atomik emisyon spektrofotometresi ile belirlenmiştir.

Bulgular: Elde edilen sonuçlar Ulusal Çevre Kalite Standartları (NEQs) ve Dünya Sağlık Örgütü'nce (WHO) konulan limitler ile karşılaştırıldı. Nehir suyu örneklerinde, ortalama BOİ, KOİ, TÇK, iletkenlik, pH ve ağır metal seviyeleri NEQs ve WHO limitlerini aşıyordu. Kamer köyünün yeraltı suyu örneklerinde, KOİ, BOİ, TÇK ve kadmiyum ve krom gibi ağır metal düzeyleri, maksimum kirlilik limitleri (MKL) altında idi. Bununla birlikte, pH, iletkenlik, demir ve manganez seviyeleri MKL sınırları üzerindeydi. Mianwali şehri yeraltı suyu örneklerinde, BOİ, KOİ, TÇK ve kadmiyum ve krom gibi ağır metaller gibi bazı parametreler MKL altında iken, iletkenlik, pH, ve ağır metaller MKL üstünde gözlendi.

Sonuç: Nehir suyu için incelenen parametrelerden çözünmüş oksijen (DO), BOİ, KOİ, TÇK, demir, manganez, kurşun, kadmiyum MKL üstünde bildirilmiştir. Kamer köyü yeraltı içme suyu ve Mianwali şehri bölgesindeki nehir suyu örneklerinde kurşun, demir ve manganez konsantrasyon düzeyleri de MCL üstünde bulunmuştur. Bölge sakinlerinin dişlerinde ve giysilerindeki paslı lekelerin sebeplerinden birisi bu olabilir. İstatistiksel lineer korelasyon çalışması metallerin kökeninin antropojenik aktivitelere ve doğal etkilere dayanabileceğini göstermektedir.

Anahtar kelimeler: Nehir suyu, yeraltı suyu, ağır metaller, antropojenik etkiler

Çıkar çatışması: Yazarların çıkar çatışması bulunmamaktadır.

Introduction

Anthropogenic influences as well as natural process degrade surface and groundwater and impair their use for drinking, industrial, recreation or other purposes [1, 2]. Owing to spatial and temporal variation in water chemistry, a monitoring program that will provide a representative and reliable estimation is necessary [3, 4]. Solid and liquid waste originating from industries and natural sources contain toxic chemicals and other substances including heavy toxic trace metals [5, 6]. People are becoming aware of the complexity of the nature and the delicate balance that exist within the global ecosystem. The effluents discharge and associated toxic compound into ecosystem represent an ongoing environmental problem due to their possible impact on communities in the receiving aquatic water and a potential effect on the human health [7].

Safe and good quality drinking water is the basis for good human health. Water provides essential elements to human beings and other living organism, but when polluted, it becomes the source of undesirable substances that are dangerous to life. The particular importance for the citizens of Pakistan is the evolution of drinking water quality due to various anthropogenic influences that make it unfit for human consumption. This pollution of water creates adverse health effects in both human and their livestock [8].

Underground water quality is greatly influenced by the quality of the corresponding fresh water from which drinking water is being derived. The main source of drinking water in Mianwali district is the underground water but river water is also being used in a few areas located around the Indus River. According to a recent report [9], the population of Mianwali district is about 1400000. There are about 259 cottage levels and small/ medium and large scale industrial units operating in this district. Industrial density of the district is given in Table 1. The scope of the study is about the evolution of water quality based on a set of specific parameters in Indus River at Kalabagh and the underground water at Kamer village and Mianwali city [10].

The hypothesis of the present study was to investigate the concentration of iron and manganese in drinking water because the people of Mianwali district often suffer from rusty spot on their teeth and clothes. In addition to this, bio-physical parameters like electrical conductivity (EC), total dissolved solids (TDS), pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and heavy metals like cadmium, lead and chromium levels were also monitored.

Materials and Methods

Study area

Indus River is the Trans Himalayan River of southern Asia and is one of the world's longest rivers; having a length of 2900 km. Annual average flow is about 207 billion cubic meters, which is twice that of Nile River. It rises in south-western Tibet and flow north-west across the valleys of the Himalayas. After reaching the Kashmir region, it continues north-westward across the Indian and Pakistani administered areas and then turns south into Pakistan (Figure 1). Indus River covers large distance between the different mountain range and leaves this mountain area at Kalabagh, the study area. Swelled by tributary rivers of the Punjab like Jhelum, Chenab, Ravi, Beas and Sutlej Rivers, it widens and flows more slowly in the desert and plain areas of Punjab and Sindh. It has been supplying water for irrigation since early times.

Sampling

The method employed for the collection of samples from underground water was 'fully flush' method [11]. Four samples from each site were collected carefully following precise instruction and detailed protocol in order to avoid any contamination during sampling and transportation. Samples were collected from November 2009 to April 2010 from frequently used household taps and Indus River surface water. Surface water samples were collected from the main flow of the river and away from slumping and scouring effects that could be found near the banks.

Table 1. Description of existing industries of Mianwali district

Sr. No.	Industry	No. of Units	Installed Capacity
1	Cement	1	450000 M.Tons
2	Cotton Ginning & Pressing	2	3 Sawgnis, 1 Press
3	Drugs & Pharmaceuticals	1	-
4	Fertilizer	1	346500 M.Tons
5	Flour Mills	7	13000 TCD
6	Oil Mills	7	-
7	Power Generation	1	23.84 Mw

Source: Ref # 9.

a)

b)

Figure 1. a) Sampling point from Indus river **b)** Sampling site locations (Latitude 32.55. Longitude 71.51667. Altitude 210)

Method and analysis

For the determination of heavy metals, samples were collected in polypropylene bottles, thoroughly cleaned by soaking for a week in 15% nitric acid and then carefully and repeatedly rinsed with deionised water. These samples were filtered by using 0.45µm Millipore filters and their pH was set at 1.0 with the addition of few drops of concentrated nitric acid for preservation. For BOD, COD, TDS determination, samples were taken in glass bottles, thoroughly rinsed with water followed by strong heating for 3 hours [11]. Analysis of heavy metals was performed by ICP-OES (Perkin-Elmer, Optima-2100). The instrument set conditions were, power 1450 W, coolant flow 13L/min, auxilary flow 0.7L/min, nebulizer flow 0.8 L/min and sample aspiration rate 2 ml/min. COD was determined by redoxtitrometric method (open-reflex method). BOD was determined by using Winkler method [12]. TDS and conductivity were determined by using a conductivity meter (WTW, model COND-720). The pH was determined by using pH meter model HANNA-25. Standards provided with the instrument were used for the calibration.

Statistical analysis

Data were expressed as mean ± standard deviation (SD). All results in this study were analyzed by the Statistical Package for Social Sciences version 12.0 (SPSS Inc., Chicago, IL, USA).

Results and Discussion

In the present study, water samples both from river and underground were investigated and compared with the set limits of national environmental quality standards (NEQs) and World Health Organization (WHO). Levels of bio-physical parameters from soil underground water of Kamer village, Mianwali city and Indus river fresh water samples are given in Table 2. Results showed that the levels exceed in case of BOD, COD, TDS, EC and pH in river water samples than their MCL. While the levels for COD, BOD and TDS were below their MCL in underground water samples of Kamer village and Mianwali city whereas the dissolved oxygen (DO), EC and pH were found above their MCL.

Higher levels for BOD, COD, TDS, EC and pH in the river water samples indicate that the river is receiving a considerable amount of pollution from anthropogenic and natural sources. Contamination from industrial and domestic waste is also important [13] because this river is receiving a considerable amount of industrial waste in the studied area. The levels for COD, BOD and TDS were within the safe limit in the Kamer village and Mianwali city underground water samples, which indicate that it is free from oxidizable organic matter. Levels of selected heavy metals (X ± SD, mg/L) from underground water of Kamer village, Mianwali city and Indus river fresh water samples are given in Table 3. Results showed that in river and under ground water samples from Kamer village and Mianwali city, the metal levels like iron, manganese and lead were exceeded than their MCL, while the levels for chromium was within the safe limits. The levels for cadmium was also within the safe limits for fresh water of Indus river and under ground water samples at Kamer village while its level was observed higher in underground water samples of Mianwali city.

Other possible sources of iron, manganese and lead in the water samples may be the rocks of Potohar range. Indus River covers its large path between these rocks and mountains which are rich in iron and manganese. The largest iron ore deposits in Pakistan were found in Mazari Tang, Marai Bela and Saman range of Kohat area. Iron ore deposits in the Potohar range especially at Kalabagh and in the salt range were estimated to be 300 tons. Three million tons iron deposits were also found in southern Chitral. Total iron reserves in Hazara district were estimated to 100 milion tons. These metals may

Table 2. Levels of bio-physical parameters from soil underground water of Kamer village, Mianwali city and Indus river fresh water (n = 4).

Parameters	River	Kamer village	Mianwali city	NEQs	WHO
TDS (mg/L)	1873.00±8.00	435.0±6.00	325.00±4.00	< 1000	< 1000
BOD (mg/L)	17.00±0.01	4.40±0.01	4.00±0.01	< 6	< 6
COD (mg/L)	45.00±1.00	6.00±0.02	6.00±0.01	< 10	< 10
DO (mg/L)	9.84±0.50	9.80±0.50	8.70±0.40	< 3	< 3
pH	8.65±0.60	8.02±0.03	8.20±0.02	6.5–8.5	< 7
EC ($S\ m^{-1}$)	0.36±0.03	0.96±0.02	0.93±0.02	0.05–0.005	0.05–0.005

TDS=Total dissolved solids, BOD=Biochemical oxygen demand, COD=Chemical oxygen demand, DO=Dissolved oxygen, EC=Electrical conductivity

Table 3. Levels of selected heavy metals (X ± SD, mg/L) from underground water of Kamer village, Mianwali city and Indus river fresh water (n = 4).

Parameters	River	Kamer village	Mianwali city	NEQs	WHO
Cadmium	0.004±0.06	0.002±0.02	0.160±0.18	< 0.01	< 0.003
Lead	1.099±0.83	0.366±0.16	1.097±0.14	< 0.05	< 0.01
Iron	0.363±0.68	0.321±0.05	0.305±0.12	<0.3	<0.3
Chromium	0.003±0.02	0.041±0.01	0.006±0.06	<0.05	<0.05
Manganese	0.397±0.04	0.330±0.13	0.481±0.15	< 0.5	<0.1

leach from rocks and enter into river water system [2].

The high concentration of iron and manganese in the Kamer village and Mianwali city water may also be due to these rocks. Rain water remains entrapped in these rocks for many days before it penetrates in the soil, due to this, it dissolves these metals. Low pH value of rain water further facilitates this dissolution process [14]. Other possible source could be the coal mining in these areas i.e. Makarwal coal mines. Concentrations of iron and manganese were always found high in the water of areas near coal mines [15] and this indicates the presence of large number of other coal mines in the region of Mianwali district and around the Indus River in the Potohar mountain range.

Temporal variation of heavy metals in a) river water, b) Kamer village and c) Mianwali city underground water samples is given in Figure 2. In the underground water from Kamer village and Mianwali city, concentration of heavy metals was higher during March and April. These seasonal variations may be due to either anthropogenic causes, such as agricultural practices, especially the use of fertilizers and biocides or wastewater discharge, or natural causes, such as water temperature, pH, redox condition, or river flow. The solubility of heavy metals in surface river water is predominately controlled by the water pH, water temperature, the river flow and the redox environment of the river system [4, 5].

pH is an important parameter of water quality that is changing chemically, slightly alkaline pH is preferable in water as heavy metals are removed by carbonates or bicarbonates precipitate [16]. A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water channels. The increase in the concentration of dissolved heavy metals in the warm period is related to the decreases of pH in those periods. A decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water. The lower pH value is found during March and April which may be the main cause of high concentration of these metals during the warm months [17].

Water temperature is higher in March and April than other studied months. When the temperature of water is high, the plants grow and die faster leaving behind matter that requires oxygen for decomposition. Trace elements accumulated to phytoplankton, may become soluble during this decay of plants. The seasonal variation of the water temperature may influence the variability of the studied metals indirectly via biological activity (decay of phytoplankton) or due to possible decrease of DO which relates to decrease in redox potential [18].

Spatial variation of heavy metals in Indus river fresh water and underground water of Kamer village and Mianwali city is given in Figure 3. Results show that the levels for lead were higher in Indus River fresh water and Mianwali city underground water samples. Varia-

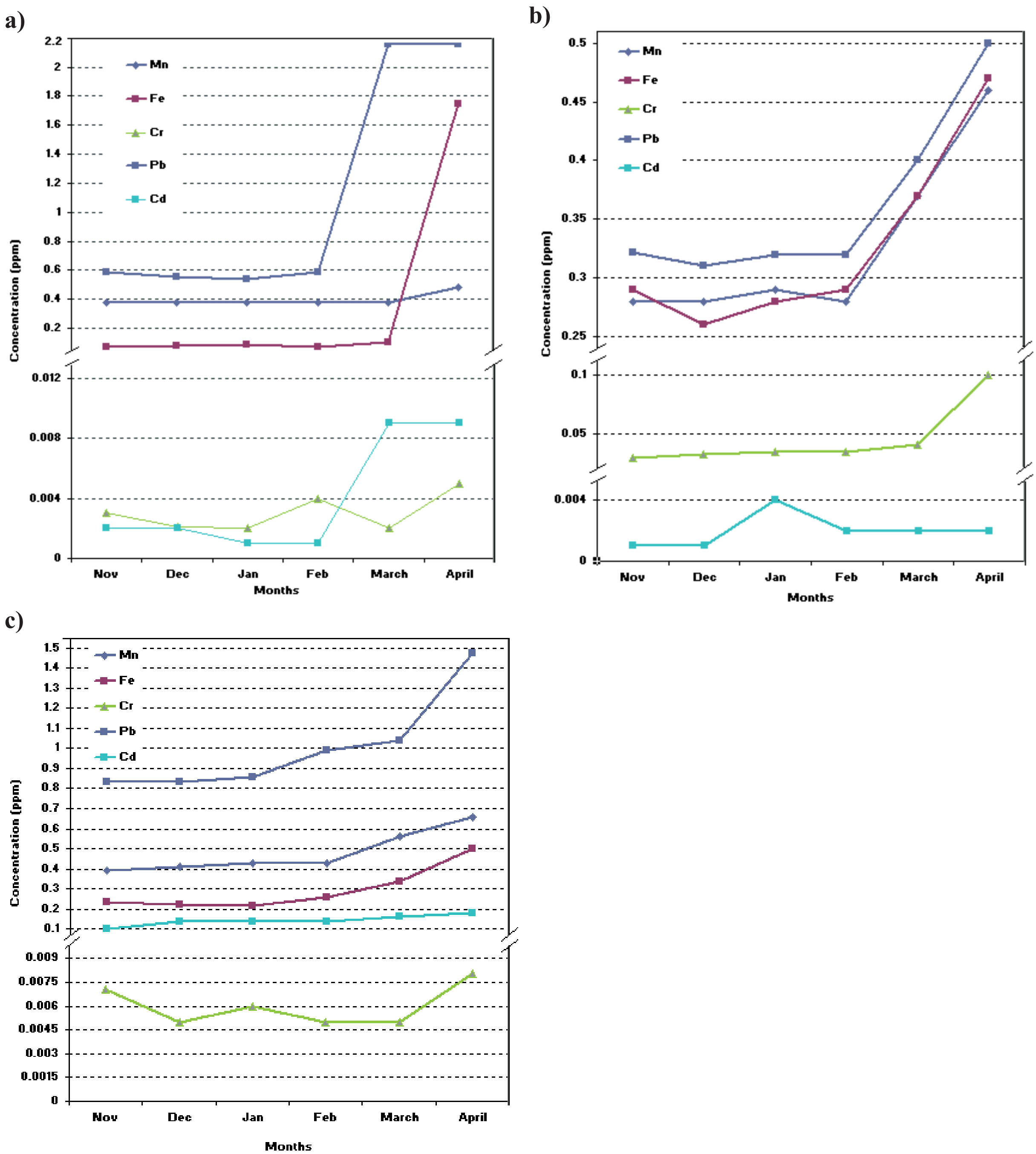

Figure 2. Temporal variation of heavy metals in **a)** Indus river water, **b)** Kamer village and **c)** Mianwali city underground water

tion of other studied metals was relatively small in the three sampling areas i.e. Indus River, Kamer village and Mianwali city**.**

Linear correlation coefficient matrix for selected heavy metals from underground water of Kamer village, Mianwali city and Indus river fresh water is given in Table 4. The statistical linear correlation study at $p<0.01$ showed strong positive correlation for manganese-cadmium ($r=0.901$), manganese-lead ($r=0.830$), lead-cadmium ($r=0.507$) and iron-lead ($r=0.253$). This strong positive correlation evidence that the metals might have their origin from anthropogenic activities and natural influences i.e. industrial and metal rich ores present in the studied area.

Conclusion

Results showed that the levels for parameters like DO, BOD, COD, TDS and heavy metals like iron, manganese, lead and cadmium were above the maximum contamination levels set by national environmental quality

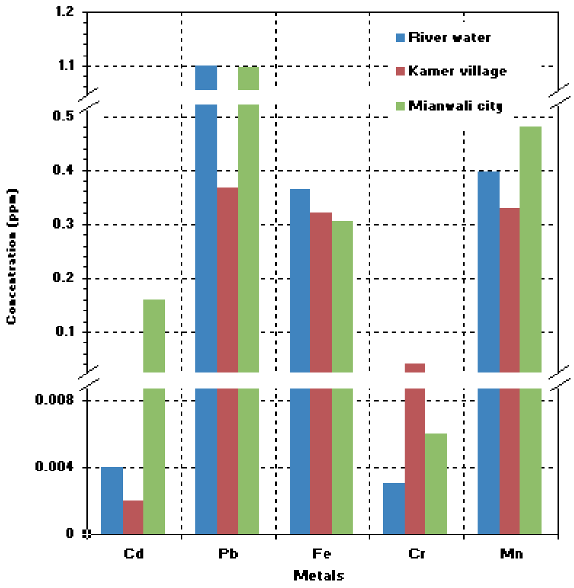

Figure 3. Spatial variation of heavy metals in Indus river fresh water and underground water samples of Kamer village and Mianwali city.

Table 4. Linear correlation coefficient matrix for selected heavy metals from underground water of Kamer village, Mianwali city and Indus river fresh water

	Cadmium	Lead	Iron	Chromium
Lead	0.507			
Iron	-0.705	0.253		
Chromium	-0.447	-0.998	-0.319	
Manga-nese	0.901	0.830	-0.329	-0.790

Values > 0.300 or < -0.300 are significant at $p < 0.01$

standards NEQs and world health organization WHO. This may be probably due to both natural and anthropogenic factors, associated with the biogeochemical cycle. The other may be due to industrial and agriculture activities in the region. The levels for the investigated parameters at Kamer village show that pH, EC and metals like lead, iron, manganese were above their MCL, while chromium, cadmium, COD, TDS were within the safe limit. The investigated higher levels for iron, manganese, lead in water may be due to coal, iron, salt mining or their leaching affects. The investigated levels for pH, EC, heavy metals like lead, iron and manganese were also found higher than their MCL in the underground water samples of Mianwali city which is located near the Potohar salt range of Pakistan. It has been seen that the people of Mianwali city and Kamer village areas have rusty spot on their teeth and cloths which may be due to higher concentration of iron and manganese present in their consuming water.

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Conflict of Interest: There is no conflict of interest among the authors who contributed to the present study.

References

[1] Wattoo MHS, Iqbal J, Kazi TG, Jakhrani MA. Monitoring of pollution parameters in waste water of tanneries in Kasur. Pak J Biolog Sci 2000; 3:960–962.

[2] Abbasi SA, Soni R. An examination of environmentally safe levels of zinc(II), cadmium(II) and lead (II) with reference to impact on channelfish *Nuria denricus*. Environ Pollut (Series A) 1986; 40: 37–51.

[3] Aswathanarayana U. Geoenvironment: An Introduction 1995; A.A. Balkema Publishers, The Netherlands.

[4] Wattoo MHS, Wattoo FH, Tirmizi SA, Kazi TG, Bhanger MI, Iqbal J. Pollution of Phulali canal water in the city premises of Hyderabad: Metal monitoring. J Chem Soc Pak 2006; 28:136–143.

[5] Wattoo MHS, Wattoo FH, Kazi TG, Tirmizi SA, Bhanger MI, Mahar RB, Iqbal J. Quality characterization of Phulali canal water for agricultural purposes. The Nucleus 2004; 41:69–75.

[6] Tariq SR, Shah MH, Shaheen N, Khalique A, Manzoor S, Jaffar M. Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water: a case study from Peshawar. Pak J Environ Manage 2006; 79:20–29.

[7] Duruibe JO, Ogwuegbu MOC, Egwurugwu JN. Heavy metal pollution and human biotoxic effects. Int J Phys Sci 2007; 2: 112–118.

[8] Iqbal MA, Gupta SG. Studies on heavy metal ion pollution of ground water sources as an effect of municipal solid waste dumping. Afr J Basic Appl Sci 2009; 1:117–122.

[9] www.mianwalionline.com/Industry.shtml [24 April 2011]

[10] www.pndpunjab.gov.pk/user_files/File/Mianwali 09.pdf [24 April 2011]

[11] Fergusson JE. Environmental Impact and Health Effects. 2008; pp.190, 720, Pergomoon, New York.

[12] Gaddamwar AG. Analytical study of rain water for the determination of polluted or unpolluted zone. Intl J Environ Sci 2011; 1:1317–1322.

[13] Hur J, Lee BM, Lee TH, Park DH. Estimation of biological oxygen demand and chemical oxygen demand for combined sewer systems using synchronous fluorescence spectra. Sensors 2010; 10: 2460–2471.

[14] Gachel GS, Slater FM, Qadri AH, Nisa, Z. Environmental impact on the conservation of the Indus River Dolphin *(Platanista minor)*. Pak J Biolog Sci 2006; 9:1497–1503.

[15] Kurshey KU. A Geography of Pakistan 1977; pp.43, 199, 4th Ed. Oxford University Press.

[16] Otero XL, Macias F. Spatial and seasonal variation in heavy metals in interstitial water of salt marsh soils. Environ Pollution 2002; 120:183–190

[17] Lohani MB, Sing A, Rupainwar DC, Dhar DN. Seasonal variation of heavy metal contamination in river Gomti of Lucknow city region. Environ Monit Assess 2008; 147:253–263.

[18] Papafilippaki AK, Kotti ME, Stavroulakis G. Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece. Global NEST J 2008; 10:320–325.