

Toxic Trace Element Pollution in Storm Water of Karachi: A Graphical Approach.

A. Zubair, Ph.D.^{*}, M.A. Farooq, M.Sc., and H.N Abbasi, M.Sc.

Department of Environmental Sciences,
Federal Urdu University of Arts, Science, and Technology (FUUAST), Karachi, Pakistan.

*E-mail: drarifzubair@gmail.com

ABSTRACT

Storm water infiltration is a cause of concern in urban areas. It mobilizes, migrates, and accumulates in groundwater as a result of infiltration. The purpose of this study is to carry out an in depth investigation to identify and quantify possible pathways of trace elements in hydrological system and their distribution pattern. Samples collected prior to and after the monsoon period were analyzed for comparison to find out the impact of storm water infiltration on groundwater pollution. Cadmium, copper, and total dissolved solid have exceeds the limit of WHO 1993 set for drinking water. However other trace metals such as arsenic, lead, iron, and zinc are well with in permissible limits. It has been observed for copper and lead that groundwater collected close to industrial area is unaffected with these two metals in certain locations. This phenomenon suggest that trace metal movements are influenced by the hydrological gradients, topography, and local geological structure such as porosity, permeability, joints, and physiochemical process in the soil. Migration of determinants with groundwater down stream is quite significant. Distribution pattern of trace metals reveals that these pollutants are accumulate towards Arabian Sea.

(Keywords: ground water, storm water, runoff, non-point pollution, heavy metals, cadmium, copper, dissolved solids, lead, arsenic, iron, zinc)

INTRODUCTION

In recent years, attention on the increasing ionic concentration of traces metals in groundwater as a result of storm water infiltration has been studied by various researchers (Ku et al., 1992; Appleyard, 1993; Wild, 1994; Hathhorn and Yonge, 1995; Pitt, 1996). This has been attributed to human interference, proliferation of industries, and recent agriculture practices in urban areas

where storm water flow recharges the aquifer. Effective retention of determinants depends upon soil types (Zubair and Farooq, 2008). Constituents such as trace metals are leached from the soil and move into aquifer systems and thus degrade water quality. Therefore it has become necessary to assess, quantify, and monitor the quality of groundwater influenced by non-point source pollution as a result of storm water infiltration in the urban environment of Karachi, Pakistan.

Infiltration experiments were undertaken to establish the suitability of soils type in terms of infiltration rates among the various soils, and to investigate the potential effects of the infiltration media on the water quality by the storm water runoff.

Karachi is a port city and major trade center of Pakistan. It is located in the northwest of Indus River delta with the Arabian Sea to its south (Figure 1), and has an arid coastal climate. The metropolitan population has grown over 12.5 million in an area of 3530 Km² (Helders, 2007). Most of the population is concentrated within the urban area of the city and encompasses an area of about 591 Km² (Zubair, 2000). It lies between latitude 24° 50' N to 25° 30' N and longitudes 66° 55' E to 67° 55' E (see Figure 1).

The city has a large number of industrial units of different sectors, such as textile, pharmaceutical, engineering, paint, paper, chemical, detergents, vegetable oils, beverages, food products, etc. These industrial units generate approximately 1.3 million liters of effluents per day (Monawwar Saleem, 2002). Most of them discharged their effluents directly to the hydrological system thus causing an imbalance to the environment. There are three major waterways passing through this mega city, namely the Hub, Lyari, and Malir rivers which have confluence with the Arabian Sea. These waterways serve an important function of carrying away storm water, particularly during the

monsoon period. It is expected that sample collected from these catchments basins contain high concentration of trace metals as these pollutants accumulate in nature over a long period. Most of these elements are toxic in nature and some are consider potential health hazards (Bubb and Lester, 1994; Hunt and Howard, 1994; Ramesh et al., 1995).

Several researchers have carried out their studies for surface and sub surface water for major ions, trace elements, and bacteria (Rahman et al., 1997; Zubair, 1998). However no attempts were made to study the distribution pattern of trace elements in groundwater as a result of storm

water infiltration and their accumulative effects on quality of groundwater. Catchment areas of the rivers are considered a major source of potable water for the area population, where piped water supply is not available or is very limited.

This study is focused on the quality of groundwater with reference to toxic trace element for arsenic, copper, cadmium, lead, iron, zinc and total dissolved solid (TDS). The present work is aimed at studying the presence of toxic metals in groundwater from storm water infiltration for their migration, dispersion and distribution patterns during the monitoring period.

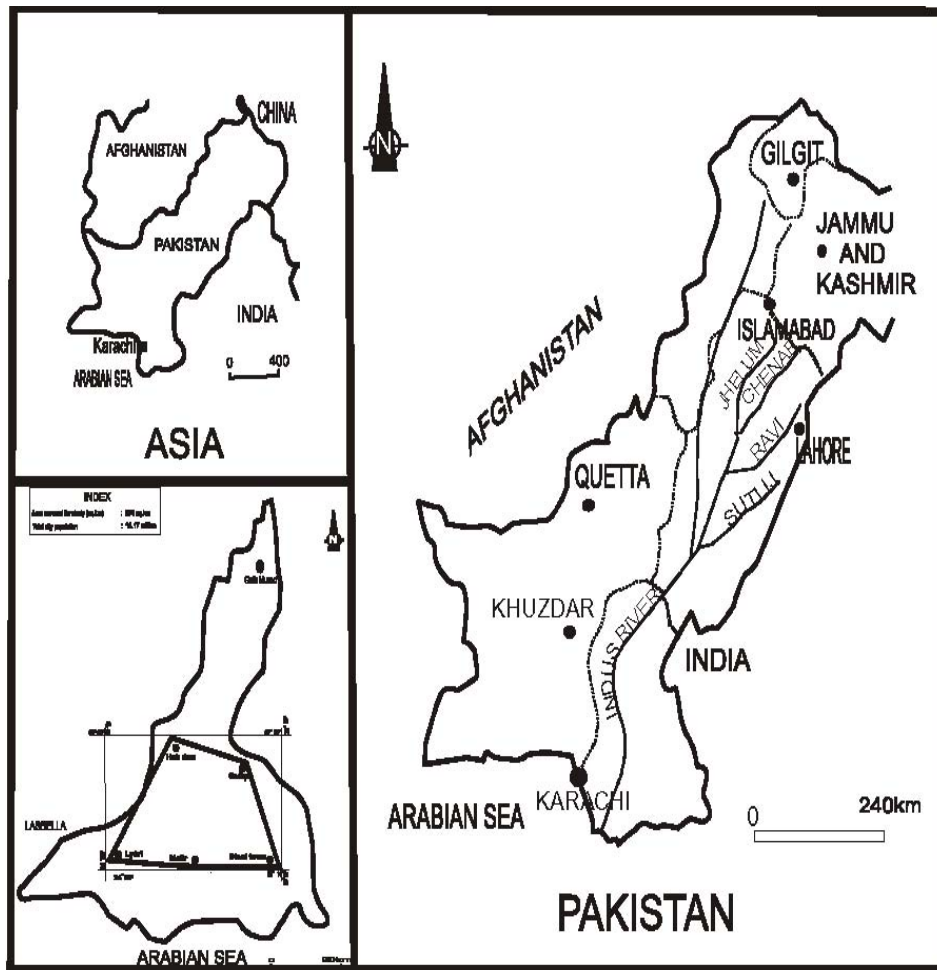


Figure 1: Map of the Study Area.

SAMPLE COLLECTION

In all, from 33 shallow wells, 132 groundwater samples were collected during the monitoring period, starting from February 2007 to November 2007 (Figure 2). The quality of water has been monitored at quarterly intervals over two rainy seasons and has been analyzed for the trace metals and total dissolved solid (TDS).

Groundwater samples collected prior to and after the monsoon period were analyzed to find out the impact of storm water on groundwater. In general, rainfall tends to be the main source of recharge of subsurface water. But this is not the case for the aquifers of Karachi. The rainfall in the city is around 200 mm per year based on the last 10 years record and the average monthly temperature ranges between 12 and 41 C (Pakistan Meteorological Department, 2007). The city received an average annual precipitation 254 mm and has an arid coastal climate (Stefan Helder, 2008).

The low precipitation/rainfall accounts for a small fraction of the total recharge (i.e., $1.9 \times 10^6 \text{ m}^3/\text{yr}$ (Rehman et al., 1997). There is also potential for recharge from sewers and drains which are designed to carry storm water out of the city. All these recharges sources eventually infiltrate and percolate down into the groundwater.

These samples cover the catchment basin of the Hub, Lyari, and Malir rivers and were collected at considerable distances from each other in order to find the impact of pollutants on hydrological system. Most of these shallow wells are regarded as potable and are used for agricultural and domestic purpose by the local population.

Each water sample was collected so as to prevent sample deterioration or contamination by any other substances. Water was sampled from the wells only when the well was pumped sufficiently long enough to ensure that samples represent the groundwater from the aquifer. In most cases the wells are regularly used by the owner.

Two liter white polyethylene bottles were used for collecting samples. The bottles were rinsed first with distilled water before filling, rinsed a further two or three times with the water being sampled, and then the water sample was taken. The samples were divided into two portions. One portion was used for trace metals determination, with immediately acidification to $\text{pH} < 2$ with 1.5 ml

concentrated nitric acid, to preserve the sample. The second portion was used for total dissolved solids (TDS) analysis.

METHODOLOGY

Standard methods for the examination of water and waste water from the USEPA were used for determination of trace metals such as arsenic, copper, cadmium, lead, iron and zinc. All of these elements were analyzed through atomic absorption spectrophotometry. While performing the analysis, two sets of internal standard were run, one at beginning and other in between the analyses, to have check the accuracy and precision of the results (Balaram, 1992). For most of the elements, the detection limits are around 1 ng ml^{-1} . Estimation of TDS was measured by using a conductivity meter.

HYDRO GEOCHEMISTRY

Groundwater contains major ions, trace metals, and other toxic pollutants, in addition to bacteria. The concentration of these substances in the aquifers is a function of the geological environment, composition of water, effect of storm water infiltration, water movement, its velocity, land use, rainfall, and recharge mechanism. Hence, the interactive relationship of water chemistry with hydrological and geological environments could be used to explain the information regarding increase or decrease of solubility of certain trace metals in groundwater.

The nature of pollution by storm water infiltration as a non-point source requires understanding of the interaction with local geological and hydrological systems. The concentrations of the trace metals present in groundwater as a result of storm water infiltration are plotted on a map of the Karachi basin. A graphic program such as SURFER is used to prepare contour maps. The concentrations of various determinants such as copper, cadmium, lead, iron, zinc and TDS in ground water are separately plotted (pre- and post-monsoon) on Karachi basin maps to define migration with hydrological gradient. Contour maps thus prepared, indicate the areas of higher and lower concentrations. Each parameter is discussed in detail are as below. In addition arsenic is also determined, but its concentration is so low or negligible that it is not considered for further study.

GEOLOGY

Physiographically, the study area falls within two major physiographic regions of Pakistan, namely the Western Highlands and Lower Indus Plain (Zaidi and Rizvi, 1989). It is almost bounded by the Hub River in the west and Malir River basin in the east (see Figure 2). To the north, hilly terrain merges into the higher hills and mountains forming the Kohistan where, as the in the south, it is bounded by Arabian Sea into which the rocky headlands are extended forming capes separated by sandy beaches.

In the Southeast, the coastal line is characterized by a coastal cliff and development of creeks. Elevations in the study area generally range between 50 m in the north and 14 m in south.

The bedrock material filling the Karachi embayment comprises marine and estuarine sediments of considerable thickness with subordinate lacustrine and lagoonal deposits. Geologically younger deposits are mainly fluvial and aeoline, composed of conglomerates, consolidated and semi consolidated gravels, and incoherent loess deposits in places.

Geomorphic evaluation and morophostructural analyses suggest non tectonic activity during the quaternary period resulted in marine regression (Achuthan, 1994). The quaternary deposits are the only lithological units spread over most part of the study area. These consist of gravel beds and alluvial deposits. The thickness of the alluvial deposits increases towards the north-west and ranges between 30 and 50 m.

MIGRATION, DISPERSION AND DISTRIBUTION PATTERN OF TRACE METALS AND TDS

An anomalous distribution of trace elements in the urban environment is a result of rapid urbanization coupled with industrialization and over exploitation of groundwater resources (Ramesh et al., 1995).

Urban storm water has been recognized as one of the major sources of pollution in the city. Due to elevated levels of certain trace elements in groundwater, it has become very important to identify the possible environmental pathways of groundwater pollution from storm water infiltration. Therefore there is an imperative need to understand their migration, dispersion, and

distribution pattern in hydrological systems in order to control them.

Arsenic

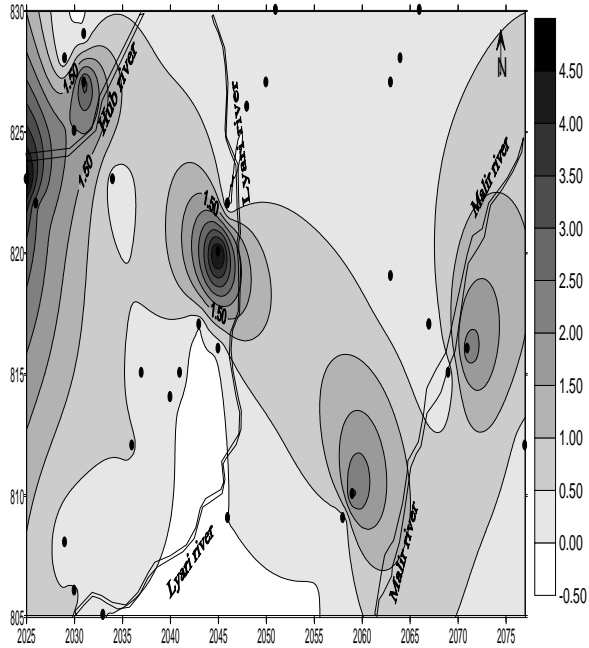
The concentration of arsenic in groundwater is less than the WHO 1993 drinking water standard for arsenic (i.e., 0.01 mg l^{-1}) during the whole monitoring period. This reveals that arsenic is either not present at all in the groundwater of the study area, or if it is present, it occurs in the negligible/non polluted range.

Copper

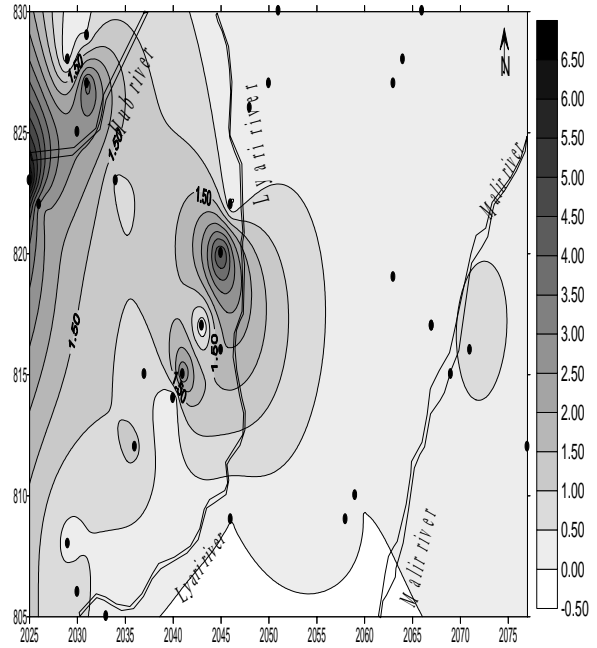
Copper is found in traces and is being released into the hydrological system by the industries located around the study area (Figure 3). Mean concentration of copper as high as 1.706 mg l^{-1} is monitored during the post-monsoon season, as a result of storm water infiltration, more than the permissible limit prescribed by WHO standard 1993. The groundwater samples in pre-monsoon season show less concentration (0.913 mg l^{-1}) of copper compared to those found in post-monsoon season. This clearly indicates that gradually copper pollutant is migrating into the groundwater system as they move south close to the Arabian Sea. In some areas copper concentration during post-monsoon season is 60 to 70 times higher than the permissible limit. There is an urgent need for control of copper migration into the natural environment especially into the groundwater. Certain locations close to industrial areas are unaffected with respect to copper pollution. This suggests that trace metal movements are mainly influenced by the hydrological gradients, topography, and local geological structure such as porosity, permeability, joints, and physiochemical processes in the soil.

Iron

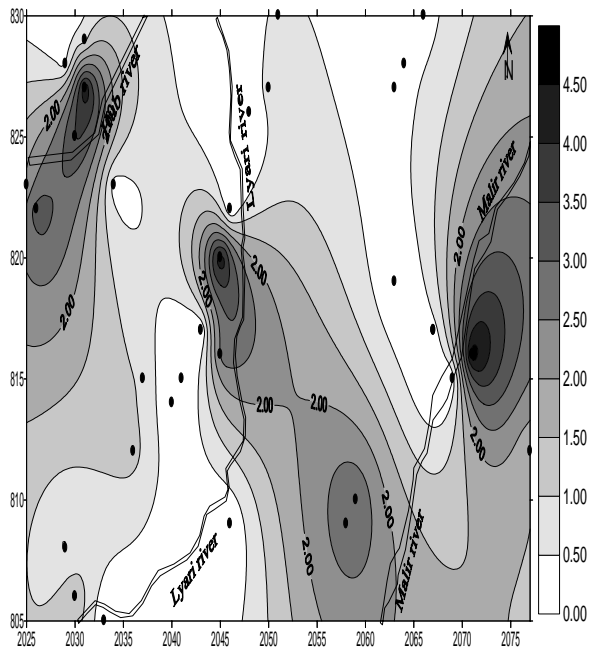
Currently iron does not show high concentration in groundwater samples, suggesting that there is very little percolation of iron from storm water to groundwater waters (Figure 4). The concentration of iron is within the permissible limit of WHO drinking water standard 1993 therefore this metal has not shown any toxic effect at present. However the influence of industrial activity in the study area is clearly visible in their migration pattern.



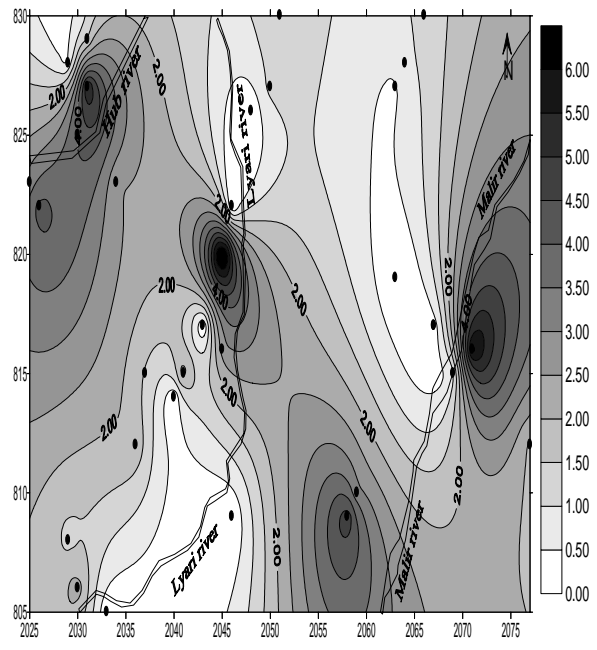
a. Pre-monsoon (Feb. 2007)



b. Pre-monsoon (May 2007)

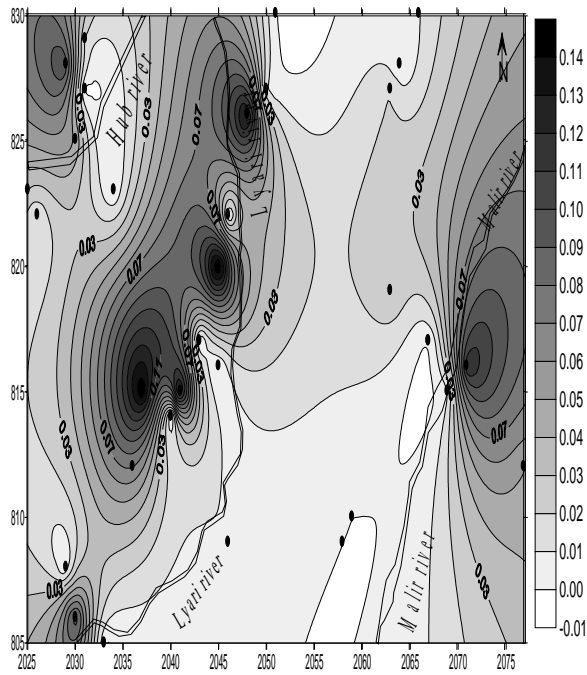


c. Post-monsoon (Sept. 2007)

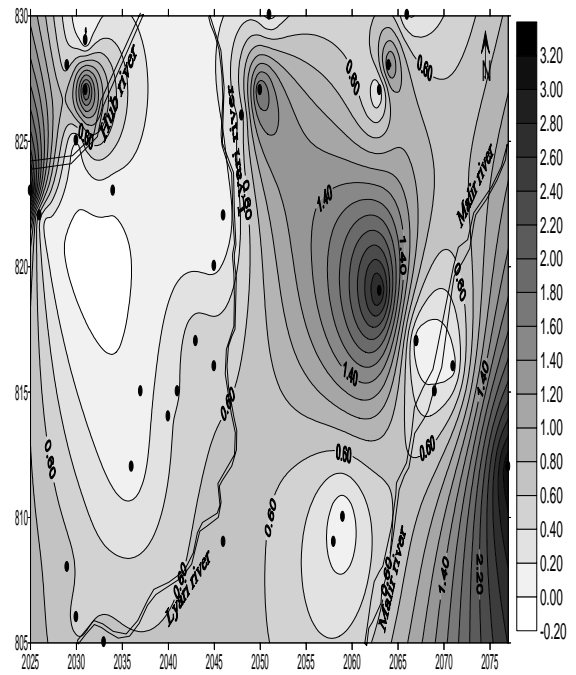


d. Post-monsoon (Nov. 2007)

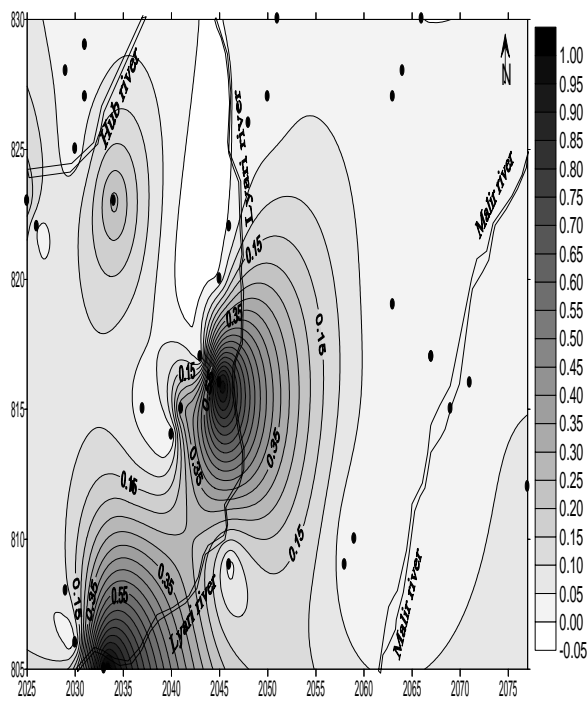
Figure 3: Contour Map Showing Distribution and Migration Pattern of Copper Concentration.



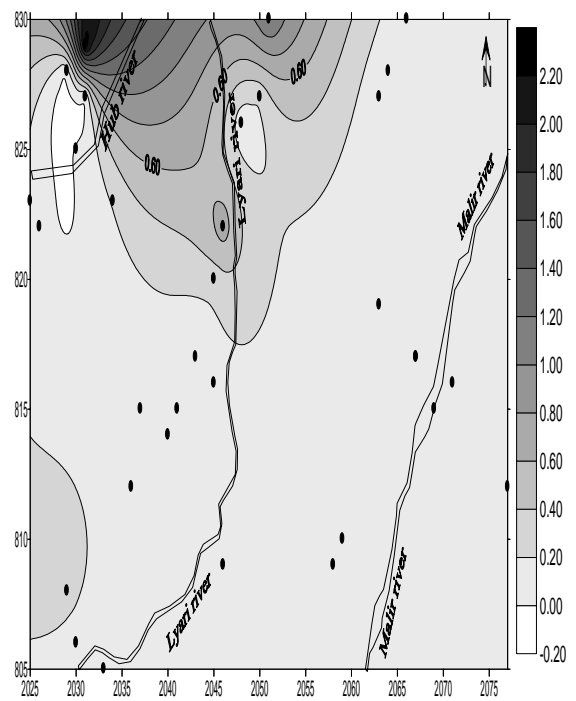
a. Pre-monsoon (Feb. 2007)



b. Pre-monsoon (May 2007)



c. Post-monsoon (Sept. 2007)



d. Post-monsoon (Nov. 2007)

Figure 4: Contour Map Showing Distribution and Migration Pattern of Iron Concentration.

The migration pattern of iron (Figure 4) demonstrates that the highest concentration is found in the north eastern and western part of the study area during pre-monsoon season where the Hub Industrial Trading Estates (HITE) and Landi Industrial Trading Estate (LITE) are located (see Figure 2). Elevated concentrations of iron are also found close to North Karachi Industrial Estates (NKIE) and Sindh Industrial Trading Estates (SITE) during post-monsoon season. This shows that elevated levels of iron concentration are restricted to the industrial zones of the city but their concentration is within the permissible limit suggesting that no industry is primarily responsible for iron contamination in storm/groundwater. The migration and their dispersion patterns suggest that gradually iron pollutant is migrating into the groundwater system as moves north to south in the study area close to the Arabian Sea.

The results of the study reveal that the concentration of iron in the groundwater samples has not reached beyond permissible limits during the monitoring period. It suggests that iron present in the surface water is getting precipitated and deposited as solid ferric hydroxide. The same is also been observed by Shiivkumar et al. (1996) in their study in India (Andhra Pradesh).

Cadmium

The WHO standard for cadmium in drinking water is 0.003 mg l^{-1} whereas the mean concentration of cadmium observed in the study area is as high as 0.04 mg l^{-1} in pre-monsoon and 0.06 mg l^{-1} in post-monsoon season. The groundwater samples in post-monsoon season shows high concentrations as a result of anthropogenic addition of effluent from surface to groundwater, especially after storm water infiltration in post-monsoon season.

High concentration of cadmium is seen in few locations (Figure 5), these have resulted in two roughly circular domains of contamination distributed in south eastern part of the study area. The distribution pattern of cadmium in groundwater samples is centered on the industrial zone of Sindh Industrial Trading Estates (SITE) (see Figure 5). Here most of the industrial activity is related to galvanized metal, painting, and the automobile industry, therefore cadmium concentration is restricted to a small area. The general migration pattern towards the south east is seen with this metal too. The result of the

cadmium shows that at present this element is close to the tolerable limits. However, it is anticipated that with increase of industrial activity, the area could increase the levels of cadmium. Therefore, there is a need to control this element at its source.

Zinc

Zinc concentrations were as high as 0.155 mg l^{-1} during post-monsoon season (Figure 6). These are within the permissible limit prescribed by WHO standard 1993. The groundwater samples before monsoon show less concentration 0.148 mg l^{-1} of zinc compared to those found in post-monsoon period. This indicates that zinc pollutant is migrating into the groundwater system as they move towards south of the study area close to the Arabian Sea. Over all, the migration patterns of zinc almost follow the same as that of copper.

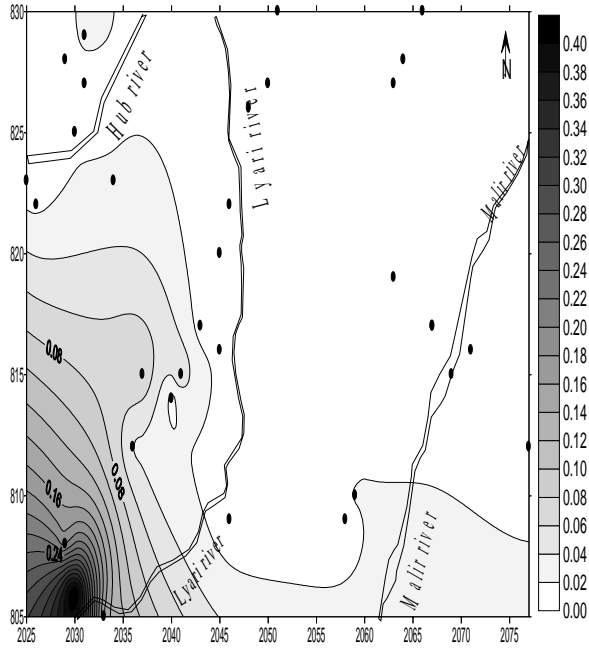
Lead

Mean concentration of lead were as high as 0.006 mg l^{-1} in pre-monsoon and 0.0065 mg l^{-1} in post-monsoon season, well within the permissible limit of 0.01 mg l^{-1} prescribed by WHO standard (1993). The distribution pattern of lead is broadly similar to the cadmium as high concentrations are restricted to south east (Figure 7). High concentrations of lead are also seen in two roughly circular domains of contamination distributed in the northern part of the study area. Storm water has shown a very little impact on the concentration of lead.

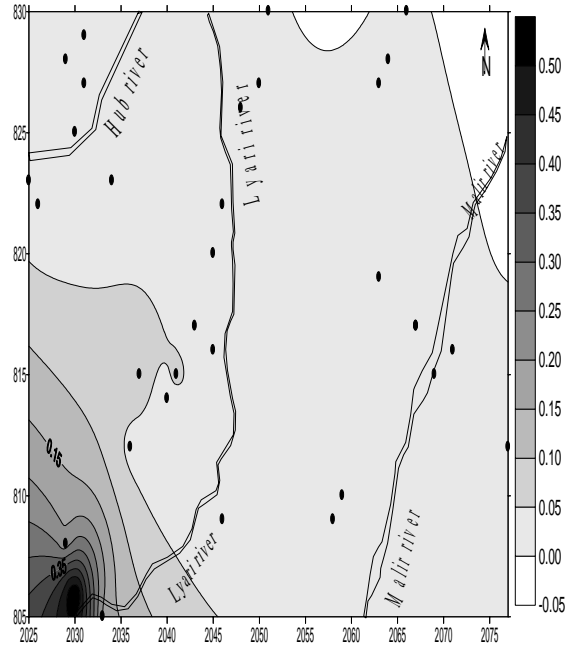
It is observed that, like copper, lead is also unaffected in many locations close to the industrial area of the city. This suggests that movements of this elements is mainly influenced by the hydrological gradients, topography, and local geological structure such as porosity, permeability, joints, and physiochemical processes in the soil.

TDS (Total Dissolved Solids)

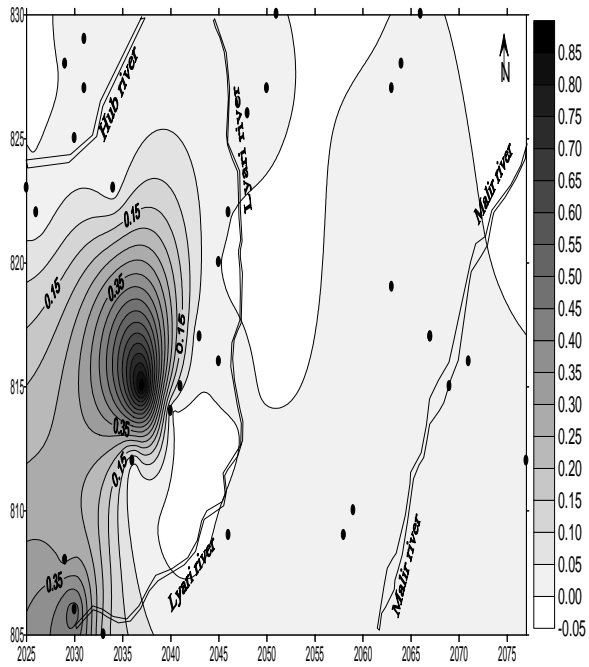
WHO permissible limit for TDS in drinking water is 1000 mg l^{-1} whereas the mean concentration of TDS is observed in study area is as high as 3712 mg l^{-1} in pre-monsoon and 2028 mg l^{-1} in post-monsoon season.



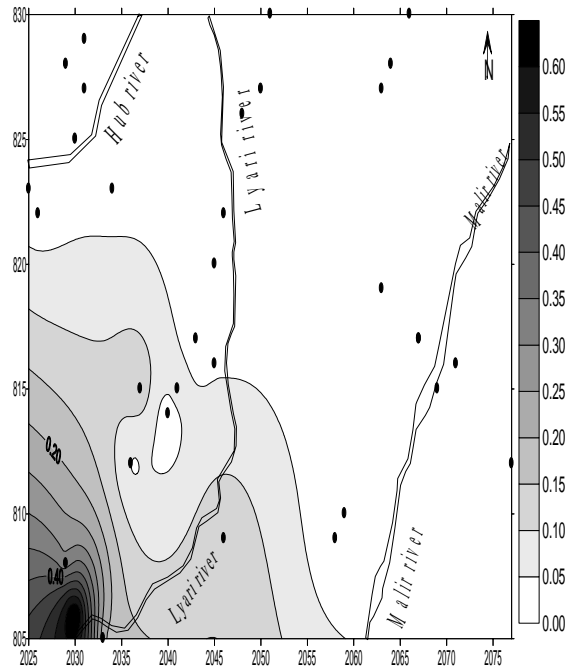
a. Pre-monsoon (Feb. 2007)



b. Pre-monsoon (May 2007)

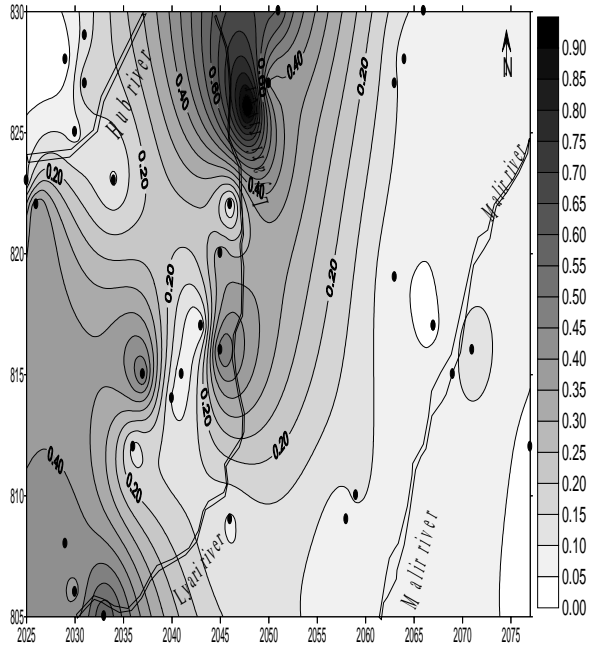


c. Post-monsoon (Sept. 2007)

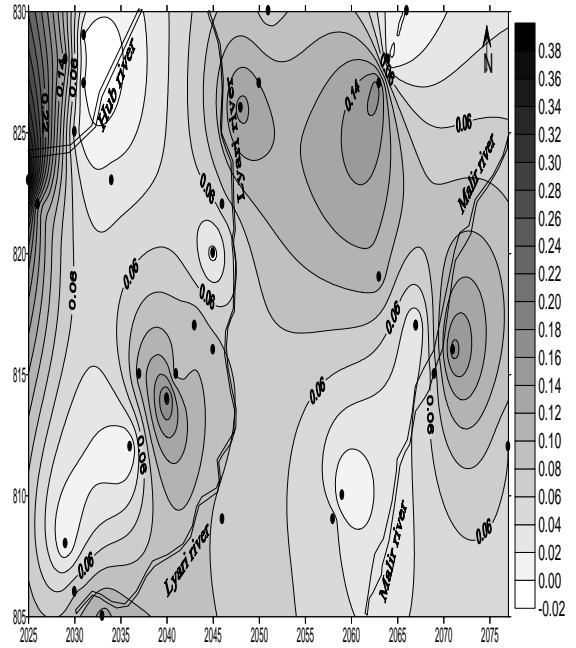


d. Post-monsoon (Nov. 2007)

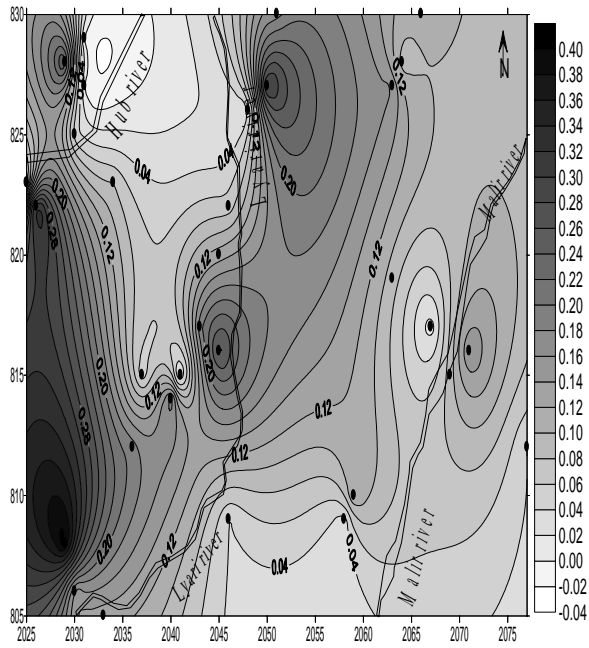
Figure 5: Contour Map Showing Distribution and Migration Pattern of Cadmium Concentration.



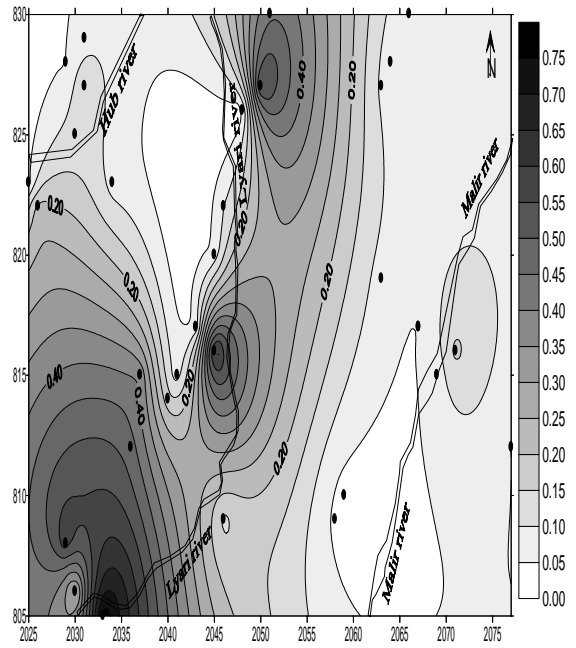
a. Pre-monsoon (Feb. 2007)



b. Pre-monsoon (May 2007)

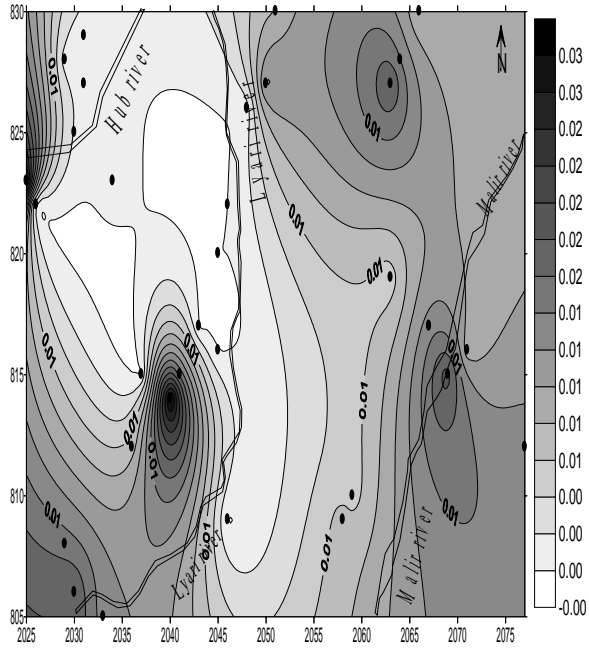


c. Post-monsoon (Sept. 2007)

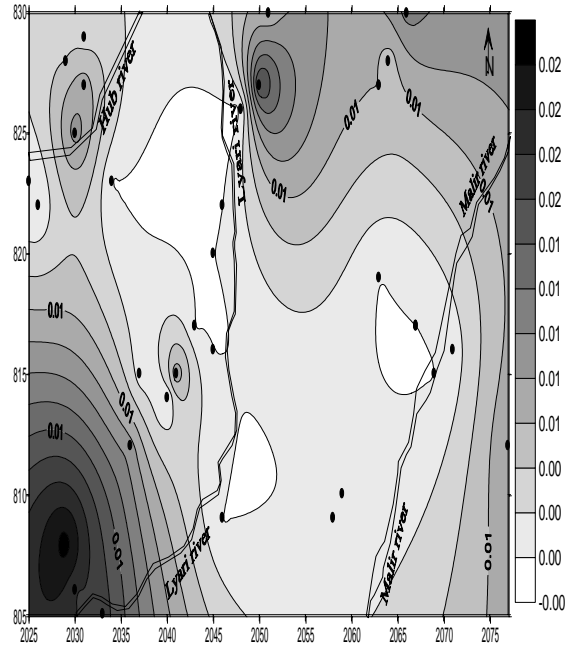


d. Post-monsoon (Nov. 2007)

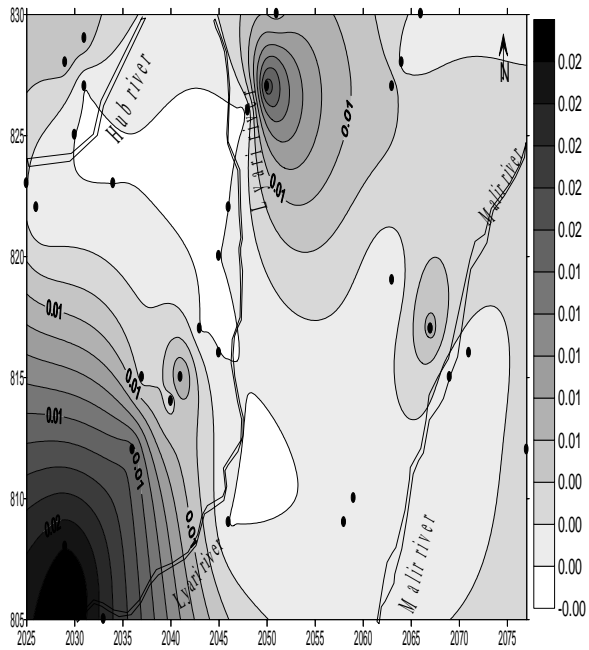
Figure 6: Contour Map Showing Distribution and Migration Pattern of Zinc Concentration.



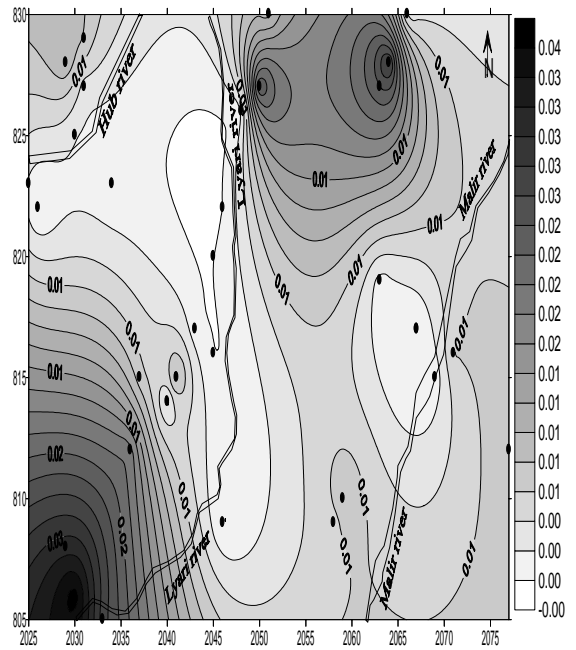
a. Pre-monsoon (Feb. 2007)



b. Pre monsoon (May 2007)



c. Post-monsoon (Sept. 2007)



d. Post monsoon (Nov. 2007)

Figure 7: Contour Map Showing Distribution and Migration Pattern of Lead Concentration.

The groundwater samples in post-monsoon season shows low concentration as a result of dilution due to rain/storm water infiltration. High concentration of TDS is seen in two locations (Figure 8). These have resulted in two roughly circular domains of contamination distributed in south eastern part of the study area. The distribution pattern of TDS in the groundwater samples is centered near the industrial zone of Sindh Industrial Trading Estates (SITE) (see Figure 8). The general migration pattern towards the south east is observed. The results show that, at present, TDS concentrations are high due to the saline nature of the groundwater.

Over all, the distribution patterns of these elements (Cu, Fe, Cd, Zn, and Pb) and TDS are centered along the industrial belt of Sindh Industrial Trading Estates (SITE) and Hub Industrial Trading Estate (HITE) located in the north and south eastern part of the study area, respectively (Figure 2). The generalized migration pattern of these pollutants demonstrates that these trace metal are migrating into the groundwater system as they move north to south of the study area close to the Arabian Sea. The migration, dispersion, and distribution patterns show the spread of pollutants and are useful in providing guidance to remedial effort.

Though the concentration of these metals does not show any toxicity at present but it is anticipated that with the increase of industrial activity in the area could increase the levels of these trace elements as well. It seems that the interaction of various components of the effluents with natural system (rocks, sediments and soils) is also responsible to enhance the level of pollution. Therefore there is a need to control these elements at source.

The migration and distribution patterns suggest that regular monitoring of groundwater samples with reference to storm water infiltration should be undertaken temporally and spatially to identify the source of toxic pollutants and other inhibitory chemicals which might affect the water around industrial zones of the study area.

DISCUSSION

Trace metals entering into the hydrological system both in the form of organometallic and inorganic metal complexes migrate down the hydrological gradient. They are accumulated in (a) different

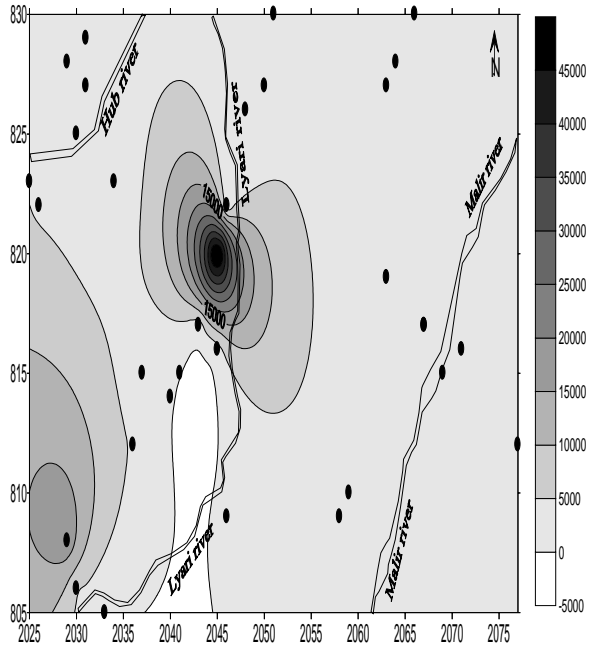
layers of soils, as these are the best known sinks of heavy metal (Dorsis and Warren, 1980; Burton, 1992); (b) aquatic plants and animals; (c) the leaves and stems of the shrubs fed with effluent water; and (d) crops grown using the contaminated groundwater.

The trace metals found in groundwater are mainly due to anthropogenic addition of municipal and industrial wastes in small landfill sites and along the banks of the rivers. This is also supported by Ramesh et al. (1995) and Zubair (1998) who found that in Madras (India) and Karachi (Pakistan), respectively, in urban environments, the human impact is many times greater than the natural input of trace elements due to sewage industrial effluent discharge by the industries. This suggests that the source of trace element in groundwater of study area is mainly from human impact and not by natural inputs.

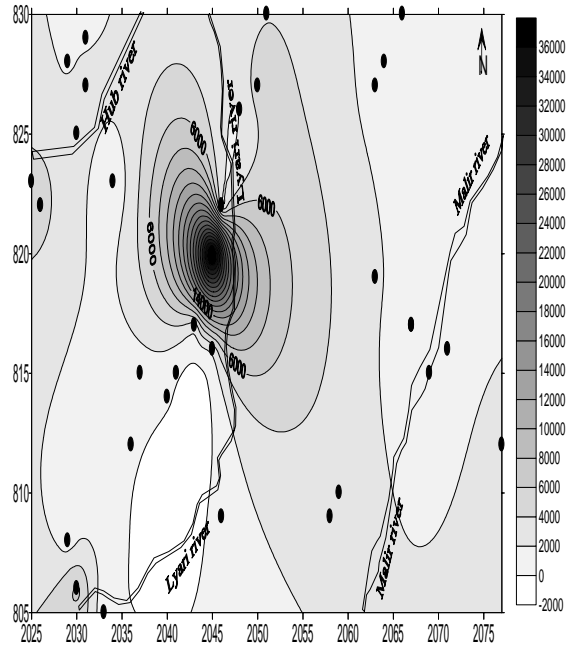
The study has also tried to identify the pathways and contamination of trace elements in the groundwater of Karachi by the impact of storm water infiltration. The anomalous distribution of trace elements is mostly man made as determined by our observation. It is anticipated that with the increase of industrial activities in the area could increase the levels of these trace elements as well. This may be the result of the interaction of various components of the effluents with natural system (rocks, sediments, and soils) responsible for an increase in the level of pollution. Therefore there is a need to control these elements at their source. Garie and McIntosh (1986) have confirmed that elevated pollutant concentrations during urban runoff storm events were short term and transient in nature.

The present study clearly shows that the degree of pollution in the groundwater of Karachi is not the results of storm water infiltration. This also is in conformity with the study of Eisen (1979) that the groundwater of Karachi is not significantly affected by total dissolved solid and trace metal.

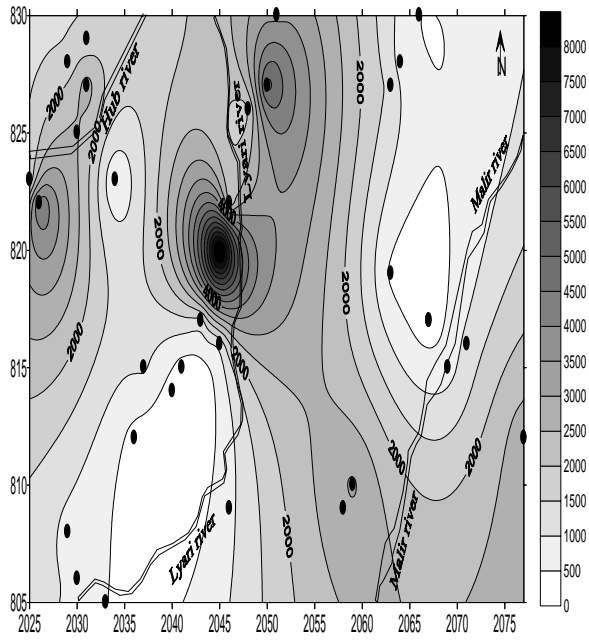
Eisen (1979) further reported that the aquifer found in sand, silt, clay, and gravel, just few meters above sea level are more contaminated with bacteria in an area of approximately 30 meter. His finding provides direct evidence for the study area, of why the groundwater of Karachi is not affected by trace metals. Our study is further supported by Malmquist and Hard (1981) that impact of storm water infiltration affects the groundwater quality only to a small extent while



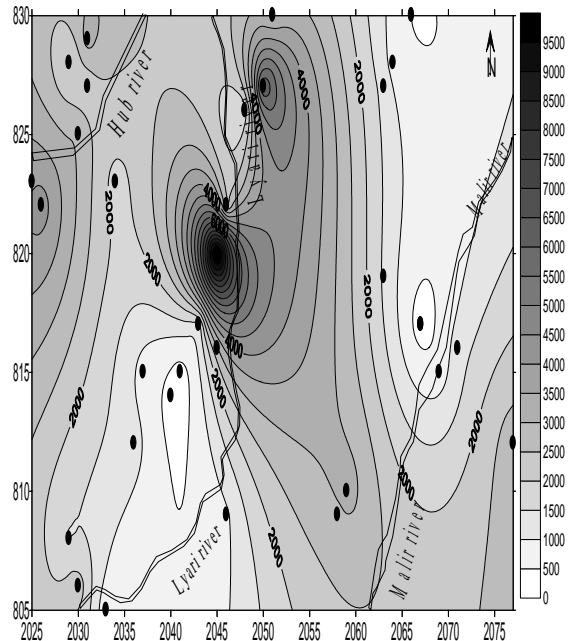
a. Pre-monsoon (Feb. 2007)



b. Pre-monsoon (May 2007)



b. Post monsoon (Sept. 2007)



d. Post monsoon (Nov. 2007)

Figure 8: Contour Map Showing Distribution and Migration Pattern of TDS Concentration.

the trace metal concentration remained within potable water range or unaffected.

It has been observed, particularly for copper and lead, that groundwater collected close to industrial areas is unaffected with these two metals in certain locations. This phenomenon suggests that trace metals movements are mainly influenced by the hydrological gradients, topography, and local geological structure such as porosity, permeability, joints, and physiochemical processes in the soil. Migration of determinants such as copper, iron, cadmium, lead, and zinc with groundwater down stream is quite significant as it increases the possibility of accumulation of pollutants in the Arabian Sea.

CONCLUSION

Certain trace elements are essential because they are absolutely necessary for life processes, whereas some are dangerous or considered potential health hazards even if present in trace quantities. They enter the human system through various pathways. The following inference is made from the data presented in this study:

- The irregular distribution of trace metals and total dissolved solids is due to man made or anthropogenic addition of effluents in nature; this is the result of poor management and over exploitation of natural resources.
- Determinants such as cadmium, copper, and total dissolved solids have exceeded the limits established by WHO (1993) many fold for drinking water. However, other trace metals, such as arsenic, are almost negligible, while lead, iron, and zinc are well with in permissible limits prescribed by WHO.
- Certain locations close to industrial area are still unaffected due hydrological gradients, topography and local geological structure such as porosity, permeability, joints and physiochemical process in the soil.
- Migration and distribution patterns of determinants such as copper, iron, cadmium, lead, and zinc with groundwater down stream is quite significant as it increases possibility of accumulation of pollutants in the Arabian Sea. The

distribution pattern of these trace metals could be used as a tools in providing guidance to curb the pollution of the study area.

This study suggests that regular monitoring of the quality of groundwater should be undertaken regularly to identify the magnitude and source of toxic pollutants which are responsible for the contamination of groundwater quality.

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ABOUT THE AUTHORS

A. Zubair completed his Ph.D. at the University of Ulster in 1998, United Kingdom. on "Ground water Pollution and its Impact on Health". His M.Phil. was on "Hydrological Studies". He has served in several R & D organization in Karachi-Pakistan in addition to serving as an Associate Professor and Director of Environment for Sir Syed University of Engineering & Technology, Karachi-Pakistan from 1988 to 2004. Since 2004 Dr. Zubair has served as a Professor and Chair of the Department of Environmental Science at the Federal Urdu University of Arts, Science and Technology, Karachi-Pakistan. To date, he has published 22 papers in national and international journals and has presented numerous papers in the

international and national conferences. His research interests are in monitoring and evaluation of groundwater and surface water, the interaction between ground surface water, contaminant studies, hydro geological and modeling studies, water resource management and conservation, and environmental chemistry. Dr. Zubair has been accepted for post doctoral research as a Fulbright Scholar (USA, August 2008).

M.A. Farooq completed his M.Sc in 1982 at the University of Punjab, Lahore, Pakistan in Geology. From 1983 to 2005, he served in the Department of Geology, Federal Urdu University of Arts, Science and Technology, Karachi-Pakistan. He is presently serving as an Associate Professor in the Department of Environmental Sciences and is involved in teaching undergraduate and graduate courses and supervising M.Sc. research projects in my environmental science. His main research interest is related to the impacts of storm water on ground water. He has published more than 7 papers and has presented numerous papers in international and national conferences on environmental studies related to environmental health.

H.N Abbasi completed his M.Sc. in Environmental Sciences in 2005 from Federal Urdu University of Arts, Science and Technology, Karachi-Pakistan. He has served as a Research Assistant in the Department (2006) and now serves as a Lecturer and is working on his doctoral research program.

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