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Impact of Stormwater on Spatial Patterns of Major Ions

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Abstract: Groundwater samples were collected from both open and bore wells over 591 km2 of Karachi, Pakistan pre- and post-monsoon 2007 to assess the potential for degrading the quality of underline groundwater resources and to evaluate transport of major ions as constituents of infiltrated storm water runoff into potable shallow aquifer system and to identify and quantify possible pathways of major ions in hydrological system and their distribution pattern. Chemical composition of groundwater in pre and post monsoon season is more or less the same although dilution of saline water by lateral flow of water during monsoon is involved. Major ions movements are influenced mainly 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.

Key words: Groundwater · Karachi · Spatial distribution · Stormwater

INTRODUCTION

Chemical compositions of groundwater are derived in general, from reactions of rainfall with rock and soil minerals. Notwithstanding the spatial variability of groundwater chemistry due to heterogeneous mineralogy and complex regional flow patterns, certain broad chemical relationships are well documented in the literature which link groundwater chemical types with groundwater movement [1, 2]. Toth [3] suggested a concise expression of the groundwater regime as the combined processes of distribution, chemistry and motion of the groundwater. The importance of hydrochemistry has led to a number of detailed studies on geochemical evolution of groundwater [4-7].

The data that have been reported in the literature, on the major ion chemistry of the groundwater in Karachi area, are related to their suitability for domestic and industrial uses [8, 9]. Eriksson [10] has observed that dissolution of air-borne salts from the Arabian Sea, which have accumulated since Pleistocene time has resulted in an increase in the salinity of groundwater. In addition to high salinity of groundwater near the Arabian Sea the presence of water is of marine origin, high rate of evaporation and non-flushing of water at deeper zone. However, in humid and semi-arid regions, throughout most of the year water infiltrating into an aquifer is relatively small. Therefore, the major influx of anthropogenic contaminant to the groundwater occurs [11-15].

The objective of the present study was to observe the change in Spatial and temporal patterns of major ions as a result of storm water infiltration, to identify the source of major ions in terms of chemical weathering of rock and to understand the relationship between mineralogy and water chemistry in the area and identify the source of salinity in groundwater / storm water.

MATERIALS AND METHODS

A survey has been conducted to establish the quality of groundwater through which storm water infiltrates into the basins. Three basins were selected for the study. All the sampling points are close to the basin and towards the hydraulically down gradient end, as determined from groundwater gradient and topographic maps in an attempt to increase the probability that the groundwater samples would be representative of the effect of storm water entering and infiltrating through the basins.

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132 groundwater samples from 33 monitoring wells were collected during the monitoring period starting during February 2006 to November 2007. The quality of water has been monitored on the basis of pre and post monsoon season (at half yearly intervals over two rainy seasons) and has been analyzed for the major ions and physical parameter. The groundwater samples collected prior to and after monsoon period were analyzed for comparative study to find out the impact of storm water. These samples cover the catchments basin of the Hub, Lyari and Malir river and were collected at considerable distances from each other. Most of these shallow wells are regarded as potable and are used for agricultural and domestic purpose by local people.

The physical parameters, pH, dissolved oxygen (DO), conductivity, salinity, total dissolved solids (TDS) and turbidity were performed on unfiltered samples with the help of Sension 156 HACH, USA. The groundwater sample analysis was carried out for major anion (chloride), cations (calcium and magnesium), alkalinity and hardness by titrimetric methods. Remaining anions (sulfate, nitrate), were determined by DR - 2800 UV VIS spectrophotometer of HACH USA.

RESULT AND DISCUSSION

Statistical analysis of the results of the total cations (TZ^+) and total anions (TZ^-) in pre and post monsoon seasons are significantly ($P<0.5$) correlated. It is implicit that the contribution of the ions other than those measured is insignificant for cations and anions charge balance.

The total dissolved solid concentration should be directly proportional to conductivity as this parameter is the sum of the ions which carry electrical charge such as Ca^{+2}, Mg^{+2}, Na^{+1}, K^{+1}, Cl^{-1}, SO_4^{-2}, CO_3^{-2} and HCO_3^{-1}. The high coefficient of determination (r^2=0.99 in both seasons) demonstrates that these eight major ions contribute significantly to the conductivity of the groundwater/stormwater samples.From the results it appears that chemical composition of groundwater in pre and post monsoon season is more or less the same although dilution of saline water by lateral flow of water during monsoon is involved [11].

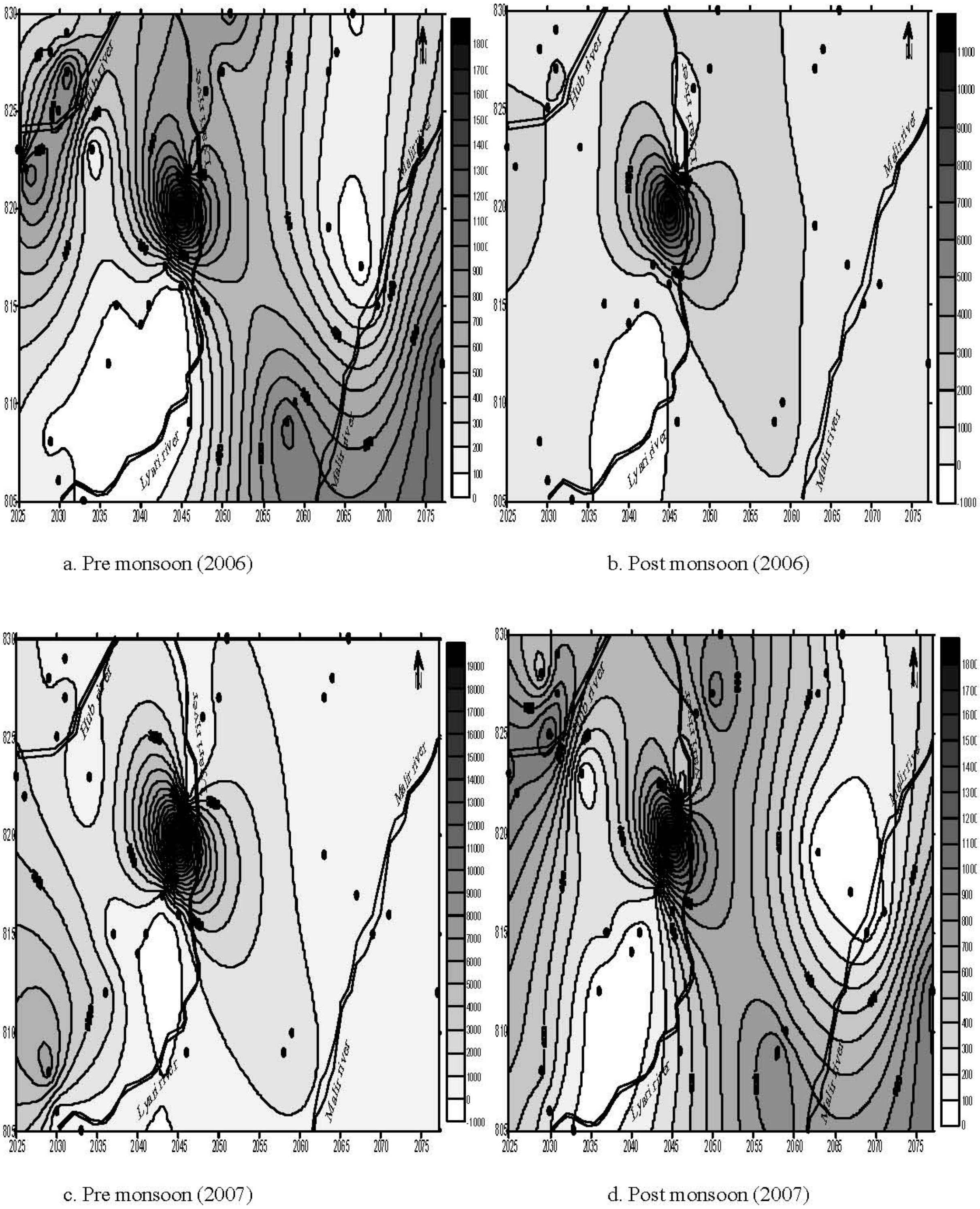
Cations: During the monitoring period pre and post monsoon season (2006 and 2007), the concentration of calcium, magnesium, sodium and potassium increases roughly linearly with the conductivity. Particularly, sodium and magnesium cations demonstrate a significant correlation with conductivity (P= 0.05). The majority of the variance is based on the mean coefficient of determination. This suggests that catchment geology is not a major factor in influencing the cations composition as concluded by Rippey and Gibson [16] in their study of fresh water in Northern Ireland (U.K).

While, the coefficient of determination for calcium is considerably lower than for magnesium and sodium, the two samples one with the highest calcium concentration mg 660 l^{-1} and other with highest conductivity 89 mS cm^{-1} have a strong influence in pre monsoon period. When these points are removed, the coefficient increases considerably to 0.62 (r^2 = 0.62). This is due to the increase of calcium concentration and conductivity suggesting a lack of precipitation of calcium carbonate in these two points particularly.

The potassium concentrations are relatively low compared to other cations as most of the samples in the pre monsoon periods (2006 and 2007) range below 30 mg l^{-1} and in post monsoon (2006 and 2007) below 20 mg l^{-1}. The concentration is very weakly related to conductivity and it is likely that the upper concentration limit is due to incorporation into clay minerals and/or being fixed by minerals [17].

Migration of Major Ions: In the central and northern part of the study area (Figs. 1and 2) the concentrations of sodium and chloride in the groundwater is high during pre monsoon season period of 2006 and 2007.This may be due to the stronger influence of evaporation / crystallization on the groundwater. It is the lack of dilution of groundwater during pre monsoon season from storm water in the regions that allows the evaporation / crystallization factor to be stronger there. This change in the composition and concentration of chloride and sodium are caused by low rainfall and high evaporation rate accompanied by a lack of dilution, leading to an increased salinity in the groundwater during the pre monsoon season. The lower concentration of sodium and chloride in the post monsoon season is mainly attributed to the storm water infiltration in the groundwater.

One sample showed a strong influence on the contour distribution in the northern part of the study area (Figs. 1and 2). This sample with very high sodium and chloride concentrations during the monitoring years 2006 and 2007 as compared to the surrounding samples is strongly influenced by local geological factors. It can be explained that high concentration of sodium and



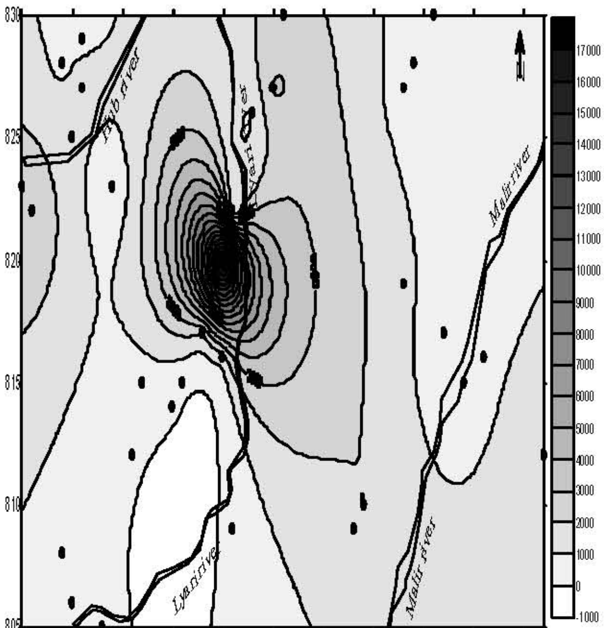
a. Pre monsoon (2006)

b. Post monsoon (2006)

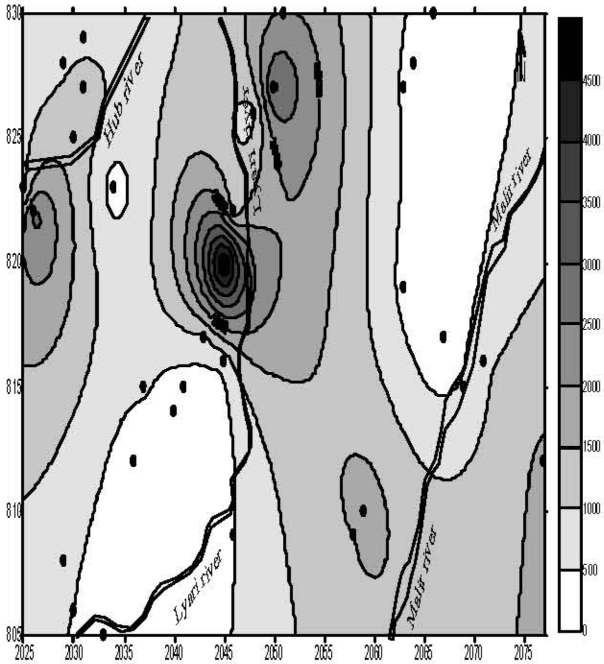
c. Pre monsoon (2007)

d. Post monsoon (2007)

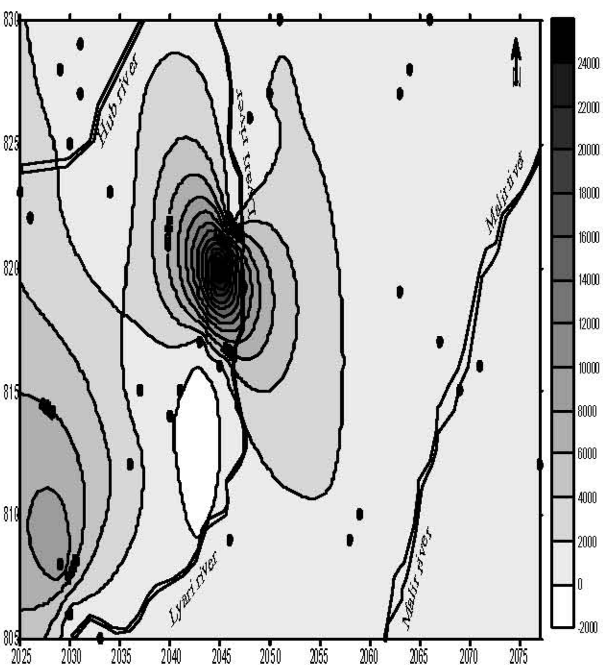
Fig. 1: Contour map showing distribution of Sodium concentration



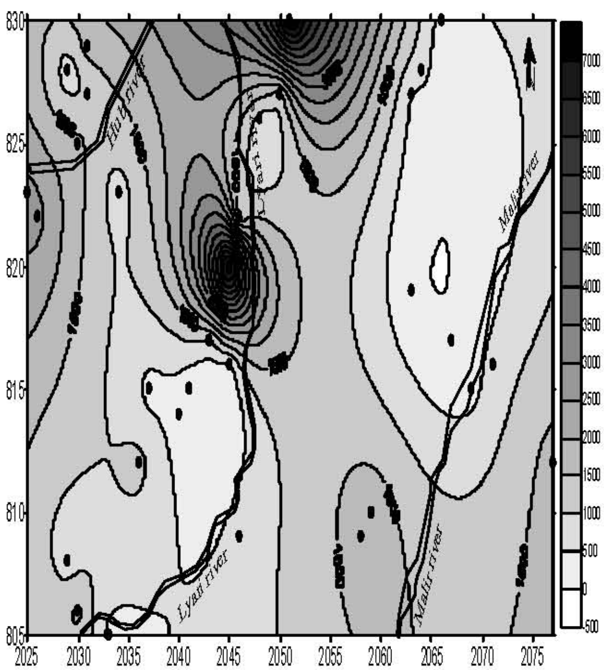
a. Pre monsoon (2006)



b. Post monsoon (2006)

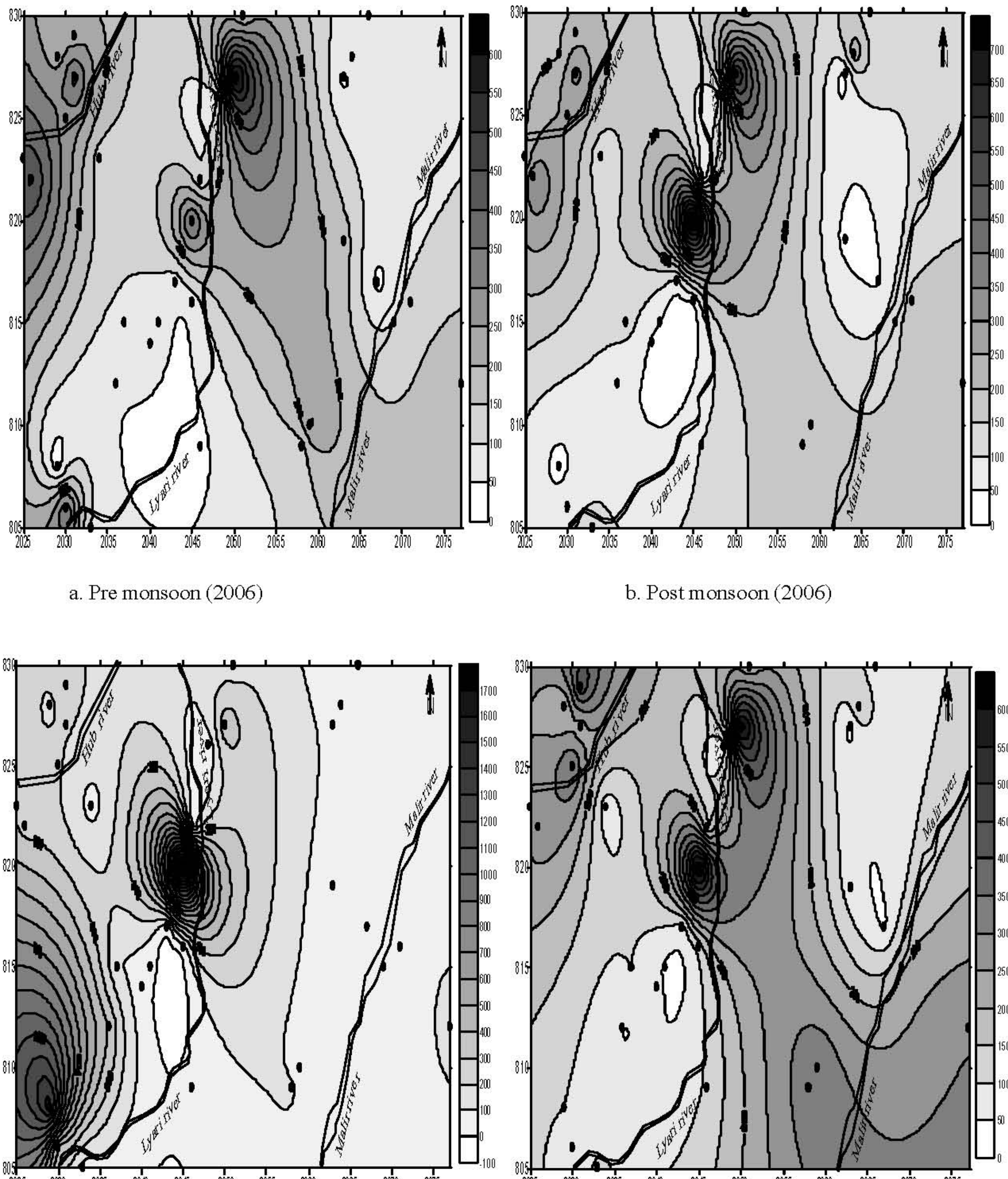


c. Pre monsoon (2007)



d. Post monsoon (2007)

Fig. 2: Contour map showing distribution of Chloride concentration.



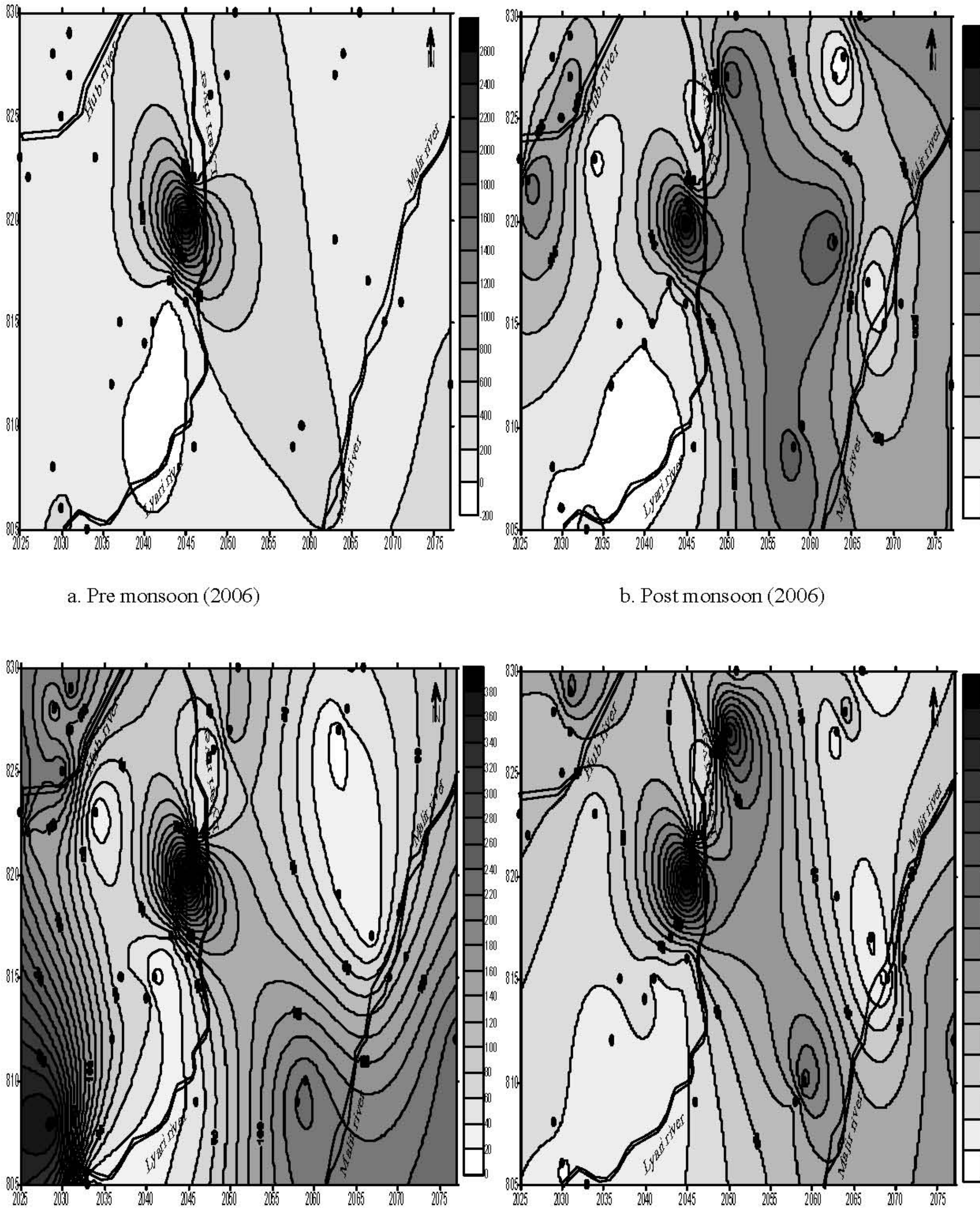
a. Pre monsoon (2006)

b. Post monsoon (2006)

c. Pre monsoon (2007)

d. Post monsoon (2007)

Fig. 3: Contour map showing distribution of Calcium concentration.



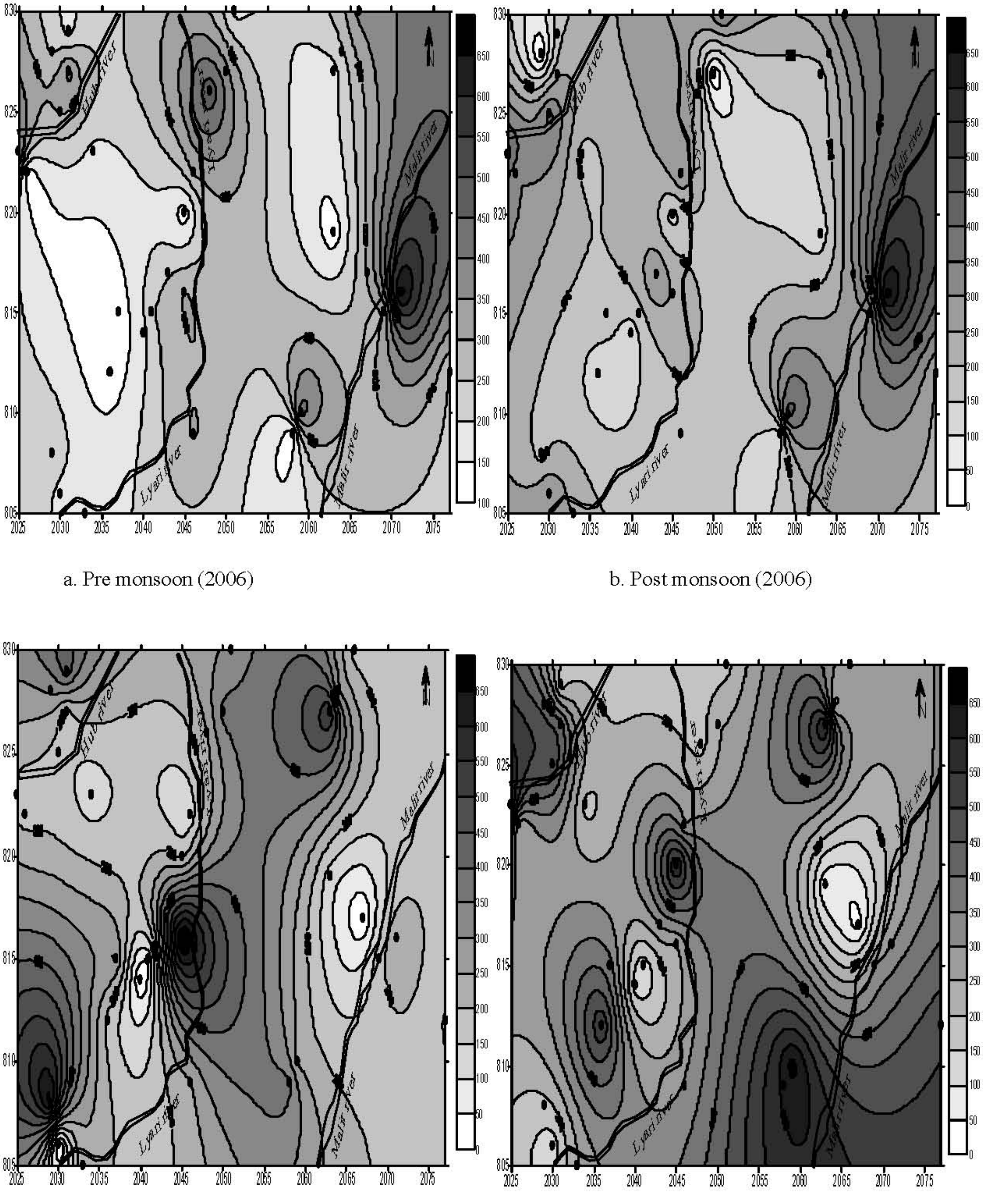
a. Pre monsoon (2006)

b. Post monsoon (2006)

c. Pre monsoon (2007)

d. Post monsoon (2007)

Fig. 4: Contour map showing distribution of Mg concentration.



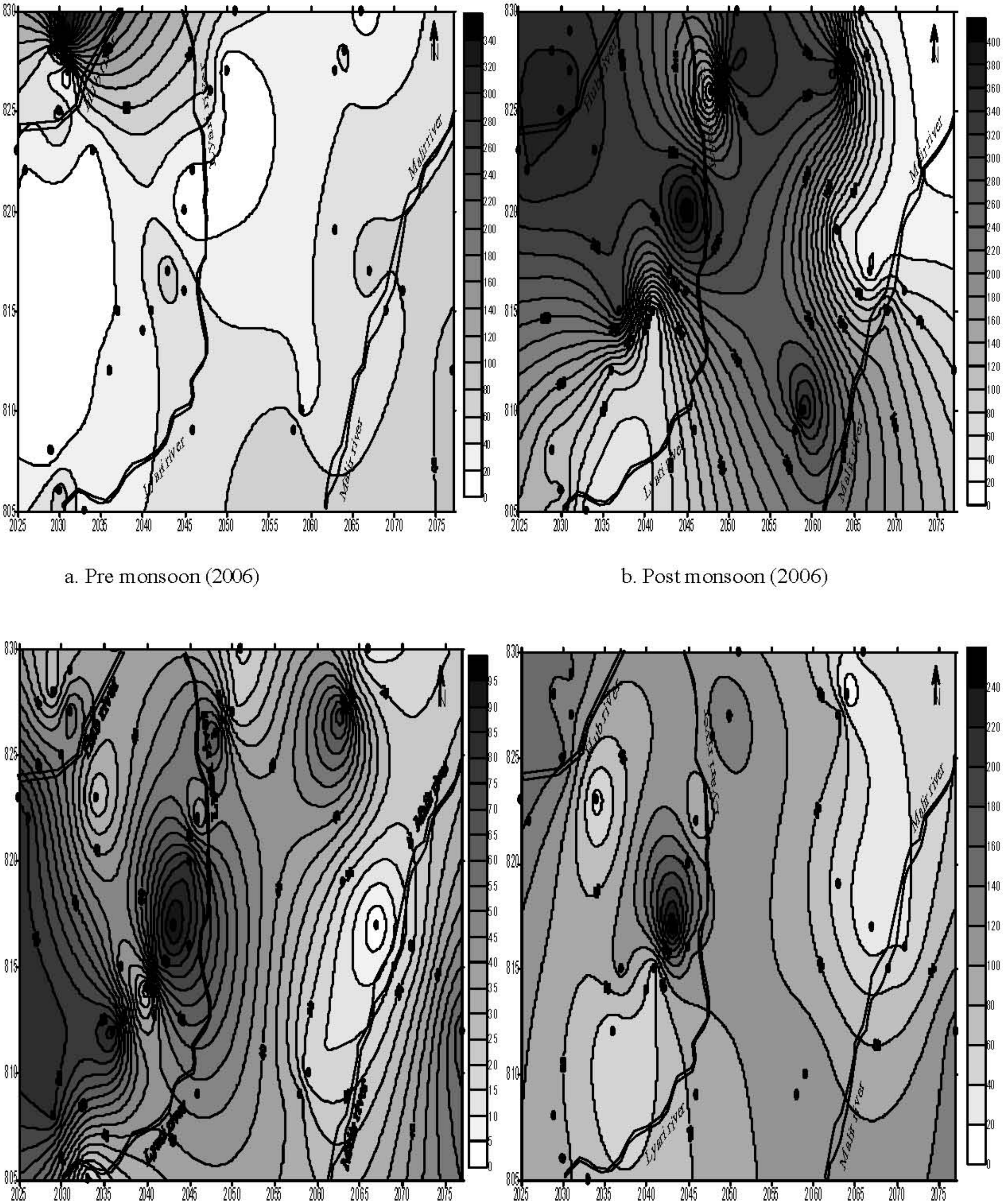
a. Pre monsoon (2006)

b. Post monsoon (2006)

c. Pre monsoon (2007)

d. Post monsoon (2007)

Fig. 5: Contour map showing distribution of Bicarbonate concentration.



a. Pre monsoon (2006)

b. Post monsoon (2006)

c. Pre monsoon (2007)

d. Post monsoon (2007)

Fig. 6: Contour map showing distribution of Sulfate concentration.

chloride ions at this location is possibly because of the geologic control. This area is exclusively dominated by clay having fine intercalation of sand in which salt accumulate and subsequently diffuse in the groundwater in the form of perched water bodies [8].

The contour map of Ca and Mg resembles that of sodium (Figs. 3 and 4) with elevated level of concentration in the specific area as shown in the figure. This is attributed to the geologic control in northern part of the study area. An anomalous concentration of magnesium in south east is observed close to the coastal area. This condition could be due to the encroachment of sea water infiltrating into the groundwater during pre monsoon. Since the sea water is relatively high in magnesium the anomalous zones are restricted to the coastal areas [18]. The contour pattern of bicarbonate (Fig. 5) broadly follows the patterns of chloride, sodium, calcium and magnesium area during the monitoring years. The concentration is high in the region because of super-saturation with calcium carbonate due to precipitation [19].

The high concentration of sulfate is in the south east part of the study area near sea (Fig. 6). This may be due to the intrusion of seawater into the adjacent groundwater. The data show that the concentration of sulfate is lower than the other anions. This is because of iron which reduced the solubility of sulfate in groundwater [20, 21]. An identical pattern is observed in all the samples taken during the monitoring period i.e. before and after monsoon season.For an analysis of the concentration and distribution of sodium, calcium and magnesium as well as bicarbonate, chloride and sulfate, thirty three (33) monitoring samples of groundwater was taken during the pre and post monsoon season in 2006 and 2007. The investigation shows that four factors determine the behavior of these major ions. These are: evaporation /crystallization, dilution of groundwater, sea water intrusion and small effect of local geology. The evaporation / crystallization process is the most important and is the dominating factor controlling the salinity of groundwater of the study area. This behavior is due to low rain fall and high rates of evaporation

The dilution of groundwater is responsible for lower salinity in specific areas, particularly in urban part where waste water is disposed of, or near the leaky water supplies and sewerage lines or near the cultivated land / farms houses.

The intrusion of sea water into groundwater does not show any significant impact except on magnesium and sulfate, which is result of intrusion of sea water into adjacent groundwater of the studied area [18].

The study revealed that local geology has not shown any significant influence on groundwater of study area. In alluvial deposit of sand, silt, gravel and clay where the large number of unconfined aquifer occurs, there are no effects of geology of chemical composition of the groundwater except in location no. 13, exclusively dominated by clay with fine intercalation of sand. Further more hydrological pathway of these aquifers also shows unconfined aquifers and is not influenced by local geology.

Using the arithmetic average concentrations of 33 monitoring samples (from the same numbers of locations), the dominant cations and anions of the groundwater of study area are in the following order during the monitoring years 2006 and 2007 i.e. pre and post monsoon season: $Cl > Na > HCO_3 > Ca > Mg > SO_4 > CO_3 > K$.

The very large number of samples with Na/(Na + Ca) ratio above 0.5 during the monitoring period (one each from pre and post monsoon seasons during 2006 and 2007) follow the evaporation / crystallization series (Fig. 7). This may suggest that low calcium and magnesium concentration makes groundwater evaporative and will leave the water dominant in sodium. It is the crystallization / precipitation of calcium carbonate as the ions in the water are concentrated by evaporation that results in the dominance of the sodium ions [22].

While there is much scattered relationship between conductivity and weight concentration ratio, the slope is significantly ($P=0.05$) different from zero. This further confirms that evaporation / crystallization is the dominant factor controlling the salinity of the groundwater. This change in composition and concentration is due to low rainfall and high rate of evaporation, which increases salinity and precipitation of calcium carbonate in groundwater.

Evaporation / Crystallization of Groundwater in Study Area: The data from this study are placed in a world context by plotting on the classic diagram of Gibbs [23] of total dissolved solid against the weight concentration ratio Na/(Na + Ca) in Fig. 7. In the study area during the monitoring period, majority of points lie within the envelope line of the evaporation / crystallization axis (Fig. 7). Also, included are few samples in pre monsoon season (2006 and 2007) showing rock dominance at the bottom left side of the figure. The slope of the descending points cluster is very similar to the slope of mid line of Gibbs diagram and the total dissolved solids of some (33) samples from each monitoring season (pre and post monsoon 2006 and 2007) at high Na/(Na + Ca) are lower than Gibbs model. An analysis of the location of the wells shows that those points which have a salinity lower then expected from Gibbs model are close to wastewaters which are disposed of or to leaky water supply and sewerage lines in the urban area or near agriculture land / farms houses in sub-urban part of the city that are causing the lower salinities in these groundwater samples. This show that anthropogenic addition disturbs these natural relationships, thus deviations from natural geochemical patterns of association indicate anthropogenic input [24].

The above mentioned factors are certainly important for groundwater in the study area. Firstly, it explains why some groundwater samples have a lower salinity (section 4.4) than expected. Next, it signifies the specific urban areas with leaking water supply pipes and sewerage lines, which reduce groundwater salinities measured in the samples. Overall, it is this factor that explains why few samples of the groundwater do not follow the Gibbs's model.

The basic Gibbs's model for the control on the concentration and composition of surface waters has been extended by W.yu. and Gibson [25] and used the interrelationship of log [(Ca lake/Na lake) (Ca rain/Na rain)] and log (TDS lake/TDS rain) to distinguish the relative importance of rock dominance, crystallization and evaporation to the salinity of surface water. High alkalinity water is mainly enriched by sodium and very little with calcium because the latter is removed as $CaCO3$ due to precipitation. The main control on the salinity of groundwater is shown by this approach to be crystallization.

CONCLUSION

It was concluded that chemical composition of groundwater in general shows more or less the same trend in both seasons during the monitoring period although dilution of the saline water by lateral flow of the groundwater during monsoon is involved. The distribution pattern of majors ions reveals that these ions are accumulate towards Arabian Sea.

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