

## THE VARIATION OF CALCIUM, MAGNESIUM, SODIUM, POTASSIUM AND BICARBONATE CONCENTRATION, pH AND CONDUCTIVITY IN GROUNDWATER OF KARACHI REGION

Arif Zubair<sup>\*a</sup> and Syed Ikramuddin Ali<sup>b</sup>

<sup>a</sup> Geological Survey of Pakistan, Karachi, Pakistan

<sup>b</sup> Institute of Human Settlement and Environment, Sir Syed University of Engineering and Technology, Karachi, Pakistan

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Groundwater in Karachi is influenced mainly by the evaporation / crystallization process as expressed by the Na/(Na+Ca) weight concentration ratio. The high coefficient of determined between conductivity and total dissolved ions concentration in meq<sup>l</sup> revealed that major ions affect the conductivity of groundwater. It was also found that groundwater quality with respect to cations is not significantly influenced by geology, particularly in the Urban area of the city, where the 90% of the population resides. The relationship between conductivity and bicarbonate concentration shows that supersaturation of groundwater with carbon dioxide is responsible for general depression of pH.

**Key words:** Groundwater, Cations concentration, Evaporation/crystallization, Supersaturation.

### Introduction

The three major mechanisms controlling world water chemistry are atmospheric precipitation, rock dominance and the evaporation-crystallization process. In defining these three controls, Gibbs (1970) used the Na/(Na+Ca) mole concentration ratio. It is also used here to help define the regional trends of major cations concentration, conductivity and pH in the groundwater of Karachi region.

### Materials and Methods

Groundwater samples (193) were collected between 1993 to 1995. Samples were uniformly taken from the study area and cover a range of altitude and geology (Fig. 1). Each sample was obtained with due care that it does not deteriorate or get contaminated with any other substances. The well was pumped sufficiently long enough to ensure that the collected sample represent the groundwater from the aquifer. In most of the cases the wells range in depth from 15 to 70 meters and are regularly used by the owners.

The pH was measured in the field using a portable meter (Lovibond 2100). Three or four groundwater samples were collected each day and the survey was completed in two years. Samples were filtered in the field through prewashed 0.45 µm membrane filters and on returning to the laboratory stored deep-frozen for later analysis. Conductivity was electrometrically (Radiometer CDM 3) measured before freezing and the calcium, magnesium, sodium and potassium concentrations

were determined by atomic absorption spectroscopy (Perkin Elmer 403), with lanthanum chloride addition for calcium. The bicarbonate concentration were determined by acid titration.

### Results and Discussion

**Total dissolved solids.** The relationship between conductivity and total dissolved ion concentration in meq l<sup>-1</sup> shown in Fig. 2 for accuracy of the data. Major ions, Ca<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> mainly originate from rock weathering and Na<sup>+</sup> and Cl<sup>-</sup> mainly

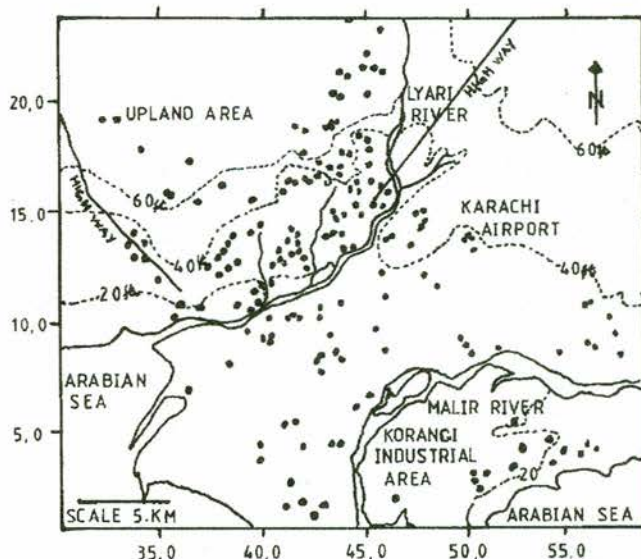


Fig 1. Sampling sites with grid reference in Karachi urban area.

\*Author for correspondence



from precipitation. Total dissolved solids are the product of the two sources modified by evaporation / crystallisation. Gibbs (1970) summarized the preceding concepts and proposed a descriptive model regarding the three processes, which are rock weathering, atmospheric precipitation and evaporation/crystallisation. The  $\text{Na}/(\text{Na}+\text{Ca})$  ratio and the total dissolved solids (TDS) Karachi groundwater are plotted in Fig. 3. The descending limb of increasing  $\text{Na}/(\text{Na}+\text{Ca})$  with decreasing TDS can be interpreted as the increasing dominance of precipitation over rock weathering in determining water chemistry. The ascending limb with increasing  $\text{Na}/(\text{Na}+\text{Ca})$  and increasing TDS, lead towards saline water and represents the evaporation / crystallisation. The Gibb's model has since been used as a standard model of world water chemistry.

The data from the present study can be placed in a world context by plotting on the classic diagram of Gibb's (1970) of total dissolved solids against the mole concentration ratio  $\text{Na}/(\text{Na}+\text{Ca})$  in Fig 3. In this study the authors found that the majority of points lie within the envelope line of the evaporation / crystallisation axis (Fig 3). Also included are some results of samples with rock dominance at the bottom left side of the diagram. The slope of the descending points cluster very similar to the slope of the mid line of Gibb's diagram and the total dissolved solids of some (52) samples are at high position in  $\text{Na}/(\text{Na}+\text{Ca})$  and their trend is lower than Gibb's model. An analysis of the location of the wells indicates that those, which have salinity lower, than expected from the Gibb's model are near to sewage wastewater's disposal sites or to leaky water supply and sewerage lines. This suggests that the groundwater recharge by sewage wastewater and leakage from water supply and sewerage lines cause the lower salinities in this case. It shows that the mixing of recharge water with saline groundwater dilutes the well water that are close to the rivers, sewage and water supply lines. These wells get recharged directly from these sources due to extremely inefficient water and sewage facilities affected by the frequent leaking, choking and overflowing. This indicates that anthropogenic addition disturbs these natural relationships, thus deviations from natural geochemical patterns of association indicate anthropogenic input (Bhosale and Sahu 1990).

Few wells (9) had lower salinity than expected from the Gibb's model, but were not close wastewaters disposal sites or to leaky water supply and sewerage lines. They are, however, close to underground water storage tanks of houses. The dilution in these cases is probably caused by leakage of the water storage tanks. Gazdar (1993) also observed this point in his study for Karachi.

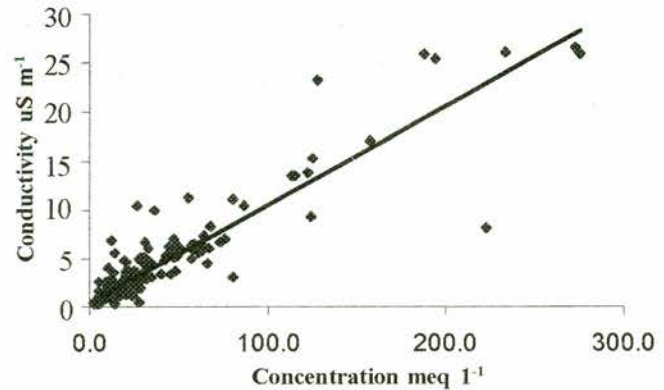


Fig 2. The relationship between conductivity ( $\text{uS cm}^{-1}$ ) and total ionic concentration ( $\text{meq l}^{-1}$ ),  $\text{uS cm}^{-1}$ ,  $0.58 + 0.1001(\text{meq l}^{-1})$ ;  $r^2$ , 0.82; n, 193.

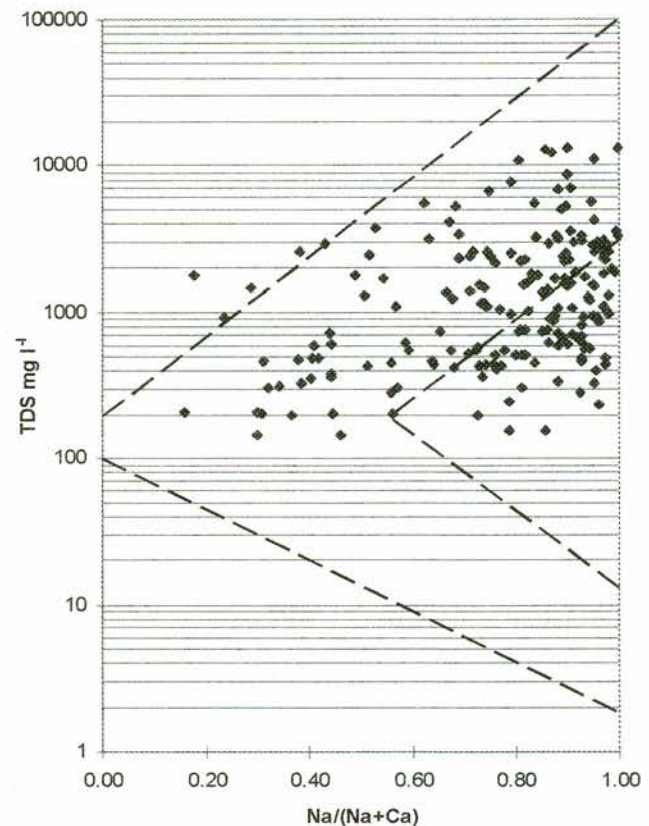


Fig 3. Gibbs Model showing evaporation crystallisation series found in groundwater of studied area. Gibbs Model (-----), Groundwater samples of Karachi (◆◆◆).

The evaporation/ crystallisation process in the study area of W. Yu and Gibson (1996) is also confirmed with our study. They developed the model for freshwater in Northern Ireland (UK). Their model also demonstrates that the main control on the salinity of groundwater is the crystallisation of salts. Use of Gibb's model further suggests that groundwater of Karachi



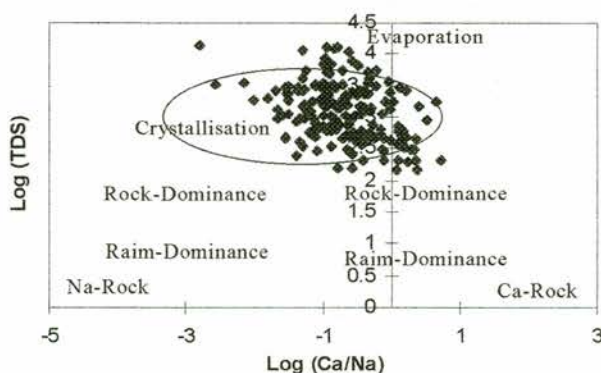
is mainly influence by the evaporation / crystallisation process.

The argument given by Ericksson (1976) for saline groundwater in an alluvial aquifer of the Dehli area (India) seems true for ground water of Karachi because of the similar climatic and geological conditions. He argue that in Dehli, as the alluvium was thoroughly washed by water about 20,000 years ago during a pluvial period, it could not have retained enough saline deposit to cause very high salinity. He also observed that the dissolution of air-borne salts from the Arabian sea. Which have accumulated since the Pleistocene, results in an increase in salinity of groundwater.

Dilution is not only responsible for lower salinities of Karachi ground waters but also for the degree of saturation. This also suggests that ground water influenced by dilution why has low/medium degree of supersaturation with calcium carbonate contrary to topographically high area of Karachi where the lack of dilution makes groundwater highly supersaturated with calcium carbonate in the absence or low rate of infiltration due to rapid runoff which is the characteristic of arid land.

This is broadly in line with Gibb's model so for the controls on the concentration and composition are concerned. However it can be well explained in the light of model extended by W yu and Gibson (1996) by establishing 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, crystallisation and evaporation to the salinity of waters. High alkalinity in waters is caused by sodium mainly, and very little with calcium because calcium is removed as a  $CaCO_3$  due to precipitation. The main control on the salinity of the Karachi groundwaters is shown by this approach (see Fig. 4).

**Cations.** In Karachi groundwaters the concentration of Ca, Mg, Na, and K increases linearly with conductivity (Figs. 5, 6, 7 & 8) particularly Na and Mg, as the slopes of these

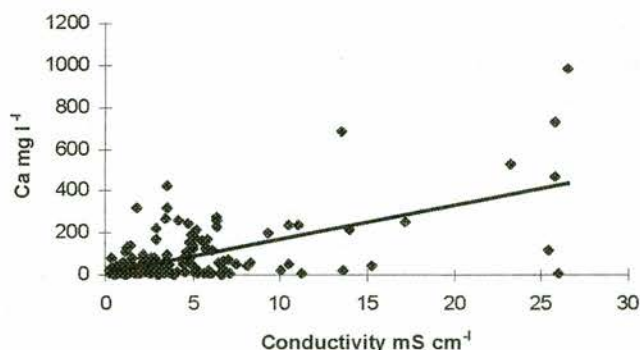


**Fig 4.** The relationship between Log (TDS) and Log (Ca/Na) indicating crystallisation of groundwater (W. yu and Gibson 1996) in Karachi area.

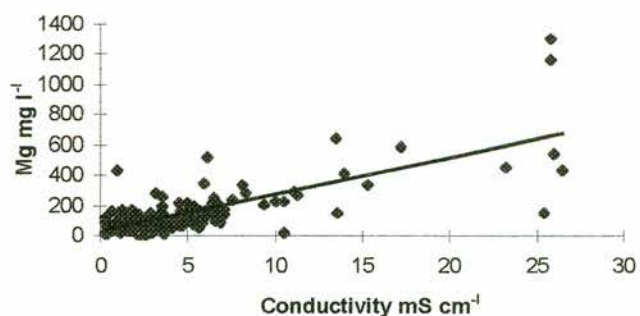
cations relationship with conductivity are significantly different from zero ( $P = 0.05$ ). Sixty percent of the variance, based on mean coefficient of determination of Ca, Mg and Na is explained by the linear relationship with conductivity (Figs. 5, 6, 7 & 8) and suggests that catchment geology is not a major factor in influencing the cations composition, as concluded by Rippey and Gibson (1984) in their study in Northern Ireland (UK).

While the coefficient of determination for Ca is considerably lower than for Mg and Na in the sample with the highest Ca concentration ( $mg\ 983\ l^{-1}$ ) which has a strong influence on this value. When this point is removed, the coefficient decreases to 0.31 ( $r^2 = 0.31$ ). This lack of a strong increase of Ca concentration with conductivity, compared to magnesium and sodium, is due to the precipitation of  $CaCO_3$ . This process maintains the calcium concentration below  $450\ mg\ l^{-1}$ , whereas the Mg rises to  $700\ mg\ l^{-1}$  and sodium to  $2000\ mg\ l^{-1}$  in Karachi groundwater.

The K concentrations are extremely low compared to the other cations, generally below  $7\ mg\ l^{-1}$ . The concentration is very weakly related to conductivity ( $r^2 = 0.25$ ) and it is likely that the upper concentration limit is due to its incorporation into clay minerals and/ or being fixed by minerals (Loughan 1969).



**Fig 5.** The relationship between ( $mg\ Ca\ l^{-1}$ ) and conductivity ( $mS\ cm^{-1}$ ),  $mg\ Ca\ l^{-1}$ ,  $11.94 + 16.20 (mS\ cm^{-1})$ ;  $r^2$ , 0.40; n, 193.



**Fig 6.** The relationship between ( $mg\ Mg\ l^{-1}$ ) and conductivity ( $mS\ cm^{-1}$ ),  $mg\ Mg\ l^{-1}$ ,  $32.91 + 24.12 (mS\ cm^{-1})$ ;  $r^2$ , 0.60; n, 193.

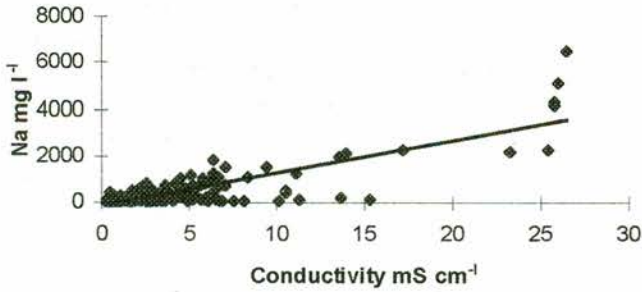


Fig 7. The relationship between (mg Na l<sup>-1</sup>) and conductivity (mS cm<sup>-1</sup>), mg Na l<sup>-1</sup>, -128.78 + 139.42 (mS cm<sup>-1</sup>); r<sup>2</sup>, 0.70; n, 193.

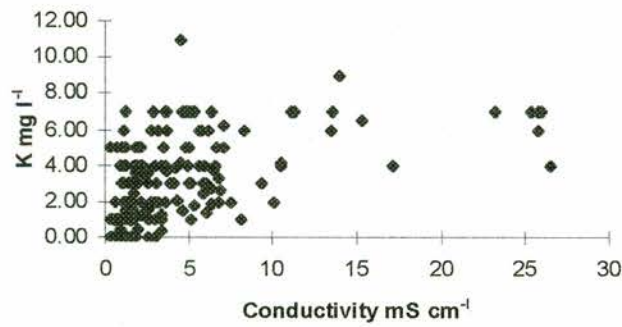
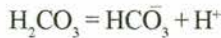


Fig 8. The relationship between (mg K l<sup>-1</sup>) and conductivity (mS cm<sup>-1</sup>), mg K l<sup>-1</sup>, 2.05 + 0.24 (mS cm<sup>-1</sup>); r<sup>2</sup>, 0.25; n, 193.

*pH*. Bicarbonate is the main carbonate species that controls pH. It is generally agreed that the carbonate system controls the pH of natural waters. Biological processes may also change the carbon dioxide concentration, which influences pH (Hutchinson 1957; Broecker and Oversby 1971; Stumm and Morgan 1996).

A simple model showing some of the characteristics of the carbonate system of natural waters is provided by equilibrating pure water with a gaseous CO<sub>2</sub> at a constant partial pressure (Stumm and Morgan 1996). The pH by the addition of a strong base or strong acid, thereby keeping the solution in equilibrium with pCO<sub>2</sub>.



Using Henry's law

$$\{H_2CO_3\} = K_H pCO_2$$

$$K_1 = \frac{\{H^+\}\{HCO_3^-\}}{\{H_2CO_3\}}$$

So,

$$\{H^+\} = \frac{K_1 K_H pCO_2}{\{HCO_3^-\}}$$

$$-\log \{H^+\} = \log \{HCO_3^-\} - \log K_1 - \log K_H - \log (pCO_2)$$

Now

$$pH = -\log \{H^+\}$$

assuming CO<sub>2</sub> in equilibrium (Stumm and Morgan 1996),  
 $-\log(pCO_2) = -\log(10^{-3.5})$

and

$$\{HCO_3^-\} = \gamma_1 [HCO_3^-]$$

Here [HCO<sub>3</sub><sup>-</sup>] is bicarbonate concentration in moles per liter and γ<sub>1</sub> is the activity coefficient.

For conversion of concentration from mg l<sup>-1</sup> to moles l<sup>-1</sup>,

$$[HCO_3^-] = \text{Concentration of bicarbonate in mg l}^{-1} / 61000$$

The values of the log function are mentioned (Stumm and Morgan 1996).

$$-\log K_H = 1.47$$

$$-\log K_1 = 6.35$$

$$-\log(pCO_2) = 3.5$$

and the value of activity coefficient calculated on the basis of 16 selected samples for supersaturation of calcium carbonate is

$$\gamma_1 = 0.9$$

These model and values were used to predict the pH of groundwaters of Karachi (Fig. 9).

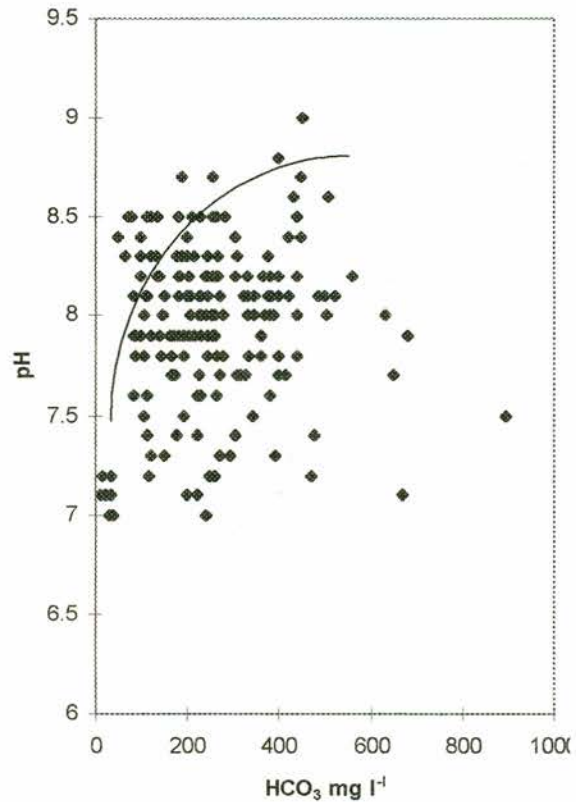


Fig 9. The relationship between pH and bicarbonate concentration. The solid lines show the theoretical curve.



There is some support for the bicarbonate control on pH. The results show that in many samples measured, the pH is less than the predicted values in groundwaters of Karachi. Similarly the low pH was also found by Rippey and Gibson (1984) in their study of freshwater in Northern Ireland (UK) and gave the assumption for the carbonate control on pH by  $\text{Ca}^{+2}$  and  $\text{HCO}_3^-$ .

Similarly for groundwater in Karachi, it is assumed that the activity coefficient of unity for using the conductivity to estimate the ionic strength and calculating the  $\text{HCO}_3^-$  activity coefficient is 0.9 for these samples. Another assumption can be drawn that  $\text{CO}_2$  is in equilibrium with water at a partial pressure of  $10^{-3.5}$ . When using the activity coefficient 0.85 and 0.95 i.e., below and above the actual value 0.9 shows no bias to the theoretical curve, so this cannot be the cause of low pH. This indicates that pH variation in groundwater is broadly determined by the bicarbonate system with carbon dioxide supersaturation depressing the pH below the background value.

Using this assumption, theoretical model shows that measured pH is less than predicted pH. The empirical relationship between pH and  $\text{HCO}_3^-$  (Fig. 9) with the empirical curve developed by Henrikson (1979) identify acidification of groundwater which shows that acidification is not responsible for the lower pH. Supersaturation of groundwater with carbon dioxide appears to be responsible for the general depression of pH from the expected background chemical values (Rippey and Gibson 1984) in the study area. Our results show that there are patterns in the concentrations of calcium, magnesium, sodium, potassium, bicarbonate, conductivity, and pH in the groundwaters of Karachi.

The supersaturation of groundwater with carbon dioxide appears to be responsible for the general depression of pH (Rippey and Gibson 1984) in relation to the expected background value. Supersaturation of freshwaters with carbon dioxide is very common (Holland 1978). Hutchinson (1957) also considers that some freshwaters are somewhat supersaturated. Garrels and Mackenzie (1971) also found that most freshwater are supersaturated with carbon dioxide.

### Conclusion

The patterns of calcium, magnesium, sodium, potassium and bicarbonate concentrations in 193 groundwater samples, which cover a wide range of geology and altitude present in Karachi urban area, are described. The  $\text{Na}/(\text{Na}+\text{Ca})$  weight concentration is used to indicate the relative importance of rock and atmospheric sources to the groundwater composition.

The above mentioned factor is certainly important for groundwaters in the Karachi area. Firstly, it explains why some groundwater samples have a lower salinity than expected. It

is also important only in specific areas, those close to where sewage wastewaters are disposed of or to leaky water supply and sewerage lines. Overall, it is this factor that explains why some of the Karachi groundwaters do not follow the Gibb's model.

Using the Gibbs approach and Wu. & Gibson models, the results show that the main control on the salinity of the groundwater is caused by the evaporation/crystallization process. The linear relationship of conductivity with cations suggests that catchment geology is not a major factor influencing the cations composition.

The results demonstrate that the groundwater of the study area is mostly saline, except in some location where dilution has occurred due to mixing with freshwater leaked from water and wastewater pipes resulting in a lower salinity than expected.

Based on the activity coefficient for low and high pH values, the models show that the measured pH is less than the predicted pH. Carbon dioxide supersaturation of groundwater is probably the reason for this.

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