

# Saturation states of carbonate minerals in a fresh-water-seawater mixing zone of small tropical island's aquifer

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**Abstract** Groundwater is a crucial resource on the Manukan Island as it is the only source of freshwater available on the island. The aquifer has deteriorated to a high degree, during the last decade. Nine domestic wells were sampled from March 2006 to January 2007 to probe the hydrochemical components that influence the water quality. Geochemical data on dissolved major constituents in groundwater samples from the Manukan Island revealed the main processes responsible for their geochemical evolution. The results using statistical analyses, graphical method and numerical model output (PHREEQC) showed that the groundwater was chemically highly enriched in Na and Cl, indicative of seawater intrusion into the aquifer as also supported from the Na-Cl signature on the Piper diagram. From the PHREEQC simulation model, calcite, dolomite and aragonite solubility showed positive values of the saturation indices (SI), indicating supersaturation which led to mineral precipitation condition of water by these minerals.

**Key words** Manukan Island; seawater intrusion; hydrochemistry; saturation index

## 1 Introduction

The solubility of a mineral involves the maximal concentrations of its components in water. Minerals present in aquifers are often in rather mixtures or solid solutions of different minerals (Appelo and Postma, 2005). Mixing of seawater with fresh groundwater is of great importance for the chemical diagenesis of carbonate rocks and sediments. Mixing of two fluids saturated in a carbonate mineral may bring about changes in the saturation state of the new solution. The two common carbonate minerals, calcite and aragonite; differ in their solubility, with aragonite being more soluble. Mixing of seawater and fresh groundwater has been interpreted as being responsible for carbonate dissolution at the time of seawater intrusion in coastal aquifers where the potential for dissolution/precipitation of calcite, aragonite and dolomite, by the mixing of seawater and fresh groundwaters, has been demonstrated theoretically (Back et al., 1979; Smart et al., 1988; Wicks and Herman, 1996).

In the fragile environment of small carbonate island's aquifer, especially for a tropical climate region,

the saturation states of various carbonate mineral species have been rarely reported. This fragile environment is rather affected by human activities induced to its chemical equilibrium, especially on the fresh groundwater chemistry. Since most of the small carbonate islands in this region are a major attraction for tourism activities, such an environment is exploitable and put under stress for its ecologic balance. Small islands have their own special physical, demographic and economic features. The prevalent issue relevant to those small islands is freshwater supply. Since the freshwater existence has become the most important source for the small islands' community, pumping from the upper phreatic zone is widely practiced for the freshwater supply. The over abstraction causes the movement of seawater into the aquifer and mixing with freshwater.

Since the mixing between freshwater and seawater in the aquifer tends to alter the fresh groundwater in the system, the potential for saturation of carbonate minerals by the mixing of fresh groundwater and seawater has been studied thoroughly. Although this process has been explained by several authors (Al-Agha, 2005; Martin et al., 2005; Wen et al., 2005), there has been only limited research on the geo-

chemical processes of mixing between freshwater and seawater in small islands' aquifer, especially in a tropical region. A hydrochemical study on seawater intrusion seems simple, given that in the majority of cases where the seawater represents extreme features in the freshwater and seawater mixture. However, this mixing process is rather complex and superimposed by other processes (Sanchez et al., 1999), which modify the characteristics of the mixing water, due to the lack of equilibrium between the aquifer matrix and the mixing water (Leboeuf, 2004). The aquifer matrix such as carbonate mineral behaves as geochemical buffers of salinization and the minerals are liable to dissolve and precipitate, dolomitization-dedolomitization and cation exchange act in opposition to changes induced by seawater intrusion (Gimenez and Morell, 1997; Jones et al., 1999).

An understanding of the geochemical processes that occur along with freshwater and seawater mixing are crucial because they affect the permeability of the rock in the aquifer in carbonate aquifers. Therefore, the main objective of this study is to study the effect of seawater intrusion toward the underlying base rock and major ions constituents in the mixing zone were studied by means of statistical analysis (descriptive statistics and correlation coefficient) and graphical method (Piper diagram). In addition, using the numerical model, PHREEQC principal saturation states of carbonate rocks in the part of the aquifer that is surrounded by a marine environment were calculated to show the extension effect of seawater intrusion to the saturation states of the major ions components in a freshwater-seawater mixing process in a closed system on the Manukan Island.

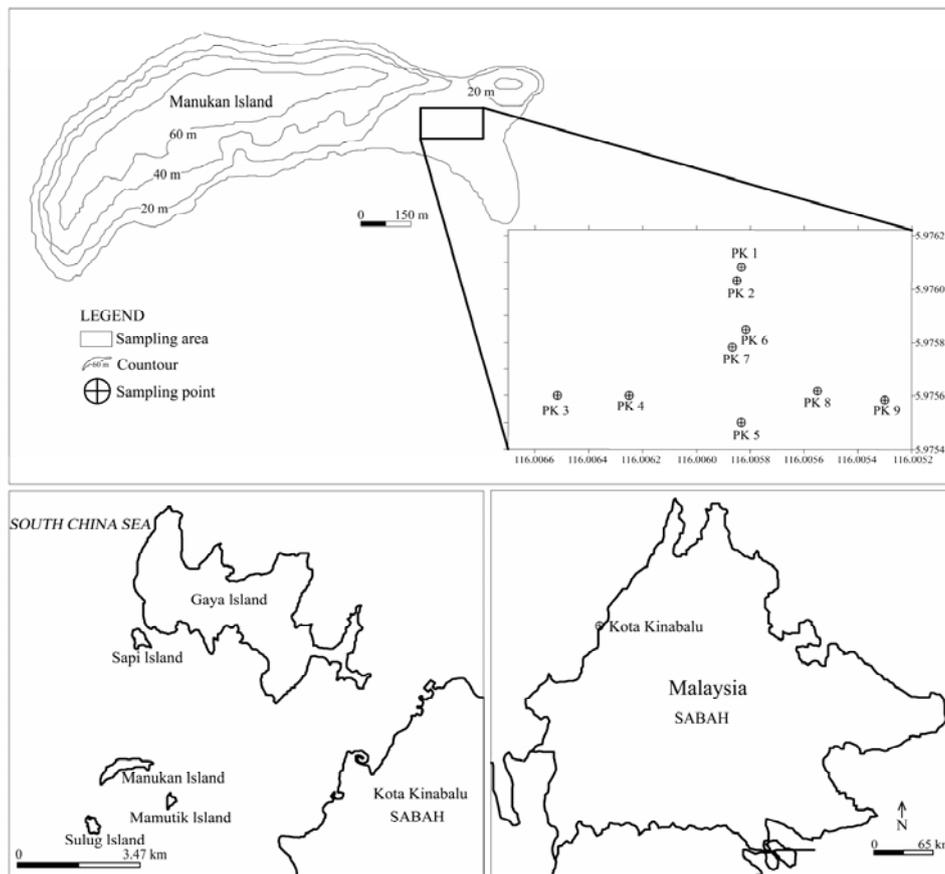


Fig. 1. Schematic map showing the geographical locality of the Manukan Island and sampling locations.

## 2 Materials and methods

### 2.1 Geography and climate

The island is located just offshore the Kota Kinabalu in Sabah, East Malaysia on the island of Borneo (Fig. 1), Manukan is one of the islands under

Tunku Abdul Rahman Parks. Covering an area of 206000 m<sup>2</sup>, the Manukan Island (5°57'–5°58'N and 115°59'–116°01'E) is the park's second largest island after the Gaya Island. It is surrounded by other magnificent small islands namely Sapi, Mamutik and Sulug and features the most developed tourist facilities that include 20 units of chalets, a clubhouse, and a few restaurants and a diving centre. Recreation facilities

include a swimming pool, a football field, squash and tennis courts. Infrastructural facilities include water support, electricity, desalination plant and sewerage system. Almost 80% of the area is covered by dense vegetation on the high relief side, while the rest 20% of the area is developed for tourism activities which are located in the low lying area of the island where the topography of the area is characterized by a relatively hilly land with maximum elevations of approximately 60 m in the western part of the island and a gradually decreasing elevation towards the eastern coast of the island. The best beach is on the eastern tip of the island. Offshore of Manukan are coral reefs, which are ideal for snorkeling, diving and swimming. The island is crescent-shaped, one and half kilometers long and three kilometers wide in the middle. The island is enacted under government's Parks Enactment 1978 and the management of the island is put under the supervision of the Sabah Parks Trustees.

The area is prevailing a warm and humid climate with annual rainfall ranging between 2000–2500 mm, and a large amount of precipitation reaches the groundwater, although there is also the possibility of recharge via groundwater movement from the hilly area. The annual temperature ranges from 21 to 32°C with humidity between 80%–90%. The climate is affected by the northeast and southwest monsoons, tropical winds that alternate the year round. The northeast monsoon blows from November to March, and the southwest monsoon from May to September and usually the periods between the monsoons are marked by heavy rainfall.

## 2.2 Geology and hydrogeology

Geologically, the Manukan Island is underlain by interbedded sandstone and sedimentary rocks classified as the Crocker Range rock formation of the western coast of Sabah. Toward the end of the Middle Miocene at about one million years ago, changes in the sea level occurred, resulting in portions of the mainland being cut off by the sea, thus giving rise to the formations observed today (Basir et al., 1991). The lower sequence of the island consists of thick yellowish-brown shale and dark grey in color and interbedded with black-grey thin sandstone while the weathered sandstones are yellowish in color, whereas the shales are brown and dark (Abdullah et al., 1997). Exposed sandstone outcrops still feature the coasts of this island, forming cliffs and deep crevasses along the shore. The sedimentary rocks of the Manukan Island dip toward the low-relief area (east-northeast), with dipping angles of 15°–45°. The folds form a slightly symmetrical syncline in the low relief area and small-scale normal faults and joint sets can be observed in several locations around the island (Abdullah et al., 1997).

An early study on the morphology of the island's aquifer conducted by Abdullah et al. (2002) revealed that the overlying rocks are approximately as thick as 11 m (in the southern area), 5.7 m (in the northern part) and 12 m (in the middle part) from the ground surface to the bedrock. In general, the low-lying profiles are thinner than those of hilly area (Fig. 2) as reported by Abdullah et al. (1997). Changes in sea level, which occurred during Quaternary, caused the formation of limestone terraces in coastal areas where the Manukan Island is formed of carbonate rocks which originated from coral deposits and was overlain by Quaternary alluviums (Basir et al., 1991). The alluviums are loose, not cemented and act as sufficient water storage which entirely depends on its thickness. A study by Abdullah et al. (2002) indicates that the medium of the aquifer consists of fine to coarse sand mixed with some fine gravels. On the lowland, the sandstone has about the same thickness, with shale and carbonate deposits. The soil map profile of the study location is shown in Fig. 3. The main association of the Manukan island is characterized by Lokan association with approximately 85% of the area. Low-lying area of the Manukan Island is characterized as Tanjung Aru association. The major elements in the soil are Mg, Ca, Si and Al, indicating the presence of carbonate minerals as underlying rocks on the island (Abdullah et al., 1997). Small aquifers may occur in the sandstone alluvium regions that often occur at sites near the coasts. Small areas and low elevations of the Manukan Island lead to very limited water storage (Aris et al., 2006).

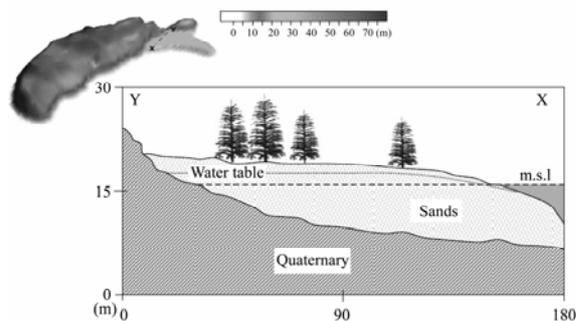


Fig. 2. 3-D elevation and aquifer cross-section Y-X of the Manukan Island.

The Manukan Island depends on shallow aquifers for its groundwater supply. Dug wells are used for extracting groundwater from its aquifer on the Manukan Island. The wells are 150 cm in diameter and vary between 55–78 cm in height from ground surface level. Data on the depth to groundwater level are not available, as some of the wells have been sealed.

### 2.3 Sampling and analysis

Groundwater samples were collected from March 2006 to January 2007 on the island. A total of 162 groundwater samples were obtained during the sampling period from 9 existing wells located on the

low-lying area of the island. Polyethylene bottles that were soaked with 1:10 HNO<sub>3</sub> acid were washed and pre rinsed with distilled water, and used to store groundwater samples based on the methods described in APHA (1995).

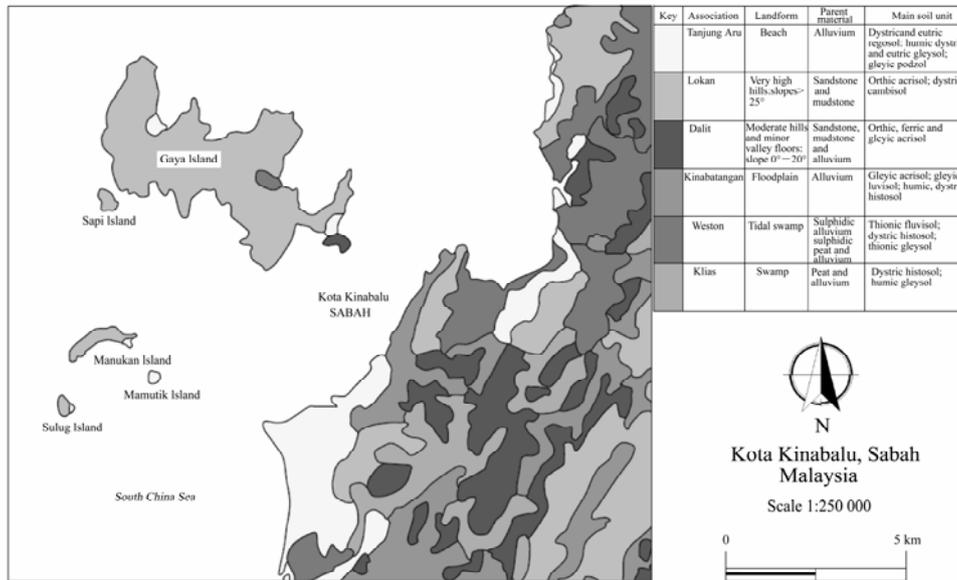


Fig. 3. Soil map of Kota Kinabalu and surrounding areas.

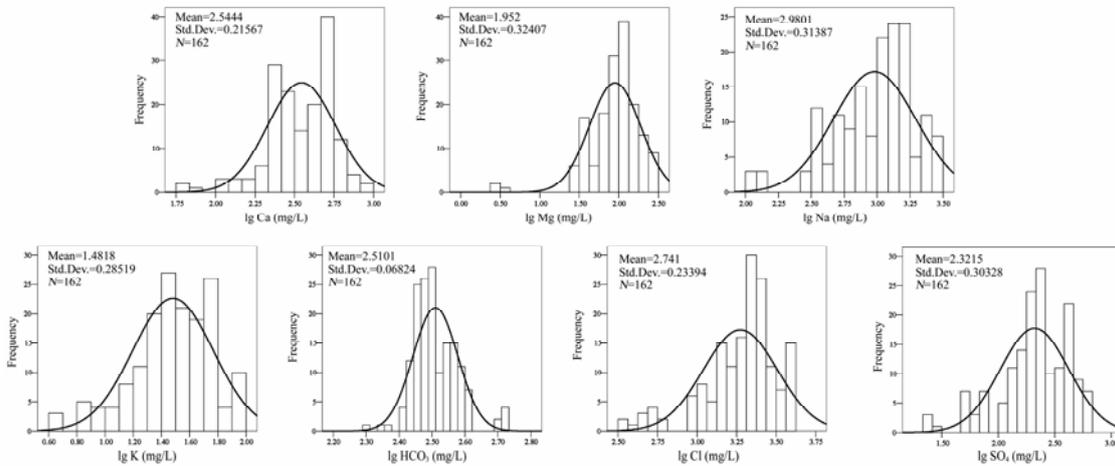


Fig. 4. Distribution of major ions.

The analysis of water samples was carried out to assess pH, temperature, electrical conductivity (EC), salinity and total dissolved solids (TDS) and ions, namely sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), bicarbonates (HCO<sub>3</sub>), chloride (Cl) and sulfate (SO<sub>4</sub>). The water pH and temperature were measured using WTW pH 315i, WTW Cond. 315i measured EC, salinity and TDS using Oaklab 13. Field measurements were done immediately following sample collection to acquire representative values of groundwater quality. The samples were transported in

an ice-filled cooler box and kept refrigerated at ~4°C prior to analysis in the laboratory. The water samples collected were filtered through 0.45 μm membrane filter paper (Millipore®) using glass filtration unit and acidified with concentrated HNO<sub>3</sub> acid to pH <2 for cation determination. Cl and HCO<sub>3</sub> were analyzed using the argentometric (AgNO<sub>3</sub> 0.1 N) and titration methods (HCl 0.1 N), respectively. Sulfate was detected by means of a HACH (DR/2040) meter. The major cations (Na, K, Ca and Mg) were determined by flame (air-acetylene burner) atomic absorption spec-

trometry (Zeeman Atomic Absorption Spectrophotometer Z-5000, Hitachi, Japan).

Statistics analysis and graphical methods were used to show the current condition of the Manukan Island. In addition, the numerical model PHREEQC (Parkhurst and Appelo, 2005) was used to set up the hydrogeochemical components of the groundwater, especially the saturation parameters for carbonate minerals (calcite, aragonite and dolomite) to test the mineral saturation and to eliminate the reactions that are thermodynamically invalid. Saturation indices (SI) are defined as  $\log(IAP/K_{sp})$ , where IAP is the ion activity product and  $K_{sp}$  is the equilibrium solubility product. SI for the selected minerals and ionic concentration changes was calculated to better understand the hydrochemical processes that take place in the aquifer during the freshwater-seawater mixing.

### 3 Results and discussion

#### 3.1 Statistical analysis (descriptive statistics)

The overall data obtained in this study are given in Table 1. The pH values vary between 6.59 and 7.97. It was found that there is no distinct grouping of these values. The temperatures of the groundwater are generally between 26 and 29°C. Significant differences are found in the salinity values, where the lowest reading was recorded in the month of July 2006 ( $0.29 \times 10^{-12}$ ) and the average value is  $2.36 \times 10^{-12}$ . The electrical conductivity (EC) varies between 0.99–12.26  $\text{mS}\cdot\text{cm}^{-1}$ . This is a good illustration of the intrusion of salt water as a result of single pumping operation. It can be seen in a general manner that the high values of conductivity observed ( $\text{EC} > 5 \text{ mS}\cdot\text{cm}^{-1}$ ) are related to seawater intrusion, as can be seen in high NaCl levels in the analyses. The EC values between 2 and 5  $\text{mS}\cdot\text{cm}^{-1}$  correspond to mixtures of fresh water and seawater in varying proportions after pumping (Freeze and Cherry, 1979; Custodio, 1991; Dazy et al., 1997). Wide ranges and great standard deviations occurred for most parameters, where the highest value was recorded in January 2007, and the

lowest value in July 2006. The basic properties of groundwater (pH, temperature, EC, salinity and TDS) and major constituents of the groundwater (Ca, Mg, Na, K) are given in Table 1. The wide distributions among the major compositions of studied groundwaters indicated that the chemical composition was affected by multiple processes, including seawater-freshwater mixing (Aris et al., 2007a). Especially the predominance of Na and Cl in groundwater indicates strong saline water impact. Of the Cl and  $\text{SO}_4$  concentrations, 100% and 57% respectively exceeded the Malaysian National Standard for raw water quality standard for Cl; 250  $\text{mg}\cdot\text{L}^{-1}$  and  $\text{SO}_4$ ; 250  $\text{mg}\cdot\text{L}^{-1}$  (MOH, 2004). Despite of the wide ranges of values, most samples are of lognormal density distribution (Fig. 4).

#### 3.2 Statistical analysis (correlation coefficient)

The hydrochemical change within the freshwater-seawater contact is rather complex by the processes between the freshwater-seawater and the aquifer's matrix that augment the ion composition of the fresh groundwater. The correlation coefficient matrix between the examined major ions, which were calculated using linear regression analysis, is given in Table 3. It was found that the correlation between Cl and/or with the major components of seawater (Na and  $\text{SO}_4$ ) is strong (Cl-Na,  $r=0.656$ ; Cl- $\text{SO}_4$ ,  $r=0.757$ ); an indication of seawater influence on the groundwater salinity. The variation of these relationships may indicate the complexity of the hydrochemical components of groundwater. In general, two main factors can be taken into consideration, which play a very important role in shaping the chemistry and quality of the water in the aquifer. These include (i) anthropogenic factor: over abstraction of freshwater and (ii) natural factors: seawater intrusion, carbonate mineral saturation condition (Aris et al., 2007b). The weak correlation between  $\text{HCO}_3$  with all studied parameters suggested that the seawater had an insignificant impact on the chemistry and behavior of  $\text{HCO}_3$  in the system.

**Table 1. The overall physico-chemical properties and major ions of groundwater in the study area ( $N=162$ )**

	Unit	Range		Mean	SD	CV(%)
pH		6.59	-	7.97	7.27	0.19
Eh	mV	-55.3	-	22.2	-17.14	15.24
Temperature	°C	26.3	-	29.4	27.89	0.74
TDS	$\text{mg}\cdot\text{L}^{-1}$	1133	-	8263	4535	1506
EC	$\text{mS}\cdot\text{cm}^{-1}$	0.30	-	12.26	4.79	1.86
Salinity	$\times 10^{-12}$	0.00	-	0.70	2.71	1.25
Ca	$\text{mg}\cdot\text{L}^{-1}$	60	-	866	390	93.14
Mg	$\text{mg}\cdot\text{L}^{-1}$	3	-	298	110	51.41
Na	$\text{mg}\cdot\text{L}^{-1}$	104	-	2780	1181	484.16
K	$\text{mg}\cdot\text{L}^{-1}$	4	-	94	37	17.30
Cl	$\text{mg}\cdot\text{L}^{-1}$	340	-	4099	2118	788.72
$\text{HCO}_3$	$\text{mg}\cdot\text{L}^{-1}$	195	-	524	328	52.03
$\text{SO}_4$	$\text{mg}\cdot\text{L}^{-1}$	25	-	660	256	121.85

**Table 2. Correlations among the major ions of the groundwater**

	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
Ca	1	0.054 <sup>a</sup>	0.000 <sup>**</sup>	0.931	0.191	0.001 <sup>**</sup>	0.265
Mg	-0.152	1	0.000 <sup>**</sup>	0.000 <sup>**</sup>	0.020 <sup>*</sup>	0.000 <sup>**</sup>	0.000 <sup>**</sup>
Na	0.366	0.459	1	0.000 <sup>**</sup>	0.017 <sup>*</sup>	0.000 <sup>**</sup>	0.000 <sup>**</sup>
K	0.007	0.905	0.618	1	0.000 <sup>**</sup>	0.000 <sup>**</sup>	0.000 <sup>**</sup>
HCO <sub>3</sub>	-0.103	-0.183	-0.187	-0.299	1	0.000 <sup>**</sup>	0.001 <sup>**</sup>
Cl	0.251	0.641	0.656	0.777	-0.340	1	0.000 <sup>**</sup>
SO <sub>4</sub>	0.088	0.886	0.696	0.952	-0.219	0.757 <sup>b</sup>	1

<sup>a</sup> Value in the upper triangle of the matrix is a significant value ( $p < 0.01^{**}$  and  $p < 0.05^*$ ); <sup>b</sup> correlation values (in the lower triangle).

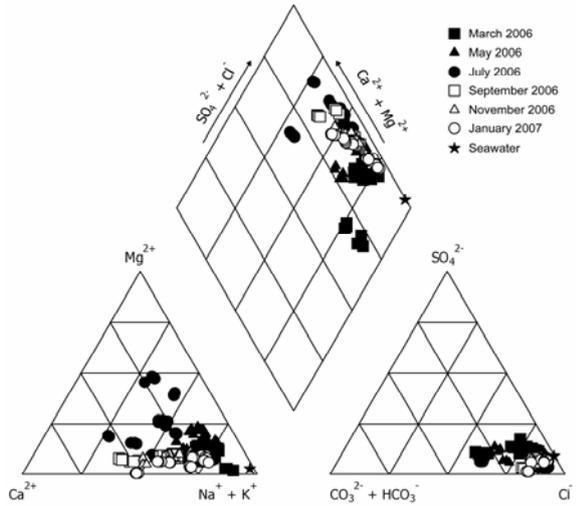


Fig. 5. Piper diagram of the studied groundwater from the Manukan Island.

**3.3 Graphical methods (Piper diagram)**

As viewed from Table 1 and Fig. 5, the groundwater is apparently saline, as indicated by its Na-Cl water type. Large proportions of the groundwater are of the Na-Cl water type, which generally indicates a strong seawater influence on the aquifer. During the sampling period, the Manukan Island aquifer waters also have Ca-Cl and Mg-Cl facies. The dominant water type of all observation wells is Na-Cl in March 2006 and May 2006 becoming Ca-Cl for observation wells PK 1 and PK 2 and becoming Mg-Cl for PK 8 during the July 2006 sampling period. During the September 2006 sampling period, only waters PK 3 and PK 8 observation wells became Ca-Cl, indicative of ion exchange between freshwater-seawater contacts. As shown in Fig. 5, in the November 2006 sampling period, groundwater from all observation wells is of the Na-Cl type while only PK 8 is of the Ca-Cl water type during the January 2007 sampling period. Unlike the chemical properties at all observation wells, the PK 8 observation well experienced a rapid ionic exchange process. Changes from Na-Cl to Ca-Cl water type show a deficit in sulfate. This concentration deficit is clearly observed in the PK 8 observation wells from the March 2006 to January 2007 sampling periods. These evolution patterns indicate that the groundwater chemistry is controlled by cation exchange reactions as well as simple mixing between

two end members (Vengosh et al., 1991; Appelo and Postma, 2005).

It is obvious that from these data, the Manukan Island aquifer has been suffering from significant seawater intrusion compared to the situation observed in 1996 (Abdullah et al., 1996).

**3.4 Numerical model PHREEQC (saturation indices)**

Saturation indices (SI) for calcite, aragonite and dolomite were calculated in order to show the extension effect of seawater intrusion on the saturation states of the major ion components in a freshwater-seawater mixing process in a closed-system. From the calculation, most of the groundwater samples are at or close to saturation with respect to calcite and dolomite (Table 3 and Fig. 6). The plot of SI of calcite versus dolomite (Fig. 6) demonstrates that the waters are supersaturated with respect to dolomite and calcite and the dolomite SI values are higher than the calcite SI values.

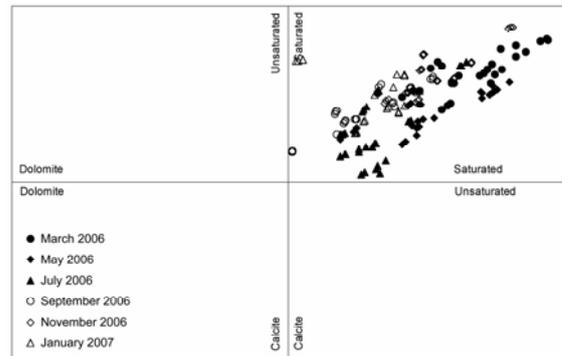


Fig. 6. Saturation indices plot for calcite and dolomite.

The supersaturation indicates the precipitation of calcium as Ca and/or Ca-Mg carbonate. The carbonate minerals dissolution leads to simultaneous exchanges of Ca and Mg with Na, so that the water remains at or slightly above saturations states with respect to the carbonate. This may signify the presence of calcareous nodules which contain a mixture of calcite and dolomite. An analysis plotting in the field data represents groundwater of the Manukan Island has come from an environment where calcite and dolomite are impover-

ished, or has undergone cation exchange process with seawater that contains high Na. Such a condition is also supported by the fact that the pH of the groundwater influenced the saturation state of calcite, aragonite and dolomite where at high pH, Ca and Mg are usually transferred to a solid phase, and, therefore, their concentrations are controlled by mineral precipitation (Hem, 1985; Lee et al., 2001).

**Table 3. Saturation indices (SI) of calcite, aragonite and dolomite of the study area**

Sampling period		Calcite	Aragonite	Dolomite
March 2006	Mean	0.87	0.73	1.66
	SD	0.16	0.16	0.41
	Range	0.58–1.14	0.44–0.99	0.81–2.35
May 2006	Mean	0.56	0.42	1.31
	SD	0.15	0.15	0.42
	Range	0.30–0.80	0.16–0.66	0.47–2.00
July 2006	Mean	0.37	0.23	0.82
	SD	0.26	0.26	0.33
	Range	0.06–0.96	-0.08–0.81	0.47–1.61
September 2006	Mean	0.57	0.44	0.69
	SD	0.19	0.19	0.38
	Range	0.24–0.84	0.10–0.69	0.03–1.31
November 2006	Mean	0.86	0.72	1.34
	SD	0.18	0.18	0.32
	Range	0.63–1.23	0.49–1.09	0.87–2.03
January 2007	Mean	0.68	0.53	0.81
	SD	0.17	0.17	0.31
	Range	0.39–0.98	0.25–0.83	0.07–1.19

The pH of groundwater influenced the saturation states of calcite and aragonite, where Ca and Mg are usually transferred to a solid phase at high pH value, and, therefore, their concentrations are controlled by mineral precipitation (Hem, 1989). There were strong correlations ( $r=0.695-0.787$ ;  $p<0.01$ ; Fig. 7) between pH and SI values of aragonite, calcite and dolomite, suggesting that the precipitation of those mineral species was due to the increasing alkalinity of groundwater (increasing pH). Hence, this may indicate that the seawater intruding into the aquifer was not the direct factor that contributes to the precipitation of minerals, but might be possibly contributed by the increasing alkalinity of groundwater due to its high pH. It was found that the recent groundwater pH of the island is significantly higher ( $p<0.05$ ) than the previous data presented by Abdullah et al. (1996). The significant increase of groundwater pH was strongly associated with the sulfate reduction processes that are accompanied by an increase in concentrations of hydrocarbonate ions.



The less significant correlation between Ca and Mg (Table 2) is possibly due to the precipitation state of dolomite, calcite and high-Mg calcite. Precipitation takes place during the cation exchange process on the calcareous rocks in the Manukan Island aquifer as an extension results from seawater intrusion as discussed previously. The cementing material of the Manukan

Island aquifer is mainly made of carbonate mineral species as indicated by an early study done by Abdullah et al. (1997).

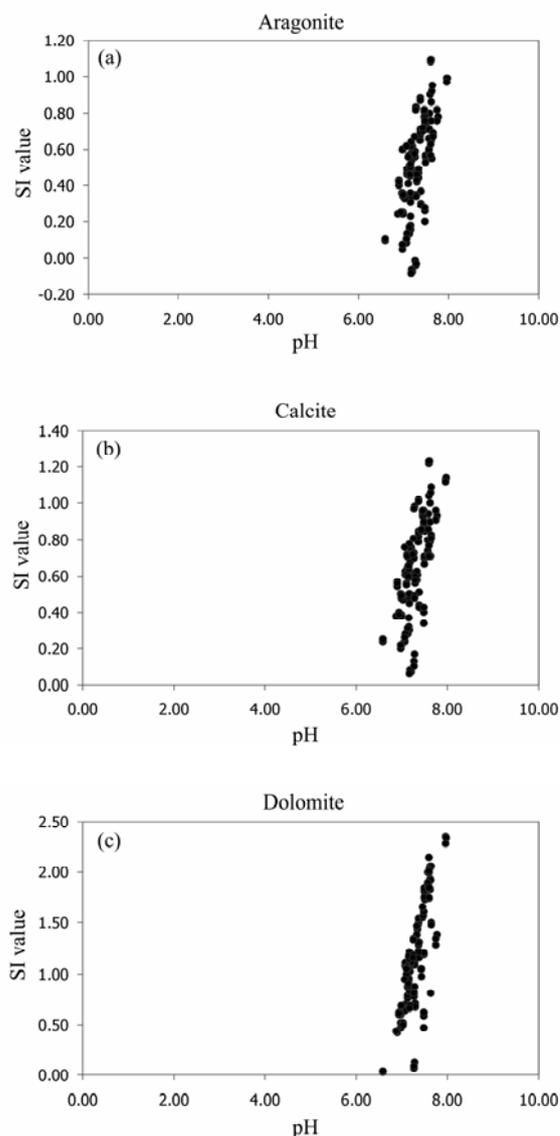


Fig. 7. Plot of SI for selected mineral species [(a) aragonite, (b) calcite and (c) dolomite] versus pH of the groundwater.

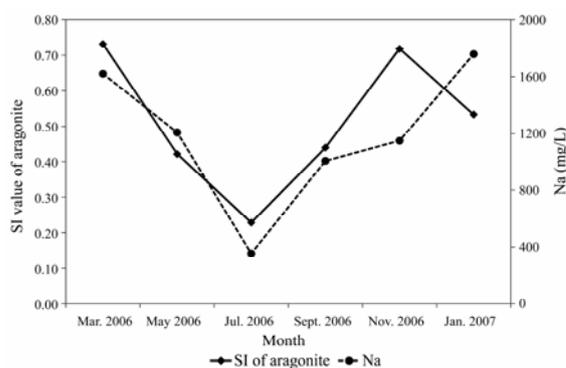


Fig. 8. SI plot of aragonite versus Na concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ) over time.

In calcite crystals, Mg substitutes Ca owing to their similarities in ionic radius and charge (Al-Agha, 1995). Such elucidation is supported by the modeling results using PHREEQC simulation package where SI of both calcite and dolomite indicates supersaturation values (Table 3). This simply means that the groundwater is undersaturated with respects to calcite and/or dolomite due to cation exchange process that takes place during the seawater intrusion. The increasing Ca concentrations in the groundwater samples recorded in March 2006–January 2007 are probably not due to calcite dissolution since the  $\text{HCO}_3^-$  does not increase so much as compared to the November 2006 and January 2007 data. Such weak correlations ( $\text{Ca-HCO}_3^-$ ;  $r = -0.103$ ) among major anions and cations revealed that dissolved salts from seawater had an insignificant impact on the  $\text{HCO}_3^-$  concentrations in the groundwater.

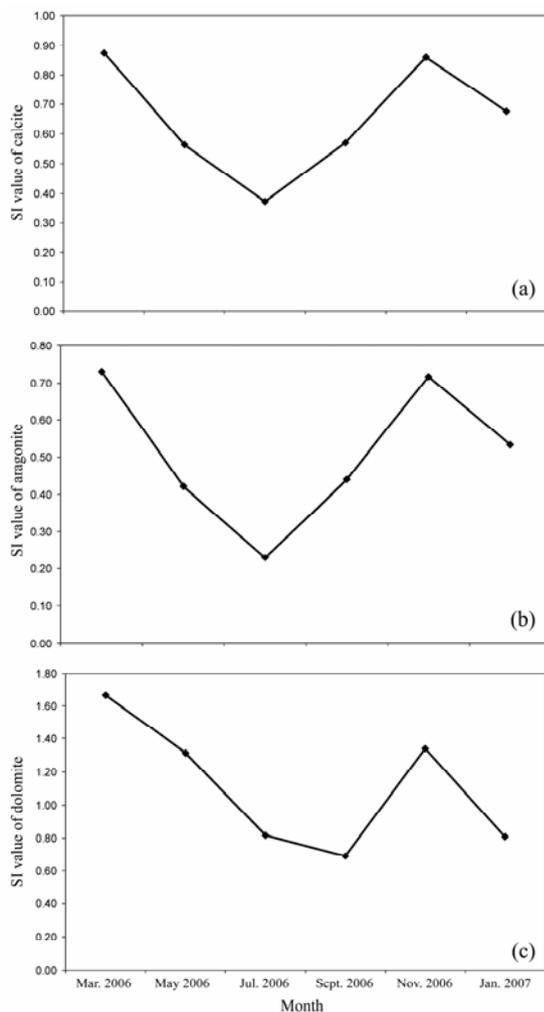


Fig. 9. Mean SI values for (a) calcite, (b) aragonite and (c) dolomite of the studied groundwater samples over time.

The trend of aragonite species is quite similar: all of the analyzed water samples are over-saturated with

aragonite. This trend suggests that Ca and Mg were not released as a result of dissolution of carbonate minerals from infiltration water while cation exchange occurs during the seawater ingestion into the aquifer. When infiltration water enters the aquifer and dissolves more carbonate bedrocks under closed condition, the water remains at or slightly above saturation conditions with respect to the carbonate minerals, even with the increasing seawater proportion penetrating the aquifer. The fact that the water remains at or slightly above saturation conditions is due to simultaneous exchange of Ca and Mg with Na. This is supported by the following Figure 8, where the increase of Na will lead to the decrease the saturation index for aragonite. Hence, the value indicates that the seawater intrusion itself was not the only factor leading to the dissolution of minerals. It was possibly one of the factors that significantly control the saturation state of the carbonate minerals.

The overall trend for studied carbonate minerals (calcite, aragonite and dolomite) over time is shown in Fig. 9. It shows fluctuation over time, which may support the view of continuous pumping activities carried out in the island may be attributed to a significant increase in seawater intrusion to the aquifer. This may lead to significant alteration on the hydrochemical balance of the groundwater as can be seen from the SI values (Table 3) and SI plot (Fig. 9).

#### 4 Conclusions

The problem of groundwater in the Manukan Island aquifer is rather complicated; represented by an over exploitation of an aquifer due to human pumping activities. Since local residents on the Manukan Island depend totally on the water derived from the aquifer for their domestic use, continuous pumping activities carried out on the island over a decade has created serious seawater intrusion to its aquifer. The over-pumping led to the deterioration of water quality by exposing deep saline water. Thus, human-induced and natural parameters play a significant role in delivering water of low quality. From the statistics analyses (descriptive statistics and correlation analysis) and graphical method (Piper diagram), it was shown that the groundwater of the Manukan Island aquifer is experiencing serious contamination from seawater. Cl and Na are found to be major pollutants of the aquifer. High concentration values of Cl and Na are attributed to the high pressure of human use, as well as the scarcity of the resource. By means of numerical model PHREEQC, saturation indices (SI) showed that the calculated values for calcite, aragonite and dolomite are positive at or close to 1, indicating the supersaturation of water by these minerals. The results showed that the influence of fluctuation over time was regu-

lated by continuous pumping activities carried out on the island due to a significant increase in seawater intrusion and significant hydrochemical imbalance to the aquifer.

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