HYDROGEOCHEMISTRY OF GROUNDWATER IN MANUKAN ISLAND, SABAH

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Abstract

Geochemical data on dissolved major consituents in groundwater samples from Manukan island reveal the main processes responsible for their geochemical evolution. The results of analysis showed that the groundwater was chemical highly enriched with Na^+ and Cl^- an indication of seawater intrusion into the aquifer as also suported 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 indeces (SI) indicating supersaturation which lead to mineral precipitation condition of water by these minerals.

Abstrak

Data geokimia yang diperoleh bagi keterlarutan utama untuk sampel air bawah tanah pulau Manukan menjelaskan proses utama yang terlibat dalam perubahan geokimianya. Keputusan analisis mendapati bahawa air bawah tanah tersebut telah didominasi dengan elemen Na^+ dan Cl^-; satu petunjuk bahawa telah berlakunya proses peneborosan air laut ke dalam akuifer seperti mana juga disokong oleh plot Na-Cl pada rajah Piper. Daripada simulasi PHREEQC, keterlarutan kalsit, dolomit dan aragonit menunjukkan nilai SI yang positif yang membawa kepada keadaan pembentukan mendakan oleh mineral tersebut.

Keywords: Manukan Island, groundwater, hydrogeochemistry, seawater intrusion, PHREEQC

Introduction

Manukan island (Fig.1) receives thousands of visitors every year. On the other hand, groundwater is the only source for regular water supply in the island. With the growing number of tourist and human activities on the islands, the demand for groundwater in these islands has increased too. Since its existence has become the most important source for the small island's community, pumping from the upper phreatic zone is widely practiced on the island. The increasing exploitation causes deterioration of groundwater. The driving force of saltwater intrusion into the aquifer is due to excess pumpage, which lowers the freshwater table, changing the direction and magnitude of groundwater gradients [12]. When seawater intrudes the aquifer, they may contaminate significant quantities of fresh groundwaters. As the groundwater concerns are heightened as vital function in sustaining life and ecology of the island, the trend of over exploitation of water resources creates a really need to understand. Currently, there is lack of studies done in tropical islands to understand the change of groundwater chemistry in such condition. Thus, this study was set up to characterize the hydrogeochemistry facies and hydrogeochemical models of the groundwater on the basis of the physico-chemical properties, by using the PHREEQC simulation model.

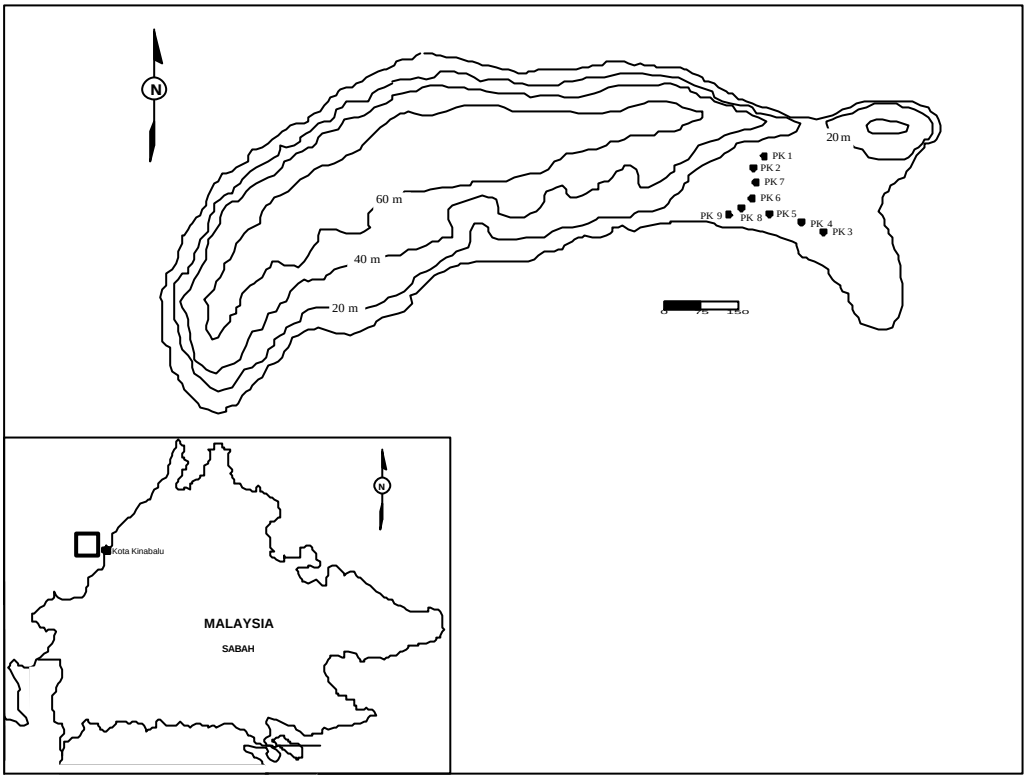

Fig. 1 Schematic map showing the geographical locality of Manukan island and its sampling locations.

Site Description

Manukan island, well known for its coral reef, situated between 5°57'-5°58' N and 115°59'-116°01' E. It has an area of 206 000 m^2, and about 80% of its area is covered by forest (Fig.1). Geologically, the island consists of interbedded sandstone and shale classified as the Crocker Formation deposited during Late Eocene to Middle Miocene [8; 2]. From the study conducted by Abdullah *et al*. [1], the thickness of the aquifer are approximately, 11 m (at the southern area), 5.7 m (at the northen part) and 12 m (at the middle part) from the ground surface to the bedrock. Geologically, Manukan island is formed of carbonate rocks and overlain by Quarternary alluvium [8]. These Quarternary alluviums (sediments) are loose, not cemented and act as good water 'storage' which it is entirely depends on its thickness. The base of the island was formed by the carbonate rocks, which originated from coral deposits.

Experimental

Polyethylene bottles were used to store groundwater samples based on the methods described in APHA [4]. Water samples were collected from 9 production wells (PK) on Manukan island in March 2006 (Fig. 1). All samples were filtered and split in a different polyethylene bottles for subsequent analyses of cations and anions. The following parameters were analyzed in the field: pH and temperature using pH 315i, electrical conductivity (EC) using Cond. 315i and total dissolved solids (TDS) using EC-TDS Scan. In the laboratory, chloride and bicarbonate were analyzed using argentometric and titration methods, respectively. The major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), were determined using flame atomic absorption spectrometry (AAS). Sulphate was detected using HACH (DR/2040) meter. Overall procedures were referred to APHA [4] and all the analyses were performed in the Water Quality Laboratory at the Universiti Malaysia Sabah. The data were analyzed to obtain simple descriptive statistics and the correlation matrix. The numerical model PHREEQC [13] was used to set up the hydrogeochemical components of the groundwater, especially the saturation parameters for carbonate (calcite, aragonite and dolomite) to test the mineral saturation and to eliminate the reactions that are thermodynamically invalid.

Results and Interpretations

Descriptive statistics

The groundwater in Manukan island contains high minerals, as shown by the EC readings, which ranged from 1660-8710 µS cm^{-1}. The EC recorded disturbances in the groundwater quality of the island. Table 1 shows the data of chemical analysis and descriptive statistics for the study area.

Table 1 Chemical analysis data and descriptive analysis of the analyzed chemical components for the study area. (All data in mg l^{-1} except for pH and EC; µS cm^{-1})

Well No.	pH	EC	TDS	K^+	Na^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}
PK 1	7.20	4953	3484	20	1286	75	385	367	1107	240
PK 2	7.37	6173	4199	31	1480	120	393	331	1532	310
PK 3	7.50	5050	3091	34	1096	111	267	365	966	250
PK 4	7.33	8703	5746	55	1910	187	283	346	2507	456
PK 5	7.75	1663	3039	12	2036	28	219	303	359	80
PK 6	7.62	6456	5312	57	1790	182	331	309	2224	416
PK 7	7.58	8096	6564	71	2393	194	415	325	2674	490
PK 8	7.63	3100	2508	10	1060	54	197	512	543	130
PK 9	7.96	6100	3867	49	1510	124	282	284	1282	333
Mean	7.55	5588	4201	38	1618	119	308	349	1466	300
Maximum	7.96	8703	6564	71	2393	194	415	512	2674	490
Minimum	7.20	1663	2508	10	1060	28	197	284	359	80
SD	0.23	2226	1381	21	449	60	77	67	837	140

The maximum (2674 mg l^1) and mean (1466 mg l^1) values of chloride exceeded the WHO [15] standards (250 mg l^1). The maximum and mean values for SO_4^{2-} were 490 mg l^1 and 300 mg l^1 respectively, exceeded the WHO [15] standard too (250 mg l^{-1}). Both chloride and sulphate contaminated the groundwater of Manukan island attributed to seawater intrusion. The SO_4^{2-} ion was never preponderant in these waters with very high mineral contents and the high concentrations were always combined with high chloride levels giving the water of sodium chloride type [6].

Correlation Coefficient

The relationship between two variables is the correlation coefficient which shows how one variable predicts the other. Associated with correlation coefficient is *r*, the multiple correlation, which is the percentage of varience in the dependent variable explained collectively by all of the independent variables.

The results of the correlation analysis are considered in the subsequent interpretation. A high correlation coefficient (near 1 or -1) means a good relationship between two variables, and a correlation coefficient around zero means no relationship. Positive values of *r* indicate a positive relationship while negative values indicate an inverse relationship. The correlation coefficient of the studied parameters are shown in Table 2.

Table 2 Correlation matrices for all data (n = 27).

	TDS	EC	Cl^-	Ca^{2+}	SO_4^{2-}	HCO_3^-	K^+	Mg^{2+}	Na^+
TDS	1								
Sig.	-								
EC	0.868	1							
Sig.	0.002	-							
Cl^-	0.975	0.940	1						
Sig.	0.000	0.000	-						
Ca^{2+}	0.615	0.609	0.623	1					
Sig.	0.011	0.011	0.073	-					
SO_4^{2-}	0.932	0.972	0.977	0.624	1				
Sig.	0.000	0.000	0.000	0.071	-				
HCO_3^-	-0.454	-0.329	-0.368	-0.396	-0.416	1			
Sig.	0.219	0.387	0.329	0.292	0.265	-			
K^+	0.907	0.879	0.915	0.505	0.953	-0.513	1		
Sig.	0.001	0.002	0.001	0.166	0.000	0.158	-		
Mg^{2+}	0.914	0.946	0.968	0.536	0.984	-0.377	0.953	1	
Sig.	0.001	0.000	0.000	0.005	0.000	0.317	0.000	-	
Na^+	0.762	0.388	0.602	0.326	0.507	-0.586	0.600	0.484	1
Sig.	0.002	0.126	0.086	0.392	0.164	0.097	0.087	0.187	-

Calcium and magnesium

There is a positive correlation of Ca^{2+} with Mg^{2+} in the groundwater of the area. These elements, Ca^{2+} and Mg^{2+}, correlate positively with alkalinity, TDS, EC, K^+ and HCO_3^-. The positive correlation between Ca^{2+} and Mg^{2+} (0.536) is attributed to the precipitation of aragonite, dolomite and calcite. Precipitation takes place during the cation exchange process which is the later effect from the seawater intrusion into the aquifer. The lower concentration of Ca^{2+} compared to Na^+, is a result from the cation exchange process that occurs naturally when seawater intrudes into the aquifer system. Presuming that Ca^{2+} is the dominant ion for the aquifer matrix of the study area, the following equation can describe the above-mentioned process [5]:

$$Na^+ + ½Ca - X_2 \longrightarrow Na - X + ½Ca - X_2 \qquad (1)$$

When Ca^{2+} exchanged with Na^+, the water becomes saturated for calcite and precipitation results [7; 9]. At high pH, Ca^{2+} and Mg^{2+} are usually transferred to a solid phase, therefore, their concentrations are controlled by mineral precipitation [10]. Such elucidation is supported by the modeling results using PHREEQC simulation package where saturation index (SI) of aragonite, calcite and dolomite indicate supersaturation values (Table 3).

Table 3 Average values for seleceted saturation indices (SI) of aragonite, calcite and dolomite of groundwaters from Manukan island along with TDS values.

Location	TDS (mg l^{-1})	Aragonite	Calcite	Dolomite
PK 1	3484	0.57	0.71	1.12
PK 2	4199	0.67	0.81	1.51
PK 3	3092	0.73	0.87	1.77
PK 4	5746	0.47	0.61	1.43
PK 5	3040	0.79	0.93	1.34
PK 6	5312	0.76	0.90	1.94
PK 7	6564	0.80	0.95	1.95
PK 8	2508	0.81	0.96	1.60
PK 9	3867	1.00	1.17	2.35

Potassium

Potassium shows positive and significance correlation with all the analyzed parameters except HCO_3^-, with a significance level of more than 0.01. Such correlation is interpreted as araising from the fact that most of these components are derived from the interaction of groundwater with the aquifer's matrix (high-Ca-calcite) which is very common in the coastal aquifer [5], part of which are certainly derived from seawater intrusion in the area [3]. The positive and significance correlation of K^+ with both Cl^- and SO_4^{2-} which is genreally very high in the sea may be interpreted in the light of seawater intrusion as well.

Sodium

The correlation between sodium and all parameters except HCO_3^- (-0.586) shows a positive correlation. The correlation between Na^{2+} and Cl^- however shows around 0.602 which is interpreted as a result of seawater intrusion. The Na-Cl correlation shows the influences of seawater and groundwater mixing. According to Mandel & Shiftan [11], the average of Na-Cl signature (0.66) is less than that of seawater (0.87). In this study, the Na-Cl signature is around 0.60 which is not as clear as theoritical correlation. This is simply means that seawater is over diluted by the groundwater as a result of aquifer recharge from infiltration. In the studied samples, two sets of strong relationship exist between major cations and anions.

1. Highly competitive relationship between ions with the same charge but different valence number, such as K^+ with Mg^{2+} and SO_4^{2-} with Cl^-.
2. The affinity between ions having different charges but the same valence number such as K^+ and Cl^-.

The variation of these relationships may indicate the complexity of the hydrogeochemical components of the groundwater. In general, two main factors can be considered that play a very important role in shaping the chemistry and the quality of the water in the aquifer. These include:

1. Anthropogenic factor: over abstraction of freshwater
2. Natural factors: seawater intrusion, carbonate saturation condition

Hydrochemical facies

Based on the major cation and anion, the groundwater composition of the island was dominated by $Na^+$and Cl^-. The groundwater type of the study area was distinguished and grouped by their position on a Piper diagram (Fig. 2). The Na-Cl facies represents 100% of the total water sample. Its source is believed to be mainly due to seawater intrusion, as Na^+ and Cl^- are the main ions that form this facies.

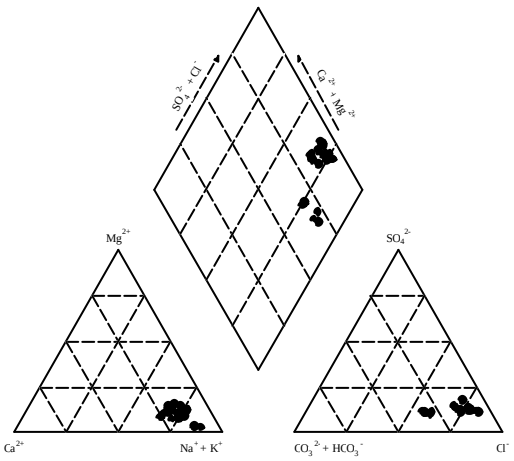

Fig. 2 Piper diagram for the studied wells.

Saturation index

For $CaCO_3$ equilibrium ini water, $CaCO_{3(s)} = (Ca^{2+} + CO_3^{2-})$, the activity product Ca^{2+} x CO_3^{2-} is a constant at any given temperature and it is defined by a thermodynamic equilibrium constant $KCaCO_3$ (K-calcite in the case of mineral calcite). The degree of calcite saturaion index ($SI_{Calcite}$), which is defined by:

$$SI_{Calcite} = \log 10 \{(Ca^{2+}) \text{ x } (CaCO_3)\} - \log 10(K_{Calcite}) \quad (2)$$

where the saturation is scaled logarithmically, as a degree of saturation in natural waters vary by orders of magnitute. For this expression a SI calcite value of 0 corresponds to calcite solubility in equilibrium state, while values of +1 and -1 correspond to 10 times and 1/10 times saturation, respectively [5]. The same was made for dolomite.

The precipitation of $CaCO_3$ and $CaMg(CO_3)$ can be assessed in terms of the SI. The saturation indices of the carbonate minerals positively show supersaturation (precipitation) of calcite and dolomite.

$$CaMg(CO_3)_2 + 2H^+ = 2HCO_3 + Mg^{2+} + Ca^{2+} \quad (3)$$

In terms of thermodynamic considerations [14], these waters are supersaturated with carbonate minerals (calcite, dolomite and aragonite) as clearly shown in Table 2 and Fig. 3.

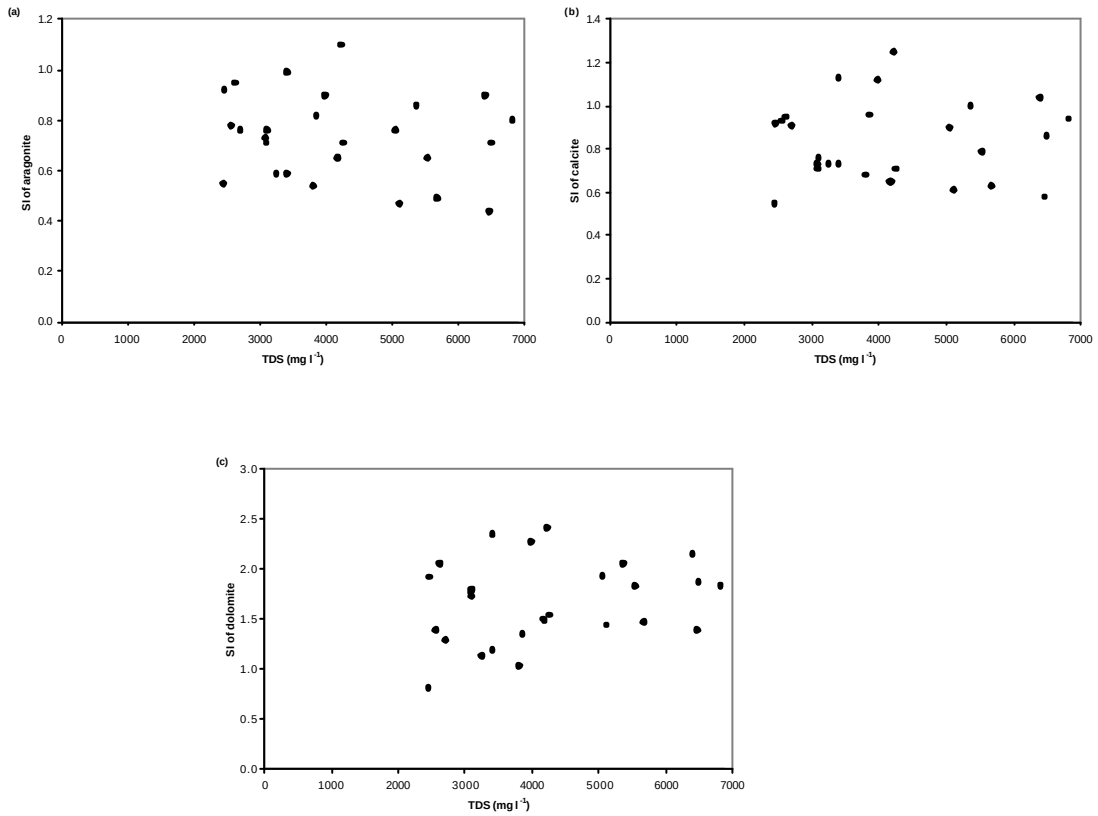

Fig. 3 Plot of calculated saturation indices (SI) of (a) Aragonite, (b) Calcite and (c) Dolomite versus total dissolved solids for the study area.

Conclusions

A diversity of geochemical processes is taking place in the fresh water-seawater contact zone in the aquifer which alter the freshwater and seawater mixture away from the theoritical composition. The problem of groundwater in Manukan island is rather complicated; it represents an over exploitation of an aquifer. The island depends totally on the water derived from the aquifer for its domestic use. The over pumping for fresh water supply contributed to the deterioration of the water quality by exposing the deep saline water. Thus, anthropogenic and natural parameters play a significant role in delivering water of low quality. Cl^- is the major pollutants of the aquifer. High concentration value of Cl^- is attributed to high preasure of human use was well as the scarcity of the resource. The regression analysis shows that there are two groups of elements that are positively and significantly correlated. Piper plots showed that Na-Cl type is the main hydrochemical facies for the groundwaters. Saturation indices of aragonite, calcite and dolomite are of positive values higher than 1, indication supersaturation which lead to mineral precipitation condition of water by these minerals.

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