Hydrogeochemistry Characteristics in Kampong Salang, Tioman Island, Pahang, Malaysia

A N Idris¹,², A Z Aris¹, S. M. Praveena³, S. Suratman², I Tawnie³, M K N Samsuddin² and A Sefei²

¹Environmental Forensics Research Centre, Faculty of Environmental Studies, 43400 UPM, Serdang, Selangor, MALAYSIA
²Hydrogeology Research Centre, National Hydraulic Research Institute of Malaysia 43300 Seri Kembangan, Selangor, MALAYSIA
³Department of Environmental and Occupational Health, Faculty of Medical and Health Science, 43400 UPM, Serdang, SELANGOR

E-mail: azrul@nahrim.gov.my

Abstract: The constituents of major ions of groundwater samples has been used to identify the chemical characteristics and the type of groundwater in the low lying area in Kampong Salang located at north-west of Tioman Island in Pahang state. This study aimed to identify the groundwater quality with some geochemical process and to understand groundwater characteristics in the low-lying aquifer of the study area. From that, forty two (42) groundwater samples were collected and analysed for various parameters. Physical and chemical parameters of groundwater such as pH, electrical conductivity (EC), total dissolved solids (TDS), Ca, Na, Mg, K, HCO₃, Cl, SO₄, NO₃, CO₃, were determined. TDS did not exceed 1,000 mg/l with a maximum of 359 mg/l for sampling activities. Generally, groundwater in the study area is fresh, based on the analytical results. Hydrochemical facies of groundwater in the study area are dominated by Ca-HCO₃ and Ca-Mg-HCO₃ water type. A software known as PHREEQC was used to calculate the saturation indices for the main mineral phases with respect to carbonate and sulphate minerals. Most of the minerals were saturated to undersaturated with respect to carbonate minerals and undersaturated with respect to sulphate minerals composition. Maximum ionic strength in the study area is 0.009 which was found 90 m from the sea. Mostly minerals from calcite and dolomite precipitation are from bedrock of pyroxene hornfels.

Keywords: Hydrogeochemistry, PHREEQC, saturation indexes, undersaturated ionic strength.
1. Introduction
Groundwater is utilised as one of the sources beside surface water for regular water supply in most of the small island. Seawater intrusion is often become a major constraint to optimal utilisation of fresh groundwater from island aquifers. Excessive groundwater abstraction, has led to large-scale lowering of groundwater tables and changing the direction and magnitude of groundwater gradients [1]. Understanding the change of groundwater chemistry is important to appreciate the characteristic of water facies in the tropical islands [2]. Coastal aquifers, particularly tropical islands, fragile in nature and the alteration of the equilibrium state between freshwater and saltwater, thereby affecting socioeconomic development and damaging the entire ecosystem. This is because coastal aquifers are usually in direct contact with the sea, creating a state of equilibrium between the freshwater and saltwater. Distortion of the equilibrium usually occurs through either an increase or a decrease in the flow of freshwater, leading to alteration of the freshwater/saltwater equilibrium interface [3].

It is pertinent to understand the hydraulic properties and hydrochemical characteristics of the groundwater as a movement below ground surface is very slow. In general, groundwater flow below ground surface along its path will increase the concentration of the chemical species [4]. The interrelationship between groundwater flow, hydrogeologic properties and hydrochemistry is related to chemical quality and lithology of the area of study.

Chemistry of groundwater depends very much on the various factor such as geology, degree of chemical weathering, rock type, quality of recharge water and inputs from sources other than water-rock interaction [5]. The interactions will result in a different groundwater quality.

This study aimed to identify the groundwater quality with some geochemical process and to understand groundwater characteristics in the low-lying aquifer of the study area. The concentrations of major and minor ions of groundwater are essential in understanding geochemical processes affecting water quality. The results of this study may contribute to the optimisation of water resources management.

2. Study Area
Kampong Salang, Tioman Island (Figure 1) with a landmass of approximately 1.5 km², most of the surface terrain is hilly with a maximum elevation of 350 m above sea level. The island is under the control of Tioman Development Authority and the study area located between 2°52.580′ to 2°52.582′N latitude and 104°09.291′ to 104°09.275′E longitude. It is one of the main area of tourists’ congregation and well known to the divers as one of the best coral reef locations in Malaysia. About 40% of Kampong Salang is a low lying area and about 60% of it’s covered by forest. The climate of the island is tropical, receiving over 2,500 mm of rainfall annually, most of it during the monsoon season between November and February, with a temperature range between 28 and 31 °C and humidity of about 80%. Groundwater levels tend to form a surface that is sub-parallel to the topography. Areas of low topography relief therefore tend to have very low groundwater gradients compared to areas with higher relief. This factor needs to be considered in relation to movement of water away from the location where it is recharged artificially. The river in the northern part of Tioman Island especially in Kampong Salang is influenced by weather condition. Salang River water level very low during the dry season where river flows into the ground as subsurface river or groundwater while during the monsoon season there are a lot of streams appearing and water flows into the main river.
3. Materials and Methods
Fourty two groundwater samples were collected from 14 wells at Kampong Salang from April, June and August 2013. The locations of sampling points are shown in Figure 1. Groundwater sampled using polyethylene bottles based on the methods described in [6]. All samples were vacuum-filtered in the field for further analyses of cations using Whatman cellulose Nylon-type Millipore filters of 0.45-um pore size. In-situ analyses were conducted in the field using multiparameter sonde YSI 6600 for total dissolved solid (TDS), electrical conductivity (EC), pH, dissolve oxygen (DO), redox potential and temperature. Chloride and bicarbonate were determined using argentometric and titration methods in the laboratory respectively. Major cations (Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$) were determined in the laboratory using inductively coupled plasma mass spectrometry (ICP-MS) model Nexion 300X, made by PerkinElmer from United State of America (USA) according to the Environmental Protection Agency (EPA). Sulfate and Nitrate were detected using HACH DR2800 Portable Spectrophotometer. All the analyses were performed in the water quality laboratory and follow the procedures referred to [6].

The statistical analysed for descriptive statistics water quality parameter presented by mean, standard deviation, minimum and maximum. The saturation parameters for carbonate (calcite, aragonite and dolomite) of hydrogeochemical components of groundwater were set up using numerical model program PHREEQC [7]. PHREEQC for windows software was used to simulate different scenarios which is based on an ion-association aqueous model.

4. Results and Discussion
4.1. Statistical Analysis
The groundwater results obtained from geochemical process occurring interaction between water and geological material which groundwater flow movement in subsurface [8]. The water quality analyses included all physical and chemical parameters. pH and electrical conductivity value ranging from 6.55 to 8.01 and 0.07 to 0.55 mS/cm, respectively. Groundwater in the study area falls under fresh type of water (TDS < 1,000). TDS value
ranges from 47 to 359 mg/l. Redox potential and salinity of the study area ranging from -138 to 177 mV and 0.03 to 8.30 ppt, respectively (Table 1).

Concentration of calcium which is derived from calcium rich mineral like pyroxenes and feldspar. The concentration ranging from 4.75 to 95.97 mg/l which may also came from corals and shells. The sources of magnesium are due to the ion exchange of minerals in rocks and soils by water. Mg and HCO$_3^-$ ions in the groundwater samples ranged from 1.08 to 23.80 and 46.36 to 336.72 mg/l, respectively (Table 2). Bicarbonate in the study area indicates the biodegradation of the organic matter in the sub surface environment [9] Na and K groundwater concentration in the study area range from 6.19 to 53.55 and 0.32 to 26.99 mg/l. Chloride and sulphate concentrations in groundwater increase from recharge to discharge area range from 11.9 to 40.7 and 0 to 52 mg/l. This is due from the intrusion of sea water. Higher nitrate concentration in groundwater was found near to sewage tank of chalet which is 15.97 mg/l. Total hardness as CaCO$_3$ is ranging from 70 to 200 mg/l is considering from moderately to hard water.

4.2. Saturation Index (SI)

Saturation index are used to evaluate the degree of equilibrium between water and minerals. Calcite, dolomite, gypsum and anhydrite saturation indices were calculated to test the possibility that SO$_4^-$ reduction and dolomitisation processes are taking place. The saturation index of a mineral is obtained from equation (1):

$$SI = \log(IAP/Kt)$$

where IAP is the ion activity product of the chemical species in solution, Kt is the equilibrium solubility product for the chemical involved at sample temperature. SI which is less than zero indicate groundwater is undersaturated which respect to the composition of the minerals. SI with greater than zero indicate the groundwater is supersaturated with respect to the particular mineral.

Figure 4 shows the plots of SI of some minerals against TDS for all the investigated groundwater. Nearly all the water samples were slightly oversaturated to undersaturate with respect to calcite, and dolomite and all samples undersaturated with respect to gypsum and anhydrite, suggesting that these carbonate mineral phases.

The saturation indices of some common carbonate (calcite and dolomite) and sulphate (gypsum and anhydrite) minerals are shown in Figure 2. Most of the groundwater samples from April, June and August 2013 are slightly to moderately undersaturated with respect to the carbonate minerals (calcite and dolomite) indicating their dissolve in the aquifer matrix. Few samples are slightly oversaturated with respect to carbonate minerals indicating that these minerals can precipitate by the aggressive groundwater. The groundwater are also moderately undersaturated with respect to sulphate minerals (gypsum and anhydrite) indicating that more sulphate minerals will dissolve to increase their saturation states. Zero concentration of sulphate in samples resulting of no saturation index of both gypsum and anhydrite in April and June 2013. In the Gibbs plot, the rock is the dominant processes controlling major ion composition of groundwater that shows in Figure 3 may have influenced the chemical composition of the study area. Table 3 shows in Ca-HCO$_3$ water type the mean values of SI$_{\text{calcite}}$ and SI$_{\text{dolomite}}$ are -0.04 and -0.71 respectively. In Ca-SO$_4$ water type the mean values of SI$_{\text{gypsum}}$ and SI$_{\text{anhydrite}}$ are -3.01 and -3.22 respectively.

![Figure 1. Saturation indices of the common carbonate and sulphate minerals in the collected groundwater samples.](image)
Seawater intrusion will increase the ionic strength and soil redox condition. Figure 5 shows the decreasing of ionic strength from north-west of the study area to south-east where the downstream is at the south-east of the study area. In this study there is a slight intrusion of seawater but not obvious significant. Calcium bicarbonate groundwater has an ionic strength of about 0.02, whereas seawater has an ionic strength of 0.70 [10][8]. Maximum ionic strength in the area is 0.009 (value is 90 m from sea).

Figure 2. Mechanism governing groundwater chemistry (after [11]).

4.3. Hydrochemical Facies
A Piper diagram (Figure 6) was created for the low-lying of Kg Salang area using the analytical data obtained from the hydrochemical analysis. In general, the sample points can be classified into 3 fields. They are i) Ca-HCO$_3$ type, ii) Ca-Mg- HCO$_3$ type and iii) Ca-Na- HCO$_3$ type. However, in the present study water types were confined to the first type. In the study area, major groundwater type is Ca-HCO$_3$ and Ca-Mg-HCO$_3$. Evaluation of the water types using piper plot suggests that there is a clear indication of the contribution from the weathering of pyroxenes in the hard rocks. In Figure 7 shows that all groundwater samples fall under the subdivision of alkaline which had been proposed by [12]. The diagram shows geochemical classification and hydrochemical parameters of groundwater. The sample was taken on April, June and August 2013 in this period dissolution of the minerals are the major processes occurring in the groundwater environment. Since the flow is sluggish there will be much time for precipitation. Dominance of Ca and Mg in the groundwater samples collected suggested an inverse ion exchange process. During this process Ca from the aquifer matrix will be exchanged by Na from the groundwater. Sluggish flow in this relatively low lying area enables sufficient rock-water interactions.

Figure 3. Plots of saturation indexes with respect to some carbonate and sulphate minerals against total dissolved solids (TDS).
5. Conclusion
The geological of the study area confirm the interaction of rock and water which precipitate calcite and dolomite minerals. These minerals are from the pyroxene hornfel which is found in the upstream of the study area. The problem of groundwater in Kg. Salang, Tioman Island is rather complicated; it represent the tidal effect of monsoon season and infiltrate into low lying aquifer area. Based on the results obtained from PHREEQC, the fresh groundwater is yet not contaminated by the seawater as there were no excessive pumping activities in the village of the island. Results of SI show that nearly all of groundwater samples were saturated to under saturated with respect to carbonate minerals and undersaturated with respect to sulphate minerals. The shielding of ion lowers the activity of dissolved species that occur around charged. Interpretation of hydrochemistry analysis indicate that groundwater in the study area is fresh. The dominant hydrochemical
Facies of groundwater is Ca-HCO$_3$ and Ca-Mg-HCO$_3$. The groundwater is considered as moderately hard to hard water that contains dissolved hardness minerals (calcium and magnesium).

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Appendixes

**Table 1.** Mean, standard deviation, minimum and maximum value of physical parameters for April, June and August 2013 of groundwater samples from 14 wells.

| Parameter | April `13 | June `13 | August `13 |
|-----------|----------|----------|------------|
| **Temp**  | Mean     | 26.63    | 26.65      | 26.87      |
|           | Standard Deviation | 0.68    | 0.70       | 0.73       |
|           | Minimum   | 25.64    | 25.84      | 26.04      |
|           | Maximum   | 28.01    | 28.20      | 28.48      |
| **EC (mS/cm)** | Mean     | 0.36     | 0.31       | 0.38       |
|           | Standard Deviation | 0.11    | 0.10       | 0.12       |
|           | Minimum   | 0.17     | 0.13       | 0.07       |
|           | Maximum   | 0.50     | 0.48       | 0.55       |
| **TDS (mg/l)** | Mean     | 231.29   | 200.86     | 244.67     |
|           | Standard Deviation | 70.81   | 62.01      | 80.64      |
|           | Minimum   | 112.00   | 83.00      | 47.00      |
|           | Maximum   | 324.00   | 311.00     | 359.00     |
| **pH**    | Mean      | 7.40     | 7.16       | 7.49       |
|           | Standard Deviation | 0.48    | 0.33       | 0.23       |
|           | Minimum   | 6.55     | 6.55       | 7.11       |
|           | Maximum   | 8.01     | 7.63       | 7.86       |
| **Redox (mV)** | Mean     | -80.14   | -22.21     | -63.02     |
|           | Standard Deviation | 85.34   | 91.32      | 59.16      |
|           | Minimum   | -205.00  | -138.00    | -141.00    |
|           | Maximum   | 149.00   | 177.00     | 35.30      |
| **Salinity (ppt)** | Mean | 0.75     | 0.15       | 0.18       |
Table 2. Value of chemical parameters of groundwater samples

| Parameters | Mean   | Median | Standard Deviation | Minimum | Maximum |
|------------|--------|--------|--------------------|---------|---------|
| $K$        | 2.60   | 1.10   | 4.54               | 0.32    | 26.99   |
| $Na$       | 13.54  | 11.20  | 9.63               | 6.19    | 53.55   |
| $Mg$       | 5.53   | 4.02   | 4.74               | 1.08    | 23.80   |
| $Ca$       | 48.43  | 49.20  | 22.31              | 4.75    | 95.97   |
| $HCO_3^-$  | 203.58 | 215.01 | 73.73              | 46.36   | 336.72  |
| $Cl$       | 16.90  | 16.04  | 4.56               | 11.90   | 40.70   |
| $CO_3^-$   | 2.19   | 1.20   | 2.49               | 0.00    | 15.00   |
| $NO_3^-$   | 0.51   | 0.30   | 0.60               | 0.00    | 15.97   |
| $SO_4^{2-}$| 4.51   | 0.02   | 9.54               | 0.00    | 52.00   |

Table 3. Statistical summary of the saturation index minerals in Kampong Salang.

| $SI_{Calcite}$ | $SI_{Dolomite}$ | $SI_{Gypsum}$ | $SI_{Anhydrite}$ |
|---------------|-----------------|---------------|------------------|
| Mean          | -0.04           | -0.71         | -3.01            | -3.22            |
| Standard Deviation | 0.62          | 1.20          | 0.77             | 0.78             |
| Minimum       | -2.03           | -4.42         | -4.40            | -4.62            |
| Maximum       | 0.92            | 1.48          | -2.02            | -2.23            |