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Discussions

Comparison of monsoon variations over groundwater hydrochemistry changes in small Tropical Island and its repercussion on quality

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Abstract

Study on the spatial and temporal distribution of groundwater hydrochemistry in the small tropical islands is important as their insular character may expose the groundwater aquifer to too many sources of pollution, especially salinization. A total of 216 groundwater samples were collected from the monitoring boreholes during two different monsoon seasons; pre- and post-monsoon. As overall, data of groundwater concentration illustrated a trend of Ca > Na > Mg > K and $HCO_3 > Cl > SO_4$ dominations with the major finding of two different groundwater types. Pre-monsoon reported Na-HCO_3 and Ca-HCO_3 types while post-monsoon were only dominated by the Ca-HCO_3 type. The statistical analysis shows the in situ parameters (Temp, pH, EC, Salinity, DO, TDS and Eh) and major ions (Ca, Mg, Na, K, HCO_3, Cl and SO_4) were strongly correlated with the monsoon changes ($p < 0.01$). From the analysis, its reveals that the seasonal changes have significantly affects the groundwater composition. While, the analytical calculations of the ionic ratio (Na vs. Cl; Cl/HCO_3 vs. Cl; Ca + Mg vs. $SO_4 + HCO_3$) describes the groundwater is influenced by the cation exchanges processes, simple mixing and water–rock interaction. Saturation indices of carbonate minerals shows strong correlationship ($p < 0.01$) with Ca constituent indicating solubility on minerals, which led to dissolution or precipitation condition of water. Results of present study contribute to a better understanding of a complex groundwater system and the hydrochemical processes related.

1 Introduction

Small tropical islands mostly are under developing area is used to be an attraction place for the tourism who wants to escape the cult of busy life. Since these islands are always filled with peoples including local community, the most important needs for life are water. The situation become interesting and complicated as small tropical islands are known to experience a scarcity of surface water where the entirely area depend on groundwater as their primary water resource. Contain in aquifer, groundwater on these islands is surrounded by more dense saltwater from the ocean. The potential for an aquifer to provide a reliable source of good quality groundwater depends on the quantity of recharge that occurs from rainfall, the physical properties of the aquifer and the abstraction of groundwater from the ground (Aris et al., 2010a). Because of their relatively small size and oceanic setting, groundwater resources are vulnerable to over-pumping and saltwater intrusion especially during droughts season caused by the climate variation.

Groundwater pollution has been documented worldwide as a result of the anthropogenic disturbances to the natural systems (Rosenthal et al., 1992), and is directly or indirectly dependent on its surrounding condition, such as the increase in nitrate content (Oakes et al., 1981), presence of organic components, infiltration of untreated wastewater and salinization by seawater encroachment (Brown et al., 2006; Aris et al., 2007). Ongoing groundwater salinization has become a major problem that is threatening groundwater resources, especially in tropical regions. According to Gaye (2001) and Rosenthal (1988), other factors affecting groundwater salinization include inflows of saline water during heavy withdrawals of fresh groundwater or the mobilization of brackish water by over-exploitation of inland aquifers. Groundwater salinization also results from the dissolution of evaporated salt (from inundation) that accumulates in the subsoil over long periods of time (Payne et al., 1979; Benyamini et al., 2005) or the flushing out of salt by precipitation from airborne salts, soil and surface area. Furthermore, the salinization of groundwater might change the normal groundwater constituents and the suitability for drinking purposes and domestic use.

A good knowledge of the groundwater conceptual model in small islands is a prerequisite to investigate the mechanisms that control the groundwater quality. The developed model aims to explain the interaction between the complex hydrogeochemical environments of small islands and their surroundings (surrounded by seawater), which makes them more susceptible to seawater disturbance. Figure 1 shows the conceptual model of a small tropical island, which was developed to understand the groundwater hydrogeochemistry process. Basically, the factors that affect the groundwater quality are the chemical reactions between the water and aquifer matrix, dissolution and precipitation of minerals (calcite, aragonite and dolomite minerals in tropical regions), pollution from seawater intrusion and infiltration of organic pollutants (herbicides and feces).

Climatology in terms of the climate changes in this study refers to the annual variation of rainfall, temperature and potential evapotranspiration (Mimikou et al., 2000). These factors affect the quantity and quality of groundwater in small islands either directly or indirectly (Green et al., 2011; Dragoni and Sukhija, 2008). From Fig. 1, tropical regions are influenced by the South-West Monsoon (pre-monsoon; May to September), mostly dry season and the North-East Monsoon (post-monsoon; November to March), particularly the wet season (Desa and Niemczynowicz, 1996; Wong et al., 2009). During the dry season (rainfall: 2.5–27 mm), groundwater is more susceptible to salinization problems as it is characterized by low precipitation with high ambient temperature as well as a high evapotranspiration rate. On the other hand, the post-monsoon is related to high precipitation (rainfall: 451–1102 mm), could influence the quantity of recharge and quality of groundwater in small islands as precipitation events lead to an improvement in the quantity and quality of groundwater (Amer, 2008; Saxena et al., 2008; Aris et al., 2007, 2010b). As the tourists mostly visit during the pre-monsoon, the consumption of groundwater by pumping could exacerbate the situation. In order to sustain groundwater availability, it is necessary to consider the impact of climate variability on groundwater. A lack of knowledge concerning these systems could limit the ability to take a national view of salinization problems in small islands. It is important to carry out detailed groundwater studies, such as groundwater monitoring and assessment, to recommend alternatives that aim at detecting and reducing such risks.

Previous studies on groundwater have been classified according to the study specification, e.g., study on hydrogeochemistry (Chen and Feng, 2013; Srinivasamoorthy et al., 2012; Currell et al., 2010), groundwater quality (Papaioannou et al., 2012; Singh et al., 2012; Isa et al., 2012), study of mineralization (Guo and Wang, 2004; Katz and Bullen, 1996; Lakshmanan et al., 2003), seasonal effect of groundwater (Brown et al., 2006; Kazama et al., 2007; Pulido-Leboeuf, 2004) and modeling (Barragán-Alarcón, 2012; Russak and Sivan, 2010; Ekwere and Edet, 2012). As expected, the issues of groundwater pollution and protecting the groundwater resources provide an important reason to study the groundwater. Scientists and engineers in developed countries have aware of the health threat posed by the contamination involving in cleaning up contaminated groundwater (Tribble, 2008). Developing area such as Kapas Island is far away in managing the sustainable of groundwater, yet, lack of expertise and information which can be applied in other tropical islands. Such hypothesis on more people attends becoming less quality of water needs to be eliminated in order to gain a sustainable development as well as concrete profitable. Due to scarcity of information and workloads on groundwater in tropical region, present study was conducted to fill the gaps and provides an understanding of groundwater hydrochemistry characteristics and the fingerprints of the groundwater pollution. Hence, with right and suitable facts, it could provide explanation and solution to the sector responsible for the variation of groundwater constituents.

The objective of this study is to reveal the important information concerning groundwater in small tropical islands, which apply to most of the study specifications listed above (hydrogeochemistry, groundwater quality, mineralization process, seasonal effects and modeling). With this information, the exact problems faced in the different circumstances (pre- and post-monsoon) and the hydrogeochemistry mechanism involved during the seasonal variation can be reviewed.

2 Site description

Kapas Island is an unconformity structure, which separates the younger rock sequence of the Kapas Conglomerate above from the older Permo-Carboniferous rock sequence below. The unconformity of this island is an important geological feature that can explain the geological history of these sequences (Shuib, 2003). The topography of Kapas Island includes a hilly area (maximum height approximately 100 m) covers 90 % of the island, while the rest is a relatively low-lying area (Fig. 2). The land use of Kapas Island, excluding the hilly area, shows that about 8 % of the area is comprised of secondary forest while the sandy coastal area constitutes only 2 %. Ecotourism activities at Kapas Island have been actively developed in the coastal area due to its accessibility.

Kapas Island was gazetted as a Marine Park, the aims of which are to protect and conserve various habitats and aquatic marine life. Kapas Island, which is relatively isolated, is also well known for its clear water, sandy white beaches and swaying palm trees. Kapas Island was chosen in this study due to the limited information available concerning the hydrogeochemistry, either pertaining to protection or preservation, and the fact that this small island has become a high water demand area due to the development of tourism activities. Kapas Island is the best location to review the impact of seasonal changes as it is situated at the monsoon interchange.

Kapas Island is located at 5°13.140′ N, 103°15.894′ E (Fig. 2) with an area of about 2 km^2 (Abdullah, 1981; Shuib, 2003). The climate is a typically tropical climate with an annual rainfall of between 451 and 1102 mm, which is influenced by the monsoon blowing from the middle of November to January. Kapas Island experiences a constant mean temperature of 29.88 °C, varying from 28 to 31 °C, and has an average daily relative humidity of around 80 %. A summary of the annual rainfall for the study area is presented in Fig. 3. A high peak in certain months, especially at the end of each year, is explained by the high rainfall intensity, usually due to the monsoon changes.

3 Methods

The sampling design for this study was based on spatial and temporal scales. A total of 216 groundwater samples with replicates were collected bimonthly (two times a month) from six constructed boreholes (specifically KW 1, KW 2, KW 3, KW 4, KW 5 and KW 6) during the pre-monsoon (August 2010–October 2010) and post-monsoon (February 2011–April 2011).

$$6\,\text{monitoring boreholes} \times \text{triplicate} \times 6\,\text{sampling campaign (each season)} \times 2\,\text{seasons} = 216\ \text{samples}$$

The locations of the constructed boreholes (monitoring boreholes) were chosen in low-lying areas with dense population as these areas are the focus for the tourism activities and concomitant pumping for groundwater abstraction is practiced. Boreholes were drilled to a depth of between 2.5–11.5 m in the aquifer (Table 1). The screening process was done before the installation of the boreholes to prevent any sand and trash penetrating into the boreholes that might cause deterioration in the samples. The hydraulic head of each monitoring borehole was measured using a water level meter before collecting the groundwater samples. Prior to the collection of the groundwater samples, the samples were pumped out for about 10–15 min to avoid any stagnant and polluted water that might interfere with the physicochemical measurement and the chemical equilibrium condition of the water.

3.1 Physicochemical parameters

The groundwater measurement consists of in situ parameters, namely, pH, redox potential (Eh), electrical conductivity (EC), salinity, total dissolved solids (TDS) (measured using Mettler Toledo, Columbus), temperature and dissolved oxygen (DO). Next, the samples were divided into another two main analyses: anions and cations. Anions, namely bicarbonate (HCO_3), chloride (Cl) and sulfate (SO_4) were determined using the titration method of HCl (APHA, 2005), titration method of $AgNO_3$ (APHA, 2005) and determination of SO_4 concentration using a HACH (DR/2000) meter (HACH, Loveland, CO, USA), respectively. It is necessary to determine anion measurements on-site, as advised by APHA (2005), to obtain representative data. For analyses of the cations, groundwater samples were filtered through a 0.45 µm Millipore filter and immediately acidified with HNO_3 ($pH < 2$) to prevent bacterial development, to block the effects of oxidation and to prevent adsorption or precipitation of cations in the groundwater samples (Appelo and Postma, 2005). Pre-treated samples were kept in a cool box before being transported to the laboratory for major ions analysis using a flame atomic absorption spectrophotometer (FAAS, Perkin Elmer, Massachusetts, USA).

The preservation and data collection of samples were done precisely to ensure the quality of data. In-situ devices were calibrated with buffer solutions before and after the field sampling to ensure that they functioned properly and accurately. The accuracy checks were undertaken to obtain a reliable analytical dataset by checking the procedure of blank measurements and a three point calibration curve when using the FAAS. The annual preventive maintenance for the FAAS was done to receive accreditation for the system and approval of the laboratories from governmental bodies. The results of triplicate analyses and average values are reported to indicate the precision of measurement.

3.2 Data analyses

Descriptive statistics and correlation coefficient analyses were calculated for groundwater samples using PASW Statistics 18.0. These techniques were used to emphasize the meaningful characterization of data, such as variability, graphical and description of similarities. The data obtained from this study are graphically presented using a Piper diagram and Schoeller diagram in order to show the mechanisms involved in the groundwater chemistry evolution. The ionic ratio was used to analyze the hydrochemistry data to amplify the hydrochemistry mechanisms in the groundwater. The ratios used in this study were Cl/HCO_3 vs. Cl, Na vs. Cl and $Ca + Mg$ vs. $SO_4 + HCO_3$ with the ionic concentrations given in miliequivalents per liter ($meq\,L^{-1}$).

In particular, the equilibrium of minerals is related to water interaction. Some minerals, such as NaCl, react faster upon contact with water. If the dissolution and precipitation occur in the same amount equally, the equilibrium is obtained. The fundamental to any description of equilibria in water is the *law of mass action* (Appelo and Postma, 2005), which states that for a reaction of the generalized type (Eq. 1) term:

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} + d\mathrm{D} \tag{1}$$

whereas, the distribution at the thermodynamic equilibrium of the species at the left and right side of the reaction is given by (Eq. 2):

$$K = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \tag{2}$$

where, K is the equilibrium constant and the bracketed quantities denote effective concentration. The superscript of a, b, c, and d are the number of moles of the reactants A and B, and the end products C and D, respectively.

For the analogue to the *law of mass action*, one can calculate with the activities, to gain the Ion Activity Product (IAP). Comparing the IAP with the K leads to an expression of the saturation conditions, or the saturation index (SI). In PHREEQC software, the SI can be calculated based on Eq. (3).

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{K}\right) \tag{3}$$

For this study, the SI for the selected minerals was calculated to gain a better understanding of the hydrochemical processes that take place in the aquifer during the mixing of freshwater and seawater. PHREEQC software 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. A negative SI value defines the dissolution process, a positive SI value explains the precipitation process, while a 0 value of SI indicates the equilibrium state of carbonate minerals.

Some of the sediment samples were submitted to nuclear agency (Malaysian Nuclear Agency) to perform an analysis of Scanning Electron Microscope-Energy Dispersive X-ray spectroscopy (SEM-EDX) to verify the existence of carbonate minerals that affect most of the hydrochemical processes in this study.

4 Results and discussion

4.1 Descriptive analyses

The results are presented in Table 2 with the mean, SD (standard deviation), Min (minimum) and Max (maximum). The average temperature and DO values are 29.71 °C and 3.32 $\mathrm{mg\,L^{-1}}$, respectively. The EC is in the range of 0.32 to 0.91 $\mathrm{mS\,cm^{-1}}$, and has a positive correlation with salinity ($r = 0.998$; $p < 0.01$) and is also strongly correlated with TDS ($r = 0.999$; $p < 0.01$). The TDS is in the range of 159 to 455 $\mathrm{mg\,L^{-1}}$, which presents the ions in the groundwater as it is strongly correlated with the major ions ($p < 0.01$; Table 3). The average salinity value in the groundwater is 0.23 ppt, while the pH and Eh show a negative correlation ($r = -0.965$; $p < 0.01$) with average values of 7.17 and 1.45 mV, respectively.

The order of cation concentrations is Ca > Na > Mg > K, while for the anions, it is $HCO_3 > Cl > SO_4$. The average concentration of Ca and Na is 64.05 and 13.37 $\mathrm{mg\,L^{-1}}$, respectively, while low concentrations of Mg and K in most cases are 5.72 and 0.77 $\mathrm{mg\,L^{-1}}$, respectively. HCO_3 is the dominant anion, which ranges from 273.08 to 372.64 $\mathrm{mg\,L^{-1}}$ with an average of 326.87 $\mathrm{mg\,L^{-1}}$. The mean values of Cl and SO_4 are 31.16 and 12.34 $\mathrm{mg\,L^{-1}}$, respectively.

4.2 Groundwater quality

The Schoeller diagram in Fig. 4 illustrates that the concentration of major ions in the different monsoon seasons explains the groundwater quality as the concentrations of major ions vary between the pre- and post-monsoon. The pre-monsoon shows a higher concentration of seawater elements (Na and Cl) while the post-monsoon displays an elevated concentration of mineral elements (Ca and Mg). The strong correlation ($p < 0.01$) between the seasons and the major ions concentration (Table 3) indicates that the monsoon changes significantly affect the groundwater quality. The hydrochemical facies of groundwater show different water types in the different monsoons. Insert (a) in Fig. 5 shows the composition of major ions during the pre-monsoon where it experienced a shift in the water type from Ca-HCO_3 (origin) to Na-HCO_3, as illustrated in the circle shapes of I and II while insert (b) for the post-monsoon might explain the ion exchange mechanism, where the groundwater has shifted back to the Ca-HCO_3 water type.

The high concentration of seawater elements of Na and Cl can be explained by the salinization process in the groundwater where it is also manifested by significant positive correlations with salinity ($r = 0.797$, 0.823; $p < 0.01$). The increase in Na concentration could be due to the cation exchange of Na (which precipitated from an inundation event) with Ca during the groundwater mixing process. The mechanism can be expressed in Eq. (4); where **X** represents the aquifer matrix. The relationship of Ca and Na concentrations can be delineated by the negative correlation value from Table 3 ($r = -0.292$; $p < 0.01$). Meanwhile, Ca has a positive correlation with Mg with $r = 0.545$ ($p < 0.01$). Both of these mineral elements increase with the dissolution of ($CaMg(CO_3)_2$) minerals (Described in saturation index sub-section). Drought season particularly in pre-monsoon have experienced quite drop of water tables as shown in Fig. 6. This is because of groundwater pumping activities are frequently practiced to meet the demand while exceeds the recharge rate levels. It allowed the up-coning of the transition zone which later on mixed with the brackish water (Fig. 1). In addition, the evaporation process of seawater (which leaves salts) may contribute to the salinization process as it is dissolved into the groundwater either by surface runoff or normal rainfall (Naseem et al., 2010). Furthermore, the infiltration of leachate that comes from the sewage piping systems may also contribute to the salinization process.

$$\frac{1}{2}\mathrm{Ca}^{+} + \mathrm{Na}-\mathbf{X} \leftrightarrow \mathrm{Na}^{+} + \frac{1}{2}\mathrm{Ca}-\mathrm{X}_2 \quad (4)$$

Elevated of mineral elements of Ca and Mg and the elevation of water tables (Fig. 6) during post-monsoon with an average increased approximately 1.21 m clearly explained the important roles of rainfall as its' groundwater recharge. The cation exchange process is assumed to take place where the reversible reaction of Eq. (4) may explain the high Ca concentration in the groundwater. Due to the wide contact of new groundwater (recharge by rainfall) with crystalline limestone and coral deposits, the groundwater in the coastal aquifer experiences another process of water–rock interactions and carbonate dissolution (Eq. 5). As rainfall (recharge) continuously during monsoon interchanges, seawater elements as well as domestic pollutants can be removed by widen the aquifer storage, distance of the transition zone and increase the groundwater table level (1.32–1.91 m from ground surface).

$$\mathrm{H_2O} + \mathrm{CaCO_3} \rightarrow \mathrm{Ca}^{2+} + \mathrm{HCO}_3^{-} + \mathrm{OH}^{-} \quad (5)$$

4.3 Ionic ratio

The calculated ionic ratios were used to verify and validate the cation exchange process that is responsible for the higher concentration of certain elements in the study area, e.g., Na during pre-monsoon and Ca during post-monsoon (Table 4). The scatter plot of the $\mathrm{Cl/HCO_3}$ ratio vs. Cl (Fig. 7a) explains the groundwater status in which the distribution shows a positive correlation with an r value of 0.964 ($p < 0.01$). Only samples from KW 6 during the pre-monsoon were isolated from others, which portray the slight interference of seawater. This can be proved as the Cl concentration correlates well with the seawater component; Na ($r = 0.915$; $p < 0.01$). The groundwater samples from the post-monsoon indicate that the groundwater was in a freshening status in which the high Cl concentration (pre-monsoon) was diluted during the post-monsoon (Fig. 4).

The plot of Na vs. Cl (Fig. 7b) indicates different mechanisms in the groundwater. The halite (evaporite salts) dissolution is responsible for the Na concentration in the groundwater in which the groundwater samples are scattered in a ratio approximately equal to 1, whereas a ratio > 1 is interpreted as the Na released from silicate weathering. In the present study, the ratios of Na vs. Cl are generally < 1, which explains that the cation exchange is the dominant process in the groundwater (Kumar et al., 2006; Lipfert et al., 2006).

The use of $Ca + Mg$ vs. $HCO_3 + SO_4$ (Fig. 7c) ratio reflects the cation exchange process and can be traced to the dissolution of carbonates in the aquifer. Most of the samples from the pre-monsoon fall below the equiline, which explains the active reaction leading to HCO_3 and SO_4 accumulation in the groundwater, while 44 % of the total samples from the post-monsoon exceed the equiline, depicting the reverse reaction of ion exchanges (Belkhiri et al., 2010; Lakshmanan et al., 2003; Wen et al., 2005), which are responsible for the dominance of the Ca and Mg concentrations in the groundwater. This mechanism can be explained by the negative relationship ($p < 0.01$; Table 3) of Ca and HCO_3. According to Reddy and Kumar (2010), the effectuation of Ca and Mg concentration is more conspicuous due to the abundance of granite (which is Kapas Island's parent rock) and post-monsoon season.

4.4 Saturation Index (SI)

Tropical aquifers are usually composed of certain carbonate materials, in which calcium carbonate is the predominant mineral, especially in shallow groundwater formations. The compaction and cementation processes of this mineral might act on the deposition as they lithify. Since the water–rock interaction contributes to the groundwater composition, the saturation states were calculated to explain the behavior of the minerals in the groundwater.

The data for the SI values are presented in Table 5. Figure 8a shows that 76 % of groundwater samples were under the dissolution process ($SI < 0$) for the minerals calcite ($CaCO_3$), aragonite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) during the pre-monsoon. This study shows that Ca has increased due to the dissolution reaction, as demonstrated in Fig. 5 and Eq. (5). Ca is strongly correlated with the saturation state of carbonate minerals, which are calcite ($r = 0.759$, $p < 0.01$), aragonite ($r = 0.759$, $p < 0.01$) and dolomite ($r = 0.662$, $p < 0.01$). The previous discussion of the correlation between Ca and Mg ($CaMg(CO_3)_2$ mineral) is explained by Eq. (6) in which Mg correlated with dolomite ($r = 0.517$; $p < 0.01$). The finding of Mg in the groundwater of the present study can be verified from a previous research (Ali et al., 2001) concerning the existence of high Mg minerals in Kapas Island. This is supported by previous ionic ratio justifications that indicate the dissolution of carbonate minerals, especially calcite and dolomite when the samples fall on the equiline (1 : 1) of the Ca+Mg vs. HCO_3+SO_4 ratio (Fig. 7c).

$$CaMg(CO_3)_2 \rightarrow 2Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \tag{6}$$

Figure 8b demonstrates the saturation state of minerals during the post-monsoon. Only 30 % of the total SI values are < 0 and most are $CaMg(CO_3)_2$ minerals. This indicates that the under saturated state of carbonate minerals during the pre-monsoon gradually increases to the equilibrium state and towards super saturated condition as the groundwater continuously reacts with the aquifer.

There are more evidences explaining the groundwater hydrochemistry mechanism. The calculated values of Ca/Mg ratio (Table 4) also reveal the dissolution of minerals involved in attaining the present hydrochemistry in the groundwater. As the points lie between 1 and < 2 in the plot, it indicates dolomite dissolution, while samples > 2 ratio (most of the samples in Table 4) shows a greater contribution of calcite (evident from the Ca concentration). On the other hand, the inverse ratio of Mg/Ca is used to distinguish the factor responsible for groundwater chemistry with respect to seawater influence (Aris et al., 2012). The ratio of Mg/Ca > 0.7 clarifies the disturbance of seawater; however, none of the samples in the present study comply with the interference (Table 4).

Figure 9 illustrates the ionic ratio of (a) Na-normalized Ca vs. Mg and (b) Na-normalized Ca vs. HCO_3 (Table 4) in which these ionic ratios are used to show that the groups of samples are influenced by seawater disturbance, silicate weathering or carbonate dissolution (Belkhiri et al., 2010). Groundwater samples tend to be grouped in the carbonate dissolution area as they increased from the seawater disturbance area and silicate weathering area towards the carbonate dissolution area; from pre-monsoon to post-monsoon seasons, with r values of 0.730 and 0.825 ($p < 0.01$), respectively.

The illustration of SEM-EDX (Fig. 10) is used to support/justify the existence of carbonate minerals – to $CaCO_3$ and $CaMg(CO_3)_2$ – which has been used to describe the groundwater mechanisms throughout the paper.

5 Conclusion

At the beginning of this article, present study has claimed the important role of groundwater in Kapas Island. This research has done vigorously to acknowledge current situation of groundwater hydrochemistry where the seasonal variations have significantly contributes. The groundwater of Kapas Island displays the domination of the $Ca > Na > Mg > K$ and $HCO_3 > Cl > SO_4$ trend. The findings that have presented suggest that the groundwater consists of different water types, both in pre ($Na\text{-}HCO_3$) and post-monsoon ($Ca\text{-}HCO_3$). This is important to decipher the chemical changes in groundwater during monsoon interchanges, also, are the best reflection of the cation exchange process. The cation exchange process was strengthened by the results of the ionic ratio's scatter plots (Cl/HCO_3 vs. Cl, Na vs. Cl and $Ca + Mg$ vs. $SO_4 + HCO_3$) and the saturation index calculation that explained the minerals behavior of water–rock interaction either in dissolved or precipitated state.

To date, the previous study of small tropical island's aquifer have issued the groundwater pollution regarding on seawater intrusion. This study has offers a better understanding on groundwater hydrochemistry of a pristine environment by providing an excellent interpretation of the results and enhanced the used of selected variables in hydrochemistry studies, as a source tracer for groundwater contaminations. Present study also compromises with the quantitative and qualitative outputs where the quantitative issues have exemplify the hydrochemistry concerns based on the elements concentration in the groundwater, signify the differences of mechanism in spatial and temporal scales and elucidate the groundwater status based on the establish guidelines. Whereas, the qualitative issues includes the evidences of affected area, comparison with previous researches on groundwater study and either to create a new databases or to improve an existing guidelines especially on small tropical islands. This information will be of value in setting priorities and allocating resources within regulatory agency. It would be fruitful to pursue further research in term of management concerns by certified the ongoing profits from tourism activities as long as the natural ecosystem remain unharmed.

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Table 1. Location and depth of boreholes at Kapas Island.

Station	Station's Coordinate		Distance from coastline (m)	Depth of boreholes from surface (m)
KW1	5°12.999 N	103°15.799 E	119	11.5
KW2	5°12.996 N	103°15.787 E	98	9.1
KW3	5°12.992 N	103°15.778 E	83	3.5
KW4	5°12.989 N	103°15.771 E	68	3.0
KW5	5°12.985 N	103°15.762 E	48	2.9
KW6	5°12.982 N	103°15.754 E	31	2.5

Table 2. Descriptive analyses for in situ and major ions of groundwater samples ($n = 216$).

Station		Temperature	pH	EC	Salinity	DO	TDS	Eh	Ca	Mg	Na	K	HCO_3	Cl	SO_4
KW 1	Mean	29.48	7.18	0.52	0.25	2.97	258.72	1.24	75.72	8.58	13.83	0.71	326.72	30.35	17.22
	SD	0.86	0.12	0.08	0.04	2.61	38.41	5.88	28.23	4.02	4.16	0.19	36.78	7.74	2.36
	Min	27.80	7.04	0.34	0.16	0.70	170.20	−13.20	24.01	3.19	5.80	0.37	244.00	17.99	14.00
	Max	30.80	7.64	0.62	0.30	7.74	311.00	9.90	116.07	15.44	20.20	1.05	366.00	45.99	20.00
KW 2	Mean	29.77	7.07	0.54	0.26	2.82	270.16	7.28	60.72	6.36	12.17	1.76	344.38	31.00	8.92
	SD	1.05	0.17	0.20	0.10	2.23	99.39	10.18	23.21	2.44	6.92	1.04	108.73	12.05	8.61
	Min	28.40	6.76	0.34	0.16	0.63	169.50	−4.80	10.40	2.19	3.13	0.58	229.36	16.00	1.00
	Max	32.20	7.27	0.91	0.45	7.88	455.00	27.00	96.70	10.40	25.20	3.89	578.28	55.98	26.00
KW 3	Mean	29.66	7.24	0.41	0.20	4.17	202.65	−3.21	54.09	5.19	9.33	0.55	273.08	22.80	11.11
	SD	0.74	0.05	0.02	0.01	2.69	12.02	2.29	26.33	1.92	3.60	0.14	19.09	4.44	2.76
	Min	28.50	7.14	0.36	0.18	1.35	181.90	−7.90	11.40	1.62	0.80	0.38	239.12	17.99	6.00
	Max	31.00	7.32	0.44	0.21	10.17	221.00	0.80	91.81	8.69	13.36	0.88	324.52	32.99	17.00
KW 4	Mean	30.07	7.23	0.39	0.19	4.47	197.32	−2.69	62.79	4.96	7.09	0.35	293.00	17.72	9.03
	SD	1.34	0.06	0.02	0.01	2.41	11.92	3.27	29.74	1.27	5.78	0.43	26.90	6.42	3.16
	Min	28.30	7.15	0.37	0.18	2.09	182.90	−7.50	14.30	2.81	1.84	0.03	244.00	11.00	4.00
	Max	33.70	7.31	0.44	0.21	9.05	220.00	2.00	95.85	7.10	24.48	1.48	341.60	32.99	14.00
KW 5	Mean	30.28	7.20	0.45	0.22	3.53	227.88	−0.78	67.22	4.41	15.57	0.48	361.43	31.96	15.06
	SD	1.76	0.08	0.11	0.05	1.67	55.00	5.23	29.23	1.45	13.07	0.46	179.42	19.77	8.65
	Min	28.60	7.07	0.32	0.15	1.72	158.80	−9.00	18.50	1.96	5.10	0.08	236.68	10.00	5.00
	Max	35.10	7.34	0.63	0.30	7.63	314.00	7.50	145.20	6.92	42.65	1.51	893.04	78.98	30.00
KW 6	Mean	30.06	7.11	0.54	0.26	2.50	269.32	4.70	63.74	4.83	22.23	0.78	362.61	53.15	12.69
	SD	1.43	0.19	0.21	0.11	0.75	105.99	12.21	28.39	1.56	21.51	0.90	118.41	50.02	5.70
	Min	27.90	6.68	0.35	0.17	1.39	174.30	−11.00	17.80	1.98	5.72	0.05	234.24	13.00	5.00
	Max	32.70	7.37	0.85	0.41	4.22	422.00	32.30	106.70	7.60	58.80	2.95	639.28	141.96	20.00

All units in mg L^{-1}, except for temperature (°C), EC (mS cm^{-1}), salinity (ppt), Eh (mV) and pH (unit less).

Table 3. Correlation coefficient for groundwater samples of Kapas Island ($n = 216$).

	Temp	pH	EC	Salinity	DO	TDS	Eh	Ca	Mg	Na	K	HCO_3	Cl	SO_4	Season
Temp	1	−0.392**	0.302**	0.296**	−0.066	0.301**	0.391**	−0.296**	−0.145*	0.192**	0.307**	0.563**	0.277**	0.060	−0.432**
pH		1	−0.810**	−0.804**	0.250**	−0.807**	−0.965**	0.080	−0.309**	−0.531**	−0.644**	−0.547**	−0.573**	0.012	0.372**
EC			1	0.998**	−0.241**	0.999**	0.845**	−0.307**	0.210**	0.790**	0.574**	0.631**	0.820**	0.256**	−0.616**
Salinity				1	−0.235**	0.999**	0.841**	−0.306**	0.205**	0.797**	0.565**	0.631**	0.823**	0.255**	−0.609**
DO					1	−0.243**	−0.232**	0.118	−0.159*	−0.123	−0.274**	−0.080	−0.202**	0.020	0.196**
TDS						1	0.843**	−0.309**	0.208**	0.794**	0.573**	0.633**	0.821**	0.260**	−0.618**
Eh							1	−0.093	0.297**	0.563**	0.660**	0.599**	0.619**	0.012	−0.356**
Ca								1	0.545**	−0.292**	−0.357**	−0.223**	−0.346**	−0.218**	0.692**
Mg									1	0.030	0.013	−0.005	−0.064	−0.071	0.224**
Na										1	0.320**	0.433**	0.915**	0.466**	−0.477**
K											1	0.513**	0.363**	−0.024	−0.457**
HCO_3												1	0.518**	0.193**	−0.500**
Cl													1	0.406**	−0.498**
SO_4														1	−0.311**
Season															1

Temp = Temperature
Correlation value (upper triangle)
Significant value (** $p < 0.01$, * $p < 0.05$)

Table 4. Summarized results of ionic ratio.

Station	Cl/HCO_3		Ca + Mg		$SO_4 + HCO_3$		Ca/Mg	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
KW 1	0.331	0.062	4.485	1.669	5.715	0.615	6.085	3.037
KW 2	0.318	0.058	3.554	1.259	5.831	1.710	6.163	2.240
KW 3	0.298	0.044	3.126	1.443	4.708	0.333	6.322	2.233
KW 4	0.214	0.064	3.541	1.563	4.991	0.486	7.486	2.705
KW 5	0.318	0.160	3.717	1.525	6.239	3.013	9.550	3.944
KW 6	0.476	0.378	3.578	1.475	6.209	2.002	8.248	3.147

Table 4. Continued.

Station	Ca/Na		HCO_3/Na		Mg/Na		Mg/Ca	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
KW 1	6.796	3.243	9.835	3.849	1.227	0.601	0.192	0.061
KW 2	8.840	6.904	14.099	10.375	1.360	0.898	0.180	0.072
KW 3	9.625	11.322	20.105	30.470	1.871	2.787	0.197	0.132
KW 4	19.848	18.569	24.599	15.834	2.363	1.898	0.168	0.110
KW 5	10.546	7.928	14.329	10.535	1.073	0.834	0.126	0.066
KW 6	8.381	6.399	12.360	8.233	0.891	0.575	0.160	0.122

Table 5. Saturation index (SI) for carbonate minerals in Kapas Island.

Station		Calcite	Aragonite	Dolomite
KW 1	Mean	0.20	0.06	−0.16
	SD	0.16	0.16	0.30
	Min	−0.18	−0.32	−0.81
	Max	0.40	0.25	0.26
KW 2	Mean	0.02	−0.12	−0.52
	SD	0.23	0.23	0.34
	Min	−0.78	−0.92	−1.25
	Max	0.25	0.11	−0.03
KW 3	Mean	0.03	−0.11	−0.51
	SD	0.26	0.25	0.35
	Min	−0.57	−0.71	−1.10
	Max	0.34	0.20	−0.05
KW 4	Mean	0.13	−0.01	−0.38
	SD	0.19	0.19	0.19
	Min	−0.29	−0.43	−0.71
	Max	0.34	0.20	−0.05
KW 5	Mean	0.18	0.04	−0.38
	SD	0.22	0.22	0.38
	Min	−0.35	−0.49	−1.21
	Max	0.85	0.71	0.62
KW 6	Mean	0.08	−0.06	−0.53
	SD	0.28	0.28	0.39
	Min	−0.44	−0.58	−1.18
	Max	0.61	0.47	0.43

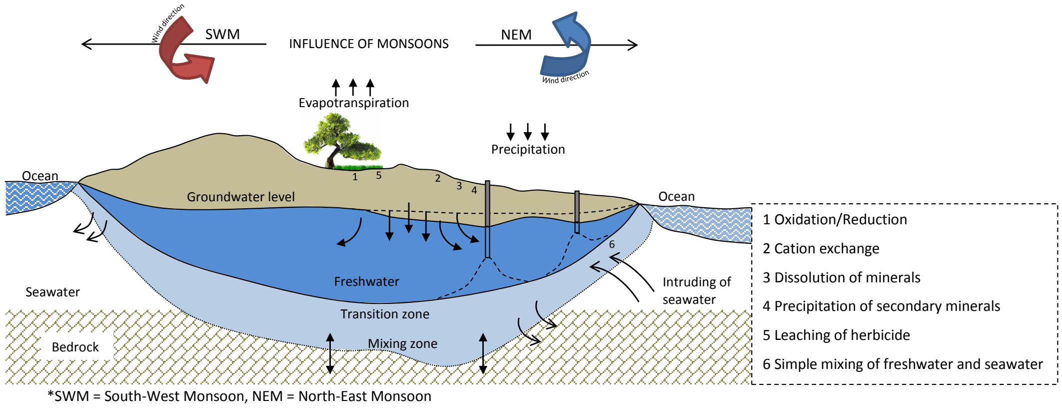

Figure 1. The complex geochemical model of groundwater in small islands (modified from Isa et al., 2014).

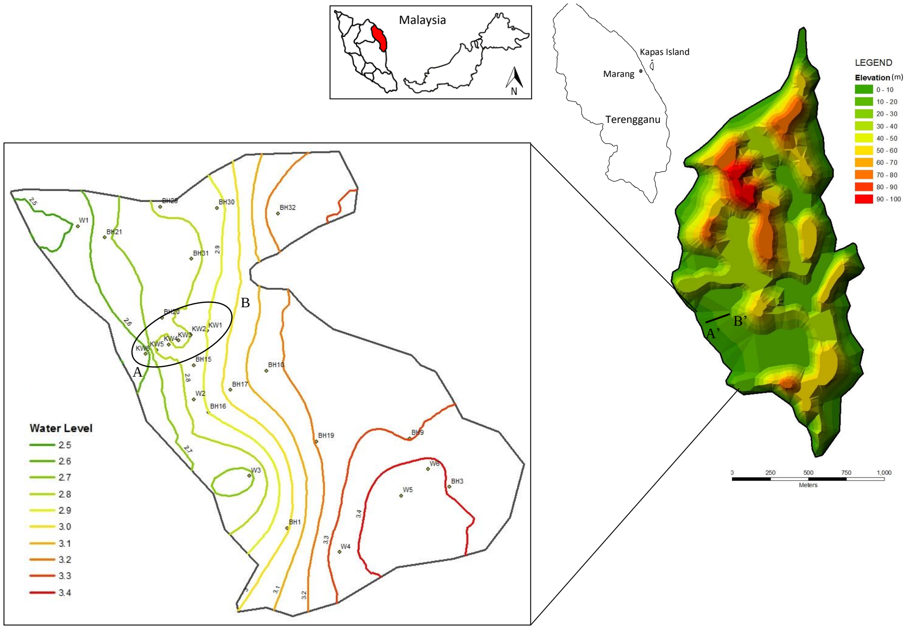

Figure 2. Schematic map showing the geographical locality of Kapas Island and the constructed monitoring boreholes.

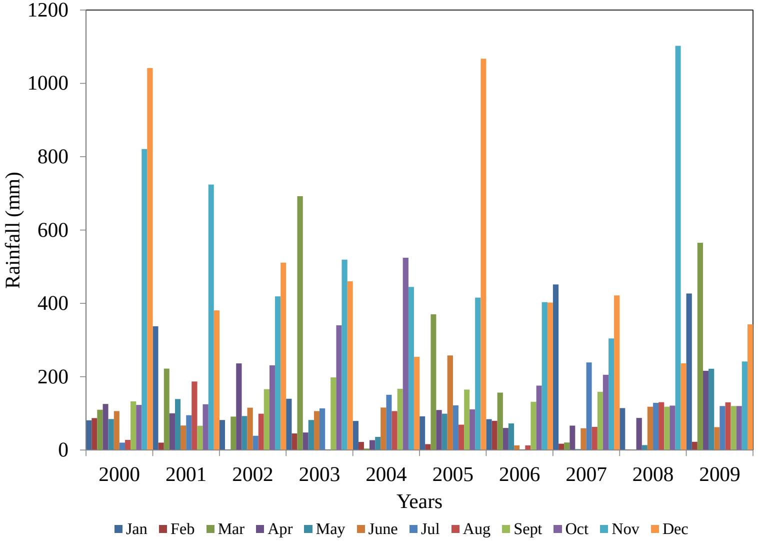

Figure 3. Distribution of annual rainfall at Marang, Terengganu (2000–2009).

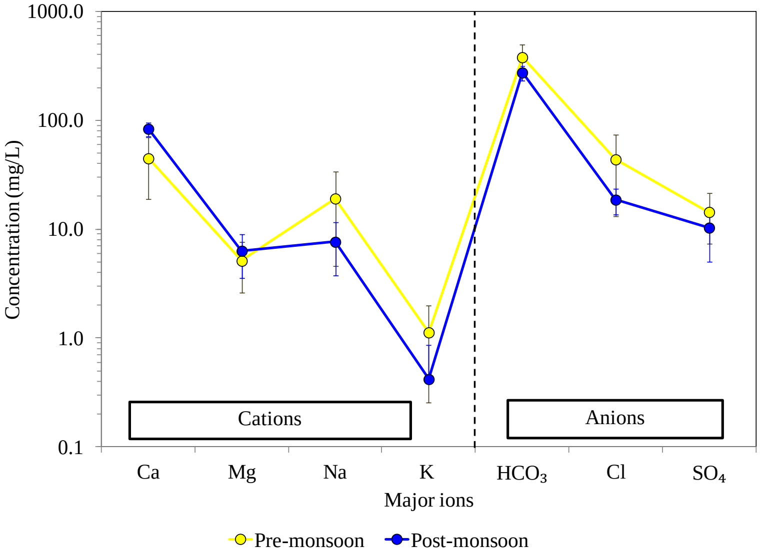

Figure 4. Schoeller diagram of concentration of major ions for the two different monsoon seasons ($n = 216$).

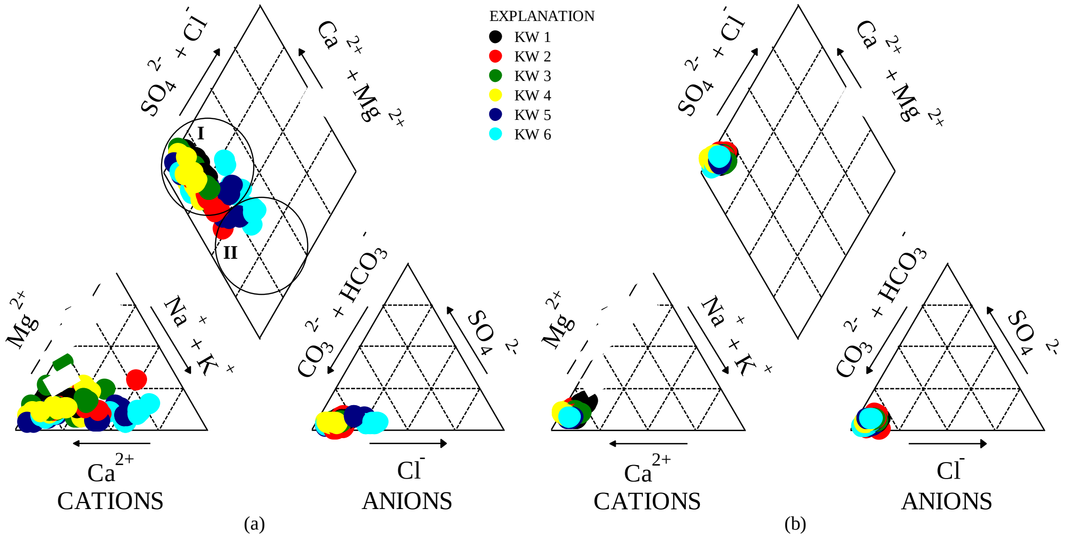

Figure 5. Schematic Piper diagram. **(a)** shows the water type for the pre-monsoon; Ca-HCO_3 water type (Circle I) and Na-HCO_3 water type (Circle II), while, **(b)** shows that the water type for the post-monsoon is Ca-HCO_3 water type.

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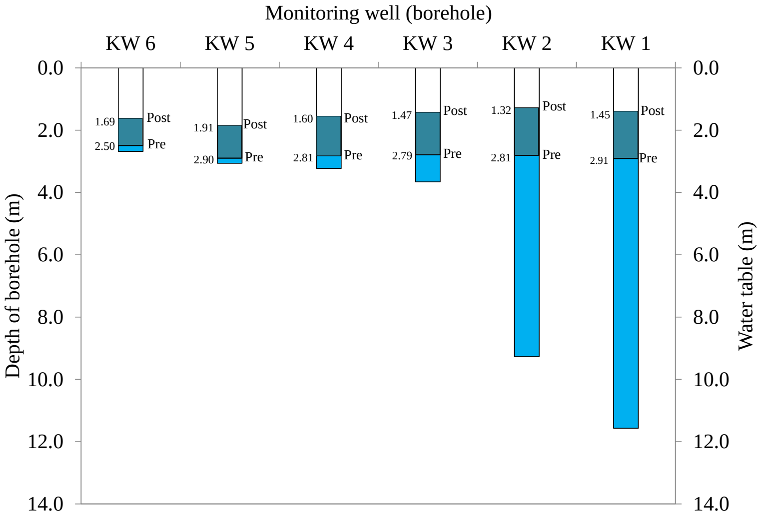

Figure 6. Illustration of average groundwater table during pre-monsoon (pre) and post-monsoon (post).

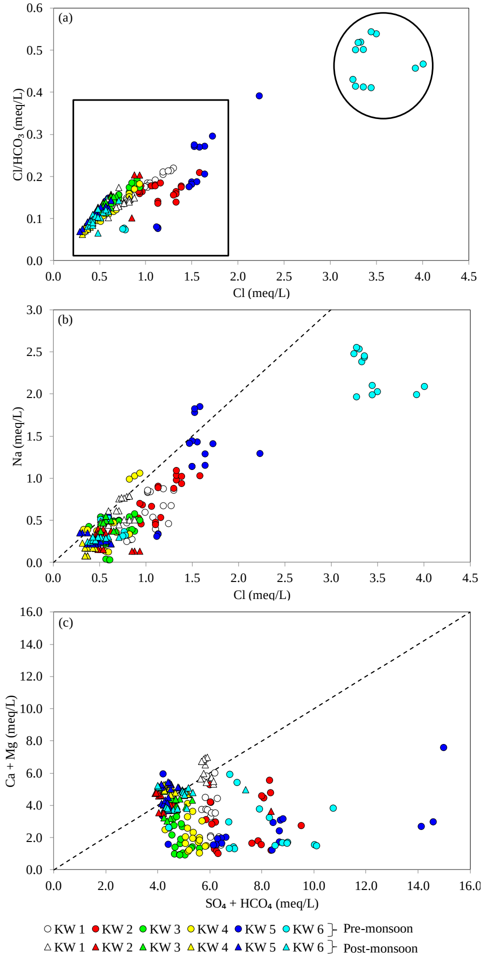

Figure 7. Ionic ratio of **(a)** Cl/HCO$_3$ vs. Cl **(b)** Na vs. Cl and **(c)** Ca + Mg vs. HCO$_3$ + SO$_4$ for present groundwater data.

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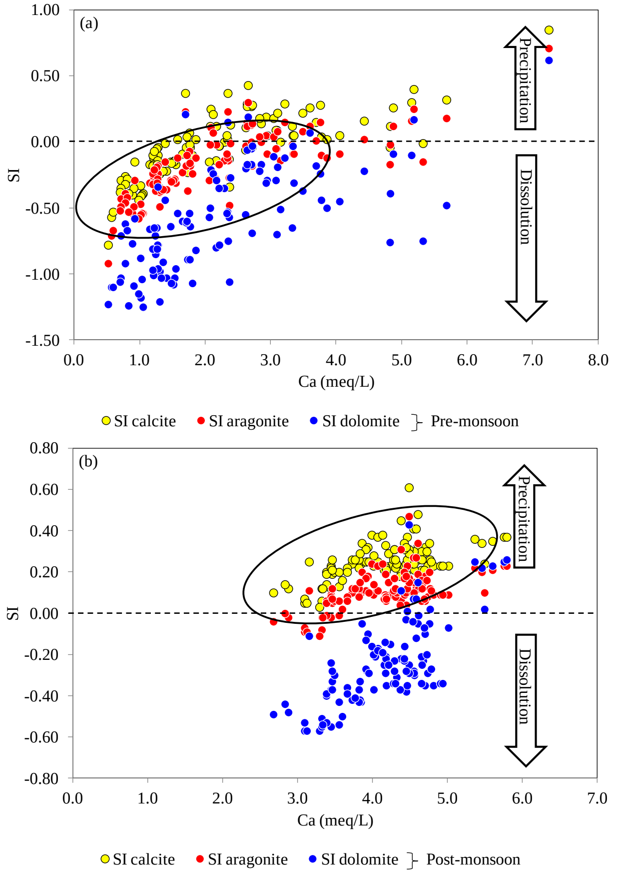

Figure 8. The saturation state of carbonate minerals (calcite, aragonite and dolomite). **(a)** demonstrates the saturation index for the pre-monsoon and insert **(b)** illustrates the saturation index for the post-monsoon. The SI value < 0 indicates the dissolution of carbonate minerals while > 0 indicates the precipitation of carbonate minerals.

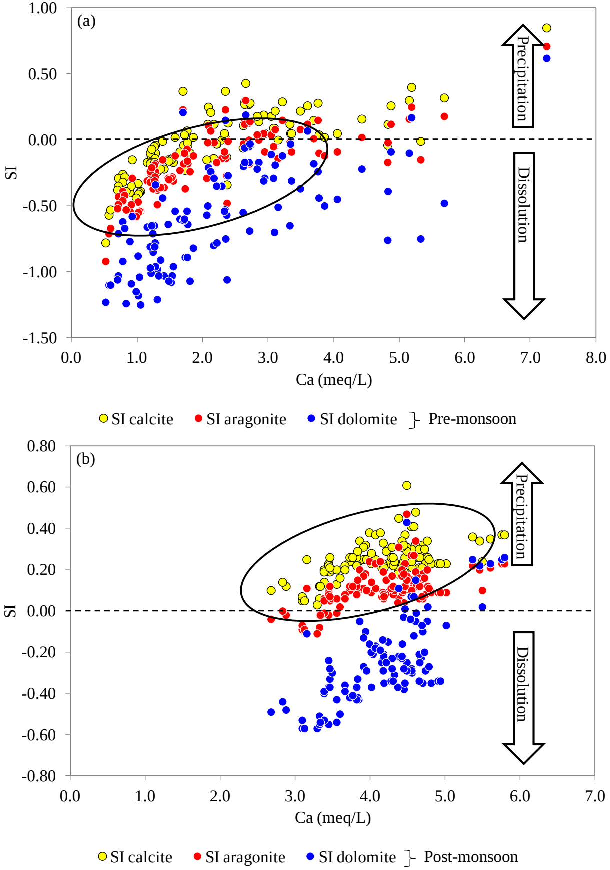

Figure 9. Scatter plot of molar ratio of **(a)** Na-normalized Ca vs. Mg and **(b)** Na-normalized Ca vs. HCO_3.

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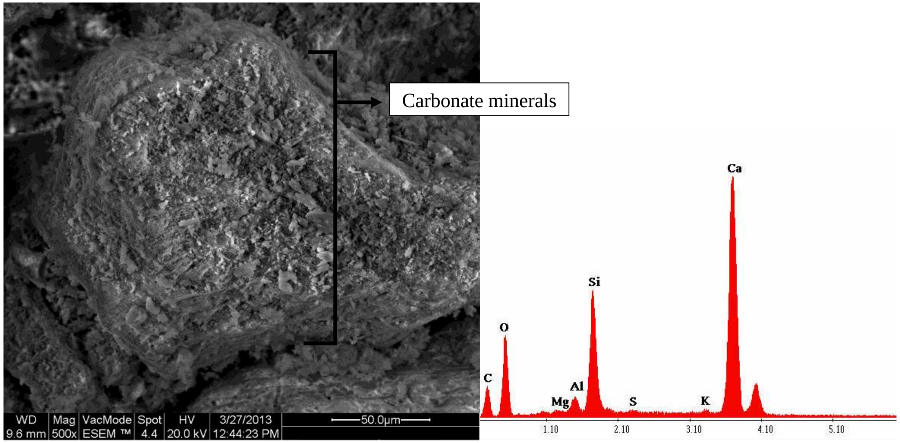

Figure 10. SEM-EDX image of sediment samples at Kapas Island.