Hydrol. Earth Syst. Sci. Discuss., 11, C4176–C4199, 2014
www.hydrol-earth-syst-sci-discuss.net/11/C4176/2014/

Hydrology and Earth System Sciences
Discussions

Interactive comment on "Comparison of monsoon variations over groundwater hydrochemistry changes in small Tropical Island and its repercussion on quality" *by* N. M. Isa et al.

N. M. Isa et al.

mi.noorain@gmail.com

Received and published: 2 October 2014

1a. The authors need to provide detailed information on the geology and hydrogeology of the site. On the Google Earth image of Kapas Island, the coastal outcrops are uniformly composed of subvertical thin-bedded strata striking north-south, probably interbedded Permo-Carboniferous sandstones and shales. There is no evidence of granite (despite the statement on p. 6417). In the relatively flat area containing the tourist resort and the bores sampled there is probably a thin surface aquifer composed at least partially of porous coral/shell sand and rubble; I presume that all the bores are screened in this material, which is apparently called the Kapas Conglomerate (p.6409).

1b. The authors need to provide the thickness, lithology and mineralogy of the surface aquifer, as well as its porosity and permeability. Figure 6 needs to be redrawn as a cross-section with a horizontal scale relative to the coastline, a vertical scale relative to sea level, the ground surface (in m asl) and the base of the surface aquifer. The likely position of the seawater/freshwater interface needs to be added.

Answer in text;

"Kapas Island has an unconformity structure, which separates the younger rock sequence of the Kapas Conglomerate above the older Permo-Carboniferous rock sequence below and it is intruded by dolerite dykes. The unconformity of this island is an important geological feature that can explain the geological history of these sequences (Shuib, 2003). The uplift that gives rise to this unconformity may be attributed to the granite emplacement found in the Eastern Belt in the Late Permian-Early Triassic time (Ali and Mohamed, 1997). Based on geologists' reports, Terengganu is dominated by meta-sediment rocks including granite. Permo-Carboniferous meta-sediment rock basically represents sandstone, mudstone, shale and silt while the conglomerate groups are signified as sandstone and mudstone (Ali et. al., 2001). These rocks have several age groups based on the similarity of other meta-sediment rocks found across the Terengganu area - Carboniferous age fossils and Permian plant fossils, where it can be concluded as the Permo-Carboniferous age. Geologies have reported several ages for the Kapas Conglomerate as it has been correlated to the Jurassic-Cretaceous Group (Rishworth, 1974) and Trembling Formation (Koopmans, 1968). Recently, it was assigned to a Triassic-Jurassic age (Mohamad Barzani 1988) and also it correlated with the Late Permian (Leman et al., 1999) or it still originates from the Jurassic-Cretaceous age (Mohamed et al., 1999). As the conclusion, the Kapas Conglomerate could be the Late Permian to Triassic age. Fig. 4 shows the structural geology of Kapas Island while Fig. 5 illustrated the cross-section of the study area with the thickness and lithology of the aquifer. Tropical aquifers are usually composed of certain carbonate materials, in which calcium carbonate is the predominant mineral, especially in shallow groundwater formations (Explanation in SEM-EDX subsection). The compaction and cementation processes of this mineral might act on the deposition as they tend to lithify. Table 1 explains other hydrological properties based on the previous and present studies done on Kapas Island."

1c. It is also necessary to provide some information on recharge to the surface aquifer. Apart from direct surface infiltration, there is likely to be runoff from the basement hills. Does this sink into the surface aquifer or flow across it, or both?

Answer in text;

"Runoff from the basement hills usually sinks directly underground, otherwise, it forms ephemeral rivers (Abdullah, 1981) that only exist in an exploitable form during heavy rain in the monsoon (North-East Monsoon).This has made Kapas Island depend entirely on groundwater resources for its freshwater supply."

1d. I presume that the tourist resort obtains its water from bores in the surface aquifer. In that case, there should be available data on bore yields; this should be added. The location of these bores needs to be shown on Fig. 2.

Answer in text:

"As for the insurance of this study, the bore yield of the resort nearby was reported as the location is stated in Fig. 2 (W1). The specific yield capacity is 47 m3/day/m. The physical properties of pH have been reported as being under a neutral condition with the average value of 7.2 while TDS and EC have an average of 274.6 mg/L and 616.3 mS/cm, respectively. The concentration of major ions are in order of Ca>Mg>Na>K and HCO3>Cl>SO4 representing the freshwater."

2. The authors attribute some of the chemical changes to cation exchange (e.g. of Na for Ca). However, the only minerals that they identify in the aquifer are carbonates and no significant cation exchange will occur on these minerals. For cation exchange to be an important process, there needs to be a substantial component of clay in the

surface aquifer. This could be derived from erosion of the basement aquifer (apparently thin-bedded shales and sandstones). The authors need to show this.

Answer in text;

"The high concentration of seawater elements of Na and Cl during pre-monsoon can be explained by the salinization process in the groundwater where it is also manifested by significant positive correlations with salinity ($r = 0.7, 0.7$; $p<0.01$). The increase in Na concentration could be due to the cation exchange of Na (residual from an inundation event/big wave that binds onto the aquifer matrix) with Ca2+ ion during the groundwater mixing process. The mechanism can be expressed in Eq. 2; where X represents the aquifer matrix (Solid phase particularly Silicate (Si) – since Si is dominant in Kapas Island after Ca as illustrated by SEM-EDX). It explains that Ca2+ ion replaced Na from the aquifer matrix and released Na+ in the groundwater. The existence of Si also can be seen in ionic ratio and saturation index subsection where certain ratios explain the Si weathering".

"The high concentration of seawater elements of Na and Cl during pre-monsoon can be explained by the salinization process in the groundwater where it is also manifested by significant positive correlations with salinity ($r = 0.7, 0.7$; $p<0.01$). The increase in Na concentration could be due to the cation exchange of Na (residual from an inundation event/big wave that binds onto the aquifer matrix) with Ca2+ ion during the groundwater mixing process. The mechanism can be expressed in Eq. 2; where X represents the aquifer matrix (Solid phase particularly Silicate (Si) – since Si is dominant in Kapas Island after Ca as illustrated by SEM-EDX). It explains that Ca2+ ion replaced Na from the aquifer matrix and released Na+ in the groundwater. The existence of Si also can be seen in ionic ratio and saturation index subsection where certain ratios explain the Si weathering."

"Fig. 12 illustrates the ionic ratio of (a) Na-normalized Ca vs. Mg and (b) Na-normalized Ca vs. HCO3 (Table 5) 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 increase 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."

3. The dominant carbonate minerals in the surface aquifer, if it contains coral/shell material, will be aragonite and calcite; dolomite is unlikely. Some of the calcite will be high-Mg calcite containing up to 4% Mg, so dissolution of this will release Mg into the groundwater (accounting for the correlation between Can and Mg). Dissolution of calcite and aragonite will release both Ca and HCO3: CaCO3 + H2CO3 = Ca2+ + 2HCO3- (this should replace reaction 5) Normally there would be a positive correlation between Ca and HCO3; the Kapas Island data apparently does not show this (Table 3). However, a standardised Schoeller plot shows that post-monsoon groundwater is enriched in both Ca and HCO3 relative to pre-monsoon groundwater; the enrichment in Ca is greater than expected just from calcite/aragonite dissolution, perhaps due to cation exchange.

Answer in text;

"The abundance of Ca and Mg concentration during post-monsoon has reported a positive correlation with r = 0.705 ($p<0.01$). Both of these mineral elements increase with the dissolution of calcite, aragonite and high-Mg minerals (CaMg(CO3)2) (Described in the saturation index sub-section). The elevation of mineral elements of Ca and Mg during post-monsoon was another important cation exchange process where it is assumed to take place by the reversible reaction of Eq. 2. Due to the wide contact of new groundwater (recharge by rainfall) with the carbonate aquifer matrix, the groundwater experiences water-rock interactions and carbonate dissolution (Eq. 3). The increase of Ca and HCO3 in Eq. 3 was justified by the correlation formed between these two elements with r = 0.278 ($p<0.01$; post-monsoon). As rainfall (recharge) continues to be observed during monsoon interchanges, seawater elements as well as domestic pol-

lutants can be removed by widening the aquifer storage, furthering the distance of the transition zone and increasing the groundwater table level where the average elevation is 1.21 m."

4. The authors collected samples in triplicate; this is to be applauded. However, when they plot the data, they should use only the median of each set of triplicates, i.e. 72 points not 216. They also need to present a table with this median data; this should replace Table 2. Charge balances need to be provided for all analyses in the table.

Answer in text;

"The sampling design for this study was based on spatial and temporal scales. A total of 216 groundwater samples with replicates were collected bimonthly/semi-monthly (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 (Aug 2010 – Oct 2010) and post-monsoon (Feb 2011 – April 2011). The calculation of 216 groundwater samples works as follows; 6 monitoring boreholes times with triplicate times with 6 sampling campaigns and times 2 seasons; 108 groundwater samples of each monsoon. It has to be clear that the triplicate times here represent the groundwater samples were taken in three different sample bottles rather than divided into three sections from a single bottle. The discussion of this paper is based on monsoons rather than each monitoring borehole since the objective is to focus on the monsoon changes."

"Besides using the charge balance, the accuracy of the analysis was employed by the measured TDS to calculate the TDS ratio, with the accepted ratio of the measured and the calculated TDS value being 1.0< measured TDS/calculated TDS< 1.2. Based on these criteria, all the groundwater samples were found to be within the ratio of 1.0 to 1.2. The excellent agreement between calculated and measured TDS means that the data collected were internally consistent and correct."

5. The Schoeller plot (Fig. 4) is the single most useful diagram. A second Schoeller plot, with the line for seawater plotted, and all three lines standardised to seawater Cl

(this automatically removes the effect of evapotranspiration), should also be added. If the rainfall composition is available, it should be plotted. This will immediately make obvious which elements have been removed/added.

Answer in text;

"The Schoeller diagram in Fig. 6 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. Based on major ion concentration in seawater, the groundwater samples in both monsoons are recognized as freshwater. However, there is a significant difference ($p<0.01$) between seasons and major ions concentration which indicates that the monsoon changes are affecting the groundwater composition. 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)."

6. Some of the KW6 pre-monsoon samples show a seawater influence, as the authors point out. This implies that the seawater/freshwater mixing zone extends 30 m inland at a depth of only 2 m (this should be shown on the redrawn cross-section). Interestingly, not all the KW6 pre-monsoon samples show this influence. This could be a tidal effect; the authors should investigate this.

Answer in text;

"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 the pre-monsoon and Ca during the post-monsoon season (Table 5). The scatter plot of the Cl/HCO3 ratio vs. Cl (Fig. 9a) 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 a slight interference of seawater, either the interference from the transition zone since KW 6 is approaching towards this particular zone or it could be tidal

effects. This can be proven as the Cl concentration correlates well with the seawater component; Na ($r = 0.907$; $p<0.01$). 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 due to the heavy rainfall. Fig.10 describes the interference of the approaching transition zone during pre-monsoon (1) and the widened aquifer during post-monsoon due to recharge by rainfall (2)."

7. The molar Na/Cl ratio for the KW6 pre-monsoon samples is 0.63; for seawater it is 0.86. This indicates a loss of Na, which could be due to cation exchange.

Answer in text;

"The plot of Na vs. Cl (Fig. 9b) indicates different mechanisms in the groundwater. The halite (residual 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 the silicate weathering. In the present study, the ratios of Na vs. Cl are generally < 1, which explain that the cation exchange is the dominant process in the groundwater (Kumar et al., 2006; Lipfert et al., 2006)."

8. The Cl content of the groundwater (in samples not affected by seawater) ranges from 10-56 mg/L, i.e. greater than the likely Cl content of rainfall. This indicates the influence of evapotranspiration; given the high humidity (80%), transpiration is likely to be more effective than evaporation.

The reviewer said that Cl contents were influence more by transpiration since the study area has high humidity. We agree to that suggestion but evaporation process may contribute to the Cl contents even though in the small amount. In our case, it is suitable to state the evapotranspiration rather than to separate the processes.

Answer in text;

"According to Gaye (2001) and Rosenthal (1988), other factors affecting groundwater salinization include the inflows of saline water during heavy withdrawals of fresh groundwater. Groundwater salinization also results from the dissolution of salt (residual salt from the evapotranspiration process during the wave over-wash event) 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 the precipitation from airborne salts, soil and surface area. Furthermore, the salinization of the groundwater might change the normal groundwater constituents and the suitability for drinking purposes and domestic use."

9. If pollution from sewage is suspected (p. 6415-6416), then NO3 analyses are needed. Interestingly, Table 2 shows that most groundwater samples have low DO and Eh values; either there is a high content of organic material in the aquifer, or this could reflect sewage input. The authors need to explore this.

Since present study is to focus on the hydrogeochemistry of monsoon changes, the anthropogenic impacts were excluded along with the statement of sewage influents. The hydrochemical composition of groundwater is controlled by many factors that include the mineralogy of the aquifer, climate variability and topography. These factors can combine to create diverse water types that change in groundwater composition spatially and temporally as the present study did.

Answer in text;

"The results are presented in Table 3. For pre-monsoon, the average temperature and DO values are 30.43°C and 2.97mg/L, respectively." "Data for post-monsoon show the average temperature and DO are 29.34 °C and 3.85 mg/L, respectively."

"The DO concentration is relatively low during pre-monsoon because the groundwater is in a closed system. Therefore, the increased DO during post-monsoon is due to the heavy rainfall which carried the O2 together into the aquifer."

"pH explains the acidity/basicity of water where both monsoons were under neutral condition while Eh refers to the redox-potential process. The detection of sulfide odors

in certain groundwater samples has revealed the existence of hydrogen sulfide (H2S) where at the same time, experiencing the unpleasant odors of H2S during the sampling campaign, one which is described as the most likely product from the sulfide reduction process."

10. Post-monsoon groundwater is more dilute than pre-monsoon groundwater and has a much less variable composition (Fig. 5). After the average compositions are standardised to Cl, pre- and post-monsoon groundwater have similar levels of K and Na, but the post-monsoon groundwater has higher levels of Ca, Mg and HCO3 (due to calcite/aragonite dissolution). Therefore the effect of rainfall infiltration during the monsoon is to dilute the groundwater (as expected), but also to cause more calcite/ aragonite dissolution. This is surprising, and the authors need to investigate the cause. Perhaps groundwater sitting in the surface aquifer since the last monsoon, with more time to dissolve the carbonate minerals, is flushed out by input during the subsequent monsoon.

Groundwater during pre-monsoon is under dissolution process (SI < 0). As the heavy rainfall during post-monsoon recharges the groundwater aquifer, the dissolution process continued until the equilibrium state was reached where the dissolution and precipitation process are equal (SI = 0). After the equilibrium state was reached, the groundwater was saturated with the Ca as the recharges continued. The results can be seen from Fig. 11b where calcite and aragonite were in super saturated condition (SI > 0).

Answer in text; "Fig. 11a shows that 76 % of the groundwater samples were under the dissolution process (SI < 0) for the minerals calcite (CaCO3), aragonite (CaCO3) and high-Mg mineral (CaMg(CO3)2) during the pre-monsoon. This study shows that Ca has increased due to the dissolution reaction, as demonstrated in Fig. 7 and Eq. 3. 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 high-Mg mineral (r = 0.662, p<0.01). The previous discussion of the correlation between Ca and Mg

(CaMg(CO3)2) is explained by Eq. 4 in which Mg correlated with high-Mg mineral (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."

"Fig. 11b demonstrates the saturation state of minerals during post-monsoon. Only 30 % of the total SI values are < 0 and most are CaMg(CO3)2 minerals. The dissolution of calcite/aragonite from the pre-monsoon gradually increases to the equilibrium state and moving towards a super saturated condition (during post-monsoon) as the groundwater continuously reacts with the aquifer. The targeted minerals which are calcite and aragonite were under precipitation condition since the groundwater aquifer is super saturated with Ca."

11. Fig 9 is missing; Fig 8 is duplicated.

Figure 9 has been restored as Figure 12

12. Much of the material on pages 6413 and 6414 could be deleted.

It has been deleted has suggested

13. There are many small grammatical errors; if the authors could prevail on a native-English-speaking colleague to check the English expression, this would improve the paper

This manuscript has made amendments about the grammatical errors by English-speaking colleagues and English editing service

Please also note the supplement to this comment:
http://www.hydrol-earth-syst-sci-discuss.net/11/C4176/2014/hessd-11-C4176-2014-supplement.pdf

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 6405, 2014.

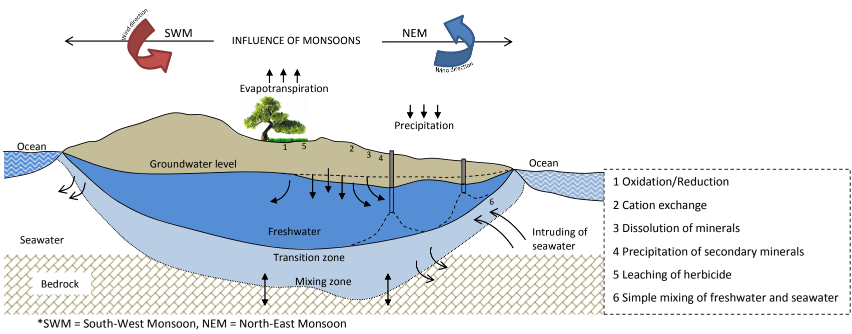

Fig. 1. The complex geochemical model of groundwater in small islands (Modified from Isa et al., 2013)

1

Fig. 1. The complex geochemical model of groundwater in small islands (Modified from Isa et al., 2013)

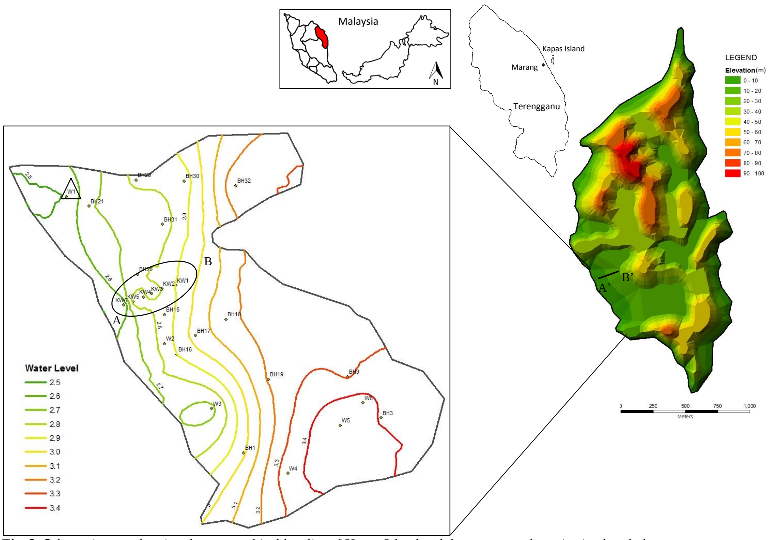

Fig. 2. Schematic map showing the geographical locality of Kapas Island and the constructed monitoring boreholes

1

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

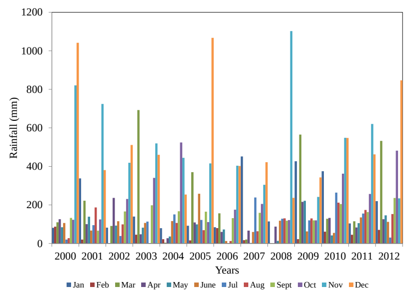

Fig. 3. Distribution of annual rainfall at Marang, Terengganu (2000-2012)

1

Fig. 3. Distribution of annual rainfall at Marang, Terengganu (2000-2012)

Fig. 4. Structural geology of Kapas Island (Modified from Shuib, 2003)

1

Fig. 4. Structural geology of Kapas Island (Modified from Shuib, 2003)

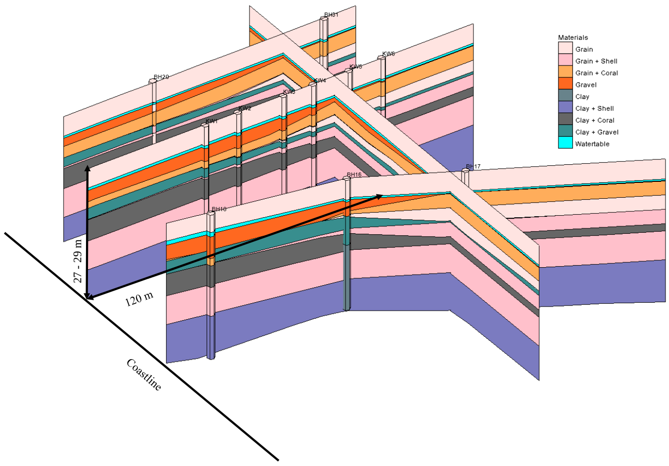

Fig. 5. The cross-section of study location in Kapas Island (KW 1, KW 2, KW 3, KW 4, KW 5 and KW 6). Other boreholes were abandoned (BH10, BH16, BH17, BH20 and BH31). The max aquifer thickness is the calcualtion of Ghyben-Herzberg equation and resistivity report from Kura et al. 2014

1

Fig. 5. The cross-section of study location in Kapas Island (KW 1, KW 2, KW 3, KW 4, KW 5 and KW 6). Other boreholes were abandoned (BH10, BH16, BH17, BH20 and BH31)

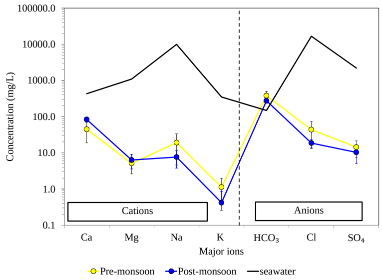

Fig. 6. Schoeller diagram of the concentration of major ions for the two different monsoon seasons (n = 216)

Fig. 6. Schoeller diagram of the concentration of major ions for the two different monsoon seasons (n = 216)

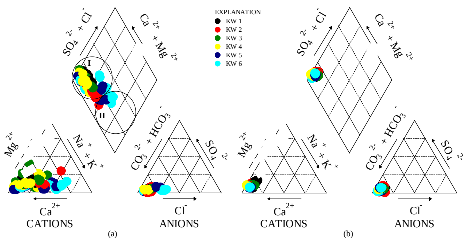

Fig. 7. Schematic Piper diagram. Insert (a) shows the water type for the pre-monsoon; Ca-HCO_3 water type (Circle I) and Na-HCO_3 water type (Circle II), while, insert (b) shows that the water type for the post-monsoon is Ca-HCO_3 water type

Fig. 7. Schematic Piper diagram

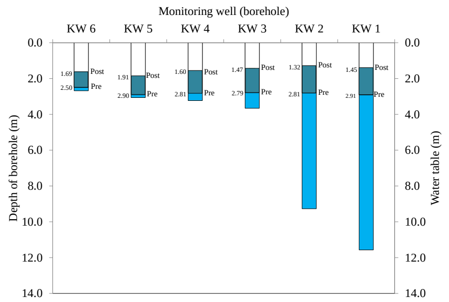

Fig. 8. Illustration of average groundwater table during pre-monsoon (pre) and post-monsoon (post)

1

Fig. 8. Illustration of average groundwater table during pre-monsoon (pre) and post-monsoon (post)

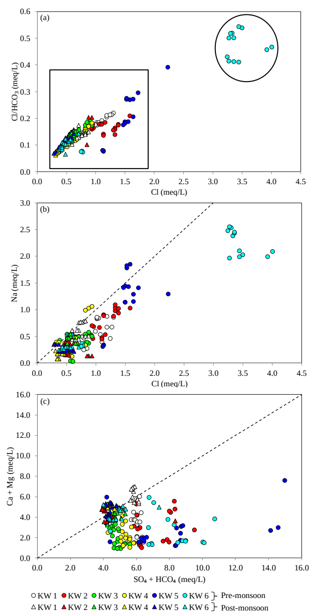

Fig. 9. Ionic ratio of (a) Cl/HCO_3 vs. Cl (b) Na vs. Cl and (c) Ca+Mg vs. HCO_3+SO_4 for present groundwater data

1

Fig. 9. Ionic ratio of (a) Cl/HCO3 vs. Cl (b) Na vs. Cl and (c) Ca+Mg vs. HCO3+SO4 for present groundwater data

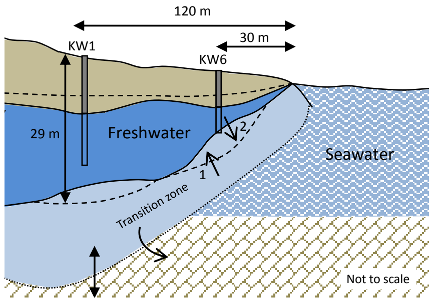

Fig. 10. The cross-section of KW 6 during the monsoon interchanges. Over the groundwater extraction during pre-monsoon, were narrowed the freshwater lens (1). Meanwhile, the opposite event reveals the widening of the aquifer storage during post-monsoon (2)

1

Fig. 10. The cross-section of KW 6 during the monsoon interchanges

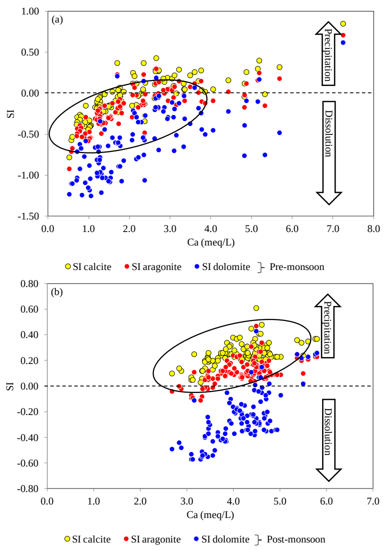

Fig. 11. The saturation state of carbonate minerals (calcite, aragonite and high-Mg mineral). Insert (a) demonstrates the saturation index for the pre-monsoon and insert (b) illustrates the saturation index for the post-monsoon. The SI value <0 indicates the dissolution of carbonate minerals while >0 indicates the precipitation of carbonate minerals

1

Fig. 11. The saturation state of carbonate minerals (calcite, aragonite and high-Mg mineral)

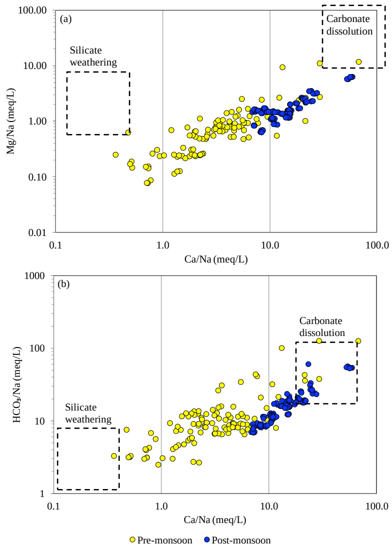

Fig. 12. The scatter plot of the molar ratio of (a) Na-normalized Ca vs. Mg and (b) Na-normalized Ca vs. HCO_3

1

Fig. 12. The scatter plot of the molar ratio of (a) Na-normalized Ca vs. Mg and (b) Na-normalized Ca vs. HCO3

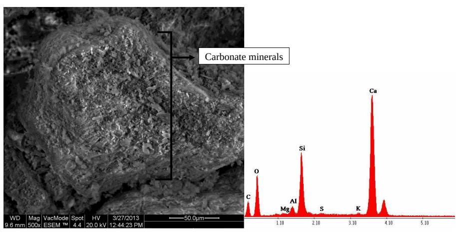

Fig. 13. The SEM-EDX image of sediment samples at Kapas Island

1

Fig. 13. The SEM-EDX image of sediment samples at Kapas Island