HYDROGEOCHEMICAL STUDY AND IRON REMOVAL OF GROUNDWATER IN NORTH KELANTAN

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FACULTY OF SCIENCE
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2. Name : 1st National Conference On Natural Resources (NCNR2010)
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   Title : Hydrogeochemical Study of North Kelantan Aquifer

4. Name : The 6th Mathematicals and Physical Science Graduate Congress 2010 (MPSGC2010)
   Date : 13th – 15th December 2010
   Place : Faculty of Science, University of Malaya, Kuala Lumpur
   Title :
   1. Selected Ion Analysis of North Kelantan Aquifer
   2. Study of the Effectiveness of Ionic Liquid as a Solvent Medium for Iron Removal in Groundwater

ABSTRACT

The hydrogeochemical study and iron removal of groundwater was carried out in North Kelantan Basin. This low-lying area is covered by alluvium deposits of Quaternary age. The thickness of the alluvium may reach up to 200 m to the coast. Patches of granite hills appear in the southeast part known as Bukit Marak and Bukit Kechik that belong to Boundary Range Granite. Granite and metamorphic rock are encountered as bedrocks. Kelantan River is the main drainage of the basin with 248 km long and covers an area of approximately 11900 km^2. Hydrology study determined the baseflow index (BFI) of the basin as 0.54. This value is influenced by diverse geological, morphological and climatological aspects of the basin. Interaction between surface water and groundwater was found in the lower part of the basin while surface runoff dominanted the process in the upper part of the basin. The total precipitation received in the basin was 30.95 x 10^9 m^3/year. Water loss via potential evapotranspiration was about 40% with 50% of runoff coefficient. Based on water balance study, recharge to the aquifer was estimated about 11% from the total precipitation received. The thick sequences of alluvium deposits form an aquifer system in North Kelantan. Three layers of aquifer were identified; Layers 1, 2 and 3 with depth interval of 20 m, 20 – 50 m and more than 50 m, respectively. These layers are separated by semi permeable clay layer. Layer 1 is known as a remarkable source of public water supply in the study area as groundwater has been exploited since 1935. Hydrochemical facies reveal that the $NaHCO_3$ and NaCl facies are prevalent in the aquifer system. The evolution of groundwater is chemically governed by the process of weathering, dissolution, ion exchange and precipitation. Geochemical modeling indicates that the ferromagnesian minerals of hematite and goethite precipitate while pyrite undergones dissolution leading to an increase of iron in groundwater. The groundwater is naturally rich with iron and exceeds the WHO (2008) acceptable limit for drinking water. Presently, conventional groundwater treatment is being used to treat the groundwater for public, agricultural and industrial purposes. Ionic liquid as a medium in liquid-liquid extraction with 1,10-phenanthroline as a chelating agent was studied as an alternative method for iron removal. Successful removal of iron was achieved with more than 95% removal from the initial concentration of groundwater samples. However, more detailed research is needed before the ionic liquid is able to replace the conventional groundwater treatment as it gives a very low recovery about 25% - 60% when reused. Furthermore, due to the ion exchange process the appearance of anion of ionic liquid also has been detected in groundwater samples.

ABSTRAK

Kajian hidrogeokimia dan pengeluaran besi dari air tanah telah dijalankan di Lembangan Utara Kelantan. Dataran lanar ini diluputi oleh enapan alluvium yang berusia Kuaterner. Ketebalan enapan alluvium dianggarkan boleh mencapai sehingga 200 m ke arah laut. Tompokan granit ditemui di bahagian timur laut kawasan kajian yang dikenali sebagai Bukit Marak and Bukit Kechik yang dikatakan berasal dari ‘Boundary Range Granite’. Lembangan ini disaliri oleh Sungai Kelantan dengan 248 km panjang yang meliputi kawasan seluas 11900 km^2. Kajian hidrologi menunjukkan bahawa indeks aliran dasar (BFI) bagi lembangan ialah 0.54. Nilai ini telah dipengaruhi oleh factor geologi, morfologi dan cuaca di lembangan. Hubungan di antara air sungai – air bawah tanah hanya berlaku di bahagian bawah lembangan manakala air larian mendominasi proses di bahagian atas lembangan. Jumlah hujan yang diterima di lembangan ialah 30.95 x 10^9 m^3/setahun. Kehilangan air melalui potensi evapotranspirasi ialah 40% dengan 50% pekali air larian. Nilai imbuhan air tanah berdasarkan kajian keseimbangan air ialah 11% dari jumlah hujan yang diterima. Jujukan tebal enapan alluvium ini membentuk sistem akuifer di Utara Kelantan. Tiga lapisan akuifer telah dikenalpasti; Lapisan 1, 2 dan 3 dengan kedalaman meghampiri 20 m, 20 m ke 50 m dan lebih 50 m. Lapisan ini telah dipisahkan oleh lapisan lempung separa telap. Lapisan 1 merupakan sumber utama bekalan air di kawasan kajian yang telah dieksploitasi semenjak tahun 1935. Fasies hidrokimia yang utama dalam akuifer sistem ialah $NaHCO_3$ dan NaCl. Evolusi air tanah secara kimia dipengaruhi oleh luluhawa, perlarutan, pertukaran ion dan pengenapan. Model geokimia menunjukkan mineral ferromagnesia seperti hematite dan goethite terenap manakala pirit mengalami pelarutan yang meningkatkan kandungan lagi besi dalam air tanah. Kandungan besi yang wujud secara semulajadi sangat tinggi dalan air tanah dan melebihi piawaian air

minuman WHO (2008). Sehingga kini, kaedah perawatan air secara tradisional telah digunakan bagi merawat air tanah untuk kegunaan awam, pertanian dan industri. Cecair ionik 1-butyl-3 methylimidazoliumbis(trifluoromethanesulfonyl)imide [C_4mim][NTf_2] sebagai medium dalam pengekstrakan cecair-cecair dengan 1,10-phenanthroline sebagai agen pengkelatan. Besi telah berjaya dikeluarkan lebih 95% daripada jumlah kepekatan awal sampel air tanah. Walau bagaimanapun, kajian yang lebih terperinci perlu dilakukan sebelum cecair ionik ini boleh dikitar semula dan dapat menggantikan kaedah perawatan air secara tradisional di mana jumlah kebolehdapatan semula yang rendah antara 25% - 60% selepas dikitar semula. Tambahan pula, proses penukaran ion yang berlaku telah menyebabkan hadirnya anion cecair ionic dalam sampel air tanah.

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With Love,
~♥nhh 2011♥~

DEDICATION

Dedicated to

My Beloved Dad and Mom

(Mr. Hussin Ahmad and Mrs. Ramlah Jopree)

also

My Beloved Siblings

(Ms. Nur Haniza, Mr. Mohd Hairi, Ms. Nur Azimah and Mr. Mohd Hafidz)

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LIST OF ABBREVIATIONS AND SYMBOLS

%	-	percent
AKSB	-	Air Kelantan Sdn. Bhd.
APHA	-	American Public Health Association
CDC	-	Centers for Disease Control
DID	-	Department of Irrigation and Drainage
DOA	-	Department of Agriculture
EC	-	Electrical Conductivity
GHM	-	German Hydrological Mission
GSD	-	Geological Survey Department
ICP-OES	-	Inductively Coupled Plasma Optical Emission Spectrometer
ILs	-	Ionic liquids
INWQS	-	Interim National Water Quality Standard
mg/L	-	Milligram per liter
MGD	-	Mineral and Geosciences Department
MLD	-	Million liter per day
MMD	-	Malaysian Meteorology Department
MOH	-	Ministry of Health
RTILs	-	Room Temperature Ionic Liquids
SAR	-	Sodium Adsorption Ratio
TDS	-	Total Dissolved Solids
WHO	-	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This research study is titled "**Hydrogeochemical Study and Iron Removal of Groundwater in North Kelantan.** The utilization of groundwater in Kota Bharu started way back since 1935 (SMHB, 2000). Groundwater contributes about 90% of the total demand for drinking water in Kelantan (Suratman, 1997). The demand for groundwater increased 2.5% per year and for the year 2010 the production demand for the whole state was estimated at 165 MLD, (Suratman, 2010). In general, groundwater in North Kelantan area is abstracted from the shallow, first aquifer layer, with the exception of Tanjung Mas area and some areas in Pintu Geng water works.

The presence of iron has been noticed in Kelantan groundwater since initial investigation of groundwater resources by the Geological Survey Department (GSD) currently known as Mineral and Geosciences Department (MGD) in collaboration with the German Hydrogeological Mission (GHM) 1971 – 1975. Investigations showed that the iron concentration was above the potable limit of 0.30 mg/L. Continuous groundwater monitoring by MGD from 1989 until 1995 also recorded high iron concentration (Ang & Loh, 1996). Therefore, iron is a major problem in Kelantan groundwater. The said iron is suspected to be originating from the deposited sediment in the Kelantan delta. However a detailed study has not been carried out to confirm the statement.

High concentration of dissolved iron, Fe(II) is by far the most common problem in associated with groundwater potability (Chapelle, 2001). The World Health Organization (WHO) has set guideline values for iron in drinking water at 0.30 mg/L. Higher concentration would cause aesthetic considerations such as metallic taste, odor, turbidity, staining of laundry and plumbing fixtures (Dutta *et al.*, 2007). In human body, the normal iron content is three to four grams. Chronic iron overload, a genetic disorder (*haemochromatosis*) is possible if the amount of iron concentration exceeds the normal level (medicinenet.com). For agriculture, high iron content in soils will turn the agriculture land into a nonproductive area (Awadalla & Noor, 1990).

Air Kelantan Sdn. Bhd. is responsible in handling the full cycle of a drinking water supply system from sourcing, treatment and distribution of treated water to consumer right up to billing and collection. For the whole state of Kelantan there are 27 waterworks, which intake comes from surface water and groundwater (Table 1.1). In total, for North Kelantan areas, there are 6 waterworks intake from groundwater that contributes for the water supply (Figure 1.1). Presently, the groundwater is treated using conventional treatment method, (detailed in Chapter 4). The conventional process works fairly well for a total concentration of iron total below 5.00 mg/L and in the absence of dissolved organic matter (Ellis *et al.*, 2000). The problem with the conventional treatment is the precipitation of iron as ferric ion after the treatment process. Only 32% forms soluble iron. Thus, Air Kelantan only controls the level of total iron concentration to meet the standard guideline for drinking water. In order to find an alternative treatment method, room temperature ionic liquid (RTILs) was used as a medium in liquid – liquid extraction to remove iron in groundwater. RTILs have been studied over a decade as green solvent for the future due to their physicochemical characteristics.

Table 1.1: List of Waterworks in Kelantan

District	Waterworks	Capacity (MLD)	Intake	Longitude	Latitude
Tumpat	Wakaf Baru	19	Groundwater	102°12’ 17.93”E	6°07’ 15.57”N
Kota Bharu	Kg. Puteh	28	Groundwater	102°14’ 30.23”E	6°05’ 47.85”N
	Tanjung Mas	10	Groundwater	102°15’ 55.71”E	6°08’ 18.49”N
	Chicha	80	Groundwater	102°17’ 03.71”E	6°04’ 42.42”N
	Pintu Geng	9	Groundwater	102°14’ 06.55”E	6°05’ 51.11”N
Bachok	Kg. Chap	4.9	Groundwater	102°20’ 40”E	5°02’ 30”N
Pasir Mas	Kelar	64	Kelantan River	102°09’ 23.87”E	6°01’ 10.68”N
Tanah Merah	Batu Gajah	2.3	Jedok River	-	-
	Bendang Nyior	1.7	Jegor River	-	-
	Bukit Remah	28	Kelantan River	102°09’112.26”E	5°48’ 11.18”N
	Kemahang	3.38	Muring River	-	-
	Kuala Tiga	1.13	Kelantan River	-	-
Machang	Merbau Chondong	40	Kelantan River	102°14’ 41.80”E	5°52’ 40.45”N
Pasir Puteh	Wakaf Bunut	9	Rasan River	-	-
Jeli	Air Lanas	2.6	Lanas River	-	-
	Jeli	4	Pergau River	-	-
	Kuala Balah	2.3	Terang River	-	-
Kuala Krai	Kg. Tualang	8.69	Kelantan River	102°11’ 34.06”E	5°31’ 18.90”N
	Pahi	16	Lebir River	102°13’ 18.57”E	5°29’ 14.95”N
	Manik Urai	7	Lebir River	102°14’ 18.43”E	5°22’ 46.95”N
	Dabong/Stong	3.77	Stong River	-	-
Gua Musang	Bertam Baru	0.5	Galas River	-	-
	Limau Kasturi	1.2	Galas River	-	-
	Aring	1.8	Aring River	-	-
	Chiku	6	Chiku River	-	-
	Sg. Ketil	13	Ketil River	-	-
	Panggung Lalat	0.7	Betis River	-	-

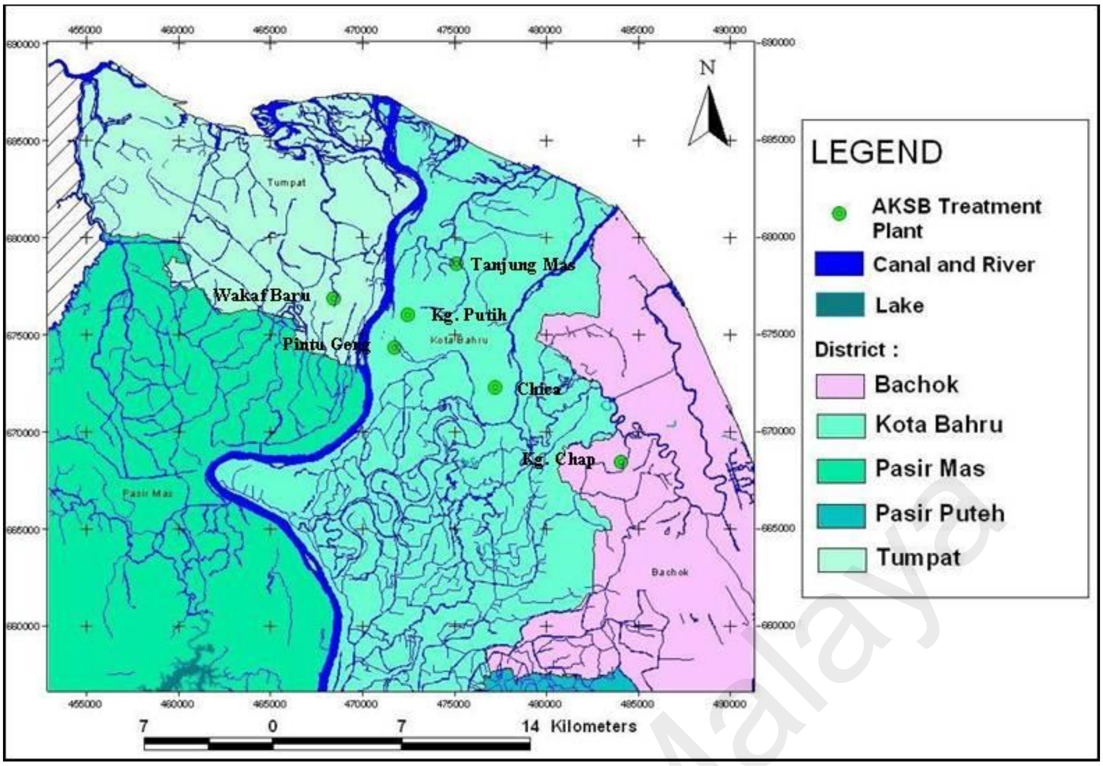


Figure 1.1: Waterworks Location in North Kelantan

1.2 OBJECTIVES

The aims of the study are:

i. To map the heavy metals concentration in each aquifer layers

ii. To study the hydrogeochemistry and evolution of the groundwater system

iii. To assess the suitability of ionic liquids based treatment method for Kelantan groundwater resources

1.3 STUDY AREA

The study area lies between longitude 102.05°E until 102.40°E and latitudes 6°N until 6.25°N (Figure 1.2). It is located at the northern part of the Kelantan state known as North Kelantan River Basin. The basin is bounded by the South China Sea in the north and east, while to the west is bounded by Thailand. Hulu Kelantan at the south marks the border of Kelantan State from Pahang State, Perak State at the south-west, while at the south-east it borders with Terengganu State.

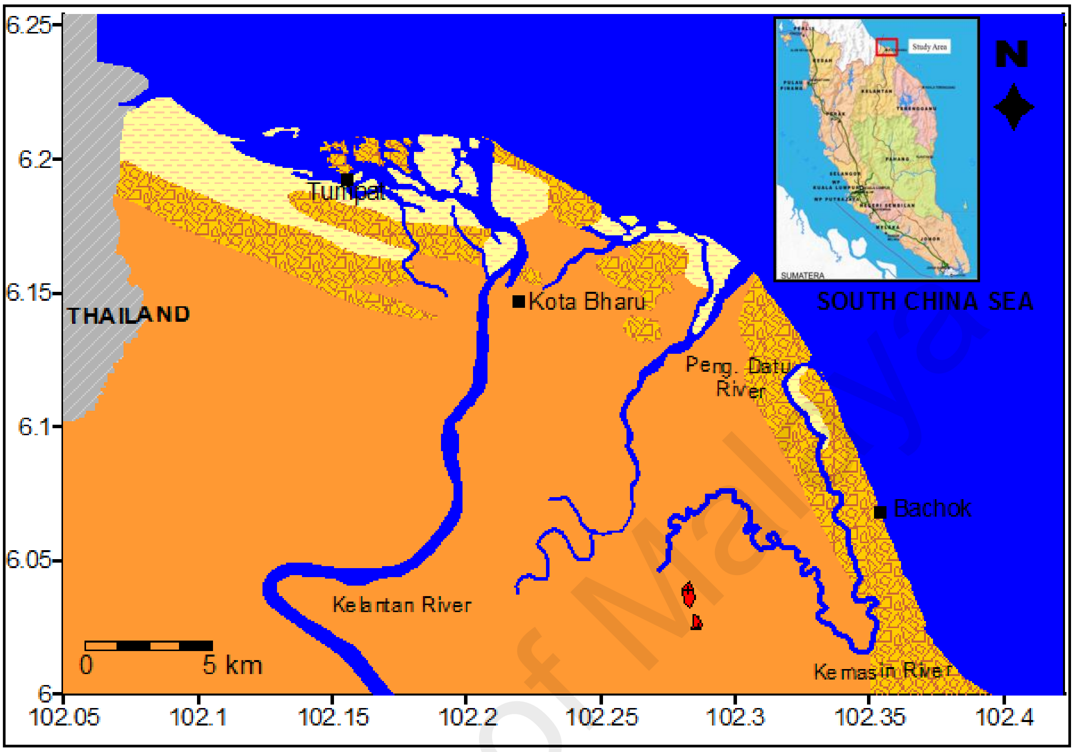


Figure 1.2: Location of the Study Area

1.4 GEOMORPHOLOGY

1.4.1 Topography

In general, the topographic features of Kelantan can be seen in Figure 1.3. This Digital Terrain Model (Ng, 2008) has been differentiated into 5 units based on mean elevation as noted in Table 1.2. Overall, the topographic features of North Kelantan is low lying unit with mean elevation less than 15 m as marked by pink rectangles in Figure 1.3. These low-lying areas represent depositional terrain and overlying unconsolidated alluvial, coastal and marine sediments of variable thickness. While the mountainous terrain mean elevation is more than 301 m. These mountains exist in the southeast part as granite intrusion (MacDonalad, 1967) known as Bukit Marak and Bukit Kechik with elevation of 373 m and 307 m.

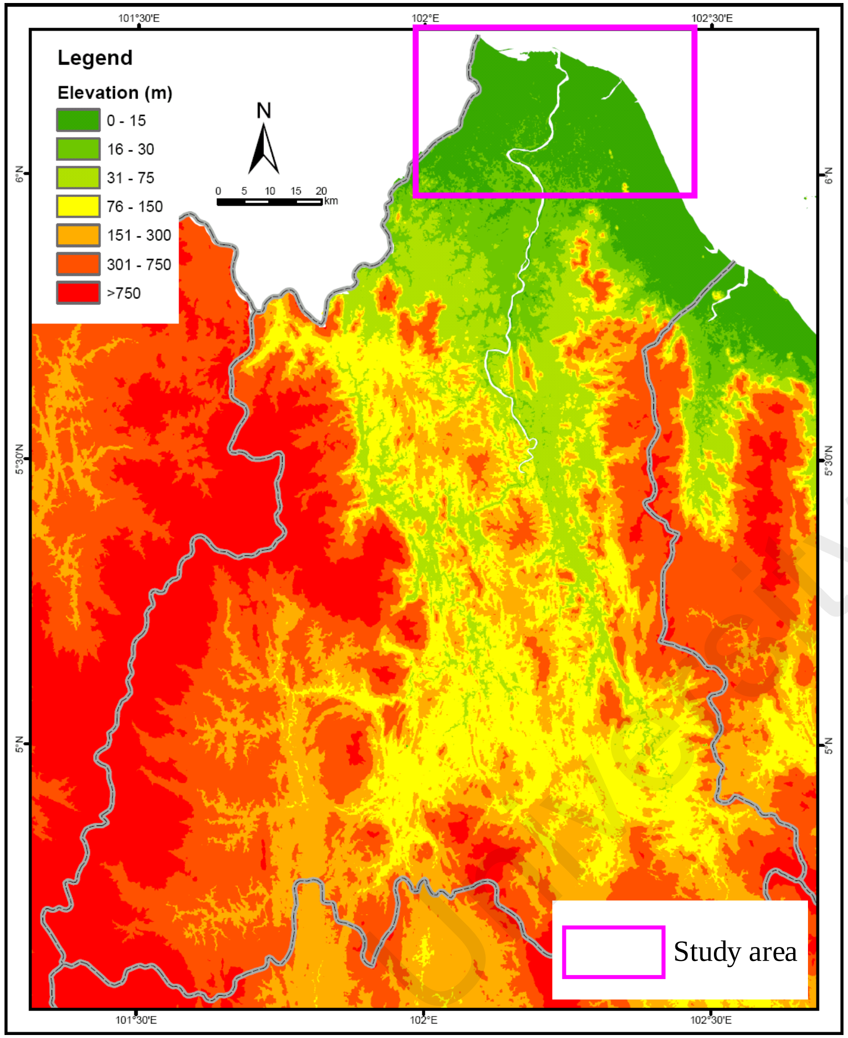


Figure 1.3: Digital Terrain Model of Kelantan Showing Mean

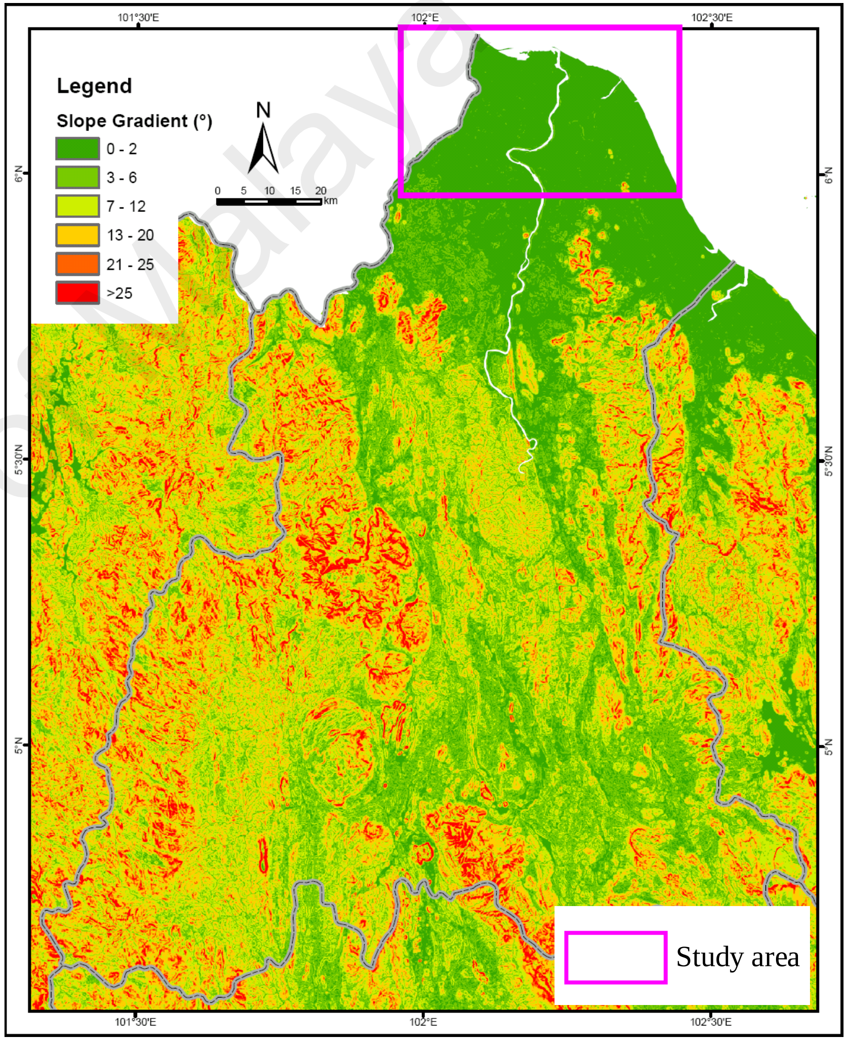


Figure 1.4: Digital Ground Slope Model of Kelantan

Table 1.2: Topographic Units according to Mean Elevations

	Topographic Unit	Mean Elevation (m above sea level)
1	Low lying	<15
2	Rolling	16-30
3	Undulating	31-75
4	Hilly	76-300
5	Mountainous	>301

Table 1.3: Slope and Terrain Classes (Leamy & Panton, 1960)

	Slope Angle	Terrain Class
1	0-2°	Level or nearly level
2	2-6°	Undulating
3	6-12°	Rolling
4	12-20°	Hilly
5	20-25°	Steep
6	>25°	Very Steep

A detailed view of the topographic features can be seen using Digital Ground Slope Model (Ng, 2008). The slope has been classed into six slope angles based on the Soil Survey Division of the Malaysia Ministry of Agriculture as noted in Table 1.3. The low lying area of North Kelantan is marked by pink rectangles (Figure 1.4) and is classed as level or nearly level terrain with very gentle ground slopes less than 2°.

1.4.2 Climate

The study area is situated in the East Coast of Peninsular Malaysia with a tropical rainforest climate. Two types of monsoon regime control the areas which influences the monthly and annual rainfall. The south west monsoon occurs from February till October with less rainfall thus hot and dry area. The north east monsoon occurs from November till March bringing heavy rainfall and contributing to high soil moisture. During this period, rainfalls are high in intensity and bring heavy storms over a large area of low lying coastal plain. Figure 1.5 shows the annual rainfall index of Kota Bharu measured at Sultan Ismail Petra Airport within year 1979 - 2008. The highest rain falls in 1999 with 3734.50 mm and the lowest rainfall in 1989 with 1540.50 mm. The mean annual rainfall is 2543.87 mm.

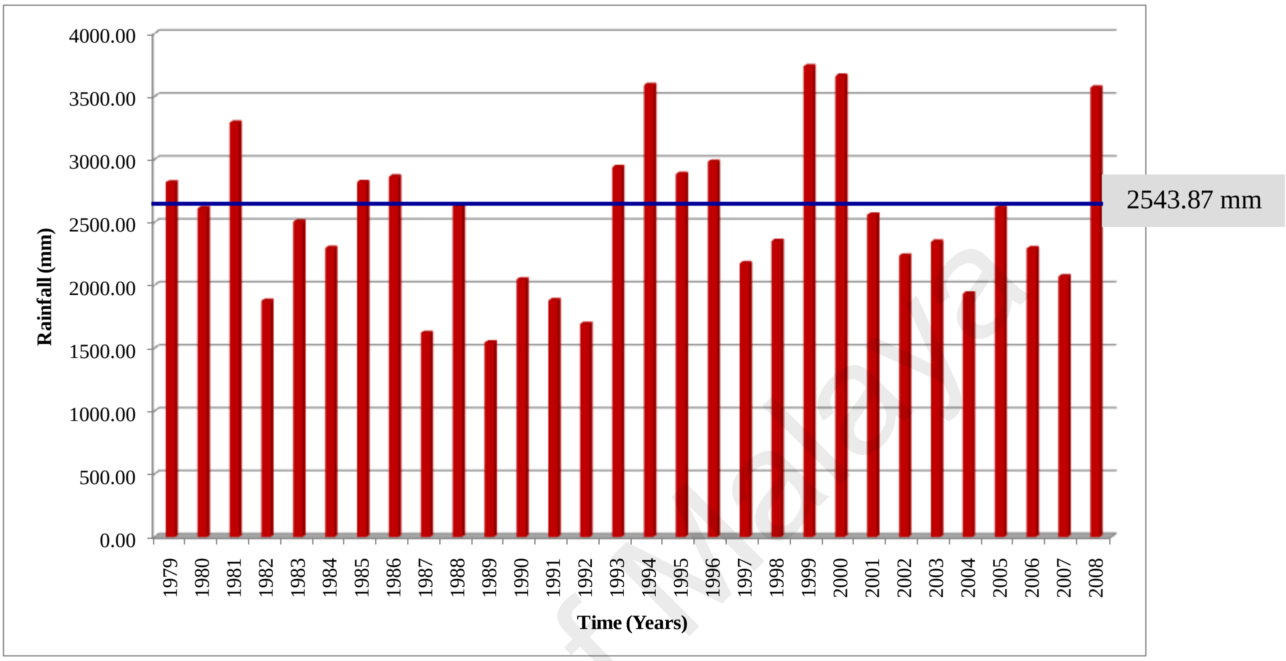


Figure 1.5: Annual Rainfall (1979 - 2008) of Kota Bharu.
Mean Annual Rainfall is 2543.87 mm

1.4.3 Drainage System

As shown in Figure 1.6, three rivers irrigate this study area. These rivers are Kelantan River, Pengkalan Datu River and Kemasin River. It demonstrates the dendritic pattern and flow from south to north-east. The Kelantan River is the main river for the state of Kelantan with 248 km length and covering an area of 11900 km^2 (Ibbitt *et al.*, 2002). This river flows northward into the South China Sea. To the east of Kelantan River are Pengkalan Datu and Kemasin river with 13.33 km and 52.60 km length, respectively. Kuala Besar, Kuala Sungai Besar and Kuala Kemasin are the main estuary. In the coastal area, there are a few beaches like Pantai Cahaya Bulan, Pantai Mek Mas and Pantai Sabak.

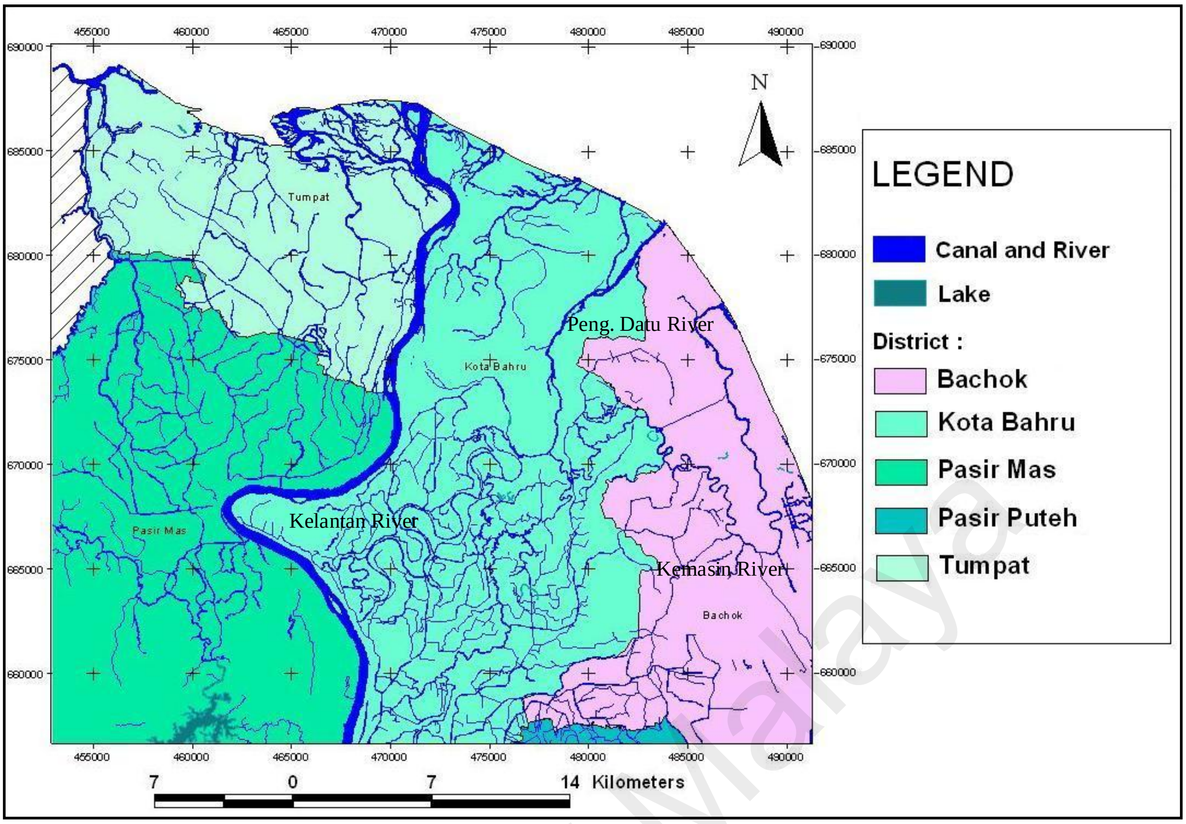


Figure 1.6: Map of Drainage System in North Kelantan

1.4.4 Land Use

Statistic shows that the total land use area is 86 343 hectare (Ha) (Department of Agriculture, 2006) which occupies the district of Kota Bharu, Tumpat and Bachok with 40 138 Ha, 18 519 Ha and 27 686 Ha, respectively. Figure 1.7 gives the percentage of main land use for Kota Bharu, Tumpat and Bachok districts. Short term crops make 34.04% of the total land use for the whole district. This is followed by plantation areas (23.77%), tree, palm and other permanent crops (15.63%), abundant grassland areas (7.02%), swamps (5.99%), settlement and associated non-agriculture areas (5.88%), water bodies (4.89%) forest (1.02%), others (1.40%) and livestock area (0.37%).

Agriculture land covers only 73.80% of the whole district with an area of 63,724 Ha. Meanwhile, the areas of land use are changed according to necessity due to continuous human activity such as municipal, housing, agricultural and others.

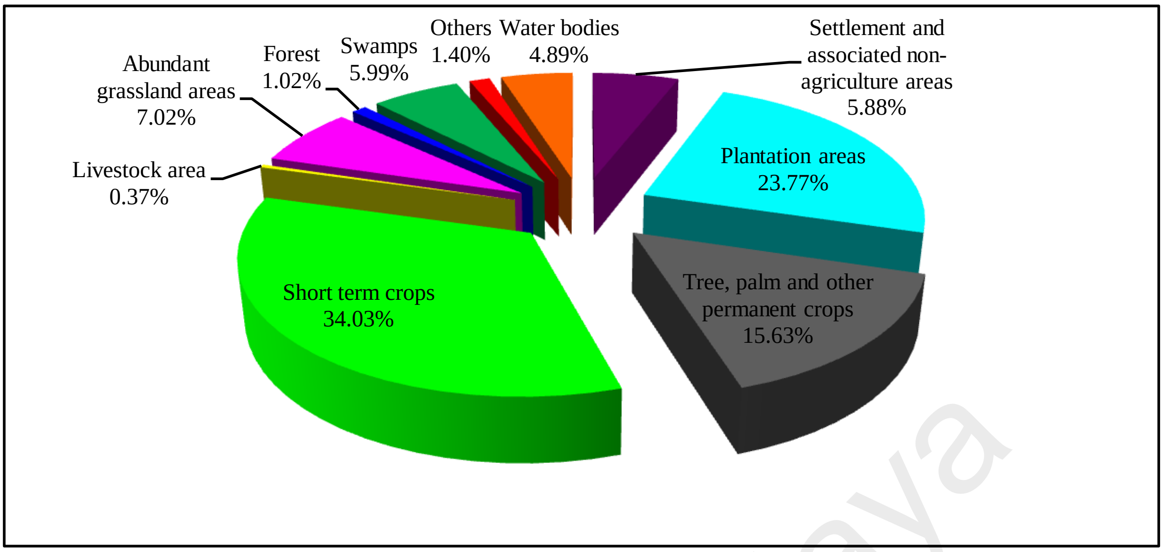


Figure 1.7: Main Land Use for Kota Bharu, Tumpat and Bachok Districts (2006)

1.5 LITERATURE REVIEW

In previous studies, numerous works had been done in this area including geology (e.g. MacDonald, 1967; Bosch, 1986 & 1988 and Noor, 1979), geomorphology (e.g. Soh, 1972; Teh, 1976; Bosch, 1988 and Raj *et al.*, 2007a & b) and hydrogeology (e.g. Ang & Kwan, 1979; Noor, 1979; Chong & Tan, 1986; Hamzah *et al.*, 1997). However, no studies have been reported on hydrogeochemistry and iron removal from groundwater.

1.5.1 Geology

The study area is a part of the coastal plain alluvium deposits during Quaternary as described by MacDonald (1967). The coastal plain was divided into marine deposits and fluviatile deposits. Complications occurred near the larger rivers in delineating these two types of deposits because large areas of marine alluvium could be swept away or covered by the river sediment. The depth, lithology and the extension of the coastal alluvium was obtained from the boring program. The alluvium extends at depth up to one hundred feet and more.

Further study by Bosch (1986 & 1988) suggested that the Quaternary deposits are divided into three formations, composed of Gula Formation, Beruas Formation and Simpang Formation.

The Gula Formation is Holocene marine deposits. This formation is made up of clay, silt, and sand with minor amounts of gravel, shell and coral deposited from the most recent major low sea level. Beruas Formation is Holocene terrestrial deposits. It consists of clay, silt, sand, gravel and peat that are deposited after the most recent major low sea-level between 15000 and 18000 years BP (before present). It is also named as the Pengkalan Member as peat is formed from *in situ* vegetation with minor intercalations of clay and silt deposited in paludal environment. This formation is also equivalent to the Young Alluvium in other parts of the Peninsular. It has been proposed to replace the Young Alluvium with the Beruas Formation. Simpang Formation is a terrestrial deposition of Pleistocene age. This formation consists of clay, silt, sand, gravel and peat that are deposited before the most recent major low sea level. It also proposed that the Old Alluvium to be replaced by the Simpang Formation. Beruas and Simpang Formation are deposited as a river channels during Holocene and Pleistocene.

Most part of the alluvial plain is underlain by Mesozoic granites but in some locality metamorphic rocks are encountered as bedrock (Noor, 1979).

1.5.2 Geomorphology

The geomorphology of North Kelantan is influenced by various physical and hydrological processes especially during north east monsoon. Kelantan delta can be divided into two geomorphic regions; to the west and east side of Kelantan River. The west region is characterized by the almost parallel three sand ridges and two distinct parallel depressions in the main land area. While the east region is made up of two vaguely areas of alluvial deposits separated by an elongated depression (Soh, 1972). In addition, Teh (1976) has classified sand ridges into Old Series and Young Series. The Old Series comprises discontinuities, parallel beach ridges about 2 km and more inland. The Young Series consists of a massive sand body with continuous parallel ridges and a few narrow swales within 2 km of the coastline. These sand ridges are the indicators of sea level changes during Holocene. The sand ridges consist of moderately sorted gravel coarse sand to poorly sorted, silty, and very fine sand. In the swales, greyish green marine sandy clay, silt and peat may be present locally. To the south of Kelantan delta stiff, white grey continental clay fills the swales (Bosch, 1988).

The coastal changes between Kuala Sungai Besar - Kuala Besar and Kuala Kemasin in consequence of breakwater construction during 1986 - 1987 and 1989 – 1991 has been studied (Raj *et al.*, 2007a & b). Littoral drift plays an important role of recession and accretion of the shorelines before and after construction. The construction of breakwater on the both sides of Kuala Sungai Besar affects the littoral drift with accretion of sediments up-drift of the southern breakwater while erosion and shoreline recession down-drift of the northern breakwater. In the present day, the littoral drift continues causing shoreline recession at Pantai Sabak and Pantai Cahaya Bulan. Northwestward transport of the eroded beach sediments result in the shoreline to advance at Pantai Mek Mas and the northwestward extension of sand spits and off-shore bar at and in the vicinity of Kuala Besar. The littoral drift has led several past coastal changes that mainly involve variation in the size of sand spits on both side of Kuala Kemasin estuary where accretion of shoreline occurs in the south side and shoreline recession occurs in the north.

1.5.3 Hydrogeology

First investigation on groundwater resources was carried out by Geological Survey Department (GSD) currently know as Mineral and Geosciences Department (MGD) working together with the German Hydrogeological Mission (GHM) on the Second Malaysian Plan (1971 - 1975). The plans cover the area of Kelantan, Terengganu, Pahang, Perlis and Sarawak. The works done during the plan involved detailed hydrogeological and geophysical studies including the construction of test and production wells.

A hydrogeological Map of Peninsular Malaysia on a scale of 1:500000 was published in 1975 by MGD as shown in Figure 1.8. This map classifies the Peninsular into various groundwater regions in accordance with their estimated yield. This classification put the coastal plains as one of the region with the highest groundwater yield (Noor, 1979). The investigation of groundwater continued to the Third Malaysian Plan (1976 - 1980) collaboration between MGD and GHM. The investigation was successfully completed for Kelantan, Terengganu, Pahang, Kedah and Perlis.

For North Kelantan River basin, early investigation in 1974 focused on the alluvial area at the east part where substantial reserves of groundwater have been proven in areas of Kota Bharu, Pengkalan Chepa, Bachok, and Pasir Puteh. During 1974-1977, detailed work in the coastal areas of Tumpat, Pengkalan Kubor and more inland of Wakaf Bharu was successfully completed. Continuous work was carried out for Pasir Mas district with construction of exploration boreholes and test well (Ang & Kwan, 1979).

Figure 1.8: Hydrogeological Map of Peninsular Malaysia

The depth aquifer layers are described by previous studies (e.g. Ang & Loh, 1975; Noor, 1979; Chong & Tan, 1986; Pfeiffer & Tiedemann, 1986; Mohammad, 1992; Mohammad & Ang, 1996 and Hamzah *et al.*, 1997). Layer 1 lies at the depth of approximately 20 m from the ground surface. Layer 2 lies at depth of 20 to approximately 50 m while Layer 3 lies at depth of more than 50 m. In some places Layer 4 has also been recognized. All aquifer layers are separated by impervious clay layer.

Previous hydrogeochemical studies (e.g. Ang & Loh, 1975; Noor, 1979; Awadalla & Noor, 1990; Mohamad, 1992; Bachik, 1994; Suratman, 1997; Mohd Aziz, 2007 and Mohd Rizalpahlavy, 2008) showed that iron concentration occurred naturally in groundwater. In general all aquifer layers showed iron concentrations exceed the WHO standard of 0.30 mg/L. The chloride concentration reported was also above the WHO standard of 250.00 mg/L especially in second layer aquifer. Nitrate concentrations in all aquifer layers were below the WHO standard of 45.00 mg/L. Certain areas in first aquifer layer had nitrate concentration above 10.00 mg/L. *E.coli* bacteria was found in the first aquifer layer. The bacteria colony was almost 40 to 230 bacteria in 100 mL groundwater samples. Hydrochemical facies indicated that groundwater changed from $NaHCO_3$ to NaCl from inland towards the coastal area.

1.5.4 General Iron Removal from Groundwater

In the past few decades, various methods have been used to remove iron from groundwater using either the conventional or advanced method. The conventional method is used for groundwater treatment in Kelantan state. This method consists of aeration, coagulation, sedimentation, filtration and disinfection. For iron removal, during aeration process, oxygen is brought into the water to convert the dissolved ferrous compound into insoluble ferric hydroxides. Then, the ferric hydroxide is removed by sedimentation and filtration processes.

Advanced method consists of (i) Ion-exchange method; (ii) Oxidation and filtration; (iii) Charcoal/ash-sand filtration; (iv) Bioremediation, as mentioned below.

In the ion exchange method, batch study using an inorganic ion exchanger of sodium titanate ion (CoTreat) was used to remove iron and other metal ions (Mn, Zn, Cu, Ni) from groundwater. The breakthrough values were below 45% and tends to decrease from 27% to 10% with the increase in the bed volume processed (Vaaramaa & Lehto, 2003).

In the oxidation combined with filtration method, oxygen or stronger oxidants such as chlorine and potassium permanganate ($KMnO_4$) are generally used for Fe^{2+} and Mn^{2+} oxidation. The solid products of oxidation ($FeOOH.H_2O$ and MnO_2) are then filtered through a granular bed, commonly green sand (Ellis *et al.*, 2000).

Charcoal/ash-sand filtration is a traditional method for iron removal. The ash-charcoal mixture is obtained from different types of firewood including bamboo. Water obtained from hand tube-well or ring-well is put in the filter system and filtered immediately, did not seem to retain iron. The use of ash or charcoal is expected to facilitate removal of iron by making the water alkaline, which precipitates iron as goethite or ferrihydrite (Dutta *et al.*, 2007)

Bioremediation for iron and manganese removal from groundwater pumped out of a hydrocarbon-contaminant obtained by oxidation and precipitation in a biological treatment plant. Iron was oxidized through aeration while manganese through the nitrification and autocatalysis process (Berbenni *et al.*, 2000).

1.5.5 Ionic Liquid as Medium for Removal of Metal Ions in Groundwater

As of date, no conclusive literature review is available on the removal of metal ions from groundwater using ionic liquids. Only batch experiments of ionic liquids with various metal ions stock solution have been reported so far.

1.6 GENERAL METHODOLOGY

To facilitate this study, techniques and methods were developed to ensure the study is scientifically sound. Figure 1.9 gives the flowchart of general methodology applied in this study.

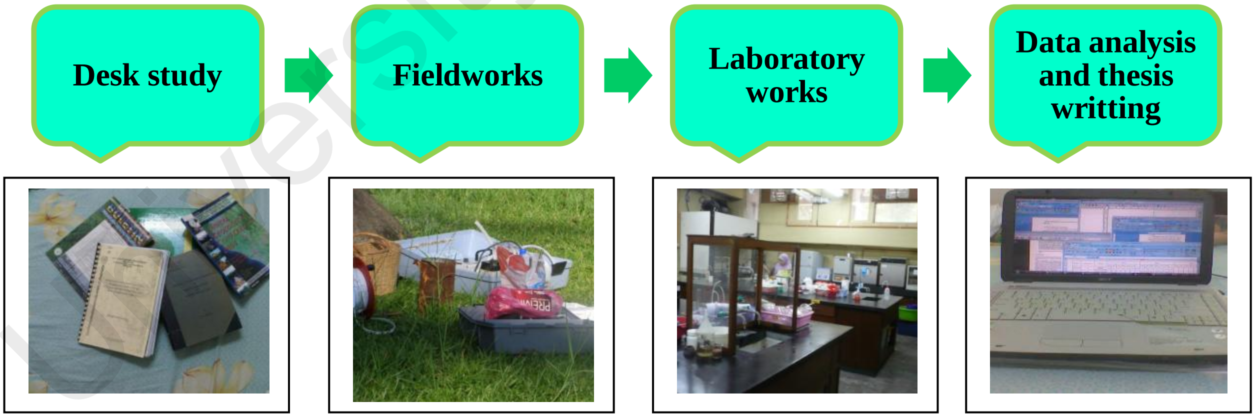


Figure 1.9: General Flow of Methodology in this Study

1.6.1 Desk Study

The first phase includes literature review, checklist and data collection for the study areas. Sources of data used in this phase were from both published and unpublished reports and journals, local or international. This phase provided a clear overview regarding the study area and gave a better understanding on the concepts and the situation of groundwater resources in Kelantan River Basin as noted in Table 1.4.

Table 1.4: Type of Data Used in this Study

Data	Scale	Department
Topography Map	1: 63360	Geology Department, University of Malaya
Geology Map	1: 50000	Minerals & Geoscience Department (MGD)
Hydogeology Map	1:500000	
Borehole Log	-	
Hydrology	-	Malaysian Meteorology Department (MMD) Department of Irrigation and Drainage (DID)
Land Use	-	Department of Agriculture (DOA)

1.6.2 Fieldwork

During fieldwork, data from literature review were validated and verified from the sampling locations. Only water level and field parameter was measured in the field. Groundwater samples were collected and preserved for laboratory analysis.

1.6.3 Laboratory

Laboratory analysis was done in Geology and Chemistry Department, University of Malaya. In Geology Department, the groundwater samples were tested for cation and anion. For cation analysis, Inductively Coupled Plasma Optical Emission Spectrometer (Perkin Elmer Optima 5300 ICP-OES) was used. Cation (13 geology elements) such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Cd^+, Mn^{2+}, Fe^{2+}, Pb^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+}, As^+ and Se^+ were determined using ICP. For anion analysis, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^- and F^-, Ion Chromatography (IC) supplied by Metrohm was used. The detailed analysis regarding metal ion removal from the standard solution was done using ionic liquid as the solvent medium for liquid-liquid extraction treatment method. Then, method analysis was applied to the groundwater samples.

1.6.4 Data Analysis and Thesis Writing

All data collected from fieldwork, laboratory experiment and government department were analyzed and interpreted. Software used were Didger 3, Surfer 7, Surfer 8, AquaChem V 5.1 integrated with PHREEQC, ArcGIS, AutoStitch and Adobe Photoshop CS3. This was followed by thesis writing.

1.7 THESIS OUTLINE

Thesis outline is guidance for thesis writing that consists of 5 chapters for this study. Chapter 1 (Introduction) discusses general overview of the study area including introduction, objective, study area, geomorphology, literature review, and a brief outline of the methodology. From here, chapter 2 – 4 has its own methodology. Chapter 2 (Geology and Hydrology), discusses about the geology, and hydrology of the study areas. Chapter 3 (Hydrogeochemistry), discusses the hydrochemical facies, groundwater quality and chemical evaluation for the three aquifer layers. Chapter 4 (Iron Removal) discusses about the treatment method with ionic liquid as a medium. Ionic liquid as a green solvent is used as a medium for this treatment with aqueous stock solution and groundwater samples. Chapter 5 (Conclusion and Recommendation), will conclude the whole of research and advocate for research improvements in the future.

CHAPTER 2

GEOLOGY AND HYDROLOGY

2.1 INTRODUCTION

Geology is the study on the history of evolution in an area from the past till the present status. Hydrology is a study on the occurrence, character and movement of water within or between the physical and biological components of the environment. Therefore, the combination of these will provide better understanding regarding the hydrogeological condition in North Kelantan.

2.2 METHODOLOGY

2.2.1 Geology

Geological studies were mostly desk study in nature. The information was gathered from previous studies, reports and books. The data was validated through field visits. All the information gathered was review in detailed to provide a good understanding regarding the general geology of Kelantan especially the main area of study.

2.2.2 Hydrology

The data was obtained from the Department of Irrigation and Drainage (DID) and Malaysian Meteorological Department (MMD) for the purpose of hydrological study. Table 2.1 shows the main components of hydrology data. Early stage, this raw data must be filtered. Filtering process involves the process of rearrange the data accordingly and checks for missing data. If there any missing data, extrapolation was used to overcome the missing data using the microsoft excel. Then, the analysis will continue with specific method.

Table 2.1: Sources and Methods Use for Hydrology Component

Data	**Station Name**	**Latitude**	**Longitude**	**Source**	**Analysis Summary**
Precipitation (P)	Pasir Mas Pump House (6021061)	06° 02' 45”	102° 10' 15”	DID & MMD	The historical record was analyzed using a common spreadsheet in excel
	Teratak Pulai (6023072)	06° 00' 20”	102° 21 30”		
	Tumpat Railway Station (6121067)	06° 11' 55”	102° 10' 10”		
	Sultan Ismail Petra Airport	6° 10' 0”	102° 17' 0”		
Discharge (Q)	Gulliemard Bridge (5721442)	5° 45' 45”	102° 09' 0”	DID	
Potential evapotranspiration (PE)	Sultan Ismail Petra Airport	6° 10' 0”	102° 17' 0”	MMD	The value was estimated using Penman Method (1948) according to hydrological procedure by DID 1991

Percipitation (P)

The Thiessen Polygon method was used to calculate areas in relationship to specific precipitation stations covering the North Kelantan River Basin. This method was used because the precipitation data show a considerable spatial variation over any region due to the differences in the type and scale of precipitation-production processes which influenced by local or regional factors (*e.g.* the topography) and by wind direction (Bayraktar et al., 2005). The area divider of stations is shown in Figure 2.1. This Thiessen Polygon was created using ESRI ArcGIS software. Then, the total mean annual precipitation was calculated using Equation 2.1. This value will be used to calculate the water balance.

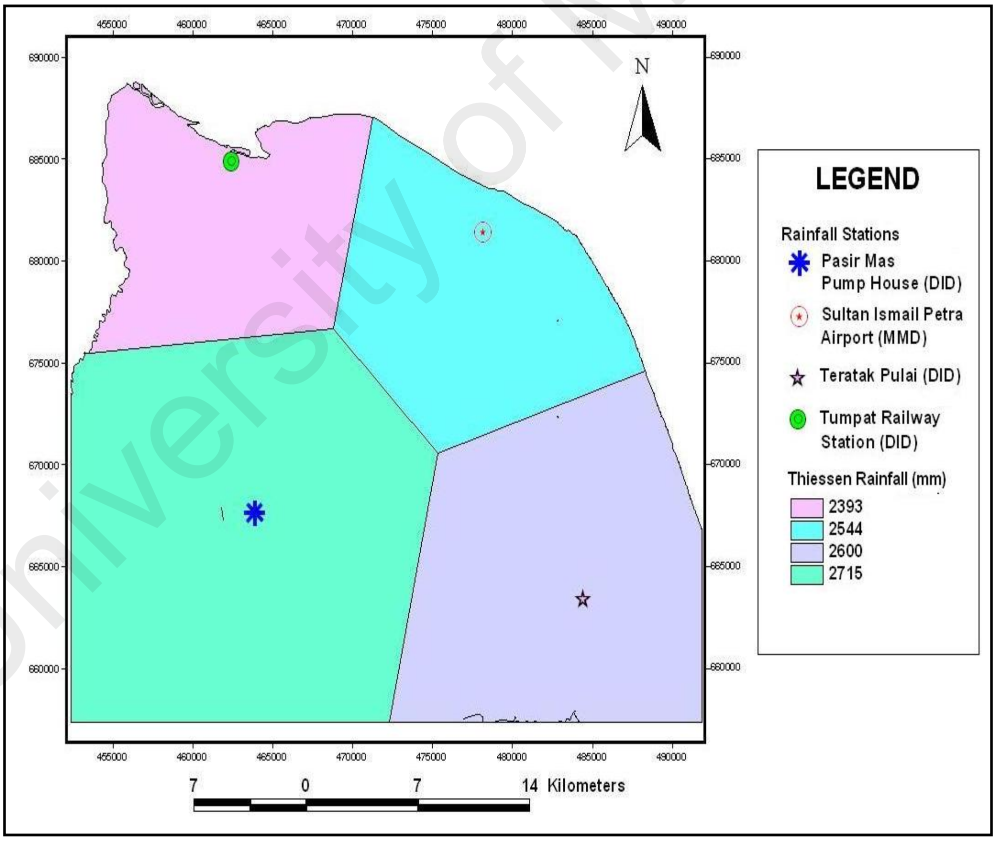


Figure 2.1: Precipitation Area Using Thiessen Polygon Method

$$P = \sum_{i=1}^{n} \frac{p_i a_i}{A} \tag{2.1}$$

Where,

p_i : is the precipitation at gauge I
a_i : is the area of the polygon surrounding rain gauge I
A : is the total basin area

Potential Evapotranspiration (PE)

The potential evapotranspiration was defined as the evapotranspiration that would occur if there is an adequate soil – moisture supply at all times. The Simplified Penman's method was used to determine the potential evapotranspiration. This method considers two terms; 1) the energy or radiation term and 2) the aerodynamic or wind and humidity term. The terms can be simplified as shown in Equation 2.2.

$$PE = \frac{\Delta H + \gamma\, f(u)\, (e_m - e_d)}{\Delta + \gamma} \tag{2.2}$$

Where,

PE : Potential evaporation in mm/day
H : Heat budget at evaporating surface in equivalent evaporation, mm/day
$f(u)$: Wind related function
$(e_m - e_d)$: Difference between the saturation vapour pressure at mean air temperature and the saturation vapour pressure at mean dew point temperature, both in mm Hg (month)
Δ : Slope of saturation vapour pressure curve of air at absolute temperature T_m, mm Hg/°C

T_m: mean air temperature in degrees absolute (°K) for day (month)

γ : Psychrometric constant, 0.49 mm Hg/°C

River Discharge

The river discharge is the amount of water that flow through the river during a given time interval. The unit express for discharge is m^3/s (cubic meters per second) or ft^3/s (cubic feets per second) (*sciencecourseware.org*). This data was used to calculate total flow and also to estimate the baseflow index (BFI) and water balance. Later, a discharge hydrograph will be plotted.

Baseflow

Baseflow was one of the components in hydrograph that reacts slowly to rainfall and is usually associated with water discharged from the groundwater storage. The baseflow index (BFI) was used as a measurement for baseflow characteristic of a catchment. The values indicated the influence of soil and geology on the river. Data from DID at the Guillemard Bridge station (5721442) was used for baseflow estimation. The baseflow was estimated using the Ineson & Downing (1964) baseflow separation method from the main river hydrograph. The area below the hydrograph is considered as baseflow, shown in Figure 2.2. Curve A extends the baseflow recession on the falling limb backwards under the peak, and the segment from the point under the peak to the point of rise is sketch in. This area was calculated using the trapezium formula of an area. Then, the baseflow index (BFI) was determined using the Equation 2.3.

$$\text{Baseflow Index (BFI)} = \frac{\text{Total baseflow (m}^3\text{/year)}}{\text{Total flow (m}^3\text{/year)}} \tag{2.3}$$

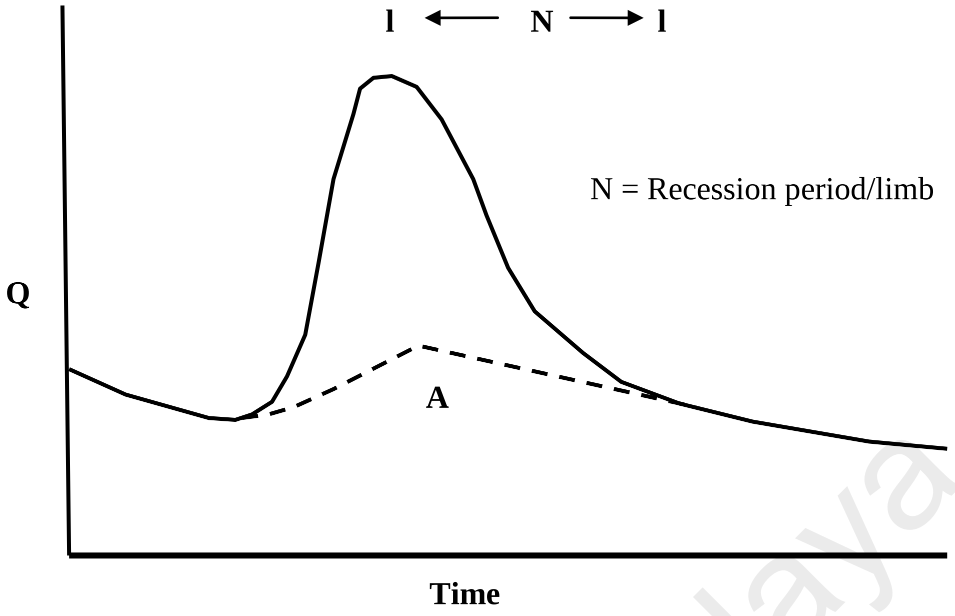


Figure 2.2: Baseflow Separation Method (Ineson & Downing, 1964)

Water Balance

The water balance or water budget for the recharge area of an aquifer was a very useful means of determining ground-water recharge (Eckhardt, 2008). Based on the hydrology data, water balance of an area can be determined. The water balance for a hydrological basin is actually an accounting of the input and the output of the water as shown in Equation 2.4.

$$\Delta S = P - (PE+Q) \tag{2.4}$$

Where,

ΔS : changes in groundwater storage (m^3/year)
P : precipitation (m^3/year)
PE : potential evapotranspiration (m^3/year)
Q : annual mean discharge (m^3/year)

2.2.3 Hydrogeology

Data was provided by Minerals and Geoscience Department (MGD). In total there are 70 monitoring wells in North Kelantan River basin located in Layers 1, 2 and 3. 29 wells are constructed in Layer 1 while 22 wells and 19 wells in Layers 2 and 3, respectively.

Monitoring well

Figure 2.3 shows a typical design of monitoring well in North Kelantan Basin. In general, the monitoring well consists of a single string of lining material placed in a borehole of 175 mm. The lining material is made up of class E uPVC pipes of 75 mm internal diameter (ID). The bottom section of the lining material is fitted with a stainless-steel screen (type 3Ø4) of 75 mm I.D. The slot opening of the screen is 1 mm wide and the length of each screened section is 1.5 m. Below each stainless-steel screen a sand-trap is fitted from 1 m length uPVC casing of 75 mm internal diameter terminated with a iPVC end-cap. The well is packed with gravel around the screen interval. The rest of the annular space is back-filled with coarse sand and bentonite pellets. The gravel pack is made up of clean, durable, evenly-shaped siliceous materials of nominal diameter (3 - 4 mm). The bentonite pellets used are ½ inch in diameter which act as an effective seal and to prevent cross-contamination among the layers (Bachik, 1989).

The JKR monitoring well design is shown in Figure 2.4. Detailed information and location of monitoring wells in North Kelantan is given in Tables 2.2 – 2.4 and Figures 2.5 – 2.7. Layer 1 may reach up to 20 m depth below the ground surface. Layers 2 and 3 are laid at depths between 20 – 50 m and more than 50 m, respectively.

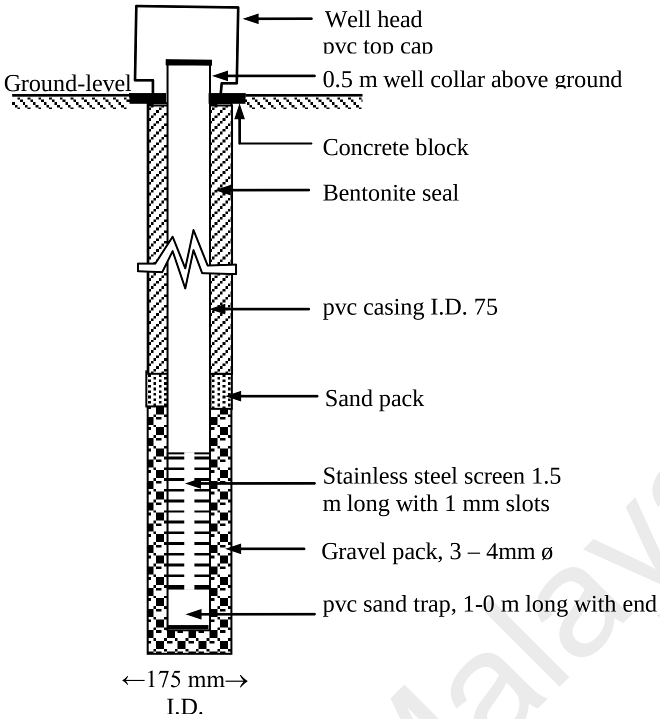


Figure 2.3: Typical Design of Monitoring Well

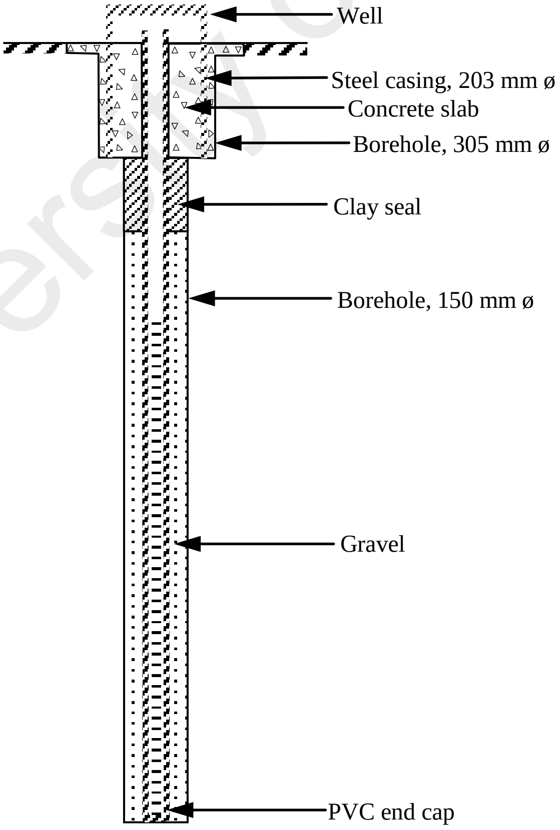


Figure 2.4: JKR Monitoring Well Design

Table 2.2: General Information of Monitoring Wells in Layer 1

Well	Location	Remarks	X (East)	Y (North)	Total Depth (m)	Screen depth (m)	Elevation (m, m.a.s.l)
KB 24	Jelawat	-	486500	664700	9.4	5.5 - 7.0	3.61
KB 27	Kubang Kerian Waterworks	-	476400	673500	14.4	10.5 - 12.0	6.42
KB 30	Pintu Geng Waterworks	-	471600	674700	14.2	9.0 - 10.5	6.01
KB 37	USM Kubang Kerian	JKR Well	477400	674200	13.0	4.0 - 11.5	4.11
KB 38	SK Demit		477300	675800	14.0	12.0 - 13.5	3.30
KB 39	Kg. Binjai		479200	672200	17.0	8.0 - 16.0	5.88
KB 40	SK Kedai Lalat		480000	675900	21.3	8.5 - 18.9	3.89
KB 41	Kg. Padang Penyadap		474300	671500	18.2	7.5 - 14.5	5.65
KB 42	SK Pasir Hor		474800	673300	12.0	3.5 - 10.5	6.18
KB 43	SK Seribong		475200	671100	16.1	7.5 - 14.5	6.26
KB 44	Kg. Kundang		476500	671100	15.5	4.5 - 14.3	5.67
KB 45	Kg. Chica		476300	672500	15.0	3.0 - 11.0	6.00
KB 46	Kg. Bunut Payong		473700	674100	15.0	3.0 - 5.4	3.77
KB 47	Wakaf Che Yeh		472300	673400	15.0	3.5 - 13.5	6.52
KB 48	Jalan Kuala Krai		471900	671100	18.0	9.5 - 14.5	4.85
KB 49	Pintu Geng Waterworks		471550	674500	15.0	5.0 - 14.0	7.44
KB 50	Kg. Huda		475600	674600	19.5	12.0 - 15.0	5.25
KB 51	SK Rambutan Rendang		475800	678900	14.6	3.0 - 7.0 8.0 - 11.6	4.99
KB 52	Kg. Langgar Tapang		477100	677500	23.0	3.0 - 9.9 12.1 - 19.8	4.91
KB 53	Wakaf Mek Zainab		472800	679200	14.5	3.0 - 12.5	2.52
KB 54	Kg. Bawah Lembah		471700	676600	15.0	5.0 - 10.5	2.00
KB 55	SK Pasir Pekan		470200	676900	13.5	7.5 - 11.2	6.53
KB 57	Wakaf Bharu Waterworks	Piezometer	467700	676600	12.0	10.0 - 11.5	6.06
KB 59	Kg. Putih Waterworks	Piezometer	471900	676200	12.0	9.7 - 11.4	7.23
KB 60	Kg. Putih Waterworks	Piezometer	471900	676200	14.0	11.5 - 13.0	6.74
KB 61	Pengkalan Chepa Waterworks	Piezometer	478150	681700	8.0	2.5 - 4.0	5.80
KB 64	Bunut Susu, Pasir Mas	-	465400	673800	8.0	6.0 - 7.5	7.09
KB 68	Panji	-	478700	678300	15.5	13.5 - 15.0	3.22
KB 69	SK Islah	Piezometer	474900	677400	10.5	8.0 - 9.5	4.25

m.a.s.l : meter above sea level

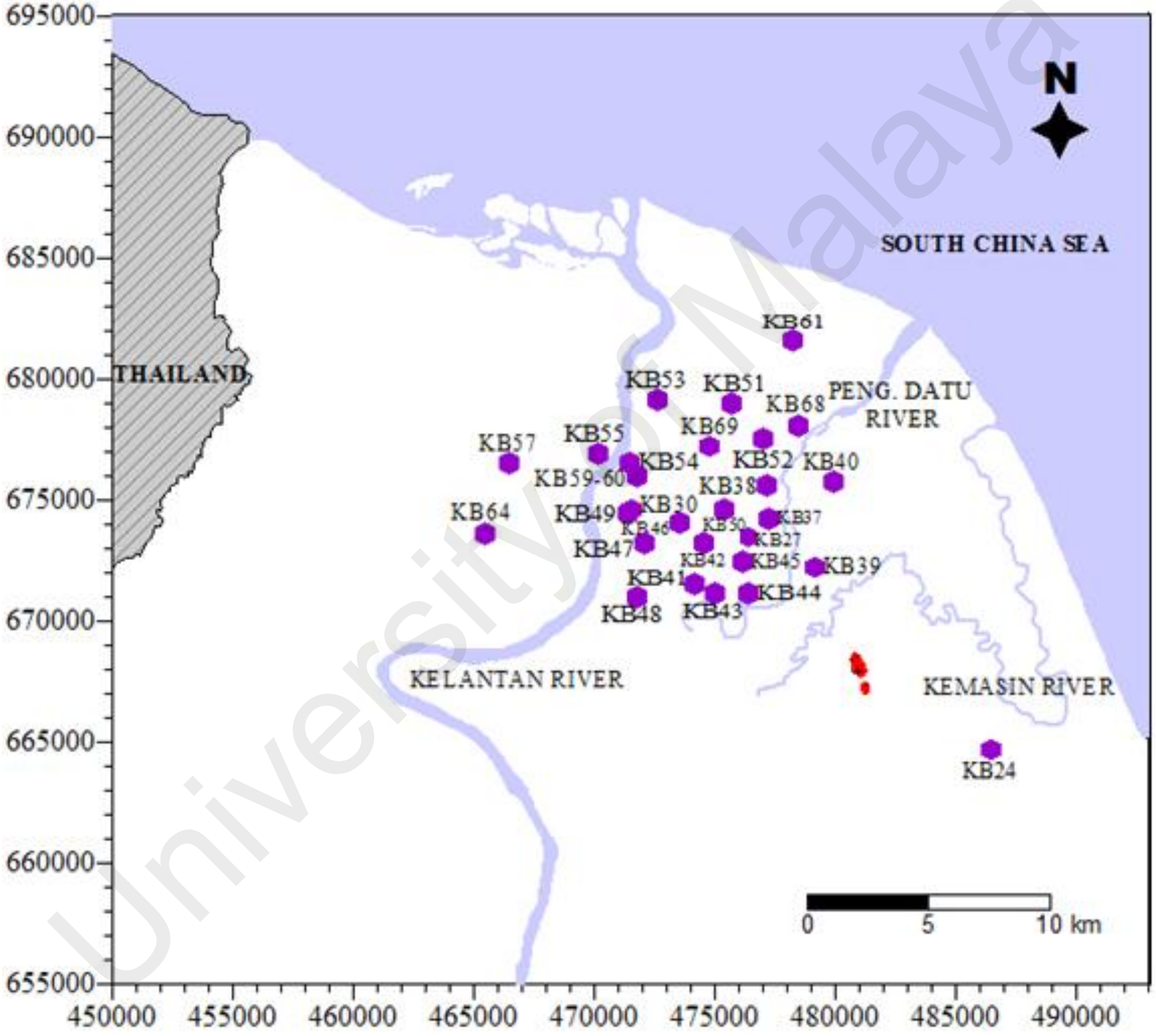


Figure 1.5: Well Locations in Layer 1

Table 2.3: General Information of Monitoring Wells in Layer 2

Well	Location	Remarks	X (East)	Y (North)	Total Depth (m)	Screen depth (m)	Elevation (m, m.a.s.l)
KB 05	Pengkalan Chepa Waterworks		478100	681700	30.0	23.0 - 24.5	5.79
KB 10	Tanjung Mas Waterworks		475200	678900	35.0	30.0 - 30.0	4.65
KB 11			475200	678900	35.0	30.5 - 32.0	4.50
KB 12			475200	678900	35.0	30.0 - 32.0	4.49
KB 13			475200	678900	35.0	30.0 - 31.5	4.41
KB 14			475200	678900	35.0	30.5 - 32.5	4.44
KB 19	Jalan Merbau		472500	678300	34.0	27.0 - 28.5	6.47
KB 20	Perol	-	472600	666200	44.8	39.5 - 41.0	8.84
KB 21			472600	666200	29.0	23.0 - 24.5	8.81
KB 22	Jelawat	-	486500	664700	50.4	46.0 - 47.5	3.61
KB 23			486500	664700	32.4	25.0 - 26.5	3.58
KB 26	Kubang Kerian Waterworks		476400	673500	39.0	52.0 - 53.5	6.44
KB 34	Beris Kubur		485700	671900	44.4	38.3 - 39.8	3.34
KB 35			485700	671900	29.2	24.0 - 25.5	3.39
KB 36	Peringat	-	477400	665900	44.3	33.5 - 35.0	5.87
KB 56	Kg. Sedar Waterworks	Piezometer	465100	683400	32.0	30.0 - 31.5	4.64
KB 58	Kg. Chap Waterworks	Piezometer	483600	668100	28.0	22.0 - 24.5	4.28
KB 62	Bunut Susu, Pasir Mas	-	465400	673800	54.0	46.0 - 47.0	7.07
KB 63			465400	673800	32.0	28.5 - 30.0	7.03
KB 66	Panji		478700	678300	135.0	40.5 - 50.0	3.48
KB 67			478700	678300	35.2	26.0 - 27.5	3.51
KB71	Loji Air Ketereh		472800	659700	41	27.0-31.0	NA

NA : not available
m.a.s.l : meter above sea level

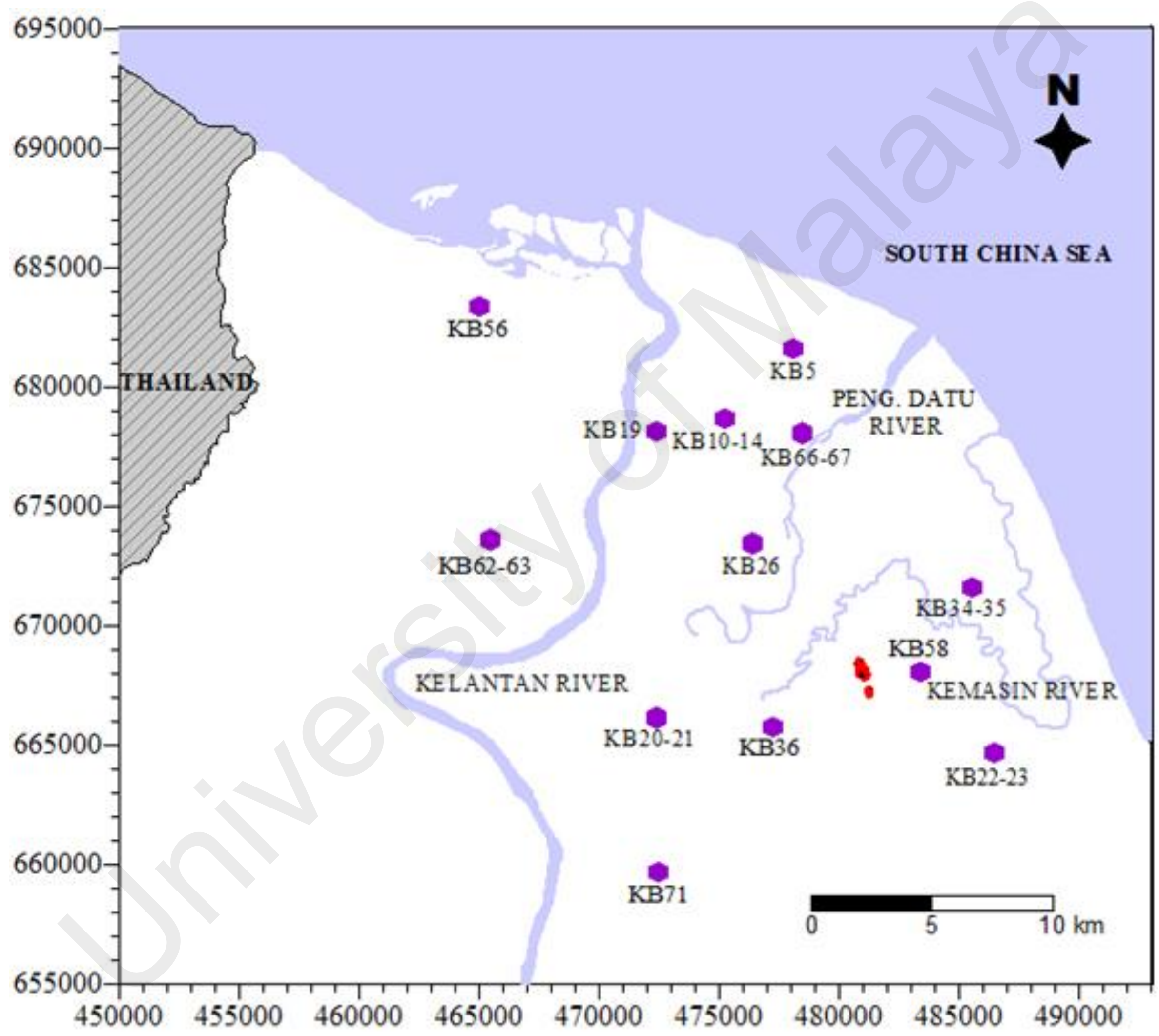


Figure 2.6: Well Locations in Layer 2

Table 2.4: General Information of Monitoring Wells in Layer 3

Well	**Location**	**Remarks**	**X (East)**	**Y (North)**	**Total Depth (m)**	**Screen depth (m)**	**Elevation (m, m.a.s.l)**
KB 1	Pengkalan Chepa Waterworks	-	478100	681700	114.0	98.5 - 100.0	5.93
KB 2		-	478100	681700	91.0	85.5 - 87.0	5.93
KB 3		-	478100	681700	73.0	67.0 - 68.5	5.87
KB 4		-	478100	681700	64.0	58.0 - 59.5	5.85
KB 6	Tanjung Mas Waterworks	-	475200	678900	140.0	127.5 - 129.0	4.48
KB 7		-	475200	678900	113.0	97.5 - 99.0	4.44
KB 8		-	475200	678900	85.0	78.5 - 80.0	4.52
KB 9		-	475200	678900	60.0	54.0 - 55.5	4.49
KB 15	Jalan Merbau	-	472500	678300	150.0	125.0 - 126.5	6.57
KB 16		-	472500	678300	113.0	108.5 - 110.0	6.58
KB 17		-	472500	678300	88.0	83.5 - 85.0	6.60
KB 18		-	472500	678300	66.0	64.0 - 65.5	6.55
KB 25	Kubang Kerian Waterworks	-	476400	673500	59.4	51.4 - 52.9	6.44
KB 28	Pintu Geng Waterworks	-	471600	674700	113.2	70.0 - 71.5	6.07
KB 29		-	471600	674700	62.2	58.0 - 59.5	6.08
KB 31	Beris Kubur	-	485700	671900	131.4	106.0 - 107.6	3.39
KB 32		-	485700	671900	101.2	93.5 - 95.0	3.60
KB 33		-	485700	671900	83.4	76.0 - 77.5	3.33
KB 65	Panji	-	478700	678300	104.0	88.5-90.0	3.37

m.a.s.l : meter above sea level

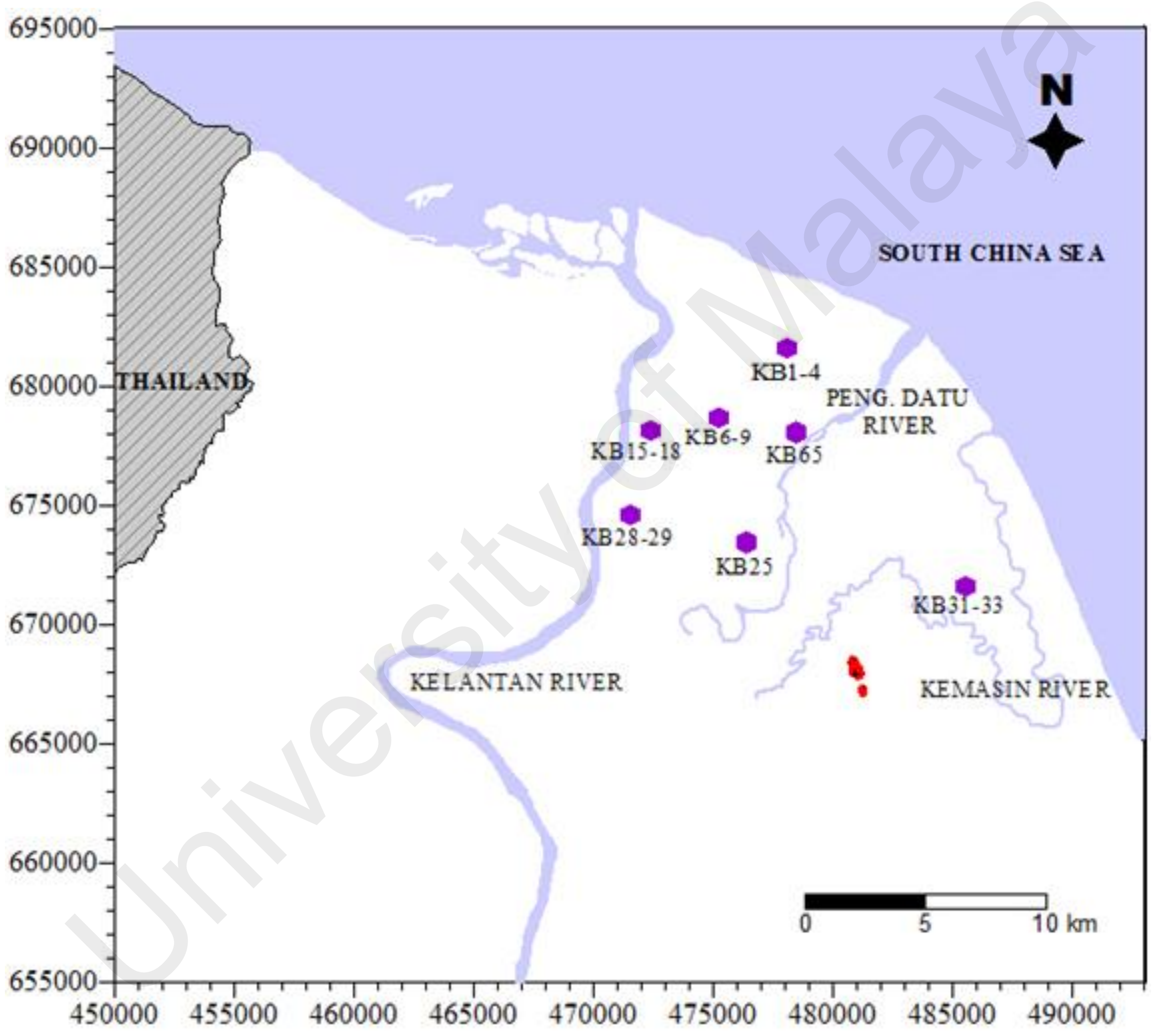


Figure 2.7: Well Locations in Layer 3

2.2.4 Conceptual Model

At the end of this chapter, a conceptual model of Kelantan River basin will be made. This model will summarize the hydrological process involved in Kelantan River basin.

2.3 RESULTS

2.3.1 General Geology of Kelantan

Early regional basis of geological work in Kelantan was carried out by Savage between the years 1922 – 1925. His work was purely reconnaissance in nature and based on inaccurate small-scale topographical maps. Later from 1951 until 1960, more work of this nature was carried out (MacDonald, 1951; Slater, 1957 and Santokh Singh, 1960). Detailed geological data on Kelantan and Peninsular Malaysia has been compiled in the book Geology of Peninsular Malaysia by Hutchison & Tan (2009). The geological formation of Kelantan ranges from Lower Paleozoic until Quaternary and can be divided into three main chronology; Paleozoic, Mesozoic and Cenozoic. Figure 2.8 shows the geological map of Kelantan.

Paleozoic

The Paleozoic formation in Kelantan was found in the central belt of Peninsular Malaysia. The bulk of the Upper Paleozoic sediments consist of marine Permian strata that occur as linear belts flanking Mesozoic sediments in the Central Belt. The Upper Paleozoic rock consists of Gua Musang Formation and Aring Formation in the south of Kelantan while it is the Taku Schist in eastern of Kelantan. The Upper Paleozoic formation is dominated by argillaceous and volcanic facies while the rest belong to calcareous and arenaceous facies. The depositional environment is typically shallow marine with intermittent active submarine volcanism starting in the Late Carboniferous and reaching it’s peak in the Permian and Triassic (Lee, 2004).

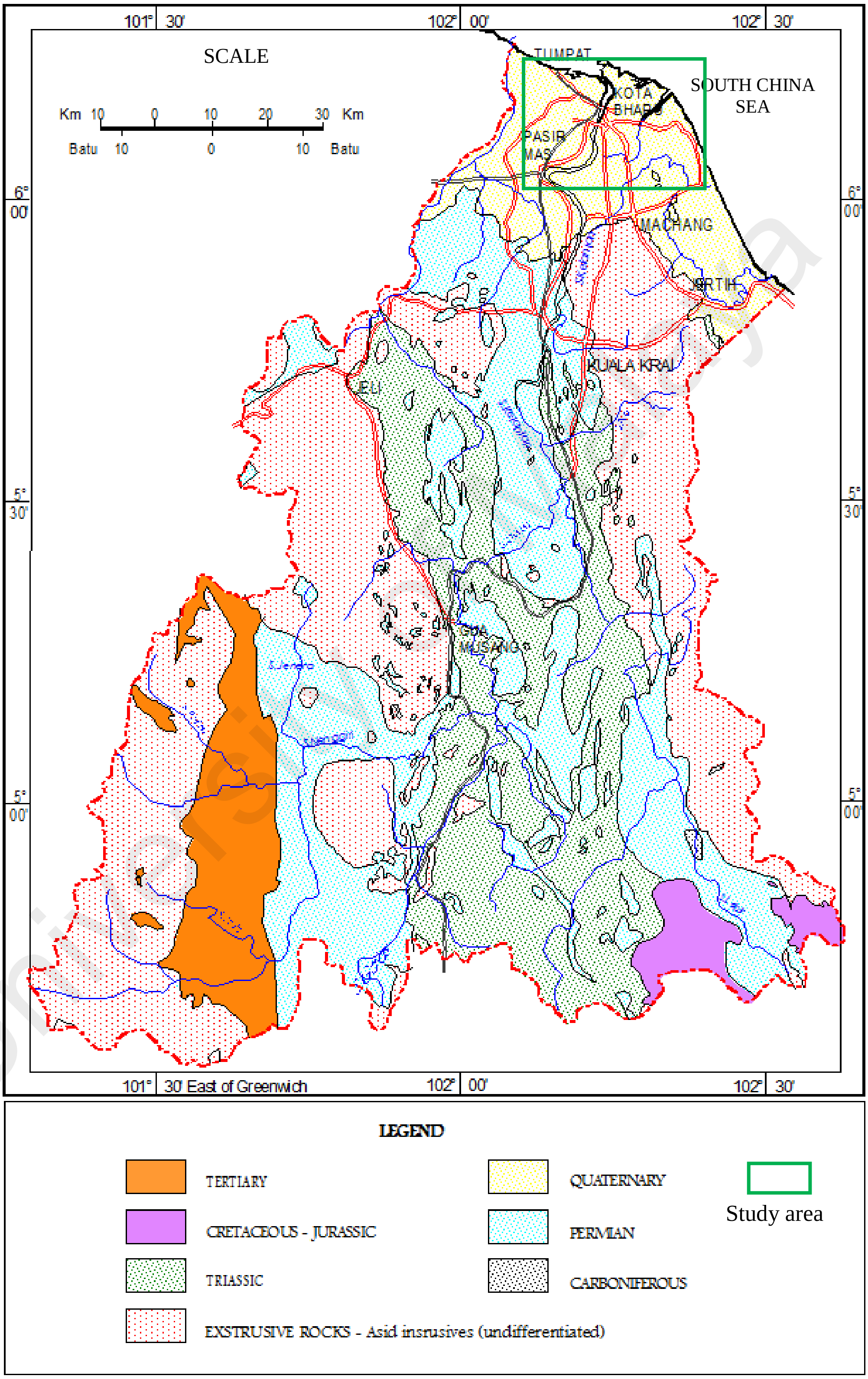


Figure 2.8: Geology Map of Kelantan

Mesozoic

The Mesozoic formation are dominant in the central belt that form continuous north – south trending belt extending beyond the international boundaries with Thailand (the Gua Musang Formation) in the north and Singapore (the Jurong Formation) in the south. The Permian – Triassic of the Gua Musang, Aring and Gunong Rabong formations in Kelantan is dominated by shallow marine clastics and carbonates with volcanic interbeds. Towards the south, deeper marine turbiditic sediment is more dominant in the Telong Formation. These turbidites are commonly tuffaceous in nature with volcanic interbeds (Leman, 2004).

Cenozoic

The Cenozoic formation is mainly represented by Quaternary sedimentary deposits. The Quaternary sediment covering part of north Kelantan consist extensively of unconsolidated to semi-consolidated boulders, gravel, sand, silt and clay that underlie the coastal and inland plain. Details about the Quaternary deposit will be discussed in Section 2.3.2.

Plutonism

The plutonic rocks in Kelantan comprised of Eastern Belt and Cretaceous plutonic rocks (Abdul Ghani, 2009). The Eastern Belt granite has been dated as Permian to Triassic age. The composition of SiO_2 ranges from 50% to 78%. The batoliths and plutons are surrounded by narrow contact metamorphic aureoles. The Eastern consists of both I and S type granite. The S type granite is responsible for the tin mineralizations that is formed by collision of continental lithosphere. The granite is characterized by K-feldspar, plagioclase, quartz biotite, hornblend, sphene, apatite, allanite, magnetite and ilmenite in granite and granodiorite.

The Cretaceous granites of Stong Complex have been dated 96 to 60 Ma (Bignell & Snelling, 1977; Darbyshire, 1988). The complex consists of Berangkat Tonalite, Kenerong Leucogranite and Noring Granite was emplaced into metasedimentary rocks comprised of silimanite and calc-silicates gneisses. The Noring granite is the largest component of Stong Complex forming oval-shaped pluton. It consists of Terang and Belimbing hornblend-bearing facies. The Noring granite is undeformed and characterized by K-feldspar, plagioclase, quartz biotite, hornblend, sphene, apatite, allanite, epidote, zircon, magnetite, pyrite and ilmenite. The Berangkat Tonalite consists of grey, partly strong foliated of megacystic monzolite-tonolite-granodiorite. The mineralogy is similar with Noring Granite. Kenerong Leucogranite is characterized by a complex network of small intrusive and is emplaced into a migmatitic metasedimentary envelope dominantly with pelitic.

Metamorphism

The Stong migmatite complex forms the mountains that lay about 8 km west of the railway town of Kemubu and Dabong (Hutchison, 2009). Three type of migmatite injection occurs through the Stong Complex which are agmatite, venite and nebulite. The granitoid layer deforms a boudins as well as into the most remarkable example of ptygmatic folds. Common rocks are finely banded hornblende-quartz schist, staurolite-garnet-biotite schist, fine-grained biotite-muscovite schist, fine-grained hornblend-biotite-quartz schist, diopside-phlogopite marble and sillimanite-garnet-biotite gneiss.

The Taku Schist is mainly pelitic schist of amphibole facies. The Kemahang granite has injected the Taku schist and incorporates large scale enclaves with Cretaceous biotite K:Ar age of 124 ± 4 Ma (Ishihara *et al.*, 1979). The predominant rock type is quartz-mica schist with subordinate quartz-mica-garnet schist and garnet-mica schist. Other rocks are amphibolites, serpentinite and granite gneiss. The mineralogy suggests that Taku Schist was metamorphosed in the Barrovian facies series. Bignell & Snelling (1977) indicated the metamorphism occurred Upper Triassic from K:Ar dating. The metamorphism age is therefore related to the Indosinian Orogeny caused by collision of Sibumasu with East Malaya same as Stong Complex.

Fault

The Lebir Fault Zone can be traced NNW-SSE trending curve-linear lineaments along Sungai Lebir near Manek Urai in Kelantan. The lineament continues to the south before terminating at the intersection with Lepar Fault in Pahang. The fault zone is at least 10 km wide, spanning the gap between the Sungai Lebir and the eastern margin of the Taku Schist near Kuala Krai. The rocks within the fault zone are deformed into brecciated metasediments, flasered granites and mylonites. Slickensides on the fault surface that is exposed along the road-cut, indicates sinistral movement (Mustafa Kamal Shuib, 2009).

2.3.2 Geology of North Kelantan River Basin

Quaternary Deposit

The study area is covered by alluvium deposits of Quaternary age. These Quaternary deposits can be divided into Pleistocene and Holocene deposit as mapped by Bosch (1986). The Pleistocene consist of the Simpang Formation while Holocene consists of the Gula Formation and Beruas Formation that was underlain by granite bedrock. Figure 2.9 shows the Geology Map of North Kelantan. The Quaternary deposits mainly consist of unconsolidated to semi consolidated gravel, sand, clay and silts that occupy in the north of Kelantan state and along the river valley (Md Hashim, 2002). The first 13 to 15 meter deposit is recent of age (Soh, 1972 and Noor, 1979) and composes of silty to clay.

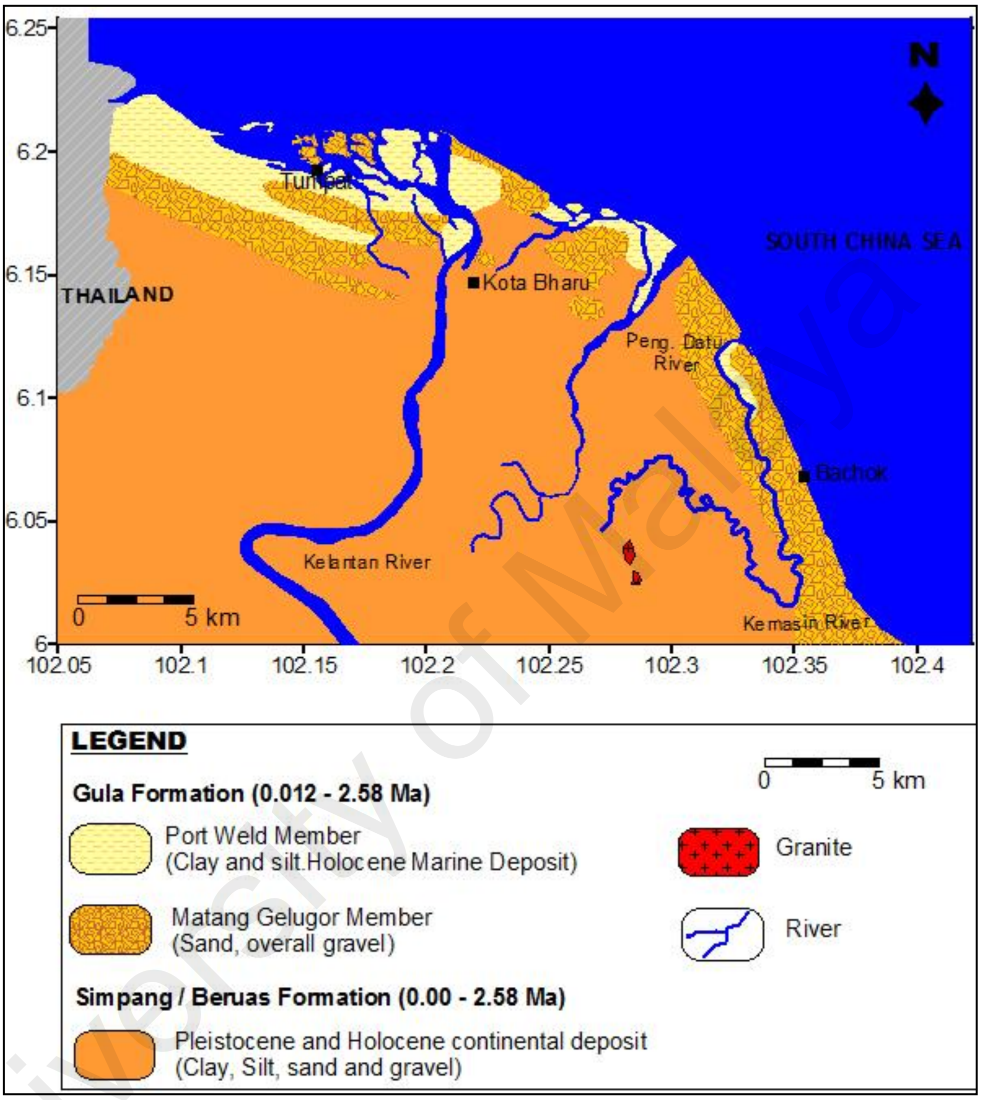


Figure 2.9: Geology Map of North Kelantan

Towards the coast, the thickness of alluvium may reach up to more than 200 m (Suratman, 1997). According to Stauffer, 1973; Pfeiffer & Chong, 1974, the unconsolidated deposit that overlays granite and sediment form in shape of thick wedge towards the sea. This sediment is complicated and made up of interstratified and intercalated deposit with marine and non-marine strata (Udie Lamasudin, 2000). The mixtures of marine and non-marine sediment build of sea level changed during the Quaternary age (Tjia, 1973).

Gula Formation

Gula Formation, mainly made up of clay and silt while sand and gravel are also present in a small amounts. The boundary is often underlain by the Simpang Formation or the bedrock with thickness of more than 40 meter. Organic matters and shells are present such as foraminifera (*Ammonia beccarii*, *Asterorotalia pulchella*), gastropod (*Coralliophila sp.*, *Natica sp.*), ostracod (*Cytherella semitalis*, *Cyprideis sp.*), pelecypod (*Anadara sp.*, *Corbula sp.*) and others. The environment of deposition is shallow marine to estuarine (Suratharalingam & Teoh, 1985 and Loh, 1992). The upper part is differentiated into Matang Gelugor Member and Port Weld Member (Suratharalingam & Teoh, 1985).

a) Matang Gelugor Member

The lithology of Matang Gelogor Member composes of the sediments varying from clayey sand to sand with rare layers of lenses of clay. Sand is mainly in the upper part while clayey sand is common in the lower part of succession. The thickness is approximately 4 meter with shallow marine (coastal) environment of deposition.

b) Port Weld Member

The lithology of Port Weld Member is predominantly clay with occasional lenses or layers of fine to medium sand and silt. The clay varies from brown-black or brownish grey to greenish grey. The clay generally consists of moderate to abundant humic materials layered or arranged in haphazard manner. The thickness is approximately 2 meter with marine origin as environment of depositional.

Simpang Formation

Simpang Formation which is Pleistocene in age, is found mainly in the center part of the study area. This formation is made up predominantly of clay, silt and sand with subordinate amounts of gravel towards the lower part of the succession. The sediments are usually mixtures of gravel, sand, silt and clay. The sand and clay are intercalated with one another. Peat and peaty clay are also present. The boundaries are unconformable basal boundary with bedrock and conformable upper boundary with Gula Formation. The thickness usually is more than 30 meter with the presence of plants fossils. The environment of deposition is fluvial (Suratharalingam & Teoh, 1985 and Loh, 1992). As stated by Suratharalingam & Teoh (1985), the formation is equivalent to the ‘Old Alluvium’ (Walker, 1956); Pleistocene sediments of Kinta Valley area are now referred as Simpang Formation.

Granite

A little patch of granite hills occurs in the southeast of the study area as shown in Figure 2.9. These granite hills are known as Bukit Marak and Bukit Kechik with 373 meter and 307 meter heights, respectively. This granite belongs to the Boundary Range Granite according to their similarities of location and mineral composition. The granite is grey in color with a lot of feldspar phenocrysts, quartz and hornblend minerals as stated by Mohd Aziz (2007).

2.3.3 Hydrology

Precipitation, P

Table 2.5 shows the annual precipitation received from 1979 until 2008 at four stations; Tumpat Railway Station, Pasir Mas Pump House, Teratak Pulai and Sultan Ismail Petra Airport. The mean annual precipitation received based on the table is 2562.94 mm. Figure 2.10 shows the distribution of mean monthly precipitation. The highest and lowest mean monthly precipitation received during December and February at Pasir Mas Pump House was 668.77 mm and 57.72 mm, respectively. High rate of precipitation received during northeast monsoon directly increases the river discharge.

Potential Evapotranspiration, PE

The potential evapotranspiration (PE) for Kelantan River Basin are based on six types of surface; Crops, Open water, Oil palm, Grass, Tropical and Towns. This value is calculated based on 17 years data using Equation 2.1. Crops show the highest rate of PE with 12735.72 mm/year (72.23%) while Oil palm shows the lowest PE with 11.99 mm/year (0.07%) as noted in Table 2.6 and Figure 2.11.

Table 2.5: Mean Monthly and Annual Precipitation

Station Name	Station No.	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Tumpat Railway Station	6121067	1979-2008	78.94	63.14	90.22	71.05	121.72	125.42	166.88	172.43	174.40	245.20	531.23	552.52	2393.17
Pasir Mas Pump House	6021061	1979-2008	95.82	57.72	70.96	80.37	149.38	149.67	184.16	226.65	210.60	245.94	554.65	688.77	2714.68
Teratak Pulai	6023072	1979-2008	98.58	73.63	121.13	65.19	112.44	130.88	181.87	168.97	231.41	264.12	582.59	569.22	2600.02
Sultan Ismail Petra Airport	-	1979-2008	78.14	59.16	123.26	95.00	107.60	116.00	154.49	157.78	183.54	260.25	646.33	562.32	2543.87
		Mean	**87.87**	**63.42**	**101.39**	**77.90**	**122.79**	**130.49**	**171.85**	**181.46**	**199.99**	**253.88**	**578.70**	**593.21**	**2562.94**

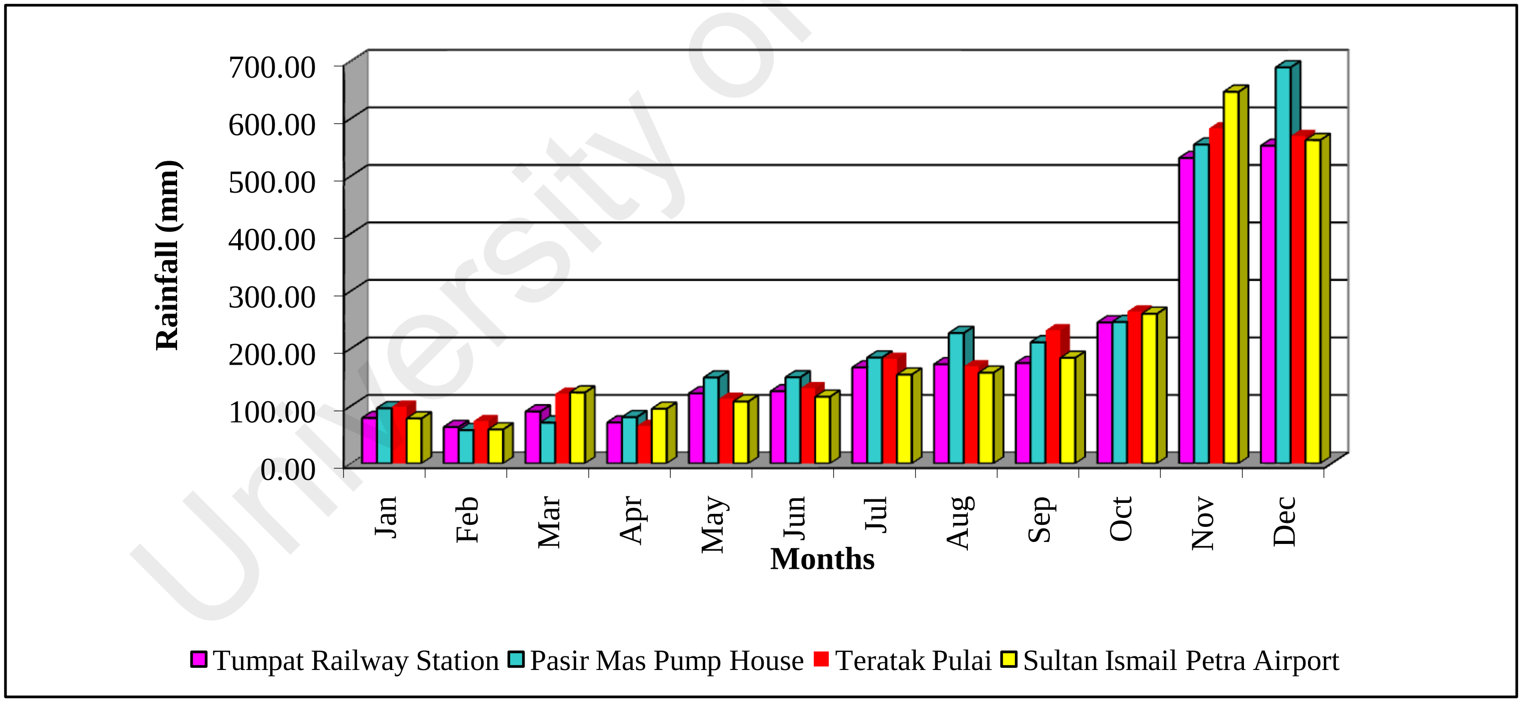


Figure 2.10: Mean Monthly Precipitation Distribution (1979 – 2008) Recorded from 4 Stations

Table 2.6: Classification of Selected Surfaces in Kelantan River Basin

Surface	**Crops**	**Open water**	**Oil palm**	**Grass**	**Tropical forest**	**Towns**
PE (mm/year)	12735.72	1911.34	11.99	1056.70	32.95	1882.28
PE (%)	72.23	10.84	0.07	5.99	0.19	10.68

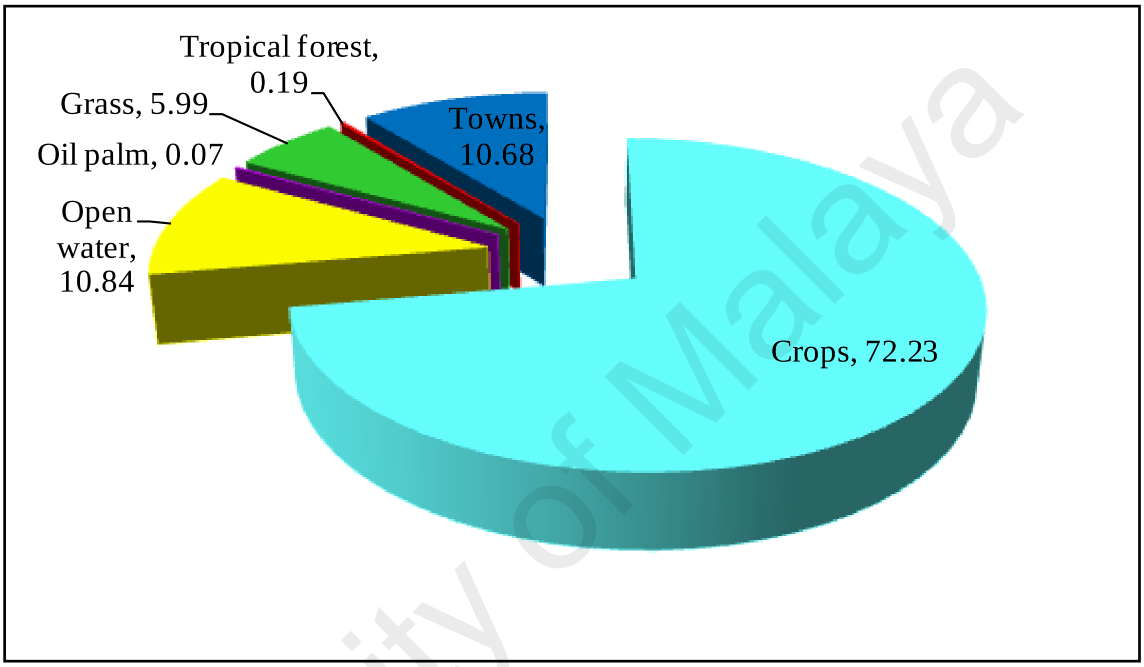


Figure 2.11: Percentage of Surface Types in Kelantan River Basin

While Figure 2.12 shows the distribution of annual PE in combination with all types of surface. The mean annual PE is 1037.12 mm/year, where 1990 shows the highest rate (1153.15 mm/year) while 1984 shows the lowest rate of PE (942.92 mm/year).

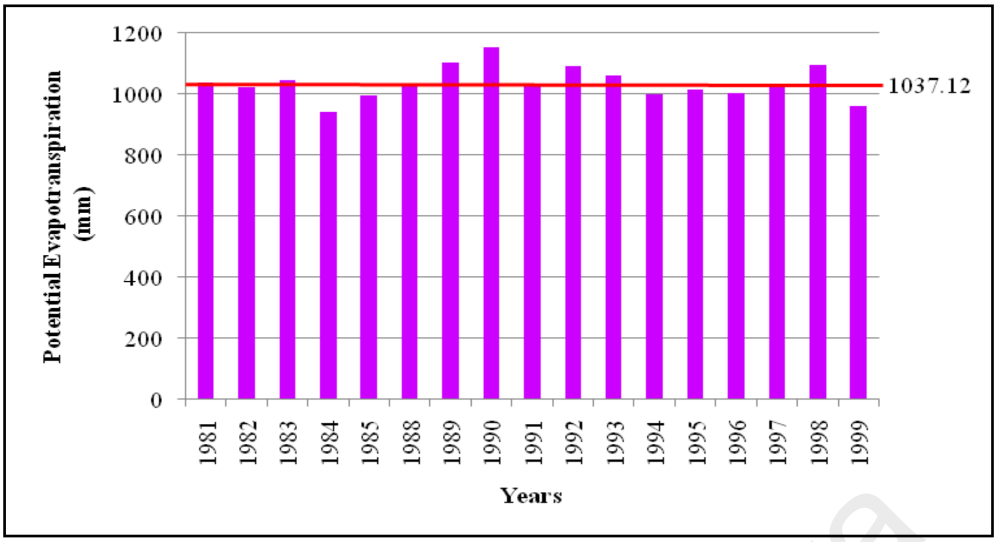


Figure 2.12: Annual Distribution of Potential Evapotranspiration (PE) with Mean Annual of 1037.12 mm/year

River Discharge

River discharge from Guillemard Bridge is used to estimate the discharge for Kelantan River Basin. The mean annual river discharge from 1979-2008 is 486.26 m^3/s as shown in Figure 2.13. The highest discharge rate is during 1994 (678.84 m^3/s) while the lowest discharge rate is during 2002 (319.16 m^3/s).

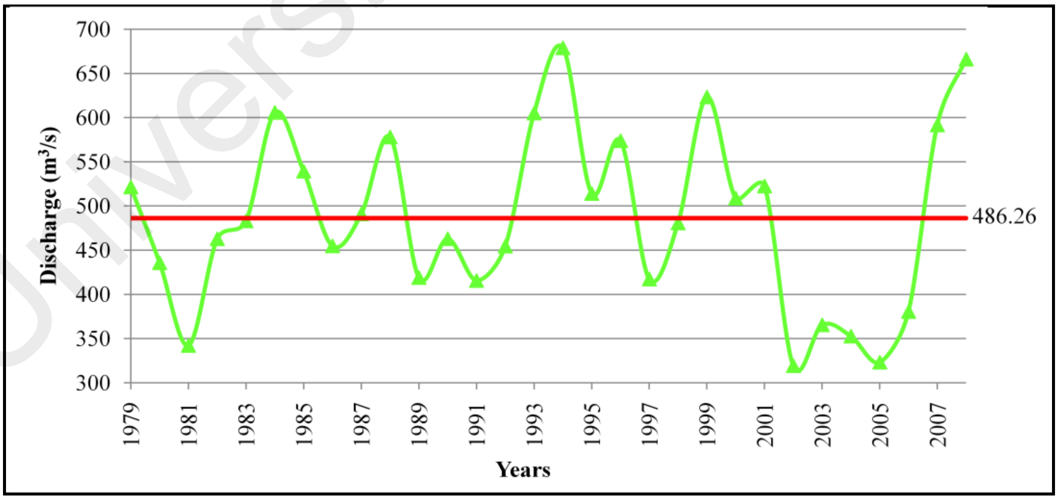


Figure 2.13: Annual River Discharge at Guillemard Bridge (1979-2008) with Mean Values of 486.26 m^3/s.

Based on river discharge data (daily discharge), a river hydrograph has been plotted for a 30 years period timespan as shown in Figure 2.14. According to this river hydrograph, the total flow is 168.52 trillion m^3/year and the mean flow is 5.62 trillion m^3/year as given in Table 2.7.

Baseflow Index

Baseflow is one of the components in hydrograph that reacts slowly to rainfall and is usually associated with water discharge from groundwater storage. Table 2.7 shows the estimated yearly baseflow value. The total baseflow for 30 years is 91.70 trillion m^3/year with mean value of 5.92 trillion m^3/year. Based on the total baseflow and total flow values, the baseflow index (BFI) of the Kelantan River Basin can be estimated using Equation 2.4. Table 2.8 shows that the baseflow index (BFI) is 0.54.

Table 2.8: Baseflow Index (BFI) of North Kelantan River Basin

Data	**Volume (trillion m^3/year)**
Total Baseflow	91.70 trillion
Total flow	168.52 trillion
Baseflow index (BFI)	0.54

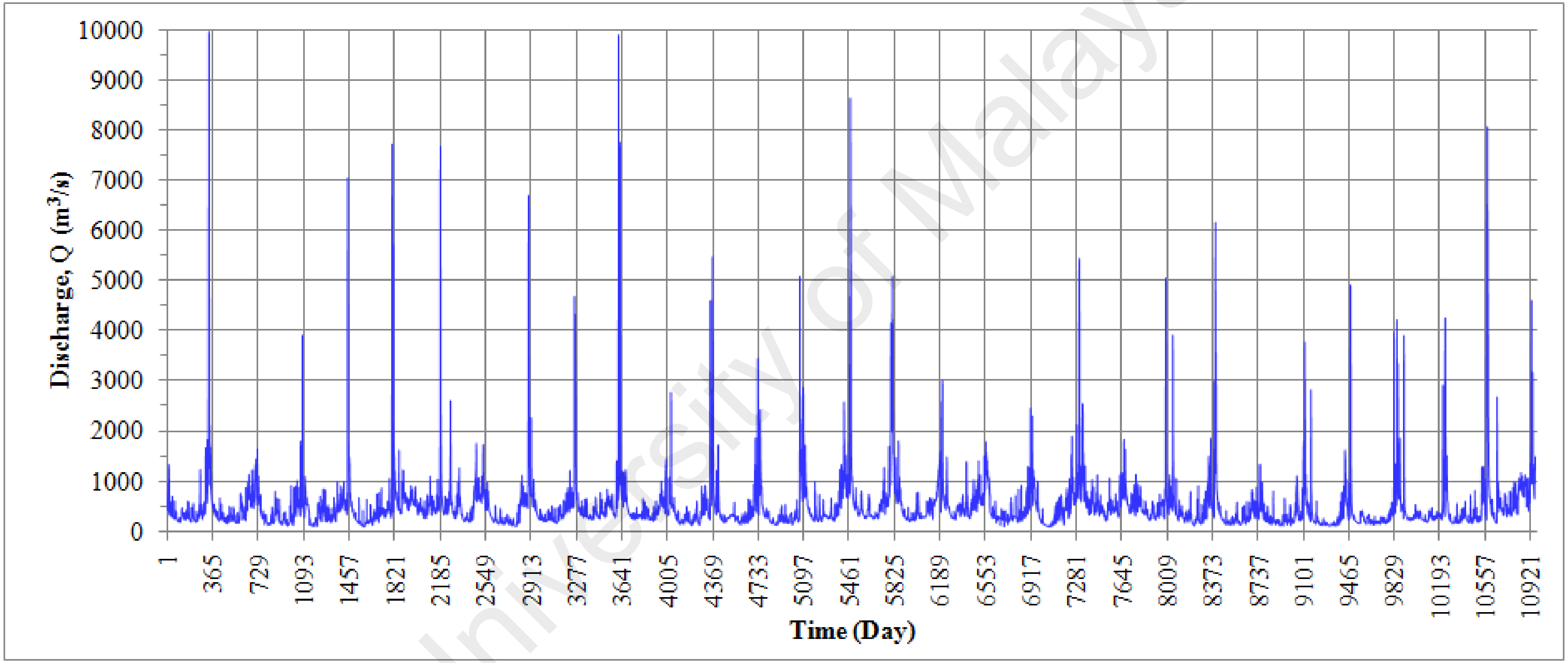


Figure 2.14: Discharge Hydrograph at Guillemard Bridge from 1979 – 2008

Table 2.7: Yearly Total Flow and Baseflow

Year	**Total flow (trillion m^3/year)**	**Baseflow (trillion m^3/year)**
1979	5.99	2.77
1980	5.05	2.82
1981	3.94	1.96
1982	5.36	2.83
1983	5.61	2.10
1984	7.01	4.37
1985	6.22	3.98
1986	5.27	2.56
1987	5.68	3.04
1988	6.68	2.99
1989	4.84	3.10
1990	5.34	3.37
1991	4.83	2.37
1992	5.23	5.12
1993	7.00	3.75
1994	7.80	4.53
1995	5.94	3.65
1996	6.62	4.43
1997	4.82	3.90
1998	5.62	2.49
1999	7.11	3.56
2000	5.87	3.20
2001	6.05	2.55
2002	3.67	2.09
2003	4.23	1.63
2004	4.08	1.46
2005	3.74	1.52
2006	4.35	2.18
2007	6.87	2.04
2008	7.70	5.34
Total	**168.52**	**91.70**
Mean	**5.62**	**3.06**

Water Balance

The total areal weighted precipitation is estimated using the Thiessen Polgyon method based on four stations is 2600.78 mm/year as given in Table 2.9. Then, the water balance for the Kelantan River Basin is determined based on Equation 2.2 and has been summarized in Table 2.10. For Kelantan River Basin, the water balance shows positive value of changes in storage with 3.27 billion m^3/year. The groundwater recharge for this basin is equivalent to this value.

Table 2.9: Calculated Average Areal Precipitation using the Thiessen Polygon Method

Station Name	Mean Annual Precipitation (mm/year)	Percent of Total Area	Area (m^2)	Area (ratio)	Areal Weighted Precipitation
Tumpat Railway Station	2393	16	172260489	0.16	388.46
Pasir Mas Pump House	2715	39	413151187	0.39	1057.06
Teratak Pulai	2600	26	278855004	0.26	683.24
Sultan Ismail Petra Airport	2544	19	196892957	0.19	472.03
Total	**10252**	**100**	**1061159637**	**1**	**2600.78**

Table 2.10: Water Balance Data for Kelantan River Basin

Data		Value (billion)	Percentage (%)
Area (m^2)	11900 km^2		
Precipitation (m^3/year)	2600.78 mm/year	30.95	100
Potential evapotranspiration (m^3/year)	1037.12 mm/year	12.34	40
Discharge (m^3/year)	486.53 m^3/s	15.33	50
Δ± Changes in storage (m^3/year)		3.27	11

2.3.4 Hydrogeology

The investigation on hydrogeology and geophysical in Kelantan was started in 1974 as mentioned in Chapter 1. The investigation was done first in the eastern part followed by the western part of Kelantan River. According to Chong & Tan (1986), in total more than 240 of test wells and observation wells had been constructed in the eastern part while 8 wells were drilled in Tumpat Area as the investigation continued in the western part (Ang &Kwan, 1979).

Based on geoelectric profile and well drilling, Kelantan River basin is covered by a thickness sequence of Quaternary deposits (Seet, 1987). The thickness is up to 200 m to the coast. This unconsolidated quaternary alluvium is underlain by Mesozoic granites but in some localities metamorphic rocks are encountered as bedrock. This deposits form an aquifer system in North Kelantan. The thickness of the aquifer is different according to the location. This aquifer is separated by an impervious clay layer with soft, blue grey clay and shells (Pfeiffer & Tieddemann, 1979). Three layers of aquifer have been identified (e.g. Ang & Loh, 1975; Noor, 1979; Chong & Tan, 1986; Pfeiffer & Tieddemann, 1986; Mohammad, 1992; Mohammad & Ang, 1996 and Hamzah *et al.*, 1997).). Layer 1 lies at depth from the ground surface to approximately 20 m. The Layer 2 lies at depth of 20 to approximately 50 m while the Layer 3 lies at depth of more than 50 m. In some places Layer 4 has also been recognized. Layer 1 consists of fine light brownish sand with grey clay and shell. Layer 2 consists of light grey, medium to coarse sand. Coarse sand with fine to medium gravel was found in Layer 3.

Hydrogeological fence diagram of North Kelantan has been constructed (Mohammad & Ang, 1996) as shown in Figure 2.15. This fence diagram separated

North Kelantan into two aquifer system; shallow and deep aquifer. Shallow aquifer refers to Layer 1 while deep aquifer refers to Layers 2 and 3. The thick sequence of alluvium can been seen in the eastern part of the Kelantan River compared to the western part. The impervious clay layers form an aquitard and aquiclud. In certain location, this clay form as lenses shape. In certain places, the shallow and deep aquifers have shown some hydraulic connection (GSD, 1993). The shallow aquifer received recharge from infiltration of precipitation, leakage from river and consumer pipe. Meanwhile, deep aquifer received recharge from shallow aquifer and surface runoff from the foot hill.

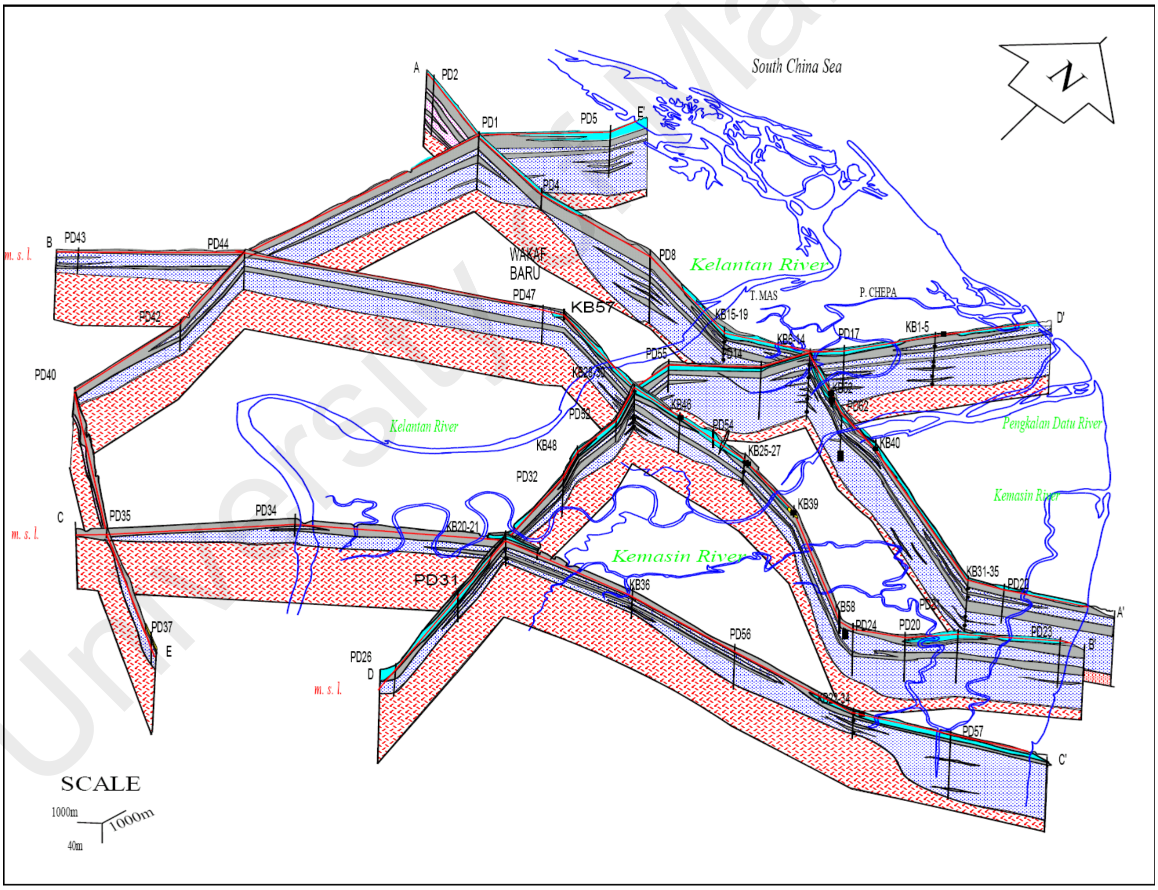


Figure 2.15: Hydrogeological Fence Diagram (Adapted from Mohammad & Ang, 1996)

The aquifer properties have been studied based on pumping test data. In total eleven localities has been selected for pumping test where six was done by Geological Survey (now MGD) and the rest by Binnie and Partners. Test conducted by MGD lasted two to five days while duration was shorter for Binnie & Partners with a maximum of 9 hours. Table 2.11 and 2.12 presents the aquifer properties (Transmissivity, Permeability and Storage) conducted by MGD and Binnie & Partners (Noor, 1979). This value was calculated using a different method as noted in the table.

According to MGD, the permeability of the aquifer ranges from 28 m/day to 337 m/day, transmissivity ranges from 336 m^2/day to 9431 m^2/day and the specific yield is 0.06. Whilst, for Binnie & Partner the range permeability, transmissivity and specific yield is 52.7 m/day to 500 m/day, 305 m^2/day to 4593 m^2/day and 0.20, respectively. Pumping test carried out on 21 test wells indicated that the mean transmissivity for Layers 1, 2 and 3 are 1200 m^2/day, 1440 m^2/day and 1320 m^2/day, respectively whilst the mean permeability for Layers 1 and 2 is 130 m/day and Layer 3 is 86 m/day (Pfeiffer and Tiedemann, 1986).

The existance of the hydraulic continuity between the shallow and lower (deep) aquifer has been demonstrated at Kg. Chap, Bachok (Noor, 1979). Pumping test was done at BH56 while the drawdown was observed in observation wells located 200 m to the west of the test well. The test indicates that the observation wells installed at different depths were affected by the pumping test. Test carried out at Kota Bharu Waterwork did not reveal any connection between shallow and deep aquifer (Pfeiffer and Chong, 1979). Therefore, whether or not the continuity is uniform throughout the basin is still to be determined. However, based on lithology of the alluvium, widespread continuity is assumed to exist between shallow and lower (deep) aquifer (Noor, 1979).

Table 2.11: Aquifer Properties (Transmissivity, Permeability and Storage) by MGD

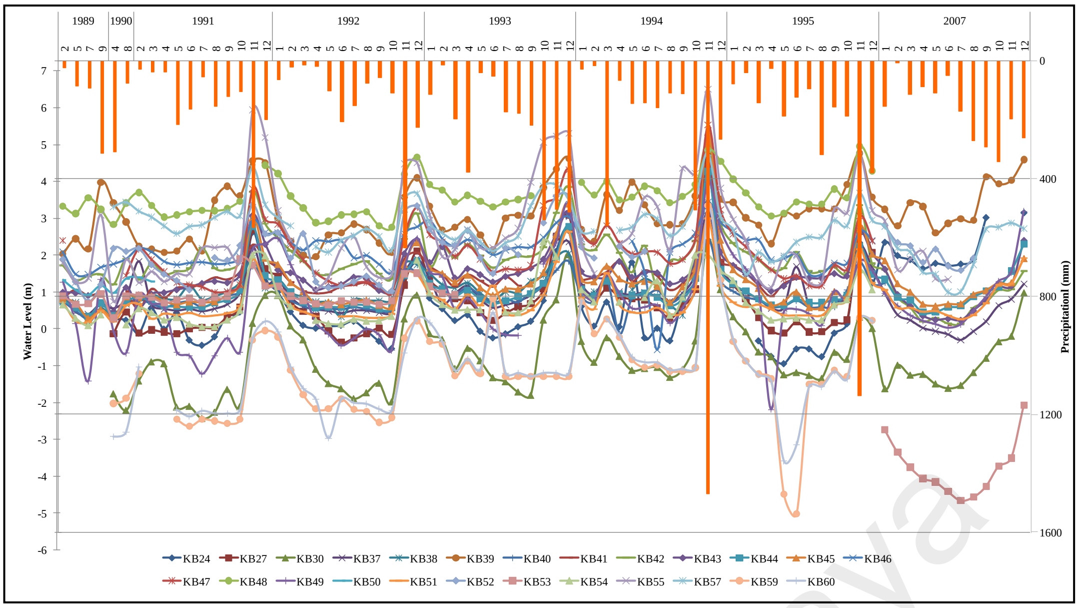
Location	Well No.	Saturated Thickness (m)	Method	Tranmissivity (m^2/d)			Permeability (m/d)			Storage		
				Early		**Late**	**Early**		**Late**	**Early**		**Late**
Pasir Puteh	Ob15	12	Boulton	763		654	64		54	1.90×10^{-3}		6.30×10^{-2}
	Ob10			509		488	42		41	8.80×10^{-2}		2.20×10^{-1}
	Ob32					336			28			3.60×10^{-2}
	Ob45					347			29			2.20×10^{-1}
	Ob70					395			33			9.90×10^{-2}
			Distance-drawdown		834			69.5				
Wakaf Baru, Tumpat	Ob10	11	Boulton	1693		1693	154		154	2.00×10^{-2}		
	Ob15			1299		1082	118		98	1.11×10^{-2}		
	Ob22			3710		3710	337		337	1.90×10^{-3}		4.40×10^{-3}
	Ob45			3387		2798	308		254	1.90×10^{-3}		3.80×10^{-2}
	Ob70			1855		1558	167		142	1.31×10^{-3}		1.77×10^{-1}
			Copper & Jacob		7791			708				
	Ob22				9431			857				
Gong Manok	Ob74	11.5	Walton		754			65.5			6.70×10^{-4}	
	Ob10				817			71			2.70×10^{-3}	
Kota Bharu	Ob20	8.4	Theis	1376		2353	164		280	6.70×10^{-2}		1.40×10^{-2}
Kg. Chap, Bachok	Ob50	17	Walton		4236			249			5.70×10^{-4}	
	Ob115				4604			271			1.70×10^{-4}	
	Ob10				3222			190			3.22×10^{-3}	
	Ob35				3966			233			5.90×10^{-4}	
	Ob23				4958			292			2.70×10^{-4}	
Tumpat	Ob10	11.2	Copper & Jacob		2449			219			6.90×10^{-4}	
	Ob15				2654			237			2.60×10^{-4}	
	Ob10		Theis		2769			247			2.90×10^{-3}	
	Ob15				2769			247			3.30×10^{-4}	
	Ob15		Recovery		3733			333			3.30×10^{-4}	
	Ob10				3584			320			3.30×10^{-4}	
			Distance-drawdown		2274			203			1.60×10^{-3}	

Table 2.12: Aquifer Properties Data (Transmissivity, Permeability and Storage) by Binnie & Partners

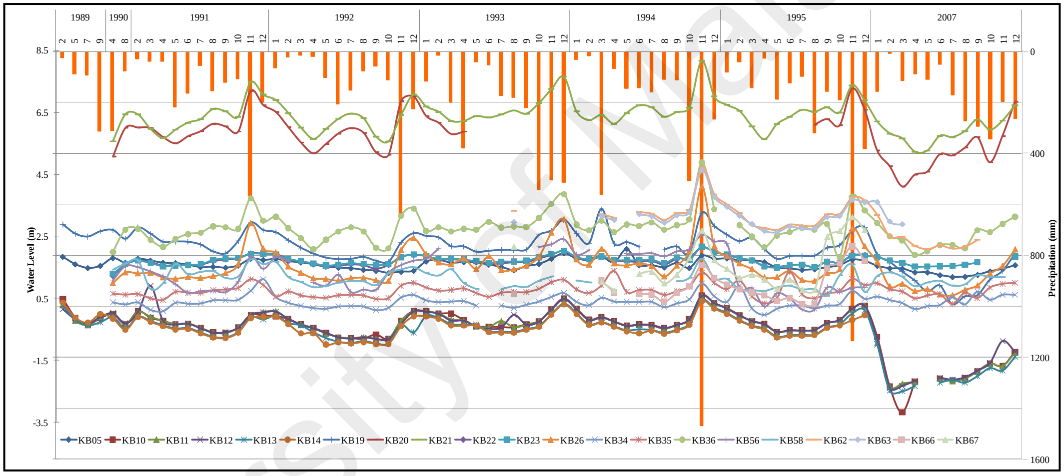
Location	Well No.	Method	Tranmissivity (m^2/day)	Permeability (m/day)	Storage
Bachok	B17	Copper & Jacob	343	52.7	2.00×10^{-2}
	B19		305	52.7	1.60×10^{-1}
Wakaf Che Yeh	B10		3752	492	4.50×10^{-1}
Kota Bharu	B3		4593	500	2.00×10^{-1}

Groundwater Level

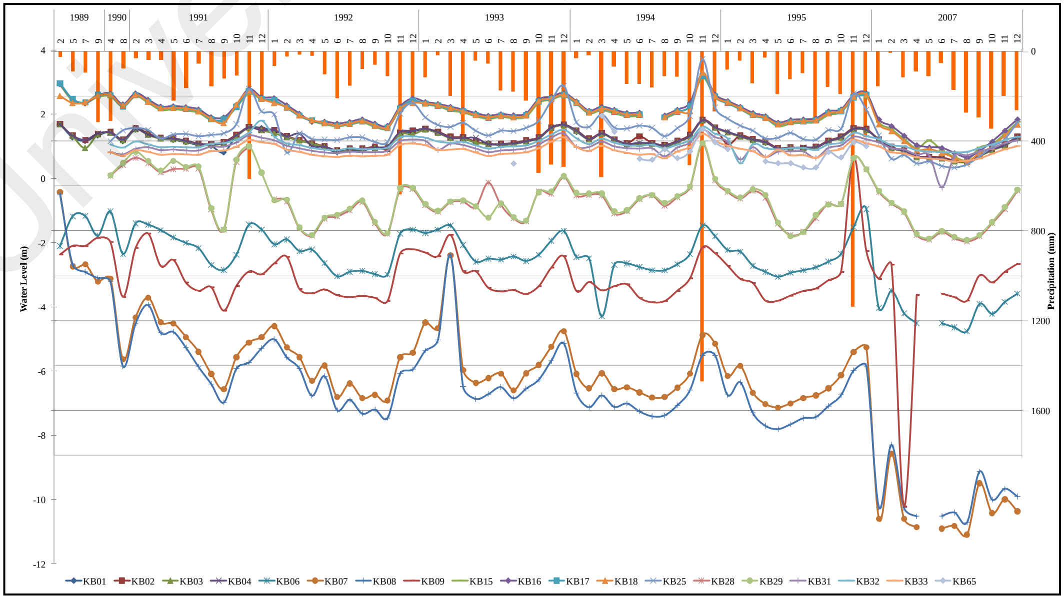
The pattern of groundwater level is strongly influence by precipitation and infiltration rate through the aquifer layers. Figure 2.16 shows the fluctuation of groundwater level in Layers 1, 2 and 3. In general, all wells in Layers 1, 2 and 3 show similar patterns in fluctuation of groundwater level. As seen from the figure, the fluctuations of groundwater levels from month to another occurred following the fluctuation of the monthly precipitation where high fluctuation occurred during north east monsoon that brings high precipitation in North Kelantan area. The highest reading of groundwater water level has been recorded in the month of November while the lowest in the month of February. The fluctuation of groundwater ranges from 0.47 – 8.36 m, 0.87 – 3.76 m and 0.87 – 10.89 in Layers 1, 2 and 3, respectively as show in Table 2.13 – 2.15.



a) Layer 1



b) Layer 2



c) Layer 3

Figure 2.16: Groundwater Level (a), (b) and (c) in North Kelantan River Basin

Table 2.13: Fluctuation of Groundwater Level in Layer 1

Well	Groundwater level (m)		
	Minimum	**Maximum**	**Fluctuation**
KB24	-0.95	3.41	4.36
KB27	-0.37	4.89	5.26
KB30	-2.44	2.42	4.86
KB37	-0.31	3.21	3.52
KB38	0.18	2.04	1.86
KB39	1.96	5.12	3.16
KB40	-0.13	2.43	2.56
KB41	0.11	4.59	4.48
KB42	0.14	5.10	4.96
KB43	0.23	4.15	3.92
KB44	0.34	4.27	3.93
KB45	0.29	5.34	5.05
KB46	-0.57	3.43	4.00
KB47	0.96	5.53	4.57
KB48	2.75	4.95	2.20
KB49	-2.19	3.99	6.18
KB50	0.92	1.39	0.47
KB51	0.18	3.00	2.82
KB52	0.75	3.60	2.85
KB53	-4.66	1.90	6.56
KB54	0.06	2.37	2.31
KB55	0.74	6.50	5.76
KB57	1.00	4.77	3.77
KB59	-5.02	3.34	8.36
KB60	-3.59	3.22	6.81

Table 2.14: Fluctuation of Groundwater Level in Layer 2

Well	Groundwater level (m)		
	Minimum	**Maximum**	**Fluctuation**
KB05	1.19	2.09	0.90
KB10	-3.17	0.59	3.76
KB11	-2.35	0.58	2.93
KB12	-2.39	0.91	3.30
KB13	-2.50	0.44	2.94
KB14	-0.99	0.41	1.40
KB19	0.31	3.38	3.07
KB20	4.11	7.26	3.15
KB21	5.23	8.17	2.94
KB22	1.23	2.15	0.92
KB23	1.29	2.16	0.87
KB26	0.60	4.10	3.50
KB34	-0.03	1.12	1.15
KB35	0.32	1.39	1.07
KB36	1.83	4.88	3.05
KB56	0.15	2.55	2.40
KB58	0.58	1.78	1.20
KB62	2.09	4.73	2.64
KB63	2.63	4.63	2.00
KB66	0.32	2.18	1.86
KB67	0.76	3.11	2.35

Table 2.15: Fluctuation of Groundwater Level in Layer 3

Well	Groundwater level (m)		
	Minimum	**Maximum**	**Fluctuation**
KB01	0.53	1.79	1.26
KB02	0.53	1.82	1.29
KB03	0.51	1.80	1.29
KB04	0.53	1.81	1.28
KB06	-4.76	-0.95	3.81
KB07	-11.10	-0.42	10.68
KB08	-10.72	-0.48	10.24
KB09	-10.22	0.67	10.89
KB15	0.57	3.14	2.57
KB16	0.65	3.26	2.61
KB17	1.58	3.19	1.61
KB18	0.52	3.29	2.77
KB25	0.34	3.72	3.38
KB28	-1.96	1.07	3.03
KB29	-1.92	1.11	3.03
KB31	-0.28	1.51	1.79
KB32	0.47	1.80	1.33
KB33	0.52	1.39	0.87
KB65	0.34	1.95	1.61

2.4 Discussion

2.4.1 Geology

Quaternary deposit of alluvium covered the whole North Kelantan River Basin. The alluvium thickness is surmissed to extend more than 200 m towards the coastal area with unconsolidated to semi consolidated gravel, sand, clay and silts. These Quaternary alluviums are classified into Holocene and Pleistocene deposits. The Holocene deposits consist of Gula Formation while Pleistocene deposits consist of Simpang Formation.

The deposition environment of Gula Formation is shallow marine to estuarine and is divided into two sub member; Matang Gelugor Member and Port Weld Member. The thickness is approximately more than 40 m and is underlain by Simpang Formation. The deposition environment of Simpang Formation is fluvial and mostly exposed in the center part of the basin with the presence of plants fossil.

Granite and metamorphic rocks form as bedrocks on these alluvium deposits. Granite exposed in the basin as granite hills known as Bukit Marak and Bukit Kechik.

2.4.2 Hydrology

Understanding river basin hydrology is important in order to manage and develop the basin. Certain elements in the hydrology cycle are very useful key factors for basin study especially for the Kelantan River Basin.

Baseflow is one of the important characters of basin hydrology. According to Lacey and Grayson (1998), baseflow is affected by geology in two ways; direct (groundwater is stored in the rocks, especially if they are highly fractured and this contributes to baseflow) and the formation of soil (different type of rocks tend to produce different types and depth of soil under the influence of weathering, plant action, etc). Hence, differences in recharge, groundwater and baseflow occur.

The baseflow index (BFI) represents the slow or delayed contribution to river flow. This may be influenced to a significant extent by basin geology (Bloomfield *et al.*, 2009). The result indicates that the BFI of the basin is 0.54. This value is affected by diverse geological, morphological and climatological aspects of the basin. For the whole basin, 70% of the river flow is on the hard rock especially in the upper part of basin. Only 30% of the basin river flows through the alluvium deposits in the lower part of the basin. More water flow as runoff in the upper part (only small amount will infiltrate through cracks) rather than infiltrating into the aquifer in the lower part of the basin. Therefore the main interaction between surface water and groundwater only occurs at the lower part that is covered by a thick sequence of alluvium. This relationship also has been demonstrated (Nathan *et al.*, 1996; Sefton and Howarth, 1998; Mwakalila *et al.*, 2002; Mwakalila, 2003; Abebe & Foerch, 2006 and Santhi *et al.*, 2008) in their region.

The basin received precipitation of 30.95 billion m^3/year. High intensity of precipitation was usually received during northeast monsoon (See Figure 2.10). The potential evapotranspiration shows that water loss in the basin is about 40% (12.34 billion m^3/year) with runoff coefficient generated about 50%. The estimated value of recharge received is 11% (3.27 billion m^3/year) according to the water balance analysis. This water surplus will eventually recharge the aquifer system during the dry season (February - October) and this storage will maintain the river flow of Kelantan River. It also indicates that this storage is useful in the development of water resources program that will minimize risk and mismanagement and hence will lead to proper utilization of the resource now and in the future.

2.4.3 Hydrogeology

The thick sequence of alluvium deposits in North Kelantan form an aquifer system. Three layers aquifer have been identified; Layer 1, Layer 2 and Layer 3 with depth of approximately 20 m, 20 m to approximately 50 m and more than 50 m, respectively. Layer 1 also known as unconfined to semi-confined aquifer (shallow aquifer) while Layers 2 and 3 are known as deep aquifers. These layers are separated by semi permeable clay layer and have hydraulic connection between the shallow and deep aquifers but the uniform of continuity is still undetermined.

The permeability, transmissivity of the aquifer ranges from 28 m/day to 337 m/day, 336 m^2/day to 9431 m^2/day with specific yield is 0.06. The groundwater level fluctuation in Layer 1, Layer 2 and Layer 3 ranges from 0.47 – 8.36 m, 0.87 – 3.76 m and 0.87 – 10.89 in Layers 1, 2 and 3, respectively.

2.4.4 Conceptual Model

Based to the geology, hydrology and hydrogeology information gained from this study, the conceptual model of North Kelantan River basin has been constructed as shown in Figure 2.17. This model summarizes all the components contributing to the hydrology cycle in the study area.

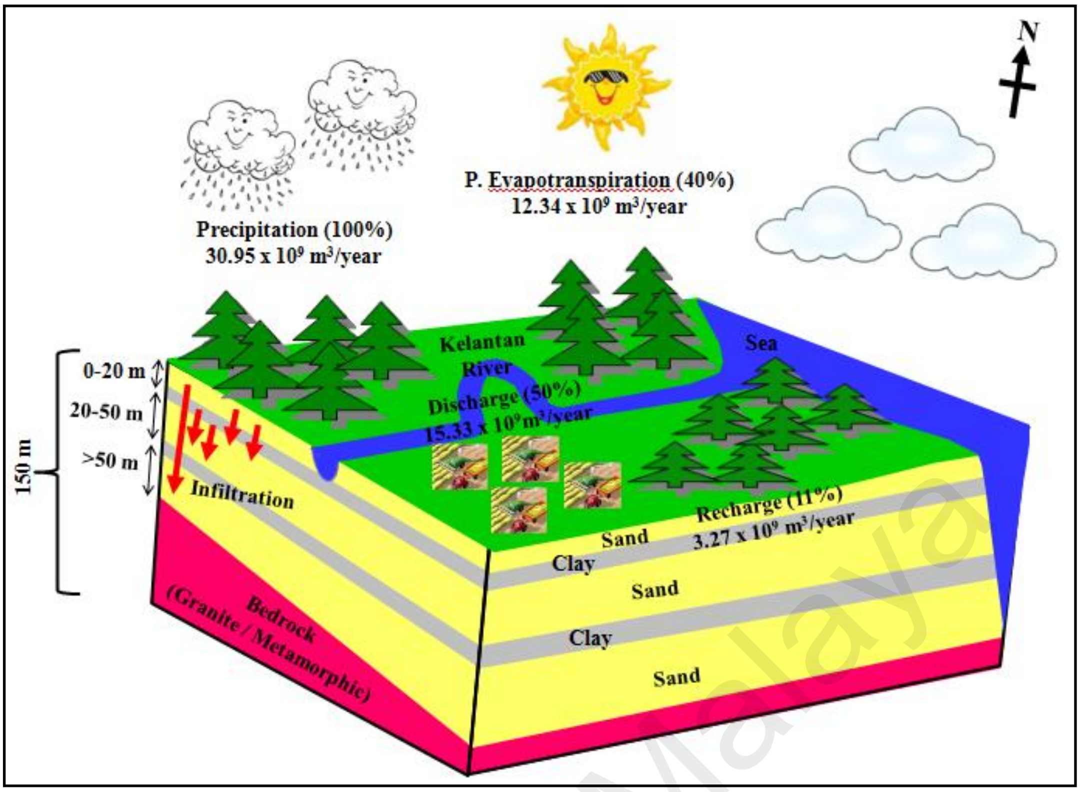


Figure 2.17: The Conceptual Model of North Kelantan River Basin

CHAPTER 3

HYDROGEOCHEMISTRY

3.1 INTRODUCTION

The hydrogeochemistry of North Kelantan groundwater is influenced by the chemistry of groundwater and its relations to the regional geology. Therefore, hydrochemical data are very useful to give a better understanding of this relationship. Apart from that, the status of groundwater quality in the basin has also been carried out.

Hydrochemical facies will be used to represent the hydrochemical data. This hydrochemical facies describes a group of groundwater with similar composition, and each facies typically has unique origin and/or pattern of evolution (Freeze and Cherry, 1979). For example, groundwater might be assigned to different hydrochemical facies if they are hosted by aquifers of differing lithology or degree of confinement. It provides some insight into the environmental processes that have affected a site in the past, and might be continue to do so in the future (Christopher & Robert, 2005). The process involves dissolution, precipitation, ion exchange and mixing. For North Kelantan groundwater, discussions of groundwater origin and evolution are based on the aquifer layers.

3.1.1 Physical Parameters (‘*in-situ’*)

Physical parameters include pH, temperature (°C), conductivity (Cond) and total dissolved solids (TDS). These parameters are usually measured in the field during sampling activity. Table 3.1 summarized some of the physical parameters.

Table 3.1: Summary of Physical Parameters

Parameters		Remarks	Reference
Physical	pH	▪ measure of hydrogen ion concentration $[H^+]$ $pH = -\log_{10}[H^+]$ ▪ main sources of hydrogen ions in natural waters (hydrolysis/dissociation/oxidation)	Hounslow (1995)
	Temperature (°C)	▪ measure of hotness expressed in Fahrenheit, Celsius or Kelvin	Britannica.com
	Color (H.U)	▪ classified according to the Hazen colour scale. ▪ The highest quality drinking water should be colourless. ▪ contributors of colour to natural water (inorganic constituents/ dissolved organic substances/ suspended particulate matters)	MOH Pakistan (2006)
	Turbidity (N.T.U)	▪ caused by suspended matter, such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, plankton and other microscopic organisms	MOH Pakistan (2006)
	Electrical Conductivity (uS/cm)	▪ measurement of the ability of material to conduct an electrical current. ▪ EC ≈ A (TDS) ▪ Unit; siemens (S) or microsiemens (µS)	Freeze and Cherry (1979) or.water.usgs.gov
	Total dissolved solid (mg/L)	▪ measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form	Freeze and Cherry (1979)
	Hardness ($CaCO_3$)	▪ sum of ions which can precipitate as “hard particles” from water ▪ expressed in meq/L or mg $CaCO_3$/L ▪ Total hardness = $2.5(Ca^{2+}) + 4.1(Mg^{2+})$ ▪ depends on pH and alkalinity, above 200 mg/L result in scale deposition, particularly on heating.	Appelo & Postma (2005)

For this study, selected physical parameters; pH, Conductivity, total dissolved solids and hardness were analyzed and discussed briefly.

3.1.2 Chemical Parameters

Chemical parameters; cations and anions are analyzed to determine the constituents in groundwater. In typical water, the major ions existing in solution are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-} and CO_3^{2-}. These major ions usually compose more than 95% of the TDS in most natural waters (Fitts, 2002). Other minor species commonly present in water include NO_3^-, F^-, Br^-, Si^{2+}, Ba^{2+}, Fe^{2+}, Li^+ and PO_4^{3-} (Hounslow, 1995). Table 3.2 shows a common classification of aqueous species.

Table 3.2: Major, Minor and Trace Constituents of Water
(Hounslow, 1995; Fitts, 2002 and Pipkin *et al.*, 2005)

Major constituents (>5 mg/L)	**Minor constituents (0.01 - 5 mg/L)**	**Trace constituents (<0.01 mg/L)**
Sodium (Na^+)	Strontium (Sr^{2+})	Aluminium (Al^{3+})
Calcium (Ca^{2+})	Iron (Fe^{2+}, Fe^{3+})	Arsenic (As^{2+})
Magnesium (Mg^{2+})	Carbonate (CO_3^{2-})	Barium (Ba^{2+})
Potassium (K^+)	Fluoride (F^-)	Bromide (Br^-)
Chloride (Cl^-)	Nitrate (NO_3^{2-})	Cadmium (Cd^{2+})
Sulfate (SO_4^{2-})	Boron (B^{3+})	Manganese (Mn^{2+})
Bicarbonate (HCO_3^-)		Zinc (Zn^{2+})
Dissolved CO_2 (H_2CO_3)		Copper (Cu^{2+})
		Selenium (Se^{2+})

According to Freeze and Cherry (1979), the constituents listed in Table 3.2 are controlled by the availability of the elements in the soil and rock through which the water passes. Major factors influencing this include geochemical constraints such as solubility and adsorption, the rate (kinetics) of geochemical processes and the sequence in which water has come into contact with the various minerals occurring in the geologic materials along the flow-path. Man-made sources also contribute to the cause of minor or trace elements. Table 3.3 summarizes the chemical parameters and their natural sources of selected cation and anion.

Table 3.3: Summary of Chemical Parameters

Parameters		**Remarks**	**Reference**
Chemical	Sodium	▪ Source: halite (NaCl), sea spray, brine, some silicate ▪ Usually results from natural ion exchange	Hounslow (1995)
	Calcium	▪ Source: calcite, aragonite, dolomite, gypsum, fluorite, plagioclase ▪ Usually affects soil quality	
	Potassium	▪ Source: potash feldspar, mica	
	Magnesium	▪ Source: dolomite, olivine, amphibole, pyroxene ▪ The main sink is montmorillonite ▪ In saline water, $MgCl_2$ is a major sink	
	Iron	▪ Exists as reduced ferrous Fe(II) or oxidized ferric Fe(III)	
	Manganese	▪ Source: pyrolusite, impurity with iron oxide, silica and carbonate ▪ Form as Mn(II) and Mn(IV)	
	Chloride	▪ Source: halite, sea spray, brines and hot spring ▪ Common sink only evaporates ▪ Naturally occurring in deep aquifer or caused by pollution (sea water/brine/industrial and domestic wastes)	
	Sulfate	▪ Source: pyrite, gypsum, anhydrite ▪ Common sink; pyrite, gypsum and sulfate reduction	
	Nitrate	▪ Primary source is atmospheric nitrogen gas ▪ Diffuse to groundwater as non-point source	

3.2 METHODOLOGY

For hydrogeochemical study, long term data from 1989 to 2006 were used for analysis and interpretation studies. Data was obtained from the Groundwater Monitoring Programmed carried out by Minerals and Geoscience Department, Malaysia (MGD).

3.2.1 Software

To evaluate the data, hydrochemical analysis and interpretation was done using Aquachem software version 5.1. This software was developed specifically for graphical and numerical analysis and modeling of water quality data. It features a fully customizable database of physical and chemical parameters and provides a comprehensive selection of analysis tools, calculations and graphs for interpreting water quality data to interpret the hydrochemical facies.

Furthermore, Aquachem features a built-in link to the popular geochemical modeling program PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution. This software is useful in the deduction of rock-water interaction.

3.2.2 Hydrochemical Facies

Hydrochemical facies for North Kelantan groundwater was interpreted by Piper Diagram using Aquachem software. These diagrams were plotted based on the ionic concentration of miliequivalent of major cations and anions to evaluate the geochemical characteristics of the groundwater. The projection of the point in the central diamond-shaped field revealed the heterogeneity of the groundwater chemical composition in this area (Silva-Filho, 2007). Four basic conclusions can be derived from multiple analyses plotted on Piper diagram. These were water type, precipitation or solution, mixing and ion exchange (Hounslow, 1995).

3.2.3 Saturation Index

Groundwater was typically makes simultaneous intimate contact with several solid mineral phases. Because mineral-solute reactions are slow and because water encounters varying assemblages of minerals as it flows, groundwater are rarely in perfect equilibrium with the mineral solids that surround it. Water may dissolve minerals from the matrix, or it may precipitate minerals and adds mass to the matrix (Fitts, 2002).

In any solution where the concentrations of these ions are known, their product may be calculated. This number was called the ion activity product (IAP). The number obtained may be compared to the solubility product of a mineral of interest. The comparison takes the form of log of the ratio, which is called the saturation index, SI (Hounslow, 1995). The details are explained in Table 3.4.

$SI = \log(IAP)/K_{sat}$

Table 3.4: Saturation Index

SI	Notation	Remarks
$SI = 0$	$IAP = K_{sat}$	the water is saturated with the mineral phase
$SI > 0$	$IAP > K_{sat}$	the water is oversaturated with respect to the mineral phase and will tend to precipitate
$SI < 0$	$IAP < K_{sat}$	the water is under saturated with respect to the mineral phase and will tend to dissolved more of the mineral if it is present.

3.2.4 Rock Source Deduction

Rock source deduction is based on the ion ratios and total dissolved solids found in the samples. These results can be used to determine the type of minerals the water samples has been in contact with during its subsurface journey or to deduce the possible origin of the water samples.

3.3 RESULTS

Physical and chemical parameters of groundwater in Layers 1, 2 and 3 are shown in Table 3.5. The standard value by WHO (2008), MOH (1992) and INWQS is given in the table for comparison of drinking water quality.

3.3.1 Physical parameters.

Temperature, °C

The mean temperature values are 29.07 °C, 29.66 °C and 30.63 °C in Layers 1, 2 and 3, respectively as stated in Table 3.5. In term of aquifer layers, the groundwater shows normal range of temperature values for tropical monsoon climate in Malaysia.

pH

The mean pH values are 5.91 (ranges of 4.50 to 7.90), 6.33 (ranges of 4.00 to 8.5) and 6.07 (ranges of 2.90 to 7.60) in Layers 1, 2 and 3, respectively as stated in Table 3.5. General distribution of pH in Layers 1, 2 and 3 are shown in Figure 3.1. The distributions are based on well location according to the groundwater flow from inland towards the sea. In general, all layers show slightly acidic chemical reaction within the groundwater system. Only KB 67 in Layer 2 shows slightly alkaline pH value of 7.88.

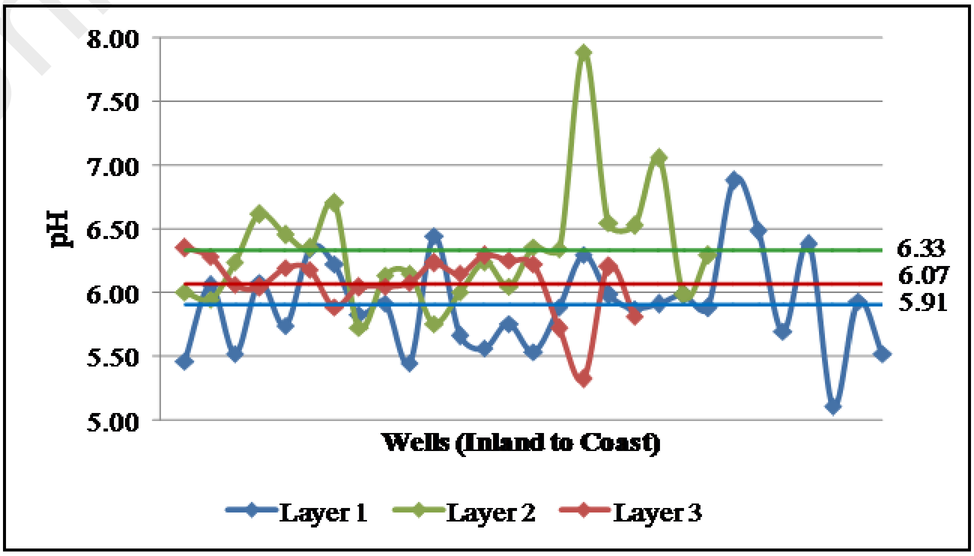


Figure 3.1: pH Value in Layers 1, 2 and 3

Table 3.5: Physical and Chemical Parameters in Layers 1, 2 and 3.

Parameters		WHO(2008)/MOH(1992)$^{\#}$/INWQS*		Layer 1 (n=29)				Layer 2 (n=22)				Layer 3 (n=19)			
				Mean	**Minimum**	**Maximum**	**Stdev**	**Mean**	**Minimum**	**Maximum**	**Stdev**	**Mean**	**Minimum**	**Maximum**	**Stdev**
Physical Parameters		Temperature (°C)		29.07	20.30	33.20	0.51	29.66	27.70	32.90	0.22	30.63	26.70	33.90	0.29
		pH(F)	6.5-9.5	5.91	4.50	7.90	0.19	6.33	4.00	8.50	0.12	6.07	2.90	7.60	0.21
		pH(L)	6.5-9.5	6.55	0.80	9.70	0.27	6.71	0.80	8.90	0.19	6.20	2.20	8.40	0.36
		Colour (H.U)	15	5.11	4.00	**60.00**	2.54	5.92	4.00	**70.00**	5.74	4.95	4.00	5.00	0.08
		Turbidity (N.T.U)	15	**28.34**	0.10	**1898.00**	77.20	**59.53**	0.30	**1580.00**	66.54	**51.92**	0.60	**1241.00**	48.60
		Electrical Conductivity (µS/cm) (F)	1000000*	153.22	44.00	460.00	28.45	1277.77	5.00	13520.00	576.76	393.61	84.00	2780.00	138.52
		Electrical Conductivity (µS/cm) (L)	1000000*	141.54	36.00	1855.00	71.86	1268.13	50.00	12770.00	393.97	356.61	20.00	2140.00	88.61
		Total Solid (mg/L)		158.70	14.00	2034.00	109.79	889.76	56.00	7112.00	549.21	237.44	15.00	1676.00	58.77
		Total Dissolved Solids (mg/L)	1000	95.19	12.00	468.00	20.59	721.31	34.00	**6784.00**	263.48	199.93	26.00	**1532.00**	59.75
Chemical Parameters	Cations (mg/L)	Ca^{2+}		9.61	1.00	95.00	5.86	27.27	0.90	201.00	11.07	12.56	0.50	49.00	2.85
		Mg^{2+}	150$^{\#}$	3.72	0.50	20.00	1.18	22.50	0.40	**204.00**	12.88	8.36	0.30	36.00	1.28
		Na^{+}	200	13.45	0.80	108.00	7.25	**202.96**	4.30	**2200.00**	146.24	28.50	1.30	**450.00**	16.71
		K^{+}		3.21	0.70	16.00	0.84	10.66	1.00	67.00	2.98	9.57	2.00	40.00	1.90
		As^{2+}	0.01	**0.02**	0.01	**0.34**	0.02	0.01	0.01	**0.09**	0.01	0.01	0.01	**0.07**	0.00
		Al^{3+}	0.2	**0.79**	0.10	**23.00**	3.80	0.14	0.10	**0.60**	0.06	0.16	0.10	**1.00**	0.11
		NH_4^{+}	1.5$^{\#}$	0.68	0.02	**13.00**	0.99	1.13	0.02	**17.00**	1.18	0.55	0.02	**12.00**	0.71
		Fe_{total}	0.3	**5.33**	0.10	**61.00**	3.40	**14.11**	0.20	**48.00**	1.89	**16.56**	0.10	**80.00**	4.36
		Mn^{2+}	0.1	**0.49**	0.10	**19.00**	1.42	**0.42**	0.10	**11.00**	0.60	**0.27**	0.10	**1.20**	0.04
		Cu^{2+}	2	0.11	0.10	0.50	0.05	0.10	0.10	0.10	0.00	0.10	0.10	0.20	0.02
		Pb^{2+}	0.01	0.02	0.01	**0.13**	0.01	0.02	0.01	**0.09**	0.01	0.02	0.01	0.05	0.00
		Zn^{2+}	3	0.17	0.10	1.60	0.22	0.36	0.10	**4.30**	0.85	0.66	0.10	**8.50**	1.81
		Sr^{2+}		0.09	0.01	0.60	0.06	0.18	0.01	2.76	0.21	0.16	0.01	4.90	0.42
		Ba^{2+}	0.7	0.16	0.10	0.60	0.06	0.67	0.10	**4.80**	0.29	0.54	0.10	**6.50**	0.38
		Hg^{+}	0.006	0.001	0.000	0.002	0.000	0.001	0.000	0.002	0.000	0.001	0.000	0.002	0.000
		SiO_2		20.96	1.30	118.00	4.38	27.56	2.00	134.00	9.18	18.68	1.30	86.00	2.80
	Anions (mg/L)	CO_3^{2-}		1.90	1.00	10.00	1.57	2.48	1.00	23.00	2.20	2.34	1.00	43.00	5.74
		HCO_3^{-}		48.04	2.00	215.90	12.77	96.11	1.00	550.00	28.23	57.52	1.00	760.00	74.94
		Cl^{-}	250	16.04	1.00	223.00	19.03	**386.09**	1.00	**3950.00**	314.91	77.24	1.00	**507.00**	29.17
		SO_4^{2-}	250	7.72	1.00	82.00	5.80	8.81	1.00	**3323.00**	141.27	2.63	1.00	22.00	0.77
		NO_3^{-}	50	5.21	0.50	**54.00**	3.30	4.47	0.50	**88.00**	5.76	2.57	0.50	34.00	1.82
		F^{-}	1.5	**3.76**	0.50	**12.00**	2.75	1.48	0.10	**47.00**	8.24	0.55	0.50	**3.00**	0.28
		PO_4^{2-}	0.2$^{\#}$	0.05	0.02	**0.41**	0.03	0.14	0.02	**1.40**	0.14	0.11	0.02	**0.89**	0.17

Bold: above the standard recommendation for drinking water
n: number of wells
Stdev: standard deviation
F: field
L: laboratory

Total Dissolved Solids (TDS), mg/L

The mean TDS values in Layers 1, 2 and 3 are 95.19 mg/L (ranges of 12.00 to 468.00 mg/L), 721.31 mg/L (34.00 to 6784.00 mg/L) and 199.93 mg/L (ranges of 26.00 to 1532.00 mg/L), respectively as stated in Table 3.5. In general, all layers show mean TDS values below 1000 mg/L.

Figure 3.2 shows the pattern of mean TDS values for wells in Layers 1, 2 and 3 in accordance to the groundwater flow direction from inland towards the coastal area. In contrast with wells in Layers 1 and 3, certain wells in Layer 2 show mean TDS values above 1000 mg/L. Increase in TDS values are influenced by the chemical and biochemical interaction between groundwater and the geological materials that it flows through (Freeze and Cherry, 1979) for a longer time span. In Layer 1, high TDS also reflects with tidal effect (Kelantan River, Pengkalan Datu River and Kemasin River) and human activity at the surface; factory disposal (Pengkalan Chepa), household area (Kota Bharu), sewage, agriculture and others.

As noted in Table 3.6, TDS values above 1000 mg/L are classified as brackish water. Therefore, Layer 2 shows a mixture between fresh and brackish water. Brackish water in Layer 2 has been recognized at KB05, KB14 and KB34 with mean values of 2594.52 mg/L, 1055.34 mg/L and 6163.04 mg/L.

Table 3.6: Simple Groundwater Classification Based on Total Dissolved Solids (TDS) (Freeze & Cherry, 1979)

Category	Total dissolved solids (mg/L)
Fresh water	0-1000
Brackish water	1000-10 000
Saline water	10 000-100 000
Brine water	More than 100 000

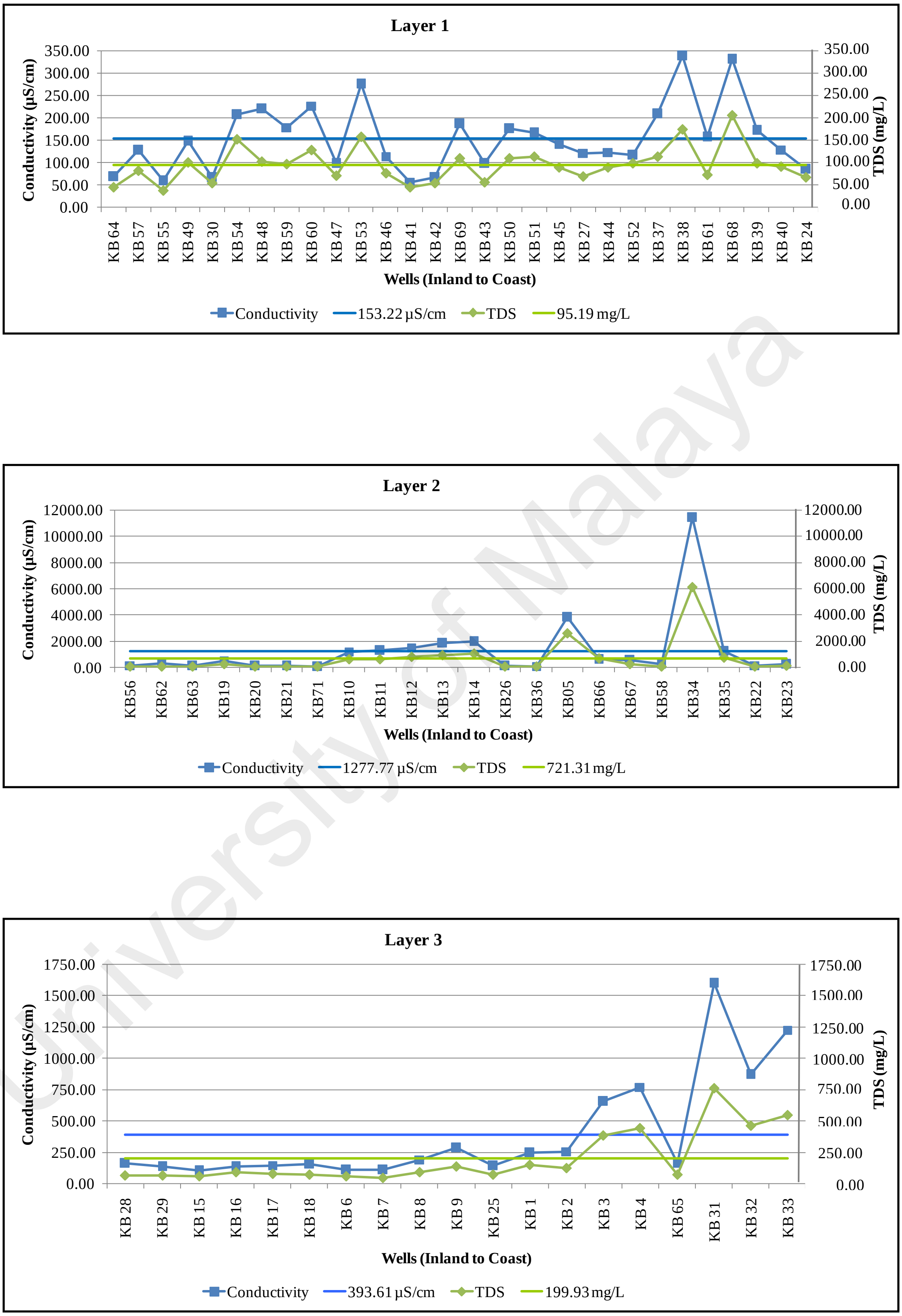


Figure 3.2: Distribution of TDS and Conductivity in Layers 1, 2 and 3

Figure 3.3 shows the mean TDS contour for wells in Layer 2. The interface between fresh water and brackish water is marked by red contour line with TDS values of 1000 mg/L. The pattern of fresh and brackish water interface in the study area is similar with the resistivity map proposed by Samsudin *et al.* (2008), enclosed in Figure 3.2. He noted that, in some inland areas between Tumpat and Bachok, the brackish water in Layer 2 can occur more than 6 km from the coast.

Electrical Conductivity (EC), µS/cm

The mean of electrical conductivity (EC) values in Layers 1, 2 and 3 are 153.22 µS/cm (ranges of 44.00 to 460.00 µS/cm), 1277.77 µS/cm (ranges of 5.00 to 13520.00 µS/cm) and 393.61 µS/cm (ranges of 84.00 to 2780.00 µS/cm), respectively as given in Table 3.5.

Figure 3.2 shows the pattern of mean EC values for wells in Layers 1, 2 and 3 in accordance to the groundwater flow direction from inland towards the coastal area. The pattern of EC values is similar to the pattern of TDS values for all Layers because EC is usually proportional with TDS. As the EC is the ability of the solution to transmit electricity and TDS is the total amount of ions in solution. Therefore the amount of TDS is proportional to the ability of aqueous solutions to conduct electricity.

Both EC and TDS in Layer 1 shows inconsistent pattern from inland toward the coast compared with Layers 2 and 3 as show in Figure 3.2. Obviously Layer 1 has been affected by tidal effect and human activity as mentioned in section 3.3.1 (total dissolved solids). It seems that ions in Layers 2 and 3 had undergone mobilization towards equilibrium with the surrounding environment and the geologic materials of the aquifer.

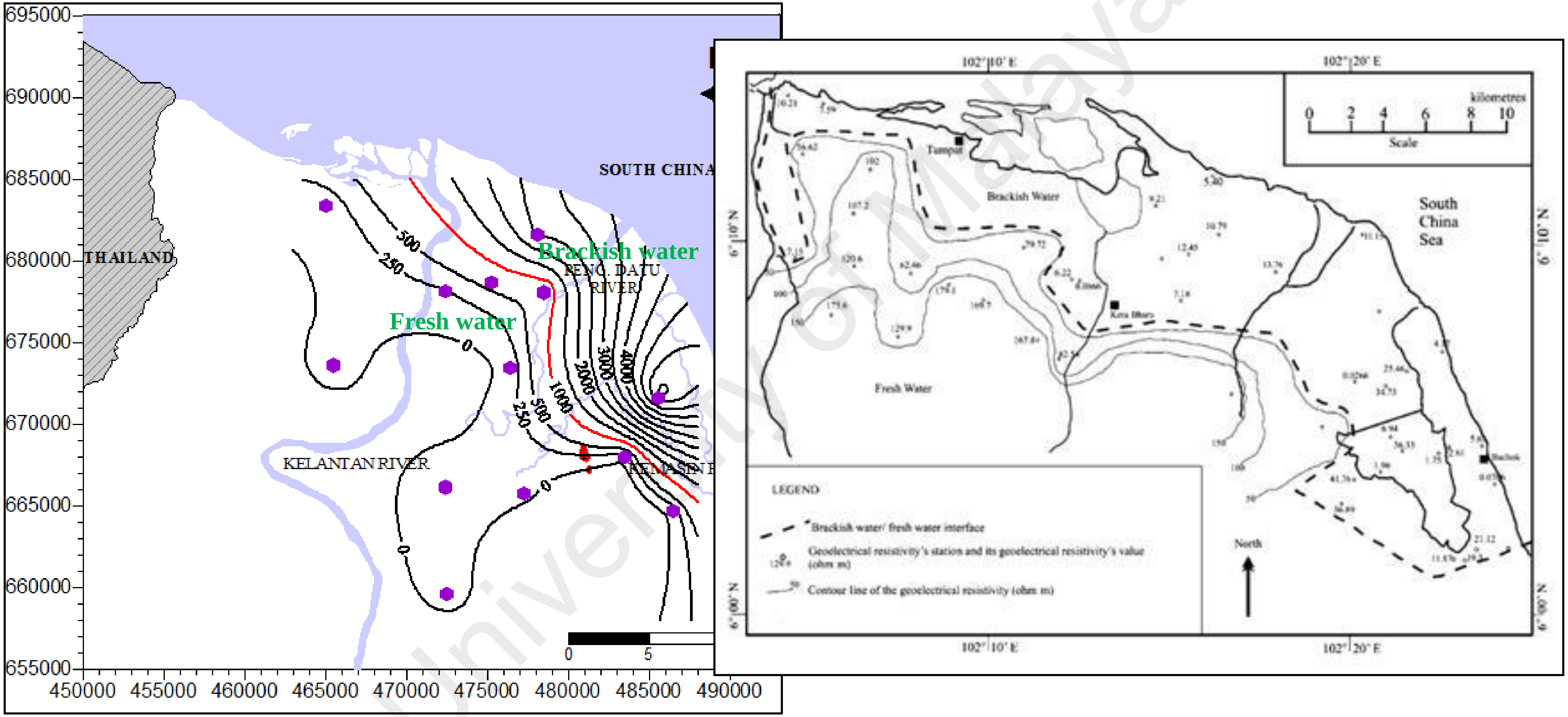


Figure 3.3: Map of TDS in Layer 2. Red Contour Line indicates the interface between Fresh Water and Brackish Water. Inlet Map shows interface between Fresh and Brackish Water using Geophysical Method by Samsudin *et al.* (2008)

High conductivity indicates high concentration of salts in water as at KB34 and KB31 in Layers 2 and 3, respectively.

3.3.2 Chemical parameters (Cations)

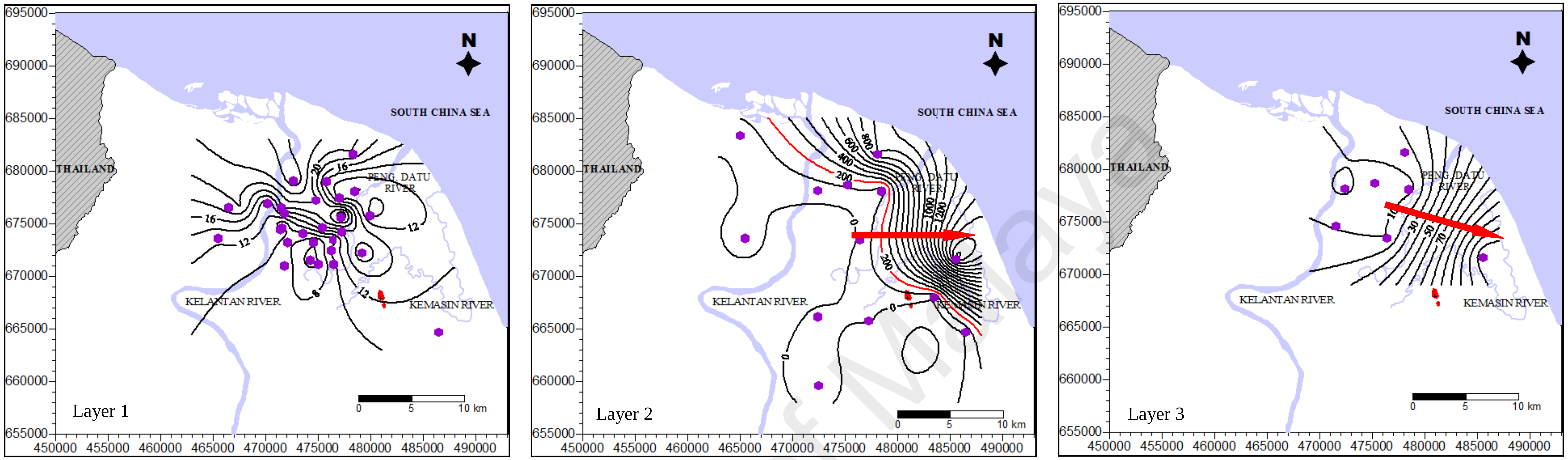
Sodium, Na^+

The mean concentrations of sodium in groundwater are 13.45 mg/L (ranges of 0.80 – 108.00 mg/L), 202.96 mg/L (ranges of 4.30 – 2200.00 mg/L) and 28.50 mg/L (ranges of 1.30 – 450.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5). KB34 in Layer 2 shows the highest concentration of sodium with 2200.00 mg/L followed by KB05 with 897.97 mg/L and KB35 with 584.04 mg/L.

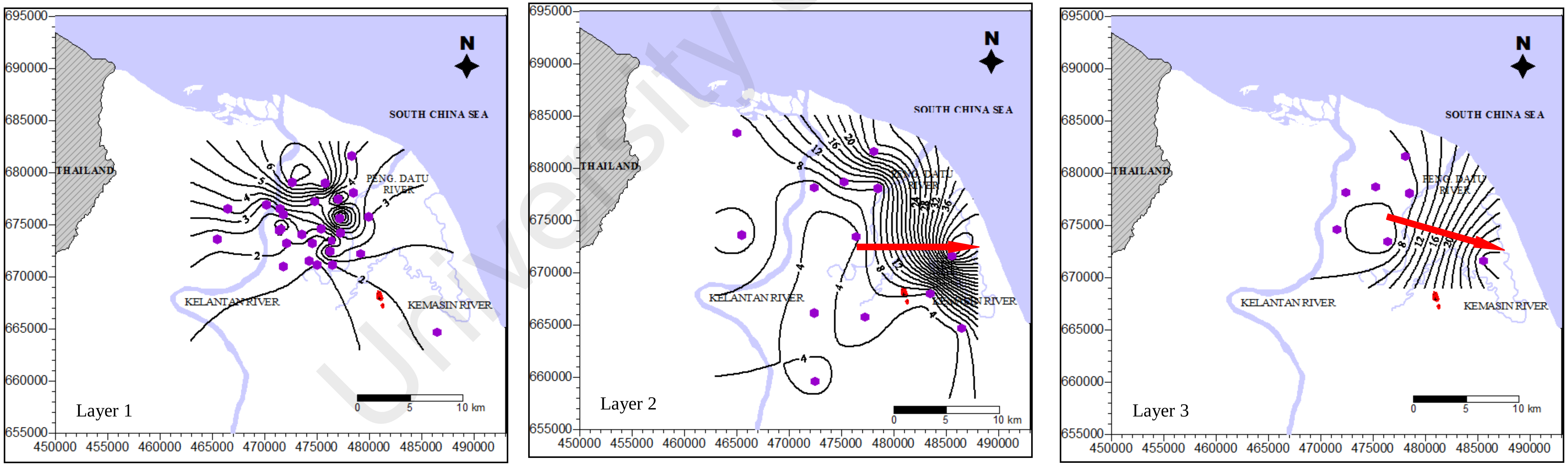
The pattern of sodium concentration contour in Layers 1, 2 and 3 is shown in Figure 3.4 (a). Obviously, Layers 1 and 3 show the mean concentration below 200 mg/L. In Layer 2, red contour line indicates the acceptable limit of sodium in drinking water as 200 mg/L. The contour pattern of sodium is also similar with TDS contour. Arrow indicates an increase in sodium values towards the sea. Layer 1 contour is affected by tidal effect from Kelantan River, Pengkalan Datu River and Kemasin River. This effect show an evidence area with high sodium is closer to the river.

Potassium, K^+

In groundwater, the concentration of potassium is low compared to sodium. The mean concentrations of potassium are 3.21 mg/L (ranges of 0.70 to 16.00 mg/L), 10.66 mg/L (ranges of 1.00 to 67.00 mg/L) and 9.57 mg/L (ranges of 2.00 to 40.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5).



a) Sodium



b) Potassium

Figure 3.4: Contour Pattern of a) Sodium; b) Potassium in Layers 1, 2 and 3

Figure 3.4 (b) shows the pattern of potassium concentration contour in Layers 1, 2 and 3. Layer 1 shows that potassium tends to concentrate in the middle of the study area at KB51 and KB38. Whilst in Layers 2 and 3 the concentration increases towards the sea as indicated by the red arrow. This pattern is similar with sodium in Layers 2 and 3. For Layer 1, the contour is reflected with agriculture activities.

Potassium is one of the main components of NPK (nitrogen: phosphorous: potassium) fertilizers used in agriculture. The usage of NPK fertilizers is dependent on the need of crop as given in Table 3.7 (Natural Resources Management and Environment Department, 2004).

Table 3.7: Recommended Fertilizer Rates for Crops on Mineral Soils

Crop	**Rates (kg/ha)**			**PPD per ha**
	N	P_2O_5	K_2O	
Paddy	90	35	25	500 (m^{-2})
Tobacco	80	205	130	17932
Rubber	109.8	163.93	281.25	450
Oil palm	128	144	200	160

PPD: plant population density

Calcium and Magnesium as Indicator for Water Hardness

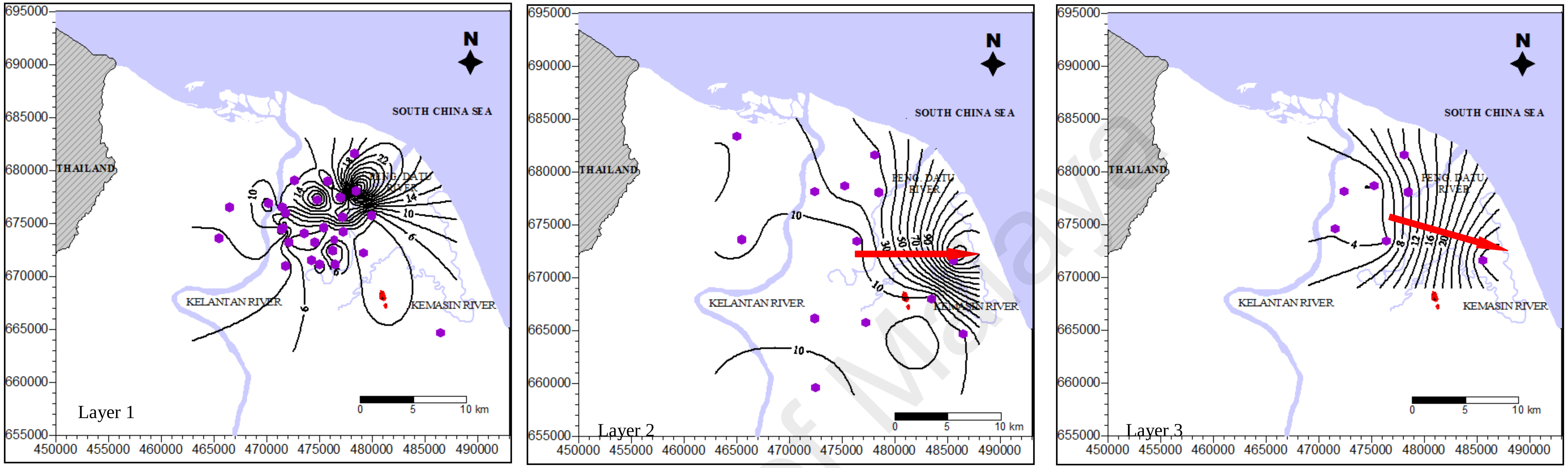
The mean concentrations of calcium in groundwater are 9.61 mg/L (ranges of 1.00 to 95.00 mg/L), 27.27 mg/L (ranges of 0.90 to 201.00 mg/L) and 12.56 mg/L (ranges of 0.50 to 49.00 mg/L) in Layers 1, 2 and 3, respectively While the mean concentrations of magnesium in groundwater are 3.72 mg/L (ranges of 0.50 to 20.00 mg/L), 22.50 mg/L (ranges of 0.40 to 204.00 mg/L) and 8.36 mg/L (ranges of 0.30 to 36.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5).

Figure 3.5 (a) and (b) shows the pattern of calcium and magnesium concentration contour in Layers 1, 2 and 3. Layer 1 shows that calcium and magnesium tends to concentrate in the middle of the study area at KB68 and KB38. Whilst in Layers 2 and 3 the concentration of calcium and magnesium increases towards the sea as indicated by the red arrow. High concentration of calcium and magnesium in Layers 2 and 3 are found at KB34 and KB4, respectively. Similar to potassium, both calcium and magnesium are used as fertilizers in agriculture. Calcium is usually used as a conditioner to improve physical condition of soil while magnesium is added as a mixture in NPK fertilizer (Natural Resources Management and Environment Department, 2004).

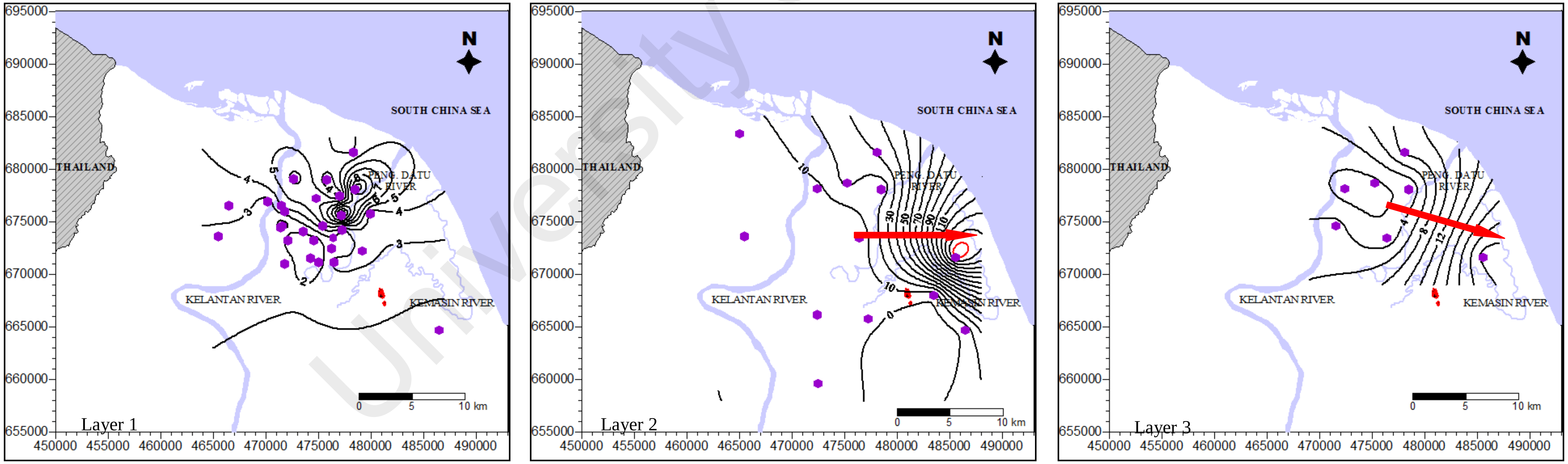
Water hardness is caused by the presence of naturally occurring calcium and magnesium in groundwater, they are dissolved as ions as water moves through soil and rocks (WSC, 2004). The total hardness values are automatically generated using Aquachem software and displayed in the samples summary report. These values have been classified according to Todd (2005) as given in Table 3.8. While Table 3.9 shows the hardness classification of groundwater in Layers 1, 2 and 3 based on Table 3.8

Table 3.8: Hardness Classification of Water (Todd, 2005)

Hardness (mg/l $CaCO_3$)	Water classification
0 – 75	Soft
75 – 150	Moderately hard
150 – 300	Hard
>300	Very hard



a) Calcium



b) Magnesium

Figure 3.5: Contour Pattern of a) Calcium; b) Magnesium in Layer 1, 2 and 3

Table 3.9: Hardness Classification in Layers 1, 2 and 3. Values in bracket are in percentage (%)

Aquifer Layer	**Hardness, mg/l $CaCO_3$ (Water classification)**			
	0 – 75 (Soft)	**75 – 150 (Moderately hard)**	**150 – 300 (Hard)**	**>300 (Very hard)**
Layer 1 (n=29)	26 (90%)	3 (10%)	-	-
Layer 2 (n=22)	12 (55%)	2 (9%)	4 (18%)	4 (18%)
Laye 3 (n=19)	14 (73%)	3 (16%)	2 (11%)	-
Total	**52 (74%)**	**8 (11%)**	**6 (9%)**	**4 (6%)**

Figure 3.6 shows the percentage of water hardness in Layers 1, 2 and 3. In general, all layers are being soft, with water hardness of 74% in the groundwater of North Kelantan. Layer 1 shows soft to moderately hard in water. Layer 2 shows all types of water hardness from soft to very hard while Layer 3 show soft to hard water hardness. Hard water exists in Layer 2 at KB5, KB10, KB11 and KB12 while Layer 3 at KB3, KB4 and KB31. Very hard water (6%) only exists in Layer 2 at KB13, KB14, KB34 and KB35.

According to Appelo and Postma (2005) high values of total hardness are related to the lithology of aquifer matrix that forms from the igneous weathering that is rich in Ca and Mg.

Iron, Fe_{total}

The mean concentrations of iron in groundwater are 5.33 mg/L (ranges of 0.10 to 61.00 mg/L), 14.11 mg/L (ranges of 0.20 to 48.00 mg/L) and 16.56 mg/L (ranges of 0.10 to 80.00 mg/L) in the Layers 1, 2 and 3, respectively (Table 3.5). High concentration of iron in Layers 1, 2 and 3 are found at KB69, KB14 and KB31, respectively.

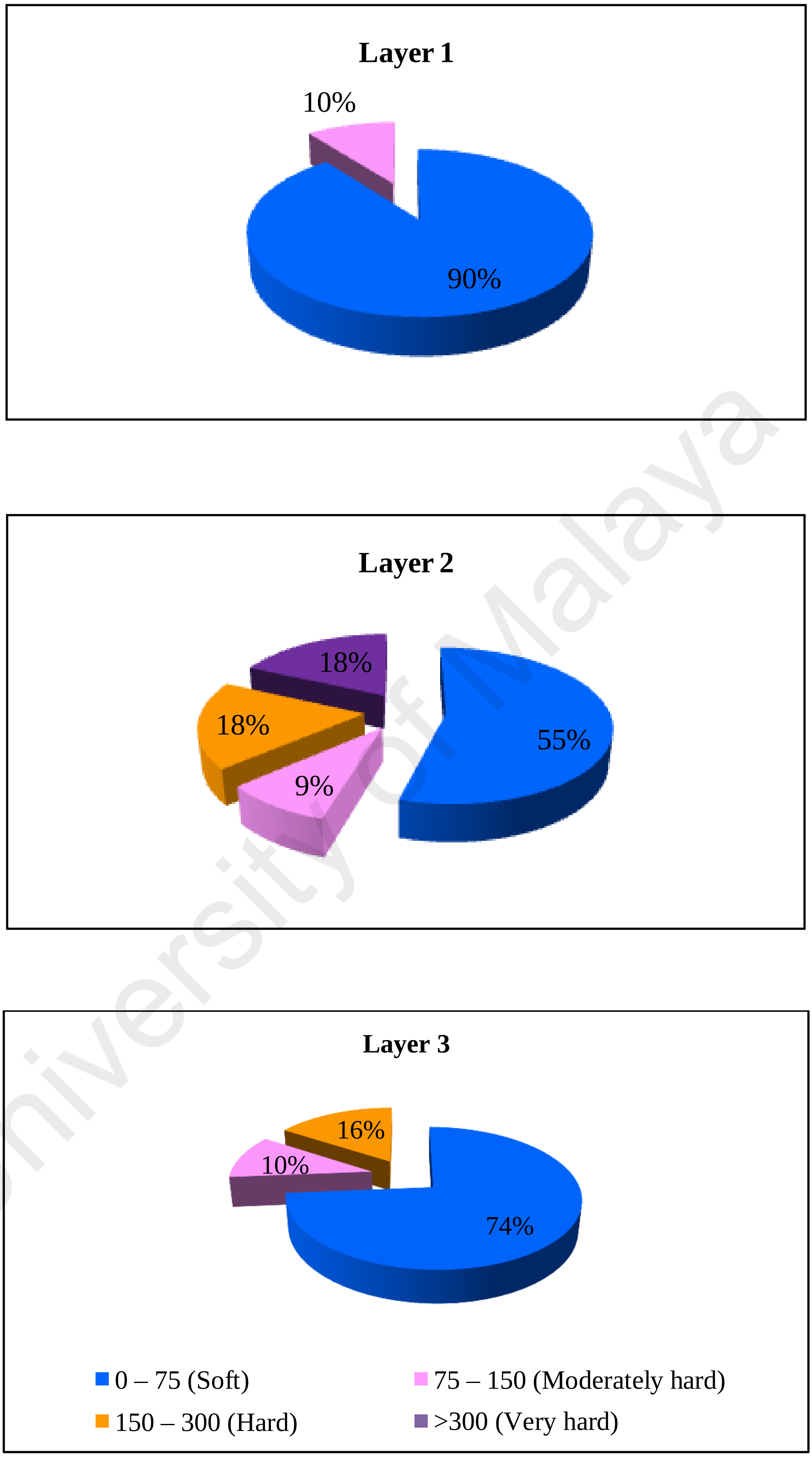


Figure 3.6: Pie Chart Percentage of Hardness in Layers 1, 2 and 3

Figure 3.7 shows the distribution of iron in Layer 1, 2 and 3. Most of the wells have iron concentration below 20.00 mg/L. All layers show mean concentration exceeds the standard value of 0.30 mg/L. High iron in groundwater is probably due to the abundant of ferromagnesian mineral from the bedrock that has undergone weathering and dissolution process.

Figure 3.8 (a) shows the pattern of iron concentration contour in Layers 1, 2 and 3. Red contour line in Layer 1 indicates the acceptable value for iron in drinking water. Iron tends to concentrate at KB69 and KB14 in Layers 1 and 2, respectively. Whilst in Layer 3 the concentration increased towards the sea as indicated by the red arrow. High concentration of iron in Layers 2 and 3 are found at KB14 and KB31, respectively.

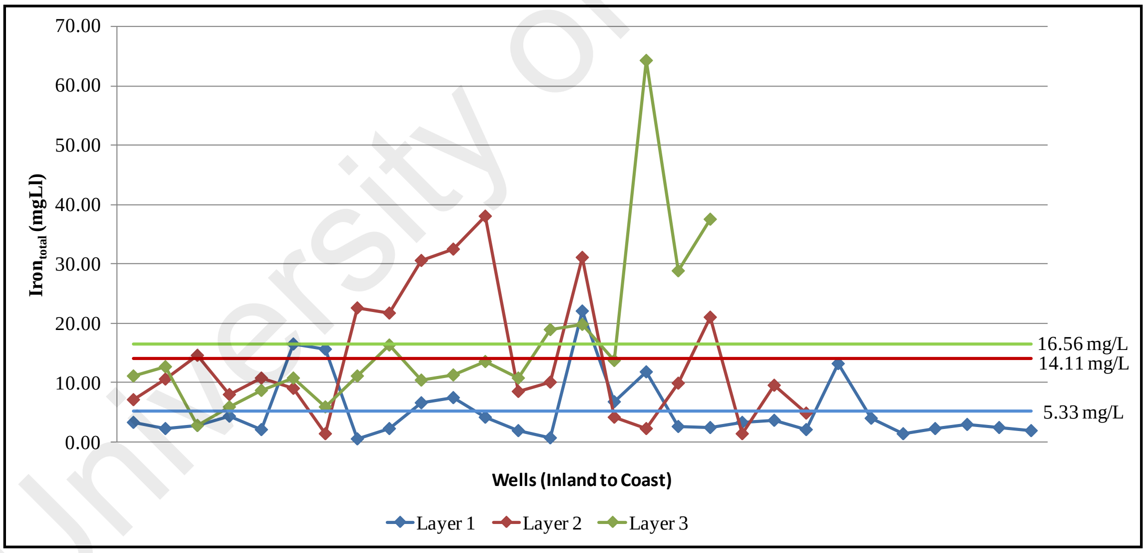
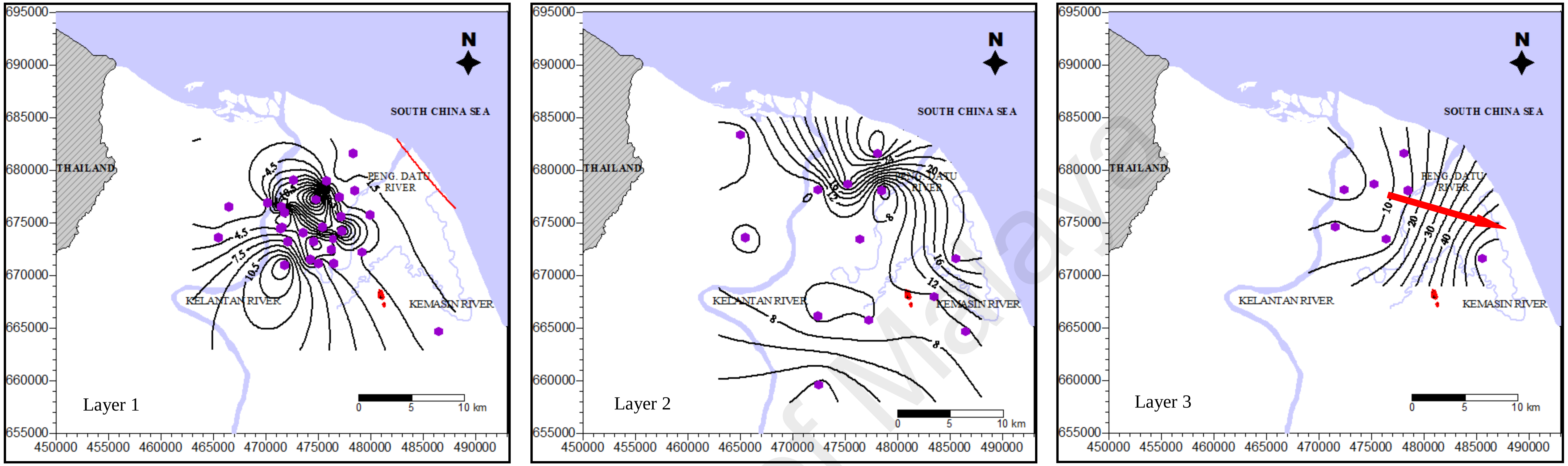
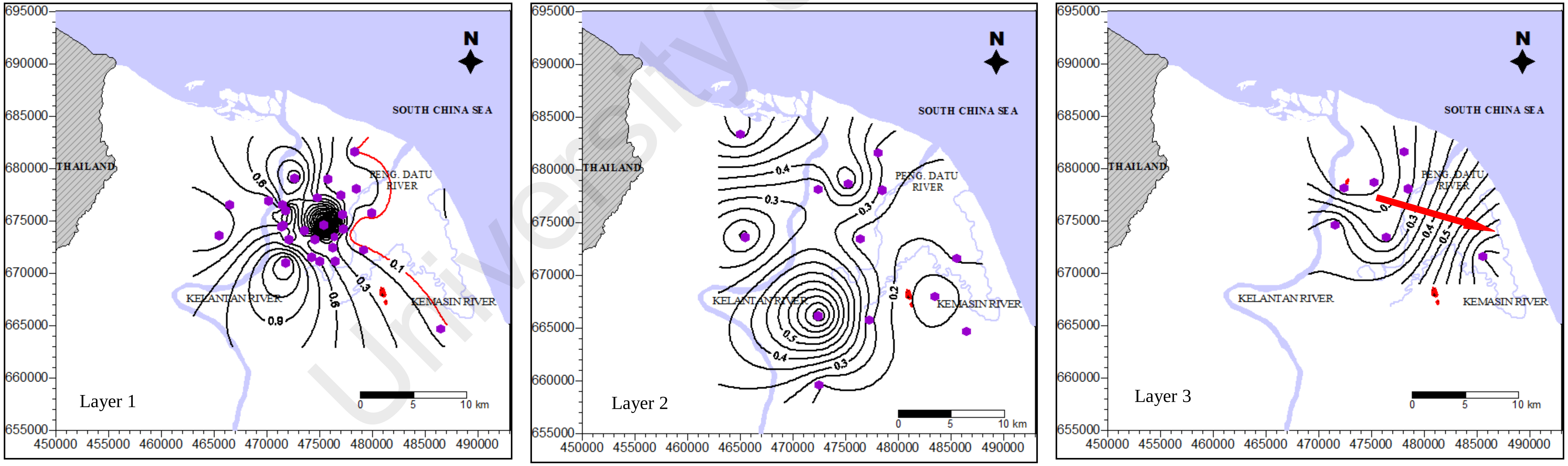


Figure 3.7: Distribution of Iron$_{total}$ in Layers 1, 2 and 3



a) Iron$_{total}$



b) Manganese

Figure 3.8: Contour Pattern of a) Iron$_{total}$; b) Manganese in Layers 1, 2 and 3.

Manganese, Mn^{2+}

The mean concentrations of manganese are 0.49 mg/L (0.10 to 19.00 mg/L), 0.42 mg/L (ranges 0.10 to 11.00 mg/L) and 0.27 mg/L (ranges of 0.10 to 1.20 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5). KB48, KB21 and KB31 show high concentration of manganese in Layers 1, 2 and 3, respectively.

Figure 3.9 shows the distribution of manganese in Layers 1, 2 and 3. Most of wells show manganese concentration below 1.00 mg/L. Only selected wells in Layers 1 and 3 show manganese concentration above 1.00 mg/L.

Figure 3.8 (b) shows the pattern of manganese concentration contour in Layers 1, 2 and 3. Red contour line in Layer 1 indicates the acceptable value for manganese in drinking water. Manganese tend to concentrate at KB50, KB14 and KB31 in Layers 1, 2 and 3 respectively. In Layer 3 the contour pattern is similar with iron where manganese concentration increases towards the sea, as indicated by the red arrow. In groundwater, manganese commonly coexist with iron but in lower concentration.

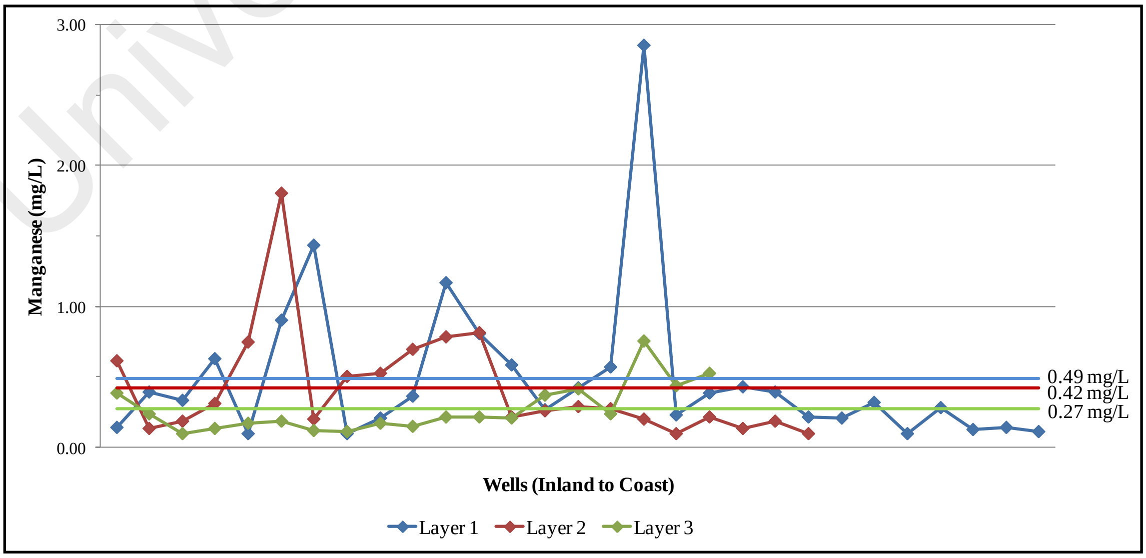


Figure 3.9: Distribution of Manganese in Layers 1, 2 and 3

Ammonium, NH_4^+

The mean concentrations of ammonium in groundwater are 0.68 mg/L (ranges of 0.02 to 13.00 mg/L), 1.13 mg/L (ranges of 0.02 to 17.00 mg/L) and 0.55 mg/L (ranges of 0.02 to 12.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5). Figure 3.10 shows the distribution of ammonium from wells in Layers 1, 2 and 3. In general, most wells show ammonium concentration below 0.65 mg/L.

Figure 3.11 shows the pattern of ammonium concentration contour in Layers 1, 2 and 3. This line also indicates the acceptable MOH (Ministry of Health, 1992) value for ammonium in drinking water of 1.50 mg/L. Only Layers 1 and 2 have ammonium concentration above the recommendation standard of MOH.

In Layer 1, high ammonium was found at KB50 (5.26 mg/L) with villages and mixed agriculture area and KB48 (3.81 mg/L) with area of paddy field plantation. High ammonium in Layer 2 are found at KB34 (6.02 mg/L) and KB35 (4.16 mg/L). Both wells are a cluster of the Beris Kubor area, which is paddy field area and close to the tobacco plantation area. High concentration of ammonium in Layer 3 is found at KB28 (1.47 mg/L). Although Layer 3 shows ammonium below the standard, action must be taken to prevent the increase of ammonium in groundwater especially non-point source of contaminant that infiltrate into the aquifer.

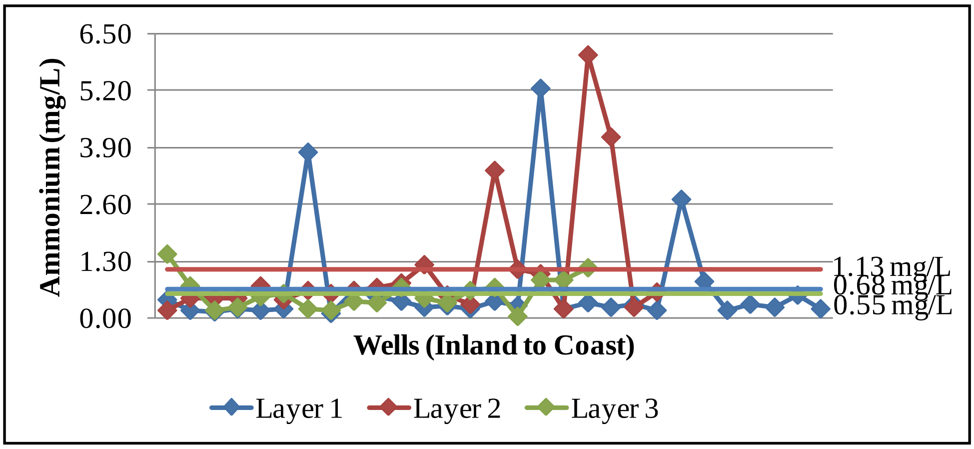


Figure 3.10: Distribution of Ammonium in Layers 1, 2 and 3

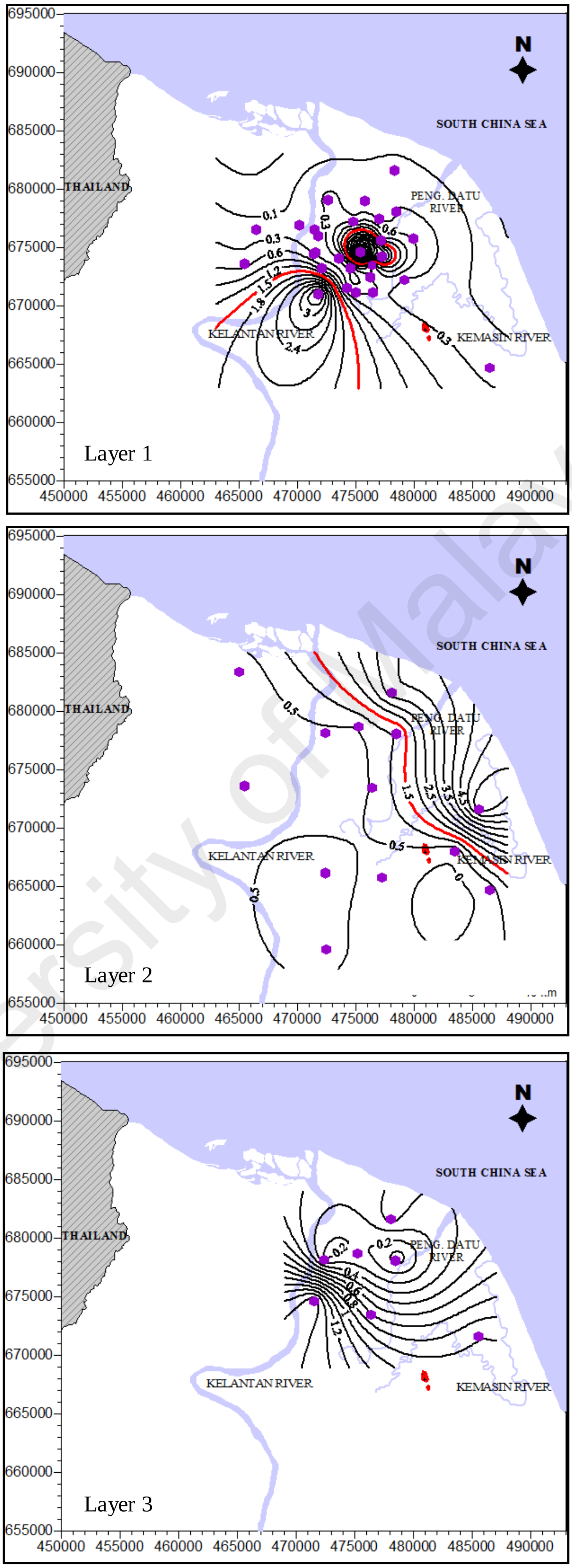


Figure 3.11: Contour Pattern of Ammonium in Layers 1, 2 and 3

Other cations

The rest of the cations such as As, Cu, Pb, Zn, Ni, Cd, Sr, Ba, Se, Hg and P are either not present or present in a very small amounts in the water samples. High amount of these cations may cause water pollution and will be hazardous if used for consumption purposes.

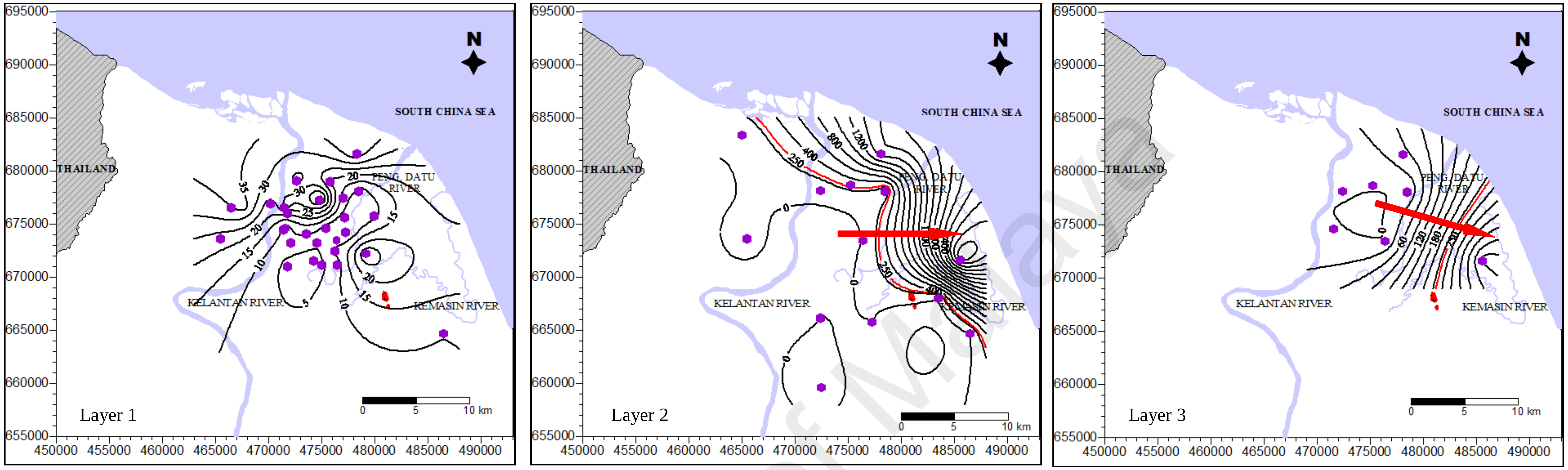
3.3.3 Chemical parameters (Anions)

Chloride, Cl^-

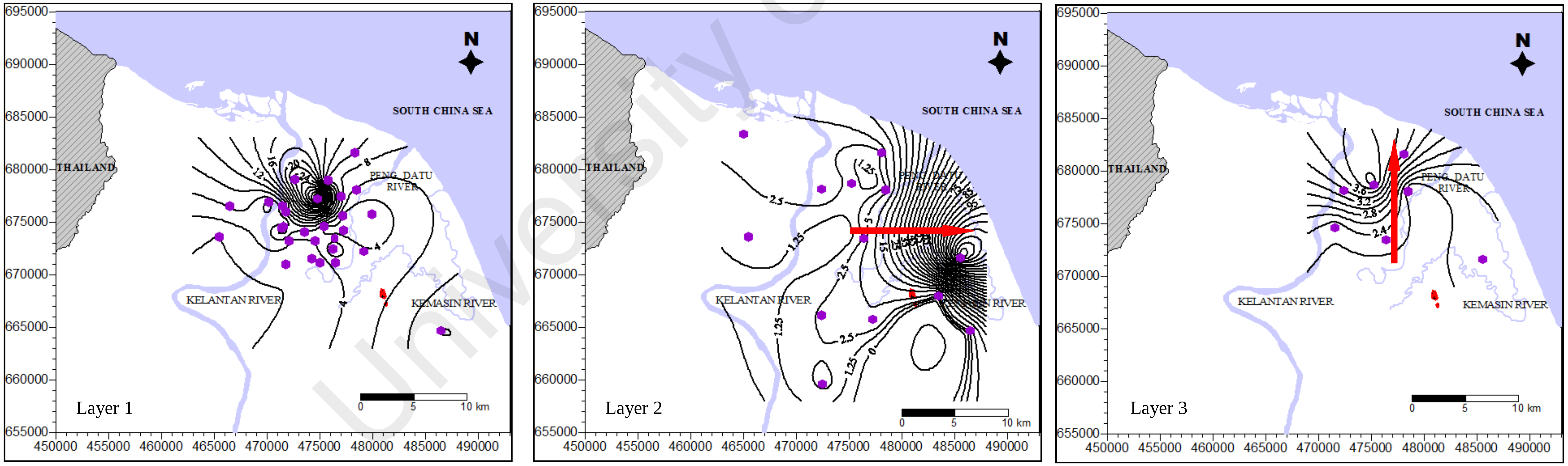
The mean concentrations of chloride in groundwater are 16.04 mg/L (ranges of 1.00 to 223.00 mg/L), 386.09 mg/L (ranges of 1.00 to 3950.00 mg/L) and 77.24 mg/L (ranges of 1.00 to 507.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5).

Figure 3.12 (a) shows the pattern of chloride concentration contour in Layers 1, 2 and 3. Red contour line indicates the acceptable value for chloride in drinking water at 250 mg/L. Chloride in Layer 1 tends to concentrate at KB69. Whilst in Layers 2 and 3 the concentration increases towards the sea as indicated by the red arrow. High concentration of chloride in Layers 2 and 3 are found at KB34 and KB31, respectively.

Based on the contour pattern, chloride shows similar trend with sodium as in Figure 3.4 (a). Both show the influence of tidal effect in Layer 1 and relatively high concentration in Layer 2 that could reflect strong influence of seawater encroachment or ancient seawater trapped in sediments.



a) Chloride



b) Sulfate

Figure 3.12: Contour Pattern of a) Chloride; b) Sulfate in Layers 1, 2 and 3

Sulfate, SO_4^{2-}

The mean concentrations of sulfate in groundwater are 7.72 mg/L (ranges of 1.00 to 82.00 mg/L), 8.81 mg/L (ranges of 1.00 to 3323.00 mg/L) and 2.63 mg/L (ranges of 1.00 to 22.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5).

Figure 3.12 (b) shows contour pattern of sulfate concentration in Layers 1, 2 and 3. Sulfate in Layer 1 tends to concentrate at KB69. Whilst in Layers 2 and 3 the concentration increases towards the sea as indicated by the red arrow. High concentration of sulfate in Layers 2 and 3 are found at KB34 and KB6, respectively. An important source of sulphate in groundwater is the oxidation of pyrite which is widely distributed in sedimentary rocks. Dissolution of gypsum and anhydrate also contribute the increase of sulphate.

Nitrate, NO_3^-

The mean concentrations of nitrate in groundwater are 5.21 mg/L (ranges of 0.50 to 54.00 mg/L), 4.47 mg/L (ranges of 0.50 to 88.00 mg/L) and 2.57 mg/L (ranges of 0.50 to 34.00 mg/L) in Layers 1, 2 and 3, respectively (Table 3.5).

Figure 3.13 shows the pattern of nitrate concentration contour in Layers 1, 2 and 3. All layers have nitrate concentration below the acceptable limit of 50.00 mg/L (WHO) for drinking water. In Layer 1, the contour is influenced by the agriculture activities as well as sewage. Layer 2 shows nitrate tends to concentrate towards the sea as indicated by red arrow. This followed the trend of groundwater flow from inland towards coastal area. KB34 (21.56 mg/L) and KB32 (5.02 mg/L) shows high concentration of nitrate in Layers 2 and 3, respectively. Both wells are a cluster of Beris Kubor area, which is a

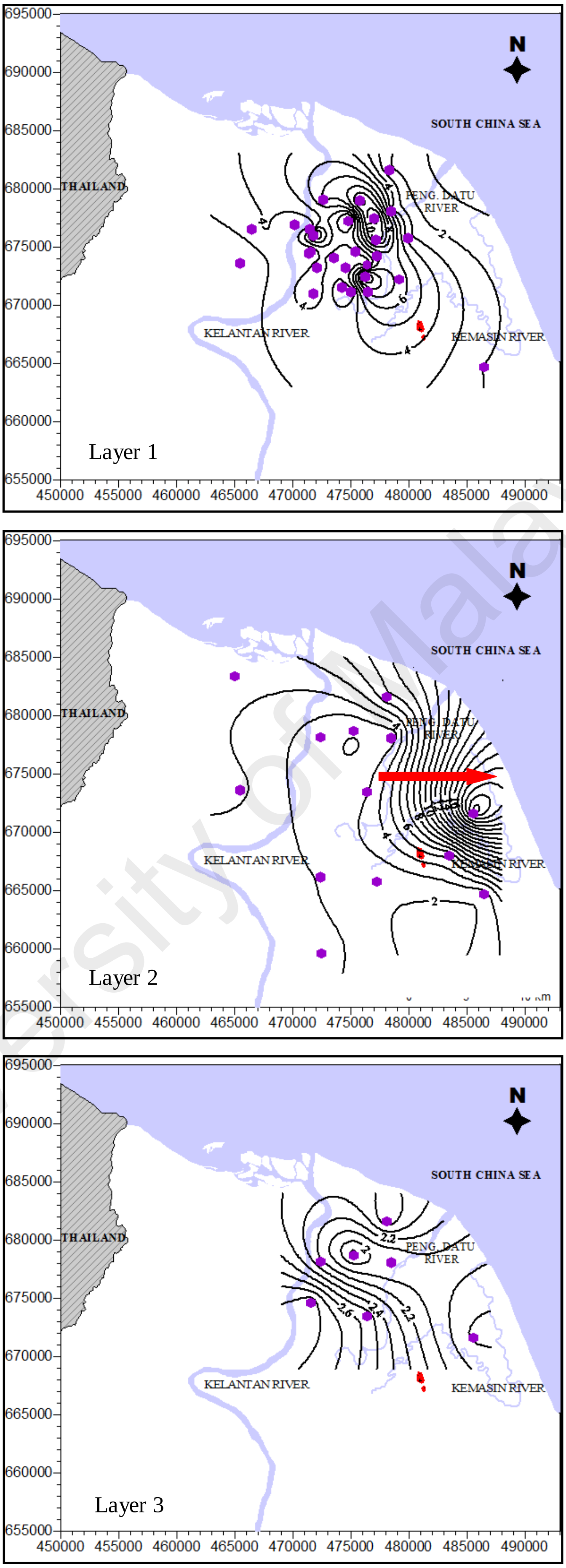


Figure 3.13: Contour Pattern of Nitrates in Layers 1, 2 and 3

paddy field area and close to the tobacco plantation area. Thus, gives direct contamination in Layer 3.

3.4 DISCUSSION

3.4.1 Relationship of Selected Chemical Parameters with Depth

Sodium and Chloride

With increase in depth, sodium and chloride in groundwater show similar pattern of ions distribution as shown in Figure 3.14. Both ions show a cluster distribution in Layers 1, 2 and 3 accordingly as indicated by the green squares. High concentration of sodium and chloride only exist at depth intervals of 20 – 50 m. The interconnection between fresh water in the aquifer and seawater at this interval give strong influence on the quality of groundwater intermixed with fresh water (Suratman, 1997). Sharp boundaries between high and low concentration of sodium and chloride reveal chemical stratification in groundwater.

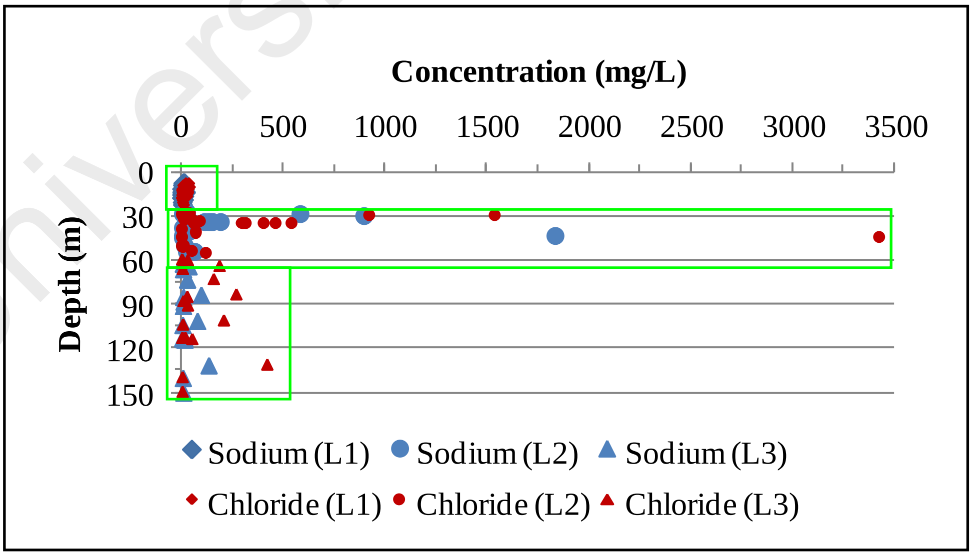


Figure 3.14: Variation of Sodium and Chloride with Depth

***Iron** *

Figure 3.15 shows the variation of iron concentration with depth. In general, the distribution of iron concentration increases with depth. The distinct trend of layers is reflected from the changes of redox condition in groundwater.

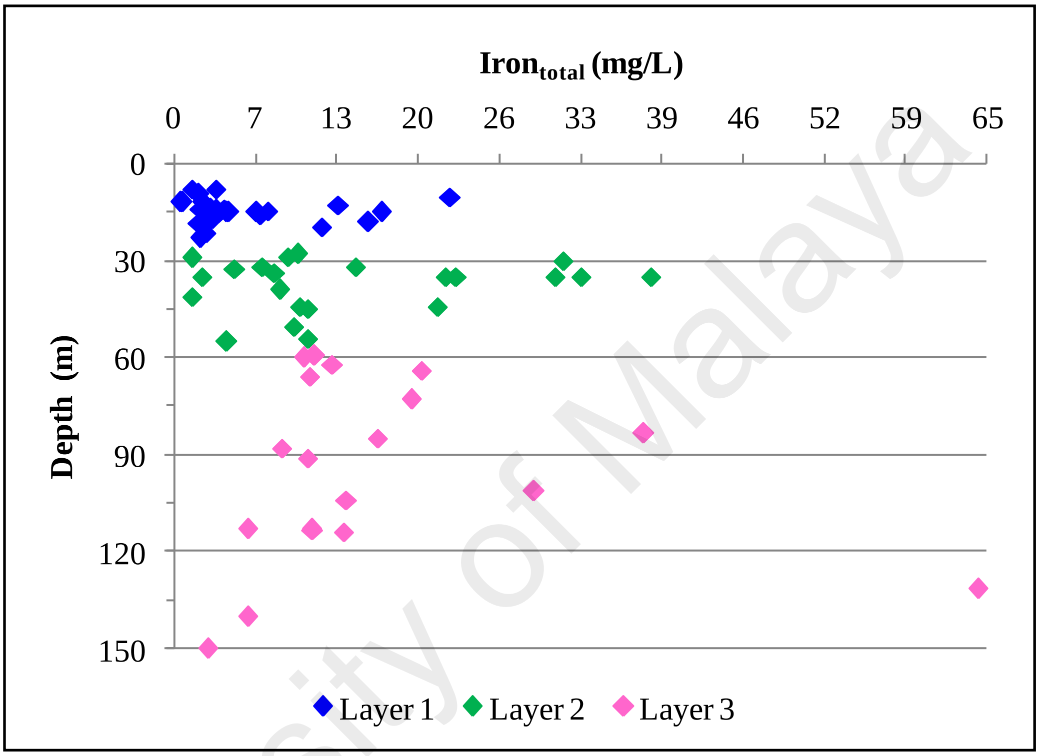


Figure 3.15: Variation of Iron $_{total}$ with depth

Low concentration of iron at the depth interval below 20 m is related to the oxidizing environment in groundwater. This unconfined aquifer, contain high amount of dissolved oxygen, therefore it creates an interface between oxidation and reduction environments. The ferrous iron in this interface region oxidizes to form ferric iron as shown in Equitation 3.1. This ferric iron is relatively immobile and will precipitate as Fe(III) oxyhydroxides in sediments; ferrihydrite, goethite, lepidocrocite and hematite (Appelo & Postma, 2005).

$$Fe^{2+} + 1/4O_2 \rightarrow Fe^{3+} + 1/2H_2O \qquad (3.1)$$

The reduction environment takes place at the depth interval above 20 m. High concentration of iron at this depth is related with the reduction of ferric iron. Microorganisms such as *Geobacter* and *Shewanella putrifaciens* play an important role in the reduction of iron. Ferric iron will be reduced to ferrous iron as given in Equatation 3.2 and become mobile in groundwater. Ferrous iron that is generated by the reduction of ferric iron remains in sediments, being sequestered in Fe(II) bearing silicates including amphiboles, pyroxene and magnetite (Chapelle, 2001; Appelo & Postma, 2005).

$$H_2 + 2Fe(OH)_3 + 4H^+ \rightarrow 2Fe^{2+} + 6H_2O \qquad (3.2)$$

Nitrate and Ammonium

Contamination of nitrate and ammonium that leach into groundwater varies depending on depth as shown in Figures 3.16 and 3.17. Both shows a decrease in nitrate and ammonium concentration with increased depth. This trend is similar as studied by Suratman (1997).

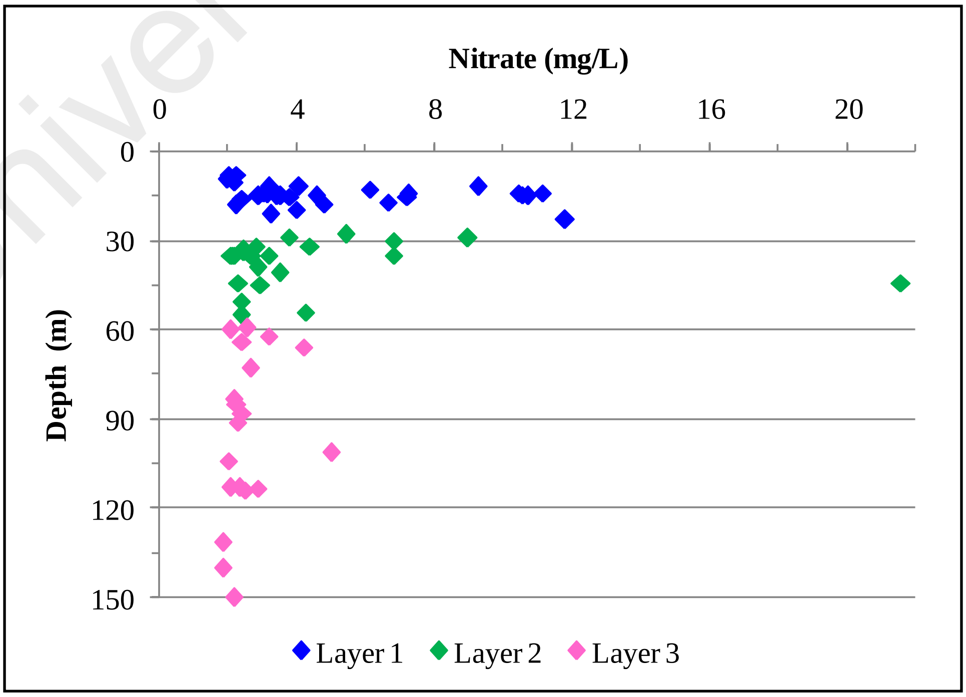


Figure 3.16: Variation of Nitrate with Depth

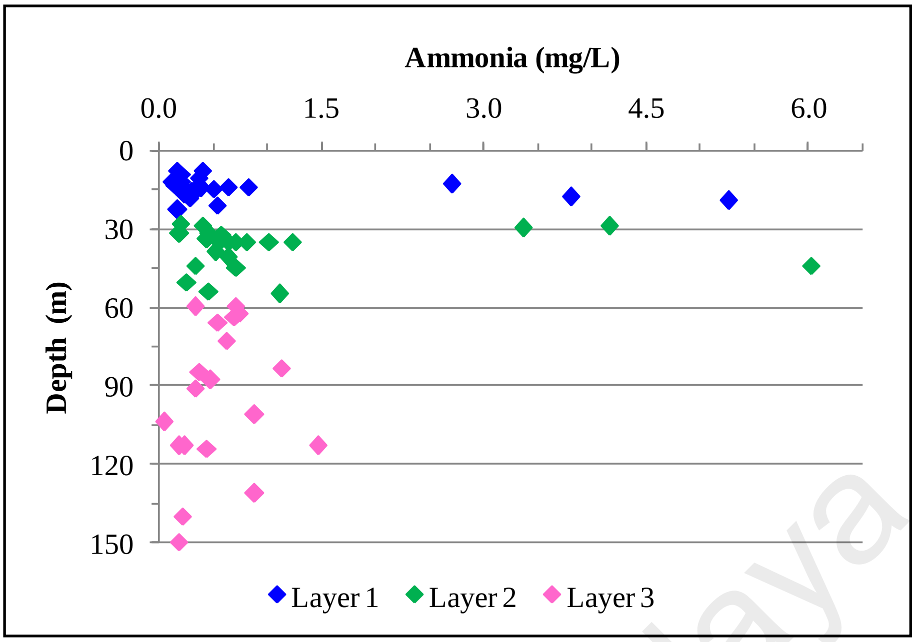


Figure 3.17: Variation of Ammonium with Depth

At depth interval below 20 m, high concentrations of nitrate and ammonium are due to direct leaches of the contaminants from the surface into the groundwater. High concentration of nitrates and ammoniums at depth interval 20 – 50 m is related with the hydraulic connectivity between Layers 1 and 2 at the surrounding areas. The downward movement to the unconfined aquifer (Layer 1) travels further in as there is no impermeable materials that block the movement. Oxidizing environment enables nitrification process which gives an excess of nitrate. Ammonium is oxidized to form nitrate as given by Equation 3.3.

$$2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ \ H_20 \qquad (3.3)$$

Deeper down, nitrate has much lower concentration. This is probably caused by denitrification of organic matter and reduction of nitrate coupled with pyrite (Appelo & Postma, 2005) as shown by the Equations 3.4, 3.5 and 3.6. This process involves the oxidation of both sulfur and ferrous iron. At this depth, iron concentration will increase as shown in Figure3.15 and the concentration of nitrate become lower very significantly.

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O \quad (3.4)$$

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 5Fe^{2+} + 10SO_4^{2-} + 2H_2O \quad (3.5)$$

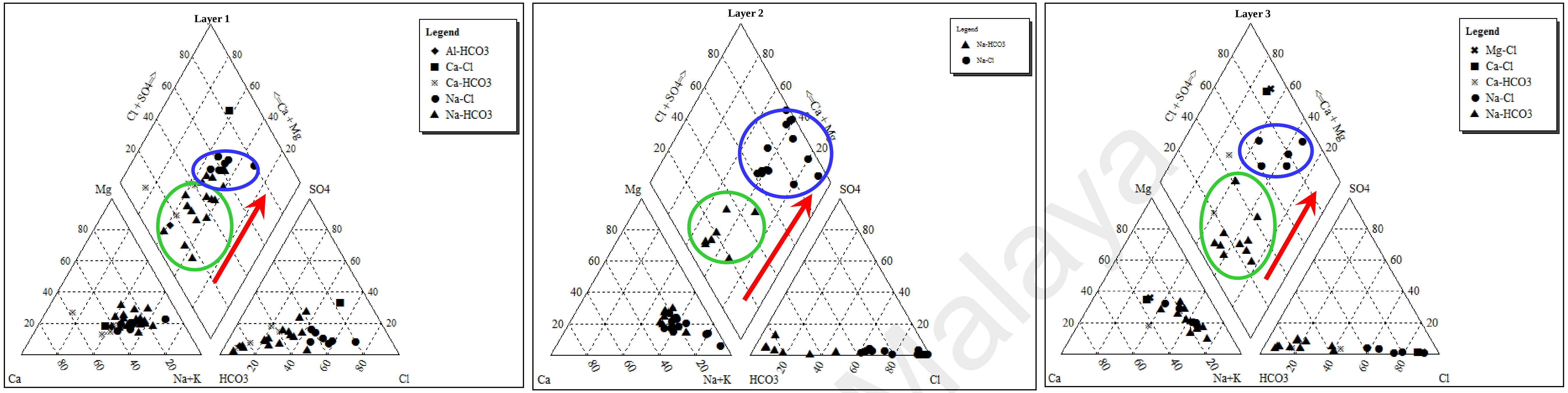
$$5Fe^{2+} + NO_3^- + 7H_2O \rightarrow 5FeOOH + 1/2N_2 + 9H^+ \quad (3.6)$$

3.4.2 Hydrochemical Fasies

General distribution of groundwater in North Kelantan is shown on Piper Diagram, Figure 3.18 (a). Based on the diagram, groundwater in the study area is characterized by different hydrochemical facies. These hydrochemical facies are influenced by the rock-water interaction that occurs in this area.

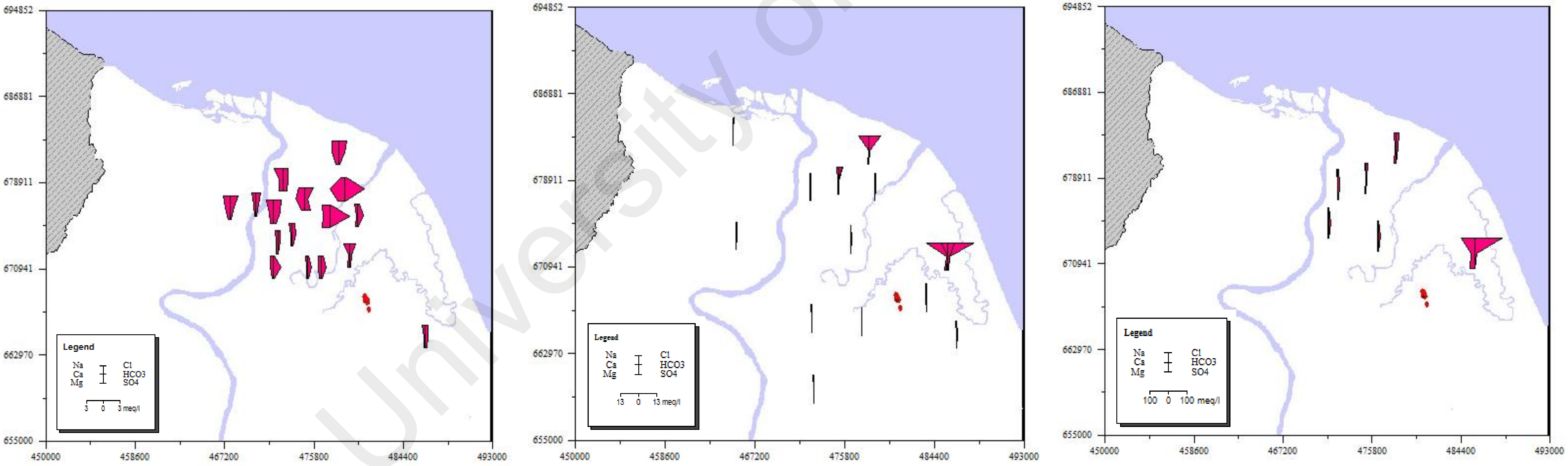
The ion concentration is plotted on Figure 3.18 (a) based on mean concentration of ion from all wells in Layers 1, 2 and 3, respectively. All layers show cluster concentration of cation in the triangle diagram with Na and K being more than 60% and Mg less than 40%. Ca on the other hand is less than 90%, 60% and 80% in Layers 1, 2 and 3, respectively. In the anion triangle, Layer 1 shows a scatter distribution of anion compared to Layers 2 and 3 that shows a cluster distribution of anion. Based on the anion triangle, in Layer 1, HCO_3 is more than 60% and SO_4 less than 40%. While in Layers 2 and 3, HCO_3 is more than 90% and SO_4 less than 20%. All layers show variable percentage of chloride.

In general, there are two main prevalent facies in this area; Na-HCO_3 facies in Layers 1 and 3 and Na-Cl facies in Layer 2 as shown in Figure 3.18 (a). Both facies show a cluster distribution in the Piper Diagram with green circle representing Na-HCO_3 facies while blue circle represents Na-Cl facies.



Groundwater flow direction from inland (up gradient) to the coast (down gradient)

a) Piper Diagram



b) Spatial Distribution of Stiff Diagram

Figure 3.18: a) Piper Diagram; b) Spatial Distribution of Stiff Diagram in Layers 1, 2 and 3

All facies occurring in Layers 1, 2 and 3 are summarized in Table 3.10. 48.57% of groundwater is contributed by Na-HCO_3 facies, 37.14% by Na-Cl facies and the rest 14.29% is contributed by mix facies (Ca-HCO_3, Al-HCO_3, Ca-Cl and Mg-Cl).

Table 3.10: Hydrochemical Facies of North Kelantan

Aquifer	Hydrochemical facies				
Layer 1 n = 29	Na-HCO_3 n =16 55.17%	Na-Cl n =7 24.14%	Ca-HCO_3 n =4 13.79%	Al-HCO_3 n =1 3.45%	Ca-Cl n =1 3.45%
Layer 2 n = 22	Na-Cl n =14 63.64%		Na-HCO_3 n =8 36.36%		
Layer 3 n = 19	Na-HCO_3 n =10 52.63%	Na-Cl n =5 26.32%	Ca-HCO_3 n =2 10.53%	Mg-Cl n =1 5.26%	Ca-Cl n =1 5.26%

From the hydrochemical facies on Piper Diagram, the groundwater flow trend can be determined. The trend of groundwater flow of North Kelantan is from Na-HCO_3 facies to Na-Cl facies from inland towards the coastal area. This follows the general trend of groundwater flow direction as marked by the red coloured arrow shown in Figure 3.18 (a). This trend is similar to the findings of Suratman (1997).

Figure 3.18 (b) represents the spatial distribution of Stiff Diagram for selected wells in Layers 1, 2 and 3, respectively. This diagram shows the chemical character according to the absolute concentrations, thereby giving an overall expression of the cation-anion balance of the groundwater. Different facies will have different pattern of Stiff diagram which is dependant on the dominant cation and anion.

3.4.3 Groundwater Evolution

Table 3.11 shows the source rock deduction in Layers 1, 2 and 3 obtained from Aquachem and PHREEQC analysis. The conclusion derived from this table is useful to determine the origin and evolution of groundwater in North Kelantan in conjunction with hydrochemical facies from Piper Diagram.

The groundwater is evolved from Ca-HCO_3/Na-HCO_3 facies to Na-Cl facies. As the groundwater flows from the inland (high hydraulic gradient) towards the coast (low hydraulic gradient), changes in geochemical composition occurs along the flow-path with the aquifer matrix until it reaches equilibrium.

Ratio of HCO_3/SiO_2 (<5) shows that this area is characterized by silicate weathering with more than 90% for all layers. This is also supported by the TDS ratio (>500) with more than 70%. The source of Na^+, K^+ and Ca^{2+} in the groundwater is from plagioclase weathering based on the (Na+K+Cl)/(Na+K+Ca+Cl) ratio. The Mg/(Ca + Mg) ratio indicates that the source of Ca^{2+} and Mg^{2+} is from the weathering or ferromagnesian mineral of the granite.

Water recharging from the surface in the inland part of the study area will infiltrate into the aquifer. The occurrence of Ca-HCO_3/Na-HCO_3 facies indicates that freshwater with low TDS value, below 1000 mg/L. The Na-HCO_3 facies become more dominant facies for freshwater compared to Ca-HCO_3 facies. Na^+ becomes the major cation in groundwater. Based on the SiO_2/(Na+K-Cl) ratio, the abundance of Na^+ is contributed by weathering of albite and ion exchange process.

Table 3.11: Ratio Source Rock Deduction in Layers 1, 2 and 3

Parameter	Attention Value	Conclusion	Layer 1							Layer 2							Layer 3						
			Mean	Min	Max	Stdev	Well	∑ well	%	Mean	Min	Max	Stdev	Well	∑ well	%	Mean	Min	Max	Stdev	Well	∑ well	%
SiO_2 (mmol/l)	> 0.5	Volcanic Glass or hydro thermal water possible	0.59	0.50	0.65	0.06	6.00	29.00	20.69	0.68	0.53	1.06	0.21	7.00	22.00	31.82							
HCO_3^-/SiO_2	>10	Carbonate weathering								12.38	10.77	15.49	2.69	3.00	22.00	13.64							
	>5 and <10	Ambiguous	5.32	5.32	5.32		1.00	29.00	3.45								7.25	5.14	9.35	2.98	2.00	19.00	10.53
	<5	Silicate weathering	2.11	1.03	4.45	0.85	28.00	29.00	96.55	2.31	0.48	5.00	1.33	19.00	22.00	86.36	2.64	1.61	4.63	0.87	17.00	19.00	89.47
SiO_2/(Na+K-Cl)	<1	Cation exchange	-1.80	-4.98	0.57	1.91	9.00	29.00	31.03	-1.09	-13.10	0.99	3.13	18.00	22.00	81.82	-0.81	-8.17	0.81	2.49	11.00	19.00	57.89
	>1 and <2	Albite weathering	1.53	1.04	1.96	0.37	9.00	29.00	31.03	1.40	1.17	1.55	0.17	4.00	22.00	18.18	1.25	1.10	1.50	0.16	6.00	19.00	31.58
	>2	Ferromagnesian Minerals	3.01	2.20	3.82	0.57	11.00	29.00	37.93								2.94	2.60	3.29	0.49	2.00	19.00	10.53
(Na+K-Cl)/ (Na+K-Cl+Ca)	> 0.2 and < 0.8	Plagioklase weathering possible	0.43	0.23	0.73	0.14	18.00	29.00	62.07	0.56	0.37	0.73	0.10	8.00	22.00	36.36	0.61	0.40	0.75	0.11	9.00	19.00	47.37
	< 0.2 or > 0.8	Plagioklase weathering unlikely	-0.19	-0.73	0.16	0.29	11.00	29.00	37.93	0.57	-1.48	2.00	1.37	14.00	22.00	63.64	1.64	-2.27	4.76	2.09	10.00	19.00	52.63
(Na/(Na+Cl)	>0.5	Sodium source other than halite - albite, ion exchange	0.65	0.52	0.85	0.10	22.00	29.00	75.86	0.76	0.57	0.87	0.12	8.00	22.00	36.36	0.72	0.57	0.86	0.10	10.00	19.00	52.63
	0.5	Halite solution								0.49	0.49	0.49		1.00	22.00	4.55							
	<0.5, TDS >500	Reverse Softening, seawater								0.40	0.34	0.47	0.05	8.00	22.00	36.36	0.35	0.33	0.36	0.02	2.00	19.00	10.53
	<0.5, TDS <500 and >50	Analysis Error	0.45	0.42	0.48	0.02	5.00	29.00	17.24	0.45	0.42	0.47	0.02	5.00	22.00	22.73	0.33	0.23	0.48	0.09	7.00	19.00	36.84
	<0.5, TDS <50	Rainwater	0.45	0.45	0.45		2.00	29.00	6.90														
Mg/(Ca+Mg)	=0.5 and HCO3-/Si>10	Dolomite Weathering																					
	<0.5	Limestone-dolomite weathering																					
	>0.5	Dolomite dissolution, calcite precipitation or seawater								0.66	0.64	0.69	0.02	3.00	22.00	13.64							
	<0.5 and HCO3-/Si<5	Ferromagnesian Minerals	0.35	0.20	0.46	0.07	19.00	29.00	65.52	12.38	10.77	15.48	2.69	3.00	22.00	13.64	0.37	0.30	0.42	0.07	3.00	19.00	15.79
			2.37	1.48	4.45	0.85	19.00	29.00	65.52	0.42	0.37	0.47	0.04	9.00	22.00	40.91	2.52	2.10	2.86	0.39	3.00	19.00	15.79
	>0.5	Granitic Weathering	0.62	0.52	0.72	0.09	4.00	29.00	13.79	2.86	0.65	5.00	1.28	9.00	22.00	40.91	0.57	0.53	0.67	0.05	10.00	19.00	52.63
			1.60	1.07	2.26	0.54	4.00	29.00	13.79	0.57	0.54	0.64	0.03	8.00	22.00	36.36	2.65	1.63	4.63	0.97	10.00	19.00	52.63
		ambiguous	0.53	0.53	0.53		1.00	29.00	3.45	1.31	0.48	2.57	0.72	8.00	22.00	36.36	0.55	0.54	0.56	0.02	2.00	19.00	10.53
			5.32	5.32	5.32		1.00	29.00	3.45								7.25	5.14	9.35	2.98	2.00	19.00	10.53
Ca/(Ca+SO_4)	0.5	Gypsum dissolution	0.53	0.52	0.55	0.02	3.00	29.00	10.34								0.54	0.54	0.54		1.00	19.00	5.26
			5.69	5.11	6.44	0.68	3.00	29.00	10.34								5.89	5.89	5.89		1.00	19.00	5.26
	<0.5, and pH <5.5	Pyrite oxidation																					
	<0.5, and pH neutral	Calcium removal - ion exchange or calcite precipitation								0.90	0.58	0.98	0.10	22.00	22.00	100.00							
	>0.5	Calcium source other than gypsum - carbonate or silicates	0.76	0.60	0.94	0.10	26.00	29.00	89.66	6.33	5.73	7.88	0.47	22.00	22.00	100.00	0.86	0.62	0.98	0.11	18.00	19.00	94.74
			5.94	5.45	6.88	0.34	26.00	29.00	89.66	1593.78	647.00	6163.00	1818.44	9.00	22.00	40.91	6.08	5.33	6.35	0.25	18.00	19.00	94.74
TDS	>500	Carbonate weathering or brine or seawater					0.00	29.00	0.00	117.15	59.00	261.00	69.82	13.00	22.00	59.09	653.50	545.00	762.00	153.44	2.00	19.00	10.53
	<500	Silicate weathering	129.79	38.00	1102.00	191.15	29.00	29.00	100.00	0.93	0.89	0.96	0.03	7.00	22.00	31.82	146.59	47.00	466.00	139.63	17.00	19.00	89.47
Cl^-/Sum Anions	>0.8 and TDS>500	Seawater or brine or evaporites															0.89	0.89	0.89		1.00	19.00	5.26
	>0.8 and TDS<100	Rainwater								0.37	0.04	0.77	0.28	15.00	22.00	68.18							
	<0.8	Rock weathering	0.23	0.05	0.52	0.14	29.00	29.00	100.00								0.27	0.05	0.74	0.23	16.00	19.00	84.21
HCO_3^-/ Sum Anions	>0.8	Silicate or carbonate weathering	0.83	0.83	0.83		1.00	29.00	3.45														
	<0.8 sulfate high	Gypsum dissolution								0.32	0.01	0.69	0.24	22.00	22.00	100.00							
	<0.8 sulfate low	Seawater or brine	0.39	0.15	0.78	0.15	28.00	29.00	96.55	0.21	0.21	0.21		1.00	22.00	4.55	0.40	0.08	0.64	0.19	19.00	19.00	100.00
SI Calcite	>0	Oversaturated with respect to calcite																					
	0	Saturated with respect to calcite								-2.12	-3.20	-0.25	0.71	21.00	22.00	95.45							
	<0	Undersaturated with respect to calcite	-2.98	-5.09	-0.96	0.87	29.00	29.00	100.00								-2.61	-3.48	-1.85	0.49	19.00	19.00	100.00

Equations 3.7 and 3.8 show an example of albite weathering/hydrolysis while Equations 3.9 to 3.11 shows other weathering products that contribute to exixting of cations in groundwater.

$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$ (3.7)

Albite Kaolinite

$2NaAlSi_3O_8 + 2CO_2 + 6H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Na^+ + HCO_3^- + 2H_4SiO_4$ (3.8)

Albite Montmorillonite

$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$ (3.9)

Anothite Kaolinite

$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 15H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4$ (3.10)

Biotite Kaolinite

$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 10H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 2H_4SiO_4$ (3.11)

Biotite Montmorillonite

Based on the $SiO_2/(Na+K-Cl)$ ratio, 56% results from cation exchange process occurring in all layers during the evolution. Clay minerals exhibit a preference for ion occupying an exchange site. Kaolinite appears as a dominant clay mineral in the aquifer as studied by Ismail (1980). The exchangeability for cation in the exchange site is according to their relative affinity. Below are general order cation exchangeability proposed by Yong (1985):

$$Li^+ < Na^+ < H^+ < K^+ < Mg^{2+} < Ca^{2+} < Al^{3+}$$

In aquifer layers, Ca^{2+} and Mg^{2+} in the groundwater will exchange with clay minerals for Na^+ as groundwater flows through them. The cation exchange process effectively increases the Na^+ concentrations at the expense of Ca^{2+} and Mg^{2+} as shown by Equations 3.12 – 3.14.

$Ca^{2+} + 2Na\text{-}X \rightarrow 2Na^+ + Ca\text{-}X$ (3.12)

$Ca^{2+} + Mg\text{-}X \rightarrow Mg^{2+} + Ca\text{-}X$ (3.13) , Na-X is Na adsorbed onto a clay mineral

$Mg^{2+} + 2Na\text{-}X \rightarrow 2Na^+ + Mg\text{-}X$ (3.14)

The HCO_3^- becomes the dominant anion in groundwater. Precipitation brings recharge into the groundwater system. Infiltration of recharge water into the aquifer layers is very common especially when there are no impermeable layers of clay overlying the unconfined aquifer. In some parts, the unconfined aquifer may represent a recharge for deeper aquifers system. As the water recharges, CO_2 rapidly dissolves (Freeze & Cherry, 1979) in aquifer layers. The dissolution of CO_2 also occurs in the soil at the partial pressure larger than atmosphere value caused primarily by root and microbial respiration (Domenico & Schwartz, 1990) as shown by Equations 3.15 – 3.17.

$$CO_2(g) + H_2O \rightarrow H_2CO_3 \qquad (3.15)$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \qquad (3.16)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \qquad (3.17)$$

This process will increase the HCO_3^- in groundwater. The main contributor of HCO_3^- is from the hydrolysis of silicate weathering as shown by Equations 3.7 - 3.11. During the evolution, groundwater is chemically in equilibrium with the surroundings of freshwater ($Na\text{-}HCO_3$).

The evolution continues with low rate of freshwater from the recharge area towards the coast, increasing the Ca^{2+} and Mg^{2+}. The Mg/(Ca+Mg) ratio shows that the source of Ca^{2+} and $Mg^{2+}$are from the ferromagnesian minerals; mafic or ultramafic rocks. Clay minerals also provide an excess of Ca^{2+} and Mg^{2+} through the reverse ion exchange process from Equations 3.12 – 3.14. Therefore mix facies (Ca-Cl and Mg-Cl facies) exists in between Na-HCO_3 and Na-Cl facies.

Towards the coastal area, groundwater is in equilibrium with Na-Cl facies. Na^+ is still the dominant cation in groundwater. The source of Na^+ is subjected to the other source of sodium; seawater based on the Na/(Na+Cl) ratio (>0.5) of 54%. The Na^+ may also be derived from the sodium salts present in the aquifer layers. This is due to the fact that the coastal area has been subjected to a series of submergence and emergence processes which leads to the increase of Na^+ compared to the inland area (Noor, 1979).

Along the flow-path, the HCO_3^- is reduced and replaced by the Cl^- as the dominant anion in groundwater. Based on the Cl-/Sum of Anions ratio (<0.8), 61% of Cl^- is the minor product from rock weathering that leaches out through the rock – water interaction. This is also followed by seawater and rainwater. Entrapped seawater in the sediments provides an excess of Na^+ and Cl^- in groundwater especially in Layer 2 which indicates possible mixing with sea water. The evolution of brackish water in Layer 2 is related with the geologic time scale. According to Sikdar *et al.*, (2001), during the late Holocene Epoch, Calcutta and Howrah were below the sea level and under the influence of brackish due to marine environment. Seawater was entrapped in the sediments as connate water during their deposition under marine conditions and later had undergone certain fundamental modifications during its period of confinement. It is believed that the same process had occurred in the study area that brought an excess of Na^+ and Cl^- in the groundwater.

These Cl^- concentrations indicate that the water in Layers 1 and 3 are fresh while in the Layer 2, there is a mixture between fresh and brackish. The variations of Cl^- concentration show that the dilution process has not been uniform. This is supported by the total dissolved solid (TDS) concentrations (Section 3.3.1-Total Dissolved Solids). Haryono *et al.* (1996) used both Cl^- concentration and resistivity data to indicate the groundwater in Layer 2 was brackish up to 5 km from the coast. The considerable amount of Cl^- suggests that the groundwater is mixed with the intrusion of seawater. However, research by Samsudin *et al.* (2008) concluded that continuous monitoring of chloride content showed no significant change with time and it was an indication that the groundwater was not affected by seasonal seawater intrusion but probably due to ancient seawater that was trapped within the sediments for a long period of time. Figure 3.19 is a simplified scheme of the groundwater evolution in North Kelantan.

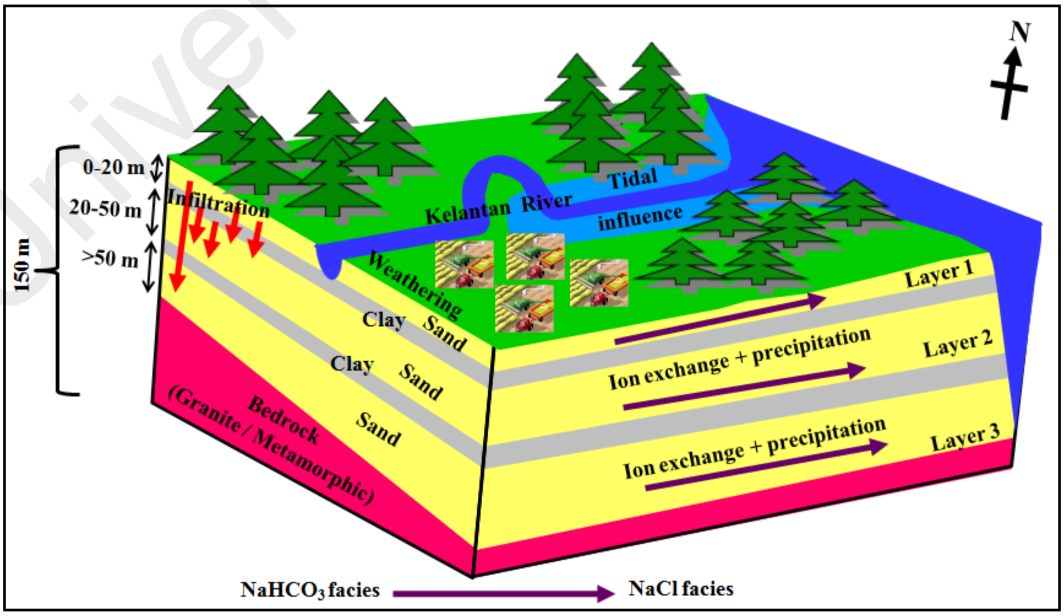


Figure 3.19: Schematic Diagram of Groundwater Evolution in North Kelantan

3.4.4 Saturation Index

Saturation index in Layers 1, 2 and 3 is shown in Figure 3.20. These values are calculated using PHREEQC. All layers show the occurrence of the same mineral phases. The mineral phases are anhydrite ($CaSO_4$), aragonite ($CaCO_3$), barite ($BaSO_4$), calcite ($CaCO_3$), dolomite ($CaMg[CO_3]_2$), fluorite (CaF_3), goethite (α-FeOOH), gypsum ($CaSO_4$), halite (NaCl), hematite (Fe_2O_3), pyrite (FeS_2), siderite ($FeCO_3$) and witherite ($BaCO_3$).

All layers show near equilibrium with respect to barite and siderite mineral. The presence of siderite usually indicates strong reducing condition and siderite becomes stable at extremely low sulfide concentration (Appelo & Postma, 2005).

All layers are under saturated with carbonates, sulfates and salts that contribute to the dissolution of ions in the groundwater. These are supported by the ratio of Na/Cl, Ca/Mg and Ca/SO_4 of the standard seawater composition as shown in Figure 3.21.

In general, in Layers 1, 2 and 3 shows Na/Cl ratios higher than seawater (0.556). This attributes to the depletion of sodium caused by cation exchange process that is associated with saltwater intrusion in coastal aquifer. Certain values are close to seawater that indicates mixing with saltwater which is consistent with high salinity values.

All layers show Ca/Mg ratio higher than sea water (0.319). High ratios may due to the enrichment of Ca by dissolution of silicate/carbonate minerals.

Table 3.12: Mean Values of Saturation Index in Layers 1, 2 and 3

Aquifer	**Anhydrite** $CaSO_4$	**Aragonite** $CaCO_3$	**Barite** $BaSO_4$	**Calcite** $CaCO_3$	**Dolomite** $CaMg(CO_3)_2$	**Fluorite** CaF_2	**Geothite** α-FeOOH	**Gypsum** $CaSO_4$	**Halite** $NaCl$	**Hematite** Fe_2O_3	**Pyrite** FeS_2	**Siderite** $FeCO_3$	**Whiterite** $BaCO_3$
Layer 1	-3.80	-3.13	-0.49	-2.98	-5.95	-1.40	5.63	-3.59	-8.37	13.29	-79.08	-1.06	-5.16
Layer 2	-3.86	-2.16	-0.54	-2.02	-3.83	-2.26	7.15	-3.66	-6.97	16.33	-86.39	-0.14	-4.16
Layer 3	-4.16	-2.75	-0.49	-2.61	-4.98	-2.79	6.74	-3.97	-8.01	15.52	-82.40	-0.16	-4.39

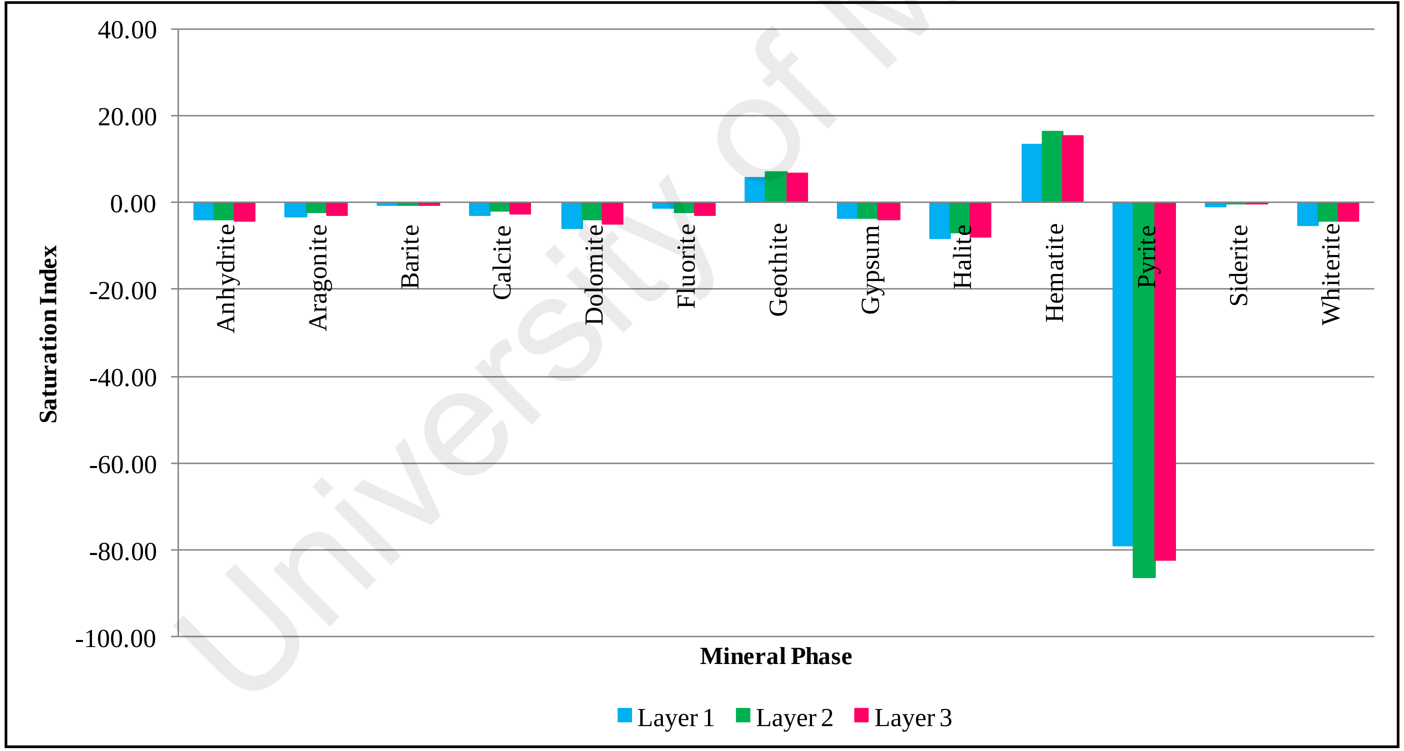
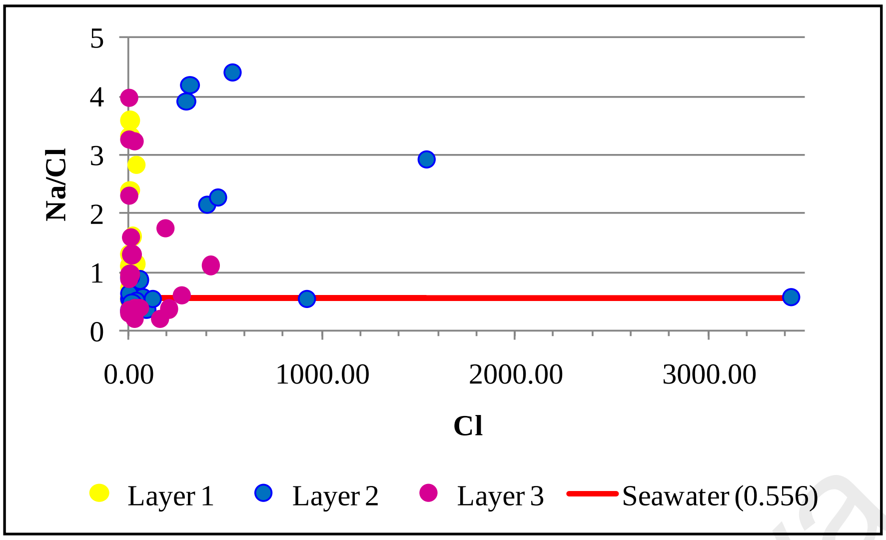
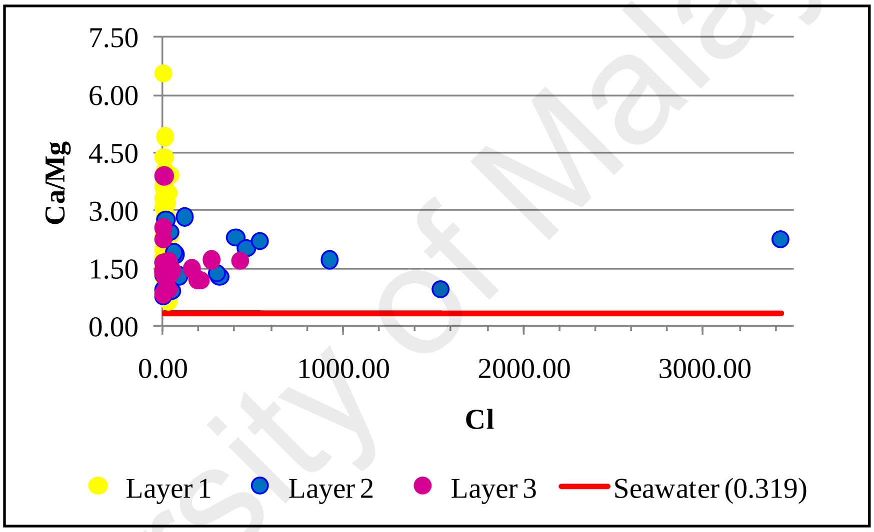


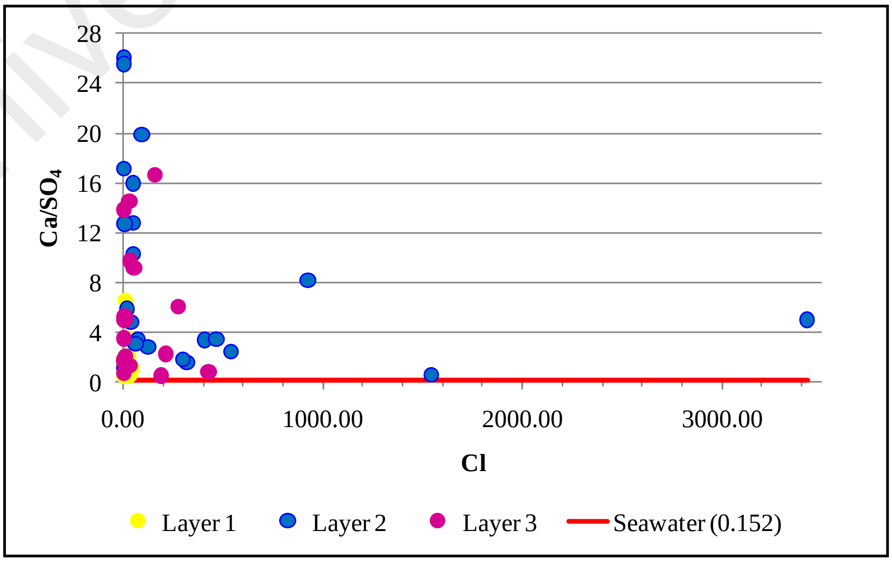
Figure 3.20: Saturation Index in Layers 1, 2 and 3.



a) Na/Cl Ratio vs Cl



b) Ca/Mg Ratio vs Cl



c) Ca/SO_4 vs Cl

Figure 3.21: Ionic Ratios of a) Na/Cl vs Cl; b) Ca/Mg vs Cl; c) Ca/SO_4 vs Cl in Layers 1, 2 and 3.

The Ca/SO_4 ratio is also higher than sea water (0.152) resulting from the dissolution of sulfates minerals (gypsum and anhydrite) that is commonly found in the Quaternary aquifer. Sulfate minerals dissolve to increase their saturation index.

All layers are highly under saturated with respect to major iron phase of pyrite mineral. Therefore iron remains dissolved after mobilization. Under an anoxic environment, dissolution of pyrite occurs and is followed by partial oxidation that reflects the increase of Fe^{2+} and SO_4^{2-} in the groundwater.

All layers are super saturated with respect to hematite and goethite minerals. Under an oxidative environment, the Fe^{2+} is released during dissolution and is precipitated as iron oxide and oxyhydroxides. This indicates that precipitations of iron phases from aquifer layers are thermodynamically favorable. Hematite precipitates more because it is more stable compared to goethite. The detection of a 'rotten egg' smell shows active SO_4^{2-} reduction which indicates possible sulfide precipitation (barite).

3.4.5 General Groundwater Quality

Drinking Purposes

Drinking water must be clear and does not have any objectable taste, colour and odour. It must be pleasant to drink and free from all harmful organisms, chemical substances and radionuclide in amounts non-hazardous to the health of consumer. All the physical and chemical parameters are considered in the assessment. These parameters are compared with the WHO, MOH and INWQS water quality standard for drinking water as given in Table 3.5. While the contour line show in Sections 3.3.1 and 3.3.2 indicates the acceptable limit of selected parameters for drinking purposed. It is observed that different layers show different ionic concentrations that exceed the guidelines limit of certain water quality standards.

Layer 1 shows pH values below the ranges of acceptable limit for drinking water (6.50 – 8.50). Based on TDS values, Layers 1 and 3 are suitable for drinking water with mean concentration below 1000 mg/L. Water with high TDS indicates more ionic concentrations, which is of inferior palatability and can induce an unfavorable physiological reaction in the consumers (Rao *et al.*, 2002).

Layer 2 shows mean concentration of sodium above the acceptable limit of 200.00 mg/L. Regarding sodium, it is believed that there is a relationship between sodium level in drinking water and the occurrence of high blood pressure; however no firm evidence supports this. Therefore, the sodium standard is only based on negative taste effects (Al-Alhmadi & El-Fiky, 2009). However, increased intake of sodium in drinking water may be problematic for people with hypertension, heart disease or kidney problems that require them to follow a low sodium diet (British Columbia Groundwater Association, 2007).

Based on the mean concentration of iron, all layers show concentration above the acceptable limit of 0.30 mg/L for drinking water. High iron will cause an unpleasant taste and smell to water, red staining to clothing and plumbing fixtures (Chaplle, 2001). Only small concentrations of iron are essential for human health benefit, because iron helps in oxygen transport in blood (Colter & Mahler, 2006). An excess of iron in human body will caused chronic iron overload-genetic disorder (*haemochromatosis*), detailed in Chapter 4.

Even though manganese shows small concentration compared to iron in groundwater but it still influences drinking water. Same trend goes to manganese, all layers show mean concentration above the acceptable limit of 0.10 mg/L for drinking water. Manganese oxides that are precipitated from domestic water supplies can cause black staining on food, laundry and sanitary ware and also can impart a metallic taste. At excessive concentrations, manganese can be detrimental to health. Evidence from occupational exposure indicates that manganese can affect neurological functions such as Parkinson's disease and Guamian amyotrophic lateral sclerosis (Takeda, 2003 & Foster, 1992). Iwami *et al.* (1994) found correlations between the concentrations of manganese in food and the prevalence of motor neuron disease in the Kii Peninsula of Japan.

Layer 2 shows mean concentration of chloride above the acceptable limit of 250.00 mg/L. Chloride does not pose health hazard to humans. An excess 250 mg/l of chloride will give rise to detectable taste in water (WHO, 2003).

All layers show mean concentration of sulfate below the acceptable limit of 250.00 mg/L for drinking water. Although, Layer 1 was not affected by high sulfate concentration, this layer shows high probability to increase of sulfate content in groundwater if no action is taken to control it. High concentration of sulfate in the drinking water could cause a cathartic action on human beings and cause respiratory problems (Rao, 1993). The presence of sulfate in drinking-water can also result in a noticeable taste. Sulfate may also contribute to the corrosion of distribution system (WHO, 2004).

All layers also show mean concentration of nitrate below the acceptable limit of 45.00 mg/L. Similar with sulfate, nitrate also shows high probability of increase in its concentration in groundwater especially in Layers 1 and 2. For example, nitrate level in most ambient groundwater in British Columbia is very low, less than 1.00 mg/L. Therefore, the presence of nitrate in groundwater greater than 3.00 mg/L usually reflects the impact of human activities on well water quality (British Columbia Groundwater Association, 2007). Nitrate is introduced into groundwater through widespread or diffuse sources, commonly called non-point sources that can hardly be detected. Leaching of chemical fertilizers or animal manure and also pollution from septic and sewage discharges are the main sources that increase the nitrate concentration in groundwater in the study area. Relatively, nitrate is considered as non-toxic. High concentrations can reduce the ability of blood to transport oxygen. In babies less than six months old, *methaemoglobinaemia* is resulted from oxygen deprivation. Nitrate has also been cited as a risk factor in developing gastric and intestinal cancer (reopure.com).

In general, comparison with drinking water quality (Table 3.5) shows that groundwater in Layers 1 and 3 are suitable for drinking water compared to Layer 2. Selected parameters need to be treated to remove or decrease the concentration in order to meet with the standard of drinking water quality. This is important to prevent from the effects that mentioned above.

Irrigation Purposes

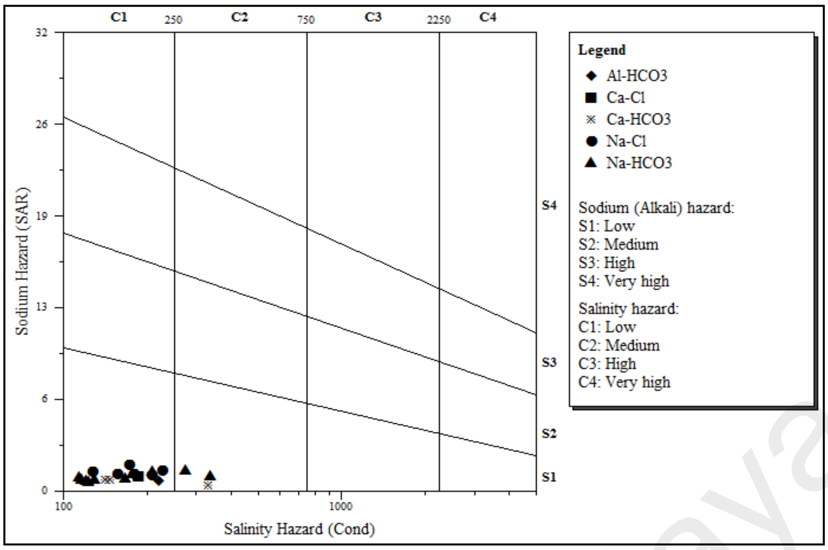
In North Kelantan, 73.80% of land area (Chapter 1) is used for irrigation. Therefore, it is important to determine the viability of groundwater for this irrigation purpose. The sodium adsorption ratio (SAR), typically expressed as sodium hazard is used for this determination. The SAR is defined by Equation 3.18. Wilcox diagram is used to illustrate the data as shown in Figure 3.22. This diagram shows the relation between sodium hazard (SAR) and salinity hazard (cond).

$$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{(\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}})/2}} \quad \text{(cations expressed as meq/L)} \qquad (3.18)$$

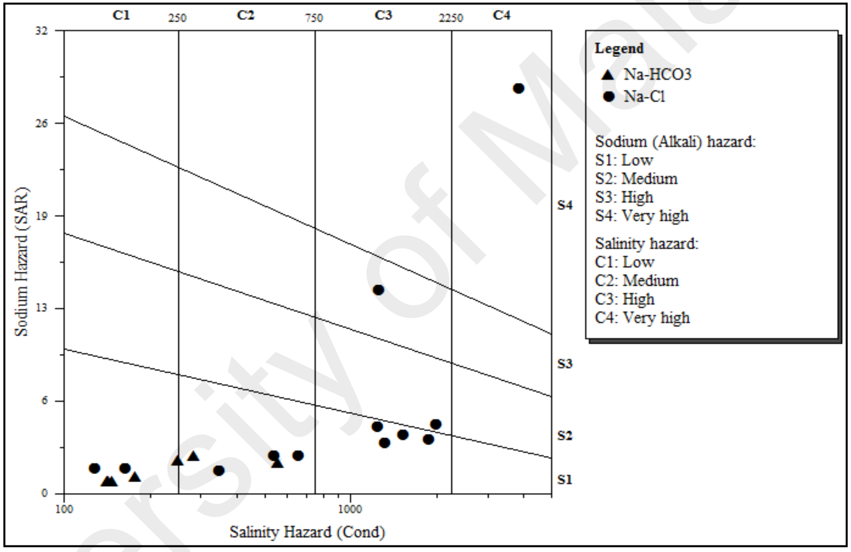
Sodium hazard is defined separately because of sodium's specific detrimental effects on soil physical properties (Bauder *et al.*, 2007). Excessive Na^+ content in irrigation water renders it unsuitable for soils containing exchangeable Ca^{2+} and Mg^{2+} ions as the soil take up Na^+ in exchange for Ca^{2+} and Mg^{2+} causing deflocculation (dispersion) and impairment of the tilth and permeability of soils (Karanth, 1994). Table 3.12 presents the general classification of irrigation water based on SAR values (Bauder *et al.*, 2007).

Table 3.12: Classification of Irrigation Water Based on SAR Values (Bounder *et al*, 2007)

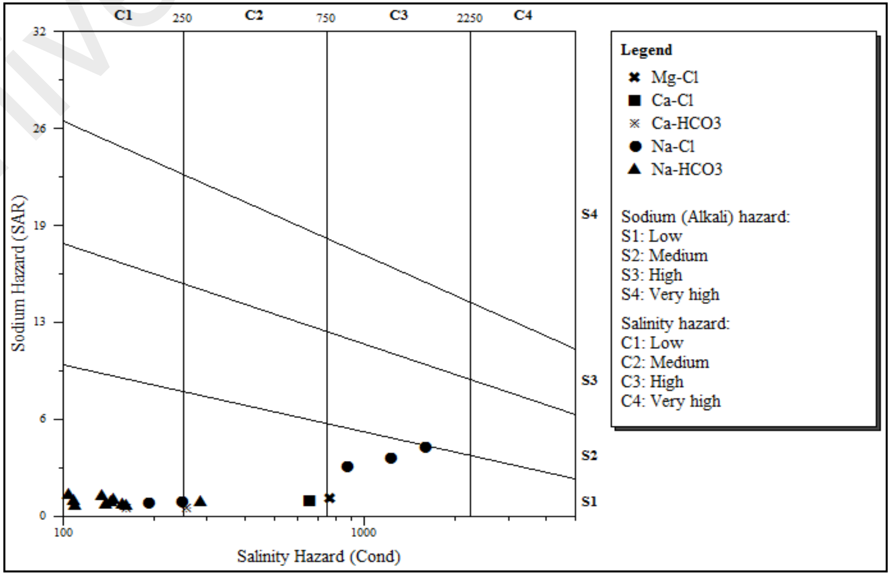
SAR values	Sodium hazard to water	Comments
1 – 9	Low	Use on sodium sensitive crops must be cautioned
10 – 17	Medium	Amendments (such as gypsum) and leaching needed
18 – 25	High	Generally unsuitable for continuous use
≥ 26	Very High	Generally unsuitable for use



a) Layer 1



b) Layer 2



c) Layer 3

Figure 3.22: Wilcox diagram (a); (b); (c) in Layers 1, 2 and 3

Salinity hazard is measured by electrical conductivity (EC) that is most influential in water quality guideline on crop productivity. The primary effect of high EC water on crop productivity is the inability of the plant to compete with ions in the soil solution for water (physiological drought). The higher the EC, the less water is available to plants, even though the soil may appear wet. Because plants can only transpire "pure" water, usable plant water in the soil solution decreases dramatically as EC increases (Bauder *et al.*, 2007). Table 3.13 shows suggested criteria for irrigation water use based on electrical conductivity. Based on Figure 3.22, very high salinity hazard (C4) has conductivity above 2250 µS/cm. Thus, by referring to Table 3.13 the water is classified in Class 4 and Class 5.

Table 3.13: Suggested Criteria for Irrigation Water Use Based Upon Conductivity (Bounder *et al*, 2007)

Classes of Water	Electrical Conductivity (µS/cm)
Class 1: Excellent	≤250
Class 2: Good	250 - 750
Class 3: Permissible[1]	760 - 2000
Class 4: Doubtful[2]	2001 - 3000
Class 5: Unsuitable[2]	≥3000

[1] Leaching needed if used.
[2] Good drainages needed and sensitive plants will have difficulty obtaining stands.

Most of the groundwater wells show variable stage of sodium hazard as well as salinity hazard. Facies in Layer 1 are classified as low sodium hazard and low salinity hazard. Only KB38 (Na-HCO_3), KB53 (Na-HCO_3) and KB68 (Ca-HCO_3) has medium salinity hazard with conductivity above 250µS/cm. Layer 2 shows a broad range of sodium hazard and salinity hazard. The Na-HCO_3 facies is classified as low sodium hazard with low to medium salinity hazard. While the Na-Cl facies is classified as low to very high sodium hazard and salinity hazard. KB5 shows very high hazard with SAR 27.93 and conductivity 3830.71µS/cm. KB35 shows high hazard with SAR 14.09 and conductivity 1241.67µS/cm. KB14 shows medium hazard with SAR 4.75 and conductivity 1980.86µS/cm. Other samples show low sodium hazard with low to high salinity hazard. Facies in Layer 3 are classified as low sodium hazard with low to high salinity hazard. Only KB31 (Na-Cl) lays in between low to medium line of sodium hazard (4.56). In general, most of the groundwaters wells are suitable for irrigation use especially from the Layer 1. Only certain groundwater wells from Layers 2 and 3 as stated above are not suitable for irrigation purposes and actions must be taken as stated in Table 3.12 and Table 3.13.

CHAPTER 4

GROUNDWATER TREATMENT FOR IRON REMOVAL

4.1 INTRODUCTION

This chapter emphasizes on an alternative method of iron removal in cases where there is an abundance of iron in groundwater. At present conventional groundwater treatment is used for iron removal. Room temperature ionic liquid (RTILs) has long been used as solvents for numerous applications. Therefore, this chapter will briefly investigate the ability of ionic liquids to act as solvents for iron removal in groundwater using liquid-liquid extraction method.

4.1.1 Problems faced in Kelantan Groundwater

In Chapter 3 (Table 3.5), the presence of iron has been detected in Kelantan groundwater. The mean concentration of iron in aquifer layers ranges from 0.54 to 80.00 mg/L. The natural source of iron and other heavy metals are said to be originating from the deposited sediment in the Kelantan basin during Holocene time. More iron enters into the solution as the groundwater ages. This is because iron is released slowly from geologic materials through rock-water interaction process.

For example, in Minnesota groundwater; concentrations of iron exceed 1.00 mg/L in aquifers occurring in geologic materials that contain large amounts of iron, such as Cretaceous and some Precambrian deposits. High concentration of iron also can be found in aquifer with reducing condition such as the buried Quaternary aquifers. The reducing conditions of aquifer are characterized by low concentrations of oxygen, nitrate and Eh values less than 250 mV. Under these conditions, microbes utilize ferric ion during food consumption. Conversion of ferric ion to ferrous ion results in dissolved iron concentrations that exceed the standard values. Aquifers occurring in low iron rocks, such as some of the Precambrian deposits, and aquifers containing oxygen, will have iron concentrations less than 0.10 mg/L (Minnesota Pollution Control Agency, 1999).

Iron is the major concern in the study area because even small amounts will seriously affect the usefulness of water for domestic and industrial purpose (Awadalla & Noor, 1990). Although iron is an essential mineral for human body, high iron also causes chronic iron overload-genetic disorder (*haemochromatosis*). According to Centers for Disease Control (CDC), a disorder can result in organ damage because of significant and excessive absorption and storage of iron from the daily diet. Over time, this excess builds up in organ tissues such as the heart, liver, pancreas, joint and pituitary. The advanced stages of *haemochromatosis* are:

i. arthritis
ii. liver disease, including an enlarged liver, cirrhosis, cancer, and liver failure
iii. damage to the pancreas, possibly causing diabetes
iv. heart abnormalities, such as irregular heart rhythms or congestive heart failure
v. impotence
vi. early menopause
vii. abnormal pigmentation of the skin, making it look gray or bronze

Statistics from Hospital Universiti Sains Malaysia (HUSM) show that only 13 cases of *Haemochromatosis* have been reported from 1996 to 2009 as stated in Table 4.1. Only 2 cases involved on children while the rest cases involved on adult.

Table 4.1: Statistics of Haemochromatosis cases from 1996 – 2009

Haemochromatosis	**Children** **(below 12 year old)**		**Adults** **(above 12 year old)**	
	Male	**Female**	**Male**	**Female**
Cases	1	1	5	6
Total	2		11	

In term of irrigation, if the iron contents are accumulated in the irrigated soils over a long period of time, the soil properties as well as the nutrient uptake will be affected because iron bearing waters favors the growth of iron bacteria which can change certain forms of dissolved iron into insoluble ferric state. The insoluble iron is deposited in the voids of soil and can seriously clog the pores of water bearing formation and the opening in a well screen which ultimately restricts the movement of water. This will reduce the soil permeability (K). Once the agriculture soils are affected due to high iron content, further utilization will turn the agriculture lands into nonproductive areas. Thus, the World Health Organization, WHO (2008) has set the guideline value of 0.30 mg/L of iron in drinking water.

4.1.2 Groundwater Abstraction in Kelantan

In northern Kelantan, most of the groundwater has been exploited from shallow aquifer for public water supplies. In total there are 6 well-fields as noted in Chapter 1 which cover the districts of Kota Bharu, Bachok and Tumpat. Table 4.2 shows that the groundwater abstraction in North Kelantan from 1974 until 1995 (Mohammad & Ang, 1996). The value was estimated from 60 monitoring wells during the time period. It shows an increase in groundwater abstraction as a result of increase in the population in these districts for water supply. While Table 4.3, show the estimated demand of groundwater in Kelantan for 2010 (Suratman, 2010). As mentioned in Chapter 1, 165 MLD is the estimation values of groundwater demand in Kelantan 2010. According

Table 4.3, the total groundwater abstraction in North Kelantan is estimated about 148 MLD. Comparing from 1995 to 2010, the demand of groundwater has increased about 75 MLD. Over the years, it shows an increase in trend of groundwater demand for water supply in North Kelantan. These trends are expected to continuously increase in the future.

Table 4.2: Groundwater Abstraction in North Kelantan from 1974 – 1995

District	**Well field**	**Groundwater abstraction (MLD)**						
		1974	**1980**	**1985**	**1988**	**1991**	**1994**	**1995**
Kota Bharu	Tanjung Mas	-	3.18	3.18	2.59	9.00	9.00	9.00
	Pintu Geng	-	4.55	3.64	2.50	12.13	19.85	19.85
	Kampung Puteh	10.46	26.14	28.94	28.94	30.75	30.75	30.75
Total		10.46	33.87	35.76	34.03	51.88	59.60	59.60
Bachok	Kampung Chap	0.09	0.14	1.68	1.68	4.55	4.55	4.55
Total		0.09	0.14	1.68	1.68	4.55	4.55	4.55
Tumpat	Wakaf Bharu	0.18	0.09	5.45	3.77	8.73	8.73	8.73
Total		0.18	0.09	5.45	3.77	8.73	8.73	8.73
Grand Total		***10.73***	***34.10***	***42.89***	***39.48***	***65.16***	***72.88***	***72.88***

Table 4.3: Estimated Kelantan Groundwater Demand for 2010

District	**Population 2010**	**Population %**	**Groundwater user (%)**	**Groundwater users**	**Groundwater Demand (m^3/day)**
Kota Bharu	509600	30.37	95	484120	96824
Bachok	142100	8.47	100	142100	28420
Tumpat	173200	10.32	65	112580	22516
Pasir Mas	212000	12.63	20	42400	8480
Pasir Puteh	134200	8	10	13420	2684
Machang	101300	6.04	10	10130	2026
Tanah Merah	133400	7.95	10	13340	2668
Jeli	48000	2.86	2	960	192
Kuala Krai	120800	7.2	2	2416	483
Gua Musang	103300	6.16	2	2066	413
KELANTAN	***1677900***	***100***	**-**	***823532***	***164706***

4.1.3 Groundwater Treatment in Kelantan

Groundwater in Kelantan is being treated using conventional treatment method. This conventional method consists of aeration, coagulation, sedimentation, filtration and disinfection. An aeration process precedes oxidation for oxygenation and removal of carbon dioxide (pH increase), sulfurs and other volatile substances. The coagulation will remove dirt and other particles suspended in water. Sedimentation takes place where heavy particles (floc) settle to the bottom and the clear water moves to the filtration. During filtration, the water passes through dual sand filtration made up with layers of fine and coarse sand that help remove small particles. Then, it is followed by the disinfection process where small amounts of chloride are added to kill any bacteria or microorganism present. Figure 4.1 shows the schematic flow of groundwater treatment done by Air Kelantan Sdn. Bhd.

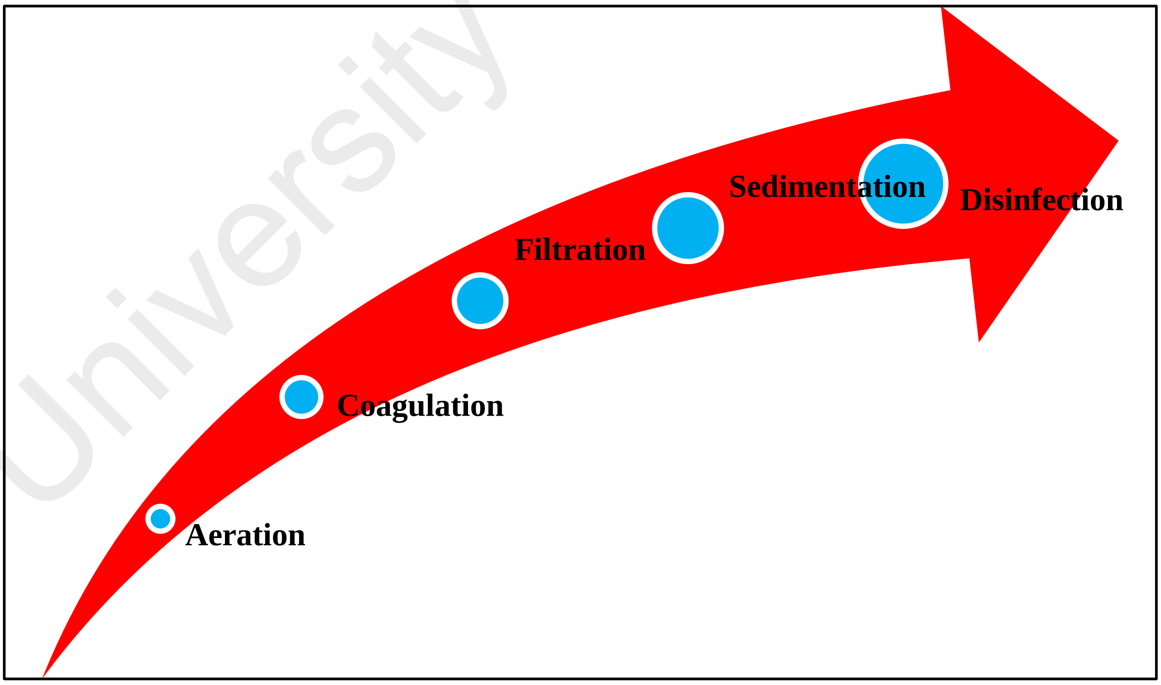


Figure 4.1: Schematic Flow of Conventional Groundwater Treatment

Recently, Air Kelantan Sdn. Bhd proposed another treatment method for groundwater. This new method is called ozonation groundwater treatment. The purpose of this method is to improve taste and color as well as to remove the organic and inorganic matters in groundwater (Kasprzyk-Hordern *et al.*, 2003). The disadvantages of ozonation are relatively its low solubility and stability in water. The application of ozonation might not be feasible from an economic point of view because of high cost and only partial oxidation of organic compound present in water. Ozone is known to be a powerful oxidant, but it reacts slowly with some organic compounds such as inactivated aromatics. In many cases, it does not provide complete oxidation of organic compounds (e.g. natural organic matter (NOM)), which results in the formation of biodegradable organic matter (carboxylic acids, carbonyl compounds).

4.1.4 General Description of Ionic Liquids

Room temperature ionic liquid (RTILs) do not contain any molecules, but they are made of ions. Ions are present in the liquid with an exactly equal number of positive and negative ions so that the whole liquid is electrically neutral (Carda-Broch *et al.*, 2003). The first RTIL, ethyl ammonium nitrate $[EtNH_3][NO_3]$ with a melting point of 12°C was discovered in 1914 during World War I (Ping Sun & Armstrong, 2010). A new class of RTILs has been reported in the 1980’s consisting of dialkylimidazolium chloroaluminate. However, these chloroaluminate ionic liquids did not receive considerable interest due to their reactivity to moisture and many chemicals (Wilkes *et al.*, 1982). The true emergence of ILs as broadly useful solvents occurred with the first development of air and moisture-stable imidazolium salts in 1992. Most of the synthesized stable RTILs contain weak complexing anions, such as BF_4^- (Wilkes & Zaworotko, 1992). RTILs have increasingly attracted attention as green, high-tech reaction media of the future. Ionic liquids (ILs) have aroused increasing interest for their promising role as alternative media for volatile solvents (Wei *et al.*, 2003).

The most common cations in ionic liquids are imidazolium, pyrrolidinium, pyridinium, tetraakylphosphonium and tetraakylammonium. While the most common anion includes halides (X^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), trifluoromethylsulfonate (TfO^-), nitrate (NO_3^-), acetate (OAc^-) and bis(trifluoromethanesulfonyl)imide (NTf_2^-). The combinations of such cation and anion can lead to a larger number of ionic liquids that can provide considerable flexibility in the selection of the most suitable pair for a specific chemical application. Figure 4.2 shows the common cations and anions in ionic liquids.

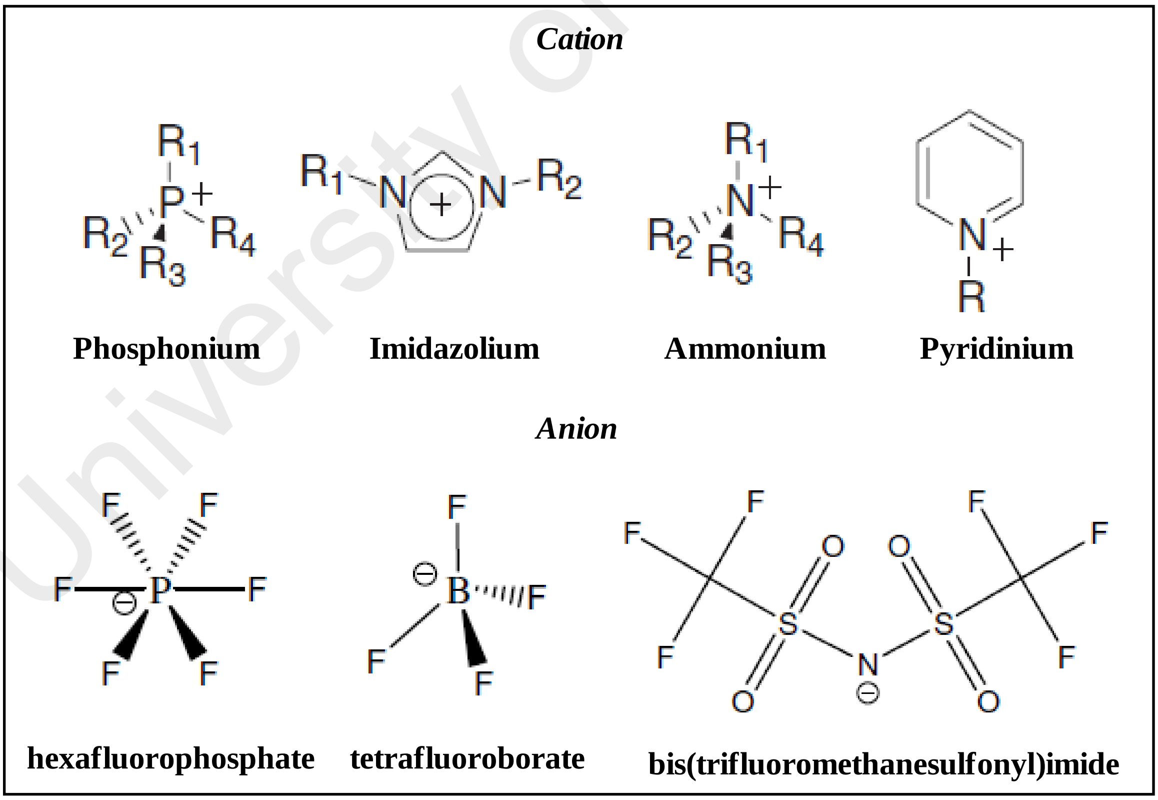


Figure 4.2: Common Cation and Anion Used in Ionic Liquids
(James & Davis, 2004; Sharma, 2008)

Ionic liquids account for their application in many fields such as catalysis, biocatalysis processing, extraction, electrochemistry or separation (Stepnowki & Zaleska, 2005). The applications of ionic liquid have expended over the past year due to their variable physicochemical properties. The main attractive physicochemical properties of RTILs are (Jonathan *et al.*, 2005 and Calda-Broch *et al.*, 2003): (i) nonvolatile at elevated temperatures; (ii) wide range electrochemical potential windows; (iii) high thermal and chemical stability; (iv) nonflammability under ambient condition; (v) media for various reaction; (vi) wide range viscosities and (vii) can be made miscible or immiscible with water and/or a number of organic solvents. Usually the term of 'Green Solvents' always refer to non-volatile, non-flammable and thermally stable ionic liquids that make such as promising replacement for the volatile organic solvents (Huddleston *et al.*, 2001).

For separation technique, the selection of RTILs is based on one of the physicochemical properties; immiscibility in water, nonvolatility and nonflammability. Water immiscibility is an important criterion because RTILs that are incorporating with hydrophobic cations and anions appear to be available for the liquid – liquid extraction (LLE) process. The nonvolatile and nonflammable RTILs is an important advantage over the conventional organic solvents (Goto *et al.*, 2003 and Goto & Shimojo, 2004).

4.1.5 Ionic Liquid as a Medium in Liquid-Liquid Extraction

Over the last ten years, numerous studies on the application of imidazolium ionic liquids as solvents for separation processes has been carried out. $[C_4mim][PF_6]$ was first applied as a solvent for the extraction of organic benzene (Roger *et al.*, 1998). Several studies show the application of ionic liquids as a medium for extraction of metal ions using LLE technique (e.g. Roger *et al.*, 2001; Visser *et al.*, 2002; Wei *et al.*, 2003;

Sheng *et al.*, 2004; Li *et al.*, 2007 and Zou *et al.*, 2008). Using the functionalized ionic liquids as an extractant and hydrophobic phase (Roger *et al.*, 2001), cadmium ($Cd^{2+)}$ and mercury (Hg^{2+}) were successfully extracted from an aqueous medium via the formation of an IL-metal complex (Visser *et al.,* 2002). The [C_4mim][PF_6] as an alternative solvent and dithizone as a metal chelator formed metal-dithizone complex with heavy metal ions. The extraction, separation and pre-concentration were achieved by controlling the pH (Wei *et al.*, 2003). BOBCalixC6 in ILs provides efficient extraction of cesium ions from aqueous solutions without the introduction of an organophilic anion in aqueous phase (Sheng *et al.*, 2004).

Successful extraction and back-extraction of inorganic mercury with [C_4tmsim][PF_6] ionic liquid using CDAA as chelating agent are also reported. This method is used to determine trace inorganic mercury in natural water with satisfactory results (Li *et al.*, 2007). The extraction of Ce(IV) along with Th(IV) and Ln(III) (Ln = Ce, Gd, Yb) nitrate by pure ionic liquid [C_8mim][PF_6] has also been tested. [C_8mim][PF_6] only showed good extraction ability for Ce(IV), poor for Th(IV) and negligible for Ln(III). Thus, the most probable extraction mechanism proposed for the study is by was anion exchange mechanism (Zuo *et al.*, 2008).

In this study, ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C_4mim][NTf_2] was used as a solvent medium in LLE together with the 1, 10-phenanthroline as an extractant (Figure 4.3). An extractant has a crucial effect on the separation and extraction efficiency (Goto & Shimijo, 2004). Therefore, the extractant that is added into an ionic liquid has to attain high distribution coefficients for cations in the LLE process (Praunitz *et al.*, 2008). In the analytical application, an extractant plays an important role because it can determine metal ions in an acid medium. It also forms complexes with metal ions in the system.

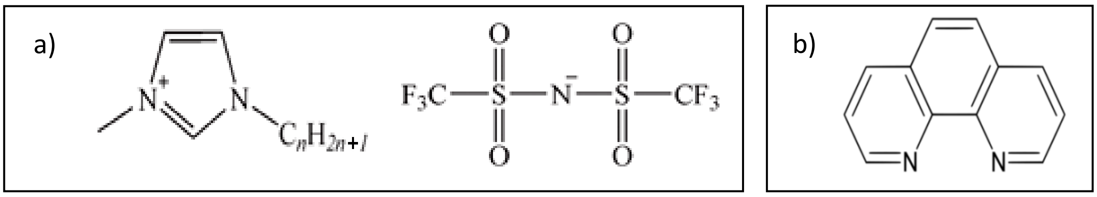


Figure 4.3: a) Structure of [C_4mim][NTf_2] and b) 1, 10-phenanthroline

4.2 METHODOLOGY

4.2.1 Sampling Points

Seven groundwater samples were collected from Department of Mineral and Geoscience (MGD) wells and private supply wells. Selection of well were based on high iron concentration for each layer of aquifer. Figure 4.4 shows the sampling locations of the selected wells. The groundwaters were sampled using peristaltic pump. Before any samples can be taken, the well should be pumped for 10 minutes or until the TDS reading give constant value to assure only a representative samples were collected. Then, the groundwater samples were filtered through Eijkelkamp filters paper (0.45 µm) into 1L polyethylene bottle. The samples were preserved in two ways; acidified or raw. The acidified samples were preserved with nitric acid at pH <2 and the raw samples were kept in a cold box with a temperature below 4°C. This samples preservation will kept the samples almost at the same condition as its actual state. The sampling and preservation method followed the APHA (1995).

Table 4.4 shows the general characteristic of the selected sampling points. The depth of wells varies from 15.0 m to 131.4 m. All layers are comprised a mixture of sand from fine to coarse and gravel in sizes.

Figure 4.4: Groundwater Sampling Point Locations

Table 4.4: General Characteristic of the Selected Sampling Points

Well	Location	Total depth (m)	Aquifer layer	Formation
KB 39	Kg. Binjai	17.0	1	Quaternary (Sand; fine to medium, greyish)
KB 54	Kg. Bawah Lembah	15.0	1	Quaternary (Sand; coarse, brownish)
KB 05	Pengkalan Chepa	30.0	2	Quaternary (Sand; fine to medium)
KB 13	Tanjung Mas	31.5	2	Quaternary (Sand; medium to coarse, grey)
KB29	Pintu Geng	62.2	2	Quaternary (Sand; coarse to very coarse with some gravel)
KB 01	Pengkalan Chepa	114.0	3	Quaternary (Sand; coarse to very coarse)
KB31	Beris Kubor Health Centre	131.4	3	Quaternary (Sand; coarse to very coarse with some gravel)

4.2.2 Chemicals and solutions

All chemicals and solvents were reagent grade and were used without purification. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C_4mim][NTf_2], 1,10-phenanthroline, and iron standard solution (1000 ppm) were supplied by Merck (Darmstadt, Germany). Lithium bistrifluoromethanesulfonylimide was supplied by Acros Organic (New Jersey, USA). Chlorobenzene (99% purity) and chloroform (99.8% purity) were obtained from Lab-Scan (Dublin, Ireland), sodium carbonate and natrium hydrogen carbonate from BDH Limited, England. Acetonitrile was supplied by Fisher Scientific (United Kingdom). Hydrochloric, sulphuric and nitric acids were obtained from Fisher Scientific (United States). Aqueous solutions were prepared using ultra-pure water with specific resistance of 18.2 MΩ-cm (PURELAB Classic by ELGA Labwater).

4.2.3 Instrumentations

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) by Perkin-Elmer (USA) was used for the determination of iron and other cations. The detection limit for ICP-OES ranges from <0.1 pbb to >10pbb depending on the elements in the periodic table. Calibration for samples analysis was done using 1ppm, 2 ppm, 3 ppm, 10 ppm and 20 ppm that contain 13 geology elements (as noted in Chapter 1). The calibration curve for standard solution should be linear through zero with correlation coefficient, $r > 0.995$. Each sample was replicate three times. The anion and ionic liquid phase were measured by 850 Professional Ion Chromatography Metrohm (Switzerland). The pH value of the extraction systems were measured with Eutech Instruments Cyberscan pH meter (Singapore) that was calibrated with pH 4.00 and 7.00 buffer standards. The conductivity, salinity and total dissolved solids (TDS) were measured using Hach sensION5 Portable Conductivity Meters (Colorado) that was calibrated with 1000 µS/cm standard solution.

4.2.4 Extraction Procedures

Figure 4.5 shows the simplified laboratory experiments. To perform the extraction mechanism, an aqueous standard solution of Fe(II) and Fe(III) ion was prepared with concentration of 20 ppm. 1 mL of [C_4mim][NTf_2] and 0.05 M of 1, 10 phenanthroline were mixed with ultrasonic agitation. Two phases will be observed when the aqueous solution is added into the ionic liquid. The biphasic system was shaken for 5 hours. The upper aqueous phase was filtered out for analysis. The initial and final solutions were analyzed using ICP-OES to determine the concentration of iron that was left in the aqueous phase. The percentage extraction of iron was calculated using Equation 4.1.

$$\text{Extraction (\%)} = 100D / [D+(V_{aq}/V_{org})], \quad D = (I-F)/F \tag{4.1}$$

where; D = distribution ratio

V_{aq} = volume aqueous (mL)

V_{org} = volume organic (mL)

I = initial concentration of aqueous (mg/L)

F = final concentration of aqueous (mg/L)

4.2.5 Stripping Procedures

For the stripping procedure of the Fe(III) ions, H_2SO_4, HNO_3 and HCl were used as stripping reagents as shown in Figure 4.5. In the extraction procedure, only 10 mL of aqueous phase containing 5 ppm of Fe(III) ion was used. The aqueous phase was shaken with 1 mL of an ionic liquid containing 0.05 M of 1,10 phenanthroline. After shaking vigorously for 5 hours, the aqueous phase was removed by filtration to separate the two phases. A 0.5 mL portion of the ionic liquid phase which contained iron-phen complex was stripped back with 2 mL of aqueous acid solution. This was followed by further vigorous shaking until equilibrium was reached. The acid solution was removed and 1 mL acid solution was diluted into 10 mL volumetric flask. The amount of iron was measured using ICP-OES to determine the recovery of the iron. The recovery factor was estimated from the ratio of metals ion in acid solution to aqueous with the correction of dilution factor (Wei *et al.*, 2003). The percentage recovery of iron was calculated using Equation 4.2.

$$\text{Recovery (\%)} = \frac{\text{Concentration of iron in acid after stripping process}}{\text{Extracted iron in IL phase}} \qquad (4.2)$$

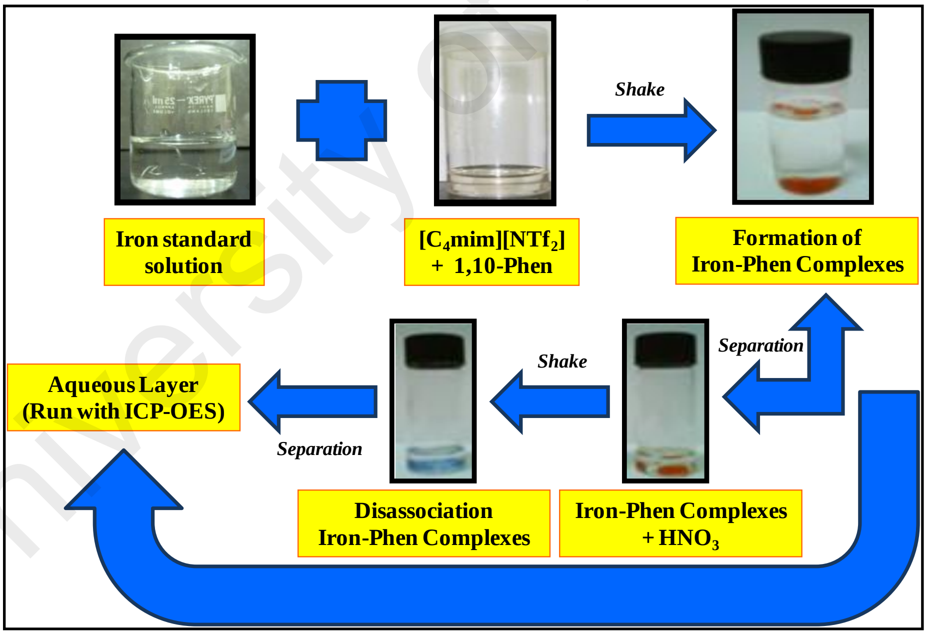


Figure 4.5: Schematic Flow of Iron Extraction and Stripping Process

4.2.6 Reuse/Recycle Procedures

Regeneration of ionic liquid take places after the extraction and stripping process were repeated for a few cycles. The recovery from each cycle shows the applicability of the ionic liquid itself for reuse.

4.3 RESULTS AND DISCUSSION

Two stages of study are involved, the first stage is using the iron standard solution and the groundwater samples is used in the second stage. In order to investigate the potential of [C_4mim][NTf_2] ionic liquid as a medium in liquid – liquid extraction several parameters were studied as listed below:

i. effect of pH
ii. effect of solvent
iii. effect of time shaking
iv. effect of phase ratio
v. effect of stripping agent

4.3.1 Effect of pH

In order to determine the optimal pH required for the extraction, it is important to study the effect of pH on the extraction efficiency of iron-phen complex with [C_4mim][NTf_2] in a wide range of pH as shown in Figure 4.6. It seems that the extraction is strongly dependent on the pH value of the extraction system (Wei *et al.*, 2003). The quantitative extraction (100%) is obtained approximately at pH around 2.5

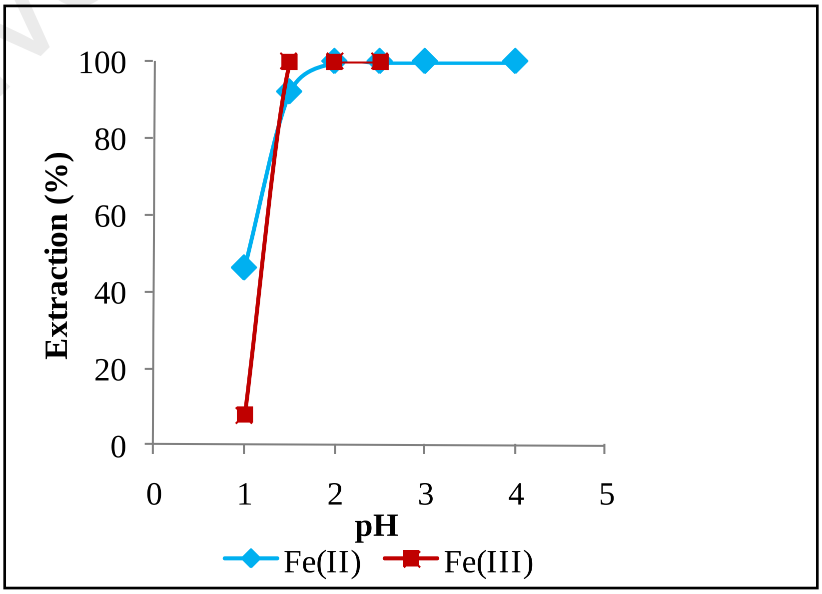


Figure 4.6: Effect of pH on the Extraction Percentage (%) of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; V_{aq}:V_{IL} = 10:0.5)

4.3.2 Effect of Solvents

The selection of solvents as the medium for extraction in this study is an important factor and it has to meet the following characteristics:

i. it should be heavier than water,

ii. it should form a binary homogenous system with water (Farajzadeh *et al.*, 2009)

iii. it should dissolve the chelating agent.

In this study, other conventional organic solvents such as chloroform ($CHCI_3$) and chlorobenzene (C_6H_5Cl) were used to carry out the extraction efficiency of Fe(II) and Fe(III) in the binary system. Figure 4.7 shows the binary phase of solvents. Ionic liquid ($[C_4mim][NTf_2]$) gives a clear phase of binary system compared to chlorobenzene and chloroform which are volatile organic compounds (VOCs). The changes in color of ionic liquid from clear to red indicate the formation of iron-phen complex. In chlorobenzene and chloroform the iron-phen complexes are still in the aqueous phase after the extraction but in ionic liquid, the iron-phen complex associates with ionic liquid. Figure 4.8 shows that the ionic liquid has higher extraction efficiency compared to chloroform and chlorobenzene at low pH. It shows that iron-phen complex has higher distribution in ionic liquid phase compared to traditional solvents.

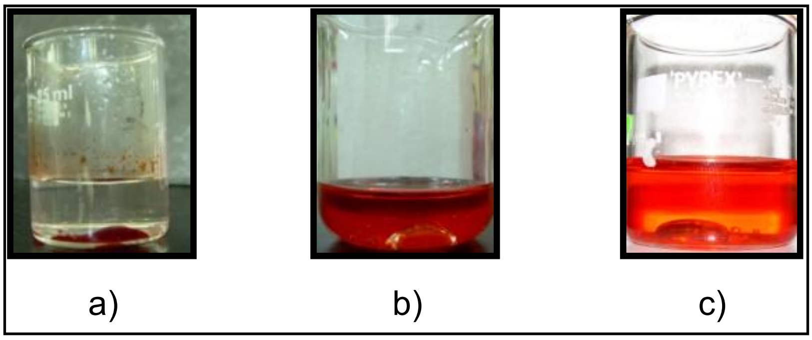


Figure 4.7: Phase Separation a) [C4mim][NTf2]; b) Chlorobenzene; c) Chloroform

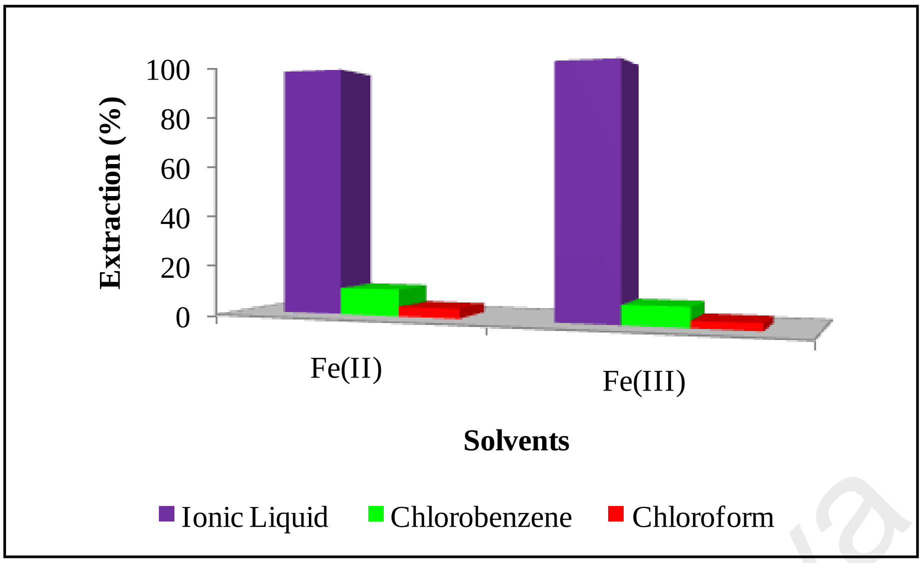


Figure 4.8: Effect on Types of Solvent on the Extraction of Fe(II) and Fe(III) Ions (Condition: [Fe(II)], and [Fe(III)] = 20 ppm; [phen] = 0.05 M; V_{aq}:V_{IL} = 10:0.5; V_{aq}:V_{CHCl3} = 10:0.5; V_{aq}:V_{C6H5Cl} = 10:0.5)

4.3.3 Effect of Time Shaking

The extraction time were performed at 5, 10, 15, 20, 60, 120, 180, 240, 300, 480, 960 and 1440 min. Figure 4.9 shows that the extraction efficiencies of Fe(II) and Fe(III) ion with [C_4mim][NTf_2] increases with time. The extraction reaches equilibrium around 300 min but the extraction time was set at 1440 min for all the experiments to ensure that all irons are fully extracted into the ionic liquid.

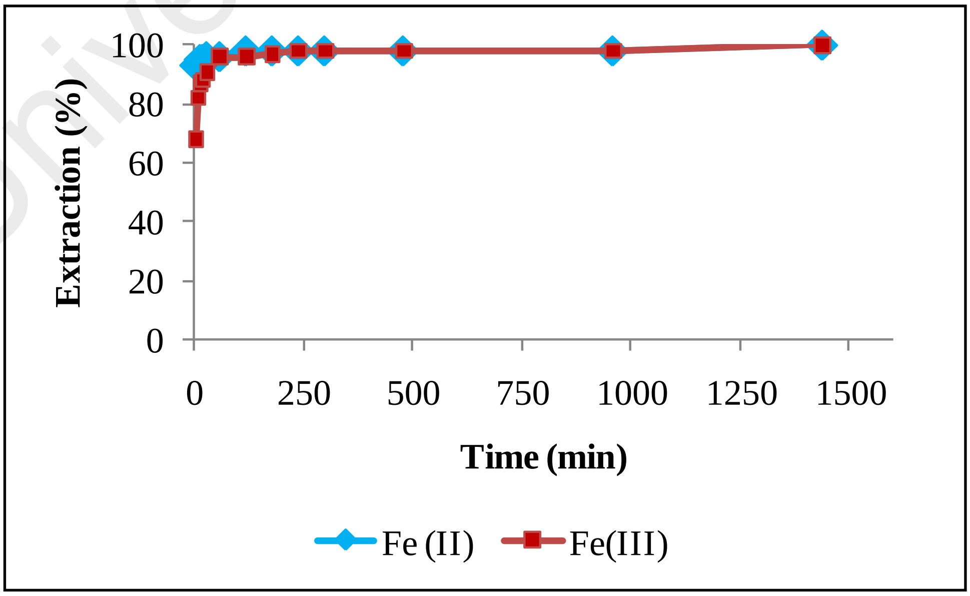


Figure 4.9: Effect of Time Shaking on the Extraction of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; V_{aq}:V_{IL} = 10:0.5)

4.3.4 Effect of Phase Ratio

The volume of ionic liquid was fixed at 0.5 mL. The extraction efficiency was obtained by changing the volumes of the aqueous phase at 10, 25, 50, 75 and 100 mL. Figure 4.10 shows the curve of extraction efficiency with different phase ratio. It shows that by increasing the ratio values, the extraction efficiency decreases. Ratio volume of aqueous to volume of ionic liquid (V_{aq}/V_{IL}) at 20 was the optimum condition for extraction. It seem that the ionic liquid shows an economic value in terms of consumption because 0.5 mL ionic liquid can extract Fe(II) and Fe(III) ion in 10 mL of aqueous phase. The percentage extraction of Fe(II) and Fe(III) ion starts to decrease at ratio V_{aq}/V_{IL} of 85. The decrease of the extraction is the result of loss in ionic liquids as volume of the aqueous phase increases.

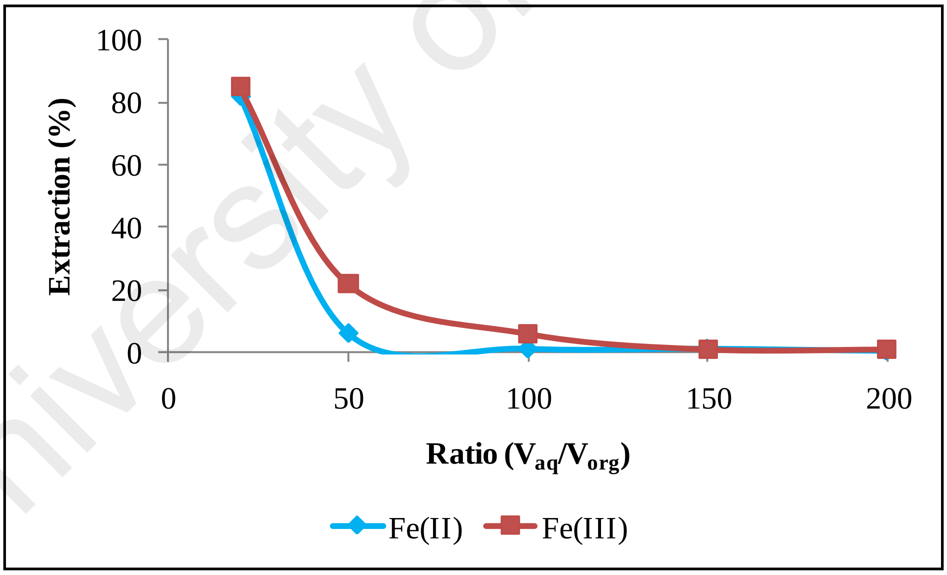


Figure 4.10: Effect of Ratio Aqueous/Organic on the Extraction of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; $V_{aq}:V_{IL}$ = 10:0.5, 25:0.5, 50:0.5, 75:0.5 and 100:0.5)

4.3.5 Effect of Stripping Agent

The purpose of stripping process is to ensure that the ionic liquid used for extraction is applicable for reuse. For this study, three types of acid were been selected, HNO_3, H_2SO_4 and HCI. During the extraction process, iron-phen complex were formed at pH value of 2.5. At pH 1.0, due to the disassociation of the iron-phen complex, low extraction value is obtained as proven by Figure 4.6. Therefore, a decrease in pH values, causes iron-phen complexes to disassociate and Fe ion removed from ionic liquid.

Figure 4.11 shows the recovery of Fe(III) with different stripping agents. It was observed that the order of stripping ability was found to be: HNO_3 > H_2SO_4 > HCI. HNO_3 was the most effective stripping agent for quantitative recovery. HNO_3 also acted as an oxidizing agent therefore stripping increases with the increase on the concentration of oxidizing agent in this LLE (Alam, 1997). 8 M HNO_3 was found to be suitable for stripping the extracted Fe(III) ion with 100% recovery. However, this stripping process leaves a problem of impurities of ionic liquid. There was no results for Fe(II) ion as regards to the inconsistent reading during the analysis.

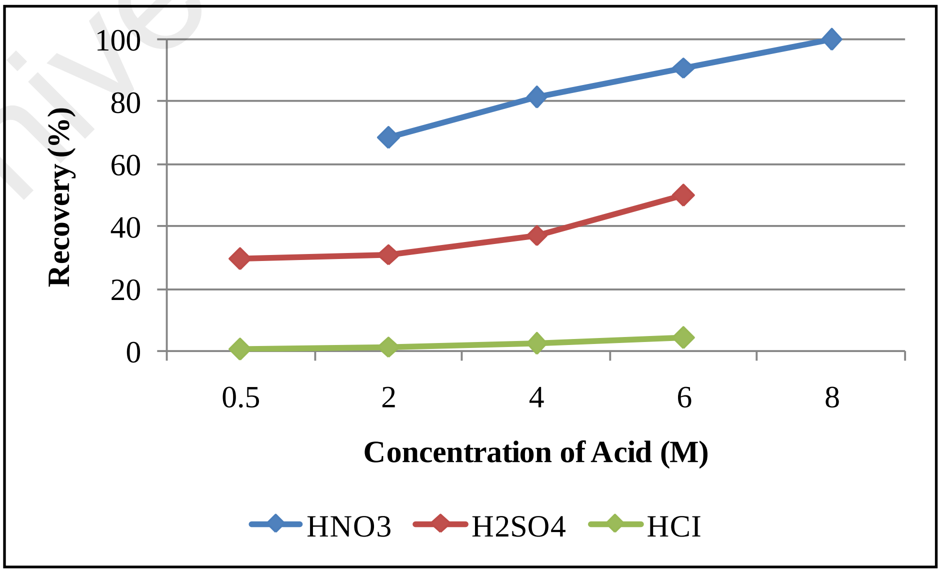


Figure 4.11: Effect of Stripping Agent on the Extraction of Fe(III) Ion (Condition: [Fe(III)] = 5 ppm; [phen] = 0.05 M; [HNO_3] = 0.5 M, 2.0 M, 6 M & 8 M; [H_2SO_4] = 0.5 M, 2.0 M & 6 M; [HCI] = 0.5 M, 2.0 M & 6 M; V_{aq}:V_{IL} = 10:1; V_{acid}:V_{IL} = 2:0.5)

4.3.6 Regeneration of Ionic Liquid

As mentioned before, the purpose of regeneration is to study the applicability of the ionic liquid itself for reuse. This will reduce the cost of using ionic liquids in LLE process. Figure 4.12 shows the recovery efficiency for each regeneration cycle. The feasibility of recycling [C_4mim][NTf_2] in LLE was determined. In the recycle process only HNO_3 solution was used. After the extraction process, the Fe(III) ion was stripped back from the ionic liquid. Then, the ionic liquid was recycled for reuse to extract Fe(III) ion in the aqueous phase. The extraction and stripping process was repeated for three cycles. The percentage of recovery decreased from cycle 1 to cycle 3 with 100%, 30% and 4% recovery. After the 2nd cycle, the ionic liquid was not suitable for the extraction of Fe(III) ion. The decrease in the recovery was observed as might be due to the loss of ionic liquid during the filtration and impurities in ionic liquid after the stripping process. Further investigation was carried out by analyzing the anion in aqueous and ionic liquid phase (Section 4.3.7).

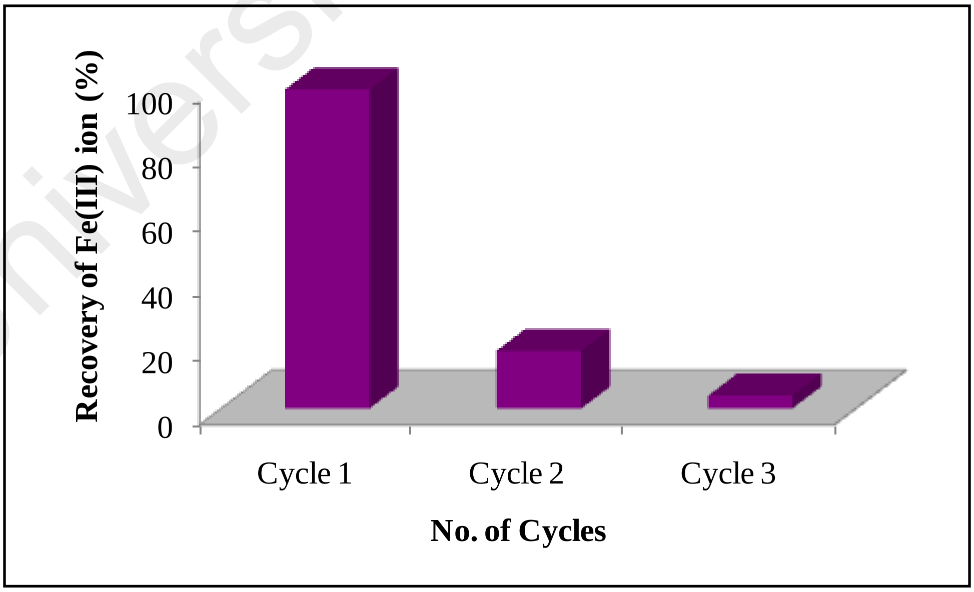


Figure 4.12: Recovery (%) of Fe(III) Ion
(Condition: [Fe(III)] = 5 ppm; [phen] = 0.05 M; [HNO_3] = 8 M; V_{aq}:V_{IL} = 10:1, 10:0.5 & 10:0.2; V_{acid}:V_{IL} = 2:0.7 & 2:0.4)

4.3.7 Application of Ionic Liquid using Groundwater Samples

Physical and Chemical Parameters

Table 4.5 shows the mean values of physical and chemical parameters of groundwater samples. In general the pH ranges from 5.42 to 6.26 that show slightly acidic groundwater condition. Most of the groundwater samples were classified as fresh water. Only KB05 was classified as brackish water as according to Freeze & Cherry, (1979) the total dissolved solid (TDS) value was more than 1000 mg/L. For sodium (Na), only KB05 showed concentration above the standard limit of 200.00 mg/L for drinking water. Most of the layers show iron (Fe) and manganese (Mn) concentration above the standard limit of 0.30 mg/L and 0.10 mg/L respectively. For anion, only chloride (Cl) showed concentration above the standard limit of 250.00 mg/L for selected groundwater samples. The standard limits are based on World Health Organization (WHO, 1984).

Removal of Metal Ions

To prove the applicability of the results obtained using the iron standard solution, study was carried out using the groundwater samples. All of the experimental conditions were chosen based on the results discussed previously.

Figure 4.13 shows that the percentage of removal of iron and other heavy metals in groundwater samples. It shows that more than 95% of iron can be removed from the groundwater samples according to the initial concentration of iron in each layer as noted in Table 4.5. Besides iron, other metal ions; Zn, Mn, and Cd too can be removed from the groundwater samples by using [C_4mim][NTf_2] ionic liquid as a solvent medium in liquid-liquid extraction treatment method.

Table 4.5: Mean Values of Physical and Chemical Parameters of Groundwater Samples

Samples			**KB54**	**KB39**	**KB13**	**KB5**	**KB29**	**KB1**	**KB31**
Aquifer			**Layer 1**	**Layer 1**	**Layer 2**	**Layer 2**	**Layer 3**	**Layer 3**	**Layer 3**
Physical parameters	**Water level (m)**		-	1.69	4.89	4.75	-	5.39	2.54
	pH		5.79	5.42	6.03	6.26	5.93	5.94	6.15
	Temp (^oC)		29.00	28.00	29.60	29.60	27.80	29.90	28.50
	Conductivity (uS/cm)		182.75	104.50	1226.00	4950.00	151.10	615.00	1352.00
	Total Dissolved Solids (TDS) (mg/L)		88.25	49.75	603.50	1413.50	71.70	299.50	669.00
	Dissolved Oxygen (DO) (mg/L)		3.55	3.65	3.80	3.15	5.50	3.35	3.10
	Salinity ($^0/_{00}$)		0.10	0.00	0.60	2.65	0.10	0.30	0.70
Chemical Parameters	**Cation (mg/L)**	**Na^+**	22.09	18.30	122.80	885.20	10.81	49.76	145.30
		K^+	7.89	1.86	14.49	47.23	3.29	12.21	42.01
		Mg^{2+}	4.28	1.24	30.39	32.90	2.79	15.94	22.92
		Ca^{2+}	20.86	1.12	46.78	26.21	20.40	18.85	32.67
		Fe_{total}	0.03	0.53	24.49	22.74	3.21	23.40	58.69
		Mn^{2+}	0.06	0.25	0.65	0.17	0.14	0.41	0.70
		Zn^{2+}	0.06	0.04	0.04	0.06	0.10	0.07	0.05
		Cd^{2+}	0.01	0.01	0.01	0.01	0.01	0.01	0.01
		Pb^{2+}	0.02	0.01	0.01	0.02	0.01	0.01	0.02
		Se^{2+}	0.02	0.02	0.00	0.01	0.01	0.01	bdl
		Cu^{2+}	bdl	bdl	bdl	bdl	bdl	bdl	bdl
		As^{2+}	bdl	bdl	bdl	0.05	0.01	bdl	bdl
		Al^{3+}	bdl	0.25	0.03	bdl	bdl	bdl	bdl
	Anion (mg/L)	**F^-**	0.07	bdl	0.13	0.08	0.40	0.14	0.05
		Cl^-	28.25	20.25	320.40	11.16	1561.19	187.30	376.90
		SO_4^{2-}	19.17	8.61	bdl	18.39	1.07	bdl	bdl
		HCO_3^-	120.10	26.60	62.40	85.70	201.60	72.80	52.60
		CO_3^{2-}	bdl	bdl	bdl	bdl	bdl	bdl	bdl
		NO_3^-	1.81	bdl	bdl	0.96	bdl	bdl	bdl
		Br^-	0.80	0.44	0.63	0.61	0.36	0.23	0.81

bdl: below detection limit

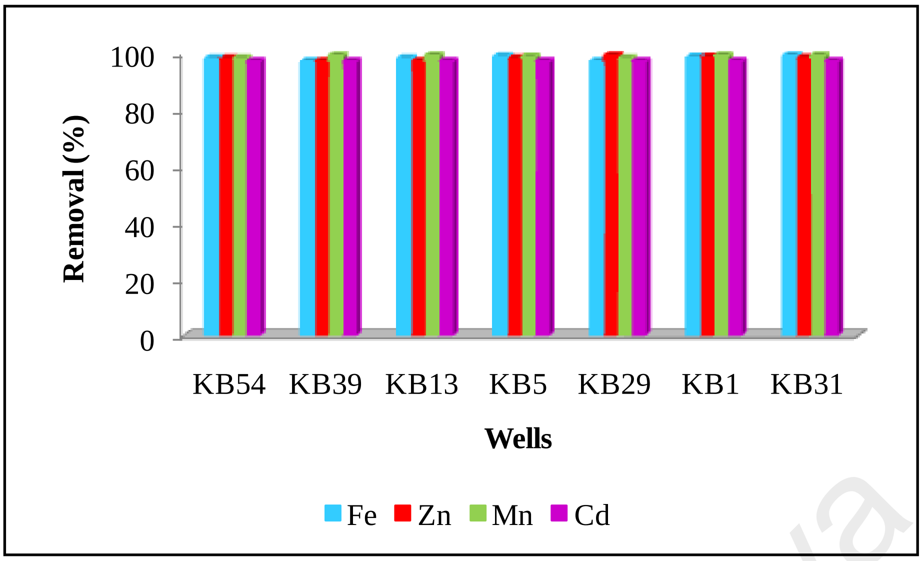


Figure 4.13: Removal of Iron and Other Heavy Metals in Groundwater Samples (Condition: [phen] = 0.05 M and V_{aq}:V_{IL} = 10:0.5)

Stripping of Ionic Liquid

In this study, 8 M of HNO_3 was used as a strippant. Figure 4.14 shows the recovery of iron from the groundwater samples. In general, the recovery ranges from 25% to 60%. The recovery values were lower compared to the laboratory experiment with iron standard solution of 100% recovery. It can be concluded that it is not very promising to reuse ionic liquid in groundwater samples because of low recovery at early stage.

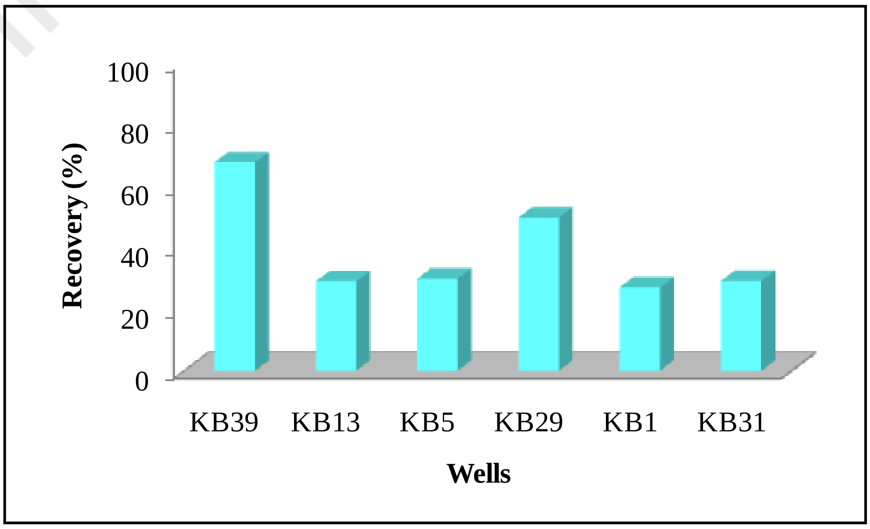
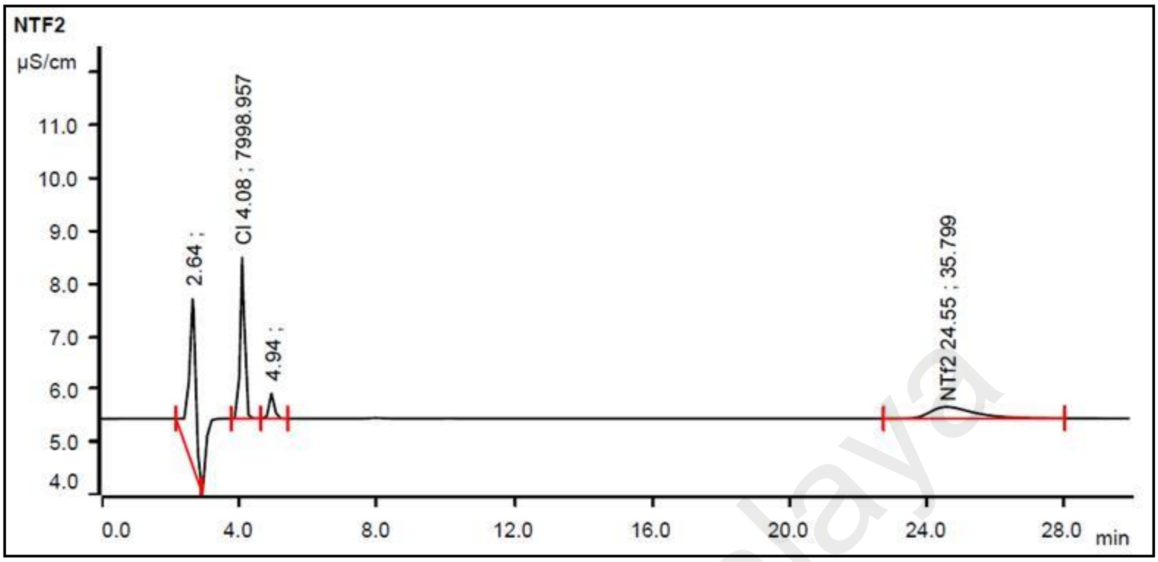


Figure 4.14: Recovery (%) of $Iron_{total}$
(Condition: V_{aq}:V_{IL} = 10:1; $V_{acid;}V_{IL}$ = 2:0.5)

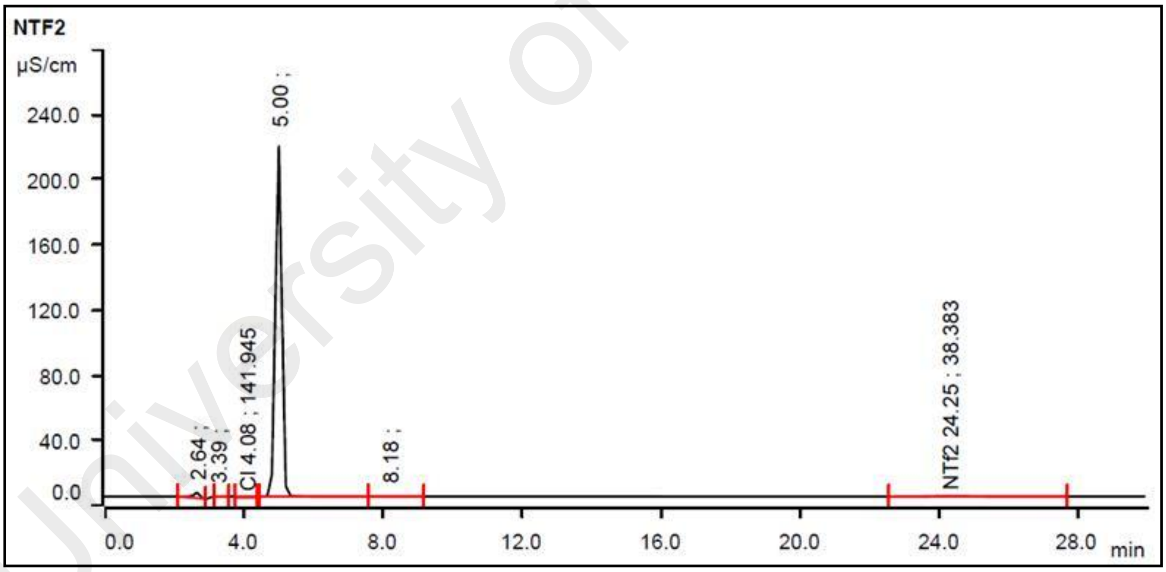
Analysis of Anion

Anion analysis was done using 850 Professional Ion Chromatography (IC) from Metrohm (Switzerland). Figure 4.15 and 4.16 shows the peak of NTf_2 anion appearing at retention time of 24.00 min (50% window) for samples KB31. It shows that NTf_2 anion from ionic liquid entered into the aqueous phase after the extraction and stripping processes. The concentration of NTf_2 in aqueous phase after the extraction was 6.43 x 10^{-3} M while after the stripping was 6.90 x 10^{-2} M. The concentration of NTf_2 in ionic liquid after the extraction was 7.84 M while after the stripping was 6.49 M. The lost of NTf_2 anion from ionic liquid suggests that the forces of attraction between the [C_4min] cation and [NTf_2] anion are not sufficiently strong enough to hold them together. Therefore NTf_2 anion of ionic liquid easily exchanges with the counter-ion in groundwater samples. Anion exchange occurs in this system as groundwater samples contain various anions as stated in Table 4.5.

Furthermore, the high concentration of strippant (8 M of HNO_3) is the main factor of impurities in IL after the stripping process. Figure 4.16 clearly shows that the presence of NO_3^- ion (retention time 4.93 min) and the loss of NTf_2 in ionic liquid phase after the stripping process. The presence of high concentration of anion in groundwater samples and strippant are the main limitations in the reuse of IL in groundwater samples. Further studies are needed to eliminate this limitation.

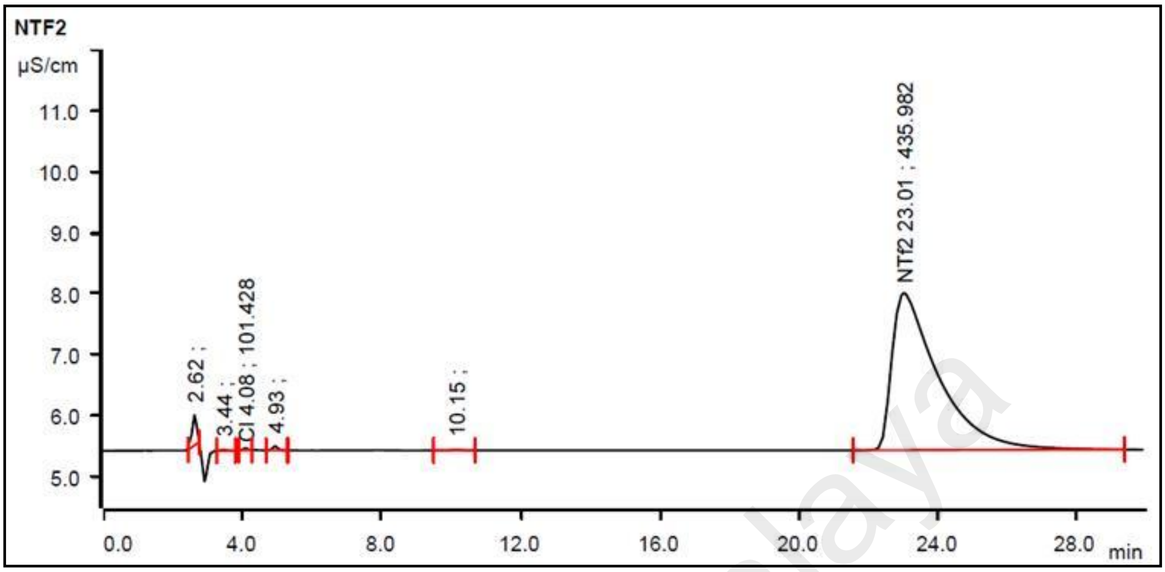


a) Aqueous phase after extraction

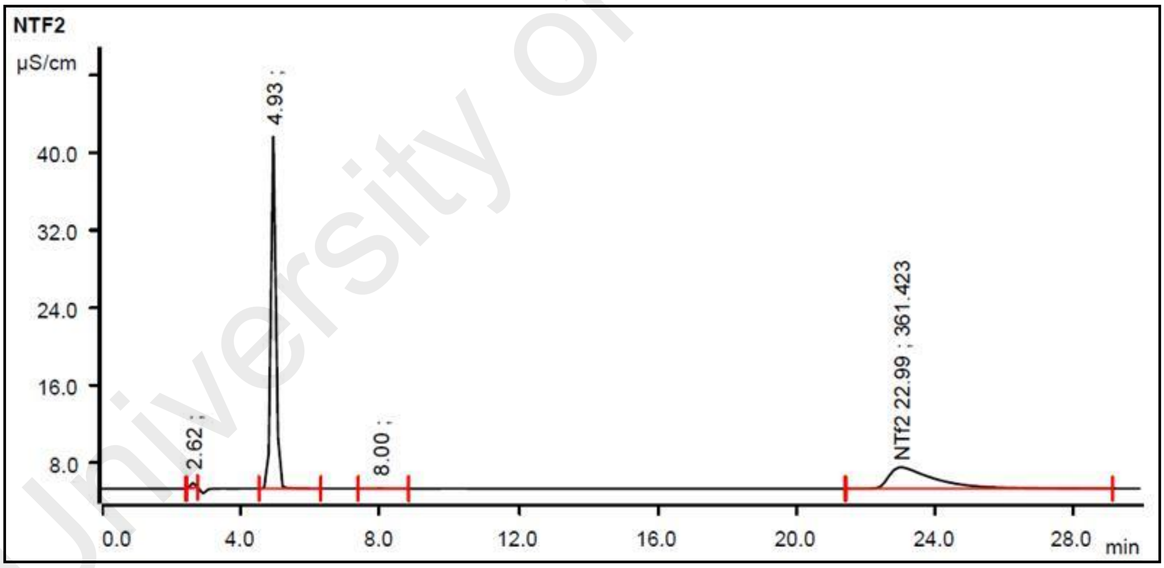


b) Aqueous phase after stripping with HNO_3 acid

Figure 4.15: Aqueous Phase Sample KB31



a) Ionic liquid phase after extraction



b) Ionic liquid phase after stripping with HNO_3 acid

Figure 4.16: Ionic Liquid Phase Sample KB31

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This chapter deals with the major conclusions drawn on the basis of hydrogeochemical study and iron removal of groundwater in the study area. Recommendations will be made based on the findings.

Conclusion

The following conclusions are drawn from the study:

1. The whole area of North Kelantan River basin is underlain by Quaternary deposits with sub formation of Gula and Simpang Formations. The thickness of the Quaternary deposits is 25 m inland and up to 200 m to the coast. This deposit is underlain by granite and metamorphic bedrock in certain locality. Bukit Marak and Bulit Kechik at the south east part appear as patches resulted from the intrusion of Boundary Range Granite in the basin.
2. This basin is drainage by Kelantan River with a length of 248 km and area of approximately 11900 km^2. The base-flow index (BFI) value of 0.54 is due to diverse geological, morphological and climatological aspects in the basin. For the whole basin, 70% of the river flows on the hard rock in the upper part of the basin and 30% of the river flows on the alluvium in the lower part of the basin. The main interaction of surface water – groundwater only occurs at the lower part of basin that is covered by alluvium deposits. While in the upper part of the basin the surface runoff dominates the process. The basin receives precipitation of 30.95x10^9 m^3/year. Potential evapotranspiration shows that about 40% (12.34 x10^9 m^3/year) of water loss from the basin with runoff coefficient of 50%. Recharge to the aquifer basin is

estimated about 11% (3.27×10^9 m^3/year) of the total precipitation based on the water balance study.

3. The alluvium deposits form an aquifer system in North Kelantan. Three aquifer layers have been identified; Layers 1, 2 and 3 with depth of approximately 20 m, 20 m to approximately 50 m and more than 50 m, respectively. These aquifer layers are separated by semi permeable clay layer and hydraulic connection exists between the layers but the uniform of the continuity is still undetermined. The permeability, transmissivity of the aquifer ranges from 28 m/day to 337 m/day, 336 m^2/day to 9431 m^2/day with specific yield is 0.06. At present, Layer 1 plays an important role as the main source of water supply for North Kelantan area.
4. Water chemistry shows that all layers have high iron concentration up to 80 mg/L and most of wells in Layers show iron concentration exceeding the WHO guideline standard of 0.30 mg/L. TDS value, classify Layers 1 and 3 as fresh water while Layer 2 as a mixture between fresh and brackish water (TDS > 1000 mg/L). As depth increases selected ions show a variation in water chemistry. Depth intervasl below 20 m shows high concentration of nitrate and ammonium. High concentration of sodium, chloride and iron are found at depth interval of 20 – 50 m. Iron remained high at depth interval of more than 50 m. Water quality shows that groundwater in Layers 1 and 3 are more suitable for drinking water purposes compared to Layer 2. Action must be taken in order to maintain the water quality as parameters above the standard limit that will result in side effects for human. While for irrigation purposes, groundwater in Layer 1 is more suitable compared to Layers 2 and 3. Layer 1 is classified as low sodium hazard (S1) with low to medium salinity hazard (C1-C2), while Layer 2 and 3 are classified as low sodium (S1) with low to high salinity hazard (C1-C3). Treatment is needed in order to control the groundwater quality of irrigation.

5. Hydrochemical facies reveal two main facies; Na-HCO_3 facies in the inland area while Na-Cl facies towards the coastal area. The intermediate facies of $CaHCO_3$, $AlHCO_3$, MgCl and CaCl has been observed in between the main facies. Based on AQUACHEM and PHREEQC analysis, the origin and evolution of groundwater in North Kelantan is influenced by weathering, dissolution, ion exchange and precipitation. An excess of sodium in groundwater are governed by silicate weathering of albite followed by dissolution. Ion exchange process especially with the clay minerals which act as impermeable layer in aquifers also increased the sodium concentration. An excess of chloride ion is attributed as a minor product due to weathering. In Layers 1 and 2, an excess of sodium and chloride ions are due to tidal effect from the river and entrapped seawater in the marine sediment during Holocene. Groundwater saturation index shows that iron minerals of hematite and goethite tend to precipitate in aquifer medium while pyrite is highly soluble in groundwater that gives high iron concentration in aquifer layers. The ferromagnesian minerals originates from the bedrock that has undergone physical and chemical weathering process.
6. The conceptual model of the aquifer system for North Kelantan River Basin is proposed and simplified in Figure 5.1. The simplification is based on the geological set up, hydrology, hydrogeology and hydrogeochemical information obtained from this study.

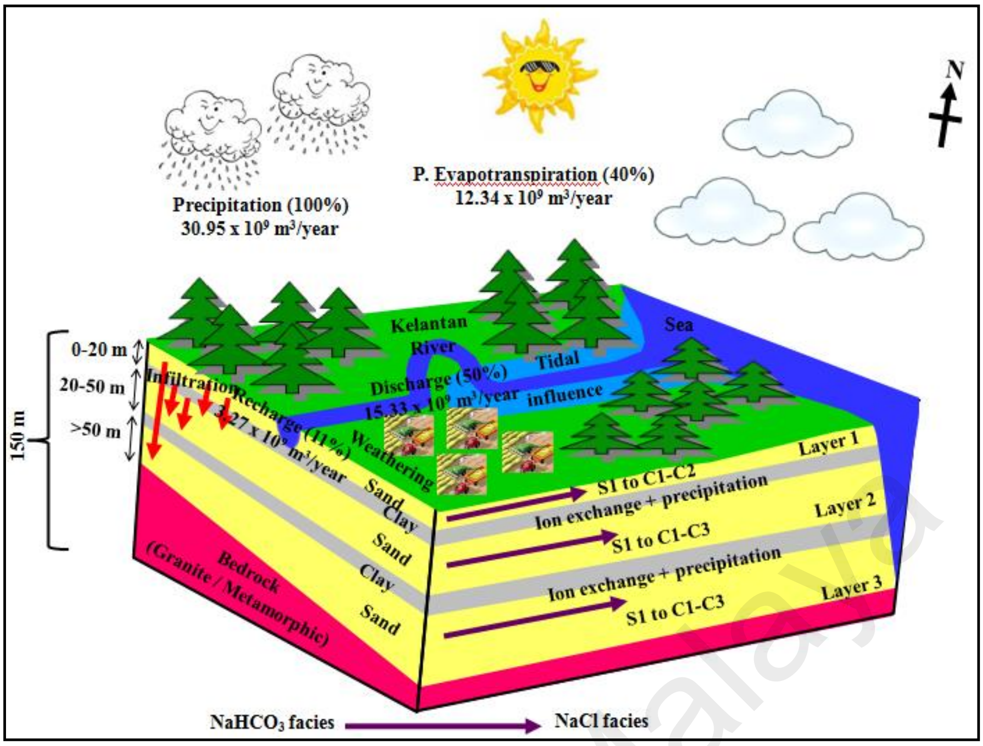


Figure 5.1: Conceptual Model of North Kelantan

7. The ionic liquid ([C_4mim][NTf_2]) as a medium in liquid – liquid extraction and 1, 10-phenanthroline as a chelating agent has been studied as an alternative method of conventional groundwater treatment. Iron was successfully removed with more than 95% removal according to the initial concentration of iron in groundwater. This method was also applied to remove manganese, cadmium and zinc from groundwater. However, [C_4mim][NTf_2] ionic liquid is not suitable to be reused for iron removal as low recovery obtained ranging from 25% to 60% in stripping process for groundwater samples. This is in regard to the appearance of [NTf_2] anion in groundwater samples as ion exchange process occurs between [C_4mim][NTf_2] ionic liquid and counter ions in the groundwater samples.

Recommendation

The following are recommendations to improve the feasibility of ionic liquid as a treatment method for groundwater with high iron concentration:

1. Further research must be done using different types of ionic liquid with different alkyl chain in order to improve the feasibility of ionic liquids as a medium in liquid – liquid extraction based on parameters studied.
2. Mass production of ionic liquids needs to be explored in the future in order to investigate field scale size of treatment.

REFERENCES

Abebe, A., Foerch, G. (2006). Catchment characteristics as predictors of base flow index (BFI) in Wabi Shebele river basin, East Africa. In: Proceedings of the Conference on Prosperity and Poverty in a Globalized World – Challenges for Agricultural Research, Tropentag, University of Bonn, October 2006. Retrived from http://www.tropentag.de/2006/

Abdul Ghani, A. (2009). Plutonism. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Alam M. S and IInoue K (1997). Extraction of rhodium from other platinum group metals with Kelex 100 from chloride media containing tin. Hydrometallurgy 46 (373-382).

Al-ahmadi, M.E. & Al-Fiky, A.A. (2009) Hydrogeochemical Evolution of Shallow Alluvial Aquifer of Wadi Marwani, Western Saudi Arabia. *Journal of King Saud University*, 21, 179 – 190.

Ang, N.K. & Loh, C.H. (1975). Hyrdogeological Investigations in Kelantan and Terengganu. Annual Report Malaysia Geological Survey

Ang, N.K. & Kwan, T.S. (1979). Groundwater Potential of the Alluvial Plain West of the Kelantan River, Kelantan. Report of Malaysia Geological Survey.

APHA, (1995). Standard Methods for the Examination of Water and Wastewater. 19th. Ed. American Water Works Association, Water Environment Federation, Washington.

Appelo, C.A.J. & Postma, D., (2005). *Geochemistry, Groundwater and Pollution* (2nd edition). A.A. Balkema Publishers, Leiden.

Aw, P.C. (1990). Fault. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Awadalla S., and Noor I. M., (1990). Groundwater condition and development in the Northern states of peninsular Malaysia. Groundwater and the Environment. Proceeding. of the seconds international groundwater conference in Kota Bahru, June 24-29

Bachik, A. R (1989). Groundwater Monitoring System in the Eastern Sungai Kelantan Area, Kelantan. Report No. GPH 05/1989, Geological Survey of Malaysia

Bachik, A. R (1994). Taburan dan Paras Nitrat di dalam Air Tanah Cetek di Lembangan Sungai Kelantan - Satu Tinjauan. Proceeding of the 25th Annual Geological Conference. Geological Survey of Malaysia p 350 – 364

Bartch, R.A., Dzyuba, S.V. & Chun. S. (2001). Influence of structural variation in room-temperature ionic liquids on the selectivity and efficiency of competitive alkali metal salt extraction by a crown ether. *Anal. Chem.*, 73, 3737-3741.

Bauder, T.A., Waskom, R.M. and Davis, J. G. (2007). Irrigation Water Quality Criteria. Extension Fact Sheet no. 0.506, Colorado State University. pp 1-5.

Berbenni, P., Pollice, A., Canziani, R., Stabile, L. & Nobili, F. (2000). Removal of iron and manganese from hydrocarbon-contaminated groundwaters, *Bioresour. Technol.*, 74, 109-114.

Bignell, J.D. & Snelling, N.J. (1977). Plutonism. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Bloomfield, J. P , Allen, D. J. & Griffiths, K. J. (2009). Examining geological controls on Baseflow Index (BFI) using regression analysis: an illustration from the Thames Basin, UK. *Journal of Hydrology*, 373, 164-17

Bosch, J.H.A. (1986). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Bosch, J.H.A. (1988). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

British Columbia Groundwater Association (2007). Water Stewardship Information Series, Nitrate in Groundwater, Feb

British Columbia Groundwater Association (2007). Water Stewardship Information Series, Sodium in Groundwater, Feb

British Geological Survey (2003). Water Quality Fact sheet: Manganese

Carda-Broch S., Bertho A. & Armstrong D.W. (2003). Solvent properties of the 1-butyl-3-methyllimidazolium hexafluorophosphate ionic liquids. *Anal. Bional Chem* 375, 191-199.

Cawte, J., Hams, G. & Kilburn, C. (1987). Manganism in a neurological ethic complex in northern Australia. *The Lancet*, 2, 1257

Chapelle, F. H. (2001). *Ground-water microbiology and geochemistry* (2nd edition). New York: John Wiley & Son

Chong, F.S. & Tan, D.N.K. (1986). Hydrogeological activities in Peninsular Malaysia and Sarawak. GEOSEA V Proceedings, Vol.II. Geological Society Malaysia, Bulletin 20, August; 827-842.

Christopher, J.D. & Robert, R. R. (2005). Defination of hydrochemical facies in the New Zealand National Groundwater Monitoring Programme. *Journal of Hydrology*, 44 (2) 105-130

Colter, A. and Mahler, R. L. (2006). Iron in Drinking Water. University of Idaho, PNW 589, June 2006.

Dai, S., Zhang, Y. & Fu, X. (2006). Comparison of extraction capacities between ionic liquids and dichloromethane. *Chin. J. Anal.Chem.*, 34 (5), 598-602.

Darbyshire, D.P.F. (1988). Plutonism. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Department of Agriculture (2006). Land used data for Kelantan State.

Domenico, P.A. & Schwartz, F.W. (1990) *Physical and Chemical Hydrogeology*. John Wiley & Sons Inc., Canada.

Dutta, R.K., Das, B., Hazrika, P., Saikia, G., Kalita, H., Goswani, D.C., Das, H.B., & Dude, S.N. (2007). Removal of iron from groundwater by ash: A systematic study of traditional method. *Journal Hazardous Materials*, 141, 834-841.

Eckhardt, K. (2008). A comparison of baseflow indices, which were calculated with seven different baseflow separation methods. *Journal of Hydrology*, 352, 168-173

Ellis, D., Bounchard, C., & Lantagne, G. (2000). Removal of iron and manganese from groundwater by oxidation and microfiltration. *Desalination* 130 (2000), 255-264

Farajzadeh, M.A., Bahram, M., Zorita, S. & Mehr, B.G. (2009). Optimization and application of homogenous liquid-liquid extraction in preconcentration of copper (II) in a ternary solvent medium. *Journal of Hardazous Materials*, 161, 1535-1543

Fitts, C. R. (2002) *Groundwater Science*. Elsevier Science Ltd., UK.

Foster, H.D. (1992). Study and interpretation of the chemical characteristics of natural water. USGS Water Supply Paper, 2254

Freeze, R.A. & Cherry, J.A. (1979). *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, N.J.

Goto, M. Nakashima, K., Kubota, F. & Maruyama, T. (2003). Ionic liquids as a novel solvent for lanthide extraction. *Analytical Sciences*, 19, 1097-1098

Goto, M. & Shimijo, K. (2004). Solvent extraction and stripping of silver ions in room-temperature ionic liquids containing calixarenes. *Anal. Chem*., 76, 5039-5044

Goto, M., Nakashima, K. & Kubota, F., Maruyama, T. (2005). Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. *Ind. Eng. Chem. Res.*, 44, 4368-4372

GSD (1993). Records of Groundwater Monitoring Wells in the Kota Bharu Area, Kelantan. Geological Survey of Malaysia. Report No. 23 GPH5 1993.

Hamzah, U., Haryono, Samsudin, A.R., Rafek, A.G. & Ali, C.A. (1997). High resolution multichannel seismic profiling: acase study at Pak Pura, Bachok, Kelantan. *Warta Geologi*, Vol.23, No.4, pp.231-237.

Han, X. & Armstrong, D.W. (2007). Ionic liquids in separations. *Acc.Chem. Res*.40, 1079-1086

Haryono, A., Abdul, R. S., Abdul G. R. & Nasiman S. (1996). Penggunaan Kaedah-Kaedah Hidrogeokimia dan Kerintangan Geoelektrik untuk Mengesan Kemasinan Air Tanah pada Akuifer Kedua di Pantai Utara Kelantan. Bulletin Geological Society, (39) 1-8

Hounslow, A.W. (1995). *Water Quality Data: Analysis and Interpretation*. CRC Press, Inc., Boca Raton, Florida.

http://www.britannica.com/EBchecked/topic/586581/temperature

http://www.reopure.com/nitratinfo.html

http://www.sciencecourseware.org/VirtualRiver/Files/pages04.html.

Huddleston, J.G., Visser, A.E., Reichert, W.M., Willauer, H.D., Broker, G.A. & Rogers, R.D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry*, 3, 156-164. DOI: 10.1039/b103275p

Hutchison, C.S. (2009). Mrtamorphism. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Ibbitt, R., Takara, K., Mohd Desa, M.N. & Pawitan, H. (2002). Catalogue of Rivers for Southeast Asia and The Pacific-eds (Volume V). The UNESCO-IHP Regional Steering Committee for Southeast Asia and the Pacific (A UNESCO-IHP Publication). March 20.

Ineson, J & Downing, R.A. (1964). The groundwater component of river discharge and its relationship to hydrogeology. *J. Inst. Water Eng*., 18: 519--541.

Interim National Groundwater Quality Standard (INWQS) for Malaysia. Retrieved from. http://www.did.sarawak.gov.my/wqis/sgsarawak/inwqsm-standards.htm

Ishihara, S., Sawata, H., Arpornsuwan, S. Busaracome, P. & Bungbrakearti, N. (1979). Metamorphism. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Iwani, O., Watanabe, T., Moon, C.S., Nakatsuka, H. & Ikeda, M. (1994). Motor neuron disease on the Kii Peninsula of Japan: excess manganese intake from food coupled with low magnesium in drinking water as a risk factor. *The Science of the Total Environment*, 149, 121-135

James, H & Davis, Jr. (2004). Task-Specific Ionic Liquids. *Lett.*, 33, 9, 1072-1077

Jonathan J., Jordy, & Mikami K. (2005). Green Reaction Media in Organic Synthesis. Publ. Blackwell Publishing Ltd.

Karanth, K.R. (1994). *Groundwater assessment, development and management*. Tata McGraw-Hill Publishing Company Limited, New Delhi, India.

Kasprzyk-Hordern, B., Ziolek, M. & Nawrocki, J. (2003). Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Applied Catalysis B. Environment*, 46, 639-669.

Lacey, C.G. & Grayson, R.B. (1998). Relating baseflow to catchment properties in south-eastern Austratlia. *Journal of Hydrology*, 204, 231-250

Lee, C.P. (2004). Paleozoic. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Leman, M.S. (2004). Mesozoic. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Li, Z., Wei, Q., Yuan, R., Zhou, X., Liu, H., Shan, H. & Song, Q. (2007) A new room temperature ionic liquid 1-butyl-3-trimethylysilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by old vapor atomic absorption spectrometry. *Talanta*, 71. 68-72

Loh, C.H. (1992). Quaternary. In: MacDonald, S. (eds) *The geology and mineral resources of north Kelantan and North Terengganu*. Geological Survey West Malysia District Memoir 10

MacDonald, S. (1967). The geology and mineral resources of north Kelantan and North Terengganu. Geological Survey West Malysia District Memoir 10

MacDonald, S. (1951). Introduction. In: MacDonald, S. (eds) *The geology and mineral resources of north Kelantan and North Terengganu*. Geological Survey West Malysia District Memoir 10

Md Hashim, M.A. (2002). Geologi dan geomorfologi kawasan Kuala Besar hingga Kuala Pengkalan Besar dengan penekanan permatang-permatang Holosen dan perubahan pantai. Unpublished B.Sc. Thesis, University of Malaya, Kuala Lumpur.

MOH. (1992). Drinking Water Quality Standard, Ministry of Health.

Ministry of Health (2009). Drinking Water Quality Standard, Ministry of Health. Retrieved from http://kmam moh.gov.my/public-user/drinking-water-quality-standard.html

Minnesota Pollution Control Agency (1999). Iron in Minnesota Groundwater. Groundwater Monitoring & Assessment Program., May

Minnesota Pollution Control Agency (1999). Sulphate in Minnesota Groundwater. Groundwater Monitoring & Assessment Program., May

Mohd Aziz, N. (2007). Kimia Air Tanah dan Taburan Bakteria dalam Akuifer Alluviium Cetek di Utara Kelantan. Unpublished B.Sc. Thesis, University of Malaya, Kuala Lumpur.

Mohd Rizalpahlavy, N.H. (2008). Hydrogeochemistry of Deep Aquifers in North Kelantan River Basin. Unpublished B.Sc. Thesis, University of Malaya, Kuala Lumpur.

Mohammad, I.C. (1992). Status Pengawasan Air Tanah di Delta Sungai Kelantan. Proceeding of the 23rd Annual Geological Conference. No.4, pp 258 - 280.

Mohamad, I.C. & Ang, N.M. (1996). Laporan Program Pengawasaan Air Tanah Semenanjung Malaysia. Geological Survey Department Malaysia. Report No. GPH 4/96.

Mwakalila, S., Feyen, J., Wyseure, G. (2002). The influence of physical catchment properties on baseflow in semi-arid environments. *Journal of Arid Environments* 52, 245–258.

Mwakalila, S. (2003). Estimation of stream flows of ungauged catchments for river basin management. *Physics and Chemistry of the Earth* 28, 935–942.

Nathan, R.J., Austin, K., Crawford, D., Jayasuriya, N. (1996). The estimation of monthly yield in ungauged catchments using a lumped conceptual model. *Australian Journal of Water Resources* 1 (2), 65–74.

Natural Resources Management and Environment Department, (2004). Fertilizer use by crop in Malaysia. Land and Plant Nutrition Management Service Land and Water Development Division. Food and Agriculture Organization of United Nations, Rome.

Ng, T.F. (2008). Topography. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Noor, I.M., (1979). Prefeasibility study of potential groundwater development in Kelantan, Malaysia. PhD Thesis, University of Birmingham, United Kingdom

Pfeiffer, D.I. & Chong, F.S. (1979). Preliminary Report of the hydrogeological Investigations in Kota Bharu. Annual Report Malaysia Geological Survey

Penman, H.L. (1948). In: EstimatingPotential Evaporation Using The Penman Procedure 1991 (Revised and Updated). Hydrological Procedure No. 17. Department of Irrigation and Drainage, Ministry of Agriculture Malaysia.

Pfeiffer, D. I. & Tieddemann. O. (1986). Hydrogeological studies and the development of groundwater in the Kelantan Coastal Plain, Malaysia. *Nat. Resour. & Development*, 24, 72-82

Pingsun & Amstrong, D.W. (2010). Review: Ionic liquid in analytical chemistry. *Analytica Chimica Acta*, 661, 1-16

Pipkin, B.W., Trent, D.D., & Hazlett, R. (2005). Geology and the Environment (4th edition). Brooks/Cole Thomson

Prausnitz, J.M., Papaiconomou, N., Lee, J.M., Salmein, J. Stosch, V.M. (2008). Selective extraction of copper, mercury, silver, and palladium ions from water using hydrophobic ionic liquids. *Ind. Eng. Chem. Res*. 47, 5080-5086.

Raj, J.K., Yusoff, I. & Abdullah, W.H., (2007a). Past and present-day coastal changes between Kuala Sungai Besar and Kuala Besar, Kelantan Darul Naim. Bull. Geol. Soc. Malaysia, 53:15-20

Raj, J.K., Yusoff, I. & Abdullah, W.H., (2007b). Past, present and future coastal changes Kuala Kemasin estuary, Kelantan State. Bull. Geol. Soc. Malaysia, 53:75-80

Rao, N. (1993). Environmental impact of industrial effluent in groundwater regime in Visakhapanam industrial complex. *Indian Jour. Geol*, 65, 35-43

Rao, N.S., Rao, J.P., Devadas, D.J., Rao, K.V., Krishna, C. & Rao, B.N. (2002). Hydrochemistry and groundwater quality in developing urbsn environment of a semi-arid region, Guntur, Andhra Pradesh. *J. Geol. Society of India*, 15, 159-166

Roger, R.D., Huddleston, J.G., Willauer, H.D., Swatloski, R.P. & Visser, A.E., (1998). Room temperature ionic liquids as novel media for “clean” liquid-liquid extraction. *Chem. Commun*., 1765-1766

Samsudin, A. R., Haryono, A., Hamzah, U. & Rafek, A. G. (2008). Salinity Mapping of Coastal Groundwater Aquifers using Hydrogeochemical and Geophysical Methods: A Case Study from North Kelantan, Malaysia. *Environ Geol*., 55, 1737–1743, doi: 10.1007/s00254-007-1124-9.

Santhi, C., Allen, P.M., Muttiah, R.S., Arnold, J.G., Tuppad, P. (2008). Regional estimation of base flow for the conterminous United States by hydraulic landscape regions. *Journal of Hydrology* 351, 139–153.

Savage, H.E., (1925).Chapter 1: Introduction. In: MacDonald, S. (eds) *The geology and mineral resources of north Kelantan and North Terengganu*. Geological Survey West Malysia District Memoir 10

Sikdar, P.K., Sarkar, S.S. & Palchoudhry, S. (2001). Geochemical Evolution of Groundwater in the Quaternary Aquifer of Calcutta and Howrah, India. *Journal of Asian Earth Science*, 19, 579-594, doi:10.1016/S1367-9120(00)00056-0.

Seet, C. P (1987). Salt Water Intrusion in Groundwater in Peninsular Malaysia - an overview. Proceeding of the International Groundwater Conference held on 22th - 26th June 1987 at Pan Pacific Hotel, Malaysia (pp E-37 - E50). Malaysia: Pan Pacific Hotel.

Sharma, P., (2008). Ionic Liquids: Synthesis, Characterization and Applications in Analytical Chemistry. M.Sc. Thesis, University of Texas at Arlington.

Slater, D. (1957).Chapter 1: Introduction. In: MacDonald, S. (eds) *The geology and mineral resources of north Kelantan and North Terengganu*. Geological Survey West Malysia District Memoir 10

SMHB Sdn. Bhd. (2000). Kajian Sumber Air Negara 2000 - 2050 (Semenanjung Malaysia) Sector Report - Jilid 04: Chapter 7 - Environmental Considerations, Chapter 8 - Supply, Planning and Development Works, Chapter 9 - Hydropower Development, Chapter 10 - Groundwater Studies.

Soh, Z.A. (1972). The geomorphology of Kelantan Delta, Malaysia. Phd Thesis, University of Malaya, Kuala Lumpur, Malaysia

Stepnowski, P. & Zaleska, A. (2005). Comparison of different advanced oxidation processes for the degradation of room temperature ionic liquids. *Journal of Photochemistry and Photobiology A: Chemistry*, 170, 45-50

Stauffer, P.H. (1973). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Suntharalingam, T. & Teoh, L.H. (1985). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Suratman, S. (1997). Groundwater Protection in north Kelantan, Malaysia: an intergrated mapping approach using modeling and gis. PhD Thesis, University of Upon Tyne, United Kingdom

Suratman, S. (2010). Current and Future R&D on Groundwater Resources in NAHRIM. 2nd Workshop on Groundwater in the Context of IWRM "Research and Development (R&D), and Capacity Building Needs in Groundwater Resource Management", NAHRIM, Malaysia

Takeda, A. (2003). Manganese action in brain function. *Brain Research Reviews*, 41, 7987

Teh, T.S. (1976). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Tjia, H.D. (1973). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Todd, D.K. & Mays, L. W. (2005). *Groundwater Hydrology* (3rd Edition). John Wiley & Sons, Inc.

Udie Lmasudin, M.I. (2000). Kajian taburan enapan resen dan perubahan pesisir pantai, Kota Bharu – Kuala Telong, Kelantan Darul Naim. Unpublished B.Sc. Thesis, University of Malaya, Kuala Lumpur.

Visser A.E., Swatloski, R.P., Reichert, W.M., Mayton, R., Sheff, S.,Wierzbicki, A., Davis, J.H. & Rogers, R.D. (2002). Task-specific ionic liquids incorporating novel cations for the coordinating and extraction of Hg^{2+} and $Cd^{2+:}$ Synthesis, characterization and extraction studies. *Environ. Sci. Technol.*, 36, 2523-2529

Walker, D. (1956). Quaternary. In: Hutchison, C.S & Tan, D.N.K., (eds). *Geology of Peninsular Malaysia*, University of Malaya and Geological Society of Malaysia, Kuala Lumpur

Wei, G.-T., Yang, Z. & Chen, J.-C. (2003). Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metals ions. *Analytica Chemica Acta*, 488, 183-192

W.H.O (2003). Chloride in Drinking-water. Background document for development WHO Guidelines for Drinking-water Quality.

W.H.O (2004). Sulfate in Drinking-water. Background Document for Development WHO Guidelines for Drinking-water Quality.

W.H.O (2008). Guidelines for Drinking-water Quality. 3rd Edition Incorporating the First and Second Addenda. Volume 1: Recommendations. World Health Organizanition, Geneva.

Wilkes, J.S., Levisky, J.A., Wilson, R.A & Hussey, C.L. (1982). Dialklimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. *Inorg. Chem*., 21 (3), 1263-1264

Wilkes, J.S. & Zaworotko, M.J. (1992). Air and water stable 1-ethyl-3-metlimidazolium based ionic liquids. *J. Chem. Soc., Chem. Commun*., 965-967

Yong, (1985). In: Domenico, P.A. & Schwartz, F.W., (eds). Physical and Chemical Hydrogeology. John Wiley & Sons, Inc., Canada.

Zuo, Y., Li, D.Q., Chen, J. & Liu, Y. (2008). The separation of Cerium(IV) from nitric acid solutions containing Thorium(IV) and Lanthanides(III) using pure [C8mim][PF6] as extracting phase . *Ind. Eng. Chem. Res.*, 47, 2349-2355.