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Major Ion Concentration Analysis and Evaluation of Malaysian-Sourced Groundwater for Drinking Water

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Groundwater makes up almost 99 % of available freshwater sources on Earth. However, Malaysia's freshwater supply comprises less than 10 % of groundwater. As the water shortage crisis becomes more severe, attention has shifted towards utilizing groundwater. However, due to progressing urbanization and the increase in population, the treatment of groundwater is necessary to ensure safe consumption. This research focuses on the hydrochemistry of groundwater samples collected from 3 different sites located in Johor, Malaysia. The main objective of this study is to establish the quality of groundwater in terms of its physicochemical properties to determine its viability to be used as drinking water. The important physical properties of groundwater such as pH, conductivity, total dissolved solids (TDS), and ion concentration analysis were conducted in the lab. The chemical composition of the groundwater was determined where major cations (Ca^{2+}, K^+, Mg^{2+}, Na^+) and anions (HCO_3^-, F^-, NO_3^-, SO_4^{2-}, Cl^-) concentrations are present in the groundwater together with several trace elements (Si, Al, As). The results of ion concentration analysis obtained for the groundwater samples were compared with the guidelines set by the Ministry of Health Malaysia (MOH) for drinking water quality to check whether it adheres to the standard values or not since excess of any mineral ions can cause severe health implications. The analysis data indicated that Ca^{2+} is the major cation present in all the samples at the highest concentration while HCO_3^- is the dominant anion that exists at an abundant concentration in all the groundwater samples. According to the analysis results obtained, it can be deduced that the groundwater samples from all three locations can be classified into the bicarbonate-calcium-rich type of water category. The groundwater samples also adhere to the quality limit set by MOH for the major ions' concentration, establishing the potential of groundwater for consumption purposes and household needs as well.

1. Introduction

Groundwater is defined as water that mostly resides in subterranean pore spaces but also in well-defined channels, such as those seen in karst formations, which are produced by the dissolving of soluble rocks like limestone (Brands et al., 2016). Groundwater may be found at any place on Earth if an extensive drilling activity is conducted to detect the source of the location, and the most exploitable groundwater is often discovered within 1 km of Earth's surface (Brands et al., 2016). It is also known to contain mineral concentrations at higher levels compared to those present in surface water. Due to the soil properties and mineral contents, the geological state has a considerable impact on the mineral composition of groundwater (Harun et al., 2019).
Groundwater is also relatively clean compared to surface water since most contaminants in groundwater are naturally filtered out as it passes through soil and rocks (Sharma and Sarma, 2011). However, due to recently increased activities of humans exploiting nature, at the namesake of industrial developments, mining, and agriculture, this source may be becoming more and more susceptible to contamination, possibly requiring proper treatment to be conducted before can be supplied as drinking water. The groundwater source which naturally contains an abundant level of mineral ions can be supplied as drinking water which is rich in specific major and minor ions that are essential for human health. These ions are also crucial to the body's ability to perform several tasks. Human health may be significantly impacted by it, either via deficiencies brought on by insufficient consumption or toxicity caused by an overabundance of nutrients (Hamzah et al., 2014). Ensuring the presence of these major ions within the permissible limit in drinking water is essential to ensure safe consumption.

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Heavy metal concentrations as well as the concentration of major and minor ions have been the subject of numerous research on the determination of major ions in groundwater. According to the results of those research, these ions vary from location to location depending on the chemical makeup of the rocks through which the groundwater moves as well as the actions of humans in that area (Hamzah et al., 2014). Prior to proposing groundwater for consumption and residential use, it is critical to assess its physicochemical properties and ion concentration. The main objective of this paper is to evaluate the potential of three Malaysian-sourced groundwater samples to be used as drinking water focusing solely on the major ions contained in the water. Although this criteria does not conclusively determine the potability of these water sources, it is an important preliminary screening that needs to be conducted. Thus, in this study, a thorough ion analysis was conducted on the groundwater collected from various places in Johor, Malaysia. This will be achieved by doing a comparative study of the results obtained from the physicochemical and ion concentration analysis with the Natural Drinking Water Quality Standard (NDWQS) set by the Ministry of Health Malaysia (MOH). The guidelines of this NDWQS were drawn based on the reference to the 2nd edition of WHO Drinking Water Quality Guidelines (Ministry of Health Malaysia, 2004).

2. Methodology

2.1 Study area

The samples were collected from three different sites in Johor, which is a state located in the south of Malaysia with a coordinate of 1°59′27″N 103°28′58″E. This state which has an equatorial climate and extraordinarily diversified tropical rainforests are also found to have an abundance of well-defined groundwater aquifers. The groundwater samples were collected from 3 deep aquifers which have a depth range of approximately 80 m to 120 m. Currently, the water sources collected at these specific locations are only being used for irrigation in agriculture, industrial usage, and as feed for livestock animals. Table 1 shows the sampling site's location, depth of the groundwater source, and the current applications of this water source. The location of the groundwater collected from the three sites is marked on the map of Johor as shown in Figure 1.

Table 1: Sample location and depth

Location	Location Code	Depth (m)
Kampung Ayer Manis, Sedenak, Kulai	A1	120
Ladang Kelapa Sawit, Kota Tinggi	A2	80
Batu Lapan, Skudai, Johor Bahru	A3	100

Figure 1: Groundwater sample collection locations

2.2 Groundwater analysis

The collected groundwater samples from the three different locations were analysed for their physicochemical properties, as well as for the major ions and trace element concentrations. The physical and chemical properties of the groundwater samples such as the temperature, pH, electrical conductivity (EC), salinity, and total dissolved solids (TDS) were checked on-site using a potable water meter. The samples were collected in sterilized glass containers and stored at a temperature of 4°C before conducting the ion analysis at the lab according to APHA guidelines. The ion analysis of anions was conducted by Ion Chromatography (F^-, NO_3^-, SO_4^{2-}, Cl^-), total metals by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (Ca^{2+}, K^+, Mg^{2+}, Na^+), ICP-MS (Al, As), total silicon by Hydrofluoric Acid (HF) Digestion, and alkalinity test for bicarbonate concentration (HCO_3^-).

Based on the ion concentration analysis results obtained, total hardness (TH) will be calculated for all three water samples based on Eq(1) (Sawyer et al., 2003). When using groundwater for drinking, household, industrial, or agricultural applications, the total hardness is a crucial water quality criterion that needs to be assessed to ensure the safe use of the source (Saha et al., 2019). TH will be calculated based on the concentration of calcium and magnesium, as they are the principal ion in charge of the TH.

$$\text{TH (mg/L)} = (Ca^+ + Mg^+) \times 50 \qquad (1)$$

The concentration of magnesium and calcium to be input in the formula for TH calculation will be in meq/L.

3. Results and discussion

3.1 On-site parameters

The physicochemical properties of the groundwater samples which were checked on-site were tabulated. The mean values of each parameter collected from the three locations were calculated and the values were compared and analysed according to the permissible limit values set for drinking water standards by the Ministry of Health Malaysia (MOH). Table 2 shows the parameter values that were measured on-site and the calculated mean value.

Table 2: On-site parameters of groundwater samples

Parameter	A1	A2	A3	Mean	MOH
Temperature (ºC)	27.33	32.73	31.69	30.6	-
Salinity (ppt)	0.01	0.01	0.02	0.013	-
TDS (mg/L)	141.0	163.0	204.0	169.3	1,000
pH	8.10	9.10	7.6	8.27	6.5-9.0
Conductivity (µS/cm)	273.32	312.20	394.82	326.78	-

The pH value is an important parameter in any assessment of water quality as it measures how well the water will react with any acidic or alkaline materials that exist in the source (Rao et al., 2012). The pH values of the samples collected from two sites (A1 and A3) are within the permissible range set by MOH which is from 6.5-9.0, while the sample from A2 has a slightly higher pH, which is 9.10. The pH values of all the locations indicate that the water is slightly alkaline as its pH value is greater than 7. This pH value is an important parameter to be checked as it influences the quality of water, and it is greatly affected by the biological and chemical parameters of the water as well as the presence of toxic compounds (Saha et al., 2019). The temperature of the groundwater has a high variation between samples from a range of 27 °C to 32 °C, and this might be due to various external conditions such as current weather during sample collection and heat transfer from the atmosphere.

A significant variation can be observed in the electrical conductivity value of the three samples and these differences can be correlated with the variation in their geochemical constituents. The electrical conductivity values of the groundwater samples collected range from 273.32 to 394.82 µS/cm with a mean value of 326.78 µS/cm. The sample from A3 records the highest EC value of all three locations. Higher electrical conductivity, a measure of a substance's capacity to conduct electricity, denotes an enrichment of salts or dissolved materials in the groundwater (Ravikumar and Somashekar, 2017). All the groundwater samples are categorised as type I which indicates a low salt enrichments class as the EC is lower than 1,500 µS/cm (Rao et al., 2012). Salinity measures the concentration of dissolved salts, such as calcium, magnesium, sodium, and potassium (Hamzah et al., 2011). As for the salinity, all three samples show relatively lower variations from 0.01 to 0.02, which indicates that the water samples do not contain many mineral salts which might occur due to saltwater intrusion. Furthermore, the total dissolved solids (TDS) of the samples also vary from 141 to 204 mg/L, with water from A3 recording the highest value as well. TDS are made up of inorganic salts such as sulphate, chloride, bicarbonates, sodium, potassium, and calcium. The TDS values can be used to categorise the type of water into freshwater (<1,000 mg/L), brackish water (1,000–10,000 mg/L), saline water (10,000–100,000 mg/L), and brine water (>100,000 mg/L) (Rao et al., 2012). All three groundwater samples collected fall under the freshwater category, as they have TDS values lower than 1,000 mg/L. The higher TDS in A3 might be due to the presence of higher dissolved solids in the water source compared to A1 and A2. The higher TDS and EC values of samples collected from A3 can also be correlated with the higher salinity value of A3, though there are no huge differences in the salinity values between the samples.

3.2 Major ion analysis

The concentration of the major ions and several trace elements present in the groundwater were analysed and the hydrochemistry of the water samples was discussed. Table 3 shows the major ion and trace element concentrations of the groundwater samples obtained from the analysis conducted. The mean values calculated were also tabulated, together with the permissible limit of each ion set by MOH that can be present in drinking water. The excess presence of any ions can cause severe health implications; hence, it is crucial to conduct a thorough ion analysis study of the groundwater before conducting other further detailed water analyses to evaluate their potential and suitability to become drinking water and for domestic uses in terms of major ion content. The total hardness which is one of the parameters used to evaluate the suitability of the groundwater to be consumed as drinking water was calculated based on the concentration of calcium and magnesium and the results were also tabulated in Table 3.

Table 3: Groundwater total hardness, major ion, and trace element concentration

Parameters	A1 (mg/L)	A2 (mg/L)	A3 (mg/L)	Mean (mg/L)	MOH (mg/L)
Calcium	40.9	14.9	24.8	26.87	-
Magnesium	2.3	1.6	1.6	1.83	150
Sodium	9.0	12.8	21.2	14.33	200
Potassium	2.3	1.1	6.6	3.33	-
Sulphate	3.2	0.8	18.7	7.57	250
Chloride	4.0	12.0	47.0	21.0	250
Fluoride	0.2	0.5	0.2	0.3	0.4-0.6
Bicarbonate	62.0	83.0	72.0	72.33	-
Nitrate	0.16	0.32	0.37	0.28	10
Aluminium	0.001	0.061	0.003	0.022	0.2
Arsenic	0.007	0.001	0.001	0.004	0.01
Silicon	<0.02	<0.02	<0.02	<0.02	-
Total Hardness	111.7	43.85	68.6	74.72	500

The mean concentration of calcium ions is the highest indicating that calcium is the major cation present in the groundwater samples followed by sodium ions. The trend of the cations present in the water samples are in the following order of $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$ and for anions are $HCO_3^{-} > Cl^{-} > SO_4^{2-}$ $F^{-} > NO_3^{-}$. The dominant anions present in the samples according to the mean value is the bicarbonate ion, followed by the chloride ion. The nitrate ion is the minor constituent present in the groundwater samples with the lowest mean concentration. Based on the similarity in the major cation and anion present in all the samples, the groundwater collected from the three sources can be classified as bicarbonate calcium-rich water, since bicarbonate and calcium ions dominate the water. In addition, trace elements such as arsenic, silicon, and aluminium are present at relatively lower concentrations than the permissible limit which indicates that these ions are present at a completely safe level to be used as drinking water.

A wide variation was observed in the sulphate, sodium, and chloride concentrations between the three samples which might be due to human activities and geological formation surrounding that area. Furthermore, sample A3 records the highest sodium, sulphate, chloride, and potassium concentrations compared to A1 and A2 which can be correlated with the higher TDS value observed for the sample as well. As a result of the high sodium concentration brought on by the groundwater's salt content, high chloride concentration (Sayyed and Bhosle, 2011) was observed as well in the A3 sample as the high sodium adds to the high chloride content. It is important to keep the sodium concentration below the permissible limit if it is to be supplied as drinking water, as drinking water with an excess sodium level can cause hypertension (Grillo et al., 2019).

On the other hand, sample A2 shows the highest bicarbonate concentration compared to A1 and A3, which can also be related to the higher alkalinity in terms of pH value observed for this sample. Bicarbonate is the dominant ion present in all the water samples, and most of the bicarbonate ions in groundwater were typically formed when carbon dioxide was dissolved in rainfall and precipitated as bicarbonate ions (Rajkumar et al., 2010). As for sulphate ion, it is present at a relatively lower concentration and within the permissible limit. An excess intake of sulphate can potentially cause adverse health effects such as vomiting and diarrhoea. Additionally, minor ions in the groundwater source; potassium (Sayyed and Bhosle, 2011) and nitrate ions (Ramesh and Elango, 2012) are commonly present due to agricultural activities that occur near the region. However, the average nitrate and potassium content of the A2 sample, which is in an agricultural area, was relatively lower than the

permitted level, proving that agricultural operations do not significantly degrade groundwater quality. Samples A1 and A3 also record lower potassium and nitrate ion concentrations which is within the permissible limit.
Furthermore, fluoride ion which is a minor anion present in the groundwater samples, is also an important criterion to assess the quality of the groundwater, as the limit cannot exceed 0.6 mg/L in the drinking water according to MOH standards. Numerous minerals found in rocks and the weathering of these rocks are two possible sources of fluoride in groundwater (Chae et al., 2006). Though fluoride is crucial for dental health, high dosage may result in dental and skeletal fluorosis (Ishaya and Abaje, 2009), hence it is important to monitor the fluoride level in drinking water. As for the analysed groundwater, all the samples record fluoride concentration within the permissible range. In summary, the concentration of all the ions is below the permissible limit set by MOH, indicating their potential to be used as drinking water as well as for domestic purposes.

3.3 Evaluation of water quality for drinking water purposes

By contrasting the physicochemical characteristics and the major ion concentration of the groundwater collected in the research region with the requirements set out for national drinking water quality guidelines by MOH, the acceptability of the groundwater for consumption as drinking water was assessed. Qualification of the groundwater samples for drinking purposes will also fit the criteria of the water samples to be used for residential applications as drinking water standards are expected to have more stringent limits.
As for the on-site parameters analysis of the groundwater samples, the TDS of all the samples was within the permissible range as set by MOH for the drinking water standard limit which is below 1,000 mg/l. For pH value, the A2 site shows a slightly higher pH compared to the limit value set by MOH, making this water highly alkaline, and less suitable to be consumed directly as drinking water. The high pH of the water can be treated with an acid injection system, where an acid solution such as aluminium sulphate and mild citric acid can be injected into the water to reduce the alkalinity (Zouhri et al., 2015). Furthermore, an anion exchange system can also be installed to treat the water of this site, where a resin in the system contains an ion normally chloride, which will be swapped with bicarbonate ion present in the water as the water flows through the system (Hu et al., 2016). As the bicarbonate ion which is the major ion causing high pH has been replaced with the chloride ion, the alkalinity of the water can be lowered.
The major affecting factors of a drinking water's quality are determined mainly by its pH value, nitrate content, TDS, and heavy metal content which were analysed thoroughly in this study. The groundwater samples from A1 and A3 are more suitable and have the potential to be used as drinking water and for domestic uses as they adhere to all the limits set for the major water quality affecting factors, while A2 also can be utilized with proper treatments implemented to reduce the alkalinity level. As for the major ion concentration analysis, it can be concluded that all the major ions and trace elements for the three samples are below the maximum permissible limit for drinking water standards according to the guidelines set by MOH. This qualifies the groundwater sources to be explored further for consumption as drinking water as they adhere to the permissible limit set for major ion concentration according to the NDWQS guidelines.
The total hardness of water is due to the excess concentration of calcium and magnesium in water. Magnesium and calcium are two crucial ions necessary for human health as they help to activate enzymes in cells. Though deficiencies of these ions can cause numerous illnesses such as osteoporosis, kidney stones, and hypertension, excess of these ions can also result in a laxative effect (World Health Organization, 2022). Thus, total hardness which is an indicator of the limit of these calcium and magnesium ions will be used to evaluate the quality of the water. The mean value of the TH obtained for the three samples is 74.72 mg/L, with A1 having the highest TH due to the higher concentration of calcium and magnesium present in this water sample. The total TH value of all the samples is below the recommended maximum value of MOH (500 mg/L) for drinking water usage indicating their acceptability to be consumed as drinking water.
According to the major ion analysis done on the samples, all the samples adhere to the standard limit and have the potential to be used as drinking water. Albeit this analysis alone is an inconclusive deciding factor to assume these water sources are safe to consume, major ion analysis is vital since any excess of the ions can cause severe health implications. Further testing on organic chemicals and emerging pollutants will be done in the future to ensure the suitability of the groundwater sources to become drinking water.

4. Conclusions

The physicochemical and major ion analysis conducted on three groundwater samples collected from different sites located at Johor indicates that water sample from two sites, A1 and A3 adheres to the standard limit set by MOH for national drinking water quality. The major ions of all the samples are within the permissible limit and will not pose any health implication risks that might occur due to the presence of excess ions if it is to be consumed as drinking water. Total hardness was also determined for the samples to evaluate their applicability for drinking water and domestic purposes, where the TH value of the three samples is below the permissible limit indicating excellent water quality. The evaluation of the groundwater in terms of the major ion analysis as per the defined objective was achieved in this study and samples A1 and A3 were chosen as the best sources which adhere to all the standard limits. Based on the results discussed, these groundwater sources are promising and have the potential to be used as drinking water in terms of the mineral ion content, though other further analyses of organic chemical and microbial hazards of the water should be done to decide conclusively if the water is potable.

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