

Hydrochemical analysis and evaluation of heavy metals in groundwater: A case study

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Abstract. The hydrochemical characteristics and the type of groundwater were identified in order to investigate the elements of major ions of groundwater samples in hydro-meteorology station located in Universiti Tun Hussien Onn Malaysia, UTHM. The objectives of the study were to measure the concentration of major ions and evaluate their chemical compositions. The measured ions were namely sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), chloride (Cl), bicarbonate (HCO_3), sulfate (SO_4), heavy metals substance such as zinc (zn), ferum (Fe), copper (Cu), and manganese (Mn). Eight (8) groundwater samples were collected between January 2018 and March 2018 from a tubewell located at the Universiti Tun Hussein Onn Malaysia, Parit Raja, Johor followed by laboratory analyses by using Standard Methods for the Examination of Water and Wastewater. The concentrations of major cations and anions were determined and the consecutive strength were $\text{Na} > \text{Mg} > \text{K} > \text{Ca}$ and $\text{Cl} > \text{HCO}_3 > \text{SO}$, respectively. Correlations among various pollutants were also observed. Strong correlations ($p < 0.01$) were found between Total Dissolved Solid (TDS) and Electric Conductivity (EC). Both TDS and EC also showed strong positive correlations with Na, Mg, and Cl ions. The dispersal of major ions in groundwater was determined using piper diagram. The major cation and anion found were Na and Cl, respectively. The type of water that predominates in the study area was Na-Cl which indicated the groundwater influence from seawater intrusion. Mean concentrations for heavy metals parameters were also identified. The values milligram per litre (mg/L) were Mn (0.20), Cu (0.01), Fe (0.50) and Zn (0.04), respectively. Overall, the selected heavy metal parameters which were Mn, Cu, Fe and Zn met the Recommended Raw Water Standard by Ministry of Health, Malaysia.

1 Introduction

Malaysia has abundance of water resources and receives an average of 3000 mm rainfall annually. Despite the general abundance quantities of surface water available to meet the demand, the water shortages have occurred fairly frequent in Malaysia.

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Population growth, municipal development, industrialization, and irrigation of agriculture as well as climate change strengthen the growing demand and pressure on Malaysian water resources thereby enhancing water pollution [1][2]. Besides pollution issues, the water supply especially from dams will not be sufficient for daily use when it is in dry period. Therefore, groundwater is one of the potential sources of water to be used in the event of drought or no other water supply in the area[3][4].

The clay type of soil that is located in the study area make the soil fails to retain much water deep into the ground[5]. However, the groundwater can still be recovered from shallow groundwater. Shallow groundwater is much easier to exploit, but it is vulnerable to pollutants such as heavy metal and its quality is easily influenced by natural water-rock interactions and anthropogenic activities[6]. Thus, shallow groundwater requires more attention and protection before it can be consumed safely. A small disturbance from human such as mining, or natural processes can easily modify the chemical constituents and quality of shallow groundwater. Therefore, the understanding of the hydrogeochemical process and water quality status is a significant component in addressing effective protection measures and implementing sustainable management of shallow groundwater[7].

This study was conducted to investigate the hydrochemical and heavy metal concentration in the study area. Major ions and heavy metal of groundwater samples were analysed and the result was compared with Raw and Drinking Water Quality by Ministry of Health Malaysia[8]. The study could serve as important information for groundwater protection and management in study area.

2 Study area

The study area is located at the hydro-meteorology station in Universiti Tun Hussien Onn Malaysia, UTHM, Johor as shown in Fig.1. Generally, the location has flat topography and surrounded with private factory, university buildings (laboratory, class and offices), and golf course. Based on geological map by Department of Mineral and Geoscience Malaysia (JMG) [9] as shown in Fig.2., this study area consisted of continental deposits from marine clay and silt soil. Based on the site observation, wet clay and silt geomaterials can be easily found in study area. The area was found to have high water content derived from high water table of lowland areas. This cause the existing of the material that demonstrated the soft soil phenomenon[10]. Besides, the high rainfall intensity which is commonly occurred in the study area also has contribute the elevation of water table thus helping to the soft soil phenomenon in this location. A study by Abidin et al. [10] was also found that this area consisted of thick clay and silt that suitable for groundwater storage and carriage. However, fine particles of clay and silk soil may course low hydraulic conductivity which influences the effectiveness of groundwater recharge [11].



Fig. 1. Hydro-meteorology station in Universiti Tun Hussien Onn Malaysia, UTHM.



Fig. 2. Geological map of study area by Department of Mineral and Geoscience Malaysia (JMG) [9].

3 Methodology

In this study, total of eight (8) groundwater samples were collected from a 30 m depth shallow borehole to determine major ions which were Na, Ca, Mg, K, Cl, SO₄, and HCO₃. Also heavy metal substances which were Fe, Cu, Zn, and Mn. All the sampling and testing procedures followed the Standard Method for the Examination of Water and Wastewater [12]. The duration of sample collection was from January 2018 until March 2018.

Groundwater was pumped out from the borehole for 10 to 15 minutes using purging pumps at a rate of 33.96 m³/day as shown in Fig. 3. before the sample collection made. Polyethylene terephthalate (PET) bottles were used to collect the samples. All sampling bottles were washed with diluted nitric acid at 10% concentration and thoroughly rinsed with distilled water prior to sample collection. In-situ measurement was carried out using a HANNA HI9829, portable multi-parameter meter to measure pH, temperature, electrical conductivity (EC), and total dissolve solid (TDS). For ions and heavy metal measurement, the groundwater samples were filtered using a 0.45 μm cellulose acetate membrane and acidified to pH < 2 using diluted nitric acid. Then the samples were stored in the cooler box with controlled temperature and immediately brought to the laboratory for further analysis. Flame Atomic Absorption Spectrophotometer (FAAS; PerkinElmer) was used to measure major cation of Na, Ca, K, and Mg while Metrohm Ion Chromatography Machine (IC) was used to measure major anion of Cl, SO₄, and HCO₃. For heavy metal concentrations of Fe, Zn, Cu, and Mn, the instrument of Inductive Couple Plasma Mass Spectrometry (ICP-MS; PerkinElmer) was used to analysed the sample.

The data from laboratory analysis was analysed using statistical analysis. In this study, statistical software IBM SPSS Statistics 20 was used for analysing descriptive statistics and correlation coefficient between variables. Piper diagram was constructed using Geochemist Workbench software to determine the major ions distribution of ground water and determination of water type.



Fig. 3. Groundwater that pumped out from the borehole using purging pumps.

4 Results and Discussion

4.1 Descriptive analysis

Physiochemical and heavy metal characteristics of collected groundwater samples at study area are shown in table 1. The pH value was found out to be natural with mean value of 7.61, with minimum and maximum values at 7.26 and 7.92 respectively. Water that falls within pH 6 until 9 can be considered as natural [13]. According to Raw and Drinking Water Quality Standard [8], the desirable limit of pH for drinking water is between 6.5 and 8.5. Therefore, all the samples were within the desired limit.

However, the groundwater samples gave high values of TDS that ranged between minimum values of 1924 mg/l and maximum values of 6359 mg/l. These high values of TDS indicated the groundwater influence from seawater intrusion [2]. The electrical conductivity of the samples also gave high values ranged from 3849 $\mu\text{S}/\text{cm}$ to 12710 $\mu\text{S}/\text{cm}$. According to Radojevic and Bashkin [14], EC related to the concentration of ionised substance in water. Thus, high value of EC and TDS in this study area indicated that high mineral content such as inorganic salts and organic matters in the water samples .

The order of major cation concentrations were $\text{Na} > \text{Mg} > \text{K} > \text{Ca}$ while anion concentration were $\text{Cl} > \text{HCO}_3 > \text{SO}_4$. The Na and Cl were found to be the most abundance cation and anion in the study area. This due to the type of soil, which was an continental deposits from marine clay and silt soil [10].

Table 1. Mean \pm std. deviation, minimum, and maximum value of physiochemical analysis of groundwater samples at hydro-meteorology station, UTHM.

	Mean \pm Std. Deviation	Minimum	Maximum
pH	7.61 \pm 0.26	7.26	7.92
Temperature	20.72 \pm 4.00	14.75	25.19
Conductivity (EC)	10215.88 \pm 2846.04	3849.00	12710.00
DO	7.56 \pm 2.83	3.77	12.02
TDS	5108.50 \pm 1424.03	1924.00	6359.00
Sodium (Na)	2024.59 \pm 602.74	888.70	2999.00
Calcium (Ca)	134.61 \pm 12.16	113.30	149.20
Magnesium (Mg)	267.14 \pm 92.12	83.41	366.70
Potassium (K)	167.57 \pm 119.02	88.60	359.10
Bicarbonate (HCO ₃)	609.63 \pm 98.93	468.00	784.00
Chloride (Cl)	3261.45 \pm 964.99	1118.14	3978.74
Sulfate (SO ₄)	141.60 \pm 37.58	60.43	177.91

4.2 Correlation

Table 2 shows the correlation coefficient between in-situ parameters, major ions parameters, and heavy metals parameters. The results from each variable parameters show very high positive correlation between EC and TDS ($r = 1.00$, $p < 0.01$) due to the constitution of ions and other organic and inorganic substances in water [14]. TDS showed high positive correlation with Na, Mg, Cl, and SO₄ with ($r = 0.907$, 0.957 , 0.918 , 0.991 ; $p < 0.01$) respectively. EC also showed high positive correlation with Na, Mg, Cl and SO₄ with value of ($r = 0.907$, 0.957 , 0.918 , 0.991 ; $p < 0.01$), respectively. This suggested that TDS and EC were controlled by these ions [15]. Mg also posed strong correlation with Na, Cl and SO₄ ($r = 0.877$, 0.909 and 0.979 ; $p < 0.01$).

4.3 Groundwater classification

The classification of groundwater types was based on a trilinear Piper diagram [16], where all major ions were used for the classification. Based on Fig. 4., the distribution of major ions were identified as Na- Cl which were marine and deep ancient ground water type [17]. The dominant ions were Na and Cl with average value of 2024.59 mg/l and 3261.45 mg/l, respectively. The groundwater samples were characterized by high EC and TDS. According to Samsudin *et al.* [18], ancient seawater that was trapped within the sediment long time ago might influence the groundwater type and characteristic.

Table 2. Correlation coefficients between in-situ parameters, major ion, and heavy metals.

	pH	Temp	EC	DO	TDS	Na	Ca	Mg	K	HCO ₃	Cl	SO ₄	Fe	Mn	Cu	Zn
pH	1	-0.740*	0.023	0.792*	0.023	0.178	-0.620	-0.022	-0.232	0.248	-0.186	0.015	-0.048	-0.108	-0.058	-0.319
Temp		1	0.489	-0.285	0.489	0.287	0.811*	0.531	-0.079	-0.227	0.669	0.512	0.345	0.051	0.286	0.235
EC			1	0.225	1.000**	0.907**	0.335	0.956**	-0.735*	-0.034	0.918**	0.991**	0.439	-0.039	0.507	0.100
DO				1	0.225	0.307	-0.247	0.208	-0.148	0.127	0.111	0.250	0.017	-0.325	-0.105	-0.514
TDS					1	0.907**	0.336	0.957**	-0.734*	-0.035	0.918**	0.991**	0.440	-0.038	0.508	0.101
Na						1	0.215	0.877**	-0.623	-0.065	0.806*	0.917**	0.132	-0.278	0.396	-0.023
Ca							1	0.533	0.172	-0.574	0.562	0.419	0.509	0.308	0.507	0.468
Mg								1	-0.620	-0.277	0.909**	0.979**	0.551	0.074	0.665	0.266
K									1	0.012	-0.430	-0.655	-0.332	0.034	-0.534	-0.240
HCO ₃										1	0.025	-0.095	-0.272	-0.089	-0.674	-0.630
Cl											1	0.941**	0.461	0.066	0.384	0.056
SO ₄												1	0.454	-0.027	0.522	0.106
Fe													1	0.796*	0.735*	0.612
Mn														1	0.497	0.668
Cu															1	0.836*
Zn																1

*. Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

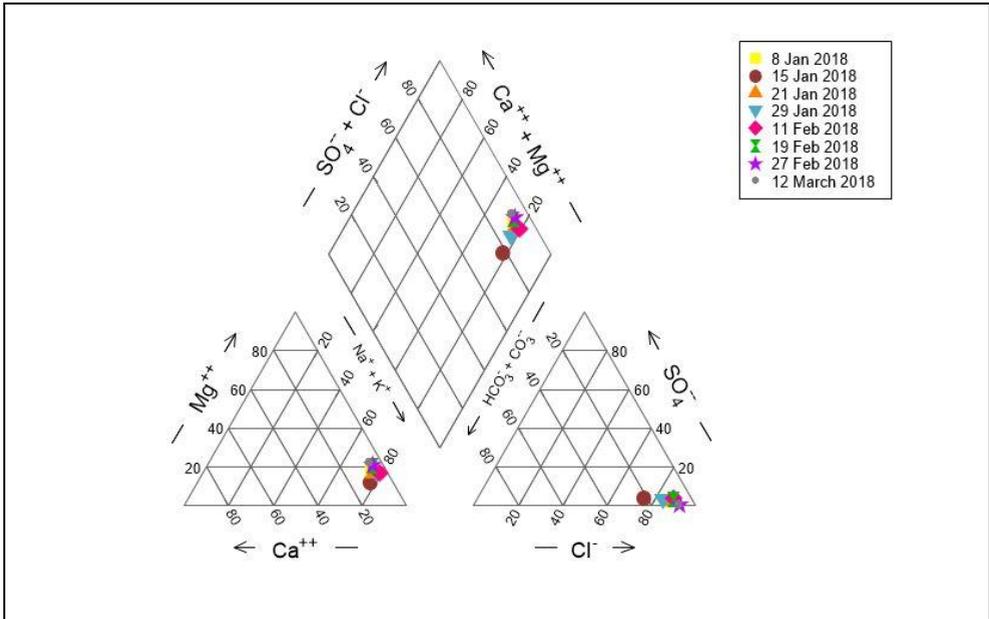


Fig. 4. The distribution of major ions using a piper plot and the determination of water type.

4.4 Heavy metal analysis

Based on Table 3, the dissolved concentrations of heavy metal substances were determined using mean value of 0.53 mg/l for Fe, 0.21 mg/l for Mn, 0.01mg/l for Cu and 0.04 mg/l for Zn. All the heavy metal parameters met the requirement of Recommended Raw Water Quality by Ministry of Health Malaysia[8]. Unfortunately, for Drinking Water Quality Standard [8], only Cu and Zn met the standard. The possible source of these metals were from natural processes or man-made influence [19]. Under natural conditions, the dissolve ions in the water are related to the mineral assemblies in rock near the ground surface [20]. Mineral texture, porosity, composition, and regional structure of rock also influenced the presence of heavy metals in the groundwater [20]. In other hand, man-made activities such as factories, dumping, and piping services also contribute to the variations of the heavy metal concentration[21]. From the observation, there were factories related to the chemical adhesive and wood based product near the study area, which directly or indirectly attributed to the contamination of the groundwater.

Table 3. The concentration values of heavy metals.

	Mean value (mg/l)	Recommended Raw Water Quality (mg/l)	Drinking Water Quality Standards (mg/l)
Ferum (Fe)	0.53	1.00	0.30
Mangense (Mn)	0.20	0.20	0.10
Copper (Cu)	0.01	1.00	1.00
Zinc (Zn)	0.04	3.00	3.00

5 Conclusion

It can be concluded that physical, hydrochemical, and heavy metal parameters in the study area were successfully analysed. The orders of major ion concentration were $\text{Na} > \text{Mg} > \text{K} > \text{Ca}$ and $\text{Cl} > \text{HCO}_3 > \text{SO}_4$. Strong correlation exist among TDS and EC due to the composition of the ions in groundwater. Also, strong correlation was found between TDS and EC with Na, Mg, and Cl ions. From the analyses of piper diagram, the major cation in the samples was Na + K, while the major ion for anions was Cl. Therefore, the dominant ions was Na–Cl, which can be categorized as marine and deep ancient water type. The mean concentrations of heavy metals of Fe, Mn, Cu, and Zn was 0.53 mg/l, 0.20 mg/l, 0.01 mg/l and 0.04 mg/l, respectively. All the selected heavy metal parameters met the Recommended Raw Water Standard by Ministry of Health, Malaysia[8]. Therefore, it can be concluded that the heavy metals in the study area will not give serious problem unless intense human interventions take place in the future. Evaluating the potential impacts, concerns, and assessing possible mitigation measures and monitoring are important steps for continuous protection of the groundwater in study area.

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