

Interaction Between Surface Water And Groundwater By Using Hydrochemical Analysis And Stable Isotope

AkhtarIzzatyRiwayat, Faculty of Civil & Environmental Engineering, UniversitiTun Hussein Onn Malaysia, Parit Raja, BatuPahat, Johor, 86400, MALAYSIA. Email: akhtarizzaty@yahoo.com.

MohdAriff Ahmad Nazri, Faculty of Civil & Environmental Engineering, UniversitiTun Hussein Onn Malaysia, Parit Raja, BatuPahat, Johor, 86400, MALAYSIA. Email: ariffn@uthm.edu.my.

RoslanzairiMostapa, Department of Environmental Tracer Application Group (ETAG), AgensiNuklear Malaysia, Kajang, Selangor, 43600, MALAYSIA. Email: roslanzairi@nuclearmalaysia.gov.my

Article Info Volume 82 Page Number: 11766 - 11775 Publication Issue: January-February 2020

Article History Article Received: 18 May 2019 Revised: 14 July 2019 Accepted: 22 December 2019 Publication: 21 February 2020

Abstract

Effective water management requires an understanding of the components of the hydrological cycle and the relationships between surface water and groundwater. One of the most important relationships traditionally found in water resource management is the interaction between surface water and groundwater. This research aim to identify the relationship between surface water and groundwater in UTHM campus by applying two method which is hydrochemical analysis and stable isotope approach. The result from hydrochemical analysis by piper diagram indicate that all surface water was characterized as freshwater types Ca2+ - Mg2+- Cl- - SO42-, while groundwater is characterized by saline water due to seawater intrusion with water types of Na+ - K+ - CI- - SO42-. Even though, the isotopic composition for δ 18O and δ 2H values of surface water were quite similar to that of groundwater samples as they varying between -4.32% to -9.74% for $\delta180$ and from -33.86% to -65.82% of the surface water samples had low salinity of chloride that less than 20 mg/l compared with groundwater with chloride concentration that more than 3000 mg/l which effects from evaporation and seawater intrusion on groundwater samples. Therefore, it indicates that the interaction between surface water and groundwater does not occur and groundwater recharges may be located outside of this study area.

Keywords: Hydrochemical, Isotope, Surface Water, Groundwater, Interaction.

I. INTRODUCTION

Sustainable development of society and required environment information regarding interaction between surface water and groundwater as both sources is the important connection in water resources [1]. In manage water resources sustainably, surface water and groundwater are necessary to be consider as it was an important component in water cycle. Water management is concerned with maintaining water quality and quantity in both sources. Surface water and groundwater are two interrelated components of a

single source and the impact on one of these components inevitably affects the quality or quantity of each other [2]. There are two types of surface water. First, it can be a source of groundwater recharge that can change the quality of groundwater while others can gain water and solutes from groundwater systems. The increase in population and rapid development has boosted the demand and use of water supply each year in Parit Raja. Moreover, in recent years, no further research related to relationships between both sources has been carried out in this flat topography area.



Hydrochemistry is a hydrological subdivision related to the chemical properties of water [3]. The chemical properties of water are determined and used as indicators of water quality. Analyzing and interpreting water chemistry can provide valuable insights into surface water and groundwater interactions. Geology and contact time between water materials and geology are factors that commonly affect hydrochemical of surface and subsurface [1]. Meanwhile, study involved isotope with combination of hydrochemical analysis have been widely implement in research related to water resources especially on groundwater management and development [4]. The evaluation of the origin of water, especially groundwater systems, often utilises the stable isotope approach to determine hydraulic parameters [5]. In addition, isotopes are used to determine the residence time of groundwater and how it is affected by meteorological and geohydrological factors [6]. Oxygen-18 (18O) and Deuterium (²H) are the most common isotopes used involve in determining the origin of water in aquifer layers and used for studying natural water circulation and groundwater movement [7]. Oxygen is often used as a measure of precipitation temperature, groundwater/mineral infraction and an indicator of processes that show isotopic fraction. Meanwhile, deuterium is extensively used as an isotope tracer in the investigation of chemical and biochemical reactions involving hydrogen.

Based on systematic analysis and interpretation of stable hydrochemical and isotope analysis, conclusions are drawn to improve water resource management and to find alternative water sources to support existing water supply in this area. The outcomes from this study also were used as a reference in future studies to improve the quality of water in the UTHM campus

II. STUDY AREA

Universiti Tun Hussein Onn Malaysia (UTHM) is located in south peninsular Malaysia at the northeast from capital of Johor Bahru with coordinates 1.8586

° N and 103.0856 ° E. The topography for this area is flat topography with an area of 54.32 acres and about 0.5 m to 2.0 m above sea level [8]. The region has a humid tropical climate with annual rainfall of about 2961 mm with temperatures between 24°C and 33°C. Fig 1 illustrates that UTHM is surrounded by marine clay deposits known as quartz deposits [9]. The formation of these soils is characterized as unconsolidated sediment that largely covers the west coast of Johor with a range of 15 km to 25 km from Muar to Kukup. Igneous intrusive rock can be found in the west of BatuPahat while over-consolidated Triassic-Jurassic sediments can be found in Aver Hitam and the eastern part of the UTHM campus. Furthermore, UTHM is located 20 km from a coastal area of PantaiRengit and has layers of sediments and fossils which formed due to tidal effects that indirectly has impact on undesirable concentrations [10]. Besides, this area and its surrounding were previously muddy and sandy coastal areas. Due to ancient saltwater intrusion during the quaternary era and impacts of karts under the land surface had causes the water to contain high concentration of calcium and chloride.



Fig. 1. Geological map of study area



III. METHOD

Samples of surface water and groundwater which involved the sampling of surface water (lakes, swale and retention pond) and groundwater (borehole) were collected at three station with bi-monthly water sampling. 1-liter polyethylene bottle were used to collect and stored each of this water samples. This bottle was rinsed with distilled water and two to three times with samples of water in the field before any water samples were collected. Before any analysis were conducted all samples of water were first filtered through 0.45 µm filter paper as to remove any residues from the water samples. The filtered samples were then diluted with a few drops of concentrated nitric acid, HNO3 to a pH of less than 2 for major concentration determination On the other hand, it was not required to add any chemicals for major anion determination.

The chemical properties for major cations (Na⁺, Mg^{2+} , K^+ , Ca^{2+}) were analysed using the Atomic Absorption Spectrometer (AAS) while for major anions (CI, SO_4^2 , NO_3) were using Ion Chromatography (IC). The concentration of anions cations in water offer qualitative and and quantitative methods for investigating the generation and involvement of water bodies. Lithology and soil characteristics that controlled by various of chemical functions was the factor that influences the hydrochemical of water [11]. Meanwhile, the concentration of physical parameters such as pH, DO, TDS, EC and temperature were determined using the Hanna HI9828 multiparameter probe. The water samples were sealed and immediately brought to the laboratory in a short time and analyzed by standard method. In this study, in-situ and laboratory tests were conducted according to APHA 2005 standards.

However, isotopes are also used with greater frequency for studies on the interaction between surface and groundwater [12]. No sample filtration or preservation is required. Water samples are first stored in 30 ml amber glass bottles directly at the source. The bottles are first rinsed with the water sample for two to three times. Details including date, location, time and source type are clearly labelled. The bottles are tightly capped to ensure that no air bubbles are trapped. During sampling, storage and transportation to the laboratory, the samples are stored properly and protected from direct sunlight.

The stable isotope analyses of surface water and groundwater data of δ^{18} and δ^{2} H were plotted in the δ -diagram of δ^{18} and δ^{2} H along with the Global Meteoric Water Line (GMWL: δ^{2} H = 8 δ^{18} O + 10) [13] and the Local Meteoric Water Line (LMWL: δ^{2} H = 7.44 δ^{18} O + 7.90) which are drawn as reference lines. The equation for LMWL was based on the latest rain data on datasets obtained from the International Atomic Energy Agency (IAEA) on the nearest rainfall station located in Johor Bahru. To determine the equation of LMWL, the isotope values of O¹⁸ and H² were plotted in Microsoft Excel with a y-axis for H² while the x-axis for O¹⁸ is illustrated in Fig. 2 The equation for this station.



Fig. 2. Graph on LMWL equation

Sources of surface water and groundwater can be distinguished by comparing the δ^{18} and $\delta^2 H$ compositions of water samples with GMWL and LMWL. The transformation relationships between both sources can be identified. The graph for isotope composition was plotted using Microsoft Excel according to its position. When the data is largely negative, all the dots (isotope value) will be located at the bottom left of the graph. The x-y axis started with 0-0 and the minor / major grid was removed



from the graph. All atomic mass numbers are in the form of 'Superscript'.

IV. RESULT AND DISCUSSION

Hydrochemical Analyses

The water samples for surface water were taken from the nearest water body while groundwater samples were taken from three boreholes in UTHM. Table 1 represented the field parameter of the water samples. In identify the total concentration of soluble salt in water bodies, EC was required as it revealed the capability of water to transmit electricity [14]. Moreover, it used to verify the content of salinity that is a hazard since it will reflect the TDS in groundwater [15]. As shown in the table above, EC and TDS groundwater ranges from 889.31 μ s/cm to 9192.00 μ s/cm and 644.40 mg/l to 4678.50 mg/l. The highest EC values of groundwater were generally observed at station C. On the contrary, EC and TDS levels of swales, lakes and retention pond were lower compared to groundwater, from 145.25 μ s/cm to 240.75 μ s/cm and 71.50 mg/l to 122.90 mg/l, respectively. Natural groundwater usually contains a higher dissolved solids concentration than surface water because it is in contact with subsurface structures which are rich in minerals. Various EC values in groundwater indicate that water samples are influenced by high salt content.

Table	1:	Physical	parameter
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Station	Sample	pН	DO	Т	TDS	EC
А	LA	5.98	6.25	26.63	102.40	173.92
	SW GW	3.99 7.43	6.95 5.36	26.17 25.98	122.90 4432.60	237.53 8621.67
В	LA	7.13	6.24	26.63	120.50	211.96
	SW GW	6.75 7.08	6.06 5.45	26.57 27.13	115.40 644.40	240.75 889.31
С	LA	6.38	7.27	26.95	121.00	219.88
	RP GW	7.26 7.28	6.88 4.42	30.00 25.16	71.50 4678.50	145.25 9192.00

*GW = Groundwater *LA = Lakes *SW = Swale *RP = Retention Pond

Meanwhile, the results of the anion and cation concentration interpreted that sodium concentration is often found naturally in groundwater and is the most abundant element in groundwater in this study area with a concentration of 214.01 mg / 1 and 2159.02 mg / 1 with an average of 1447.18 mg / 1 as indicated in Table 2. The high concentration of Na⁺ could be due to saltwater intrusion [16] or naturally occurring brackish water of aquifers as the water samples have TDS of more than 1000 mg/l. In contrast, surface water has low concentrations ranging from 6.68 mg/l to 19.59 mg/l. The chloride (Cl⁻) concentrations was high for groundwater with values ranging from 397.11 mg/l to 7412.84 mg/l while surface water has low concentrations ranging from 10.43 mg/l to 40.21 mg/l. The observation could be made based on the results which indicate the influence of seawater for a long period of time. Besides, the results were supported by [17], who explained that UTHM and its surrounding areas were previously muddy and located near the coastal area. Therefore, the water in the area contains high levels of calcium and chloride due to ancient water intrusion at quaternary areas and the impact of karts under the land surface respectively.

While, magnesium (Mg^{2+}) and calcium (Ca^{2+}) are the major ions that are readily available in groundwater. Mg^{2+} and Ca^{2+} come from rocks such



as clay and dolomite. A high concentration of Ca^{2+} which was 100 mg/l and Mg²⁺ with a concentration of 50 mg/l in the groundwater, can harm humans [18]. Table I shows that calcium concentration varies between 12.58 mg/l and 22.49 mg/l with a mean of 17.70 mg/l in surface water. Meanwhile, calcium concentration varies between 73.71 mg/l and 239.99 mg/l with a mean of 143.87 mg/l for groundwater. A high concentration of these minerals could mean that groundwater does mix slightly with seawater.

The organic sources or industrial and agricultural chemicals is the causes of nitrate (NO_3) concentration in natural water. It is the end product of aerobic stabilization of organic nitrogen and the product of conversion of nitrogenous material. However, nitrate concentration that exceeding 50 mg/l could lead to blue syndrome amount infants or cyanosis [19] and cancer in adults. even though is an essential of protein in all living organisms. The concentration of nitrate varies between 4.07 mg/l and 20.54 mg/l in surface water. Meanwhile, the concentration of nitrate varies between 59.00 mg/l and 83.33 mg/l in groundwater. The location of study area that is surrounded by an oil palm plantation located around 1 km from the observation point could be the reason for high value concentration of nitrate. Oil palm plantations are often prone to high fertilizer usage.

Large amounts of chemical data from surface water analysis and groundwater analysis require an effective method of classifying, organizing and presenting data to assist in the analysis and interpretation of hydrochemistry. The hydrochemical analysis was used for the interpretation of results. Major ions existing in both water samples were analysed and discussed. A software called Geochemist Workbench was used in the interpretation of major ions for statistical analysis. Results from the hydrochemical analyses were plotted in a Piper diagram in the form of a graph. The classification of surface water and groundwater is based on dominant cations and

anions present and these can be displayed graphically in a piper diagram. The relative concentrations of the major ions in percent mg/l are plotted on cation and anion triangles and later projected to a quadrilateral representing both cations and anions. The diagrams were classified into four hydrochemical facies based on different anion and cation dominance as shown in Table 3. Hydrochemical facies are useful in providing an initial idea of the complex hydrochemical processes the surface. Determination of beneath the hydrochemical facies has been used in chemical evaluation of surface and groundwater for decades. In addition, it can provide sufficient information on the chemical quality of water, especially its origin [20].

The piper diagram in Fig. 3 illustrates the chemical analysis of surface water and groundwater. This diagram contains two triangle that presented the percentage distribution on milliequivalent basis of major anion and cation. The groundwater for stations A, B and C demonstrate that of Type III facies for the entire observation period. CI^{-} and Na^{+} + K^+ is the major anion and cation that dominantly formed in this water type. The relative concentration of ions occurs in the Na⁺ and $K^+ > Ca^{2+} + Mg^{2+}$ and $Cl^{-} + SO_4^{2-} > HCO_3^{-}$ sequences. This fact can be explained because of possible seawater intrusion occurring in the study area. Meanwhile, surface water samples were subjected to the Type IV facies where alkaline $(Ca^{2+} - Mg^{2+})$ and strong acids $(Cl^{-} SO_4^{2-}$) were dominant. This factor may explain that the surface water sample is characterized by a mixture of Ca^{2+} - Mg^{2+} - CI^{-} - SO_4^{2-} types as it is an open system as described in Table 2. In general, the concentration distribution between cations is Na⁺> $Ca^{2+} > K^+ > Mg^{2+}$ while the anions show a similar distribution pattern of $Cl^{-} > SO_4^{2-} > NO_3^{-}$ for both surface water and groundwater samples. The result from piper diagram in Fig. 3 clearly showed that all surface water was characterized as fresh water while groundwater is characterized by types of saline water due to seawater intrusion.



Therefore, it indicates that interactions between these two sources did not occur in this study area and that the charge may be located outside this area. The results explain why lakes and balances are remaining in good quality and better for industries and households than groundwater. While the groundwater in this aquifer has been invaded by seawater and cannot be used for any other purpose before any treatment is performed.



Fig. 3. Piper diagram of water samples at UTHM campus

Station Sample K^+ Na ⁺ Ca ²⁺ Mg ²⁺ Cl ⁻ SO_4^{2-} NO ₃ ⁻ HCO ₃ LA 5.41 15.78 22.08 3.34 24.43 36.25 12.04 9.61	-
LA 5.41 15.78 22.08 3.34 24.43 36.25 12.04 9.61	2
	•
A SW 5.09 19.59 16.49 4.56 21.15 53.48 20.54 0	~
GW 144.63 2159.02 117.90 211.13 5972.63 193.47 59.00 282.4	0
LA 6.23 17.06 22.49 4.77 40.42 30.40 4.07 13.23	
B SW 5.60 15.13 17.70 3.02 24.41 29.42 14.86 13.10	
GW 21.71 214.01 73.71 40.79 397.11 130.65 82.20 61.10	
LA 3.75 15.20 12.58 3.87 22.87 36.92 16.17 4.75	
C RP 4.04 6.68 14.88 2.63 10.43 24.25 12.98 17.88	
GW 90.31 1968.50 239.99 240.01 7412.84 245.59 83.33 85.13	

Table	2:	Major	anion	and	maior	cation	sampl	les ar	alvsis ((mg/l)	
1 auto	4.	major	amon	ana	major	cation	Samp	us ai	iary sis v	(Ing/I)	

*LA = Lakes *RP = Retention Pond *GW = Groundwater *SW = Swale

Facie	es Water Type	Туре	December 2017 – April 2018
1	$Ca^{2+} - Mg^{2+} - HCO_3^{-}$	Type I	None
2	Na^+ - K^+ - HCO_3^-	Type II	None
3	$Na^{+} - K^{+} - CI^{-} - SO_{4}^{2-}$	Type III	GWA, GWB, GWC
4	$Ca^{2+} - Mg^{2+} - CI^{-} - SO_4^{-2-}$	Type IV	SWA, SWB, RPC, LAA, LAB, LAC
*GWA	= Groundwater Station A *	GWB =	= Lakes Station A $*LAB = Lakes$ Station
Ground	water Station B *G	WC =	B *LAC = Lakes Station C *RP =
Ground	water Station C *SWA =	Swale	Retention Pond Station C
Station	A *SWB = Swale Station I	3 *LAA	

Stable Isotope

In indicate the interaction between surface water and groundwater and source of groundwater recharge, isotope is known for its effectiveness in identifying those issue. To identify the sources and mechanism of recharge both essential relation between δ^2 H and δ^{18} O was used. In line with [21], its pointed that surface water was significantly affected by evaporation while shallow groundwater is less, and deep groundwater is practically unaffected. Table 4 tabulated the result for isotopic composition of different water. Isotopic composition for rainfall (RW) shows that isotopic ranges from – 2.91% to -9.14% for δ^{18} O and from -29.32% to - 52.54% for δ^{2} H. While, composition of surface



water (lakes, swale and retention pond) ranges from -4.32% to -9.74% of for δ^{18} O and from -33.86% o to -65.82% of for δ^2 H. Fig. 4 illustrated the stable composition of surface water and groundwater with those rainfall at the study area. The Global Meteoric Water Line (GMWL: $\delta^2 H = 8 \delta^{18} O + 10$) and Local Meteoric Water Line (LMWL: $\delta^2 H = 7.44 \ \delta^{18} O +$ 7.90) are drawn as reference line. The point that closer to or on the GMWL and LMWL line probably recharged directly from the local precipitation with slightly evaporation [22]. The equation for LMWL was based on datasets obtained from International Atomic Energy Agency (IAEA) on the nearest rainfall station that located at Johor Bahru. The isotopic compositions of groundwater samples in the area range from -4.96% to -6.96% o for δ^{18} O and from -38.14% to -59.10% o for δ^2 H for Station A and Station C which most of the samples are influenced by evaporation.

Observations can be made involving stable isotopes in groundwater samples compared to rainfall and surface water. The isotope analysis identified that there is interaction between surface water and groundwater at station A as well as Station C. Both sources seemed to be in a similar cluster, as illustrated in Fig. 4(a) and Fig. 4(c). This signifies that it has the same origin as the water scattered in the series of the δ -diagram of precipitation. Hence, distinct evidence showed that the main contributions were from local rainfall and slightly evaporated surface waters. The result from isotopic composition of groundwater verify that this source is mainly originated from evaporated evaporation. Isotopic composition of groundwater that enriched with heavy isotopes clarify that effect

of evaporation was clear in the groundwater samples.

The process is quite similar to the hydrologic cycle. Surface water (lakes, swales and retention ponds) at both locations was recharged from evaporated precipitation and when it reaches the ground (surface water), it will go through the evaporation process which enriches the isotopic composition. In addition, there are several observations that can be made about the stable isotope in groundwater compared to rainfall and surface water. Isotope proportions of groundwater samples were distributed throughout the LMWL. Therefore, it could be said that the groundwater samples were highly affected by evaporation and the recharged was by evaporation precipitation. Interval of rainfall, evaporation, intensity, temperature and condensation in recharge and drainage area were the factors that influenced the isotopic composition of oxygen and deuterium for infiltrating waters and precipitation.

Meanwhile, compared to Station A and Station C, Station B shows a different pattern in terms isotopic composition as illustrated in Fig. 4(b). The stable isotope of groundwater samples shows that the value of δ^2 H ranges from -81.96 %_o to -78.23 %_o and the δ^{18} O values varies from -11.66 %₀ to -9.58 %₀. The isotopic composition of groundwater at Station B was significantly lighter compare to rainwater, which indicate that this source was highly evaporated possibly from seepage of meteoric water in the past.Besides, the groundwater sources at this point was probably influenced by ancient groundwater where the weak connectivity between these sources was due to clay layers and interrupted aquifers.

Table 4. Isotopie composition in unicient water									
Sample	December 2017		January	January 2018 Fe		February 2018		March 2018	
	δ^{18} O	$\delta^2 H$	$\delta^{18}O$	$\delta^2 H$	$\delta^{18}O$	$\delta^2 H$	$\delta^{18}O$	$\delta^2 H$	
LA_LA	-9.74	-63.26	-6.22	-53.28	-4.79	-46.60	-4.32	-41.36	
SW_LA	-6.99	-47.31	-7.86	-58.85	-4.49	-34.42	-6.05	-36.70	
GW_LA	-6.96	-59.10	-6.83	-56.60	-6.12	-54.50	-5.74	-50.76	
LA_LB	-8.95	-65.82	-5.17	-42.75	-4.43	-45.08	-6.77	-42.52	
SW_LB	-7.54	-33.86	-5.97	-45.63	-4.86	-45.56	-7.26	-43.63	

 Table 4: Isotopic composition in different water



*

GW_LB	-11.66	-81.96	-11.45	-83.66	-9.77	-81.83	-9.58	-78.23
LA_LC	-7.50	-56.60	-5.11	-46.88	-5.88	-47.79	-5.31	-47.52
RP_LC	-6.75	-51.51	-5.18	-45.40	-4.68	-38.63	-5.42	-44.81
GW_LC	-6.55	-45.26	-4.96	-38.40	-5.16	-38.14	-6.89	-41.11
RW	-2.91	-29.32	-8.15	-48.88	-7.82	-51.08	-9.14	-52.54

SW = Swale *LA = Lakes *GW = Groundwater *RW = Rainwater *RP = Retention Pond



🔹 Rainwater 👔 Lakes Station A 🖕 Swale Station A 🔺 Groundwater Station A ____ Linear (GMWL) _____ Linear (LMWL)



🔹 Rainwater 🍙 Lakes Station B 🖕 Swale Station B 🔺 Groundwater Station B _____ Linear (GMWL) _____ Linear (LMWL)



Fig. 4. Relationship between the δ^{18} O and δ^{2} H of all the water samples at (a) Station A (b) Station B (c) Station C

V. CONCLUSION

Overall, sodium is the dominant cation while chloride is the dominant anions both in surface water and groundwater in the study area. The influence of high concentration of Na⁺ was due to saltwater intrusion into wells or due to naturally occurring brackish water of aquifers as the water samples has TDS more than 1000 mg/l. Meanwhile, based on graphical method from piper diagram illustrates that the surface water samples were characterized by Ca^{2+} - Mg^{2+} - CI^{-} - SO_4^{2-} type as fresh water, while groundwater is characterized as saline water due to seawater intrusion. Meanwhile, for isotope analysis the isotopic composition for δ^{18} O and δ^{2} H values of surface water were quite similar to groundwater samples at Station A and Station C, indicate that both sources appeared in the same cluster which means they originate from the same origin as the water scattered in the series δ precipitation diagram. The main contribution is from local rainfall and the slightly evaporated surface Furthermore, based water. on the isotope composition of groundwater indicates that this source is mainly originated from evaporated rainfall.

The isotopic composition of groundwater samples was enriched with heavy isotopes, which verify that the effect of evaporation was clearly in that water samples. Although the isotope compositions for the values of δ^{18} O and δ^{2} H surface water are relatively similar to groundwater samples at Station A and Station C, these surface water samples have lower salinity compared to groundwater samples.The evaporation and seawater intrusion in the study area may explain why groundwater is affected by these

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factors rather than interactions with surface water. However, difference to Station B as this point has depleted isotope composition which indicates that groundwater sources in this point probably influence by the ancient groundwater which the weak connectivity between these sources was due to clay layer and interrupted aquifer. result from piper diagram and isotope test did not support each other in verifying that these sources had an interaction. Therefore, this identifies that interactions for surface and groundwater may not occur and recharge for groundwater may be located outside of this study area. This result explained why surface water remained in good quality and suitable to be used for household while groundwater was seriously intruded by seawater.

VI. ACKNOWLEDGMENT

The author would like to acknowledge Research Fund E15501 Universiti Tun Hussein Onn Malaysia (UTHM) and GeranPenyelidikanPascasiswazah (GPPS) Fasa 2/2019.

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