Hydrochemistry temporal variation of Anjani Underground River, Jonggrangan Karst, Java Island, Indonesia

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Abstract. Anjani underground river was one of the biggest water resource in Jonggrangan Karst. The objective of this research was to describe hydrochemical temporal variation which was expected to assist in defining the aquifer conditions that recharge Anjani underground river in more detail. Sampling was carried out for one year covering dry and wet seasons, as well as the flood events. The hydrochemical analysis was conducted based on dissolved major ion concentration and physicochemical properties. In addition, SIcalc and log PCO2 were calculated to understand the temporal variation of aggressiveness on calcite mineral. The results showed that all water samples performed HCO3-Ca type. The chemical constituent in water varied temporally which showed high during dry season and decreased during wet season. The high chemical constituent during dry season was caused by the domination of slow-flow (diffuse) so the water had a longer residence time in aquifer, allowing water-rock interaction to be more intensive. Meanwhile, the low dissolved constituent during wet season was caused by input from quick-flow that changed water-rock interaction into dilution by precipitation process. Generally, all water samples was saturated with respect to calcite, except during flood events. One of the factors that affected this condition was CO2 supply from the allogenic river that allowed the dissolution process to be more intensive.

1. Introduction

Karst is a landform which is formed by the dissolution process on soluble rocks [15] that is characterized by its appearance and unique hydrological conditions [8]. Karst landform is widely spread in various continents and occupies 10-15% of the total land area on earth [8]. As an aquifer [6], karst has a high potential for water resources. However, on the other side, karst is also vulnerable on pollution and various human activities [6]. Moreover, karst aquifer is known to have a heterogeneous-anisotropic property which distinguishes it from the other rocks formation, causing the hydrological conditions of karst aquifer to be complex.

The sustainable karst water resources management requires an understanding of the karst system characteristics [14]. Karst hydrological experts apply several methods to learn the karst aquifer, including the characterization of structure with geological and geomorphological approach, karst system delineation with geological mapping, tracer test, water balance, and the characterization of aquifer by hydrodynamics and hydrochemistry [1], as well as the characterization of local properties by tracer test and pumping test [4]. Moreover, the hydrochemical approach provides significant information on the characterization of the karst aquifer system and is complementary to the description of karst aquifer development seen from its flow properties aspect [9].
This research was conducted in Anjani underground river as part of Karst Jonggrangan, Purworejo Regency, Central Java. Anjani Cave has an important role for the community around, which is the water resources provider for them. The objectives of this research were: (1) to understand the temporal variation of its chemical content in Anjani underground river and (2) to recognize the relationship between the chemical content and the discharge of Anjani underground river to support the characterization of its aquifer conditions.

2. Methodology

2.1. Research Location

Karst Jonggrangan has a total area of 17.6 km² and is located on the border between Kulonprogo Regency, DIY, and Purworejo Regency, Central Java. Physiographically, Jonggrangan Karst is located on the peak of Kulonprogo Mountain. Jonggrangan Karst, geologically, is located on Jonggrangan Formation which consists of conglomerate, tuff-contented marl, and limestone-contented sandstone with lignite inserts at the bottom. According to [13], the limestone of Jonggrangan Karst was deposited during ocean shrinkage phase on tidal zone environment to open ocean.

Its location which is at the peak of Kulonprogo Mountain causes Jonggrangan Karst area has a high rainfall. Rainfall data during the period of 2008 to 2017 at Kaligesing Sub-District rain station showed that the mean annual rainfall of 2563 mm. Meanwhile, the mean monthly temperature in Jonggrangan Karst was 24.1°C.

Anjani Cave is located in the northwest part of Jonggrangan Karst and administratively located in Tlogoguwo Village, Kaligesing Sub-District, Purworejo Regency, Central Java (Figure 1). Anjani underground river is recharged by three allogenic rivers, namely Jumbleng Sawah, Kali Cebong, and Kali Setro [10]. Anjani underground river then comes out like a waterfall which is located in the southwest part of Anjani Cave. The catchment area calculation based on water balance which had been carried out showed that the catchment of Anjani underground river was 3.69 km² [7].

2.2. Method

The data in this research were obtained during a year (March 2018 to March 2019) to accommodate the flow conditions during the dry and wet season. The data obtained include water level data, discharge, the concentration of major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻, SO₄²⁻), and physical-chemical properties of water (pH, EC, TDS, and temperature).

Water level data in Anjani underground river was recorded automatically by automatic water level logger (HOBO U-20L) with an interval recording in every 15 minutes. The discharge measurement was carried out 10 times using the velocity area method, while the flow velocity was measured using a current meter and float. The discharge data was then processed to be stage-discharge rating curve to obtain the formula of water level and discharge relationship. The formula was then applied on recorded water level data so that the hydrograph of Anjani underground river during the research period was obtained.
Chemical water data was obtained through water sampling with the interval of every month during the dry season and every two weeks during the wet season. The sampling was also carried out during flood events period with the interval of every two hours to describe aquifer responses on the change of flow conditions in more detail. The concentration of Ca$^{2+}$ and HCO$_3^-$ were measured by titration using calcium test kit and alkalinity test kit, while the concentration of Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, dan SO$_4^{2-}$ were analyzed at the laboratory. The concentration of Mg$^{2+}$ and Cl$^-$ were analyzed through volumetric analysis. The concentration of Na$^+$ and K$^+$ were analyzed through colorimetric analysis, while the concentration of SO$_4^{2-}$ was analyzed through turbidimetric analysis. In addition, the value of the saturation indices on calcite mineral (SI$_{\text{calcite}}$) and partial pressure of CO$_2$ gas (PCO$_2$) was also calculated using PHREEQC software [14]. Saturation indices with respect to calcite are formulated as below:

$$SI_{\text{calcite}} = \log \left( \frac{(Ca^{2+})(CO_3^{2-})}{K_c} \right)$$

where SI$_{\text{calcite}}$ is Saturation index of calcite, Ca$^{2+}$ is the concentration of Ca$^{2+}$ in water, CO$_3^{2-}$ the concentration of CO$_3^{2-}$ in water, and K$_c$ is equilibrium constants for calcite dissolution. Meanwhile, the partial pressure of CO$_2$ gas is formulated as below:

$$PCO_2 = \frac{[HCO_3^-][H^+]}{K_1K_{CO_2}}$$

where PCO$_2$ is the partial pressure of CO$_2$ gas in water, [HCO$_3^-$] is bicarbonate ion activity, [H$^+$] is hydrogen ion activity, K$_1$ is equilibrium constants of dissolution reactions on the temperature of 25$^\circ$C, and K$_{CO_2}$ is equilibrium constants of CO$_2$ gas in water. Then, the chemograph interpretation was also carried out to describe the temporal variation of hydrochemical conditions.

3. Results and discussion
3.1. Stage-discharge rating curve and discharge hydrograph

Stage-discharge rating curve of Anjani underground river is shown in Figure 2. Water level and discharge had a high correlation, shown by the $R^2$ value of 0.9668. Such an equation was written as below:

$$\text{Discharge} = 1131.8(\text{Stage}) - 45.013$$  \hspace{1cm} (3)

![Figure 2. Stage-discharge rating curve of Anjani underground river](image)

Figure 2 showed the hydrograph of Anjani Cave during the research period. The discharge fluctuation in Anjani underground river was high enough which showed the lowest discharge of 43.27 l/s, while the highest discharge reached 1441.04 l/s. The dry season occurred from March until October 2018, while the wet season occurred from October 2018 until March 2019 which was characterized by several flood events.

![Figure 3. Discharge hydrograph of Anjani underground river (March 2018 - March 2019)](image)

3.2. Hydrochemistry of Anjani underground river

During the research period, all the samples (24 samples) which were analyzed showed the range of pH which tended to be neutral to base (6.7-8.1 with an average of 7.4). Meanwhile, TDS and fluid conductivity (EC) had a considerable fluctuation, 205-429 $\mu$S/cm (average of 292 $\mu$S/cm) and 103-213 ppm (average of 145 ppm), respectively. Meanwhile, water temperature showed a small fluctuation, which was 22.6-23.9 °C.
The major cations with the highest concentration were Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^+\) > K\(^+\), respectively. The concentration of Ca\(^{2+}\) had a range from 50 to 104 with an average of 73 mg/l, the concentration of Mg\(^{2+}\) from 2.42 to 13.61 with the average of 6.93 mg/l, the concentration of Na\(^+\) from 5 to 11 with the average of 8 mg/l, and the concentration of K\(^+\) from 1 to 5 with the average of 2 mg/l. Meanwhile, the major anion sequence from the highest to the lowest was HCO\(_3^-\) > SO\(_4^{2-}\) > Cl\(^-\). The concentration of HCO\(_3^-\) had a range from 164.75 to 307.5 with the average of 215.74 mg/l, the range of the concentration of SO\(_4^{2-}\) was from 7.3 to 8.1 with the average of 7.7 mg/l, and Cl\(^-\) had a range from 2 to 5.5 with an average of 3.6 mg/l. All the samples had a positive value of Saturation Index (SI) with respect to calcite mineral dan the negative value of log PCO\(_2\), except during the flood events. SI\(_{\text{calcite}}\) had a range from -0.63 to 1.09 with an average of 0.23. Meanwhile, log PCO\(_2\) value had a range from -2.53 to -1.29 with an average of -2.3. The concentration of major ion from 24 water samples of Anjani groundwater river was plotted on the piper diagram to show groundwater chemical type. All the samples had the same groundwater chemical type, which was HCO\(_3^-\)-Ca type (Figure 4).

![Figure 4. Piper Diagram of Anjani underground river](image)

### 3.3. Temporal variation of hydrochemistry

The chemograph in Anjani underground river during the research period is shown in Figure 5. TDS, EC, Ca\(^{2+}\), HCO\(_3^-\), and SI\(_{\text{calcite}}\) tended to show a high value during the dry season and low during the wet season. Meanwhile, temperature and PCO\(_2\) showed a low value during the dry season and tended to be high during the wet season. TDS, EC, pH, Ca\(^{2+}\), HCO\(_3^-\), and SI\(_{\text{calcite}}\) had an inverse relationship with discharge, thus they had a high value during the dry season. In contrast, the temperature and log PCO\(_2\) showed the directly proportional relationship to discharge, thus their value was low during the dry season.
The chemical conditions of the aquifer is a function of residence time and flow conditions [3]. During low water conditions (the dry season), the water tends to move slower than in high water conditions (the wet season), quick flow conditions decrease the contact duration (short residence time) between the water and the rocks so the dissolved chemical content is low [5]. The high concentration of dissolved ions during the dry season was caused by water-rock interaction as the dominant process in the aquifer which caused much-dissolved constituent in the water. Meanwhile, the low concentration during the wet season was caused by dilution process by precipitation, thus decreasing the ion concentration in water [11]. The domination of water-rock interaction process during the dry season was proved by the high value of SI calcite during the dry season, where such conditions showed that the dissolution process had been intensive in the aquifer, thus when the water reached the sampling location, its condition had been saturated with calcite. The difference in chemical content based on the season was also caused by the difference of contact duration between water and rocks. Furthermore, it showed that the aquifer of Anjani underground river had developed and allowed the duration difference of water-rocks contact through the mechanism of different flow velocity. During the wet season, the water that flowed through conduit fracture would have the short contact with rocks which made the rocks had not adequate time to change the water chemical composition so the chemical content in the water was low.

The sampling was also carried out during the flood events on 22-23 January 2019. The concentration of \( \text{Ca}^{2+} \) and \( \text{HCO}_3^- \) showed good relation to water level fluctuation, while pH and DHL showed the good relationship at the beginning of flood events, but fluctuated at the end of flood periods (Figure 6). The concentration of \( \text{Ca}^{2+} \), \( \text{HCO}_3^- \), and DHL increased at the beginning of flood events, indicating the presence of old water pushed out by infiltrated rainwater (piston effect) [6, 8]. This is caused by the imbalance between the dissolution kinetics and flow velocity, which is the water flow that is too fast when the flood occurred and make the water is not able to reach the thermodynamic equilibrium [12].

During the flood period, the concentration of \( \text{Ca}^{2+} \) and \( \text{HCO}_3^- \) decreased which showed the arrival of rainwater at the sampling point. Then, \( \text{Ca}^{2+} \) dan \( \text{HCO}_3^- \) increased until the end of flood events, this was probably caused by the dissolution process that had already happened due to the presence of \( \text{CO}_2 \) supply so the concentration continued to increase or because of the recession period which was slowly re-dominated by diffuse storage. Meanwhile, the fluctuating pattern of EC and pH at the middle to the end of flood events was probably affected by the sinking stream (allogenic) which recharged Anjani underground river. EC and pH which was fluctuating indicated the different arrival time of water from each sinking stream. The three sinking streams are the surface river with the different characteristics so that they probably have different flow concentration-time as well.
Figure 5. Chemograph of Anjani underground river (Maret 2018-Maret 2019)
3.4. Water aggressivity with respect to calcite mineral

The water aggressiveness on dissolving calcite mineral which was shown by $\text{SI}_{\text{calcite}}$ value in Anjani underground river during the research period is shown in Figure 7. Groundwater is aggressive on calcite mineral when in unsaturated condition ($\text{SI}_{\text{calcite}} < 0$), in contrast, the water is not aggressive when in saturated condition ($\text{SI}_{\text{calcite}} > 0$) [2]. All the samples showed the saturated condition on calcite ($\text{SI}_{\text{calcite}} > 0$), except during the flood events. Temporally, the value of $\text{SI}_{\text{calcite}}$ showed an upward trend when entered the dry season and decreased as well as fluctuated in the wet season. The presence of fluctuation depended on rain events. The value of $\text{SI}_{\text{calcite}}$ (which the majority had been saturated), indicated that the dissolution had been intensive inside the aquifer so that when the water reached the sampling location, its condition had been saturated with calcite and it was not aggressive to dissolve calcite minerals to any further extent.

Then, the temporal variation of log $\text{PCO}_2$ value in Anjani underground river during the research period is shown in Figure 8. Log $\text{PCO}_2$ also fluctuated which was controlled by season but had the inverse relationship with $\text{SI}_{\text{calcite}}$. Log $\text{PCO}_2$ showed a high value during the wet season and low during the dry season. The high value during the wet season was caused by the presence of CO$_2$ supply from rainwater.

The flood events on January 22-23 2019 showed the lowest $\text{SI}_{\text{calcite}}$ value (undersaturated) and the highest value of log $\text{PCO}_2$ during the research period. $\text{SI}_{\text{calcite}}$ which was on undersaturated condition showed that the water was still aggressive to dissolve calcite mineral. This condition was affected by
CO\textsubscript{2} supply that was transported by rainwater during the flood events so allowed the calcite dissolution reaction to occur.

![Figure 8. Temporal variation of log PCO\textsubscript{2} in Anjani underground river (March 2018-March 2019)](image)

### 4. Conclusions

The hydrogeochemical conditions in Anjani underground river varied temporally. The dissolved constituents in the water tended to be high during the dry season and low during the wet season. This was caused by the slow flow domination during the dry season which caused the long contact between water and rocks (the dominance of water-rock interaction process) so that there was an equilibrium of water with the rocks around it. In contrast, the low chemical content during the wet season was caused by the input water that flowed quickly (quick flow) through the conduit void which caused the short contact between water and rocks. As a result, the rocks had not had the time to change the water chemical composition. Besides, the addition of water volume which entered into the aquifer during the flood events caused the dilution process that decreased the chemical concentration in the water (the dominance of the dilution process by precipitation).

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