Flood water hydrogeochemistry characteristics in Pindul Cave, Gunungsewu Karst Area, Indonesia

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Abstract. Pindul cave located in Gunungkidul Regency, Gunungsewu Karst Area, Indonesia has a unique characteristic which is dominated by surface rivers (allogenic recharge) and groundwater (autogenic recharge). The main purpose of this study is to analyze temporal variation of flood water hydrogeochemistry in Pindul Cave. Water sampling for flood hydrogeochemistry analysis is taken in the wet season for three selected flood events. Parameters of hydrogeochemistry analysis consist of major dissolved element (Ca²⁺ and HCO₃⁻); conductivity; total dissolved solid; SI calcite; log PCO₂; and pH. The result shows that there was correlation between flood discharge and hydrogeochemistry parameters. The hydrogeochemistry of flood events in Pindul Cave typified by a low value of calcium and bicarbonate and high CO₂ gas content in water that indicated the dilution by precipitation processes. Pindul Cave also show the negative value of calcite during flood event which mean that groundwater is unsaturated, so it becomes aggressive towards calcite. According to the flood water hydrogeochemistry characteristics, Pindul Cave is dominated by conduit flow from the large-fracture that already developed.

1. Introduction

Karst is a landform formed from the dissolving process of soluble rocks such as limestone, dolomite, and gypsum [1]. The dissolution process forms a unique hydrological system, where the karst hydrological system is strongly influenced by secondary porosity so that water enters the underground flow system [2]. Therefore, the subsurface karst hydrological system is more developed than the surface hydrological system and causes dry conditions on the surface [3].

Karst aquifers also have heterogeneous-anisotropic that distinguish them from aquifers in other rock formations, so that the hydrogeological conditions of karst aquifers are complex [4]. The complexity of the karst hydrological system is shown by the dualism in the karst hydrological system, namely the dualism of the recharge mechanism (allogenic and autogenic), infiltration dualism (seepage and concentrated), and porosity/flow dualism (conduit and fracture) [5]. This condition causes karst aquifers that are able to provide abundant water sources. But on the other hand, karst aquifers are also considered vulnerable to pollution by various kinds of human activities.

Pindul Cave as part of the Gunungsewu Karst Area, Gunungkidul has a very important role in providing water resources. According to [6], water resources in Pindul Cave come from surface rivers (allogenic recharge) and groundwater (autogenic recharge). The underground river that flows in Pindul Cave is widely used for agricultural irrigation and tourism [7]. The tourism developed in Pindul Cave
is cave tubing, where tourism activities are heavily influenced by conditions during floods. Because of the importance of Pindul Cave, understanding the characteristics of karst aquifers is very important to support water resource management.

Karst aquifer characterization can be done by looking at its hydrogeochemical conditions. Hydrogeochemistry is one approach to explain the dissolution processes and interactions with the constituent rocks through the chemical characteristics of karst groundwater [8]. The hydrogeochemistry of karst tends to be controlled by the karstification process, namely the chemical dissolution of limestone by water containing CO₂. The karstification process that occurs will determine the development of karst. Therefore, temporally hydrogeochemistry is a method that can be used to describe the karstification process and the characteristics of karst aquifers [9].

This study was conducted with the aim of analyzing the hydrogeochemical variations during temporal floods in Pindul Cave. This research is important to know the characteristics of the flood so that good and appropriate management can be carried out. In addition, the water resources in this location are also widely used by the surrounding community for irrigating rice fields and other water needs. This research is also expected to add to the literature review, especially the development of karst aquifers and their comparison with other karst hydrological conditions on the island of Java, Indonesia.

2. Methodology

This research was conducted by water sampling in Pindul Cave during the flood period. Sampling was carried out in 3 flood periods. The sampling period is 1 hour for the first and second flood events, and 2 hours for the third flood event. The hydrogeochemical approach method for the characterization of karst aquifers is carried out by testing chemical and physical parameters (pH, DHL, TDS, and temperature) as well as major ions of water (Mg²⁺, Na⁺, K⁺, Ca²⁺, SO₄²⁻, Cl⁻, HCO₃⁻).

Physical and chemical testing of water is carried out with a portable water checker with direct measurements in the field on pH, electric conductivity (EC), Total Dissolve Solid (TDS), and temperature. The measurement of the major ion content of HCO₃⁻ and Ca²⁺ was carried out directly in the field using the titration method, while the content of the major ions of Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻ was carried out in the laboratory. Volumetric method was used to test the content of Mg²⁺ and SO₄²⁻, and flame photometry method was used to test Na⁺ and K⁺. All samples were brought to the laboratory on the day or the following day after collection.

The results of field and laboratory data for major ions are calculated Charge Balance Error (CBE) as validation so that the data represents its natural condition [10]. Natural conditions of water have the same amount of negative ions and positive ions in units of meq/l [11]. The CBE calculation formula is written in equation (1) [8].

\[
E = \frac{\sum \text{Kation} - \sum \text{Anion}}{\Sigma \text{Kation} + \Sigma \text{Anion}} \times 100
\]  

(1)

E is the CBE value (%), cation is the number of Mg²⁺, Na⁺, K⁺, Ca²⁺ ions, and anions = The number of SO₄²⁻, Cl⁻, HCO₃⁻ ions. Calcite saturation index (SI) value was calculated with PHREEQC software. The input data are major chemical content, temperature, EC, and pH. The equation (2) for the calcite saturation index is as follows [1].

\[
SIc = \log \frac{[\text{CO}_3^-][\text{Ca}^{2+}]}{K_{sp} \text{CaCO}_3}
\]  

(2)

[CO₃⁻⁻] is the activity of bicarbonate ions, [Ca²⁺] is the activity of calcium ions, Ksp CaCO₃ is the solubility product of calcite (10⁻⁸.48). The value of CO₂ partial pressure is also calculated with the help of PHREEQC software. The calculation of CO₂ partial pressure is written in the equation (3) [8].

\[
P_{CO_2} = \frac{([\text{HCO}_3^-][H^+]}){K_1 K_{CO_2}}
\]  

(3)
PCO$_2$ is the partial pressure of CO$_2$ gas in water, [HCO$_3$-] is bicarbonate ion, [H$^+$] is hydrogen ion, K1 is the constant equilibrium of the dissolution reaction at 25°C, and KCO$_2$ is the constant balance of CO$_2$ gas in water.

The calculated data is presented by making a hydrochemograph. A chemograph is a scaled graph that presents the temporal relationship between flow rate and chemical properties of water (Plagnes, 2001). The chemographs in this study included information on time paired with discharge and concentration of Ca$^{2+}$ and HCO$_3$-, log PCO$_2$, SI calcite, temperature, pH, DHL, and TDS.

3. Result and Discussion

3.1. Temporal variation of discharge, major ions, and physical parameter

Sampling of water at the time of flooding was carried out on three measured flood events in Pindul Cave. The first flood event was carried out on January 1, 2021. The highest flow rate measured in the first flood event was 5,319.8 liters/second during the second sampling. The second flood event occurred on February 24, 2021 with the highest discharge of 8,990.7 liters/second which occurred during the second sampling. The third flood event occurred on 19-20 March 2021 with the highest discharge of 4,901.7 liters/second which occurred during the first sampling.

The process of dissolving rocks in karst landforms which involves various physical and chemical reactions [12], will affect the hydrogeochemical conditions of groundwater. Hydrogeochemical data on three flood events are shown in Table 1. In general, the content of the dominant dissolved elements (calcium and carbonate) decreased significantly at the time of the highest discharge measured during sampling. In addition, the chemical and physical parameters of water such as pH, electric conductivity, and total dissolved solids also decreased significantly. This is influenced by the water dilution process which is characterized by an increase in water level. Other factors that affect the hydrogeochemical content are rain, evapotranspiration, ion exchange, mineral deposition, mixing processes, and the influence of human activities [11].

Temporal variations of electric conductivity, pH, major ions (Ca$^{2+}$ and HCO$_3$-), and discharge are depicted on the hydrochemograph (Figure 1). In general, the hydrochemograph patterns of the three flood events tend to be the same. The pattern of electric conductivity, pH, calcium, and carbonate is inversely proportional to the discharge. The first sample in flood events 1 and 2 was taken before the highest flood discharge occurred so that the first sample was in the rising climb period. In the rising climb period, the discharge increased while the electric conductivity, pH, calcium, and carbonate decreased. The discharge begins to decrease during the recession period, while the electric conductivity, pH, calcium, and carbonate increase. This shows that at the time of rising limb to peak discharge the diffuse flow is replaced by conduit with a dilution process, then during recession slowly the diffuse flow begins to dominate again [13]. The water-rock interaction process causes the dominant dissolved element content to slowly begin to rise during the recession period.
Table 1. Flood Water Hydrogeochemistry variation of Pindul Cave.

| Date     | Time | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | Na⁺ (mg/L) | K⁺ (mg/L) | pH  | EC (μS/cm) | TDS (ppm) | Temp (°C) | Discharge (l/sec) |
|----------|------|-------------|-------------|------------|-----------|-----|------------|------------|-----------|------------------|
| 27/01/2021 | 01:00 | 14.0        | 7.3         | 12.0       | 2.0       | 9.9 | 353.9      | 12.0       | 7.6/6     | 263              | 3.954,6         |
| 27/01/2021 | 02:00 | 6.0         | 7.0         | 6.0        | 2.0       | 5.5 | 207.5      | 6.0        | 7.1/0     | 182.0           | 5.319,8         |
| 27/01/2021 | 03:00 | 58.0        | 9.7         | 6.0        | 2.0       | 6.0 | 201.4      | 7.0        | 7.0/8     | 165.0           | 4.651,1         |
| 27/01/2021 | 04:00 | 50.0        | 7.3         | 6.0        | 2.0       | 3.5 | 170.8      | 8.0        | 7.0/4     | 138.0           | 4.115,1         |
| 27/01/2021 | 05:00 | 46.0        | 2.4         | 6.0        | 2.0       | 3.0 | 152.5      | 7.0        | 7.0/2     | 130.0           | 4.375,6         |
| 27/01/2021 | 06:00 | 42.0        | 2.4         | 6.0        | 2.0       | 2.0 | 146.4      | 10.0       | 7.0/3     | 119.0           | 4.343,5         |
| 27/01/2021 | 07:00 | 38.0        | 2.4         | 6.0        | 2.0       | 2.0 | 109.8      | 11.0       | 6.9/7     | 113.0           | 4.282,4         |
| 27/01/2021 | 08:00 | 36.0        | 2.4         | 6.0        | 2.0       | 2.0 | 122.0      | 11.0       | 6.9/7     | 111.0           | 4.231,3         |
| 27/01/2021 | 09:00 | 38.0        | 2.4         | 6.0        | 2.0       | 2.5 | 134.2      | 9.0        | 7.0/3     | 117.0           | 4.246,2         |
| 27/01/2021 | 10:00 | 42.0        | 2.4         | 6.0        | 2.0       | 2.5 | 140.3      | 14.0       | 7.0/6     | 116.0           | 4.203,7         |
| 27/01/2021 | 11:00 | 42.0        | 9.7         | 6.0        | 2.0       | 3.0 | 146.4      | 8.0        | 7.0/5     | 117.0           | 4.255,6         |
| 27/01/2021 | 12:05 | 42.0        | 5.8         | 6.0        | 2.0       | 2.5 | 152.5      | 9.0        | 7.1/0     | 119.0           | 2.959,1         |
| 27/01/2021 | 16:21 | 44.0        | 7.3         | 6.0        | 2.0       | 3.0 | 158.6      | 9.0        | 7.1/5     | 129.0           | 2.763,0         |
| 24/02/2021 | 00:45 | 92.0        | 9.1         | 14.0       | 1.0       | 8.4 | 292.9      | 22.0       | 7.4/1     | 212.0           | 7.345,5         |
| 24/02/2021 | 01:45 | 32.0        | 1.9         | 7.0         | 2.0       | 1.5 | 103.7      | 19.0       | 7.1/2     | 72.0            | 8.990,7         |
| 24/02/2021 | 02:45 | 22.0        | 1.9         | 7.0         | 2.0       | 1.5 | 79.3       | 42.0       | 7.0/8     | 48.0            | 2.655,1         |
| 24/02/2021 | 03:45 | 21.0        | 4.3         | 4.0         | 2.0       | 0.6 | 73.2       | 40.0       | 7.0/1     | 46.0            | 5.112,5         |
| 24/02/2021 | 04:45 | 22.0        | 2.4         | 4.0         | 2.0       | 1.0 | 85.4       | 29.0       | 7.0/8     | 52.0            | 4.479,8         |
| 24/02/2021 | 05:45 | 24.0        | 2.4         | 4.0         | 2.0       | 1.0 | 91.5       | 31.0       | 7.1/5     | 55.0            | 2.963,5         |
| 24/02/2021 | 07:45 | 28.0        | 2.4         | 4.0         | 2.0       | 1.5 | 97.6       | 19.0       | 7.1/2     | 62.0            | 2.359,2         |
| 24/02/2021 | 09:45 | 30.0        | 2.4         | 4.0         | 2.0       | 1.0 | 103.7      | 24.0       | 7.1/6     | 69.0            | 2.339,1         |
| 24/02/2021 | 11:45 | 33.0        | 2.4         | 8.0         | 2.0       | 1.5 | 115.9      | 15.0       | 7.2/0     | 70.0            | 2.318,7         |
| 24/02/2021 | 13:45 | 40.0        | 3.4         | 8.0         | 2.0       | 1.0 | 140.3      | 15.0       | 7.3/1     | 78.0            | 2.976,3         |
| 19/03/2021 | 00:45 | 84.0        | 13.2        | 10.0       | 2.0       | 8.0 | 268.5      | 23.0       | 7.3/1     | 201.0           | 4.901,7         |
| 20/03/2021 | 01:45 | 32.0        | 5.4         | 7.0         | 2.0       | 3.0 | 97.6       | 20.0       | 7.1/5     | 101.0           | 4.141,9         |
| 20/03/2021 | 03:45 | 34.0        | 3.4         | 3.0         | 2.0       | 3.0 | 103.7      | 31.0       | 7.1/0     | 89.0            | 3.544,1         |
| 20/03/2021 | 05:45 | 36.0        | 3.9         | 7.0         | 2.0       | 2.5 | 109.8      | 24.0       | 7.1/0     | 89.0            | 3.347,6         |
| 20/03/2021 | 08:50 | 48.0        | 4.9         | 7.0         | 2.0       | 4.0 | 146.4      | 18.0       | 7.2/2     | 108.0           | 2.247,7         |
| 20/03/2021 | 11:45 | 50.0        | 3.4         | 7.0         | 2.0       | 4.0 | 152.5      | 19.0       | 7.2/3     | 108.0           | 2.165,5         |
Figure 1. Hydrochemograph of Flood Event in Pindul Cave.

3.2. **Temporal variation of discharge, SI calcite, log PCO₂**

Temporal variations of SI calcite and log PCO₂ are shown in **Table 2**. SI calcite at the time of flooding in Pindul Cave was negative, especially during the recession period. A negative SI value of calcite indicates that the groundwater is undersaturated, so that it becomes aggressive towards calcite. Rainwater tends to be aggressive and unsaturated, so a negative SI value of calcite indicates the influence of conduit flow in a karst aquifer [8]. Therefore, the groundwater in Pindul Cave during a flood event has an aggressive nature towards calcite minerals.

Limestone dissolution process involves CO₂, so the aggressiveness of the water is also influenced by the CO₂ content in the water. A high PCO₂ value indicates that there is conduit fracture in a karst aquifer [13]. Based on PCO₂ log analysis, Pindul Cave has experienced conduit development due to an increase in PCO₂ values during flood events.
Table 2. Discharge, SI Calcite, and Log PCO₂ variation of Pindul Cave.

| Flood Event 1 | Flood Event 2 | Flood Event 3 |
|---------------|---------------|---------------|
| Date          | Time | SI Calcite | Log PCO₂ | Discharge | Date          | Time | SI Calcite | Log PCO₂ | Discharge | Date          | Time | SI Calcite | Log PCO₂ | Discharge |
| 27/01/2021    | 01:00 | 0.87 | -2.04 | 3.95 | 24/02/2021 | 00:45 | 0.77 | -2.02 | 7.34 | 19/03/2021 | 00:45 | 0.42 | -1.92 | 4.90 |
| 27/01/2021    | 02:00 | -0.14 | -1.70 | 5.31 | 24/02/2021 | 01:45 | -0.68 | -1.85 | 8.99 | 20/03/2021 | 01:45 | -0.46 | -1.93 | 4.14 |
| 27/01/2021    | 03:00 | -0.20 | -1.70 | 4.65 | 24/02/2021 | 02:45 | -1.00 | -1.92 | 6.55 | 20/03/2021 | 03:45 | -0.47 | -1.95 | 3.54 |
| 27/01/2021    | 04:00 | -0.57 | -1.73 | 4.11 | 24/02/2021 | 03:45 | -1.12 | -1.87 | 5.11 | 20/03/2021 | 05:45 | -0.42 | -1.98 | 3.34 |
| 27/01/2021    | 05:00 | -0.46 | -1.75 | 3.71 | 24/02/2021 | 04:45 | -0.96 | -1.85 | 4.37 | 20/03/2021 | 08:50 | -0.15 | -1.99 | 3.24 |
| 27/01/2021    | 06:00 | -0.50 | -1.78 | 3.44 | 24/02/2021 | 05:45 | -0.83 | -1.90 | 3.96 | 20/03/2021 | 11:45 | -0.08 | -1.99 | 3.16 |
| 27/01/2021    | 07:00 | -0.73 | -1.84 | 3.28 | 24/02/2021 | 07:45 | -0.75 | -1.85 | 3.59 | 20/03/2021 | 14:45 | -0.07 | -1.99 | 3.17 |
| 27/01/2021    | 08:00 | -0.90 | -1.80 | 3.21 | 24/02/2021 | 09:45 | -0.63 | -1.87 | 3.39 | 20/03/2021 | 17:45 | -0.06 | -1.99 | 3.13 |
| 27/01/2021    | 09:00 | -0.57 | -1.81 | 3.17 | 24/02/2021 | 11:45 | -0.49 | -1.84 | 3.18 | 20/03/2021 | 20:45 | -0.05 | -1.99 | 3.12 |
| 27/01/2021    | 10:00 | -0.49 | -1.83 | 3.08 | 24/02/2021 | 13:45 | -0.21 | -1.88 | 2.97 | 20/03/2021 | 23:45 | -0.04 | -1.99 | 2.96 |
| 27/01/2021    | 11:00 | -0.48 | -1.80 | 3.01 | 24/02/2021 | 15:45 | -0.19 | -1.87 | 2.95 | 20/03/2021 | 00:45 | -0.03 | -1.99 | 2.94 |
| 27/01/2021    | 12:00 | -0.41 | -1.83 | 2.95 | 24/02/2021 | 17:45 | -0.11 | -1.86 | 2.93 | 20/03/2021 | 03:45 | -0.02 | -1.99 | 2.92 |
| 27/01/2021    | 16:25 | -0.33 | -1.86 | 2.76 | 24/02/2021 | 21:45 | -0.04 | -1.89 | 2.74 | 20/03/2021 | 06:45 | -0.01 | -1.99 | 2.73 |

The temporal pattern of variations in Log PCO₂, SI Calcite, and Discharge in Pindul Cave is shown in Figure 2. SI Calcite decreased during the rising climb period and continued and increased at the end of the recession period. SI Calcite has the opposite relationship. In contrast to SI calcite, log PCO₂ shows an increase in line with the increase in discharge during the rising climb period and shows a fluctuating graph in the recession period. Log PCO₂ and discharge have a linear relationship.
4. Conclusion and Future Works

Based on the research, Pindul Cave has karst characteristics that can be shown through its hydrogeochemical content. The content of calcite, carbonate, pH, electric conductivity, and total dissolves has an inverse relationship with the discharge. The decrease in hydrogeochemistry in these parameters is due to dilution by precipitation. The existence of a water-rock interaction process causes the dominant dissolved element content to slowly begin to rise during the recession period. The negative SI value of calcite in the recession period indicates that the groundwater is undersaturated, so that it becomes aggressive towards calcite. The pattern of increasing Log PCO₂ content indicates that there is conduit fracture in a dominant karst aquifer during a flood event.

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