Hydrogeochemical and groundwater aggressiveness assessment in the epikarst aquifer: a spatial and temporal analysis

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Abstract. The ability of water to dissolve rocks, which is indicated by groundwater aggressiveness, controls the rate and extent of the current karstification process. This study aimed to analyze the hydrogeochemistry and characteristics of groundwater aggressiveness in an epikarst aquifer, both temporally and spatially, using seven (7) major ions, namely Ca$^{2+}$, HCO$_3^-$, Mg$^{2+}$, K, Na, SO$_4^{2-}$ and Cl$^-$ as parameters. These ions were then plotted into a Piper diagram to find out the hydrogeochemical facies of the groundwater. Meanwhile, the groundwater aggressiveness was analyzed in PHREEQC software. Nine (9) springs were each sampled one time for the spatial analysis. As for the temporal observation, seven (7) samples were collected from one spring. The results revealed that the hydrogeochemistry of the epikarst aquifer was composed of Ca$^{2+}$ HCO$_3^-$ groundwater, indicating that the limestone (calcite) dominates the lithology of the aquifer. Moreover, temporal variations were detected in the groundwater aggressiveness levels, namely high in the rainy season, but low in the dry season. Spatially, the aggressiveness of groundwater emerging to the selected springs also varied depending on the development of the underlying karst aquifers.

1. Introduction
Analyzing hydrogeochemical facies based on major ions reflects the chemical reaction transpiring when water flows through pores and rock fractures, and this information helps to understand the source of the analyzed water [1-3]. Groundwater reaction with limestone is a critical process that shapes the chemical composition of groundwater in karst aquifers [4] and subsequently determines the rate and extent of the karstification. The ongoing karstification process relies on the ability of water to dissolve rocks, which is expressed in groundwater aggressiveness. Groundwater aggressiveness is influenced by PCO$_2$ content. The higher the PCO$_2$ concentration, the stronger the ability of water to dissolve rock minerals. PCO$_2$ increases in winter and the alternative change between summer and winter significantly affects solutional groundwater aggressiveness [5]. Groundwater aggressiveness in rocks, especially in karst landforms, is vital in determining the dissolution and sedimentation stages occurring in karst aquifers. This property is indicated by the saturation index (SIc) and is related to three phases, namely (1) undersaturated water (a state at which water can still dissolve rock minerals), (2) equilibrium (the dissolution process stops), and (3) supersaturated water (precipitation starts to occur) [4]. For the reasons above, the rate of water aggressiveness varies temporally.

Gunungsewu Karst is a tropical karst that is influenced by seasons (rain and dry). Seasonal differences cause variations in aggressiveness characteristics. This paper describes the characteristics of hydrogeochemistry and groundwater aggressiveness in epikarst aquifers. Hydrogeochemistry explains
about the dominant types that work in the research area. Aggressiveness explains the ability of groundwater to dissolve rocks both spatially and temporally.

2. Methods

2.1. Research location
The research location is the eastern part of the Gunungsewu Karst Area. Like all karst in this landscape, the limestone in the east originates in the Wonosari-Punung Formation—which consists of massive reef limestone in the south and bedded limestone in the north ([6], [7], [8], [9])—with a thickness of more than 650 m and volcanic and clastic rocks underneath it [8]. Rudstones, packstones, and framestones that dominate the reef limestone are rocks of high variations. Breccias have unusual clay matrices, identifiable biohermal structures, and intercalation of volcanic ash lenses and carbonate [8]. Volcanic ash lenses are the product of eruptions of the surrounding volcanoes. The Wonosari Plateau is mainly composed of bedded limestone protruding in the north and northeast directions. The complex of the Mediterranean lithosol and rendzina covers more than 90% of the study area. Other types of soil exist in a small percentage, including black grumusol and reddish-brown lithosol complex distributed in the northeast. More than half of the land is used for dry agricultural practices. Settlements and rain-fed rice fields are the second and third-largest land use in the study area [10]. These land-use proportions are attributable to the topography of the region, i.e., hills with moderate to steep slopes, that restricts the expansion of built-up land. The location of the study area and the distribution of springs are presented in Figure 1.

![Figure 1. The spring distribution map of the study area.](image)

2.2. Hydrogeochemical and Aggressiveness
Spatial variation in aggressiveness was determined by taking one sample each from nine (9) springs. As for its temporal fluctuation, it was analyzed by collecting seven (7) samples from one spring, namely Kakap Spring, to represent the rainy and dry seasons. Water aggressiveness is indicated by saturation index. This characteristic defines at which state rock dissolution in a karst aquifer occurs. The saturation index was calculated using Equation 1.
\[ SI_{\text{CaCO}_3} = \log_{10} \left( \frac{[CO_3^{2-}] [Ca^{2+}]}{K_{sp} \text{CaCO}_3} \right) \]  

(1)

Where SI < 0 indicates unsaturated groundwater that retains its high solutional aggressiveness toward rocks. On the contrary, SI > 0 represents a saturated condition in which groundwater can no longer dissolve rocks. At this state, calcification leans toward crystallization or solid material formation as groundwater loses its aggressiveness. SI = 0 shows that the karstification process is in equilibrium. The water aggressiveness was analyzed in PHREEQC software.

3. Results and Discussion

3.1. Hydrogeochemical

Based on the piper diagram presented in Figure 2, the springs in the study area are chemically composed of calcium and bicarbonate. The major chemical elements were found in low concentrations except for HCO\(_3\)- and Ca\(^{2+}\) (see Table 1). HCO\(_3\)- and Ca\(^{2+}\) were present with high levels, and the Ca\(^{2+}\) content was significantly higher than Mg\(^{2+}\), these results are in line with several other studies conducted in the Gunungsewu Karst Area which canonical landform [11-13]. With Ca\(^{2+}\) having a higher concentration than Mg\(^{2+}\), the study area is therefore dominated by calcite limestone instead of dolomite limestone. Groundwater aggressiveness shows the ability of groundwater to dissolve rocks (i.e., limestone in karst areas). It is a strong determinant of the karstification process taking place in a karst landscape. The spatial distribution of aggressiveness was analyzed from the nine samples of spring water in the study area. The aggressiveness calculation results are summarized in Table 2.

![Figure 2. The piper diagram of springs in the study area.](image)

3.2. Aggressiveness Groundwater

Based on Table 2, six (6) springs have high aggressiveness, as apparent from their saturation indices, i.e., SI\(_{\text{Ca}}\) < 0. This finding signifies an ongoing karstification process. The other three (3) springs have a low aggressiveness, as evidenced by SI\(_{\text{Ca}}\) > 0. In other terms, the karstification process has reached saturation and therefore turned into calcite deposition instead. Low water aggressiveness is attributable to small flow discharge [14], which indicates that the spring has a fissure flow. The temporal variation in groundwater aggressiveness was observed at one spring (Kakap). This spring was sampled repeatedly.
in the rainy and dry seasons. The temporal fluctuation of the groundwater aggressiveness is presented in Table 3.

**Table 1.** The Major Chemical Elements of Springs in the Study Area

| Springs | Ca$^{2+}$ (mg/L) | Mg$^{2+}$ (mg/L) | Na$^+$ (mg/L) | K$^+$ (mg/L) | Cl$^-$ (mg/L) | SO$_4^{2-}$ (mg/L) | HCO$_3^-$ (mg/L) | pH | Temp (°C) | EC (µmhos/cm) |
|---------|-----------------|-----------------|---------------|-------------|--------------|-----------------|-----------------|-----|-----------|----------------|
| Nampu   | 98.00           | 34.26           | 86.00         | 2.00        | 118.00       | 9.00            | 274.59          | 118 | 28.50     | 798.00         |
| Karanglo| 137.00          | 4.86            | 22.00         | 2.00        | 6.00         | 7.00            | 451.55          | 28.50| 28.60     | 630.00         |
| Kropak  | 144.00          | 47.14           | 15.00         | 1.00        | 2.00         | 2.00            | 433.24          | 28.50| 28.80     | 589.00         |
| Kakap   | 154.00          | 6.87            | 12.00         | 1.00        | 5.00         | 6.00            | 488.13          | 28.50 | 28.70   | 601.00        |
| Braholo | 122.00          | 17.01           | 31.00         | 2.00        | 11.00        | 5.00            | 347.81          | 28.50 | 24.50   | 542.00        |
| Beton   | 128.00          | 0.73            | 14.00         | 2.00        | 6.00         | 4.00            | 414.94          | 28.50 | 24.30   | 555.00        |
| Lebak   | 124.00          | 11.50           | 15.00         | 1.00        | 4.00         | 3.00            | 421.04          | 28.50 | 24.30   | 555.00        |
| Waru    | 120.00          | 13.85           | 14.00         | 2.00        | 8.60         | 4.00            | 412.43          | 28.50 | 24.60   | 523.00        |
| Kali Petung | 129.00    | 3.38            | 9.00          | 1.00        | 4.50         | 6.00            | 421.01          | 28.50 | 26.80   | 614.00        |
| Dlingo  | 118.00          | 15.55           | 10.00         | 1.00        | 7.40         | 10.00           | 433.21          | 28.50 | 24.60   | 608.00        |

**Table 2.** The spatial variation of spring water aggressiveness in the study area

| Springs   | Q (l/s) | SI calcite | Process  |
|-----------|---------|------------|----------|
| Nampu     | 1       | -0.25      | Unsaturated |
| Karanglo  | 7       | -0.09      | Unsaturated |
| Kropak    | 2       | 0.08       | Unsaturated |
| Kakap     | 80      | -0.02      | Unsaturated |
| Beton     | 120     | -0.31      | Unsaturated |
| Lebak     | 6       | -0.11      | Unsaturated |
| Waru      | 6       | 0.08       | Saturated |
| Kali Petung | 0.017   | 0.53       | Saturated |
| Dlingo    | 0.029   | 0.5        | Saturated |

Table 3 shows that water aggressiveness analysis at Kakap Spring has a temporal variation. This variation is grouped according to the season. In the dry season, the spring had a saturation index of averagely above 1, indicating saturated water that ceases the dissolution process. With low aggressiveness, the dominant process occurring in the groundwater flow is calcite deposition. This condition is associated with small water flow discharge, which is typical of base flow or diffuse system. The opposite is true for the rainy season, where the saturation index was below 0, indicating an ongoing dissolution or karstification process. Based on the description above, the aggressiveness has a distinct temporal pattern. The groundwater emerging in the observed springs has weak aggressiveness because its flow discharge decreases. If the water flows too rapidly, it allows a very short period for rock-water interaction, and, most of the time, rock dissolution cannot occur in this condition. Meanwhile, if the water flows at a considerably slower rate, the physicochemical reaction in the rock dissolution process ceases because the water tends to reach saturation fast [14].

**Table 3.** The temporal variation of groundwater aggressiveness, as identified from Kakap spring.

| Sampling time       | Discharge (Liter/s) | SI calcite | Processes |
|---------------------|---------------------|------------|-----------|
| Dry season 1        | 119.83              | 1.14       | Saturated |
| Dry season 2        | 84.50               | 1.13       | Saturated |
| Dry season 3        | 113.71              | 1.04       | Saturated |
| Dry season 4        | 80.18               | 1.22       | Saturated |
| Rainy season 1      | 142.70              | 0.34       | Saturated |
| Rainy season 2      | 350.81              | -0.02      | Unsaturated |
| Rainy season 3      | 998.39              | -0.16      | Unsaturated |

The amount of discharge that affects water aggressiveness depends on rainwater supply because dry seasons lead to saturated conditions, while rainy seasons contribute to a state of unsaturation. The CO$_2$ amount required in the dissolution reaction increases as rainwater enters the aquifer. It implies that Kakap Spring has a developed conduit system, as apparent from the wide discharge fluctuations between
the two seasons. At the beginning of the rainy season, the calculated samples showed SI > 0. In other terms, the groundwater can no longer aggregate rocks. During this period, the flow discharge was still low, and the CO₂ supply could not produce karstification. However, the SIca was smaller than the previous period, meaning that dilution by rainwater has occurred.

4. Conclusion

The hydrogeochemistry of the epikarst aquifer was composed of Ca²⁺HCO₃⁻ groundwater, indicating that the limestone (calcite) dominates the lithology of the aquifer. Moreover, temporal variations were detected in the groundwater aggressiveness levels, namely high in the rainy season, but low in the dry season. Spatially, the aggressiveness of groundwater emerging to the selected springs also varied depending on the development of the underlying karst aquifers.

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