Variation of Saturation Indices (SI\textsubscript{cal}) with respect to Calcite Mineral at Kalisirah and Jumbleng Springs, South Gombong Karst, Central Java, Indonesia

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Abstract. This research was conducted in two main springs, namely Kalisirah and Jumbleng springs, located on the north side of the South Gombong karst area, Central Java, Indonesia. The objective of this study was to determine the temporal variation of the saturation indices with respect to the mineral calcite in the two springs. Water samples were taken 24 times at each spring during dry, rainy, and flood events. Electrical Conductivity (EC), pH, temperature, calcium (Ca\textsuperscript{2+}) and bicarbonate (HCO\textsubscript{3}-) were measured directly in the field, while other major elements such as Mg\textsuperscript{2+}, Na\textsuperscript{+}, K\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-} were analyzed in the laboratory. Furthermore, the calculation of the Saturation Indices with respect to the calcite mineral (SI\textsubscript{cal}) and carbon dioxide partial pressure (logP\textsubscript{CO2}) was carried out. The analysis results show that temporarily, the SI\textsubscript{cal} value is generally higher during low discharge (dry season) and decreased during high discharge (rainy season). When compared, Jumbleng Springs has a stronger relationship between decreased discharge and an increase in SI\textsubscript{cal}. Meanwhile, the variation of SI\textsubscript{cal} increase (during the dry season) is also followed by a decrease in log P\textsubscript{CO2}, which indicates the dominance of the calcite precipitation process when the carbon dioxide content in the water is minimal.

1. Introduction

Karst is an area formed by the dissolution process of rock [1] [2]. The soluble rocks that make up the karst landscape include limestone, dolomite, gypsum, and rock salt. The dissolution process in karst areas requires a solvent medium in melted ice, rain, surface river flows, and underground flows. The dissolution process produces a system of cracks, fissures, caves and water conduits in the karst aquifer [3]. Karst aquifers resulting from the dissolution process have complex non-uniform (heterogeneous) void dimensions and have anisotropic systems. Through this complex aquifer, karst areas present hydrological and ecological features that are very important for human life, immaculate water storage systems. Managing water quality and quantity in karst areas is essential for a clean water storage system. Especially in the era of the COVID-19 pandemic, the need for clean water tends to increase along with the implementation of a healthy lifestyle such as washing hands with running water [4] [5].

One of the efforts related to the management of karst aquifers is water quality management. Water quality management in karst areas is closely related to its hydrogeochemical composition. The dissolution process of carbonate rocks strongly influences the hydrogeochemical composition of the karst aquifer. Therefore, it is imperative to study the law of dissolution of carbonate rocks in karst aquifers to understand groundwater environmental conditions comprehensively. Dissolution of carbonate rocks in karst formation is part of the carbon, water and calcium cycle that occurs at the lithosphere, hydrosphere, atmosphere and biosphere interphase [6]. The result of this cycle produces a mechanism known as the CO\textsubscript{2}–H\textsubscript{2}O–CaCO\textsubscript{3} (carbon dioxide-water-limestone) mechanism. The
presence of CO$_2$ (carbon dioxide) dissolved in water will form H$_2$CO$_3$ (carbonic acid), which will dissolve various carbonate rock substrates [7]. Based on these conditions, the presence of CO$_2$ is very influential on the process of karst formation, especially the presence of dissolved CO$_2$, which causes water to be aggressive in dissolving carbonate rocks.

The chemical reaction between water and minerals in carbonate rocks is reversible between the dissolution and precipitation processes. Therefore, an assessment process is needed between the dissolution and precipitation processes. One of the methods to define the dissolution process and mineral precipitation in carbonate rock (calcite) is by calculating SI Calcite (SI$_{calc}$) and log P$_{CO_2}$. SI calcite (SI$_{calc}$) will describe the dissolution and precipitation process phase, while log P$_{CO_2}$ will describe the supply of CO$_2$ in the water, which can stimulate the dissolution of calcite minerals.

This research was conducted based on the law of carbonate rock dissolution, which was analyzed temporally. The study was conducted in 2 springs, namely Kalisirah Spring and Jumbleng Spring, located in the South Gombong karst. Both of these springs rely on the local community to meet their daily clean water needs. The purpose of this study was to determine the variation of SI Calcite in each spring to determine the dissolving or precipitation phase of the calcite mineral during the study period.

2. Site Description

The research location is part of the Karangbolong Mountains in the southwest of Kebumen Regency, Central Java. The Karangbolong Mountains are composed of volcanic breccia units (Gabon Formation), limestone units (Kalipucang Formation), and limestone-sandstone units and alluvium (Halang Formation) [8]. The South Gombong karst area is located in the Kalipucang Formation of the Middle Miocene age. The bottom of this formation is composed of shale, calcareous claystone and calcareous sandstone with polymic breccia inserts. The upper part of this formation consists of coral limestone with a carbonate content of up to 95.5%, which belongs to the pure limestone group [8].

South Gombong Karst is one of the most well-developed karst landscapes and is an example of typical tropical karst. South Gombong Karst is dominated by polygonal karst morphology formed from interconnected karst hills and separated by compound closed basins. This compound closed basin is specifically called the cockpit. The characteristic morphology in this karst is a conical hill with a sharper slope compared to karst formations in other areas in Indonesia [9].

The aquifer component in the South Gombong karst is composed of an epikarst zone, vadose limestone and water-saturated limestone [9]. In general, most of the hydrological conditions are dominated by the subsurface flow. This subsurface flow presents the appearance of springs with varying discharges. The springs with the largest discharge in the northern part of this karst are Kalisirah and Jumbleng springs (Figure 1.). These two springs are located close to each other but have different flow input sources, and the Kalisirah spring is sourced from the Pocung Cave and Candi Cave. The water flow from Pocung Cave flows towards Jeblosan and Kaliwinong springs and then appears at Kalisirah springs [10]. The stream from the Candi Cave flows towards the Kaliwinong Spring and appears at the Kalisirah Spring. Meanwhile, Jumbleng Spring is the output of the stream originating from Ponor Banjirian. Both springs are located in Sikayu Village, Buayan District, Kebumen Regency, Central Java. These two springs have an essential role in meeting domestic and agricultural water needs for residents in Sikayu Village and its surroundings.
Figure 1. Tracer test results showing the direction of flow in Kalisirah and Jumbleng Spring

3. Methods

Data collection of dissolved major ion content in Kalisirah and Jumbleng springs was obtained from laboratory tests on the elements Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, and SO$_4^{2-}$ and direct titration testing in the field using an alkalinity test kit for the content of Ca$^{2+}$ and HCO$_3^-$ ions. In addition, the parameters of pH, temperature, TDS (Total Dissolved Solids), DHL (Electrical Conductivity), and discharge were also measured along with the time of sampling in the field. Based on the parameters mentioned above, 24 samples for each spring were obtained in the period from February 2019 to March 2020. In summary, the 24 samples showed the average, maximum and minimum values, as shown in Table 1.
Table 1. Statistics of Hydrochemical Parameters in Kalisirah and Jumbleng Springs.

| Parameters | Kalisirah | Jumbleng |
|------------|-----------|----------|
|            | Average   | Min      | Max      | Average | Min | Max      |
| Discharge  | 226.5     | 22.8     | 697.9    | 71.4    | 13.1 | 193.3    |
| Na⁺        | 8.3       | 5.0      | 12.0     | 8.5     | 6.0  | 12.0     |
| K⁺         | 1.5       | 1.0      | 2.0      | 1.5     | 1.0  | 5.0      |
| Mg²⁺       | 11.4      | 4.7      | 19.2     | 13.9    | 2.4  | 24.4     |
| Ca²⁺       | 87.6      | 71.3     | 109.0    | 80.6    | 42.2 | 110.0    |
| HCO₃⁻      | 318.3     | 237.9    | 421.0    | 300.0   | 158.6| 378.3    |
| Cl⁻        | 3.7       | 2.4      | 4.5      | 4.1     | 2.0  | 5.5      |
| SO₄²⁻      | 11.8      | 1.0      | 25.0     | 12.9    | 5.0  | 29.0     |
| Ph         | 7.1       | 6.8      | 7.7      | 6.8     | 6.4  | 7.3      |
| Temperature (°C) | 26.3  | 25.2     | 26.8     | 26.3    | 24.9 | 27.2     |
| Ec (µs/cm) | 543.3     | 444.0    | 668.0    | 505.8   | 330.0| 668.0    |
| TDS (ppm)  | 274.1     | 228.0    | 340.0    | 271.1   | 156.0| 336.0    |

The SIcal and log P CO₂ were calculated using the Phreeqc software [11]. SIcal and log P CO₂ analyzes were carried out to determine the nature of water on the level of solubility with respect to calcite minerals (CaCO₃). A positive SIcal value (SIcal > 0) indicates the state of the water has been saturated with carbonate minerals, so it is difficult to dissolve the carbonate rock (it tends to be in the precipitation phase), but when the SIcal value shows a negative value (SIcal < 0), it indicates the water condition is unsaturated (aggressive), so it can still dissolve carbonate rocks. Calculations are carried out using Phreeqc software with the following calculation formula:

\[
SI_{cal} = \log 10 \frac{[CO₃^{2-}][Ca^{2+}]}{K_c}
\]  

where:
- SI_{cal} = saturation indice of calcite mineral A
- Ca^{2+} = Ca^{2+} dissolved in water
- CO₃²⁻ = CO₃²⁻ dissolved in water
- K_c = equilibrium constant for calcite

Furthermore, the definition related to CO₂ that affects the dissolution process in the aquifer is carried out by calculating P CO₂ (partial pressure of CO₂ gas in water). The following equation calculates the log P CO₂ value:

\[
P_{CO₂} = \frac{[HCO₃^-][H^+]}{K_1 \cdot K_{CO₂}}
\]

where HCO₃⁻ is the activity of the bicarbonate ion, [H⁺] is the activity of the hydrogen ion, K_1 is the equilibrium constant for the dissolution reaction at 25°C, and K_{CO₂} is the constant equilibrium of CO₂ gas in water. Knowledge of the effect of the CO₂ variable in karst aquifers can provide a comprehensive picture of the karstification process in karst formation [12].
4. Result and Discussion

4.1 Temporal SI_{cal} variation

SI_{cal} variation in both springs during the dry season was dominated by positive values (Figure 2). From the figure, it can be concluded that there is an inverse relationship between SI_{cal} and Log P_{CO2} with a strong correlation ($R^2 = 0.83$ for Kalisirah Spring and $R^2 = 0.94$ for Jumbleng Spring). This correlation means that the SI_{cal} value gradually increases as the Log P_{CO2} value gradually decreases (Figure 3). This indicates that there has been a change in water conditions that are aggressive to non-aggressive (SI_{cal} > 0). This condition is related to the presence of CO$_2$, where the CO$_2$ content in the water will increase the water solubility of carbonate rocks [13]. On the other hand, when the level of CO$_2$ in the water decreases, it will increase the value of the saturation index and decrease its solubility in carbonate rocks [14]. The decrease in CO$_2$ during the dry season is controlled by the lack of microorganisms that produce CO$_2$ in the soil [15] and rainwater's absence of vertical diffuse flow into the epikarst [7]. Due to the decrease in CO$_2$ pressure in the aquifer, there is a change in conditions from saturated to very saturated (Kalisirah Spring) and aggressive to saturated at Jumbleng Spring (Table 2).

![Figure 2. SI_{cal} and Log P_{CO2} variation](image)

Water that is poor in CO$_2$ content comes from a closed system where the voids are not directly connected to the surface so that the CO$_2$ gas content is poor [16]. The flow from this closed system is stored and released through micropores and small cracks known as diffuse storage. The characteristics of the flow released from the diffuse storage have a long storage duration and an extended-release...
duration (slow-flow) [17], with a smaller amount of discharge. The relationship between SI_{cal} and discharge during the dry season shows that a decrease in discharge correlates with an increase in the SI_{cal} value (Figure 4). This condition means that the longer the water stays in the diffuse storage, the more saturated the flow will be and the smaller the discharge will be.

Table 2. The criteria for SI_{cal} values of Kalisirah and Jumbleng springs.

| Location | Seasons | Range       | Criteria               |
|----------|---------|-------------|------------------------|
| Kalisirah| Dry     | 0,14 to 0,72| Saturated to over-saturated |
|          | Rainy   | 0,33 to -0,30| Saturated to aggressive |
| Jumbleng | Dry     | -0,17 to 0,40| Aggressive to saturated |
|          | Rainy   | 0,08 to -1,00| Moderately saturated to highly aggressive |

In the rainy season, SI_{cal} variation was found in both springs moving to negative values (Figure 3). This value indicates that the flow conditions are becoming more aggressive. In this condition, it appears that the character of Kalisirah Spring changes from saturated water to aggressive, and Jumbleng Spring which is slightly saturated becomes very aggressive. This condition is caused by rainwater entering the aquifer with high CO₂ content. This fact is evidenced by the relationship between SI_{cal} and log P_{CO2} values; it can be seen that a low SI_{cal} value accompanies a high Log P_{CO2} value. As the supply of CO₂ in the aquifer increases, the nature of the water will become more aggressive. This aggressive water condition will significantly affect the development of karst geomorphology, such as the formation of cavities and widening existing fissures in the karst aquifer [18].

Figure 3. Relationship between SI_{cal} and log P_{CO2}

Furthermore, the relationship between SI_{cal} and discharge is presented in Figure 4. Based on the relationship between the discharge value and SI_{cal}, it can be seen that the greater the discharge flow, the more aggressive the water conditions. This condition is related to water coming from an open system with a void/conduit directly connected to the surface, so it is rich in CO₂ gas supply. The flow from this open system is stored and released through large voids. Characteristics of large voids in karst aquifers can be found in conduit and fissure storage. Some experts mention the naming of this storage as conduit-fissure storage. The characteristics of the flow released from conduit-fissure deposits have a storage duration and a faster flow release (quick-flow) with a more considerable amount of discharge. Short water residence causes the dissolution process to be short so that the character of the water is unsaturated. Therefore, the flow released through a more significant discharge has a more aggressive character (undersaturated) than usual.
In general, Kalisirah and Jumbleng springs are supersaturated during the dry season and tend to be aggressive (undersaturated) during the rainy season. This condition indicates that the dominance of the precipitation process to calcite occurs in the dry season, while the dominance of the dissolution process occurs during the rainy season. The precipitation process occurs when the CO2 content is low, while the dissolution process occurs when the CO2 content is high. Water with low CO2 content comes from a closed system that flows slowly (slow-flow) with supersaturated water, while the flow with a high CO2 content comes from an open system that flows quickly with aggressive water (undersaturated).

4.2 Spatial Analysis

The relationship between SI_calc and discharge in Kalisirah Spring has a less intense relationship throughout the year. This condition is caused by the binding of CO2 supply by carbonate with a short duration because it has a thick epikarst layer. Therefore, rapid precipitation occurs even before the hydrograph recession occurs. Basically, the dissolution and precipitation processes are reversible, meaning that when the carbonate rock dissolution process has reached its maximum point, it will return to the equilibrium point until the water becomes saturated again.

Jumbleng Spring has more aggressive water conditions than Kalisirah Spring. This condition indicates that Jumbleng Spring has a conduit cavity that has developed in its aquifer so that there is a supply of CO2 gas that triggers the dissolution process. Here, there is a strong relationship between SI_calc and log P_CO2 in the dry season, and it is also found that the relationship between SI_calc and discharge even has a high correlation in the rainy season. This condition means that the decreasing level of CO2 influences the precipitation process in the aquifer, and the dissolution process depends on the water input that enters the aquifer.

The relevant theory regarding the dissolution phenomenon in Jumbleng Spring is the variation in the size of the void conduit. That is, the void has irregular dimensions, so there is a barrier when water flows in it (Figure 5). This condition will impact the rotation of the flow that occurs in the aquifer because there are two energy releases in different directions. This non-uniform cavity condition will cause the flow to crash in the conduit at high speed, and a wave reversal will occur so that water storage pockets are formed [19]. The rotation of the flow in the aquifer causes the binding of CO2 to be infinite [20], causing the saturation process is getting longer. The flow rotation also causes the dissolution process to be controlled by the kinetic energy of the input stream that enters the aquifer. Therefore, the SI_calc value strongly relates to the discharge and causes a weak relationship with the log P_CO2 during the rainy season.
5. Conclusion and future works

Kalisirah and Jumbleng springs have saturated conditions during the dry season and are aggressive during the rainy season. This condition indicates the dominance of the precipitation process on calcite minerals in the dry season, while the dominance of the dissolution process occurs during the rainy season. The precipitation process occurs when the CO₂ content is low, while the dissolution process occurs when the CO₂ content is high. Water with a low CO₂ content comes from a closed system passed slowly by saturated water, while water with a high CO₂ content comes from an open system that is passed quickly by aggressive water. Both springs have a thick epikarst layer so that during the dry season, the relationship between S_{kal} and log P_{CO2} becomes very strong.

In terms of conclusions, further research is still needed regarding the condition of the aquifers in Jumbleng and Kalisirah Springs either through isotope methods, water tracing, aquifer memory systems or other methods that can display the characters of the two flow systems. Conditions related to voids in karst aquifers in this research are still only inferred from existing theories such as research from [19] on maze caves and experiments from [20] on open-closed systems.

Acknowledgements

This research was funded by the RTA-2021 Grant Universitas Gadjah Mada, No contract: 3143/UN1.P.III/DIT-LIT/PT/2021.

6. References

[1] Gillieson D 1996 Caves: processes, development, management (Blackwell, Oxford)
[2] Ford D C and P W Williams 2007 Karst Hydrogeology and Geomorphology (Wiley, Chichester)
[3] White W B 1988 Geomorphology and Hydrology of Karst Terrains (New York: Oxford University Press)
[4] Hendrasari R S 2020 Studi peningkatan kebutuhan air bersih pada masa pandemi covid-19 di kota Yogyakarta Proc. Seminar Nasional Unimus 3
[5] Campos M A S, Carvalho S L, Melo S K, Gonçalves G B F R, dos Santos J R, Barros R L and Abreu R R P 2021 Impact of the covid-19 pandemic on water consumption behaviour Water Supply J.

[6] Yuan D 1997 Sensitivity of karst process to environmental change along the pep II transect Quaternary International 37 105-113

[7] Pu J, Yuan D, Zhao H and Shen L 2014 Hydrochemical and pCO<sub>2</sub> variations of a cave stream in a subtropical karst area, chongqing, sw china: piston effects, dilution effects, CO<sub>2</sub> and buffer effects Env. Earth Sci. 71 4039-49

[8] Ruswanto, Badri I and Anwar A 2003 Inventarisasi geologi lingkungan kawasan karst gombong, kabupaten kebumen, jawa tengah Report (Departemen ESDM: Direktorat Tata Lingkungan Geologi dan Kawasan Pertambangan)

[9] Haryono E and Trijuni Putro S 2017 Polygonal karst morphology of Karangbolong area, Java-Indonesia. *Acta Carstologica* 46 1

[10] Astuti E S, Rahmawati A I, Setyawan A, Alghozali Q, Agniy R F, Fauzi D R, Mahrizkhal D S, Nurkholis A, Pratama A D, Dwiputra D S and Laksono G E 2020 A groundwater tracing investigation to determine kalisirah karst springs catchment area, kebumen regency, central java IOP Conf. Series: Earth and Env. Sci. 451 1 012072

[11] Parkhurst D L and Appelo C A J 1999 User’s guide to phreeqc (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations *US Geol. Surv. Wat-Resour. Invest.* 312 4259-99

[12] Liu Z, Groves C, Yuan D, Meiman J, Jiang, D, He S and Li Q 2004(b) Hydrochemical variation during flood pulses in southwest peak cluster karst: impacts of caco<sub>3</sub>-h<sub>2</sub>o-co<sub>2</sub> interactions, *Hydrological Processes* 18 2423-37

[13] Xiao N, Li S and Lin M 2017 Experimental investigation of CO<sub>2</sub>-water-rock interactions during CO<sub>2</sub> flooding in carbonate reservoir *Open J. of Yangtze Oil and Gas* 2 108

[14] Haryono E and Adji T N 2004 *Pengantar Geomorfologi dan Hidrologi Karst* (Yogyakarta: Kelompok Studi Karst Fakultas Geografi Universitas Gadjah Mada)

[15] Cosford J, Qing H, Mattey D, Eglington B and Zhang M 2009 Climatic and local effects on stalagmite δ13C values at lianhua cave, china *Palaeogeography, Palaeoclimatology, Palaeoecology* 280 235-244

[16] Adji T N, Haryono E, Fatchurohman H and Oktama R 2016 Diffuse flow characteristics and their relation to hydrochemistry conditions in the petoyan spring, gunungsewu karst, java, indonesia Geosciences J. 20 381–390

[17] Chang W, Wan J, Tan J, Wang Z, Jiang C and Huang K 2021 Responses of spring discharge to different rainfall events for single-conduit karst aquifers in western hunan province, china *International J. of Env. Research and Public Health* 18 5775

[18] Kaufmann G, Gabrovšek F and Romanov D 2016 Dissolution and precipitation of fractures in soluble rock *Hydrology and Earth System Sci. Discussions* 1 30

[19] Palmer A N 2001 Dynamics of cave development by allogenic water *Acta Carsologica* 30 13-32

[20] Buhmann D and Dreybrodt W 1985 The kinetics of calcite dissolution and precipitation in geologically relevant situations of karst areas: 2. closed system *Chemical Geology* 53 109-124

[21] Mahrizkhal D S 2021 Karst aquifer characterization using hydrogeochemical variation and flow release approach at kalisirah and jumbleng springs, south gombong karst area Thesis (Yogyakarta: Faculty of Geography Universitas Gadjah Mada)