Analysis of dissolved carbon sequestration potentials at several springs in karst landscape, wonogiri regency

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Abstract. This study aimed to analyze the potential of dissolved carbon sequestration in several springs distributed over the Wonogiri Karst area—a carbon sink. It employed a survey method and collected momentary data at eight sampled springs. The main parameters were calcium, alkalinity, and discharge. The springs varied in discharge, ranging from 1 L/s to 140 L/s, and were found into two classes, namely class 3 and class 5. These springs showed the characteristics of perennial flows. The alkalinity and calcium content was distributed almost uniformly, except for Nampu Spring that had small levels in both parameters. The potentials of dissolved carbon sequestration in the eight springs varied between 4.3 x 10^8 and 9.3 x 10^9 m^3/year, with the smallest level found in Nampu Spring and the largest one in Kakap Spring.

1. Introduction
Carbon dioxide (CO_2) is the most contributing gas to the greenhouse effect in the atmosphere [1]. This effect involves an increase in temperature and, subsequently, global warming, which has initiated climate change and extensively affected human life. An example includes the intensification of disasters and its accompanying threats of more severe casualties and material losses. Another climate change impact is the decline in economic quality, starting from economic collapse until food insecurity following crop failure due to disasters and seasonal changes.

There has been a lack of karst studies in the tropics, particularly in Wonogiri Karst area. This situation is quite concerning because, based on karst theory, tropical karst is the ideal form of karst development. Several studies have shown that the ability of karst to sequester carbon is within the range of 0.01-0.07 PgC/year depending on rock dissolution ([2], [3], [4], [5]). These figures are measured based on the chemical process in karstification. However, [6] obtained a much higher value (0.7052 PgC/year) by combining the dissolution of carbonate rock, the global water cycle, and the photosynthesis process. Even though many have realized that karst is a strategic medium for climate change research, studies have only been carried out in humid to subtropical karsts. Karst becomes essential in the carbon cycle because it requires H_2O and CO_2 in its dissolution.

Until recently, analysis of karst and its relation to climate change has been mostly conducted in the cold-climate regions to the subtropics. Since the tropics theoretically provide an environment for ideal karst development, information about the amount of CO_2 absorbed in the dissolution process can define the essential function of tropical karst landform in the context of climate change. Also, it can be further used as a reference in planning adaptation to climate change whose impacts are also felt on a local scale in Gunungkidul Karst, viz. decreased rainfall and elevated temperature by 0.04-0.047 [8].
Wonogiri Karst is a karst landform developing in the tropics that can be used to observe the potential of CO$_2$ sequestration. Modeling has been performed by looking at the variations between the catchment areas of developing and non-developing karsts.

2. Methods
This survey research was conducted at Wonogiri Karst (Figure 1), and the research object was springs. The sample size was eight springs with varying levels of discharge. Employing the float method, the flow discharge measurement was performed once at every spring. The alkalinity and calcium levels were determined in situ, each using alkalinity and calcium test kits. As for the dissolved carbon potential (C), it was analyzed based on equilibrium reactions during the dissolution process of carbonate rocks. The equation used to calculate it was as follows [9]:

$$C = Q \cdot \left[ \frac{HCO_3^-}{2} \times \frac{12}{61} \right]$$

Where HCO$_3^-$ is the annual concentration of HCO$_3^-$ in waters (g/L) and Q is annual water discharge (L/s). Meanwhile, the satellite images were analyzed to delineate the area of Wonogiri Karst.

![Figure 1 Research Location](image-url)
Table 1. Tools and Materials and Their Functions in the Research

| No | Materials                        | Functions                                      |
|----|----------------------------------|------------------------------------------------|
| 1  | Landsat images                   | Interpretation of land use, the boundary of the karst area |
| 2  | Topographical Maps of Indonesia | Research map location, the boundary of the karst area |
| 3  | Geological Maps                  | Interpretation of the lithology and the boundary of the karst area |
|    | Field Survey Tools               | Functions                                      |
| 1  | EC meter                         | Conductivity measurement                       |
| 2  | GPS                              | Positioning (samples, observation points, etc.) |
| 3  | Titration-based alkalinity test kits | Measurement of water alkalinity |
|    | Laboratory Equipment             | Functions                                      |

3. Results and Discussion

3.1. Description of Wonogiri Karst

Wonogiri Karst is part of Gunungsewu Karst stretch in the east of Yogyakarta. It covers an area of about 29,672.1826 ha from the total area of Wonogiri Regency, that is, 182,236.0236 ha. The research site is bordered by Eromoko and Giriwoyo Districts (north), Pacitan Regency in East Java Province (east), Indian Ocean (south), and Gunung Kidul Regency in the Special Region of Yogyakarta (west). Based on the UTM projection, it is located between 472911.59 - 495763.48 E and 9122533.37 N - 9092271.99 N.

Just as Gunungsewu Karst, the limestone in Wonogiri Karst is formed in Wonosari-Punung Formation that is composed of massive coral reef limestone in the south and layered limestone in the north ([10], [11], [12], [13]). Limestone thickness reaches more than 650 m with volcanic and clastic rocks in the base [12]. Reef limestone has highly diverse constituent rocks. However, rudstones, packstones, and framestones are predominant. Breccia consists of unusual clay matrices, identifiable biothermal structures, and carbonates with interspersed lenses of volcanic ash [12]. Layered limestone protrudes toward the north and northeast and dominates the Wonosari Plateau.

The three types of soils with the order of the smallest to the largest percentage in the study area are black grumusol, reddish-brown lithosol complex, and Mediterranean lithosol-rendzina complex (covering more than 90%). Both black grumusol and reddish-brown lithosol complex are found only in the northeastern part of the study area.

Dry agricultural area dominates more than half of the land uses in the study area, followed by settlements and rainfed rice fields [14]. This land utilization is attributable to the topographic conditions, i.e., hills with moderate to steep slopes that constrain the growth of built-up areas.

3.2. Discharge

The springs in the study area differed in discharge. Based on the Todd and Mays' classification, they were divided into three classes, namely class 3 (two springs) and class 5 (six springs). The highest discharge (up to 140 L/s) was detected at Kakap Spring, whereas the smallest one (1 L/s) was at Nampu.
Spring. These discharges are influenced by the size of the recharge area or the developing cavity system. The former defines the amount of rainwater ‘caught’ by the area, while the latter is associated with the amount of water stored in the spring. Springs with small discharge are the results of a diffuse cavity system, whereas high discharge comes from springs with a conduit system. The discharge levels of the sampled springs are illustrated in Figure 2. These springs flow throughout the year, indicating that all of them are perennial. Springs in the karst area are one source of clean water that is relatively easy to utilize, especially in the dry season during which the karst ground is dry and arid due to undeveloped surface flow.

![Figure 2. Spring discharge in the research area](image)

Nearly all of the sampled springs are used to meet the water demand of the households. Two springs with copious discharge, namely Kakap and Beton, provide water for domestic, agricultural, and fish farming practices. Kakap Spring is the source of the water managed by the Regional Drinking Water Company, which distributes clean irrigation water to farmlands in Giriwoyo Village, while Beton Spring is used not only for domestic purposes but also for a fish hatchery in Pracimantoro District.

3.3. Alkalinity and Calcium Content
The calcium content of the spring water varied between 98 and 144 mg/L. The lowest concentration was identified in Nampu Spring, while the highest one was in Lebak and Kropak Springs. Calcium is an essential element for living organisms, particularly in bone formation. In natural waters, calcium is usually less than 15 mg/L. Based on the SNI standard, it must be more than 75 mg/L. However, in karst regions, the concentration of calcium is commonly within the range of 30-100 mg/L [15].

The calcium content in most sampled springs was very high. It is related to carbonate rock solution and, therefore, proves that the karst in the study area is composed of calcite limestone (CaCO$_3$). High calcium can make waters hard, but it tends to be harmless and can even reduce the toxicity of some compounds.

Compared with calcium, bicarbonate was found at higher levels—i.e., in the range of 274.56-451.55 mg/L. The lowest and highest bicarbonate contents were measured at Nampu Spring and Karanglo Spring, respectively. The bicarbonate ion is the product of karst dissolution that represents carbon dioxide content in water.

Carbon dioxide in surface water and groundwater mainly comes from CO$_2$ in the air. The other sources are CO$_2$ contained in the soil and unsaturated zone between the soil surface and water table and CO$_2$ produced by plants nearby the water and oxidation of organic materials. Some of them can affect
the level of bicarbonate in waters. Bicarbonate, the output in the reaction of limestone dissolution, can be used to identify the current dissolution rate in karst areas [16]. The bicarbonate concentrations in the sampled springs are listed in Table 2.

3.4. Carbon Sequestration

The carbon sequestration potentials of the sampled springs ranged between 4.3 x 10^8 and 9.3 x 10^9 mg/year (Table 3). The lowest potential was found in Nampu Spring, whereas the highest one was in Kakap Spring. These levels are influenced by the size of the recharge area and the flow system that is currently developing in the area. Small sequestration potential likely indicates a small recharge area and diffuse flow system. Field observation found that the discharge fluctuation between the rainy and dry seasons was low, representing a diffuse flow system. On the contrary, springs with high carbon sequestration like Beton and Kakap produced high discharge with a developed flow system, called conduit. Conduit flow is characterized by, for instance, wide discharge fluctuation between the rainy and dry seasons.

| Springs | Q (L/s) | HCO\textsubscript{3} (mg/L) | F (mg/year) | Style |
|---------|---------|-----------------|-------------|-------|
| Nampu   | 1       | 274.59          | 425,875,585.60 |       |
| Karanglo| 7       | 451.55          | 4,902,322,898.00 |     |
| Kropak  | 2       | 433.24          | 1,343,867,866.00 |     |
| Kakap   | 140     | 427.14          | 92,746,238,636.00 |     |
| Braholo | 1.2     | 347.81          | 647,323,445.50 |      |
| Beton   | 120     | 414.94          | 77,226,183,974.00 |     |
| Lebak   | 6       | 421.04          | 3,918,073,999.00 |      |
| Waru    | 6       | 384.43          | 3,577,392,142.00 |      |
| Total   |         |                 | 1.84787E+11   |      |

The sequestration of dissolved carbon in the sampled springs is proportional to the size of the recharge area during the one-time sampling. One-time sampling does not reflect the average sequestration in one year, given that the highest discharge variation occurs in springs with conduit flow. Calculating the average value is not realistic considering that the recharge area of springs in karst regions is difficult to determine. More precise estimation can be performed with continuous measurement in the field, especially one in the rainy season and one in the dry season. One sample of spring for continuous analysis can provide more detailed data on carbon sequestration.
4. Conclusion
The springs varied in discharge, ranging from 1 L/s to 140 L/s, and were found into two classes, namely class 3 and class 5. These springs showed the characteristics of perennial flows. The alkalinity and calcium content was distributed almost uniformly, except for Nampu Spring that had small levels in both parameters. The potentials of dissolved carbon sequestration in the eight springs varied between $4.3 \times 10^8$ and $9.3 \times 10^9$ mg/year, with the smallest level found in Nampu Spring and the largest one in Kakap Spring.
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