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29-Nov-2021

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Reviewer: 1

Comments to the Author
The following article is found to be interesting and informative. The title of the manuscript is well written.
Suggestion on abstract
The abstract is concise, however, still can be well structured. Being based on the objective, the objective can be developed more with classifications of the doline than just groundwater flow. In the result, the author mentioned statistical analysis while no details on the statistical method were used in the result and discussion. I suggest it better to remove the sentence stating statistical analysis.

Comments on manuscript
Overall

1. The authors have tried to provide the details on the doline water, their hydrochemistry and the contribution of groundwater, however, much of the information provided are repeating.
2. The details provided in the result and discussion can be used in the introduction section and can be made more concise. The result section contains more descriptions of the analyzed result.
3. The obtained results are interesting and much more information can be provided from the data presented. I suggest the authors categorize the result in table form, add some maps if possible for better clarity. The result section can be rewritten by explaining obtaining results at first and discussed later with the references. For example; The paragraph "The physical properties of doline water generally show conditions that are clear to turbid, tasteless and odorless......." can be emphasized at first.
4. The authors are suggeted to have thorough english check before submission and follow the written style of scientific paper.

Specific
1. I suggest the authors to add the significance of doline for the study area and its importance in the introduction section.
2. Similarly, the details on the hydrogeology, water label to be presented in the materials sections are missing and are mentioned in the result section. Some parts of the result sections can be mentioned in the materials section.
3. Among 45 doline samples, the authors selected only 10 samples for the manuscript. What are the criteria for using only 10 samples? Please mention.
4. Please mention the method used in the physio-chemical parameters on the field as well as in the laboratory.
5. The paragraph on Page 6 "The amount of groundwater recharge........" has to be rewritten. In the same paragraph, please change the sentence "drought occurs" as this misleads the meaning as drought is the climatic condition than just doline.
6. I better suggest authors to present stiff diagram in the map form than in chart as its difficult to locate each loactions.
7. Page 8 paragraph starting with "Fig 6 shows that......" Instead of stating weathering of the minerals during dry, I suggest the authors to mention about contribution of weathering than specifically indicate weathering. Similarly, the one increment of Ca minerals might be the reason of Calcite dissolution than weathering. Please make sure by referring other authors.
8. The summary paragraph is not clear and has to be rewritten. Although, weathering is seen during the dry sesaon, the increment of Na+K might be one of the major from the evaporation and land use too. Please add some discussion adding references. Additionally, the authors are suggested to find any relationbetween overland flow surrounding the doline than concluding directly into the regional conduit flow. The authors are suggested to mark dolines with regional flow (if possible).
9. The authors mentioned silicate weathering in the conclusion section where thery havent't discussed anything about the silicate weathering in the result sections. Please add some sentences regarding silicate weathering that may have made change to doline water with some reference.

Figures
10. Fig 1. Mentioning all the sampled location is baseless.
11. Fig 3 is not clear. Please remake.

Reference
12. Please ensure the manuscript follows the journal reference style of mentioning all authors name rather than et al.
13. Mention if the journal is not in english language stating (in indonesian) in the references.

Reviewer: 2

Comments to the Author
The manucript is written well organized but some mistakes grammar. It would be better if proof reading to provide more impression in the writing. Figures need to provide in high quality and format table in the top format instead of center.

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16-Mar-2022

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Sincerely,
Takashi Nakamura
Associate Editor, Journal of Water and Environment Technology
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[Editor's Comments]

[Reviewer(s)' Comments]
Reviewer: 1

Comments to the Author
The research entitled “doline” got a lot of potential in the water resource development from the area of Indonesia and carries good scientific facts and figures. Although, authors made significant changes after the first review processes I still find a room to modify. For the first authors are suggested to know the significance of separating the paragraphs in the results and discussion. Similarly, authors are missing the correct citation processes. Since JWET is an emerging scientific journal, authors are strictly suggested to maintain the scientific pattern in the manuscript. I personally am interested to accept this paper, however, will wait one more time if authors modify near to the suggested points and not miss the comments reviewers and editor provides and suggest ensuring to ask someone who has better scientific paper writing command than entrusting Grammarly. Meanwhile, I would like authors to check thoroughly before submitting as I couldn’t see important figures.

For specific comments please find the attached pdf with comments mentioned in it.

Specific comments
1. Add it's after whether i.e. whether it's local or regional in the introduction section.
2. In the study area, the author mentioned "All dolines". Better to quantify the dolines than mention all. For eg. If 45 dolines are available write, nearly 45 dolines are available in the study area….
3. Same question following the comments from last time. Why author uses only 10 dolines for the analysis, why not all 46. Instead of mentioning it in the response sheet, I request the author to mention the exact reason why they used 10 samples. Additionally, mark the location of your interest i.e., either bigger dots or change the size of the analyzed 10 spots in the figure.
4. In the regional section, make ensure your intended meaning is correct for heights/ low. Please check whether it is high/ low or only height.
5. In field data of doline, why did only the EC meter get the equipment name and why not in the pH and TDS. Also please provide the precision of the device.
6. What's the use of SNI and APHA in laboratory data? I request the author to go through some other journals to write in the correct style. It's a bit confusing when you state the sentence saying, … particularly SNI and APHA have testing methods. What does that mean? Do you mean reader to go look at the methods? Please restructure the sentence.
7. In the result and discussion in the lithology section please merge the paragraph as separating paragraphs doesn't make sense here.
8. In doline condition section, better to refer to some of the papers than stating to go through the table "Climate changes can also ….. and turbidity (Table 3)." Simply looking at the data many thought on variation appears. Although, the climate might have a direct or less impact better to refer to some paper than just mentioning data. Since the climate effect and your objective don't match, I better suggest removing this discussion as the author hasn't presented long-term climate data.
9. In the hydrochemistry section, change hydrochemical to hydrochemistry of water and groundwater,…… Also, the two paragraphs are hydrochemical of water and ….. and Surface water and groundwater contains…. Can be used in the introductions section than writing up here as this can be a base in defining why and what can be done for the groundwater development from a future perspective.
10. Please mention the exact value of the precipitation from the paper you extracted than just citing it as "the information about precipitation can be seen". Most readers won't have time to go through other papers while reading you and break the flow reading other papers.
11. The three sentences, "The figure also shows the highest rainfall… ", "it means that there was a strong difference…..", and "therefore, the facies…….". How are these three sentences connected to each other? Some connecting sentences are missing. How rainfall caused Ca increase. Define the increase of Ca in the groundwater of the karstic environment, cite the sentences and then write about your result. This will lead your sentence to a valid point and will help you discuss rainfall and hydrochemistry.
12. Following the line, "Its condition triggers the dilution processes in the rainy season, then……." You mention dilution, do you mean dilution occurs in Na only and not in Ca? This sentence can be used as a connecting sentence for the previous one however you have to cite why Ca increased and Na decreased during the rainy season. There are many papers defining such information as Ca in rainfall is higher and it dissolves Ca from karts. Please ensure.
13. Please check the meaning of the work decomposition. Check if it's dissolution.
14. In the hydrogeological system, please make sure you are using the correct words. Please change to … "which can occur to groundwater fluctuation" to "low or no rainfall".
15. In a sentence, "Meanwhile, the anthropogenic process has not….." and the preceding paragraph "The difference in the main ion content in dolines water……." There is a contrast to the statement author is mentioning. Please check the connection between the sentences.
16. "In summary, the hydrogeological …….." paragraph, there is the repetition of the information. Please remove those. For those not described above can be used in the previous paragraphs than separating the paragraphs. The last line of this paragraph gives no meaning, please make sure to explain in a systematic manner.
17. Please check the grammatical structure of "other aspects that may affect the hydrogeochemical changes….."
18. In table no. 2 and 3, the information is repetitive like pH and EC. Please ensure not repeating the information.

Reviewer: 2

Comments to the Author
All the comments are well collected.

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[Reviewer(s)' Comments]
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However, please make sure you correct all the grammer during proofreading.

Reviewer: 2
I have verified that the comments have been properly corrected.
However, I strongly recommend that the "native English check".
For example, by English editing service.

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Today I have submitted my revision of manuscript through your OJS.
In this email I also attach the document.
I'm waiting for the next good news.
Thank you very much

Best regards,
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Groundwater Contributing to Doline Hydrochemistry in Panggang and Wonosari - Baron Hydrogeological Subsystems, Indonesia

T. Listyani R.A.[a], Ridayati [b]

[a] Department of Geological Engineering, Institut Teknologi Nasional Yogyakarta, Indonesia

[b] Department of Civil Engineering, Institut Teknologi Nasional Yogyakarta, Indonesia

ABSTRACT

The Panggang and the Wonosari-Baron Hydrogeological Subsystems are part of the Gunungsewu karst landscape in Gunungkidul Regency, Yogyakarta, Indonesia. This landscape has many dolines as one of the epikarst of the phenomenon. These dolines usually classified as solution dolines. This study aims to determine the presence or absence of groundwater flow in doline based on hydrochemical characteristics. Hydrochemical data were collected during the dry and rainy seasons, supplemented by water doline sampling on the ten selected dolines. Data were taken from the field and laboratory, both in physical (color, taste, odor, and turbidity) and chemical (pH, EC, and ionic content) properties of water. The hydrochemical analysis was performed using Stiff and Gibbs diagrams. The doline's water has Ca and Na-bicarbonate facies during the dry season but tends to change to Ca-bicarbonate facies in the rainy season. The water-rock interaction process and precipitation found strongly influence the hydrochemistry of dolines water. The hydrogeological system involves conduit-type groundwater flow. The groundwater is interpreted to contribute to the water doline based on its hydrochemistry, both locally and regionally.

Keywords: doline, karst, hydrochemistry, water, groundwater

Corresponding author: T. Listyani R.A., E-mail: lis@itny.ac.id

INTRODUCTION

Hydrochemical studies of the Gunungsewu karst area have been developed by several experts [1-4]. The research has been done in the Panggang and Wonosari-Baron subsystems of the Gunungsewu karst hydrogeological system. This region is located in the southern part of Java Island, Indonesia. Gunungsewu karst is an area that has good groundwater potential, although it often experiences drought in the dry season. Groundwater studies in this area are critical to revealing the water potential of the karst region. In particular, hydrochemical studies of water in the karst area, both groundwater and surface water, are interesting to be studied to understand water's genetics.

For karst regions, a study of chemistry is essential because hydrochemical properties reflect the mechanism of groundwater flow in karst rocks [5, 6]. The hydrochemical study in this research is focused on the phenomenon of water dolines. Doline is a funnel that allows direct surface water transmission to the bedrock aquifer. Doline may appear as isolated formations or clusters that give a mottled tone to the ground [6].

Dolines are limestone basins with diameters ranging from a few meters to one kilometer and depths from a few meters to one kilometer. Some dolines are grassy hollows, while others are stony basins bordered by cliffs [7]. Doline is the most fundamental characteristic of closed depression in karst. According to its origin, it can be further divided into several forms such as solution (true karst), collapse, break, buried, caprock, and suffosion dolines [8]. Dolines in the research area are generally solution dolines.

The hydrograph characteristics of karst aquifers have been studied in Gunungsewu, especially in underground springs and rivers, which show temporal and spatial variations [2]. Studies on karst spring have also been carried out [9]. The results show that water that can dissolve carbonate rocks usually affects the current karstification process rate. Spatial/temporal analysis of the karst subsurface river shows that hydrochemistry of karst water, especially in total dissolved solids (TDS) and pH, was affected by precipitation during the flow process [10]. On the other hand, the quality and origin of groundwater, including the transport mechanism, can support the conservation of existing water resources, such as springs, wells, and river water [11], and protect fresh groundwater [12]. The hydrochemistry in karst doline water has not been studied specifically, so this paper aims to complement the karst research, especially Gunungsewu. The origin of doline water in the research area also needs to be examined to see the contribution of groundwater flow based on the hydrochemistry of doline water.

This study aims to determine the hydrogeological system concerning the water doline phenomenon and is expected to complement the knowledge of the karst hydrogeological system in the area. By hydrochemical analysis, this study will reveal the genetics of surface water present in the doline, whether the water only comes from rainwater or is there a contribution from groundwater that supplies doline water. Doline is essential to learn and know groundwater's contribution to them locally and regionally.

The hydrochemistry of water and groundwater affects its quality. For example, surface water and groundwater may have different qualities in terms of salt content. This difference in quality can be studied to determine the two effects.

MATERIALS AND METHODS

Study area

The research area is the western part of the Gunungsewu Karst Landscape Area, especially in Panggang Subdistrict and its surroundings (see **Fig. 1**). Field hydrogeological surveys have been carried out in and around its surroundings, emphasizing areas with doline morphology. There are 45 dolines available in the study area as the subject of this study.

Regional hydrogeology of Gunungsewu

The research area is part of the physiographic zone of the Southern Mountains of Central-East Java [13]. This zone consists of three sub-zones, namely the Baturagung Sub-zone in the north, the Wonosari plateau sub-zone in the middle, and the Gunungsewu Sub-zone in the south. The Gunungsewu Sub-zone is a karst hill that spreads relatively west-east.

The configuration of Gunungsewu karst bedrock varies with highs/lows, ridge/basin, and subsurface valleys, causing differences in the direction of groundwater flow, thus forming a hydrodynamic zone separation in this area. Based on the hydrodynamics, pattern, and distribution of the springs, the hydrogeological system in the Gunungsewu area can be divided into three subsystems, from west to east, namely Panggang, Wonosari –Baron, and Sadeng Sub-systems [1]. This research was conducted in two hydrogeological subsystems, namely Panggang and Wonosari-Baron. In the Panggang area, a bedrock ridge extends with a relatively west-east axis parallel to the South Coast, with a maximum depth of approximately 50 m from the surface.

The Panggang Sub-system has several endokarst and exokarst phenomena, including underground rivers and karst springs. Underground rivers and the karst springs may be interconnected. A single conduit tunnel developed significantly in the region by tracing groundwater flows in springs and underground rivers in the Purwosari area [14].

Field data of doline

Field data collection was carried out on several dolines, including geological and hydrogeological data. Geological data is collected based on morphology, rock, and geological structures. Hydrogeological data were obtained by observing rocks to determine their potential as aquifers and groundwater quality data. Doline water quality data includes pH, TDS, and EC obtained using Hanna brand pH-meter, TDS-meter, and EC-meter. This equipment is calibrated using a standard solution before being used in the field. Field data collection was taken for two seasons, namely at the end of the dry season in September -

October 2019 and the middle of the rainy season in March 2020.

Forty-five dolines were recorded in the study area, both large and small dimensions. Dolines are generally round in shape, and some dolines are slightly elongated/oval. Ten dolines were selected with a large enough volume of water for hydrochemical testing in the laboratory. The reason for choosing the ten dolines is that other dolines are often found dry in the dry season, so sampling cannot be done.

Laboratory data

The selected doline water samples were then tested in the laboratory to determine their physical and chemical properties. Parameters tested include color, turbidity, pH, EC, and the content of ions/chemical compounds. The ionic/chemical compounds included HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, K^+, Na^+, Mg^{2+} cations, and SiO_2 (see **Table 1**). Then, laboratory data are used for hydrochemical analysis by representing Stiff and Gibbs diagrams [15]. Major cations such as Ca^{2+}, Na^+, Mg^{2+}, and K^+ were measured using ion chromatography. Ion SO_4^{2-} were analyzed by spectrophotometer, while HCO_3^- and Cl^- were determined by alkalinity and argentomeric titration methods, respectively. The groundwater facies is determined based on the dominant anions and cations values, where the facies naming is determined by the ions content of > 25%.

Hydrogeological and hydrochemical analysis

The hydrogeological analyses were carried out by describing the rock exposed in the field, analyzing the aquifers responsible for groundwater flow, water media, and the type of flows around the doline. These hydrogeological characteristics largely determine the pattern of subsurface water flow through the type of rock porosity. In comparison, hydrochemical analysis determines the chemical facies of water through the Stiff diagram. The diagram of the relationship between chemical ions and TDS through the Gibbs diagram is significantly helpful in interpreting the hydrochemical process of water.

RESULTS AND DISCUSSION

Hydrogeological characteristics of the doline area

Lithology

Karst regions have a specific hydrogeological character [6] because the constituent rocks, such as limestone and dolomite, are highly susceptible to chemical dissolution [16]. The limestones that make up the study area are dominated by reef limestones consisting of boundstone and packstone and layered limestone in the form of wackestone [1]. Wackestone exhibits a matrix-supported texture, with grains generally < 1 mm. The grain types are mostly calcite and foraminifera fossils that have undergone a lot of dissolution, leaving many pores. Dissolution occurs from the grain and matrix parts. Packstone exhibits a grain-supported texture with moderate sorting. Granules are generally < 1.5 mm in size, composed predominantly of foraminifera, mollusks, and algae. The apparent porosity is vuggy and interparticle type. The apparent porosity is of the moldic and vuggy type.

Reef limestones supported the karst hydrogeological system in the study area as the karst landscape's dominant constituent. Occasionally, layered limestone or tuffaceous sandstone are found to be relatively thin.

Aquifer

Non-karst aquifers form aquifer systems with the diffuse flow and karst aquifers with conduit flow. The potential aquifer in the Gunungsewu area is the limestone of the Wonosari Formation. In addition, there are also non-karst, perched aquifers in a karst limestone-free aquifer system [1]. Karst aquifers have cavity porosity with conduit flow, while non-karst aquifers are supported by intergranular porosity and diffuse flow.

Limestone aquifers are generally free aquifers bounded by an impermeable layer of Tertiary bedrock. This aquifer is highly developed due to the support of secondary permeability in cavities with small to large dimensions, such as underground caves.

Water media

Reef and layered limestones are good water media in karst. These rocks have experienced quite intensive tectonics activity, as evidenced by the many cracks and fractures. In addition to the joint structure, geological structures in the form of faults may be present in the study area.

The existence of geological structures in the form of faults, fractures, or cracks causes the development of secondary porosity, namely crack porosity, in addition to intergrain porosity. The dissolution also increases the porosity of limestones to form cavities that sometimes have relatively large dimensions, thus allowing the underground caves and rivers to occur.

Cavity porosity triggers the conduit groundwater flow. The cavities formed from the dissolving of easily soluble limestone can even form karst caves. This limestone dissolution is strongly supported by rainfall levels and is influenced by climate change.

Flow type

Shallow, free aquifers support the hydrogeological system in the study area. Groundwater flow is dominated by the conduit system and can be a source of doline water support (**Table 2**). Diffusion flow can occur in soil or weathered rock near the surface to very shallow depths.

Doline's condition over the season

The physical properties of doline water generally show clear to turbid, tasteless, and odorless conditions in both dry and rainy seasons. On the other hand, the seasons affect physical changes, especially cloudiness and color, which is uncertain. Doline turbid water can be brownish white or greenish to brown (Table 3).

Dolines with small dimensions include Gandu (D5), Sambi (D7), Klepu (D32), Pengos (D23), Sumuran (D37; **Fig. 2a**), Sade (D43), and Belik (D44) dolines. These small dolines have a length of only a few meters in diameter, not more than 50 m. Dolines with large dimensions include Dendengwelut (D6), Towet (D21), Suci (D27), Winong (D28; **Fig. 2b**), Boromo (D29), Namberan (D30), and Gadel (D35). These large dolines reach a length or diameter of > 100 m.

Seasonal differences affect the volume of groundwater discharge [17]. It also applies to the amount of dolines water. In the dry season, the dolines water is generally much less, and there are even some dry dolines, for example, Gandu (D5), Jombor (D8), Miriledok (D4), Suci (D27), Pengos (D33), and Sumuran (D37) dolines. However, several dolines still showed a fairly large volume of water, including Towet (D21), Jambeanom (D26), Boromo (D29), Namberan (D30), Monggol (D31), and Omang (D42) dolines. According to information from residents, Towet doline never dries up, even though there is a long dry season.

In the rainy season, many dolines have abundant water. It means that the water on the doline is strongly supported by rainfall. However, some doline was found in almost dry (little water) to dry conditions. Dolines that are almost dry in the rainy season include Gandrung (D18) and Wuni (D39) dolines. Dolines that dry in the rainy season include (D14), Pengos (D33), Depok (D36), Sade (D43), and Belik (D44) dolines.

Groundwater recharge may vary linearly with monthly rainfall [18], as well as doline conditions. In the rainy season, precipitation can be the main water source in the dolines. Seasonal changes will usually affect the quantity of dolines water. Dry or less water occurs due to significant fluctuations in doline water. If the doline comes into contact with groundwater, the groundwater table is probably below the bottom of the dolines.

Hydrochemistry of doline water

To fulfill the needs of drinking water, water quality needs to be evaluated. The hydrochemistry of water and groundwater determines water quality in an area. Various studies have successfully evaluated water quality, including solutions to improve water quality with RO devices to reduce dissolved organic carbon [19].

Surface water and groundwater contain different salts with different concentrations, depending on the sources and the number of soluble constituents present in the geological formations through which the waters passes [20, 21]. Therefore, the hydrochemical characteristics can be studied to determine the genetics of water.

The hydrochemical facies of water doline during the dry season is dominated by Ca,Na-bicarbonate facies, while in the rainy season, it generally shows the Ca-bicarbonate facies. From the Stiff diagram, it can be seen that, in general, the major ions content of doline during the rainy season tends to decrease in concentration (**Fig. 3**). It means that rainfall results in a dilution of the major ions concentration. Although the enrichment of HCO3 accompanies the increase in EC during the rainy season^{-} and Ca^{2+} ions, rainfall significantly affected the decrease in the concentration of these major ions. Karst groundwater in the tropics in Cenozoic rocks usually has low EC variability [22], as does karst in this study area.

Information on precipitation can be seen in **Fig. 4**. The figure shows no precipitation in the study area at the time of the first water sampling (September 2019), and the highest was in March 2020, when the second sampling was carried out. It means that there is a large difference in rainfall in the two sampling periods. There was no rain from August to October 2019, while in the rainy season, the lowest rainfall was 131 mm/month in November 2019, and the highest was 422 mm/month in March 2020 [23]. The doline water facies tend to be of the Ca- bicarbonate type in the rainy season, accompanied by lower EC values than in the dry season. The high Ca content in the rainy season indicates that the dissolution of limestone is getting more intensive.

The hydrochemistry of doline water is affected by rock dissolution, which can be accelerated by the presence of weathered rock. The data plot on the Gibbs diagram (**Fig. 5**) shows that the influence of rock factors dominates the doline waters in the study area. This means that the hydrochemistry of water doline is determined mainly by the rock composition and controlled by the supply of elements derived from the dissolution of rock minerals.

Seasonal variations of water doline hydrochemistry can be seen in the different facies. The doline may be strongly supported by rainfall in the rainy season but should be another water source in the dry season. If there is a contribution from the groundwater, the conduit-type flow dominates the groundwater. The contribution of groundwater is very likely to occur, as evidenced by the presence of dolines that remain wet during the long dry season.

Hydrogeological system in doline and surrounding areas

The character of the groundwater recharge system in the Gunungkidul area, apart from originating from the local area, can also be supplied from other surrounding areas. Stable isotopes data from previous researchers supported an understanding of the hydrogeological system in this area. Based on the characteristics of stable isotopes, it is known that groundwater in this area is associated with intermediate and regional recharge systems [3].

Most of the groundwater in underground springs and rivers in the karst region comes from groundwater saturated with $CaCO_3$ with diffusion flow systems in the epikarst zone. The diffusion flow then develops into groundwater flow with a conduits (cavities) system. Flow diffusion usually occurs in porous or dense jointed media [24].

Groundwater in the study area is connected with the regional recharge system from the non-karst hills in the north and the local recharge system from the Gunungsewu karst area [3]. Groundwater flows in underground rivers and can appear as karst springs. In addition, groundwater can also appear on the surface mixed with rainwater and contribute to the surrounding doline.

Then, groundwater hydrochemistry is important to provide information about its aquifer and the water in the surrounding area. Groundwater in the karst hydrogeological systems can contribute to doline water. Doline, which is dry in the long dry season, indicates a lack of groundwater supply to the doline, which can occur due to groundwater table fluctuation, which causes the groundwater table to fall below the doline depth.

Based on the Gibbs diagram analysis, the significant variation in the dry season compared to the rainy season indicates a significant dissolution effect and the dominant hydrochemical process. The considerable variation in the dry season by ignoring local rains significantly affects groundwater, especially in some doline which still has large water volumes (Towet, Namberan, Monggol, Omang dolines). A large water supply from groundwater may come from a regional flow system or non-karst hills [3]. This is also supported by a graphical analysis of Ca^{2+}/Na^{+} *vs* HCO_3^{-}/Na^{+} or Mg^{2+}/Na^{+} [25], which shows silicate weathering as a hydrochemical process in the study area (**Fig. 6**).

Fig. 6 shows that minerals weathering is more dominant in the dry season. In contrast, in the rainy season, there is a lot of weathering of carbonate minerals and the dissolution of carbonates. This graph does not appear to be fully appropriate, considering that the research area is located in a karst hydrogeological subsystem. However, from the chart, it can be interpreted that in the dry season, there is weathered clay material dissolved in water dolines. The clay material may be supported by water-rock interactions from non-karst hills carried by regional groundwater flows, consistent with the previous findings [3].

The hydrochemical variation of doline water during the dry season is supported by wide variations in the content of Ca^{2+} and HCO_3^{-}. It shows that rock dissolution can vary from place to place, usually triggered by the amount of water in the water-rock interaction process. In addition, the duration of the flow process and the distance traveled can also provide variations in the ion content. It means the groundwater supplying doline water may vary as a local, intermediate or regional system which also accounts for differences in the duration and distance traveled by the draining process.

In the dry season, groundwater plays a vital role in determining the hydrochemistry of doline water.

Then in the rainy season, doline water is strongly influenced by rainfall. Weathering and mineral dissolution are the main processes during the dry or rainy season. The evaporation and enrichment of water chemical elements were also observed to occur more frequently during the dry season. Hydrochemistry is strongly influenced by rainfall during the rainy season and provides a dilution effect. Meanwhile, the anthropogenic processes have not become dominant in both the rainy and dry seasons.

The difference in the main ion content in the dolines water in the two seasons can also be caused by land use or anthropogenic aspects [15], although the intensity is small [26]. It can be triggered by surface runoff [27, 28] or fertilizer contamination from cultivated farms [13, 29].

In summary, the hydrogeological system in the study area involving the doline water facies can be seen in **Fig. 7**. This figure shows that doline water can come from local rain or be supported by groundwater flow in local, medium, or regional systems through conduit-type flows. However, it is possible that dolines only depend on rainwater and are not connected to groundwater. Dolines like this are usually dry in the dry season.

CONCLUSIONS

Hydrochemical studies in the Gunungsewu karst area have been done on the Panggang and Wonosari-Baron subsystems to determine the relationship between dolines water and groundwater. The hydrogeological system of the study area determines the hydrochemistry of doline water. The geological structure is in the form of fairly dense joints so that it helps the flow process as a porous aquifer media, supported by dissolving limestone. Seasonal changes cause water doline to fluctuate, where some dolines may dry up, especially during the dry season.

The dissolution process of limestone minerals primarily determines the hydrochemistry of doline waters. The Gibbs diagram shows that rock dissolution plays a significant role in deciding the hydrochemistry of doline water. In addition, the relationship between ions shows the dominant influence of silicate weathering, which is interpreted to originate from distant silicate rocks through regional groundwater flows. Another aspect affecting hydrochemical changes in dolines water, even if small, is land use or anthropogenic activities.

Groundwater flow systems that supply doline water may be local and regional. Dolines waters are supported by conduit-type groundwater flow. The contribution of regional groundwater flows is supported by water doline hydrochemistry, supported by differences in water facies in different seasons. Moreover, rainfall as a source of local groundwater and doline water recharge can also affect the hydrochemistry of doline water.

The contribution of groundwater to doline water indicates that some dolines have water dependent on groundwater flow. It should be understood that doline in some places has a relationship with leaks in other areas, even at quite a distance.

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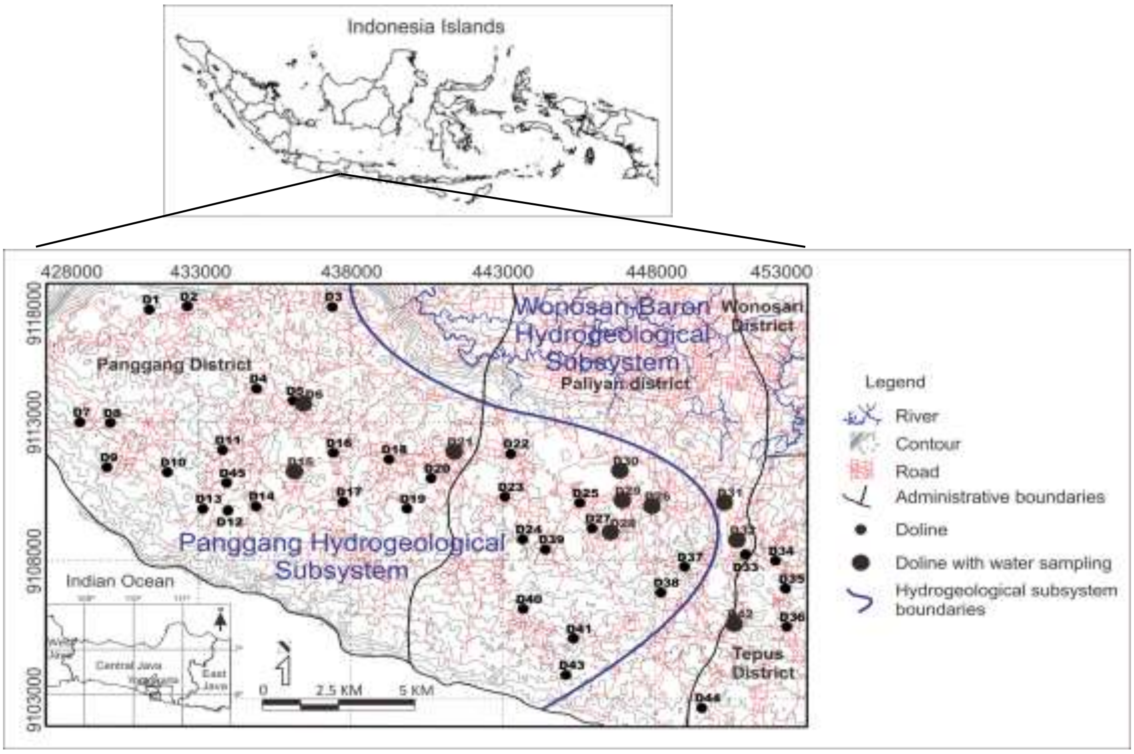

Fig. 1 Map of the location of dolines in the study area.

Table 1 The laboratory data of doline water chemical properties.

Parameter (mg/L)	D6	D15	D21	D26	D28	D29	D30	D31	D32	D42
	Dry Season									
HCO_3^-	146.4	250.1	122	189.1	350.4	274,5	140.3	140.3	267.1	91.5
Cl^-	7.0	6	8.5	32	42	37	17.5	6	12.5	10.5
SO_4^{2-}	6	8	2	9	8	8	8	2	16	4
Ca^{2+}	27.86	54.35	26,33	38.31	68.66	50.47	27.16	27.53	41.18	11.14
K^+	6	4	6	8	13	9	6	4	27	7
Na^+	8	25	25	59	93	82	49	25	59	31
Mg^{2+}	8.22	5.8	2.89	1.93	1.45	2.42	4.35	1.45	9.15	1.45
SiO_2	14.94	14.054	10.496	13.41	13.258	12.846	10.364	9.624	11.001	4.244
	Rainy Season									
HCO_3^-	68.3	47.5	59.4	59.4	97.9	77.2	68.3	68.3	74.2	80.1
Cl^-	0.6	0.6	0.6	0.6	6.5	0.6	0.6	0.6	2	0.6
SO_4^{2-}	16	20	10	10	9	10	10	10	6	8
Ca^{2+}	17.6	11.2	12.8	16.72	20.7	15.92	19.1	14.33	16.72	19.9
K^+	4	2	3	4	5	3	3	3	4	4
Na^+	10	3	7	10	23	7	7	10	13	10
Mg^{2+}	2.43	3.4	4.37	2.42	1.45	1.93	1.93	1.45	1.45	0.48
SiO_2	6.562	6.163	5.025	7.624	6.574	2.756	6.208	7.008	4.451	3.058

Table 2 Hydrogeological characteristics of the study area.

Parameter	Groundwater	Doline Water
Lithology	Reef & bedded limestone of Wonosari Formation	Reef & bedded limestone of Wonosari Formation
Characteristics	Shallow aquifer	Associated with shallow aquifer
Water media	Densely fracture - porous; cave & underground river	Surface water bodies
Flow type	Conduit system	Local rainfall, diffuse flow in soil, supported by conduit groundwater flow

Table 3 The physical/chemical properties of water dolines.

Doline	D6	D15	D21	D26	D28	D29	D30	D31	D32	D42
Parameter	DRY SEASON									
T (ºC)	30.2	26.3	31.8	33.2	31.8	30.1	31.2	31.7	29.8	32.4
pH	8.8	7.4	8	10.1	9.5	9.1	9.6	9	9	9.8
TDS (mg/L)	104	241	103	180	299	260	133	83	160	82
EC (µS/cm)	248	418	204	304	374	322	296	136	156	151
Turbidity (NTU)	19	16.1	2.2	89	143.5	243.5	136.5	1.3	122.5	37.8
Color (TCU)	46	8	24	88	94	148	94	19	83	23
	RAINY SEASON									
T (ºC)	31.8	34	31.6	33	30.8	29.8	30	27.7	27.6	32
pH	8.9	8	9.2	9.4	9.4	9.1	8.4	8.4	8.1	9.1
TDS (mg/L)	59	46	53	53	76	53	48	52	55	45
EC (µS/cm)	148	70	116	100	174	122	132	110	104	116
Turbidity (NTU)	35.6	37.6	15.7	41.7	19	28.8	29.8	14.2	13.5	19.3
Color (TCU)	106	200	28	64	33	40	40	22	15	7

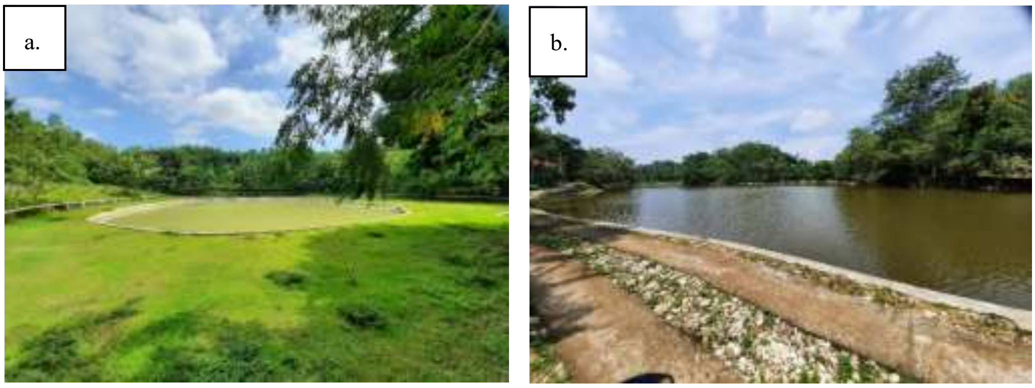

Fig. 2 (a) Sumuran (D37) doline is an example of small dimension doline. (b) Winong (D28) doline represents the large doline.

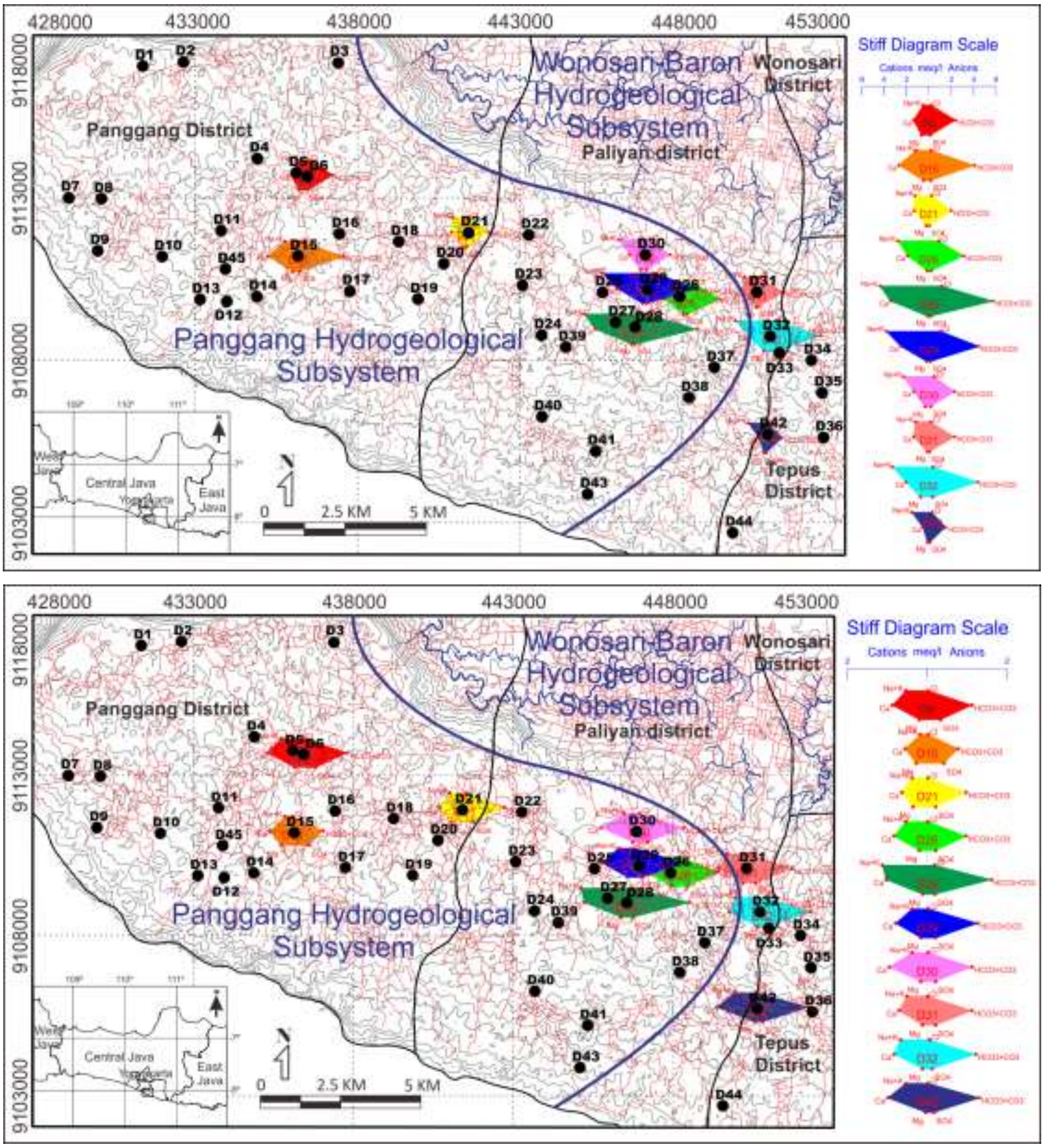

Fig. 3 Stiff diagrams of water samples in dry season (top) and rainy season (bottom).

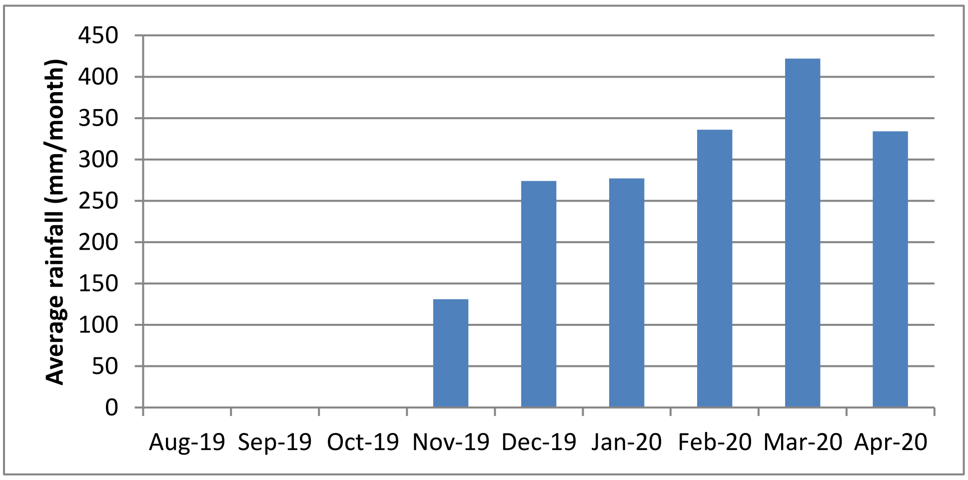

Fig. 4 Average rainfall in study area [23].

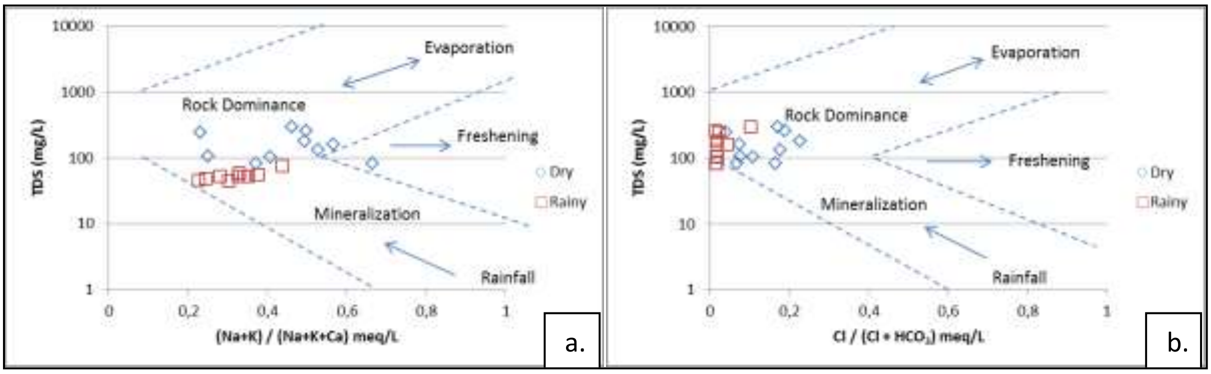

Fig. 5 Plot of water doline hydrochemical data on the Gibbs Diagrams, shows the relationship between alkaline ions *vs* TDS (a) and major ion *vs* TDS (b).

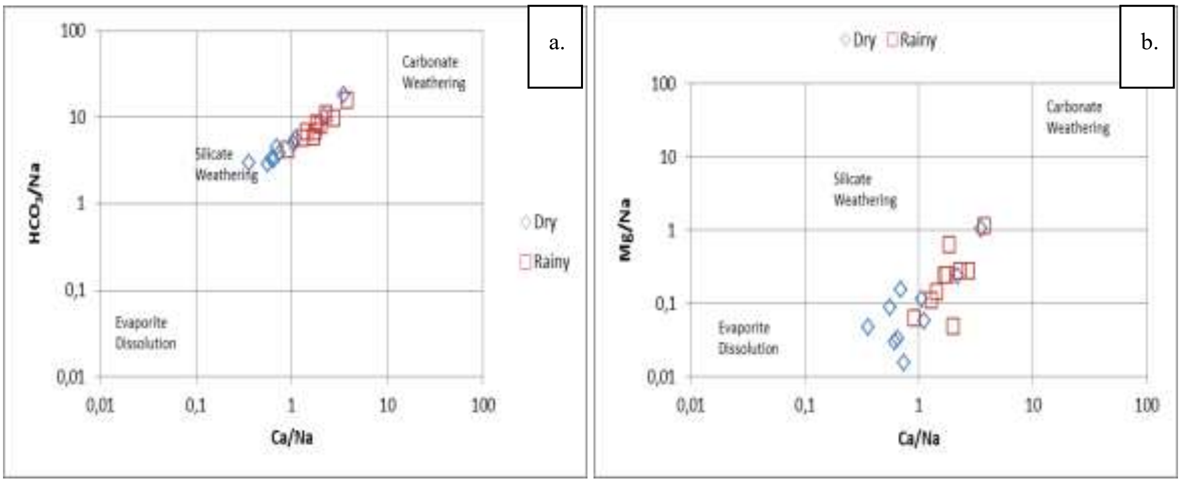

Fig. 6 Relationship of several hydrochemical parameters [25] in study area show (a) Na normalized HCO_3^- *vs* Ca^{2+} plots and (b) Na normalized Mg^{2+} *vs* Ca^{2+} plots.

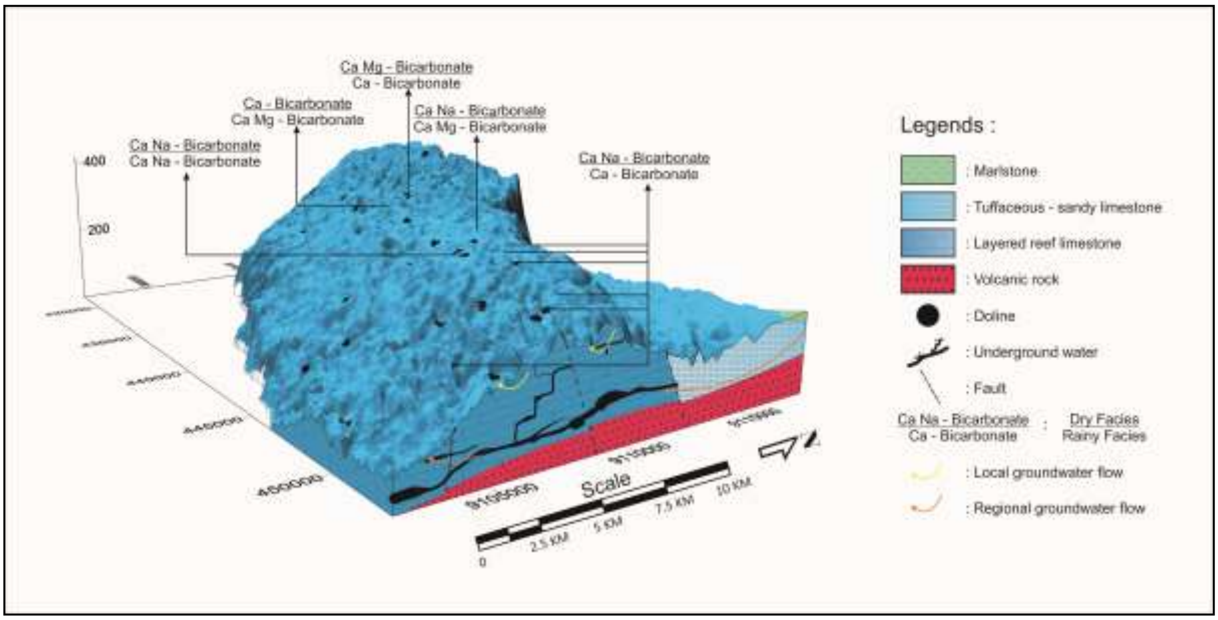

Fig. 7 Schematic diagram of the 3D hydrogeological system of the doline in the study area (modification from [1]).

Groundwater Contributing to Doline Hydrochemistry in Panggang and Wonosari - Baron Hydrogeological Subsystems, Indonesia

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ABSTRACT

The Panggang and the Wonosari-Baron Hydrogeological Subsystems are part of the Gunungsewu karst landscape in Gunungkidul Regency, Yogyakarta, Indonesia. This landscape has many dolines as one of the epikarst of the phenomenon. These dolines usually classified as solution dolines. This study aims to determine the presence or absence of groundwater flow in doline based on hydrochemical characteristics. Hydrochemical data were collected during the dry and rainy seasons, supplemented by water doline sampling on the ten selected dolines. Data were taken from the field and laboratory, both in physical (color, taste, odor, and turbidity) and chemical (pH, EC, and ionic content) properties of water. The hydrochemical analysis was performed using Stiff and Gibbs diagrams. The doline's water has Ca and Na-bicarbonate facies during the dry season but tends to change to Ca-bicarbonate facies in the rainy season. The water-rock interaction process and precipitation found strongly influence the hydrochemistry of dolines water. The hydrogeological system involves conduit-type groundwater flow. The groundwater is interpreted to contribute to the water doline based on its hydrochemistry, both locally and regionally.

Keywords: doline, karst, hydrochemistry, water, groundwater

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INTRODUCTION

Hydrochemical studies of the Gunungsewu karst area have been developed by several experts [1-4]. The research has been done in the Panggang and Wonosari-Baron subsystems of the Gunungsewu karst hydrogeological system. This region is located in the southern part of Java Island, Indonesia. Gunungsewu karst is an area that has good groundwater potential, although it often experiences drought in the dry season. Groundwater studies in this area are critical to revealing the water potential of the karst region. In particular, hydrochemical studies of water in the karst area, both groundwater and surface water, are interesting to be studied to understand water's genetics.

For karst regions, a study of chemistry is essential because hydrochemical properties reflect the mechanism of groundwater flow in karst rocks [5, 6]. The hydrochemical study in this research is focused on the phenomenon of water dolines. Doline is a funnel that allows direct surface water transmission to the bedrock aquifer. Doline may appear as isolated formations or clusters that give a mottled tone to the ground [6].

Dolines are limestone basins with diameters ranging from a few meters to one kilometer and depths from a few meters to one kilometer. Some dolines are grassy hollows, while others are stony basins bordered by cliffs [7]. Doline is the most fundamental characteristic of closed depression in karst. According to its origin, it can be further divided into several forms such as solution (true karst), collapse, break, buried, caprock, and suffosion dolines [8]. Dolines in the research area are generally solution dolines.

The hydrograph characteristics of karst aquifers have been studied in Gunungsewu, especially in underground springs and rivers, which show temporal and spatial variations [2]. Studies on karst spring have also been carried out [9]. The results show that water that can dissolve carbonate rocks usually affects the current karstification process rate. Spatial/temporal analysis of the karst subsurface river shows that hydrochemistry of karst water, especially in total dissolved solids (TDS) and pH, was affected by precipitation during the flow process [10]. On the other hand, the quality and origin of groundwater, including the transport mechanism, can support the conservation of existing water resources, such as springs, wells, and river water [11], and protect fresh groundwater [12]. The hydrochemistry in karst doline water has not been studied specifically, so this paper aims to complement the karst research, especially Gunungsewu. The origin of doline water in the research area also needs to be examined to see the contribution of groundwater flow based on the hydrochemistry of doline water.

This study aims to determine the hydrogeological system concerning the water doline phenomenon and is expected to complement the knowledge of the karst hydrogeological system in the area. By hydrochemical analysis, this study will reveal the genetics of surface water present in the doline, whether the water only comes from rainwater or is there a contribution from groundwater that supplies doline water. Doline is essential to learn and know groundwater's contribution to them locally and regionally.

The hydrochemistry of water and groundwater affects its quality. For example, surface water and groundwater may have different qualities in terms of salt content. This difference in quality can be studied to determine the two effects.

MATERIALS AND METHODS

Study area

The research area is the western part of the Gunungsewu Karst Landscape Area, especially in Panggang Subdistrict and its surroundings (see **Fig. 1**). Field hydrogeological surveys have been carried out in and around its surroundings, emphasizing areas with doline morphology. There are 45 dolines available in the study area as the subject of this study.

Regional hydrogeology of Gunungsewu

The research area is part of the physiographic zone of the Southern Mountains of Central-East Java [13]. This zone consists of three sub-zones, namely the Baturagung Sub-zone in the north, the Wonosari plateau sub-zone in the middle, and the Gunungsewu Sub-zone in the south. The Gunungsewu Sub-zone is a karst hill that spreads relatively west-east.

The configuration of Gunungsewu karst bedrock varies with highs/lows, ridge/basin, and subsurface valleys, causing differences in the direction of groundwater flow, thus forming a hydrodynamic zone separation in this area. Based on the hydrodynamics, pattern, and distribution of the springs, the hydrogeological system in the Gunungsewu area can be divided into three subsystems, from west to east, namely Panggang, Wonosari –Baron, and Sadeng Sub-systems [1]. This research was conducted in two hydrogeological subsystems, namely Panggang and Wonosari-Baron. In the Panggang area, a bedrock ridge extends with a relatively west-east axis parallel to the South Coast, with a maximum depth of approximately 50 m from the surface.

The Panggang Sub-system has several endokarst and exokarst phenomena, including underground rivers and karst springs. Underground rivers and the karst springs may be interconnected. A single conduit tunnel developed significantly in the region by tracing groundwater flows in springs and underground rivers in the Purwosari area [14].

Field data of doline

Field data collection was carried out on several dolines, including geological and hydrogeological data. Geological data is collected based on morphology, rock, and geological structures. Hydrogeological data were obtained by observing rocks to determine their potential as aquifers and groundwater quality data. Doline water quality data includes pH, TDS, and EC obtained using Hanna brand pH-meter, TDS-meter, and EC-meter. This equipment is calibrated using a standard solution before being used in the field. Field data collection was taken for two seasons, namely at the end of the dry season in September -

October 2019 and the middle of the rainy season in March 2020.

Forty-five dolines were recorded in the study area, both large and small dimensions. Dolines are generally round in shape, and some dolines are slightly elongated/oval. Ten dolines were selected with a large enough volume of water for hydrochemical testing in the laboratory. The reason for choosing the ten dolines is that other dolines are often found dry in the dry season, so sampling cannot be done.

Laboratory data

The selected doline water samples were then tested in the laboratory to determine their physical and chemical properties. Parameters tested include color, turbidity, pH, EC, and the content of ions/chemical compounds. The ionic/chemical compounds included HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, K^+, Na^+, Mg^{2+} cations, and SiO_2 (see **Table 1**). Then, laboratory data are used for hydrochemical analysis by representing Stiff and Gibbs diagrams [15]. Major cations such as Ca^{2+}, Na^+, Mg^{2+}, and K^+ were measured using ion chromatography. Ion SO_4^{2-} were analyzed by spectrophotometer, while HCO_3^- and Cl^- were determined by alkalinity and argentomeric titration methods, respectively. The groundwater facies is determined based on the dominant anions and cations values, where the facies naming is determined by the ions content of > 25%.

Hydrogeological and hydrochemical analysis

The hydrogeological analyses were carried out by describing the rock exposed in the field, analyzing the aquifers responsible for groundwater flow, water media, and the type of flows around the doline. These hydrogeological characteristics largely determine the pattern of subsurface water flow through the type of rock porosity. In comparison, hydrochemical analysis determines the chemical facies of water through the Stiff diagram. The diagram of the relationship between chemical ions and TDS through the Gibbs diagram is significantly helpful in interpreting the hydrochemical process of water.

RESULTS AND DISCUSSION

Hydrogeological characteristics of the doline area

Lithology

Karst regions have a specific hydrogeological character [6] because the constituent rocks, such as limestone and dolomite, are highly susceptible to chemical dissolution [16]. The limestones that make up the study area are dominated by reef limestones consisting of boundstone and packstone and layered limestone in the form of wackestone [1]. Wackestone exhibits a matrix-supported texture, with grains generally < 1 mm. The grain types are mostly calcite and foraminifera fossils that have undergone a lot of dissolution, leaving many pores. Dissolution occurs from the grain and matrix parts. Packstone exhibits a grain-supported texture with moderate sorting. Granules are generally < 1.5 mm in size, composed predominantly of foraminifera, mollusks, and algae. The apparent porosity is vuggy and interparticle type. The apparent porosity is of the moldic and vuggy type.

Reef limestones supported the karst hydrogeological system in the study area as the karst landscape's dominant constituent. Occasionally, layered limestone or tuffaceous sandstone are found to be relatively thin.

Aquifer

Non-karst aquifers form aquifer systems with the diffuse flow and karst aquifers with conduit flow. The potential aquifer in the Gunungsewu area is the limestone of the Wonosari Formation. In addition, there are also non-karst, perched aquifers in a karst limestone-free aquifer system [1]. Karst aquifers have cavity porosity with conduit flow, while non-karst aquifers are supported by intergranular porosity and diffuse flow.

Limestone aquifers are generally free aquifers bounded by an impermeable layer of Tertiary bedrock. This aquifer is highly developed due to the support of secondary permeability in cavities with small to large dimensions, such as underground caves.

Water media

Reef and layered limestones are good water media in karst. These rocks have experienced quite intensive tectonics activity, as evidenced by the many cracks and fractures. In addition to the joint structure, geological structures in the form of faults may be present in the study area.

The existence of geological structures in the form of faults, fractures, or cracks causes the development of secondary porosity, namely crack porosity, in addition to intergrain porosity. The dissolution also increases the porosity of limestones to form cavities that sometimes have relatively large dimensions, thus allowing the underground caves and rivers to occur.

Cavity porosity triggers the conduit groundwater flow. The cavities formed from the dissolving of easily soluble limestone can even form karst caves. This limestone dissolution is strongly supported by rainfall levels and is influenced by climate change.

Flow type

Shallow, free aquifers support the hydrogeological system in the study area. Groundwater flow is dominated by the conduit system and can be a source of doline water support (**Table 2**). Diffusion flow can occur in soil or weathered rock near the surface to very shallow depths.

Doline's condition over the season

The physical properties of doline water generally show clear to turbid, tasteless, and odorless conditions in both dry and rainy seasons. On the other hand, the seasons affect physical changes, especially cloudiness and color, which is uncertain. Doline turbid water can be brownish white or greenish to brown (Table 3).

Dolines with small dimensions include Gandu (D5), Sambi (D7), Klepu (D32), Pengos (D23), Sumuran (D37; **Fig. 2a**), Sade (D43), and Belik (D44) dolines. These small dolines have a length of only a few meters in diameter, not more than 50 m. Dolines with large dimensions include Dendengwelut (D6), Towet (D21), Suci (D27), Winong (D28; **Fig. 2b**), Boromo (D29), Namberan (D30), and Gadel (D35). These large dolines reach a length or diameter of > 100 m.

Seasonal differences affect the volume of groundwater discharge [17]. It also applies to the amount of dolines water. In the dry season, the dolines water is generally much less, and there are even some dry dolines, for example, Gandu (D5), Jombor (D8), Miriledok (D4), Suci (D27), Pengos (D33), and Sumuran (D37) dolines. However, several dolines still showed a fairly large volume of water, including Towet (D21), Jambeanom (D26), Boromo (D29), Namberan (D30), Monggol (D31), and Omang (D42) dolines. According to information from residents, Towet doline never dries up, even though there is a long dry season.

In the rainy season, many dolines have abundant water. It means that the water on the doline is strongly supported by rainfall. However, some doline was found in almost dry (little water) to dry conditions. Dolines that are almost dry in the rainy season include Gandrung (D18) and Wuni (D39) dolines. Dolines that dry in the rainy season include (D14), Pengos (D33), Depok (D36), Sade (D43), and Belik (D44) dolines.

Groundwater recharge may vary linearly with monthly rainfall [18], as well as doline conditions. In the rainy season, precipitation can be the main water source in the dolines. Seasonal changes will usually affect the quantity of dolines water. Dry or less water occurs due to significant fluctuations in doline water. If the doline comes into contact with groundwater, the groundwater table is probably below the bottom of the dolines.

Hydrochemistry of doline water

To fulfill the needs of drinking water, water quality needs to be evaluated. The hydrochemistry of water and groundwater determines water quality in an area. Various studies have successfully evaluated water quality, including solutions to improve water quality with RO devices to reduce dissolved organic carbon [19].

Surface water and groundwater contain different salts with different concentrations, depending on the sources and the number of soluble constituents present in the geological formations through which the waters passes [20, 21]. Therefore, the hydrochemical characteristics can be studied to determine the genetics of water.

The hydrochemical facies of water doline during the dry season is dominated by Ca,Na-bicarbonate facies, while in the rainy season, it generally shows the Ca-bicarbonate facies. From the Stiff diagram, it can be seen that, in general, the major ions content of doline during the rainy season tends to decrease in concentration (**Fig. 3**). It means that rainfall results in a dilution of the major ions concentration. Although the enrichment of HCO3 accompanies the increase in EC during the rainy season^{-} and Ca^{2+} ions, rainfall significantly affected the decrease in the concentration of these major ions. Karst groundwater in the tropics in Cenozoic rocks usually has low EC variability [22], as does karst in this study area.

Information on precipitation can be seen in **Fig. 4**. The figure shows no precipitation in the study area at the time of the first water sampling (September 2019), and the highest was in March 2020, when the second sampling was carried out. It means that there is a large difference in rainfall in the two sampling periods. There was no rain from August to October 2019, while in the rainy season, the lowest rainfall was 131 mm/month in November 2019, and the highest was 422 mm/month in March 2020 [23]. The doline water facies tend to be of the Ca- bicarbonate type in the rainy season, accompanied by lower EC values than in the dry season. The high Ca content in the rainy season indicates that the dissolution of limestone is getting more intensive.

The hydrochemistry of doline water is affected by rock dissolution, which can be accelerated by the presence of weathered rock. The data plot on the Gibbs diagram (**Fig. 5**) shows that the influence of rock factors dominates the doline waters in the study area. This means that the hydrochemistry of water doline is determined mainly by the rock composition and controlled by the supply of elements derived from the dissolution of rock minerals.

Seasonal variations of water doline hydrochemistry can be seen in the different facies. The doline may be strongly supported by rainfall in the rainy season but should be another water source in the dry season. If there is a contribution from the groundwater, the conduit-type flow dominates the groundwater. The contribution of groundwater is very likely to occur, as evidenced by the presence of dolines that remain wet during the long dry season.

Hydrogeological system in doline and surrounding areas

The character of the groundwater recharge system in the Gunungkidul area, apart from originating from the local area, can also be supplied from other surrounding areas. Stable isotopes data from previous researchers supported an understanding of the hydrogeological system in this area. Based on the characteristics of stable isotopes, it is known that groundwater in this area is associated with intermediate and regional recharge systems [3].

Most of the groundwater in underground springs and rivers in the karst region comes from groundwater saturated with $CaCO_3$ with diffusion flow systems in the epikarst zone. The diffusion flow then develops into groundwater flow with a conduits (cavities) system. Flow diffusion usually occurs in porous or dense jointed media [24].

Groundwater in the study area is connected with the regional recharge system from the non-karst hills in the north and the local recharge system from the Gunungsewu karst area [3]. Groundwater flows in underground rivers and can appear as karst springs. In addition, groundwater can also appear on the surface mixed with rainwater and contribute to the surrounding doline.

Then, groundwater hydrochemistry is important to provide information about its aquifer and the water in the surrounding area. Groundwater in the karst hydrogeological systems can contribute to doline water. Doline, which is dry in the long dry season, indicates a lack of groundwater supply to the doline, which can occur due to groundwater table fluctuation, which causes the groundwater table to fall below the doline depth.

Based on the Gibbs diagram analysis, the significant variation in the dry season compared to the rainy season indicates a significant dissolution effect and the dominant hydrochemical process. The considerable variation in the dry season by ignoring local rains significantly affects groundwater, especially in some doline which still has large water volumes (Towet, Namberan, Monggol, Omang dolines). A large water supply from groundwater may come from a regional flow system or non-karst hills [3]. This is also supported by a graphical analysis of Ca^{2+}/Na^{+} *vs* HCO_3^{-}/Na^{+} or Mg^{2+}/Na^{+} [25], which shows silicate weathering as a hydrochemical process in the study area (**Fig. 6**).

Fig. 6 shows that minerals weathering is more dominant in the dry season. In contrast, in the rainy season, there is a lot of weathering of carbonate minerals and the dissolution of carbonates. This graph does not appear to be fully appropriate, considering that the research area is located in a karst hydrogeological subsystem. However, from the chart, it can be interpreted that in the dry season, there is weathered clay material dissolved in water dolines. The clay material may be supported by water-rock interactions from non-karst hills carried by regional groundwater flows, consistent with the previous findings [3].

The hydrochemical variation of doline water during the dry season is supported by wide variations in the content of Ca^{2+} and HCO_3^{-}. It shows that rock dissolution can vary from place to place, usually triggered by the amount of water in the water-rock interaction process. In addition, the duration of the flow process and the distance traveled can also provide variations in the ion content. It means the groundwater supplying doline water may vary as a local, intermediate or regional system which also accounts for differences in the duration and distance traveled by the draining process.

In the dry season, groundwater plays a vital role in determining the hydrochemistry of doline water.

Then in the rainy season, doline water is strongly influenced by rainfall. Weathering and mineral dissolution are the main processes during the dry or rainy season. The evaporation and enrichment of water chemical elements were also observed to occur more frequently during the dry season. Hydrochemistry is strongly influenced by rainfall during the rainy season and provides a dilution effect. Meanwhile, the anthropogenic processes have not become dominant in both the rainy and dry seasons.

The difference in the main ion content in the dolines water in the two seasons can also be caused by land use or anthropogenic aspects [15], although the intensity is small [26]. It can be triggered by surface runoff [27, 28] or fertilizer contamination from cultivated farms [13, 29].

In summary, the hydrogeological system in the study area involving the doline water facies can be seen in **Fig. 7**. This figure shows that doline water can come from local rain or be supported by groundwater flow in local, medium, or regional systems through conduit-type flows. However, it is possible that dolines only depend on rainwater and are not connected to groundwater. Dolines like this are usually dry in the dry season.

CONCLUSIONS

Hydrochemical studies in the Gunungsewu karst area have been done on the Panggang and Wonosari-Baron subsystems to determine the relationship between dolines water and groundwater. The hydrogeological system of the study area determines the hydrochemistry of doline water. The geological structure is in the form of fairly dense joints so that it helps the flow process as a porous aquifer media, supported by dissolving limestone. Seasonal changes cause water doline to fluctuate, where some dolines may dry up, especially during the dry season.

The dissolution process of limestone minerals primarily determines the hydrochemistry of doline waters. The Gibbs diagram shows that rock dissolution plays a significant role in deciding the hydrochemistry of doline water. In addition, the relationship between ions shows the dominant influence of silicate weathering, which is interpreted to originate from distant silicate rocks through regional groundwater flows. Another aspect affecting hydrochemical changes in dolines water, even if small, is land use or anthropogenic activities.

Groundwater flow systems that supply doline water may be local and regional. Dolines waters are supported by conduit-type groundwater flow. The contribution of regional groundwater flows is supported by water doline hydrochemistry, supported by differences in water facies in different seasons. Moreover, rainfall as a source of local groundwater and doline water recharge can also affect the hydrochemistry of doline water.

The contribution of groundwater to doline water indicates that some dolines have water dependent on groundwater flow. It should be understood that doline in some places has a relationship with leaks in other areas, even at quite a distance.

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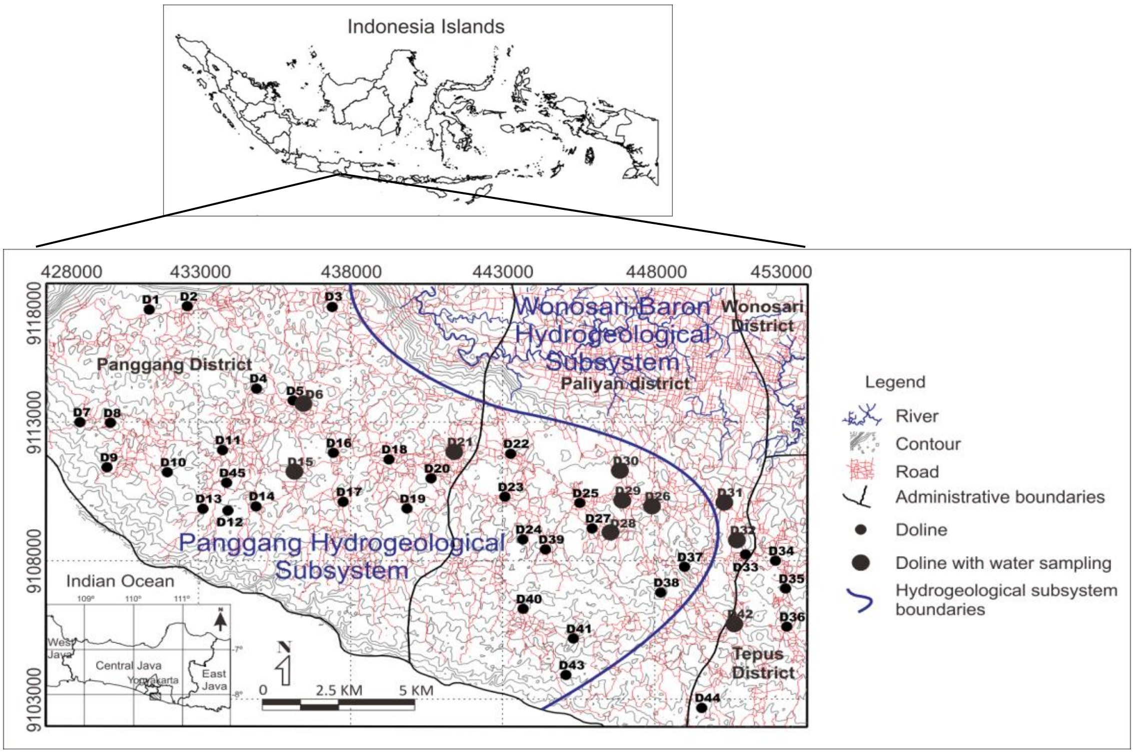


Fig. 1 Map of the location of dolines in the study area.

Table 1 The laboratory data of doline water chemical properties.

Parameter	D6	D15	D21	D26	D28	D29	D30	D31	D32	D42
(mg/L)	Dry Season									
HCO_3^-	146.4	250.1	122	189.1	350.4	274,5	140.3	140.3	267.1	91.5
Cl^-	7.0	6	8.5	32	42	37	17.5	6	12.5	10.5
SO_4^{2-}	6	8	2	9	8	8	8	2	16	4
Ca^{2+}	27.86	54.35	26,33	38.31	68.66	50.47	27.16	27.53	41.18	11.14
K^+	6	4	6	8	13	9	6	4	27	7
Na^+	8	25	25	59	93	82	49	25	59	31
Mg^{2+}	8.22	5.8	2.89	1.93	1.45	2.42	4.35	1.45	9.15	1.45
SiO_2	14.94	14.054	10.496	13.41	13.258	12.846	10.364	9.624	11.001	4.244
	Rainy Season									
HCO_3^-	68.3	47.5	59.4	59.4	97.9	77.2	68.3	68.3	74.2	80.1
Cl^-	0.6	0.6	0.6	0.6	6.5	0.6	0.6	0.6	2	0.6
SO_4^{2-}	16	20	10	10	9	10	10	10	6	8
Ca^{2+}	17.6	11.2	12.8	16.72	20.7	15.92	19.1	14.33	16.72	19.9
K^+	4	2	3	4	5	3	3	3	4	4
Na^+	10	3	7	10	23	7	7	10	13	10
Mg^{2+}	2.43	3.4	4.37	2.42	1.45	1.93	1.93	1.45	1.45	0.48
SiO_2	6.562	6.163	5.025	7.624	6.574	2.756	6.208	7.008	4.451	3.058

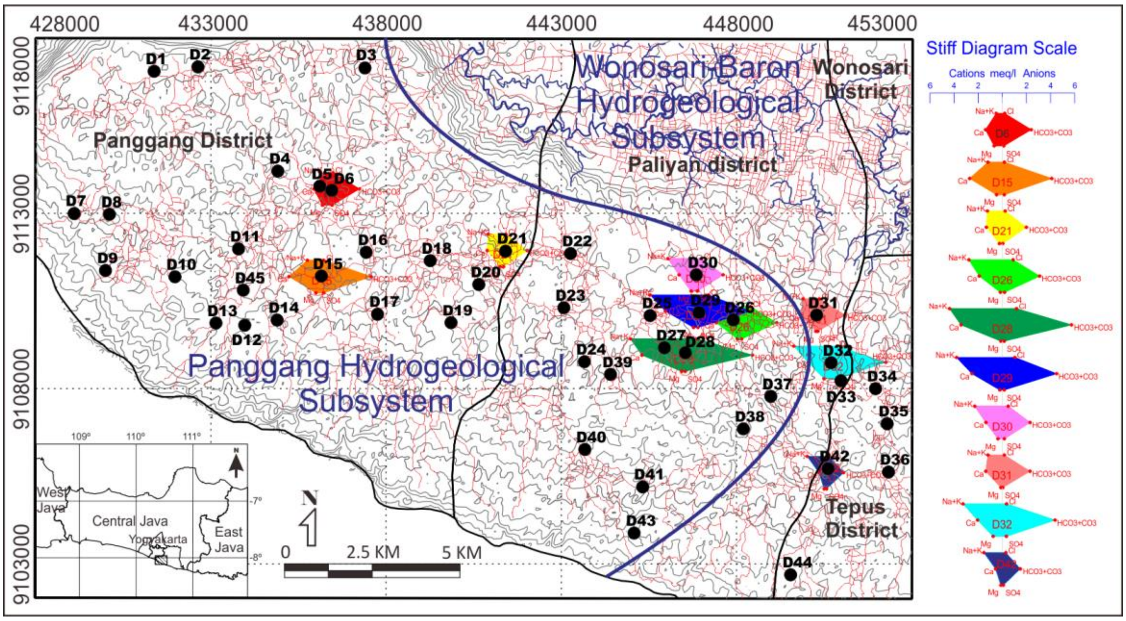
Table 2 Hydrogeological characteristics of the study area.

Parameter	Groundwater	Doline Water
Lithology	Reef & bedded limestone of Wonosari Formation	Reef & bedded limestone of Wonosari Formation
Characteristics	Shallow aquifer	Associated with shallow aquifer
Water media	Densely fracture - porous; cave & underground river	Surface water bodies
Flow type	Conduit system	Local rainfall, diffuse flow in soil, supported by conduit groundwater flow

Table 3 The physical/chemical properties of water dolines.

Doline	D6	D15	D21	D26	D28	D29	D30	D31	D32	D42
Parameter	DRY SEASON									
T (ºC)	30.2	26.3	31.8	33.2	31.8	30.1	31.2	31.7	29.8	32.4
pH	8.8	7.4	8	10.1	9.5	9.1	9.6	9	9	9.8
TDS (mg/L)	104	241	103	180	299	260	133	83	160	82
EC (µS/cm)	248	418	204	304	374	322	296	136	156	151
Turbidity (NTU)	19	16.1	2.2	89	143.5	243.5	136.5	1.3	122.5	37.8
Color (TCU)	46	8	24	88	94	148	94	19	83	23
	RAINY SEASON									
T (ºC)	31.8	34	31.6	33	30.8	29.8	30	27.7	27.6	32
pH	8.9	8	9.2	9.4	9.4	9.1	8.4	8.4	8.1	9.1
TDS (mg/L)	59	46	53	53	76	53	48	52	55	45
EC (µS/cm)	148	70	116	100	174	122	132	110	104	116
Turbidity (NTU)	35.6	37.6	15.7	41.7	19	28.8	29.8	14.2	13.5	19.3
Color (TCU)	106	200	28	64	33	40	40	22	15	7

Fig. 2 (a) Sumuran (D37) doline is an example of small dimension doline. (b) Winong (D28) doline represents the large doline.



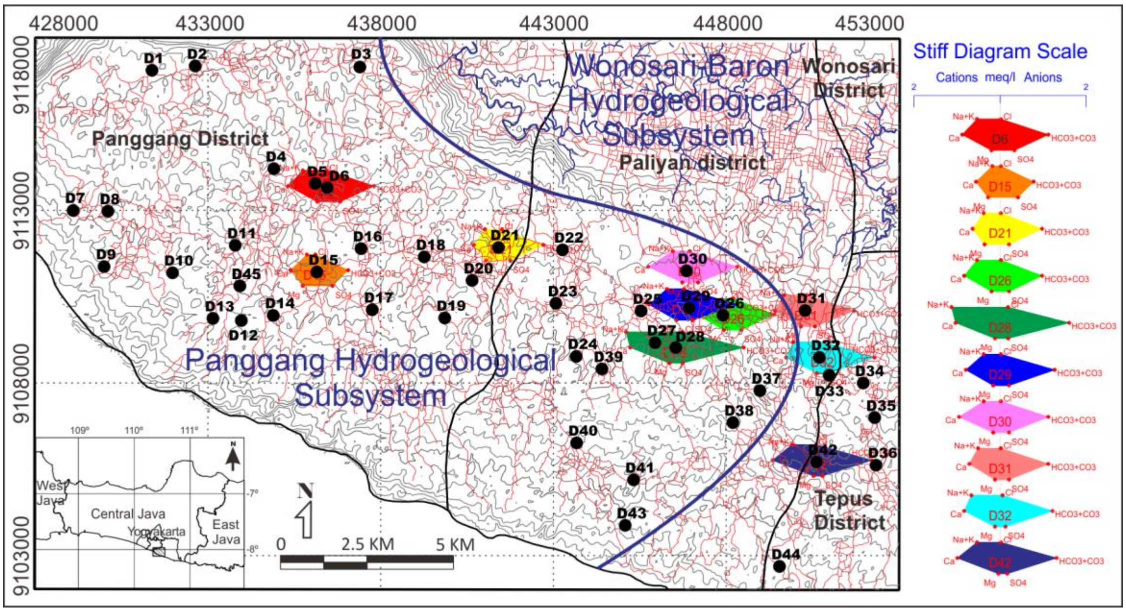


Fig. 3 Stiff diagrams of water samples in dry season (top) and rainy season (bottom).

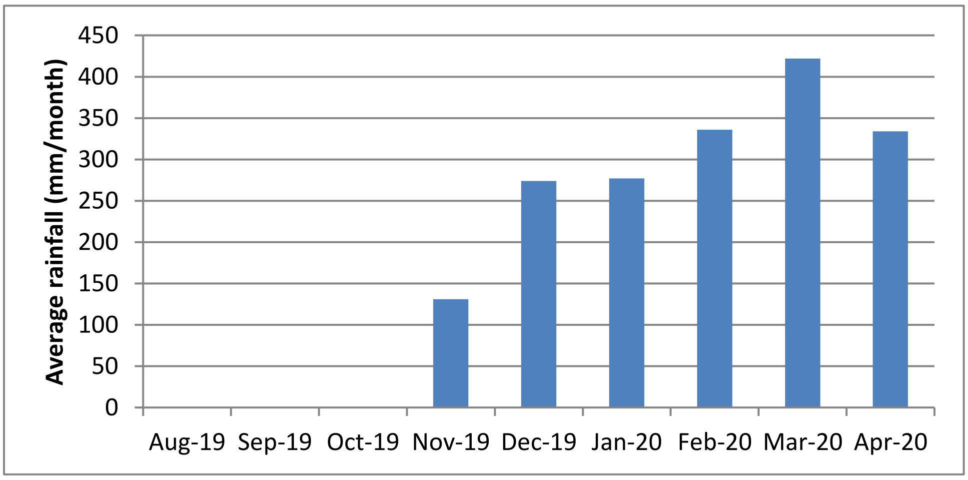


Fig. 4 Average rainfall in study area [23].

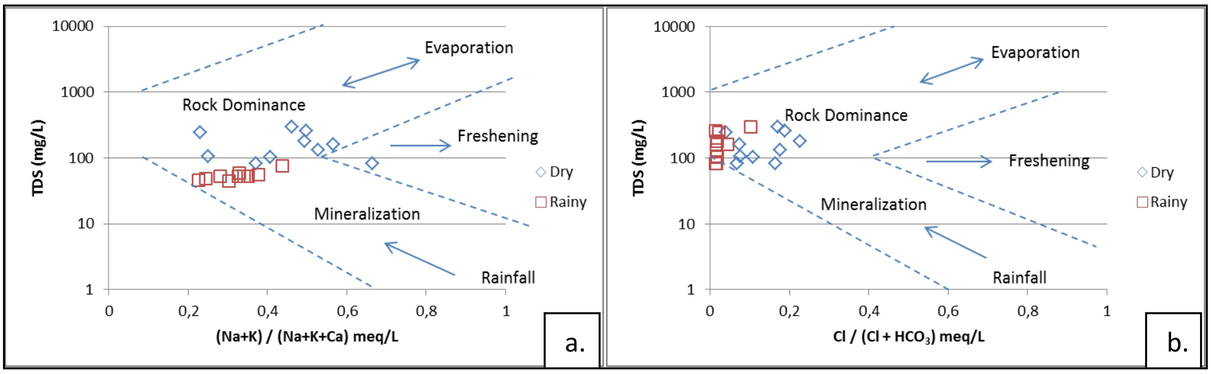


Fig. 5 Plot of water doline hydrochemical data on the Gibbs Diagrams, shows the relationship between alkaline ions *vs* TDS (a) and major ion *vs* TDS (b).

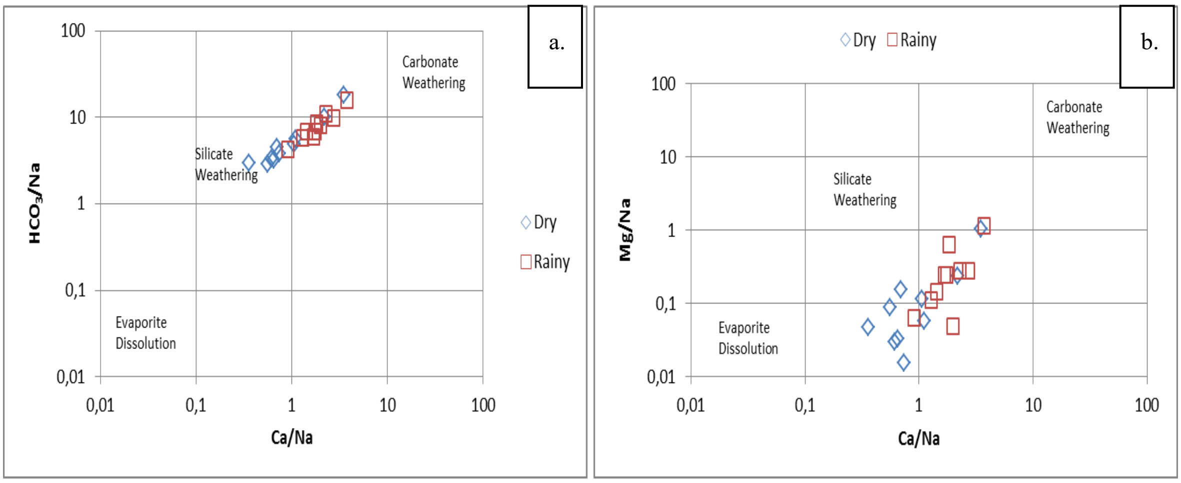


Fig. 6 Relationship of several hydrochemical parameters [25] in study area show (a) Na normalized HCO_3^- *vs* Ca^{2+} plots and (b) Na normalized Mg^{2+} *vs* Ca^{2+} plots.

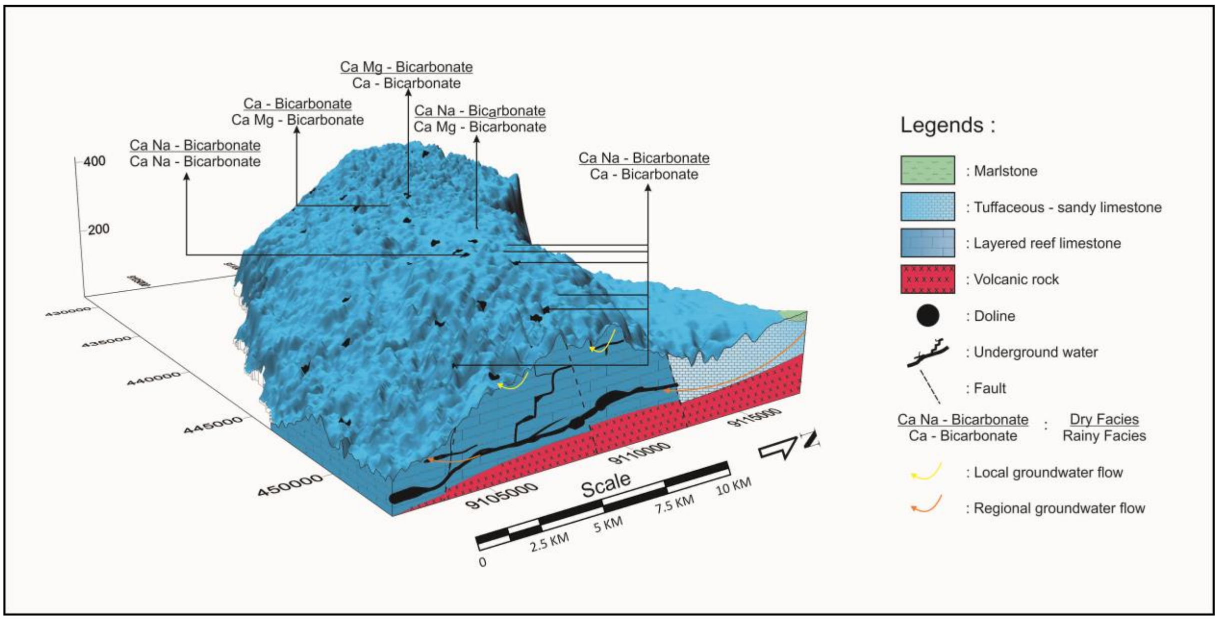


Fig. 7 Schematic diagram of the 3D hydrogeological system of the doline in the study area (modification from [1]).

Author Response to JWET on May 30, 2022

Groundwater Contributing to Doline Hydrochemistry in Panggang and Wonosari - Baron Hydrogeological Subsystems, Indonesia

Authors: T. Listyani R.A.[1]* and Ridayati[2]

The authors have summarized their replies to the Reviewers' comments in this response letter. A revised manuscript is submitted addressing all the comments to the Journal of Water and Environment Technology for possible publication.

<table>
<tr><td>No</td><td>Reviewer Comments</td><td>Author Response</td></tr>
<tr><td>Reviewer-1</td><td>The manuscript submitted after the revision can be almost accepted for publication. However, please make sure you correct all the grammer during proofreading.</td><td rowspan="2">I have checked the grammar of our manuscript in two steps:
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<tr><td>Reviewer-2</td><td>I have verified that the comments have been properly corrected. However, I strongly recommend that the "native English check"</td></tr>
</table>

The authors appreciate the valuable comments from the Reviewer.

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Listiani RA <lis@itny.ac.id>

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Kepada: lis@itny.ac.id, ridayati@gmail.com

30-May-2022

Dear Dr Listyani R.A.:

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Thank you for your fine contribution. On behalf of the Editors of the Journal of Water and Environment Technology, we look forward to your continued contributions to the Journal.

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August 16, 2022

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On behalf of the editorial board of "Journal of Water and Environment Technology (JWET)", we appreciate your cooperation for publishing the new issue Vol.20, No.5 (2022. 10).

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