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 in the field and laboratory, both in physical (color, taste, odor, turbidity) and chemical (pH, EC, and ionic content) properties of water. The hydrochemical analysis was performed using Stiff and Gibbs diagrams. Generally, in the dry season, water doline has Ca and Na-bicarbonate facies, while it tends to change to Ca-bicarbonate facies in the rainy season. The water-rock interaction process and precipitation 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

The research has been done in 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 also interesting to be learned to understand water's genetics. Hydrochemical studies of the Gunungsewu karst area have been developed by several experts [1-4].

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

Doline is a limestone basin with a diameter ranging from a few meters to a kilometer and a depth ranging from a few meters to a kilometer. Some dolines are grassy hollows, while others are stony basins bordered by cliffs [7]. The doline is the most fundamental characteristic of close depression in karst. According to its genesis, it can be further split into several forms: solution (the true karst doline), collapse, dropout, buried, caprock, and suffosion doline [8]. The 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, showing temporal and spatial variations [2]. A study on karst spring has also been carried out [9]. The results show that water can dissolve carbonate rocks usually influences the current karstification process rate. The spatial/temporal analysis of the karst subsurface river shows that karst water's hydrochemical, especially in total dissolved solids (TDS) and pH, were affected by precipitation during flow processes [10]. On the other hand, the quality and origin of groundwater, including its transport mechanism, can support the conservation of existing water resources, such as springs, wells, and river water [11], and protect the fresh groundwater [12]. The hydrochemistry in karst doline water has not been studied specifically, so this paper wants to complement the karst research, especially Gunungsewu. The origin of doline water in the research area also needs to be examined to see the groundwater flow contribution based on doline water's hydrochemistry.

This paper intends to discuss the hydrochemistry of doline water in the Gunungsewu karst region. It may be expected to complement the karst hydrogeological system's knowledge in the area. This study aimed to determine the hydrogeological system concerning the water doline phenomenon. By hydrochemical analysis, this study aims to reveal the genetics of surface water present in doline,

whether the water only comes from rainwater or is there a contribution from groundwater that supplies doline water. The dolines are essential to learn to know the groundwater contribution to them, whether local or regional.

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MATERIALS AND METHODS

Study area

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

Regional hydrogeology of Gunungsewu

The research area is part of the Southern Mountains physiographic zone of Central - East Java [13]. This zone consists of three sub-zones: 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 west-east relatively.

The bedrock configuration of Gunungsewu karst varies with heights/lower ridges/basins, and subsurface valleys, which has led to differences in groundwater direction flow, thus forming a hydrodynamic zone separation in this area. Based on these hydrodynamics, the 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 pamely Panggang and Wonosari-Baron. In the Panggang area, there is an elongated ridge of bedrock 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. The underground river and the karst springs may be interconnected. Tracing groundwater flows in springs and underground rivers in the Purwosari area indicates a single conduit tunnel significantly developed in the area [14].

Field data of doline

Field data were collected on several dolines, including geological and hydrogeological data. Geological data were 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 pH-meter, TDS-meter, and Hanna brand EC-meter. Field data was taken for two seasons, at the end of the dry season in September - October 2019 and the middle of the rainy season in March 2020.

45 dolines were recorded in the study area, both large and small dimensions. The doline is generally round in shape, and some dolines are slightly elongated/oval. Ten selected dolines with a large enough volume of water were chosen for hydrochemical testing in the laboratory.

Laboratory data

The selected doline water samples were then tested in the laboratory to determine their physical and chemical properties. The parameters tested include color, turbidity, pH, EC, and the content of ions/chemical compounds. The ionic/chemical compounds included HCO₃⁻, Cl⁻, SO₄², Ca²⁺, K⁺, Na⁺, Mg²⁺ cations, and SiO₂ (**Table 1**). Then, the laboratory data were used for hydrochemical analysis by representing Stiff and Gibbs diagrams [15]. Ion chromatography was used to determine the Ca²⁺, Na⁺, Mg²⁺, and K⁺ ions. A spectrophotometer was used to examine the SO₄²⁻ ions. Titration was used to quantify Cl⁻ and HCO₃⁻ ions. Some standards, particularly SNI (2004-2009) and APHA (2012) have testing methods. Groundwater facies are determined based on the values of dominant anions and cations, 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 aquifer responsible for groundwater flow, water media, and the type of flow that develops around doline. These hydrogeological characteristics largely determine the pattern of subsurface water flow through the type of rock porosity.

Meanwhile, hydrochemical analysis determined water's chemical facies through the Stiff diagram, the relationship diagram between ions and TDS through the Gibbs diagram. The diagram of the relationship between the significant chemical ions helped interpret the water's hydrochemical process.

RESULTS AND DISCUSSION

Hydrogeological characteristics of doline area

Lithology

Karst regions have a specific hydrogeological character [6] because the constituent rocks, like limestone and dolomite, are highly susceptible to chemical dissolution [16]. The limestones that composed the study area are dominated by reef limestones consisting of boundstone and packstone and layered limestone in the form of wackestone [1].

Wackestone shows a matrix-supported texture, with grains generally < 1 mm. The grain types are mostly calcite and fossil foraminifera that have undergone much dissolution, leaving many pores. The apparent porosity is of the moldic and vuggy type. Dissolution occurs from part of the grain and

matrix. Packstone shows a grain-supported texture with moderate sorting. The granules are generally < 1.5 mm in size, composed predominantly of foraminifera, mollusks, algae. The apparent porosity is of the vuggy and interparticle type.

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

Aquifer

Non-karst aquifers form the aquifer system with the diffuse flow and karst aquifers with conduit flow. The potential aquifer in the Gunungsewu area is the limestone of the Wonosari Formation. Besides, there are also non-karst, perched aquifer in the 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 rock bedrock. This aquifer is highly developed because of secondary permeability support in cavities with small to large dimensions as underground caves.

Water media

Reef and layered limestones are good water media in karst. In general, these rocks have undergone quite intensive tectonics, as evidenced by many cracks and fractures. Besides the joint structure, a geological structure in the form of a fault may be present in the study area.

Existence geological structures in the form of faults, fractures, or cracks cause the development of secondary porosity, namely crack porosity, in addition to intergrain porosity. The dissolution also increases the porosity of the limestone to form cavities that are sometimes of relatively large dimensions, allowing the occurrence of underground caves and rivers.

The porosity of the cavity triggers the conduit flow of groundwater. The cavities formed by dissolving limestone are easily dissolved and can even form karst caves. This limestone dissolution is strongly supported by rainfall and is affected by climate change.

Flow type

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

Doline condition over the season

The physical properties of doline water generally show clear to turbid, tasteless, and odorless conditions in either the dry or rainy season. Turbid water doline can be brownish white or greenish to brown. Climate changes can also affect the quality of dolines water, including the color and turbidity (**Table 3**). Unfortunately, the influence of seasons on physical changes, especially cloudiness and color, is uncertain.

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 or only a few meters in diameter, not more than 50 m. The doline with large dimensions include Dendengwelut (D6), Towet (D21), Suci (D27), Winong (D28; **Fig. 2b**), Boromo (D29), Namberan (D30) and Gadel (D35). These large dolines were reached a length or diameter of > 100 m.

Seasonal differences affected the discharge volume of groundwater [17]. It also applies to the quantity of dolines water. In the dry season, the water of dolines is generally much less, and there are even some dry doline, for example Gandu (D5), Jombor (D8) Miriledok (D4), Suci (D27), Pengos (D33), and Sumuran (D37) dolines. However, some dolines still show 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, the Towet doline never dries up, even though there is a long dry season.

In the rainy season, many dolines have abundant water. It means 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 during 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.

The recharge of groundwater may vary linearly with monthly rainfall [18], as well as doline conditions. In the rainy season, precipitation can be the primary water source on 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 is in contact with the groundwater, the groundwater table is probably below the bottom of the dolines.

Hydrochemistry of doline water

Hydrochemical of water and groundwater determine the quality of water in an area. To fulfill drinking water, water quality needs to be evaluated. Various authors have successfully evaluated the water quality, including the 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 their sources and the number of soluble constituents present in the geological formations through which these waters pass [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 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 the dilution at the major ions concentration. Although the increase in EC during the rainy season is accompanied by enrichment of HCO₃⁻ and Ca²⁺ ions, rainfall significantly affects the decrease in the concentration of these major ions. Karst groundwater in the tropics in Cenozoic rocks usually has a low variability of EC [22], as does karst in the study area.

The information about precipitation can be seen in [23] **Fig. 4**. The figure shows no rainfall in the research area during the first water sampling (September 2019). The second period of water sampling was done in March (2020), the month with high rainfall. The figure also shows the highest rainfall, which reached 422 mm/month in March 2020. It means that there was a strong difference in rainfall in the two sampling periods. Therefore, the facies of dolines water tend to be Ca-bicarbonate and reduce its EC value. Its condition triggers the dilution process in the rainy season, then reduces Na-dominance in the hydrochemistry of water.

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

The seasonal variations of water doline hydrochemistry can be seen in the difference of its facies. The doline may be strongly supported by rainfall in the rainy season, but it should be other sources of water in the dry season. If there is a contribution from the groundwater, then the groundwater is dominated by a conduit-type flow. The existence of a groundwater contribution is very likely to occur, as evidenced by the presence of doline, which remains 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 areas around it. The stable isotopes data from the previous researcher supported understanding the hydrogeological system in this area. Based on the characteristics of stable isotopes, it is known that the groundwater in the area is associated with

recharge systems that are intermediate and regional [3].

Most of the groundwater in underground springs and rivers in the karst region comes from groundwater saturated with CaCO₃ with diffusion flow systems in the epikarst zone. The diffusion flow then develops into a groundwater flow with a conduit (cavity) system. Flow diffusion usually occurs in porous or dense jointed media [24].

Groundwater in the study area shows a connection with the regional recharge system from non-karst hills in the north and the local recharge system from Gunungsewu karst area [3]. The 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, the hydrochemical of groundwater is important to give information about its aquifer and the water in the surrounding area. Groundwater in the karst hydrogeological system may contribute to doline water. Doline, which is dry in the long dry season, shows a lack of groundwater supply to doline, which can occur due to groundwater fluctuation, which causes the groundwater level to fall below the depth of doline.

The significant variation in the dry season compared to the rainy season indicates a significant dissolution effect, also the dominant hydrochemical process. It has been proven based on the analysis of the Gibbs diagram.

The considerable variation in the dry season, ignoring local rains, shows a significant influence on groundwater, especially in some doline which still has large water volumes (Towet, Namberan, Monggol, Omang dolines). A lot of water supply from groundwater may come from a regional flow system or from non-karst hills [3]. It is also supported by the analysis of Ca²⁺/Na⁺ vs HCO₃⁻/Na⁺ or Mg²⁺/Na⁺ charts [25] that indicate silicate weathering as a hydrochemical process in the study area (**Fig. 6**).

Fig. 6 shows that weathering of minerals is more dominant in the dry season. In contrast, in the rainy season, weathering of carbonate minerals begins to occur a lot, in addition to carbonate dissolution. This graph seems not entirely appropriate, considering that the research area is in the karst hydrogeological subsystem. However, it can be interpreted from the graph that during the dry season, there is weathered clay material dissolved in water doline. 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 a wide variation in the Ca²⁺ and HCO₃⁻ content. It shows that rock dissolution can vary from place to place, which is

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 ion content. It means, the groundwater that supplies doline water can vary as a local, intermediate or regional system which also marks the difference in duration and distance traveled by the draining process.

During the dry season, groundwater plays an important role in determining the hydrochemistry of doline water. Then in the rainy season, doline water is greatly influenced by rainfall. In general, weathering and mineral dissolution are the main processes during the dry or rainy season. The process of evaporation and enrichment of chemical water elements was also observed to occur more frequently during the dry season. The hydrochemical is greatly influenced by rainfall during the rainy season and gives a dilution effect. Meanwhile, the anthropogenic process has not become dominant in both the rainy and dry seasons.

The difference in the main ion content in dolines water in the two seasons may 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 agriculture [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 doline only depends on rainwater and is not connected to groundwater. Doline like this is usually dry in the dry season. However, in dry doline, which is usually supported by groundwater, it can also occur when the groundwater level falls below the bottom of the doline.

CONCLUSIONS

Hydrochemical study in the Gunungsewu karst area has been done at the Panggang and Wonosari-Baron subsystems to determine the relation between dolines water and groundwater. Seasonal changes cause water doline fluctuation, where some of the dolines may be dry, especially during the dry season. The hydrogeological system of the study area determines the hydrochemistry of doline water. The geological structure is fairly dense joints that help the flow process as a porous aquifer medium, supported by limestone dissolution.

The dissolution process of limestone minerals primarily determines the hydrochemistry of doline waters. The Gibbs diagram shows that rock dissolution 5 ays a significant role in determining the hydrochemistry of doline water. In addition, the relationship between ions shows the dominant influence of silicate weathering, which is interpreted to originate from silicate rocks that are far away through regional groundwater flows. Other aspects that may affect the hydrochemical changes in dolines water are land use or anthropogenic, although small.

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

The contribution of groundwater to doline water indicates that some dolines have water that depends on groundwater flow. It should be understood that doline in some places has links with leaks in other places, even in places quite far away.

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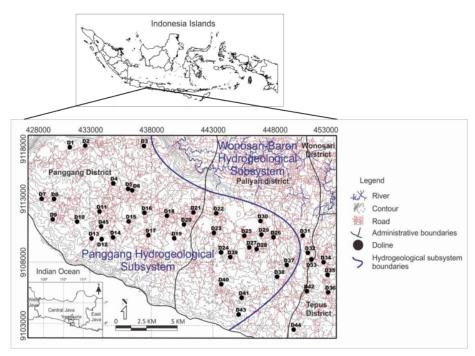


Fig. 1 Map of the location of dolines in the study area.

Table 1 Field and laboratory data of doline water chemical properties.

Para- meter*	Dry Season									Rainy Season										
	D6	D15	D21	5 1220	D28	D29	D30	D31	D32	D42	D6	D15	D21	5 1926	D28	D29	D30	D31	D32	D42
pH	8.8	7.4	8	10.1	9.5	9.1	9.6	9	9	9.8	8.9	8	9.2	9,4	9.4	9.1	8.4	8.4	8.1	9.1
EC	248	418	204	304	374	322	296	136	156	151	148	70	116	100	174	122	132	110	104	116
HCO3	146.4	250.1	122	189.1	350.4	274,5	140.3	140.3	267.1	91.5	68.3	47.5	59.4	59.4	97.9	77.2	68.3	68.3	74.2	80.1
Cl	7.0	6	8.5	32	42	37	17.5	6	12.5	10.5	0.6	0.6	0.6	0.6	6.5	0.6	0.6	0.6	2	0.6
SO ₄ ²	6	8	2	9	8	8	8	2	16	4	16	20	10	10	9	10	10	10	6	8
Ca ²⁺	27.86	54.35	26,33	38.31	68.66	50.47	27.16	27.53	41.18	11.14	17.6	11.2	12.8	16.72	20.7	15.92	19.1	14.33	16.72	19.9
K*	6	4	6	8	13	9	6	4	27	7	4	2	3	4	5	3	3	3	4	4
Na [*]	8	25	25	59	93	82	49	25	59	31	10	3	7	10	23	7	7	10	13	10
Mg ²⁺	8.22	5.8	2.89	1.93	1.45	2.42	4.35	1.45	9.15	1.45	2.43	3.4	4.37	2.42	1.45	1.93	1.93	1.45	1.45	0.48
Si O ₂	14.94	14.054	10.496	13.41	13.258	12.846	10.364	9.624	11.001	4.244	6.562	6.163	5.025	7.624	6.574	2.756	6.208	7.008	4.451	3.058

^{*}All parameters in mg/L unit except pH

Table 2 Hydrogeological characteristics of the study area.

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

Table 3 The physical properties of water dolines.

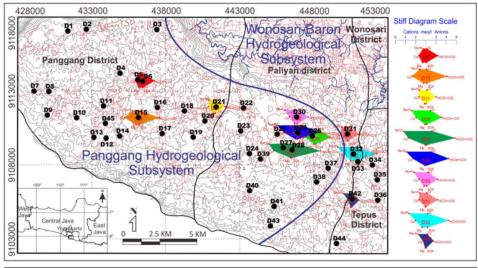
Doline	D6	D15	D21	D26	D28	D29	D30	D31	D32	D42		
Parameter		DRY SEASON										
T(°C)	30.2	26.3	31.8	33.2	31.8	30.1	31.2	31.7	29.8	32.4		
рH	8.8	7.4	8	10.1	9.5	9.1	9.6	9	9	9.8		
TDS (mg/L)	104	241	103	180	299	260	133	83	160	82		
EC (µS/cm)	248	418	204	304	374	322	296	136	156	151		
Turbidity (NTU)	19	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 (°C)	31.8	34	31.6	33	30.8	29.8	30	27.7	27.6	32		
рH	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		





 $\textbf{Fig. 2} \ (\text{a}) \ \text{Sumuran (D37) doline is an example of small dimension doline}.$

(b) Winong (D28) doline represents the large doline.



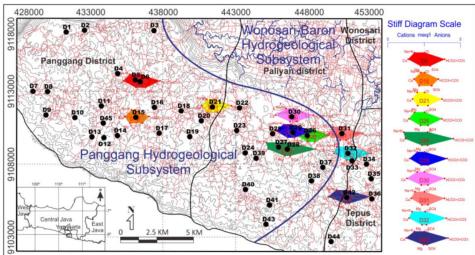


Fig. 3 Stiff diagrams of water samples in dry season (top) and rainy season (bottom).

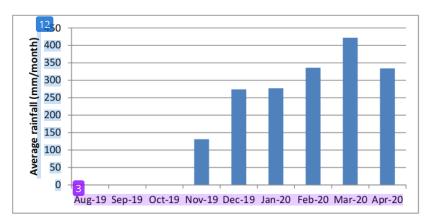


Fig. 4 Average rainfall in study area [23].

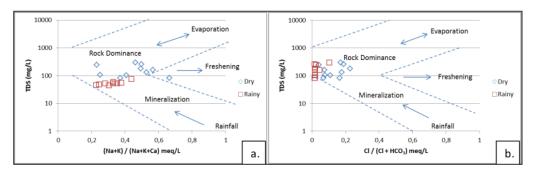


Fig. 5 Plot of water doline hydrochemical data on the Gibbs Diagrams, shows the relationship between alkaline ions *vs* TDS (a) and major ion *vs* TDS (b).

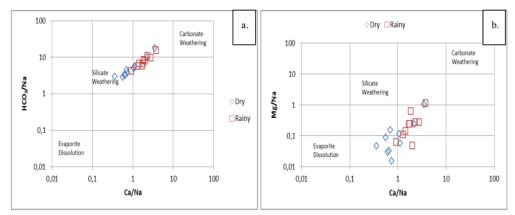


Fig. 6 Relationship of several hydrochemical parameters [25] in study area show (a) Na normalized $HCO_3^- vs Ca^{2+}$ plots and (b) Na normalized $Mg^{2+} vs Ca^{2+}$ plots.

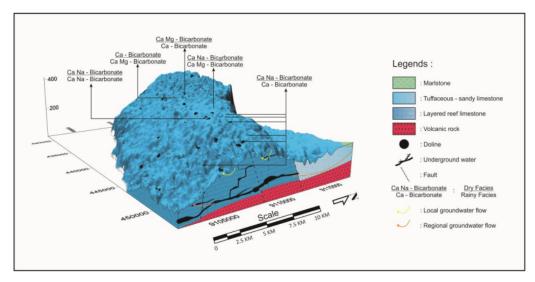


Fig. 7 Schematic diagram of the 3D hydrogeological system of the doline in the study area (modification from [1]).

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