

The Origin Groundwater of Rawadanau in Serang Banten, Indonesia

Priyo Hartanto^{1,2}, Rachmat Fajar Lubis², Boy Yoseph CSS Syah Alam¹, and Hendarmawan¹

¹Faculty of Geological Engineering, Universitas Padjadjaran, Jatinangor, Sumedang 45363, Indonesia

²Research Center for Geotechnology, Indonesian Institute of Sciences, Jln. Sangkuriang, Bandung 40135, Indonesia

Correspondence to: Priyo Hartanto (priyo.hartanto@lipi.go.id ; priyo17001@mail.unpad.ac.id)

Abstract

Rawadanau, located in Serang, Banten, is the main water supply for the Cilegon industrial area, West Coast of Java, Indonesia, has geothermal potential. Understanding groundwater origin and quality is an essential factor in determining appropriate actions to save water supply sources. This paper aims to answer the groundwater origin that fills the Rawadanau, whose rocks are composed of volcanic products with evidence of the main elements of water chemistry and stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$). Analysis of pH, temperature, EC, HCO_3^- is carried out in the field, while other chemical elements and stable isotopes are analyzed in the laboratory. Groundwater found consists of hot springs, cold springs, dug wells, river water. Hierarchical analysis clusters based on water chemistry and stable isotopes can be grouped into two, cluster K (K1 and K2) and clusters L, respectively. Data of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the spring waters in the Rawadanau indicate that they are of meteoric origin, and there has been evaporation from several springs. Water comes from meteoric water with stable isotopes content of $\delta^{18}\text{O}$ between -6.39 to -4.82 ‰ and $\delta^2\text{H}$ between - 41.35 to -31.30 ‰, which has been controlled by two main mechanisms, namely rock dominance, and evaporation dominance. Aquifers are composed of product volcanic with the dominant composition rock of porphyritic andesite, basaltic andesite, and andesite. The multivariate statistical analysis results besides pH and SO_4 , all parameters (cation and anions) showed significant correlation. There are four groundwater facies, namely Ca-HCO_3 , Ca-Mg-HCO_3 , Mg-Ca-HCO_3 , and Na-Cl .

KEYWORDS

Rawadanau, Indonesia, origin, stable isotope, hydrochemical, spring

1 INTRODUCTION

The study of Rawadanau groundwater is needed to understand its origin in hydrochemical and isotope characteristics to explain groundwater supply actual conditions in the study area. Groundwater is the most important freshwater resource at Rawadanau and provides almost all of the

water needs at the industrial area Cilegon the present time. Rawadanau Sub-Basin has an area of 375 km² (KEMEN-ESDM, 2017), is the primary source and supplier of water fulfillment for the Cilegon industrial area. Rawadanau also has geothermal potential with several hot springs locations being found. More than 100 companies in the industrial area of Cilegon depend on the Rawadanau water reserves, which are collected by damming the Cidanau River (Hartanto, Delinom, & Hendarmawan, 2019). Existing water comes from rainwater, river water, springs flowing through several river branches before entering the Cidanau River.

Stable isotopes can be used tracers in the groundwater environment to understand water origin in a hydrologic cycle (Taniguchi, Nakayama, Tase, & Shimada, 2000). Stable isotopes do not decay over geologic time. The stable isotopes of oxygen and hydrogen in water are ¹⁶O, ¹⁷O, ¹⁸O, and ¹H and ²H, respectively, whose values are expressed in δ (Tweed et al., 2019). Isotopes provide vital records that occur in thermal and nonthermal groundwater so they can play an essential role in hydrogeological investigations (Oyuntsetseg, Ganchimeg, Minjigmaa, Ueda, & Kusakabe, 2015). Hydrochemical and isotopes can be an effective method to solve various hydrology and hydrogeology problems (Clark & Fritz, 2013; Liu et al., 2015). The origin, evolution, and formation of hot springs can be explained using hydrochemical and trace stable isotopes.

This study to determine to answer groundwater origin as a supply of Rawadanau using new evidence covering the main elements of water chemistry and stable tracer isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) from springs, dug wells, and surface water. Then the data is processed with statistics for grouping and classification of sources and some frequently used models.

2 GENERAL SETTING

Rawadanau is located on the west side of Java Island at a morphology between 100 to 1350 meters above sea level (asl) (Figure 1), located in Serang province of Banten Indonesia. The research area is located at coordinates between 06° 07' 10" - 06° 19' 10" South Latitude and 105° 51' 30" - 106° 03' 00" East Longitude. The Cidanau River is the main river research area and flows to the Sunda Strait. Based on meteorological data between 1996 to 2014, the average annual rainfall is 2806 mm (Hartanto et al., 2019). Rainy days occur throughout the month, where above ten days/month occurs between November to May, the intensity of monthly rainfall is above 200 mm, except from May to October. Minimum rainy days, occurring less than five days/month occur in August and September (Figure 2), with average monthly rainfall intensity of 61.2 mm/month and 56.6 mm/month, respectively. The average dry peak occurs from August to September (intensity 50 mm/month), while the peak rainy season from December to February with are intensity above 300 mm/month (Figure 3), respectively. The southern side of the research area is Mount Parakasak (990 meters asl), Mount Karang (1739 meters asl), Mount Asepun (1081 meters asl), the north side is Mount Gede (741 meters asl), and the east side is Mount Kupak (361 meters asl).

Rawadanau covers approximately 375 km², with the constituent rocks being the product of Mount Garung and Karang-Pulosari Volcano and alluvium (Alam, Itoi, Taguchi, & Yamashiro, 2014; Mulyadi, 1985; Suryadarma & Fauzi, 1991). Two fault systems control Rawadanau, namely Garung and Wangun system. Both of them have the same straight line pattern, namely NW-SE with rocks consisting of porphyritic andesite, basaltic andesite, and andesite formed since the Pleistocene era (Suryadarma & Fauzi, 1991). The discovery of hot springs containing solfatara around Rawadanau, which are the slopes of Mount Karang-Pulosari and Mount Garung, shows the remnants of volcanic activity and geothermal manifestations (Mulyadi, 1985).

Lithostratigraphy study area is comprised of Rawadanau deposits (Qr) consisting of gravel, clay sand, mud, and pumice crust. Colluvium sediment (Qk) form of ruins, talus, and dumping of volcanic ruins. Coral volcanic rocks (Qvk), composed of volcanic breccia, lava, tuff, and lava, are inseparable. Young volcanic rock deposits (Qhv) are composed of volcanic breccia, lava, tuff, lava flows, and other volcanic eruptions (Mount Asepun, Mount Parakasak). Upper Banten tuff (Qvtb) consists of tuff, pumice tuff, sandy tuff (at the top) and crystal tuff, rocky pumice tuff, glass tuff, and clay tuff insert at the bottom. Young Lake Volcanic Rock Deposits (Qvd) is composed of lava flows composed of andesite or basalt flapping, volcanic breccia, and tuff. Lower Banten tuff (Qptb), composed of breccias, agglomerates, pumice tuffs, lapilli tuffs, and sandy tuffs. Old Lake Volcanic Rocks (Qpd) form of lava flow composed of andesite or raised basalt, volcanic breccia, and tuff.

Based on hydrogeology, the study area aquifers are divided into cleft flow aquifers and inter-grain spaces, aquifers through fractures, fractures, channels, cavities, and small productive aquifers and rare groundwater areas. Discharged areas include active, productive aquifers (discharge more than 5 liters/second), medium productive aquifers (discharge less than 5 liters/second), and rare groundwater (Suryaman, 1999).

3 MATERIALS AND METHODS

3.1 Water sampling and analysis

Water sampling was carried out at the peak of the dry season in September 2019. A set of 28 samples were taken, consisting of dug wells, cold spring, rivers, and hot springs. The 28 sample locations include seven rivers, five wells, and 16 springs. Several water parameters are measured directly (in situ measure) using the Water Checker Toac portable devices, including pH, temperature, electrical conductivity (EC), and salinity. All samples were put in 500 ml polyethylene bottles for major ion (anions and cations), analyzed at the Water Laboratory of Research Center for Geotechnology Indonesian Institute of Sciences based on APHA 2005. Titrations analysis (Ca^{2+} , Mg^{2+} , HCO_3^- , and Cl^-), flame photometry (Na^+ and K^+), and spectrophotometry (for analysis of SO_4^{2-} , and SiO_2). HCO_3^- analysis carried out directly on the same day after collection, titrated using / with 0.01 or 0.1 M HCl against methyl orange and Bromocresol green indicators (APHA, 2005). The results analysis of the physical and chemical are presented in Table 1. Minimum raw elements are analyzed as

information to be used as drinking water (Appelo & Postma, 2005). The accuracy of the chemical analysis of water is verified by calculating the charge balance error (CBE) where the error is generally less than about 5% (Freeze & Cherry, 1979) with the equation:

$$\%CBE = \frac{\sum Z_{mc} - \sum Z_{ma}}{\sum Z_{mc} + \sum Z_{ma}} \times 100 \quad (1)$$

Where $\sum Z_{mc}$ is total cations in equivalent, $\sum Z_{ma}$ is total anions in equivalent.

For isotope analysis (^2H and ^{18}O), the sample was put in a 100 ml polyethylene bottle analyzed at the Hydrochemical Laboratory of the Center for Groundwater and Environmental Geology, the Geological Agency of Indonesia using the Picarro L-2130-i analyzer. The results of the stable isotope analysis (^2H and ^{18}O) are presented in Table 2. For isotope analysis (^2H and ^{18}O), the sample was put in a 100 ml polyethylene bottle analyzed at the Hydrochemical Laboratory of the Center for Groundwater and Environmental Geology, the Geological Agency of Indonesia using the Picarro L-2130-i analyzer. The results of the stable isotope analysis ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are presented in Table 2.

The TDS value is considered an essential value in determining water use and describing inorganic salts' presence and correlates with EC (Logeshkumaran, Magesh, Godson, & Chandrasekar, 2015; Rusydi, 2018). In this study, the TDS value is not measured directly, because this parameter is correlated with EC, usually expressed by a simple equation (Clark & Fritz, 2013; Rusydi, 2018):

$$\text{TDS (mg/L)} = 0.65 * \text{EC (}\mu\text{S/cm)} \quad (2)$$

The interpretation of water types based on major ions is plotted in two basic triangles as the percentage of cations and milliequivalent anions of water chemistry using the Piper Diagram (Piper, 1944). Simultaneously, to understand the processes that occur in groundwater using the Gibbs Diagram (Chintalapudi, Pujari, Khadse, Sanam, & Labhasetwar, 2016; Gibbs, 1970; Marandi & Shand, 2018). To process statistical data used SPSS V26.

3.2 Statistical analysis

Perform statistical analysis, and the first step is to perform clustering based on the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$. From clustering, it is obtained as in Figure 4. Some of the chemical properties of water are related to one another (Marsal, 1987). From the clustering results, the descriptive statistics and the correlation of each element are analyzed. The statistical analysis of all physical and chemical parameters, including minimum, maximum, mean, standard deviation, and coefficient of variance are presented in Table 3.

The main water elements can be easily determined using a box plot (Boateng, Opoku, Acquah, & Akoto, 2016; Srinivasamoorthy, Gopinath, Chidambaram, Vasanthavigar, & Sarma, 2014; Tizro & Voudouris, 2008). The large concentration range of elemental content against standard deviation shows that the chemical composition of groundwater has been influenced by processes including

water-rock interactions and anthropogenic influences (Boateng et al., 2016; Srinivasamoorthy et al., 2014). Increase of main water element concentration illustrated in box-plot and whisker images (Figure 5). The box-plot shows the upper and lower quartiles; the maximum and minimum values are shown as lines. The abundance of the main elements of anions in water is $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$ and the cations is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, respectively.

4 RESULTS

4.1 Hydrochemical characteristics

The hydrochemical analysis results, univariate of each cluster, are shown in Table 1 and Table 4. The primary ions, value a charge balance error in water, is still at the allowable level between -4.96 up to -2.21, while the mean error as -4.05.

The groundwater pH study area generally ranged from 5.7 to 7.7. Sub-cluster K1 had an average pH of 6.5, Sub-cluster K2 had an average pH of 6.7, and Cluster L had an average pH of 6.9, respectively. Water temperature ranges from 23.5 to 51.8 °C (mean 32.1 °C), sub-cluster K1 average temperature of 34.0 °C, sub-cluster K2 averages 33.2 °C and cluster L averages 28.3 °C, respectively. Hot springs found in sub-clusters K2 and K1. The study area's water salinity ranged from 0.0 to 0.2% (mean 0.04%), and the R-value ranged from 2.6 to 216.0 ohm-m (mean 52.9 ohm-m). At Batukuwung spring (around location 29S), the water temperature reached 65 °C (Hochstein & Sudarman, 2008). More than 37.8 °C can classify as hot springs (Alfaro & Wallace, 1994). Even if the water temperature is more than the average surface temperature in general or more than 36.7, it can be said to be hot springs (Pentecost, Jones, & Renaut, 2003).

The electrical conductivity (EC) Sub-cluster K1 ranges from 75 to 2410 $\mu\text{S}/\text{cm}$ (mean 845.8 $\mu\text{S}/\text{cm}$), Sub-cluster K2 from 46 to 2850 $\mu\text{S}/\text{cm}$ (mean 834.4 $\mu\text{S}/\text{cm}$), Cluster L is between 73 and 612 $\mu\text{S}/\text{cm}$ (mean EC 73 $\mu\text{S} / \text{cm}$), respectively. Indicates groundwater has low salinity properties. An increase TDS value followed by an increase EC value is caused by the dissolving process that occurs when it flows due to evaporation, ion exchange resulting in an increasing concentration (Delinom, 2009; Liu et al., 2015; Tóth, 1999). Sub-cluster K1 and sub-cluster K2, respectively, the mean EC values of 845.5 $\mu\text{S}/\text{cm}$ and 834.4 $\mu\text{S}/\text{cm}$, respectively, indicate that the existing groundwater contains many rock dissolved minerals.

TDS value is considered an important value in determining water use. Total dissolved solids concentration (TDS) ranged from 46.0 to 1852.5 mg/L, TDS sub-cluster K1 ranged from 75.4 to 1566.5 mg/L (mean 549.8 mg/L), sub-cluster K2 ranged from 29.9 to 1852.5 mg/L (mean 542.4 mg/L) and cluster L between 47.5 and 397.8 mg/L (mean 187.6 mg/L), respectively.

Abundance of the main element cation (Figure 5 and Table 4) $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, respectively. In general, content of the sequential cations is Ca^{2+} (between 8.0 and 116.8 mg/L) $> \text{Na}^+$ (1.1 to 212.3 mg/L) $> \text{Mg}^{2+}$ (2.5 to 86.7 mg/L) $> \text{K}^+$ (0.6 to 102.4 mg/L), respectively. The Ca content of the K1 sub-cluster ranged from 16.4 to 102.8 mg/L (mean 42.5 mg/L), the K2 sub-cluster ranged

from 8.0 to 116.8 mg/L (mean 36.8 mg/L) and cluster L ranged from 11.4 to 62.2 mg/L (mean 30.3 mg/L). The high Ca^{2+} content is caused by enrichment due to the dissolution of Ca-plagioclase minerals (Alam et al., 2014; Appelo & Postma, 2005).

The content of Mg^{2+} sub-cluster K1 ranged from 4.6 to 86.7 mg/L (mean 27.9 mg/L), sub-cluster K2 ranged from 2.5 to 78.6 mg/L (mean 22.1 mg/L) and cluster L ranged from 3.7 to 46.8 mg/L (mean 11.6 mg/L), respectively. Rocks composed of Tufa caused high Mg^{2+} content (Appelo & Postma, 2005). The groundwater has passed through aquifers composed of tuffs and andesitic rocks.

The Na^+ content of the K1 sub-cluster ranged from 2.1 to 86.7 mg/L (mean 28.9 mg/L), the K2 sub-cluster ranged from 1.1 to 212.2 mg/L (mean 43.7 mg/L) and cluster L ranged from 1.7 to 38.7 mg/L (mean 13.3 mg/L), respectively. Some locations where very high Na^+ content (31S and 33S) is thought to be formation water.

The K^+ content K1 sub-cluster ranged from 2.9 to 56.6 mg/L (mean 18.5 mg/L), the K2 sub-cluster ranged from 1.1 to 102.4 mg/L (mean 21.2 mg/L) and the L cluster ranged from 0.6 to 18.1 mg/L (mean 5.0 mg/L), respectively. The presence of K^+ in water is result from dissolving igneous rock minerals (Appelo & Postma, 2005).

The abundance of the main elements of anions in water (Figure 5 and Table 4) is $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$, respectively. HCO_3^- (between 34.3 and 624.7 mg/L) $> \text{Cl}^-$ (between 6.9 and 771.0 mg/L) $> \text{SO}_4^{2-}$ (between 2.1 and 14.90 mg/L) $> \text{CO}_3^{2-}$ (between 0.0 and 58.9 mg/L), respectively. The HCO_3^- content - sub-cluster K1 ranged from 68.5 to 624.7 mg/L (mean 255.5 mg/L), sub-cluster K2 ranged from 34.3 to 373.3 mg/L (mean 137.1 mg/L) and cluster L ranged from 47.4 to 543.0 mg/L (mean 160.8 mg/L), respectively. The presence of carbonates and bicarbonates as dissolution of the remaining carbonate minerals commonly contained in igneous rocks (Appelo & Postma, 2005).

Carbonate (CO_3^{2-}) was generally only detected at K2 sub-cluster between 0.0 and 58.9 mg/L (mean 16.0 mg/L), and K1 sub-cluster, only one saw (26S) with a value of 7.8 mg/L and one L cluster (28R) of 4.2 mg/L.

The chloride content of the K1 sub-cluster was 8.3 to 298.0 mg/L (mean 84.4 mg/L), the K2 sub-cluster was between 6.9 to 771.0 mg/L (mean 134.2 mg/L), and the L between cluster 8.3 to 38.6 mg/L (mean 24.3 mg/L), respectively. Likewise, the high Na^+ content, followed by the high Cl^- content in several locations, is probably sourced from formation water flowing at hot springs (13S, 31S, and 33S).

The sulfates (SO_4^{2-}) content of the K1 sub-cluster ranged from 2.2 to 3.6 mg/L (mean 2.5 mg/L), the K2 sub-cluster ranged from 2.1 to 14.2 mg/L (mean 5.4 mg/L) and the L cluster ranged from 2.3 to 14.9 mg/L (mean 5.9 mg/L), respectively. The low SO_4^{2-} content proves that the study area's water source has not been contaminated by anthropogenic factors or mineral dissolution, rich in sulfates. Low-sulfate groundwater is pristine freshwater (Appelo & Postma, 2005).

During September, at peak dry season, silica (SiO_2) in groundwater varies from 34.24 mg/L to 157.07 mg/L. SiO_2 content was found in all clusters, SiO_2 sub-cluster K1 between 52.6 to 128.4 mg/L

L (mean 103.0 mg/L), K2 sub-cluster between 37.6 to 157.1 mg/L (mean 88.9 mg/L), and cluster L between 34.2 to 85.6 mg/L (mean 54.1 mg/L), respectively. The presence of silica indicates the dissolution of rock constituent minerals, which are usually closely related to geothermal (Giggenbach, 1981).

The results plotted on a piper diagram yield two dominant water types: Ca-Mg- HCO_3 -Cl, Ca-Mg- HCO_3 . And 2 locations (31S and 33S) were showing the Na-Cl type (Figure 6). Calcium-magnesium bicarbonate facies reflects the geology and climate of the study area. Besides, the research area is composed of volcanic rock products, so the groundwater interacts with mineral compounds in the aquifer between the groundwater and the rocks it passes through (Alam et al., 2014). Ion exchange occurs between $\text{Na}^+ + \text{K}^+$ ions in water and soil Ca^{2+} and Mg^{2+} during the water's residence time in the rock. Several locations show a high Cl content, indicating that the water has undergone some transport and produced relatively high Cl^- (Freeze & Cherry, 1979).

4.2 Correlation analysis

Several chemical properties of water are related to each other (Marsal, 1987). Pearson's correlation coefficient is used to measure and find the strength of any linear relationship between two numerical variables. The results of the correlation matrix between 17 chemical water parameters are calculated and presented in Table 5. Pearson's correlation coefficient values range between +1 and -1, where values close to 0.00 do not indicate a linear relationship (Tabachnick & Fidell, 2013). An r value of +1.00 or -1.00 indicates one of the perfect predictability when the other is known. Based on Pearson's correlation, the positive correlation is significant and high ($r > 0.7$).

As in Table 5, a positive, robust, and consistent correlation is shown by temperature, EC, and salinity with almost all variables from the correlation test result. In addition, a powerful correlation was shown by sodium with potassium, calcium, magnesium and chloride ($r = 0.80 - 0.98$), between potassium and calcium, magnesium, chloride ($r = 0.82 - 0.94$), between calcium and magnesium, bicarbonate, chloride ($r = 0.81 - 0.94$), between magnesium and bicarbonate ($r = 0.86$), respectively. The powerful and positive correlation between Ca^{2+} , Mg^{2+} , and Na^+ is probably a manifestation of the ion exchange process that has taken place during the dissolution of silicate minerals (Adams, Titus, Pietersen, Tredoux, & Harris, 2001; Yunhui Zhang et al., 2018). Strong correlation between sodium and carbonate ($r = 0.69$), potassium with carbonate ($r = 0.60$), magnesium with chloride ($r = 0.78$), carbonate with chloride ($r = 0.62$). The content of silica (SiO_2) has a strong correlation with major ions ($r = 0.60 - 0.79$), this indicates that the dissolution of the minerals that make up the rock produces silica minerals, which are usually closely related to geothermal (Giggenbach, 1981). The correlation between SiO_2 and temperature can be seen in Figure 7.

Figure 7 shows a robust correlation between temperature (T) and silica (SiO_2); an increase in temperature will also offset the more effective SiO_2 content. This SiO_2 can be used as a reliable geothermometer guide in geothermal investigations (Yuqi Zhang et al., 2019). The graph shows that

the springs have a temperature between 41.3 to 51.8 °C (S7, S11, S12, S13, S29, S31, S33) with SiO₂ concentrations ranging from 119.4 to 157.1 mg/L. The increase in concentration mainly comes from dissolving rocks containing SiO₂ during groundwater circulation in the rock.

4.3 Water stable isotopes

A graph representing the relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ regarding the global meteoric water line is presented in Figure 8. From that graph show that the K1 sub-cluster and K2 sub-cluster are distributed adjacent to the global meteoric water line (GMWL) as described by Craig (1961). The local water meteoric line in the study area refers to Jakarta's closest model (Lubis et al., 2008); the equation used is $y = 8x + 10$. Cluster L under GMWL shows that it has been heavily influenced by evaporation so that enrichment occurs. Cluster L is heavier than sub-clusters K1 and K2, and this indicates that the groundwater from sub-cluster K1 and sub-cluster K2 has interacted a lot with rocks on its way.

Cluster analysis is based on the dependence of several water quality parameters. This study was carried out with an approach based on the stable isotope content ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in water (Figure 4). Consider the use of stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) because they are both durable and do not decay over a geological period (Clark & Fritz, 2013; Liu et al., 2015; Tweed et al., 2019). The dendrogram graph based on the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Figure 4) shows two groups, namely K, consisting of 20 samples and L composed of 8 samples. Cluster K includes sub-cluster K1; there are 9 locations (6S, 7S, 8S, 10S, 11S, 12S, 13S, 20S, and 26S). The lightest isotope content of Sub-Cluster K1, maximum $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (-6.1 ‰ and -39.6 ‰), minimum (-6.4 ‰ and -41.3 ‰), mean (-6.3 ‰ and -40.5 ‰), respectively. The sample from the springs tends to be lighter so that the isotope content is depleted.

The K2 sub-cluster contains 11 samples 2R, 27S, 17W, 22S, 29S, 24R, 25S, 19R, 31S, 23S and 33S. The isotope content of Sub-Cluster K2 is generally heavier than Sub-cluster K1; the sample consists of springs, dug wells, and rivers. The full contents were $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (-5.6 ‰ and -36.5 ‰), minimum (-6.1 ‰ and -39.2 ‰), with a mean (-5.9 ‰ and -38.2 ‰), respectively.

There are 8 locations: cluster L, including sub-cluster L1 (7 samples) and sub-cluster L-2 (1 sample), the water sources are dominated by dug wells and rivers. Cluster L includes eight samples, consisting of wells and rivers covering 16W, 21R, 3W, 4W, 5W, 15R, 28R, and 1R. The full contents were $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (-4.8 ‰ and -31.3 ‰), minimum (-5.5 ‰ and -35.1 ‰), with a mean (-5.1 ‰ and -33.6 ‰), respectively.

5 DISCUSSION

5.1 Groundwater geochemical characteristics

The hydrochemical analysis result showed that groundwater pH generally ranged from 5.7 to 7.7; the water temperature was between 23.5 to 51.8 °C. A water temperature of more than 36.7 °C indicates

hot springs (Pentecost et al., 2003). There is a water temperature of up to 51.8 °C, which is more than 36.7 °C, and silica (SiO₂) is found as an indication of geothermal (Pentecost et al., 2003; Yuqi Zhang et al., 2019); the process that takes place shows the dissolution of the minerals that make up the rock and produces silica minerals (Giggenbach, 1981). The hot springs (13S, 31S, and 33S) contain high levels of Na⁺ and Cl⁻, possibly from formation water that comes out as springs or as seawater trapped in aquifers (Villegas, Paredes, Betancur, Taupin, & Toro, 2018).

Hydrochemistry is influenced by the interaction between water and the medium in which it passes, in this case, rock, changes in water's chemical characteristics depending on the type of rock and the water composition. Water is predominantly bicarbonate (HCO₃⁼), and the main cation is Ca²⁺ dominant from the main anion content. Overall, the piper diagram (Figure 6) of water types are generally Ca-HCO₃ and Mg-HCO₃. Water facies like this show that groundwater is still relatively pristine, such as rainwater. The rocks that make up the research area are volcanic products, groundwater in the course of mineral compounds in the aquifer between the groundwater and the rocks it passes through (Alam et al., 2014). According to the piper diagram (Figure 6), the SO₄ content is relatively small, not more than 14.9 mg/L, proving that groundwater is freshwater that is still original (Appelo & Postma, 2005) because high SO₄ is related to the use of pesticides or fertilizers (Villegas et al., 2018).

5.2 Groundwater isotope characteristics

The local meteoric water line in the study area refers to the nearest meteoric, namely GMWL Jakarta (Lubis, Sakura, & Delinom, 2008), the equation used is $y = 8x + 10$. Plotting the relationship between δ²H and δ¹⁸O (Figure 8) has at least two patterns: a) coincide with the GMWL, which is occupied by the K-1 and K-2 Sub-clusters; b) the pattern that tends to move away from the GMWL is occupied by the L sub-cluster. The K-1 and K2 sub-clusters almost coincide with the GMWL, indicating that the groundwater is affected by local climate and local topography (Lee, Wenner, & Lee, 1999).

Dendrogram graph analysis based on the stable isotopes ¹⁸O and ²H (Figure 4) produces two groups: K of 20 sites, and L of 8 sites. Sub-Cluster K1 of cold-springs (6S, 8S, 10S, 20S, and 26S) and hot-springs (7S, 11S, 12S, 13S), mean isotope content of δ¹⁸O and δ²H are -6.3 ‰ and - 40.5 ‰, respectively (Table 4). Sub-Cluster K2 isotope content of river water samples (2R, 24R, 19R) well water (17W) cold springs (27S, 22S, 25S, 23S) and hot-springs (29S, 31S, 33S), average isotope content δ¹⁸O and δ²H are -5.9 ‰ and - 38.2 ‰, respectively. Cluster L includes sub-sub-clusters L1 (7 locations) of dug well (3W, 4W, 5W, 16W) and river water (21R, 15R, 28R) and sub-cluster L-2 (1R). The mean content δ¹⁸O and δ²H are -5.1 ‰ and - 33.6 ‰, respectively. Of the 8 locations, there are probably 4 locations, namely that the river water (1R, 15R, 21R, and 28R) is evaporated water.

Although the type of water is relatively the same, dominated by springs, the isotope content of Sub-Cluster K2 is generally heavier than Sub-Cluster K1. K1 sub-cluster more depleted indicates

that these samples are characterized by water with a longer residence time in the aquifer. Furthermore, the same kind of water is from river water; Sub-Cluster K2 contents isotope is lighter than sub-cluster L.

5.3 Groundwater Interactions

Study the mechanism of groundwater evolution, Gibbs (1970) provides a simple solution by making a semi-logarithmic graph of the relationship between TDS versus the ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$. Three mechanisms form the graph: dominance precipitation, dominance rock, and evaporation dominance (Gibbs, 1970; Srinivasamoorthy et al., 2014).

Plotting the data on the Gibbs chart, which compares TDS with the ratio of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ and ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ water, produces two groups, namely evaporation dominance, and rock dominance. Based on the Gibbs graph, which reflects the relationship between TDS and the $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio (Figure 9.a), it is divided into two groups, namely evaporation dominance for sub-cluster K1 (7S, 11S, 12S, 13S) and sub-cluster K2 (17W, 29S, 31S, 33S) and rock dominance for K1 sub-clusters (6S, 8S, 10S, 20S, 26S), K2 sub-clusters (2R, 27S, 22S, 24R, 25S, 19R, 23S) all L clusters (16W, 21R, 3W, 4W, 5W, 15R, 28R, 1R), respectively.

The graph shows the comparison between TDS and the ratio of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ (Figure 9.b), divided into two groups. Evaporation dominance (7S, 11S, 12S, 13S, 17W, 29S, 31S, 33S) samples 31S and 33S lead to saline-water (rich in chloride) and rock dominance for K1 sub-clusters (6S, 8S, 10S, 20S, 26S) and K2 sub-clusters (2R, 27S, 22S, 24R, 25S, 19R, 23S)) as well as all L clusters (16W, 21R, 3W, 4W, 5W, 15R, 28R, 1R), respectively.

The results of plotting data on the Gibb chart through the TDS ratio of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ and the ratio of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ are generally in the area of rock dominance and evaporation dominance (Gibbs, 1970; Marandi & Shand, 2018; Srinivasamoorthy et al., 2014). That indicates that there is an area of evaporation from several springs. Also, samples from river water, wells, and cold springs are heavily influenced by dissolution and weathering of the minerals that make up volcanic rocks from tuff and andesite, generally containing feldspar (Alam et al., 2014; Appelo & Postma, 2005).

6 CONCLUSIONS

The study examines groundwater origin at Rawadanau with a stable isotope approach ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and hydrochemical, which shows good results. There are two sub-clusters from grouping using stable isotopes: the K cluster and the L cluster. The isotope content ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of cluster K is lighter than the L cluster. Stable isotope data ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) show that the groundwater that fills Rawadanau comes from local meteoric, which in their course has experienced evaporation dominance and rock dominance factors, as shown in the Gibbs diagram. The effect of evaporation and interaction with a rock when groundwater flows causes lighter isotopes and various water types.

The type of groundwater in Rawadanau is influenced by mineral dissolution and mineral content from the weathering of volcanic rocks. They were comprising porphyritic andesite, basaltic andesite, and andesite. The chemical compositions are mainly influenced by volcanic dissolution. The enrichment of weathered igneous rock products at peak dry season produces four types of groundwater. River water and cold springs are predominantly Ca- HCO₃ types. At the same time, hot springs have three types of water, including Mg-Ca- HCO₃ -Cl, Ca-Mg- HCO₃, and Na-Cl.

ACKNOWLEDGMENTS

The authors express his appreciation and gratitude to the Deputy for Earth Sciences of the Indonesian Institute of Sciences (LIPI), By-Research Program (LIPI), Group colleagues at Research Center for Geotechnology (LIPI) to support this research and discussion. Also, the academic community of the Faculty of Geological Engineering UNPAD for their invaluable critiques during the writing of this report.

ORCID

Priyo Hartanto <https://orcid.org/0000-0001-7759-6947>

Rachmat Fajar Lubis <https://orcid.org/0000-0002-5430-7169>

REFERENCES

- Adams, S., Titus, R., Pietersen, K., Tredoux, G., & Harris, C. (2001). Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. *Journal of Hydrology*, 241(1–2), 91–103.
- Alam, B. Y. C. S. S. S., Itoi, R., Taguchi, S., & Yamashiro, R. (2014). Spatial Variation in Groundwater Types in the Mt. Karang (West Java, Indonesia) Volcanic Aquifer System Based on Hydro-Chemical and Stable Isotope ([delta] D and [delta]¹⁸ O) Analysis. *Modern Applied Science*, 8(6), 87–102. <https://doi.org/10.5539/mas.v8n6p87>
- Alfaro, C., & Wallace, M. (1994). Origin and classification of springs and historical review with current applications. *Environmental Geology*, 24(2), 112–124. <https://doi.org/10.1007/BF00767884>
- APHA. (2005). Standard Methods for the Examination of Water and Wastewater. APHA. 2005. *Standard Methods for the Examination of Water and Wastewater. 21st Ed. American Public Health Association, Washington DC, 1220p*. <https://doi.org/10.2105/SMWW.2882.216>
- Appelo, C. A. J., & Postma, D. (2005). Geochemistry, groundwater and pollution. 2nd. Ed. *Balkema, Rotterdam*.
- Boateng, T. K., Opoku, F., Acquah, S. O., & Akoto, O. (2016). Groundwater quality assessment using statistical approach and water quality index in Ejisu-Juaben Municipality, Ghana. *Environmental Earth Sciences*, 75(6), 489. <https://doi.org/10.1007/s12665-015-5105-0>
- Chintalapudi, P., Pujari, P., Khadse, G., Sanam, R., & Labhasetwar, P. (2016). Groundwater quality assessment in emerging industrial cluster of alluvial aquifer near Jaipur, India. *Environmental Earth Sciences*, 76(1), 8. <https://doi.org/10.1007/s12665-016-6300-3>
- Clark, I. D., & Fritz, P. (2013). *Environmental Isotopes in Hydrogeology*. Lewis Publishers New York.

- Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, 133(3465), 1702–1703. <https://doi.org/10.1126/science.133.3465.1702>
- Delinom, R. M. (2009). Structural geology controls on groundwater flow: Lembang Fault case study, West Java, Indonesia. *Hydrogeology Journal*, 17(4), 1011–1023. <https://doi.org/10.1007/s10040-009-0453-z>
- Freeze, R. A., & Cherry, J. A. (1979). Groundwater: Englewood Cliffs. *New Jersey*.
- Gibbs, R. J. (1970). Mechanisms controlling world water chemistry. *Science*, 170(3962), 1088–1090. <https://doi.org/10.1126/science.170.3962.1088>
- Giggenbach, W. F. (1981). Geothermal mineral equilibria. *Geochimica et Cosmochimica Acta*, 45(3), 393–410.
- Hartanto, P., Delinom, R. M., & Hendarmawan, H. (2019). Kualitas Air pada Puncak Musim Kemarau di Daerah Rawa Danau Kabupaten Serang. *RISSET Geologi Dan Pertambangan*, 29(1), 13–25. <https://doi.org/10.14203/risetgeotam2019.v29.1021>
- Hochstein, M. P., & Sudarman, S. (2008). History of geothermal exploration in Indonesia from 1970 to 2000. *Geothermics*, 37(3), 220–266.
- KEMEN-ESDM. (2017). *Peraturan Menteri ESDM No. 2 Tahun 2017 tentang Cekungan Airtanah di Indonesia*. Jakarta (In Indonesian): Kementerian Energi dan Sumber Daya Mineral.
- Lee, K.-S., Wenner, D. B., & Lee, I. (1999). Using H-and O-isotopic data for estimating the relative contributions of rainy and dry season precipitation to groundwater: example from Cheju Island, Korea. *Journal of Hydrology*, 222(1–4), 65–74.
- Liu, F., Song, X., Yang, L., Zhang, Y., Han, D., Ma, Y., & Bu, H. (2015). Identifying the origin and geochemical evolution of groundwater using hydrochemistry and stable isotopes in the Subei Lake basin, Ordos energy base, northwestern China. *Hydrology & Earth System Sciences*, 19(1). <https://doi.org/10.5194/hess-19-551-2015>
- Logeshkumaran, A., Magesh, N. S., Godson, P. S., & Chandrasekar, N. (2015). Hydro-geochemistry and application of water quality index (WQI) for groundwater quality assessment, Anna Nagar, part of Chennai City, Tamil Nadu, India. *Applied Water Science*, 5(4), 335–343. <https://doi.org/10.1007/s13201-014-0196-4>
- Lubis, R. F., Sakura, Y., & Delinom, R. (2008). Groundwater recharge and discharge processes in the Jakarta groundwater basin, Indonesia. *Hydrogeology Journal*, 16(5), 927–938.
- Marandi, A., & Shand, P. (2018). Groundwater chemistry and the Gibbs Diagram. *Applied Geochemistry*, 97, 209–212. <https://doi.org/10.1016/j.apgeochem.2018.07.009>
- Marsal, D. (1987). *Statistics for geoscientists (translated from German by D. F. MERRIAM)* (1st ed.). Pergamon Press.
- Mulyadi. (1985). The Geophysical Investigation of Banten Geothermal Area, West Java. *7th NZ Geothermal Workshop*, 201–206.
- Oyuntsetseg, D., Ganchimeg, D., Minjigmaa, A., Ueda, A., & Kusakabe, M. (2015). Isotopic and chemical studies of hot and cold springs in western part of Khangai Mountain region, Mongolia, for geothermal exploration. *Geothermics*, 53, 488–497. <https://doi.org/10.1016/j.geothermics.2014.08.010>
- Pentecost, A., Jones, B., & Renaut, R. W. (2003). What is a hot spring? *Canadian Journal of Earth Sciences*, 40(11), 1443–1446.
- Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water-analyses. *Eos, Transactions American Geophysical Union*, 25(6), 914–928.

<https://doi.org/10.1029/TR025i006p00914>

- Rusydi, A. F. (2018). Correlation between conductivity and total dissolved solid in various type of water: A review. *IOP Conference Series: Earth and Environmental Science*, 118(1), 12019. IOP Publishing.
- Srinivasamoorthy, K., Gopinath, M., Chidambaram, S., Vasanthavigar, M., & Sarma, V. S. (2014). Hydrochemical characterization and quality appraisal of groundwater from Pungar sub basin, Tamilnadu, India. *Journal of King Saud University-Science*, 26(1), 37–52. <https://doi.org/https://doi.org/10.1016/j.jksus.2013.08.001>
- Suryadarma, & Fauzi, A. (1991). Hydrothermal Alteration of The Garung Banten Geothermal Area West Java. *Proc.13th New Zealand Geothermal Workshop*, 193–197. Retrieved from <https://www.geothermal-energy.org/pdf/IGAstandard/NZGW/1991/Suryadarma.pdf>
- Suryaman, M. (1999). Peta Hidrogeologi Indonesia, Skala 1:100.000, lembar 1109-2 (Cikarang) dan 1110-2 Anyer., *Direktorat Geologi Tata Lingkungan, Bandung*.
- Tabachnick, B. G., & Fidell, L. S. (2013). *Using multivariate statistics* (6th ed.). Pearson Boston, MA.
- Taniguchi, M., Nakayama, T., Tase, N., & Shimada, J. (2000). Stable isotope studies of precipitation and river water in the Lake Biwa basin, Japan. *Hydrological Processes*, 14(3), 539–556.
- Tizro, A. T., & Voudouris, K. S. (2008). Groundwater quality in the semi-arid region of the Chahardouly basin, West Iran. *Hydrological Processes: An International Journal*, 22(16), 3066–3078. <https://doi.org/10.1002/hyp.6893>
- Tóth, J. (1999). Groundwater as a geologic agent: an overview of the causes, processes, and manifestations. *Hydrogeology Journal*, 7(1), 1–14.
- Tweed, S., Leblanc, M., Cartwright, I., Bass, A., Travi, Y., Marc, V., ... Kumar, U. S. (2019). *Stable Isotopes of Water in Hydrogeology*. <https://doi.org/10.1002/9781119300762.wsts0154>
- Villegas, P., Paredes, V., Betancur, T., Taupin, J. D., & Toro, L. E. (2018). Groundwater evolution and mean water age inferred from hydrochemical and isotopic tracers in a tropical confined aquifer. *Hydrological Processes*, 32(14), 2158–2175. <https://doi.org/10.1002/hyp.13160>
- Zhang, Yunhui, Xu, M., Li, X., Qi, J., Zhang, Q., Guo, J., ... Zhao, R. (2018). Hydrochemical characteristics and multivariate statistical analysis of natural water system: A case study in Kangding County, Southwestern China. *Water*, 10(1), 80.
- Zhang, Yuqi, Zhou, X., Liu, H., Yu, M., Hai, K., Tan, M., & Huo, D. (2019). Hydrogeochemistry, geothermometry, and genesis of the hot springs in the Simao Basin in southwestern China. *Geofluids*, 2019.