Seasonal variability of nitrate flux in the Northern part of Karangbolong Karst Aquifer, Central Java

Elisabeth Supi Astuti1,* and Eko Haryono1,2
1Department of Environmental Geography, Faculty of Geography, Universitas Gadjah Mada, Indonesia
2Karst Research Group, Faculty of Geography, Universitas Gadjah Mada, Indonesia

Abstract. Kalisirah Springs and Jumbleng Spring are located in the northern part of Karangbolong Karst Area, Kebumen Regency. Tracer tests for underground rivers and field surveys indicate that the catchment areas of these two karst springs have the dominant land use of dry land farm and plantation. The condition of the catchment area will affect the chemical content of water resources in karst aquifers. Dry land farm and plantation use fertilizer in the process of planting, but in practice, there is nitrogen lost due to the washing process by rainwater. Karst landforms also have cavities and fissures that allow applied fertilizer to enter the karstic aquifer directly. This study aims to determine the nitrogen flux fluctuations in the form of nitrate (N) in Kalisirah Springs and Jumbleng Springs along with their relationship with discharge and rainfall. The data used in this study were primary data, which included data of the water level, rainfall, water chemistry samples, and the agricultural planting calendar. The N content was analyzed using hydrograph to determine the response of N flux to the discharge. Recording the amount of N used in agricultural activities in the catchment area was conducted by calculating the area of agricultural land use using Topographic Map of Indonesia, and the triangulation method was used to determine fertilizer characteristics in the catchment area. Kalisirah catchment area lost 56.09 % N, while the Jumbleng catchment area lost 57.53 % N. The extent of this loss is influenced by land use conditions which will have implications for the number and frequency of fertilization.

Keywords: Catchment area, karst spring, agriculture, nitrogen loss, N flux

1 Introduction

Karst landforms have unique hydrological characteristics where the rock dissolves easily and has well-developed secondary porosity [1]. The karst region has cavities that allow contaminants from the surface enter directly to the karst aquifer. Pollutants will move through underground channels [2]. Watersheds can have a significant influence on flow ecosystems [3]. Addition to karst aquifers derived from the precipitation process above allows the area with the upstream part of agriculture to make a major contribution to the presence of nutrients in the groundwater flow. The entry of nutrients in karst aquifer can be caused by washing the soil by rain [4]. The existence of a cavities that connect the land surface in the karst region to the subsurface river system can contribute to the burden of groundwater pollutants in karst aquifers [5]. This research will examine the fluctuations in the concentration of N in the Karangbolmong Karst aquifer using nitrate hydrograph.

Karangbolong karst areas is one of the well-developed karst areas [6]. Kalisirah and Jumbleng Spring (Figure 1) are located in Sikayu Village, the northern part of the Gombong karst area. The land uses of the area are dry land farm, plantation farm, settlements, and shrub (Figure 2). Agricultural land needs nutrients to increase land productivity. Nutrient is a chemical element in the soil that is useful for helping plant growth [7].

Fig. 1. (a) Kalisirah Springs and (b) Jumbleng Springs

Nutrients consist of Nitrogen (N), Potassium (K), and Phosphorus (P). Nitrogen is a nutrient that is needed by plants in greater quantities compared to phosphorus and potassium. Nitrogen content in the soil is 0.06 % to 0.5 % in the upper layer and 0.02 % to 2.5 % in the lower layer [8]. Nitrogen demand by plants causes fertilizer to be applied to plants, but in the process, some nitrogen is lost from the soil. Loss of nitrogen from the soil can be caused by joint washing of drainage, erosion, evaporation, wind, microorganisms, and plant absorption [4].
Fig. 2. Landuse Maps of Kalisirah and Jumbleng Catchment Area

Kalisirah and Jumbleng catchment area are dominated by agricultural land use. The dominant land use in the catchment area can affect the nutrient content in karstic aquifers because karstic regions have cavities that allow surface contaminants to enter the karst aquifer system directly. This study aims to determine the number of nutrients lost from agricultural land and enter karstic aquifers.

2 Research methodology

2.1. Study sites

The Karangbolong Karst is a located at the southern zone of Java between 106°28'–109°14' E and 7°38'–7°45' S with area of 4,34 ha. The average rainfall in the Karangbolong Karst is around 3 000 mm yr⁻¹ [6]. Based on the rainfall, this region is included in the tropical climate (A) of tropical monsoon (Am) type. This climate type is characterized by the presence of fairly dense forests. This region is an approximate temperature of 25 °C to 29 °C.

This area is located on a fault block that is elevated and forms a plateau morphology [9]. The limestone in this area is dominated by boundstone and packstone from Kalipucang Formation [10]. The Kalipucang Formation overlap is not aligned with the Gabon Formation and overlays the Halang Formation (Figure 3) [11].

Fig. 3. Cross Section of the Karangbolong Karst Area [11]

Although geologically this region is relatively young, karst morphology and cave systems in this area have developed well [12]. At Karangbolong Karst, a cockpit was found that developed on the inside (above the plateau). The formation of the cockpit leaves the conical hills that are elongated in shape. Longitudinal formation indicates that the formation of valleys and cockpits is controlled by burly. On some cone hills, uvala is also found. Karangbolong Karst is one of the tropical karst typified by conical hills and aligned valley [6].

The Karangbolong Karst has several large springs, two reported are Jumbleng Springs and Kalisirah Springs located in the northern part of the Karangbolong Karst. Both of these springs flow throughout the year and are the main source of air for residents in the vicinity. The direction of underground flow is known by the tracing method that has been carried out by [13]. The water footprint shows the different flow systems of the two springs. The main system of the Jumbleng catchment area is Banjiran Ponor that empties the Jumbleng Springs, while the Kalisirah catchment area system is the Pocung Cave that empties the Jeblosan Cave and reaches the Kalisirah Springs [13]. Kalisirah Springs has a fairly large discharge (92 L s⁻¹ to 1 358 L s⁻¹). The condition of the water is relatively clear but turns turbid shortly after rain and discharge increase. Unlike the Kalisirah Springs, Jumbleng Springs has smaller discharges (5 L s⁻¹ to 142 L s⁻¹) with clearer water.

The use of agricultural land around Kalisirah Spring and Jumbleng Spring is dominated by plantation dry land farm and dry land dry land farm, the two springs have different characteristics of agricultural land area (Table 1). Kalisirah catchment area has wider dry land dry farm land use, while the Jumbleng catchment area is dominated by plantation dry land farm land use. Dry land farm in this area are planted with annual crops such as chili, vegetables, corn, cassava, crops, and sago. Meanwhile, plantation farm are dominated by woody plants such as coconut trees, melinjo trees, mahogany trees, albias trees, albizia trees, teak trees, and other woody plants.

| Landuse     | Percentage (%) | Area (ha) | Percentage (%) | Area (ha) |
|-------------|----------------|-----------|----------------|-----------|
| Shrub       | 9              | 16        | 0              | 0         |
| Dry land farm | 46            | 82        | 20             | 26        |
| Settlement  | 9              | 16        | 20             | 26        |
| Plantation farm | 37         | 66        | 37             | 48        |
| Total       | 100            | 180       | 100            | 77        |

Source: Indonesian Topographic Map (2019)

Kalisirah catchment area has an area of 1 799 257 m², much more extensive than the area of Jumbleng watershed which is 657 687 m². The area of agricultural land in the Kalisirah and Jumbleng watersheds is quite large compared to other land uses (Figure 2). The area of agricultural land in the Kalisirah catchment area covers 82.3 % of the total area of the catchment area, while in Jumbleng catchment area the area is 86.1 %.
2.2. Methods
The data used in this study were primary data, which included data of the water level, rainfall, water chemistry samples, and the agricultural planting calendar. The water level data was obtained by installing a Hobo U-30 water level logger which was calibrated using an air pressure logger on both springs. Rainfall data is obtained by installing an automatic rain gauge with tipping bucket on the upstream of both flow systems. Water samples for nitrate analyses were taken for 8 mon (January 2019 to August 2019) under various water level conditions to represent the dry and rainy seasons. The water sample was then analyzed at the Environmental Health and Disease Engineering Center (BTKLPP Yogyakarta) using APHA 2012, Section 4500-N03B method. Recording the amount of N used in agricultural activities in the catchment area was by calculating the area of agricultural land use using Topographic Map of Indonesia data in 2018. Interviews with agricultural field officers and heads of farmer groups are carried out to determine fertilizer characteristics in the catchment area.

2.3. Data analysis
Nitrate flux analysis is performed using regression analysis to determine the relationship between daily nitrate-N load versus flow rate. The formula obtained from the nitrate rating curve is used to calculate the value of nitrate concentrations under various discharge conditions, to then make a nitrate hydrograph. The nitrate hydrograph links the concentration of nitrate with time. The making of nitrate hydrograph aims to find out the fluctuation of nitrate concentrations in the spring and its relationship to discharge, rainfall events, and fertilizing characteristics. The spatio-temporal analysis was also carried out to compare spatial variations and temporal nitrate flux in the two karst springs.

3 Results and discussions
3.1. Results
Nitrate Loads at Kalisirah Springs and Jumbleng Springs have the same characteristics but the amount is different, where the N load on the Kalisirah Springs is higher. Nitrate load increases with flowrate (Figure 4). Nitrate load with discharge at Kalisirah and Jumbleng Springs has a positive direct relationship with the amount of R² values are 0.97 and 0.99 using linear regression that indicates a relationship between discharge and N load.

\[ y = 0.2848x + 1.0807 \quad R^2 = 0.9986 \]

\[ y = 0.3800x + 3.3188 \quad R^2 = 0.964 \]

Fig. 4. Nitrat Load vs Discharge of (a) Kalisirah Spring and (b) Jumbleng Spring. Source : Data processing (2019)

N requirements for agricultural land in the study site (Table 2) were obtained by interviews and processed using triangulation techniques. Plants grown in the dry land farm include nutmeg, chili, legumes, vegetables (barren, tomato, and eggplant), corn, cassava, sago, and cardamom. Plantation farm are dominated by hardy woody plants such as teak trees, mahogany trees, acacia trees, coconut trees, melinjo trees, alisias trees, albizia trees, and banana trees. Woody trees only need fertilizer at the beginning of their growth, whereas when they are more than 5 y.o these trees are no longer fertilized. The characteristics of these types of plants make a dry land farm need more fertilizer than a plantation farm.

Table 2. Fertilization (N) on Kalisirah Catchment Area and Jumbleng Catchment Area

| Landuse (g m⁻²) | Nitrogen Needs (kg) |
|----------------|---------------------|
| Dry land farm  | Plantation farm     |
| Jan            | 600.77              |
| Feb            | 823.63              |
| Mar            | 192.72              |
| Apr            | 1.0807              |
| May            | 0.00                |
| Jun            | 0.00                |
| Jul            | 0.00                |
| Aug            | 2.4176              |
| Sep            | 0.00                |
| Oct            | 346.05              |
| Nov            | 1.0807              |
| Dec            | 1.0807              |
| Total          | 1.0807              |

Nitrogen input in the Kalisirah catchment area is higher than that of the Jumbleng catchment area (Figure 5). The high level of nitrogen input in the Kalisirah catchment area is due to the greater area of the Kalisirah catchment area. Besides, the dominant land use in the Kalisirah catchment is a dry land farm that requires more N than a plantation farm. The highest N requirement in Kalisirah catchment area occurred in November which was 14 950 kg, while in Jumbleng Springs the highest N requirement in January was 7.214 kg.

Fig. 5. Graph of N Input on Kalisirah Catchment Area and Jumbleng Catchment Area

3.2 Discussions
Nitrogen input in Kalisirah catchment area is higher than in Jumbleng DTA (Figure 6). The high level of nitrogen input in the Kalisirah catchment area is due to the greater area of the Kalisirah catchment area. Besides, the dominant land use in the Kalisirah catchment area is a dry land farm that requires more N than a plantation farm. The highest N requirement in Kalisirah catchment area occurred in November which was 14 950 kg, while in Jumbleng catchment area the highest N requirement in October was 5.012 kg.
Load N fluctuations in Kalisirah Springs and Jumbleng Springs have the same characteristics. The value of N load in both springs is high when the discharge is high, whereas when the discharge is low the N load decreases. Temporal variation in nutrient content is related to precipitation [14–16]. Load N is dynamic and high during the rainy season, whereas in the dry season the value decreases with the low discharge and rainfall. The average N load in Kalisirah Springs is 89 kg d⁻¹, while in Jumbleng Springs the value is lower at 12 kg d⁻¹. The value of N load in Kalisirah Springs is relatively high, which is 529 kg d⁻¹ during the peak of the rainy season. This N load is close to the highest N load in the karst area of Gunungsewu whose value has been studied by [17] of 400.876 kg d⁻¹. The high value of nitrate load is due to the stable nature of nitrate compounds. Nitrate is also the end result of the nitrogen cycle so that its presence is high in nature [18].

Fig. 6. N Flux Hydrograph on Kalisirah Catchment Area and Jumbleng Catchment Area

The total N load in Kalisirah Springs for 309 d measurement was 29596 kg. In Jumbleng Springs, the total N load for 258 d of measurement was 3493 kg. The comparison between N inputs in Kalisirah Springs and Jumbleng Springs for the period 16 February 2019 to 29 September 2019 is 8.8:1. The significant difference in N load in the two springs during 225 d of measurement is influenced by the discharge and area of agricultural land in the catchment. The flowrate on Kalisirah catchment area is greater than Jumbleng catchment area. Land use in the form of a wider dry land farm in the Kalisirah catchment area also plays a role in the magnitude of the N flux value in the Kalisirah catchment area, because the need for fertilizer for the dry land farm is greater than the need for fertilizer for the plantation farm.

Nitrogen balance is a quantitative comparison between N (input) and N (output) inputs which has implications for the balance and sustainability of agricultural land [19]. N inputs originate from fertilization and N outputs calculated are N in the waters [20]. The loss of N in Kalisirah catchment area is higher than in Jumbleng catchment area (Table 3). Kalisirah catchment area experienced an N loss of 56.09 %. Agricultural land in Kalisirah catchment area requires 52766 kg of fertilizer from November to September, while the amount of N in water reaches 29596 kg. Fertilization is more intense during the rainy season. The dominance of agricultural land in the form of land in Kalisirah catchment area that requires a lot of fertilizer causes the amount of leaching N in the region. This triggers high N in water which has implications for the estimated magnitude of N loss in the Kalisirah catchment area. The catchment area in the form of agricultural land will affect the high levels of nutrients in the water due to fertilization [21]. The Jumbleng catchment area is estimated to have an N loss of 57.53 % during the 9-mon measurement (February to October 2019). The recorded N requirement is 6 072.25 kg, while the N value in the spring is 3 493.32 kg. Fertilization in the Jumbleng catchment area is mostly done at the beginning of the rainy season, so the output value is quite large when the peak of the rainy season occurs due to the accumulation of N in leached soil and entering the aquifer system.

Table 3. N Balance of Kalisirah Catchment Area and Jumbleng Catchment Area

| Month    | Kalisirah | Jumbleng |
|----------|-----------|----------|
|          | Input     | Output   | Input     | Output   |
| January  | 14 414.82 | 4 208.75 | -         | -        |
| February | 2 823.63  | 3 258.16 | 662.77    | 594.16   |
| March    | 3 163.80  | 3 844.77 | 855.04    | 600.59   |
| April    | -         | 3 542.03 | -         | 432.96   |
| May      | -         | 2 042.81 | -         | 411.01   |
| June     | -         | 2 389.31 | -         | 354.87   |
| July     | -         | 1 990.46 | -         | 325.45   |
| August   | 10 530.10 | 1 819.06 | 2 471.67  | 276.61   |
| September| 1 474.21  | 1 653.09 | 346.03    | 255.36   |
| October  | 1 736.73  | 1 242.68 | -         | -        |
| November | 1 950.79  | 1 793.82 | -         | -        |
| December | 5 408.96  | 2 054.00 | -         | -        |
| Total    | 52 766.33 | 29 596.25 | 6 072.25 | 3 493.32 |

N loss (%) | 56.09 | 57.53

The difference in N losses in the Kalisirah catchment area and Jumbleng catchment area is due to land use characteristics. Jumbleng catchment area has a greater percentage of agricultural land compared to the Kalisirah catchment area. A large amount of fertilization in the field can cause N saturation. N saturation is a condition where the addition of N in the field exceeds the N requirement [22]. This can cause quite a lot of N in the soil so it is easily leached.

4 Conclusion and recommendation

The concentration of N₂ in the form of nitrate (NO₃⁻) in Kalisirah Springs and Jumbleng Springs has the same characteristics. Low nitrate concentration during rainfall and high discharge. The mean nitrate concentration in Kalisirah Springs (4.62 mg L⁻¹) is higher than the average nitrate concentration in Jumbleng Springs (3.64 mg L⁻¹). Comparison between N outputs in Kalisirah Springs and Jumbleng Springs for the period of February 16, 2019 - September 29, 2019, is 8.8:1. The N yield in Kalisirah Springs is 0.0181 kg m⁻² yr⁻¹ and in Jumbleng watershed the value is 0.0068 kg m⁻² yr⁻¹. The difference in N load and N yield which is quite significant in these two springs is influenced by the discharge and area of agricultural land in the catchment area. The Kalisirah catchment area is recorded to have lost N by 56.09 %, while the Jumbleng catchment area has lost N by 57.53 %. The extent of this
loss is influenced by land use conditions which will have implications for the number and frequency of fertilization.

This study only calculates the N input value of agricultural activities based on the type of land use, namely plantation farm and dry land farm. Therefore, making a vegetation cover map in the catchment area can be done to analyze fertilization more specifically and in detail. This will be very helpful in analyzing the characteristics of fertilization. Research on N input from household waste also needs to be carried out to determine other sources of N input apart from agricultural land in aquifers. Research on N input from household waste will help improve the accuracy of N balance calculations because in this study the N input used only comes from agricultural activities.

The authors would like to thank Persatuan Rakyat Penyelamat Karst Gombong (PERPAG) for supporting our research and assistance with field work also a place to stay when conducting the research.

References

1. D. Ford, P. Williams, *Karst Geomorphology and Hydrology*, London: Chapman and Hall (1989)
2. T. Adji, Indonesian Cave and Karst Journal, 2,1 (2006)
3. P.C. Frost, L.E. Kinsman, C.A. Johnston, J.H. Larson, Watershed Discharge Modulat, 90,6: 1631–1640 (2017)
4. N. G. Darmono, Suwardi, Darmawan, Journal Zeolit Indonesia, 8,2: 89–96 (2009)
5. A. Cahyadi, E.A. Ayuningtyas, B.A. Prabawa, Indonesian Journal of Conservation, 2,1:23–32 (2013), ISSN: 2252-9195 (2013)
6. E. Haryono, S.T. Putro, Suratman, Sutikno, Acta Carsologica, 46:63–72 (2017)
7. J. Sartohadi, et al., *Pengantar Geografi Tanah*. Yogyakarta: Pustaka Pelajar (2012)
8. M. Alexander, *Introduction to Soil Microbiology*. 2nd ed. Jhon Wiley and Sons. Inc: New York. (1997)
9. R.W. Bemmelen, *The Geology of Indonesia. General Geology of Indonesia and Adjacent Archipelagoes*. Government Printing Office, The Hague, (1970)
10. B. Brahmanto, *Perkembangan bentangalam Karst Gombong Selatan, dengan Geologi Sebagai Faktor Kendali.*- PhD thesis. Institut Teknologi Bandung, pp. 182. (2005)
11. S. Asikin, *Geologi Struktur Indonesia dan Stratigrafi Jawa Tengah*. Bandung: ITB Press., (1992)
12. L. Bernard, L. Josiane, C. Locatelli, G. Robert, R. Setiawan, L. Sitepu, F. E. A. Winarto, *Expédition Spéléologique Sur Le Karst de Karangbolong (java, Indonésie)- Fédération Française de Spéléologie*, Report Number: 61, (2003)
13. E.S. Astuti, A.I. Rahmawati, A Setyawan, Q. Alghozali, R.F. Agniy, D.R. Fauzi, D.S. Mahrizkhal, A. Nurkholis, A D. Pratama, D.S. Dwiputra, G.E. Laksono, A.D. Siswanto, T.N. Adji, E. Haryono, A Groundwater Tracing Investigation to Determine Kalisirah Karst Springs Catchment Area, Kebumen Regency, in *Proceedings of the 3rd International Conference on Environmental Resources Management in Global Region*, ICERM, 14 Nov 2019, IOP Conference Series: Earth and Environmental Science, 451, Yogyakarta, Indonesia (2020)
14. S. Li, W. Liu, S. Gu, X. Cheng, Z. Xu, Q. Zhang, Journal of Hazardous Materials, 162,2–3:1340–1346 (2009), https://doi.org/10.1016/j.jhazmat.2008.06.059.
15. B.J. Mahler, D. Valdes, M. Musgrove, N. Massei, Journal of Contaminant Hydrology, 98,1–2:36–49 (2008), https://doi.org/10.1016/j.jconhyd.2008.02.006.
16. K. Kyllmar, M. Bechmann, J. Deelstra, A. Iital, G. Blicher-Mathiesen, V. Jansons, A. Povilaitis, Agriculture, Ecosystems and Environment, 198, 4–12 (2014), https://doi.org/10.1016/j.agee.2014.07.005.
17. T. Oehler, E. Eiche, D. Putra, D. Adyasari, H. Hennig, U. Mallast, N. Moosdorf, Journal of Hydrology, 565:662–671 (2018), https://doi.org/10.1016/j.jhydrol.2018.08.077.
18. United Nations Environment Programme and the World Health Organization, *Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes*. (R. Bartram, Jamie and Ballance, Ed.) (1st ed.). London: Chapman & Hall, (1996)
19. U.M. Sainju, *Determination of Nitrogen Balance in Agroecosystems*, MethodsX, 4(June), 199–208 (2017), https://doi.org/10.1016/j.mex.2017.06.001
20. M. Musgrove, S.P. Opsahl, B.J. Mahler, C. Harrington, T.L. Sample, J.R. Banta, Science of the Total Environment, 568:457–469 (2016), https://doi.org/10.1016/j.scitotenv.2016.05.201.
21. A. Burg, Heaton, Israel. J Hydrol 204:68–82 (1998)
22. J.D. Aber, K.J. Nadelhoffer, P. Steudler, J.M. Melillo, *BioScience*, 396:378–386 (1989)
23. https://doi.org/10.2307/1311067
24. https://doi.org/10.1051/e3sconf/202020006009