Published Online First: July, 2024
https://doi.org/10.21123/bsj.2024.10610
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

Temporal Variation of Nitrate Concentrations in Karst Spring in the Western Part of the Gunungsewu Karst Area, Java Island, Indonesia

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Received 04/01/2024, Revised 05/05/2024, Accepted 07/05/2024, Published Online First 20/07/2024

Abstract

The presence of nitrate in water has become a concern for many environmentalists because it has reduced the quality of water used to meet people's clean water needs. The study of the temporal variation of nitrate in water flow is expected to provide a complete understanding of the influencing factors that need to be managed to control the nitrate concentration in water. This study aims to analyze the temporal variations in the nitrate concentration at the Guntur Spring, one of the springs in the Gunungsewu Karst Area that plays a role in the provision of clean water. The data used in this research include data on nitrate concentration in spring water, rainfall, and spring discharge. Sampling was carried out every two weeks from February 2018 to March 2019 to understand the temporal variation in nitrate concentrations. Discharge and rainfall data were obtained from automatic recording during the same period as water sampling for nitrate analysis. The result shows that the nitrate concentration throughout the year in the Guntur Spring does not exceed the quality standard. The good water quality is caused by the natural filtration process that is still going well due to the low level of karstification that is still dominated by fissure flows. In addition, this research has found that the most influential variation in nitrate concentration in the spring flow at Guntur Spring is the cropping pattern in the area.

Keywords: Nitrate, Karst Spring, Cropping Pattern, Karst Development, Temporal Variation.

Introduction

Nitrate is an element that is often found in agricultural areas[1,2]. Nitrate in karst areas generally comes from fertilizers used in agricultural areas[3]. This is generally caused by excessive fertilization that causes the plants to be unable to absorb all of the nitrate elements in fertilizer. Nitrates from fertilizers that are not absorbed by plants will be carried by rainwater and enter the karst river system[4,5]. In karst areas where there are no surface rivers, nitrate will immediately move to the underground river or karst aquifer[6,7]. The impacts caused by excessive nitrate entering river systems and groundwater can cause environmental problems in the form of eutrophication[8,9] and health problems in the form of methemoglobinemia and cancer[10-12]. The quality standard for nitrate content in water has been set as the tolerable limit. Some of the quality standard limits that are widely used are international regulations set by the World Health Organization (WHO) and domestic regulations such as those set

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out in the Regulation of the Minister of Health (PERMENKES) of the Republic of Indonesia Number 90 of 2002, which provides safe concentration limits of nitrate in water of <50 mg/l.

Several cases around the world demonstrate that nitrate from agricultural activities is among the primary sources polluting groundwater[13-15], and the majority of developing countries have a large contribution to polluting groundwater with nitrate from agricultural products[8,9]. The process of nitrate entering the groundwater system is also observed in several regions in Indonesia, one of which occurs in the Gunungsewu karst area[16-18]. The unique thing about the polluting process in the study area is that the nitrate at this location enters the underground river system through a sinkhole or ponor which is the outlet of an allogenic river and comes out in the spring[19,20]. This process in karst areas is deemed unusual since the nitrate entry system in this area occurs directly and quickly without any filtering through widening fissures and conduit passages formed by the dissolution process[21,22].

Agriculture is the main economic sector that develops in the Gunungsewu karst area. The prevalent land use in Gunungsewu Karst is in the form of mixed gardens and moors, as well as several rainfed rice fields[23], inducing it to have a high vulnerability to nitrate pollution[24]. The dominance of these three land uses is estimated to contribute significantly to the nitrate input into the karst hydrological system, primarily due to fertilizer usage[11,25,26].

Guntur Spring is one of the springs in the Gunungsewu Karst Area that is used to meet the clean water needs of around 500 families in the area[26]. Pollution that occurs in this spring can have an impact on the quality of the spring, resulting in harm to nearby society. Therefore, temporal monitoring is vital Given that karst areas have high groundwater vulnerability, as well as the dynamics caused by seasonal changes and changes in land use/cover at the study site by the cultivation process of agricultural crops such as corn, peanuts, cassava, dryland rice and other crops.

This research aims to carry out temporal analysis and investigate the temporal variation patterns of nitrate concentrations in Guntur Spring. This research specifically conducted a multi-temporal study over one year to determine the characteristics of the nitrate content in Guntur Spring and its relationship to rainfall, spring discharge, and cropping patterns in the Gunungsewu Karst Area. This research also aims to determine the specific characteristics of nitrate pollution caused by agricultural activities in tropical karst areas controlled by the Asian-Australian monsoon system. This monsoon system causes the Gunungsewu karst area (which is located on the island of Java and acts as the center of the monsoon) to have two contrasting seasons, namely the dry season and the rainy season[27]. These two seasons are likely to have an impact on the characteristics of nitrate pollution at the study location with different pollution behavior in each season[5,15,28]. It is also hoped that the results of this research will be able to identify factors that must be considered in managing water resources in karst areas in the future, especially related to the potential of nitrate water pollution.

Materials and Methods

Guntur Spring is located in Purwosari District, Gunungkidul Regency, Yogyakarta Special Region, Indonesia. Administratively, the study location is part of the southern mountains of the island of Java, and astronomically, Guntur Spring is located at coordinates 110.436 E (Longitude) and -7.992 S (Latitude) (Fig. 1). Hydrogeologically, Guntur Spring is situated in the Panggang Hydrogeological Sub System, which is the westernmost part of the Gunungsewu Karst Area[21,29,30], which is the westernmost part of the Gunungsewu Karst Area. The rocks found at the study site primarily belong to the Wonosari Formation limestone, consisting of reef limestone that was deposited over ancient volcanic rocks dating back to the Tertiary period[31,32,33]. The catchment area of Guntur Spring is dominated by land use in the form of mixed plantations, rainfed rice fields, and moors[24,34].

The data used in this research includes nitrate concentration data in spring flows, rainfall and spring discharge. Nitrate concentration data are generated from the analysis of samples that were taken every two weeks. The sampling was carried out from 7 February 2018 to 16 March 2019 and a total of 27 water samples were taken from the study area.

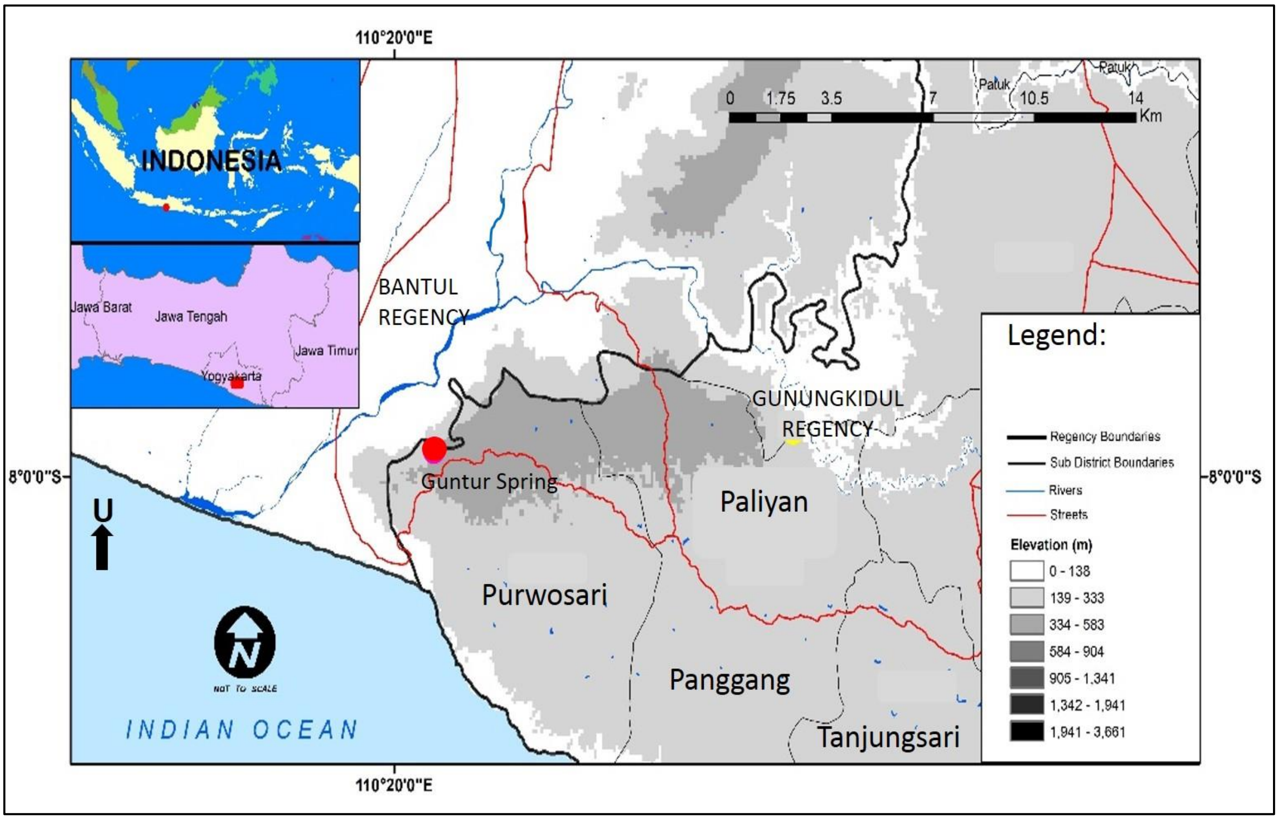

Figure 1. Map of Study Area (Source: Topography Map Scale 1:25,000 from Geospatial Information Agency, Republic of Indonesia).

Spring discharge data was obtained from automatic recording using an automatic water level logger, while the rainfall data used was acquired from an automatic weather logger. Both tools are set to record the data for every 15 minutes. However, it should be noted that the data used in this research is discharge data for two weeks which has been averaged, and rainfall data which has been summed up for two weeks.

The nitrate concentration data in the spring flow was analyzed for quality standards based on the water quality standards stated in the Regulation of the Minister of Health of the Republic of Indonesia number 90 of 2002, where based on this regulation the quality standard value for nitrate is <50 mg/l.

Temporal analysis of data taken at the research location was carried out in pairs, namely on the nitrate concentration variables and bi-weekly rainfall, as well as the nitrate concentration variables and spring discharge data. Temporal analysis by pairing the two variables is used to visually analyze the similarity of temporal variation patterns between the two variables. Correlation in each pair of variables was analyzed using the linear regression method.

In-depth interviews with agricultural farmers and society at the study location were also conducted to determine cropping patterns and land cultivation behavior in the study area which could influence variations in nitrate concentrations in the spring flow at the study location. The results of the cropping pattern analysis were then linked to the nitrate content in Guntur Spring to determine the effect of cropping patterns on nitrate concentrations.

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Results and Discussion

The results of the analysis of nitrate concentrations in Guntur Spring show that during the monitoring period, all nitrate concentration values at the research location were below the quality standard value (50 mg/l) (Table 1). These results show that nitrate concentrations throughout the year in Guntur Spring were in line with the quality standard. This is considered quite unforeseen considering that the study location has a total water catchment area of 30.7 ha[35] with 76% of the area consisting of agricultural land in the form of rainfed fields and rice fields[36,37] which has intensive fertilization intensity[38], whether using chemical fertilizers or manure which has the potential to pollute groundwater in the study area.

Table 1. Bi-weekly Discharge, Rainfall and Nitrate Concentration Data at Guntur Spring

Date	Discharge (L/s)	Rainfall (mm/2 weeks)	Nitrate (mg/L)	Quality Standard Information
February 7, 2018	100.79	27.20	1.56	Samples Meet Quality Standards
February 15, 2018	99.29	26.40	1.08	Samples Meet Quality Standards
March 9, 2018	73.35	19.40	18.15	Samples Meet Quality Standards
March 28, 2018	76.07	14.20	17.30	Samples Meet Quality Standards
April 9, 2018	85.97	6.00	16.95	Samples Meet Quality Standards
April 23, 2018	58.17	4.20	11.15	Samples Meet Quality Standards
May 7, 2018	2.88	1.20	5.67	Samples Meet Quality Standards
May 21, 2018	2.01	0.00	3.00	Samples Meet Quality Standards
June 7, 2018	1.80	0.00	2.30	Samples Meet Quality Standards
June 21, 2018	1.75	0.00	2.20	Samples Meet Quality Standards
July 7, 2018	1.70	0.00	2.20	Samples Meet Quality Standards
July 21, 2018	0.85	0.00	1.40	Samples Meet Quality Standards
August 7, 2018	0.80	0.00	1.20	Samples Meet Quality Standards
August 21, 2018	0.70	0.00	1.10	Samples Meet Quality Standards
September 7, 2018	0.60	0.00	1.20	Samples Meet Quality Standards
September 21, 2018	0.30	0.00	0.80	Samples Meet Quality Standards
October 7, 2018	0.20	0.00	0.30	Samples Meet Quality Standards
October 21, 2018	0.20	12.00	0.30	Samples Meet Quality Standards
November 4, 2018	9.20	14.00	7.20	Samples Meet Quality Standards
November 18, 2018	10.20	46.00	14.40	Samples Meet Quality Standards
December 4, 2018	35.00	56.00	5.14	Samples Meet Quality Standards
December 18, 2018	42.20	52.00	4.20	Samples Meet Quality Standards
January 8, 2019	76.00	43.00	3.40	Samples Meet Quality Standards
January 24, 2019	74.00	34.00	3.20	Samples Meet Quality Standards
February 11, 2019	72.00	42.00	13.20	Samples Meet Quality Standards
February 28, 2019	68.70	52.00	9.20	Samples Meet Quality Standards
March 16, 2019	80.00	78.30	4.30	Samples Meet Quality Standards

Sources: Field Data, Analysis Data and Laboratory Analysis Results

Nitrate concentrations in groundwater in karst areas where land use is dominated by the agricultural sector are generally quite high[11,39,40]. This happens because the development of conduit (passages with a diameter of more than 10 mm) formed by the dissolution process makes it easier for water and pollutants to flow into the aquifer system of karst areas[41-43]. Generally, in karst areas, the natural water filtering process by soil and rock does not occur since water from the surface will flow through dissolution passages or conduits, not through intergranular voids of rock or soil grains[44,45]. The low level of nitrate concentration in the research area despite being located in a karst area is due to a low level of tunnel development in the water catchment area of Guntur Spring, namely at level 5, where the groundwater flow that supplies Guntur Spring is still dominated by fissure flow (flow in dissolution passages are small, less than 10 mm in diameter or in the form of cracks) with conduit that have just starting to develop[46-48]. This answers the question of why the nitrate content in Guntur Spring has relatively low concentrations despite having a large water catchment dominated by agricultural land. The dominance of fissure flows in Guntur Spring also shows that the natural filtration process by rocks and soil is still going well, unlike in most karst areas that have developed large conduit over time.

The nitrate concentration in groundwater from Guntur Spring has an average of 5.63 mg/l, with a maximum nitrate concentration value of 18.15 mg/l, and a minimum concentration of 0.30 mg/l. Fig. 2 shows that temporally nitrate concentrations in the Guntur Spring increase during the rainy season and decrease during the dry season. The decrease of nitrate concentration in Guntur Spring in the dry season begins from 21 May 2018 to 21 October 2018, while the increase of nitrate concentration in Guntur Spring in the rainy season fluctuates following the rainfall that occurs in the area from 21 October 2018 to 21 May 2018. This aligned with the results of a study by Chen et al.[40], Huebsch et al.[49], Al-Kenzawi et al.[50]; and Wang et al.[51] which states that high rainfall intensity may cause surface flow on agricultural land to bring nitrate more intensively into groundwater. Meanwhile, during the dry season, the lack or even absence of rainwater causes no surface flow which carries nitrate into the aquifer system to form, thus decreasing the concentration of nitrate in the Guntur Spring.

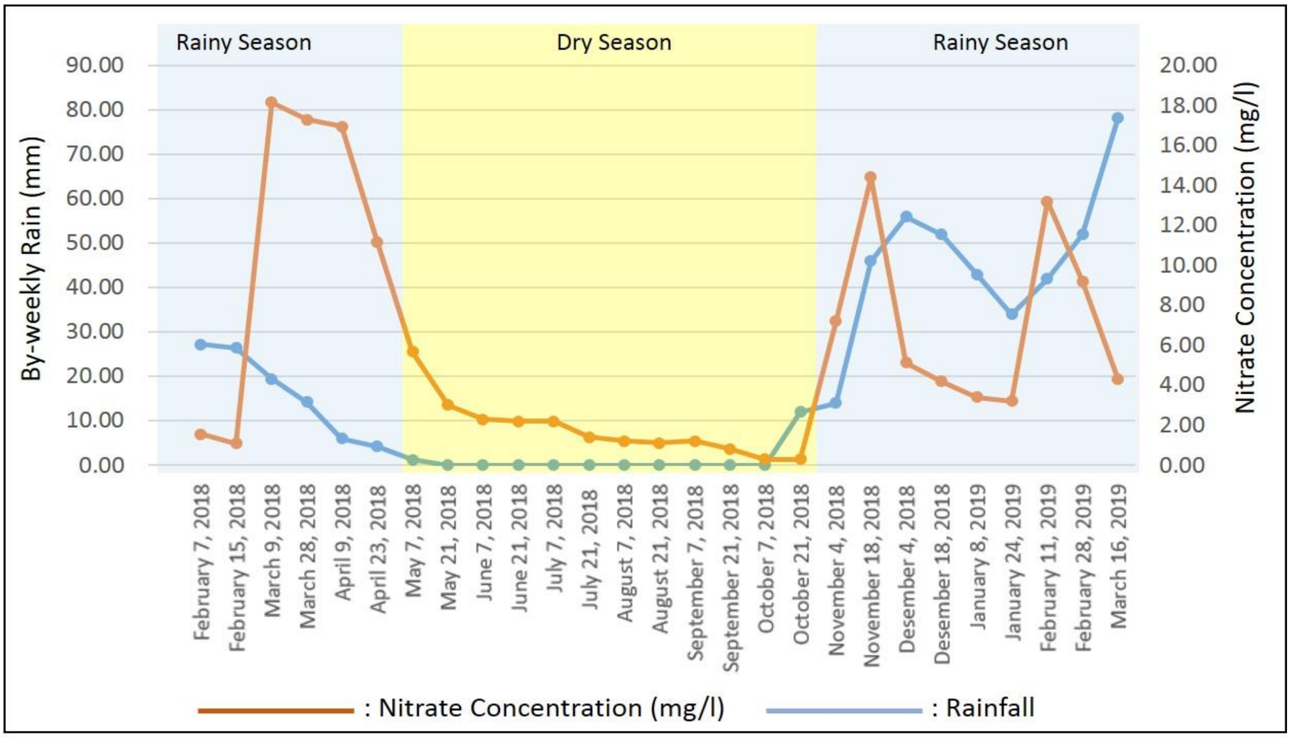

Figure 2. Temporal Graph of Bi-weekly Rainfall and Nitrate Concentration in Guntur Spring

A linear correlation was also found in the temporal graph showing the discharge values and nitrate concentration at Guntur Spring in one year (Fig. 3). In this figure, it can be observed that when the spring discharge is considerably high, the nitrate concentration also tends to increase. As previously explained, this happens because the water flow carries nitrate into the groundwater, thus higher water volume in spring may result in higher nitrate concentration. A large volume of spring discharges occurs in the rainy season when Guntur Spring receives replenishment from internal runoff and infiltration through fissures and diffuses (flow between rock grains). The Guntur Spring does not have allogenic recharge (a charge that comes from outside the karst area), but it has internal runoff

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P-ISSN: 2078-8665 - E-ISSN: 2411-7986

recharge, namely recharge from surface flow on the doline which enters the underground river system through sinkholes or conduit. The existence of this passages will make it easier for pollutants including nitrates to enter the groundwater system in Guntur Spring.

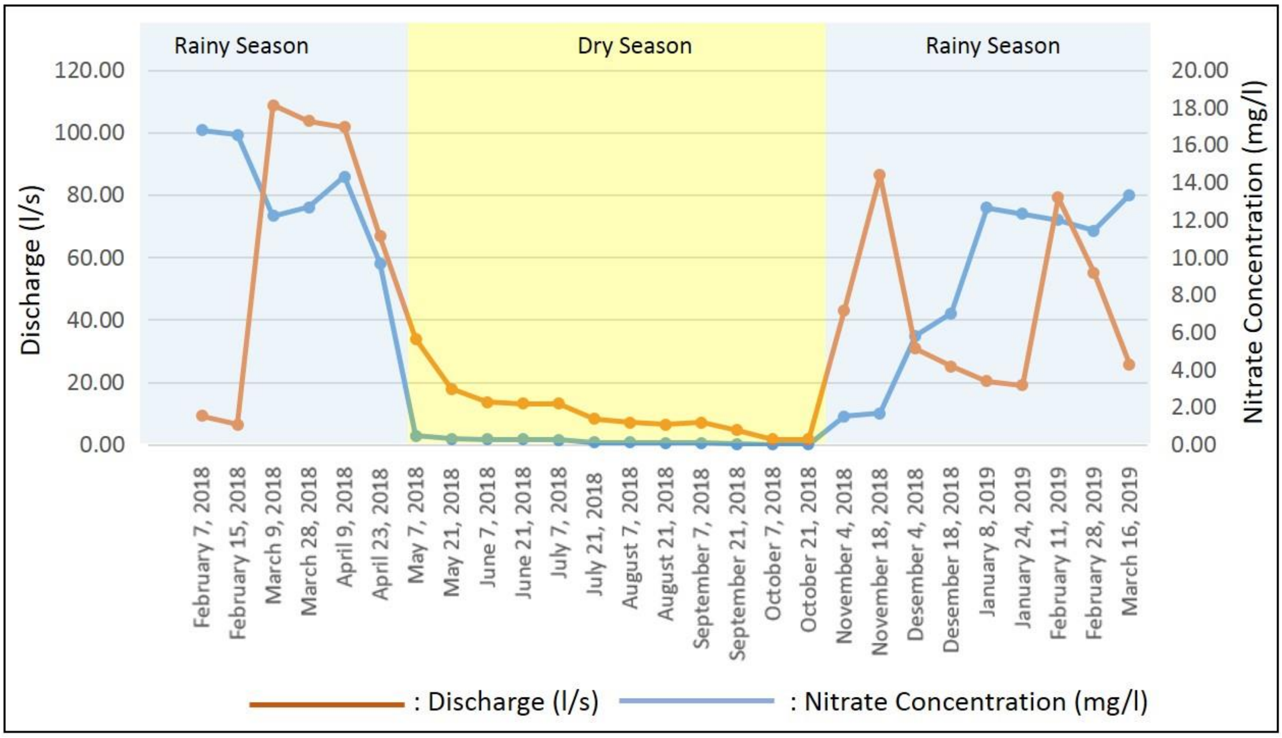

Figure 3. Temporal Graph of Discharge and Nitrate Concentration in Guntur Spring

Although temporally the nitrate concentration appears to be related to rainfall and discharge, the correlation graph in Fig. 4 and Fig. 5 shows that these two parameters evidently have a low correlation with the value of the nitrate concentration. In general, based on the correlation graph, both parameters show a positive relationship with nitrate content, even though the correlation value is small. Based on the R^2 value in Figs. 4 and 5, the r value which shows the correlation value between two parameters can be calculated. Based on the correlation value, the relationship between discharge and nitrate concentration has a greater correlation value (r = 0.45) compared to the correlation value between bi-weekly rainfall and nitrate concentration (r = 0.22). This condition occurs because rainfall and water discharge can indeed cause nitrate to be carried into the karst aquifer, but on the other hand it will cause a dilution process that causes nitrate levels to appear to decrease[52].

The results of this study found that the main factor affecting nitrate concentrations in groundwater at Guntur Spring is the cropping pattern. This can be observed in Fig. 6 which shows that the beginning of each planting season is always followed by an increase in nitrate concentration of water that comes out of Guntur Springs. This occurs because, at the beginning of the planting season, the land is open since the plants being sown have not yet grown, resulting in the process of erosion and fertilizer absorption occurring quite intensively. This is also further strengthened by the fact that the nitrate concentration graph then decreases along with the growth of crops, which generally consist of dryland rice and secondary crops.

The start of the rainy season every year always changes depending on the rainfall that occurs that year. The climate conditions at the study location are greatly influenced by the monsoon phenomenon which is formed as a consequence of Indonesia's location between two continents, namely the Asian Continent and the Australian Continent. Cahyadi et al.[27] stated that the study location includes a zone that is part of the monsoon center. Despite being the

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center part of the monsoon, as a maritime continent Indonesia is influenced by many climate phenomena, thus shifts in the start of the rainy season often occur. It can be seen that the start of the second planting season in 2017-2018 occurred in February 2018, while in 2018-2019 it occurred in mid-January 2019.

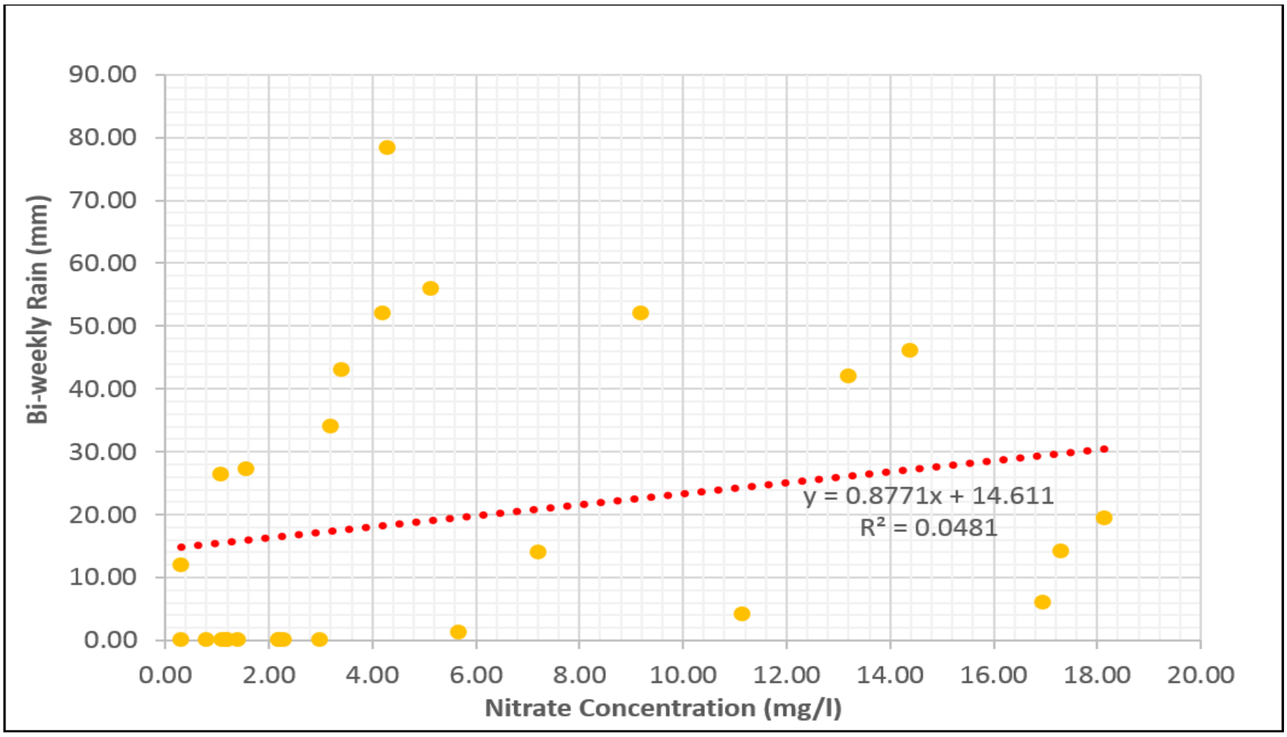

Figure 4. Correlation Graph of Bi-weekly Rainfall and Nitrate Concentration

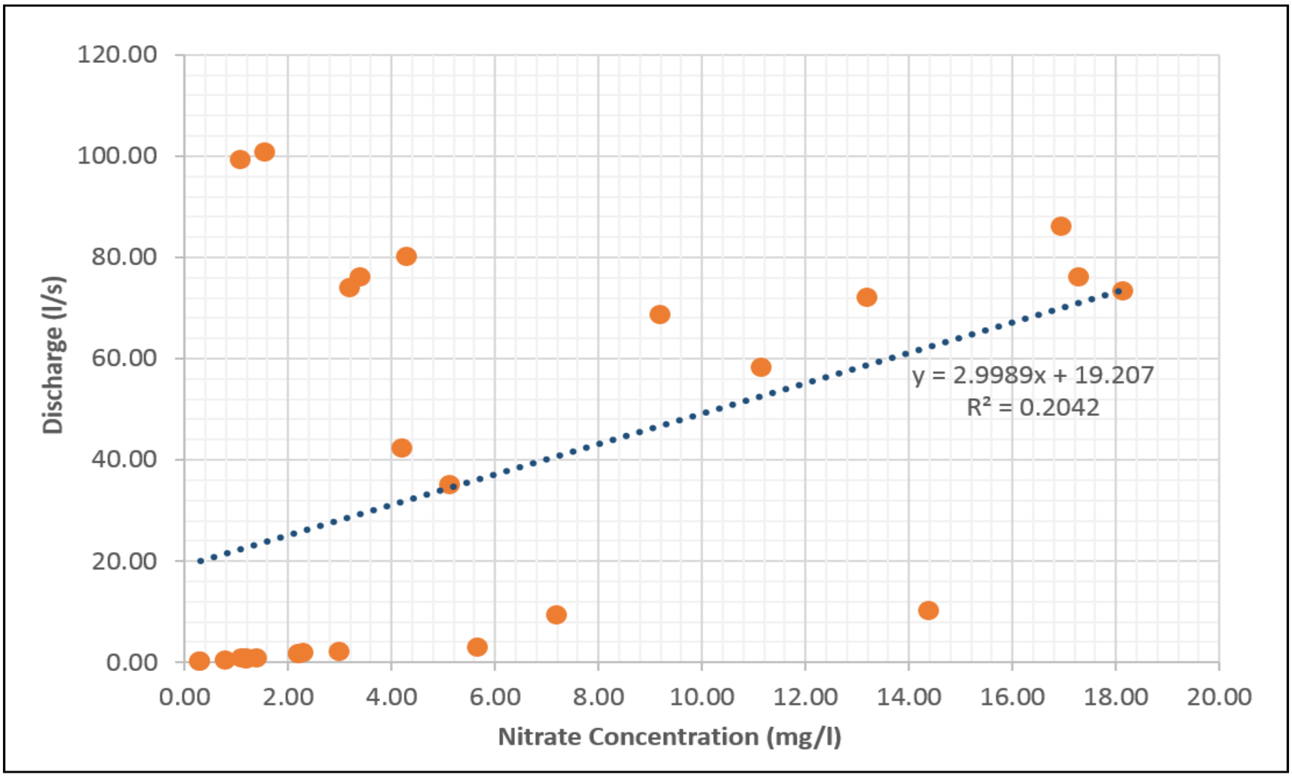

Figure 5. Correlation Graph of spring flow discharge and nitrate concentration

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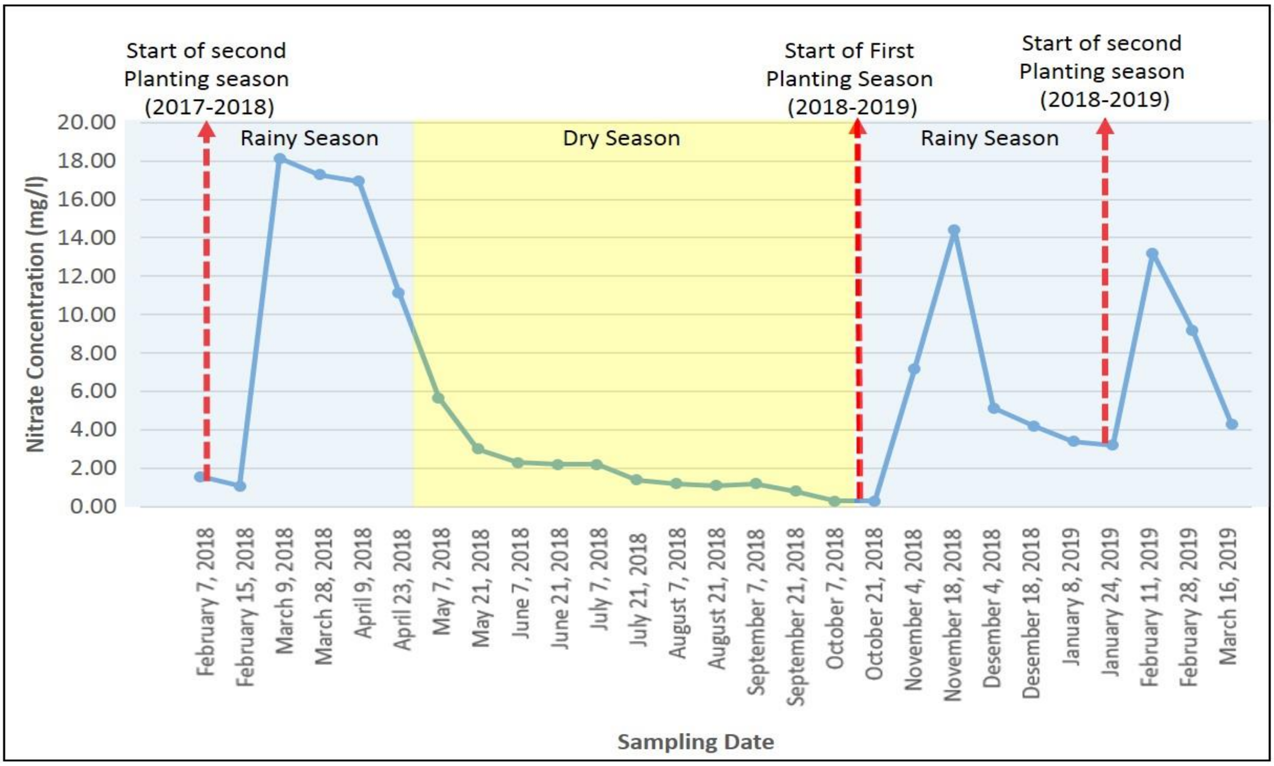

Figure 6. Temporal Variation of Nitrate Concentration and Its Correlation to Cropping Patterns in the Guntur Springs Karst Drainage Basin

Based on the results of the study above, control of nitrate concentrations in groundwater flows or underground rivers at the study location in Guntur Springs and its surroundings can be done by applying fertilizer in more appropriate amounts at the start of the planting period. Providing the right amount of fertilizer at the beginning of the planting season can reduce the amount of fertilizer that will not be absorbed by plants, thereby reducing nitrate concentrations in the soil and surrounding groundwater. One additional measure involves applying mulch to the soil at the start of the planting season, which mitigates the accelerated erosion caused by insufficient vegetation coverage. Moreover, safeguarding ponors or swallow holes, sinkholes, and conduits directly connected to underground rivers by constructing embankments or utilizing organic plant debris can further diminish the influx of soil directly into the karst aquifer system.

Long-term use of water from Guntur Springs for drinking water requires further processing to reduce pollutants and other physical, chemical, and biological aspects. Several methods that can be implemented include sedimentation methods, the use of coagulants, filtration, and bioremediation using several plants that can reduce pollutants in the water[53,54,55]. In addition, regular and real time monitoring by taking samples to ensure the suitability of Guntur Spring as a drinking water source is also something that needs to be done[56,57,58] by the responsible agency[59, 60,61] with the involvement of the surrounding community[62,63,64].

Conclusion

Temporal variations in nitrate concentration in Guntur Springs show concentration values that increase during the rainy season and decrease during the dry season. However, the overall nitrate concentration in Guntur Springs throughout the year is generally still below the quality standards applicable at the research location. This condition is influenced by the character of the karstification level of the Guntur Springs Karst Drainage Basin which is still dominated by fissure flows that have just formed conduit. The low level of karstification at the research location makes it possible for natural filtration processes to occur by soil and rocks. The analysis results also show low correlations between nitrate concentration and other variables, namely biweekly rainfall and spring discharge. Research shows that the main factor behind a high concentration of nitrate in the flow of Guntur Springs is the cropping pattern in the nearby area. This is observed from the nitrate concentration value which increases significantly at the beginning of the planting season and gradually decreases along with the growth of seasonal crops planted on agricultural land.

Acknowledgment

The researcher would like to thank all parties who have helped with this research. We would like to express our gratitude to the government bodies who have granted us research permission and provided a lot of assistance during the research, particularly to the government of Dringo Hamlet, Girijati Village, Purwosari District, Gunungkidul Regency, Yogyakarta.

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of write the name of the university or center of which you received the approval.

Authors' Contribution Statement

A.C. and I.A.R contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

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Published Online First: July, 2024
https://doi.org/10.21123/bsj.2024.10610
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

التباين الزمني لتركيزات النترات في نبع الكارست في الجزء الغربي من منطقة جونونجسيوو كارست، جزيرة جاوة، إندونيسيا

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الخلاصة

أصبح وجود النترات في الماء مصدر قلق للعديد من علماء البيئة لأنه أدى إلى انخفاض جودة المياه المستخدمة لتلبية احتياجات الناس من المياه النظيفة. من المتوقع أن توفر دراسة التغير الزمني للنترات في تدفق المياه فهمًا كاملاً للعوامل المؤثرة التي يجب إدارتها للتحكم في تركيز النترات في الماء. تهدف هذه الدراسة إلى تحليل التغيرات الزمنية في تركيز النترات في نبع جونتور، أحد الينابيع في منطقة جونونجسيو كارست والذي يلعب دورًا في توفير المياه النظيفة. تشمل البيانات المستخدمة في هذا البحث بيانات عن تركيز النترات في مياه الينابيع، وهطول الأمطار، وتصريف الينابيع. تم إجراء أخذ العينات كل أسبوعين من فبراير 2018 إلى مارس 2019 لفهم التباين الزمني في تركيزات النترات. تم الحصول على بيانات التصريف وهطول الأمطار من التسجيل التلقائي خلال نفس فترة أخذ عينات المياه لتحليل النترات. وتظهر النتيجة أن تركيز النترات على مدار العام في نبع جونتور لا يتجاوز معايير الجودة. ترجع جودة المياه الجيدة إلى عملية الترشيح الطبيعية التي لا تزال تسير بشكل جيد بسبب انخفاض مستوى الكارستات الذي لا تزال تهيمن عليه تدفقات الشقوق. بالإضافة إلى ذلك، وجد هذا البحث أن الاختلاف الأكثر تأثيرًا في تركيز النترات في تدفق الربيع في جونتور سبرينج هو نمط المحاصيل في المنطقة.

الكلمات المفتاحية: النترات، نبع الكارست، النمط المحصولي، تطور الكارست، التباين الزمني.