Nitrate contamination level in groundwater of the randublatung basin and its surroundings

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Abstract. The community of Randublatung basin and its surroundings (Grobogan, Blora, and Bojonegoro Regencies) using groundwater for agricultural, farming, and daily needs. However, these activities can contaminate the groundwater through nitrate and chloride in fertilizers, pesticides, animal waste, and household waste. Therefore, it is crucial to know the amount of nitrate and chloride content in the groundwater of The Randublatung basin and its surroundings. This research aims to analyze nitrate and chloride content and the ratio between ions in the groundwater of The Randublatung basin and its surroundings to find contaminant resources. The method to analyze the nitrate and chloride content is using Ion Chromatography. The analysis result from 35 samples of groundwater shows that the average nitrate content in dug wells samples is 10.06 mg/L, while the average from pump wells is 6.31 mg/L. The average chloride in dug wells samples is 43.65 mg/L, and the average from pump wells is 54.57 mg/L. These nitrate and chloride level are still in safe category based on Health Ministry Indonesia and WHO. The nitrate: chloride ratio in dug wells is 1:5, 1:9 from pump wells. The ratios indicate that the nitrate's resource is associated with the on-site sanitation and will increase if there is no mitigation action to the contaminant resource.

1. Introduction
Groundwater is a water resource to fulfill the community's daily needs, agriculture, and farming, for example, the people of Randublatung basin and its surroundings. The basin's location is in Grobogan, Blora, and Bojonegoro Regencies, as seen in Figure 1. Based on the physiological condition, Randublatung Basin is between two hills of Randublatung Depression Zone [1]. The two hills are Rembang Hills on the north side and Kendeng Hills on the south side.

In 2020, Grobogan Regency had 1.02% of population growth with 51.789 Ha of paddy field and 199.584 of livestock [2]. While in Blora Regency in the same year, the population growth is 0.64% with 253.776 Ha of paddy field and 175.326 of livestock [3]. In 2020 Bojonegoro Regency has 0.23% of population growth and 4.398 Ha of agricultural land [4]. The population growths indicate the increase in domestic, agriculture, and farming activities.

Meanwhile, these activities will also produce contaminants, such as nitrate and chloride, in fertilizers, animal waste, and household waste [5]. Then, the contaminants will enter the soil and mix with groundwater. This is how there is nitrate and chloride content in groundwater.
Groundwater that consumable is groundwater with nitrate content less than 50 mg/L [6, 7]. Consuming groundwater with higher nitrate content can cause methemoglobinemia or blue baby syndrome in infants and gastrointestinal cancer in adults [5, 8]. While chloride affects the acceptability of groundwater [9, 10]. The ratio between nitrate and chloride can determine the source of nitrate. If the nitrate:chloride ratio is between 1:1 and 8:1, then the nitrate is likely from faecal source [11-14]. Therefore, it is crucial to know the nitrate and chloride content of groundwater in Randublatung Groundwater Basin and its surroundings so that later steps can be taken to prevent groundwater contamination from getting worse.

Nitrate and chloride content in groundwater can be identified with Ion Chromatography. This method was applied in 2015 on Eğirdir Lake, Turkey [15], 2019 on Tehran, Iran [11], and 2020 on North Maluku [16]. According to the studies mentioned, this research uses Ion Chromatography to determine the nitrate content in the groundwater of Randublatung Groundwater Basin and its surroundings. Samples that tested were 35 samples of groundwater from dug wells and pump wells.

This research aims to analyze nitrate and chloride content and the ratio between ions in the groundwater of The Randublatung Groundwater Basin and its surroundings to find the contaminant resources. It is hoped that this research can provide an overview of the condition of groundwater in Randublatung Groundwater Basin and its surroundings.

Figure 1. Study area of the research and the locations of groundwater sampling from pump wells (♦) and dug wells (●)

2. Methodology
The groundwater samples are from dug wells and pump wells. From 35 samples, 20 are from dug wells, and 15 are from pump wells. Samples were kept in the HDPE bottle and the cooling box. The cooling box is used to prevent microbial activity and carbonate deposition in the samples for anions testing [17].

Analysis of nitrate and chloride content in the groundwater is using Ion Chromatography Metro Ohm 850 Professional IC. Before the testing, samples have to be filtered with 0.2 µm filter. The amount of sample used for testing is about 50 ml.

Nitrate resources analysis is using a comparison chart between nitrate content and chloride content in the groundwater [11-14]. The anions testing result was plotted on the diagram, and then the nitrate:chloride ratio can be obtained.
3. Results and discussions

The result of nitrate and chloride content in the groundwater of Randublatung Basin, shown in Table 1, and Figure 2 shows the nitrate distribution. Nitrate and chloride content measured in mg/L. The average nitrate content in dug wells groundwater is 10.06 mg/L (range 0.34 mg/L to 52.04 mg/L). There is one sample that reaches the limitation of nitrate content for drinking water that is 50 mg/L [6, 7]. The sample is SGL 03 that located in the northeast side of the basin. The formation of rock in this location is Tambakromo Formation that consists of claystone, marl, and limestone [17, 18]. SGL 03 administratively is located in Kedungtuban District of Blora Regency. The high concentration of nitrate in SGL 03 can be caused by the high activity of agriculture in Kedungtuban District. There are 16 districts in Blora Regency, where the 10% of agriculture activity is in Kedungtuban District [3].

While in the groundwater of the pump well, the average is 6.31 mg/L (range 0 mg/L to 29.72 mg/L). There is no sample that reaches the limitation of nitrate content for drinking water, but the highest is in sample SGC 01. The nitrate level above 10 mg/L shows that the groundwater has been affected by the surface activities [5]. From the nitrate level in dug wells and pump wells samples, the groundwater from pump wells is likely safer than groundwater from dug wells.

The chloride level is generally high in sewage and manure; thus, chloride is an indicator of sewage [13]. The chloride content is 43.65 mg/L average (range 2.83 mg/L to 117.50 mg/L) in dug wells samples, while in the pump wells samples is 54.57 mg/L average (range 4.64 mg/L to 271.36 mg/L). The chloride content in the dug wells samples is still within the limits permitted by WHO and Ministry of Health Indonesia for consumption as drinking water. While in the pump wells samples there is one sample that exceeds the permissible limit. The sample is SGC 01. SGC 01 is highest in both parameters, nitrate and chloride of pump wells samples.

Geologically, formation of rock in the location of SGC 01 is Alluvial Deposits that consist of sand and gravel that have high permeability [17, 18]. Hydrogeologically, this formation of rock is potential to be an unconfined aquifer [19]. SGC 01 location is near the Bengawan Solo River (on the north side of the river). Based on the lithology and hydrogeology condition, the substance from surface can easily get into the ground. Administratively, SGC 01 is in the Cepu District of Blora Regency. Based on population density, Cepu District is the most populous district in Blora Regency. Therefore, the chloride concentration in SGC 01 is very high.

Table 1. Nitrate and chloride content in the groundwater of Randublatung Groundwater Basin

| No. | Sample Name | Nitrate (NO₃⁻) mg/L | Chloride (Cl⁻) mg/L | No. | Sample Name | Nitrate (NO₃⁻) mg/L | Chloride (Cl⁻) mg/L |
|-----|-------------|---------------------|---------------------|-----|-------------|---------------------|---------------------|
| 1   | SD 01       | 5.60                | 2.83                | 11  | SGL 03      | 52.04               | 78.89               |
| 2   | SD 04       | 1.89                | 20.76               | 12  | SGL 04      | 16.12               | 25.17               |
| 3   | SG 02       | 4.84                | 91.08               | 13  | SGL 08      | 0.34                | 117.50              |
| 4   | SGB 03      | 27.40               | 56.38               | 14  | SGL 09      | 7.12                | 26.68               |
| 5   | SGC 10      | 1.44                | 22.53               | 15  | SG 18       | 2.97                | 18.84               |
| 6   | SGC 20      | 9.98                | 91.09               | 16  | SGB 72      | 2.93                | 3.38                |
| 7   | SGC 30      | 37.28               | 90.45               |          |            |                      |                     |
| 8   | SGC 01      | 4.78                | 28.06               |          |            |                      |                     |
| 9   | SGB 03      | 6.54                | 11.46               |          |            |                      |                     |
| 10  | SGC 02      | 11.53               | 15.44               |          |            |                      |                     |
| 11  | SGC 03      | 0.09                | 12.21               |          |            |                      |                     |
| 12  | SGC 04      | 0.00                | 61.81               |          |            |                      |                     |
| 13  | SGC 29      | 0.19                | 24.23               |          |            |                      |                     |
| 14  | SGC 30      | 0.30                | 17.81               |          |            |                      |                     |
| 15  | SGC 412     | 0.99                | 36.84               |          |            |                      |                     |
| 16  | SGC 03      | 29.72               | 271.36              |          |            |                      |                     |
| 17  | SGC 01      | 115.03              | 32.08               |          |            |                      |                     |
No. | Sample Name | Nitrate (NO₃⁻) mg/L | Chloride (Cl⁻) mg/L | Nitrate (NO₃⁻) mg/L | Chloride (Cl⁻) mg/L
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18 | SG 135 | 1.22 | 18.99 |
19 | SGB 14 | 1.21 | 9.40 |
20 | SGB 16 | 6.28 | 33.18 |

**Figure 2.** Nitrate content distribution in groundwater of Randublatung basin and surroundings

The ratio between nitrate and chloride content is shown in Figure 3. On the pump well samples, the ratio between nitrate and chloride is 1:9 and on the dug well is 1:5. The positive ratio also appears in Tehran, Iran, where the nitrate: chloride ratio shows that the nitrate content comes from sewage [11]. The same thing is also shown in the research in Dharapuram, India, where the nitrate: chloride ratio indicates that the nitrate content is from domestic sewage or agricultural inputs [12]. The positive ratio also appears in South China, where the nitrate: chloride ratio of almost 1:1 indicates that nitrate comes from anthropogenic sources, such as sewage and manure [13]. In Nagpur, India also shows a positive correlation between nitrate and chloride, which indicates that surface activities (domestic solid waste and fertilizers) causing nitrate pollution [14]. So that in this research, the ratio between nitrate and chloride indicates that nitrate’s resources are associated with on-site sanitation.
4. Conclusions

The conclusions of this research are:

a. The nitrate content in groundwater of Randublatung basin and its surrounding from dug wells samples is 10.06 mg/L average with the lowest is 0.34 mg/L and the highest is 52.04 mg/L. While the nitrate from pump wells samples is between 0 mg/L to 29.72 mg/L with 6.31 mg/L average. The number of samples that have a nitrate value above the Health Ministry of Indonesia and WHO permitted value is 1 sample of dug wells and none from pump wells samples. From nitrate concentration levels indicate that groundwater from pump wells is likely safer than the groundwater from dug wells;

b. The chloride content in groundwater from dug wells is between 2.83 mg/L to 117.50 mg/L and 43.65 mg/L on average. While the chloride content in pump wells is between 4.64 mg/L to 271.36 mg/L with 54.57 mg/L on average. There is no sample that exceeds the limit allowed by WHO and Ministry of Health Indonesia on dug wells samples, but 1 sample of pump wells samples exceeds the limit. Based on chloride level, the groundwater from dug wells is likely safer than groundwater of pump wells;

c. The ratio of nitrate content and chloride content of dug wells samples is 1:5, while samples from pump wells show a 1:9 ratio. The ratio indicates that nitrate's resources are associated with on-site sanitation and will increase if there is no mitigation action to the contaminant resource.

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