The impact of nitrogen fertilizer on the aquatic environment in the Upper Tondano watershed, North Sulawesi Province

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Abstract. Nitrogen fertilization is needed as a source of nitrogen in the growing plants. Nitrogen in the environment will undergo transformation in the form of compounds such as nitrate (NO\(_3\)-) and nitrite (NO\(_2\)-). The transformation from nitrogen to nitrate, nitrite, will have a negative impact on the aquatic environment namely the formation of toxic conditions. The main purpose of this research was to study the residual nitrogen fertilizer in the outlet of paddy irrigation upper Tondano Watershed and to evaluate the residual nitrogen fertilizer in the outlet of paddy irrigation upper Tondano Watershed 5-years period (2015-2019). Water quality sampling was carried out using a composite sampling method at two sample locations in River Panasen, in situ measurement of water temperature parameters, and pH. Analysis of the parameters of nitrate and nitrite was carried out in the laboratory. Data were analyzed using descriptive statistics. The results showed that the concentration nitrate of 0.933-153 mg/l (according Government standard PP No. 82/2001 nitrate 10 mg/l), and nitrite of 0.001 mg/l-0.52 mg/l exceed PP No. 82 /2001 quality standard (0.006 mg/l).

1. Introduction
Nitrogen fertilization is needed in the vegetative period. Nitrogen is indispensable for the growth and development of plants. The forms of nitrogen in the environment undergoes a transformation as part of the nitrogen cycle like nitrification and denitrification [1]. The presence of nitrogen in the environment has both positive and negative effects because nitrogen in the environment will undergo transformation into the forms of NO\(_3\), and NO\(_2\) compounds, through the processes of nitrification, nitrate reduction, denitrification [2]. Nitrate is a nutrient for the growth of aquatic plants and algae. Nitrite is a toxic compound that can kill water organism. The forms of nitrogen in the environment undergo a transformation as part of the nitrogen cycle. The forms of nitrogen transformation in the environment are nitrification, nitrate reduction and denitrification.

Nitrogen is a major component of plants and animals. Weathering of organic matter produces ammonia, and when oxygen is available the ammonia turns into nitrate. Intensive agricultural activity in the Tondano watershed has been going on for years and has resulted in agricultural residues that have the potential to reduce the quality of surface water such as rivers. River Panasen is a river that crosses the upstream rice fields of Tondano watershed and the river flows into Lake Tondano.

Irrigation channels will carry the remains of nutrients from fertilization activity, in particular, the use of urea fertilizer. Urea [CO (NH\(_2\)\(_2\))] would be hydrolyzed to produce ammonium nitrate, and plants absorb those nutrients in form of ammonium (NH\(_4\)+) and nitrate (NO\(_3\)-), is not absorbed by the plants it will flow into the irrigation channels and water bodies ie rivers. This is correlated with the residual nitrogen in the outlet channel and irrigation upper Tondano Watershed.
The main purpose of this research was to study the residual nitrogen fertilizer in outlet of the paddy irrigation Tondano Watershed. The next interesting point was to evaluate the residual nitrogen fertilizer in outlet of the paddy irrigation upper Tondano Watershed 5-year period (2015-2019).

2. Methods
The materials used for this study were water samples of River Panasen (figure 1), aquadest, tissue, name label to mark containers and writing instruments. This study also need tools for taking water samples (water sampler, icebox, GPS and in situ measurements (pH meter, and thermometer), and equipment in the laboratory, i.e., spectrophotometer. The primary data for water quality were obtained by taking directly water samples from two sampling points of River Panasen (Fig.1) and then analyzed in accredited KAN laboratory, WLN (National Accreditation Committee Testing Laboratory LP- 433-IDN). Sampling points and water samples were determined based on river water flows [3]. Method of sampling was composite sampling [4].

The parameters observed in laboratory were nitrate, nitrite, while pH and temperature were measured directly in the field. Nitrate and nitrite refers to the APHA Method [5]. Water classification is based on Nitrate value; below 10 mg/l, and nitrite below 0.006 mg/l is according to the quality standard [6].

Figure 1. Water sampling location

The data obtained in this study were analyzed using the Spectrophotometry Method. Next, the results compare with Quality Standard according to Government Regulation number 82/2001 Regarding Water Quality Management and Water Pollution Control [6]. Finally, it is analyzed using descriptive statistics.
3. **Results and Discussion**

The results showed that nitrogen transformed into nitrate in the river Panasen of the Tondano watershed. The concentration of nitrate was 0.153-0.933 mg/l and still met water quality standard based on PP No. 82/2001 (nitrate 10 mg/l).

![Figure 2](image-url)

Figure 2. Nitrate concentration in the Upper Stream of Tondano watershed

Figure 2 shows the concentration of nitrate in the upper part of river Panasen in Tondano watershed. The results showed that the concentration of nitrate was 10 mg/l, which still met the quality standard based on Government Regulation number 82/2001. Distribution of nitrate is more concentrated at the river outlet [7].

The results also showed that the transformation of nitrogen to nitrite in the upper river Panasen in Tondano Watershed. The concentration of nitrite was 0.001-0.52 mg/l. This concentration has exceeded the quality standard based on Government Regulation PP 82/2001 (nitrite 0.006 mg/l) as shown in figure 3.
Figure 3 shows that the nitrate concentration fluctuates for each month in each year. The highest concentration was in September and March. Based on the data recorded, in September 2016 the nitrate concentration in River Panasen 1 was 0.25 mg/l and in River Panasen 2 was 0.52 mg/l. In September 2018, the nitrate concentration in River Panasen 1 was 0.073 mg/l and in Panasen 2 was 0.023 mg/l. In March 2016, the nitrate concentration in River Panasen 1 was 0.074 mg/l and in River Panasen 2 was 0.084 mg/l and In March 2018 the nitrate concentration of River Panasen 1 was 0.212 mg/l and in River Panasen 2 was 0.084 mg/l. In March 2019 the nitrate concentration in River Panasen 1 was 0.093 mg/l and in River Panasen 2 was 0.28 mg/l. This condition is caused by the fact that in September and March the time was for farmers to fertilize using nitrogen fertilizer, including Urea (CO (NH)\(_2\)) fertilizer. In lowland rice plants, in the other month farmers generally do not carry out fertilizing activities. This was based on the results of interviews with farmers about fertilization time. Nitrogen residues in aquatic environments can undergo nitrification. Nitrification is the oxidation of ammonia to nitrate and takes place under aerobic conditions.

Based on data recorded, the concentration of nitrite has exceeded quality standards. In June 2018, the nitrite concentration in River Panasen 1 was 1.45 mg/l and River Panasen 2 was 0.084 mg/l). In June 2019 the nitrite concentration of River Panasen 1 was 0.005 mg/l and River Panasen 2 was 0.135 mg/l). This tendency is the same as the condition of nitrate which is the highest concentration found in March and September. The high concentration of nitrates in the river Panasen is caused by the application of nitrogen fertilizer such as Urea (CO (NH)\(_2\)) in paddy fields and horticulture land [8]. The residue of dominant agricultural waste comes from leaching residues during fertilization in agricultural activities about 77% of the catchment area is used for intensive agricultural cultivation land, and forest, settlements, swamps and solfatara [9].

Transformation of nitrogen into nitrite through the process of nitrate reduction and denitrification. Nitrate reduction is nitrate as an electron receptor that always produces Nitrite (NO\(_2\)) at pH 7 following the chemical reaction.
1/2 \text{NO}_3 + 1/4 \text{(CH}_2\text{O}) \rightarrow 1/2 \text{NO}_2 + 1/4 \text{H}_2\text{O} + 1/2 \text{CO}_2

4. Conclusion
The highest concentration of nitrate and nitrites found in the upper part of River Panasen in Tondano watershed. There is an increasing concentration of nitrate and nitrite residues in the upper part of River Panasen in Tondano watershed during 5 years period (2015-2019). The concentration of nitrate and nitrite has exceeded the standard level of quality in March and September. This condition is caused by the fact that in September and March the time was for farmers to fertilize using nitrogen fertilizer. Nitrogen residues in aquatic environments can undergo nitrification. Transformation of nitrogen into nitrite through the process of nitrate reduction and denitrification.

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