Nitrate and Phosphate Contents on Sediments Related to The Density Levels of Mangrove Rhizophora Sp. in Mangrove Park Waters of Pekalongan, Central Java

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Abstract. Mangrove Park waters area of Pekalongan City, Central Java, used to be an aquaculture field, now turning the function into a restoration-based mangrove area, and now it has undergone rehabilitation. The conditions may affect the distribution of nitrate and phosphate content. The objective of this study was to determine the content of nitrates and phosphates in sediments related to the density levels of mangrove Rhizophora sp. The method used in this research was a descriptive method, and sampling was done by purposive sampling method. Water and sediment sampling were conducted at three stations respectively, representing: no mangrove area but used as a residential and tourist area (station 1); less dense mangrove (station 2); and, the previously aquaculture field - or medium dense mangrove (station 3). The results showed that the content of nitrate and phosphate in the whole sediment showed a low fertility rate. Average nitrate content for station 1, station 2 and station 3 were 0.86 mg/100 g, 0.94 mg/100 g and 0.81 mg/100 g, respectively. The average phosphate content at each station were 1.14 mg/100 g, 0.04 mg/100 g and 0.05 mg/100 g, respectively. Except to the station 1 that was no vegetation anymore, the mangrove density levels at two other stations at study sites were relatively low to medium; at station 2 was 0.8 ind/10 m² and at station 3 was 1.2 ind/10 m². The role of nitrate and phosphate were for mangrove growth at the site.

Keywords: Nitrate, Phosphate, sediment, water, mangrove density

1. Introduction

Mangrove is an ecosystem with high organic productivity, and high biota diversity [1-2]. Mangroves usually grow in tropical and subtropical regions, growing only on coastal protected from wave action [3]. The role of mangroves other than as abrasion holder also has an ecological function as a provider of nutrients for aquatic biota [4].

Mangrove can bind sediment dissolved from the river [5]. The mangrove efficiency of suspended bonding of water column depends on various factors such as particle size, salinity, the tidal, and wide area of intertidal zone [6]. The value of binding efficiency can be very high at 15-44% [7]; 30-60% [8]; even up to 80% [9]. The presence of mangroves causes a lack of water movement to give a significant effect on the sedimentation of fine sedimentary particles that tend to congregate at the bottom [10]. Due to typical and dense root systems, it can cause soluble particles in water to settle around their roots, thus forming a collection of sedimentary layers [11]. Sediments that exist around this mangrove vegetation are then mixed with the litter [5]. Nutrient elements of organic matter will be deposited in the sediments and will be distributed by environmental factors [5]. This condition makes
the mangrove forest as a contributor of nutrients to other ecosystems in the vicinity [5]. Nitrate in the waters comes from the breakdown of organic and inorganic nitrogen in soils derived from the decomposition of organic materials with the help of microbes [12]. Phosphate in waters naturally comes from weathering of rocks and also decomposition of organic matter [13].

Mangrove density is influenced by the growth factor of the mangrove. According to Hossain and Nuruddin [14], mangroves typically grow in areas that have large river mouths, and their streams are rich in mud and sand. Mangroves derive nutrients from inorganic mineral ions and organic matter as well as from nutrient recycling internally through detrital based food web [5][15]. Inorganic nutrients such as N and P are essential nutrients that are needed by the organism because it can not be replaced by other elements. Nitrate (NO₃⁻) and phosphate (PO₄³⁻) are the major nutrients that determine the stability of vegetation growth such as mangroves [2]. Inorganic nutrient sources are rain, surface flow, sediment, seawater, and degraded organic materials [2]. Nitrate (NO₃⁻) is the main form of nitrogen in natural waters and is a major nutrient for plant growth [16]. NO₃⁻ is easily dissolved in water and stable [17]. This compound is produced from the perfect oxidation process of nitrogen compounds in the waters. Nitrification which is the process of oxidizing ammonia to nitrite and nitrate with the help of microorganisms is an important process in the nitrogen cycle [5].

Nitrification is a process consisting of two reactions namely the oxidation of ammonia to nitrite and subsequently oxidation of nitrite to nitrate [5]. The decomposed organic matter is the source of ammonia, which is the beginning of nitrate formation through the breakdown of organic and inorganic nitrogen present in soil and water with the help of microbes and fungi [5]. According to Reef et al [2], in mangrove ecosystems, nitrogen fixation is found to occur in sediments even though only a few centimeters at the top of the sediment layer [18], nitrogen fixation in sediments with upper mangrove vegetation is higher than the plantless sediments present above it, due to differences in detritus content present in the soil.

According to Kolliopoulos et al [19], the phosphorus element is not found in free form as an element but in the form of dissolved organic compounds (orthophosphates and polyphosphates) and particulate organic compounds. Phosphorus forms complexes with iron and calcium ions in aerobic conditions, soluble and deposited in sediments. The phosphorus present in seawater comes from the decomposition of dead organisms [20]. Orthophosphates are a form of phosphorus that can be directly exploited by aquatic plants, while polyphosphates must be reduced to orthophosphate before use. Phosphorus in the form of phosphate is a necessary micronutrient in small amounts but is essential for aquatic organisms [19]. Phosphate deficiency can also inhibit plant growth. Monovalent orthophosphate anions (H₂PO₄⁻) and divalent (HPO₄²⁻) are absorbed by plants from 50% of total soil solution at almost neutral pH (pH 6-7). At pH 4-6, H₂PO₄⁻ is absorbed about 100 percent, and at pH 8, H₂PO₄⁻ is absorbed by 20 percent and HPO₄²⁻ is 80 percent of total P [21].

In sediments, the main source of phosphorus is from terrestrial sediments that are eroded and agricultural fertilizers carried by streams [22]. The source of phosphorus (P) from anthropogenic activity can increase the level of soil erosion from soil to sea by about 300% [23]. Other fractions of soluble phosphate which are partially in the form of colloids are derived from the excretion of the organism and from the resulting autolysis of dead organisms [24]. The existence of various forms of phosphate in the ocean is controlled by biological and physical processes [25][24]. In sediments, these phosphate minerals are absorbed by hydrolyzed sediments, especially clays [26]. Increased orthophosphate is proportional to the increase in sediment concentration. Suspended materials may also carry the absorbed phosphate therein [26].

Pekalongan city is one of the urban areas in Central Java Province which has a tourism object based on learning place and mangrove restoration. Mangrove Park Pekalongan City was established in 2013 and is under the authority of DPPK (Dinas Pertanian, Peternakan, dan Kelautan / Department of Agriculture, Husbandry, and Ocean) of Pekalongan city. Land area used for mangrove restoration reached 5.7 Ha with more than 50% planted with various types of mangroves, and dominated by mangrove species of Rhizophora sp. The condition of the waters in Mangrove Park, Pekalongan is generally calm not affected by the currents or sea waves.

Mangrove park Pekalongan city, formerly a pond that has long not functioned. At the location is now built mangrove tourist attractions entitled restoration and used as a place of learning mangrove.
This is because the existing mangrove conditions in the region of Pekalongan increasingly apprehensive.

Research on the content of nitrates and phosphates in mangrove sediments has been widely practiced. But specifically in the waters of Mangrove Park, Pekalongan has never done research on nitrate and phosphate. Logically, the older the mangrove will be the more nitrogen content. This is because the root system is getting stronger so the plants can precipitate the mud that contains many nutrients. Also explained by Alongi [27], that the N content along with the increase in height and diameter of trees on Rhizophora sp mangrove species, but unlike the phosphate content in sediments have no linear relationship to tree age. The value of phosphate content is probably more influenced by input other sources derived from industry and fertilizer. While the total value of total organic carbon content is more influenced by the source of input from the river and the location around the mangrove plant.

Based on these considerations, the research on the content of nitrate (NO₃) and phosphate (PO₄) in the sediment to the level of mangrove density of Rhizophora sp in Mangrove Park waters, Pekalongan is necessary. The aim was to find out the content of nitrate (NO₃) and phosphate (PO₄) in the sediment in the waters of mangrove park, Pekalongan and its relation to mangrove density. Sediments play an important role in the provision of nutrients and stability of plant growth, because the sediment is the storage of chemical compounds accumulated from compounds in the water column. Described by Chaubey et al [28], observation of boundary nutrient content can help identifying the relationship between nutrient availability and plant growth. The results of this study were expected to provide information about the presence of nitrate and phosphate in the mangrove sediments in the waters of Mangrove Park, Pekalongan City to become a reference in the management of the mangrove forest at the future.

2. Methodology
This research was conducted in Mangrove Park waters, Pekalongan City in January 2016. The research material used was water and sediment samples, taken from three stations (station 1 = settlement & tourism, no mangrove, station 2 = less mangrove density, station 3 = previously aquaculture field - or moderate mangroves density). Distance between stations one to another is 87-94 meters. Determination of the station based on purposive sampling, and each station was done repetition sampling 3 times (Figure 1). The coordinates of each station was determined using the Global Positioning System (GPS) tool. Water samples were analyzed for Total Organic Matter (TOM) and Biological Oxygen Demand (BOD₅), while sediment samples were analyzed for nitrate (NO₃) and phosphate (PO₄) conducted at BPIK ((Balai Pengujian dan Informasi Konstruksi), Semarang. Measurement of parameters of the waters was done to support the research results. All data obtained were analyzed descriptively and the results were interpreted through histogram tables and graphs and the results of those analyzes were compared with the quality standard.
Figure 1. Study Site at the Pekalongan Mangrove Park Central Java

Water sampling was done at each substation. Samples of 600 ml of water were taken directly from the surface of the waters by using a polyethylene bottle [29], then TOM and BOD5 were tested [30].

Sediment sampling was conducted at each substation of 500 g taken at a depth of ± 20 cm using sediment grab. Sediment samples were analyzed for phosphate, nitrate, and sediment grain analysis. Phosphate analysis used Ascorbic Acid method and read the absorbance using spectrophotometer at wavelength of 880 nm [31]. Analysis of nitrate content by brucin method using spectrophotometer at 410 nm wavelength [31]. Sediment grain measurement analysis was performed to find out the substrate type with the method of sieving and hydrometer analysis and the result was read according to triangle of USDA texture triangle [32].

The measurement of environmental parameters was carried out directly during in situ sampling which includes temperature, salinity, pH, dissolved oxygen (DO) measurements.

Calculation of mangrove density at each station was done to determine the condition of mangrove vegetation. Calculation method of mangrove was by using plot sampling method. Samples were taken randomly from selected sampling point by using transect method (Figure 2.) which was expected to represent the characteristics of each station.

Figure 2. Plotting Method: 10 m x 10 m for Tree Category; 5 m x 5 m for Sapling Category; and, 1m x 1m for Seedling Category
Calculation of the amount of mangrove tree stands was done at an altitude of ± 1.3 m and has a diameter at Breast Height or dbh ≥ 10 cm in subplots of 10 m x 10 m; Sapling counting (seedling) with stem diameter 2≤ dbh <10 cm and height> 1 m; And Seedling sample calculation (seedlings) were performed on mangrove vegetation with height <1 meter in subplot measuring 1 m x 1 m [33]. According to Pellegrini et al [33], the density is the number of individuals per unit area. The calculated density value has an ind /m² unit, using the formula:

\[
\text{Density} = \frac{\text{Number of individuals of a species in all plots (ind)}}{\text{Plot area (m²)}}
\]  

(1)

3. Results and Discussion

3.1. Water Quality Measurement, Phosphate & Nitrate in Sediment and Substrate Type

In situ field, water quality measurements and the results of phosphate nitrate analysis on sediment and substrate type ex situ (laboratory) were presented in Table 1.

Table 1. Water Quality Measurement, Phosphate and Nitrate Analysis in Sediments and Substrate Type at Study Site (X ± SD, n=3)

| Station | Water Quality | Sediment Analysis | Substrate Type |
|---------|---------------|------------------|----------------|
|         | pH Air | Salinity (ppt) | Temperature (°C) | DO (mg/L) | BOD₅ (mg/L) | TOM (mg/L) | NO₃ (mg/100 g) | PO₄ (mg/100g) | N:P Ratio |
| I       | 7.30-  | 24.00-  | 30.00-  | 8.30- | 11.04- | 24.76- | 0.86±0.65 | 1.14±0.09 | 0.75:1  |
|         | 8.70-  | 26.00-  | 31.00-  | 8.70 | 12.60 | 25.40 | 0.94±0.19 | 0.04±0.02 | 23.5:1  |
| II      | 7.90   | 24.00-  | 29.80-  | 5.90- | 16.50- | 29.15- | 0.94±0.19 | 0.04±0.02 | 23.5:1  |
|         | 6.30-  | 26.00-  | 30.30-  | 7.30 | 17.00 | 29.69 | 0.81±0.32 | 0.05±0.001 | 16.2:1  |
| III     | 6.87   | 27.00-  | 29.80-  | 4.20- | 16.30- | 26.99- | 0.81±0.32 | 0.05±0.001 | 16.2:1  |

Standard Quality

| pH | Salinity | Temperature | DO | BOD₅ | TOM | NO₃ | PO₄ | N:P |
|----|----------|-------------|----|------|-----|-----|-----|-----|
| 7- | 8.5(*)   | 0-34(*)     | 28-32(*) | >5(*) | 20(*) | 0.01- | 0.03- | 30(*) |
| 8(*)|         |             |     |      |     |     |     |     |

Sources: *) [34]  ***) [35].

Based on the results of the measurement of water quality at the site, it could still support the life and growth of the mangrove optimally because it was still in the range of existing quality standards according to the [34].

3.2. Nitrates (NO₃) in Sediments

Based on the result of measurement of nitrate content (NO₃) in sediment, the result showed that varied 0.81-0.94 mg /100 g. The highest nitrate content was in station II of 0.94 mg/100 g; Station I of 0.86 mg/100 g and the lowest at station III is 0.81 mg/100 g. (Table 1 & Figure 3).

Decomposition of mangrove litter is related to bacterial activity that is influenced by chemical physics parameters such as temperature, salinity, and pH. The salinity value affects the number of littering, the higher the salinity, the more litter produced [36]. However, salinity is negatively correlated with decomposition rate of mangrove litter, the higher the salinity, the slower decomposition rate of mangroves, and the lower the decomposition rate, the faster. The measured salinity at the time of observation in the three station locations had a low value that was between 24-27
ppt when compared with the quality standard according to Decree of the State Minister of Environment No. 51 of 2004 that was 0-34 ppt.

Figure 3. NO₃ and PO₄ Contents in Sediments at the Study Site at the Pekalongan Mangrove Park

The content of nitrates in sediments is also influenced by the rate of nitrification. According to Reef et al [2], the most significant environmental factors in controlling nitrification rates are pH, temperature, substrate, and oxygen (DO) availability.

According to Hossain and Nuruddin [15], pH is a determinant of the absence of nutrients absorbed by the soil and affect the development of microorganisms. Low pH causes the nitrification process to run slowly so that the resulting nitrate is low. In contrast, high pH (base) is the optimum pH for nitrification process. It is proven that the content of NO₃ in sediment at station II has a higher value than other stations, presumably because the pH at station II approaching the value of 8 is around 7.50-7.90.

At high pH (base) ammonia the degradation of organic matter can be present in non-ionized form (NH₃) which is toxic, otherwise low pH ammonia present in ionized form (NH₄⁺) [2]. By dissolved oxygen the ammonia compound (NH₃ and NH₄⁺) will undergo oxidation process to nitrate (NO₃). This oxidation process is assisted by nitrification bacteria nitrosomonas and nitrobacter bacteria [2]. Nitrification reaction according to APHA [35] as follows:

$$2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- (\text{nitrit}) + 4\text{H}^+ + 2\text{H}_2\text{O} \text{ (Nitrosomonas bacteria)} \quad (2)$$

$$2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^- \text{ (Nitrobacter bacteria)} \quad (3)$$

The nitrite compound (NO₂⁻) produced is a compound between the oxidation of the ammonia compound, which then continues to produce nitrate (NO₃⁻) by the aid of nitrobacter bacteria.

The high content of nitrate in sediment at station II was also due to the type of substrate in the location dominated by silt which was 60%, while in station I and III sand was dominated by 53% and 58% respectively (Figure 4). In accordance with the results of research [16], the higher the percentage of silt or Clay in the sediment, the higher the nitrate content.
According to Zhu et al [37], the smaller sediment size, the greater the availability of nutrients N and P in the substrate, as well as the larger the size of the sediment the availability of N and P elements is lesser [38]. This is because the fine-textured soils have a larger surface area so that the ability to hold water and provide high nutrients, while sand-textured soils have a smaller surface area making it difficult to hold water and nutrients [39]. Silt and clay particles have a higher ability to trap nutrients because they have finer particles than sand [40].

The content of nitrates in sediments is also influenced by the content of organic matter in the waters. According to Reef et al [2], the availability of nutrients in mangrove production is controlled by various biotic and abiotic factors such as tidal inundation, elevation in the tidal framework, soil type, redox status and soil microbial activity, plant species, litter production and decomposition [2]. The total organic matter content (TOM) in station II has a higher value than other stations that is equal to 29.15-29.69 mg/L. The amount of TOM content in these waters is suspected to come from the mangrove litter, waste disposal from human activities, considering that in the area other than close to the residential area is also the center of the area based tourist attractions and mangrove restoration. The decomposition of organic matter will increase the number of soil organisms and result in increased phosphate and organic nitrate in the network of microorganisms and can improve the environment to be more suitable for plant growth.

Based on the results of nitrate content analysis on sediments in the study sites belong to the classification of less fertility, because the value ranged from 0.81 to 0.94 mg/100 g. According to Effendi [41], nitrate content < 0.227 mg/L (< 2.27 mg/100 g) classification of less fertility; 0.227-1.129 mg/L (2.27-11.29 mg/100 g) classification of moderate fertility; and 1.130-11.250 mg/L (11.30-112.50 mg/100 g) classification of high fertility.

In Mangrove Park waters, Pekalongan is still possible to do mangrove growth effort, because almost every location of TOM content station ranges from 24.76-29.69 mg/L. According to Afu, [35] waters condition with organic matter content of 0.01-30 mg/L is still possible to do coastal conservation effort (support growth of mangrove).

3.3. Phosphate (PO₄) in Sediments

The result of measurement of phosphate content (PO₄) at the site, obtained an average value of 1.14 mg/100 g (station I); 0.04 mg /100 g (station II); and 0.05 mg/100 g (station III) (Table 1 & Figure 3).

At the station 1, it showed that the high content of phosphate was derived from the remnants of agricultural waste (fertilization), considering the Mangrove Park in Pekalongan city was once a farming area. Phosphate comes from terrestrial deposits that are eroded and from domestic waste input (detergent) deposited into the sediments. According to Childers et al [22], the main source of phosphorus in sediments is from terrestrial sediments that are eroded and agricultural fertilizers carried by streams, as well as from domestic waste [42]. Anthropogenic activity can also increase the level of soil erosion from the ground to the sea by about 300% [23]. According to Zhuang et al [43], suspended...
materials may also carry the phosphate absorbed therein. Reported by Vicente [44], organic matter in sediments also contributes to phosphorus retention by sediments.

The content of phosphates in sediments is influenced by the type of substrate. According to Strauch et al [15], sandy soils tend to have higher PO₄³⁻ alkalinity than litter dominated soil. This statement is by the results of research in Mangrove Park that at the station I has the highest phosphate value compared to stations II and III, suspected because the type of substrate is dominated by sand (sand) by 53%.

The high content of phosphate at station I is suspected due to the absence of mangrove vegetation grown on the site so that most of the phosphate is not utilized and settles in sediment. This condition is supported by the condition of waters in Mangrove Park which tend to calm and not much affected by the tides so that the content of phosphates in the sediment tends to be high.

Based on the measurement of phosphate content in sediment, the station I belong to very good fertility, while station II and III belong to low fertility. According to Effendi [41], the phosphate content of 0.00-0.20 mg/100 g classified as low fertility, 0.21-0.50 mg/100 g classified as sufficient fertility, 0.51-1 mg/100 g classified as good fertility, and phosphate values > 1 mg/100 g belong to excellent fertility.

3.4. Relationship of N:P with Mangrove Rhizophora sp Density

Based on the calculation of mangrove density, for station I was not found mangrove plant, while station II has a density of 0.8 individuals/10 m² and station III 1.2 individuals/10 m² (Table 2).

| Plant Category | Station I (ind) | Station II (ind) | Station III (ind) |
|----------------|----------------|-----------------|-------------------|
| Seedling       | -              | 6 ± 1,73        | 9 ± 2,64          |
| Sapling        | -              | 1 ± 0,57        | 1 ± 0,58          |
| Tree           | -              | 1 ± 0,57        | 2 ± 1,00          |
| Total          | -              | 8               | 12                |
| Density (ind/10 m²) | -            | 0,8             | 1,2               |

Note: - : no mangrove

Based on the calculation of mangrove density level, in Mangrove Park Pekalongan the site was moderate density. According to Giesen [45], the medium category of mangrove density if having ≥1000 - <1500 trees/hectare.

In Mangrove Park location, Pekalongan is dominated by Rhizophora sp. This is by the type of substrate in the location that is dominated by sand and silt substrate. According to Windusari et al [46], mangrove vegetation grows on substrate variation (sand, clay, and silt) where the condition of organic materials also varies according to substrate composition. Mangrove vegetation is more fertile at low salinity; high salinity mangroves consume more energy to maintain water balance and ion concentration than for primary production and growth [47]. This is proven on the salinity content at the research sites in Mangrove Park has a lower value that ranges from 24-27 ppt compared to the standard quality of 0-34 ppt.

The growth and structure of mangroves, in addition, to correlating with soil chemical physics characteristics also correlates with the ratio of nitrate to phosphate, soil moisture content, sedimentation rate, and soil quality [14].

The ratio value of N: P in sediment at station I is N:P = 0.75: 1; Station II ratio N:P = 23.5: 1; and station III ratio N:P = 16.2: 1. According to Sofawi et al [10], the N: P ratio on the substrate above 30 is considered to be evidence of P-limitation and N: P ratio less than 25-30 is considered to indicate N limitations. Based on this, the location of the study was classified as the criterion of N limitation, since in the third station has an N:P ratio of 0.75 to 23.5. The low value of the ratio is thought to be due to nutrients re-utilized by mangroves for growth. Mangrove requires elements of N and P for
growth and primary production. Nitrogen (NO$_3$-N) was required mangroves for protein formation, improved vegetative growth of plants and photosynthesis [16]. While phosphates are nutrients that are needed by all organisms for energy synthesis (ATP, NADPH), nucleic acids, protein and amino acid formation, and other important compounds [48].

Giesen et al [45], said that environmental factors such as tides, substrate textures also affect mangrove growth. The mangrove litter that is submerged in river water or tidal will experience faster decomposition, as well as nitrogen-rich organic materials will be broken-down quickly [16]. This statement is evidenced by the observations at station II that have high TOM will result in high nitrate decomposition of organic material, and silt particles (silt) have a higher ability to trap nutrients because it has finer particles than sand. Therefore, the ratio value of N:P generated at station II is higher than other stations.

The availability of nutrients is related to the allocation of root biomass. According to McKee [49], when nutrient availability (N:P ratio) is high enough, mangrove seeds will invest more in above ground biomass (by maximizing carbon acquisition) than at root, while when nutrient availability is low, mangrove seeds divert the source to improve root biomass. This is evident at the site at station 3 has a ratio of N:P is lower than station 2, it is suspected that the nutrient is used for the growth of root biomass so that the organic material produced is low.

4. Conclusion
The conclusion that can be drawn from this research is nitrate content (NO$_3$) and phosphate (PO$_4$) on sediment in Mangrove Park waters, Pekalongan is still classified into less fertility category, which ranged from 0.81-0.94 mg /100 g (nitrate ) and 0.04-1.14 mg /100 g (phosphate). Mangrove density in Mangrove Park is classified into medium density, which is about 0.8 ind /10 m$^2$ - 1.2 ind/10 m$^2$. The role of nitrate and phosphate for mangrove growth is to help regenerate the growth of mangroves itself. The high content of phosphate at station I was thought to be derived from the remnants of agricultural waste (fertilization) considering the Mangrove Park in Pekalongan city was once a farming area and from domestic waste input (detergent) deposited into the sediments.

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