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Distribution Analysis of Nitrate and Phosphate in Coastal Area: Evidence from Pangkep River, South Sulawesi

Waode Rustiah[1*], Alfian Noor[1], Maming[1], Muhammad Lukman[2], Baharuddin[3], Andi Tenri Fitriyah[3]

[1] *Department of Chemistry, Faculty Mathematic and Natural Science, Hasanuddin University, Indonesia.*
[2] *Marine Science Department, Faculty of Marine Science and Fisheries, Hasanuddin University, Indonesia.*
[3] *Faculty of Agriculture, University of Bosowa, Indonesia.*

[*] *Corresponding author's e-mail: waoderustiah79@gmail.com*

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ABSTRACT

Nitrate and phosphate nutrient and the other oceanographical parameter are part of an indicator to evaluate the quality of the water environment. Our research aims to determine the nitrate and phosphate levels in the water and sediment along the Pangkep coastal area. The research was conducted in February 2018 in coastal Pangkep using five sampling stations. Physico-chemical parameters of the water, such as temperature, pH, salinity, and dissolved oxygen were measured directly, whereas nitrate and phosphate parameters were analyzed using a spectrophotometer. In addition, nitrate and phosphate parameters from the sediment were measured using an atomic absorption spectrophotometer. The sediment nitrate values ranged from 0.026-0.442 mg/L, and the water nitrate values ranged from 0.018-0.063 mg/L. Moreover, the phosphate values from sediment ranged from 0.019-0.306 mg/L, and the phosphate values from the water ranged from 0.13-0.056 mg/L. The results show decreasing values of nitrate and phosphate concentration in the water and sediment starting from the estuary to the sea. The highest values were indicated in the estuary, which represents a eutrophic condition in the environment. Nutrient enrichment in coral reefs occurs and mixes with oceanographic conditions resulting in oxygen depletion and changes in benthic community structure.

Keywords:
Nitrate; phosphate; water quality; coast of Pangkep

1. Introduction

The coastal zone, especially estuaries, has received many anthropogenic additions from many sources (Bayram *et al.*, 2013; Strokal and Kroeze, 2013). For example, the Tallo River, which stretches alongside Makassar City, South Sulawesi, ending in the Makassar Strait, is known to have dense residences and several industries that directly connect to the river. Moreover, the coastal area of Pangkep has received large-scale runoff from agricultural activity, mining, fish farming, and domestic waste, which has caused accumulated organic and inorganic materials. Organic matter entering the water is determined by several factors, such as the river debit or runoff intensity, catchment area, rainfall intensity, and intensity of the organic matter (phosphate (P) and nitrogen (N)) in the mainland (Lihan *et al.,* 2008; Chazottes *et al.,* 2008).

Prolonged increased anthropogenic runoff will trigger the accumulation of organic matter in sediment form. Sedimentation is one of the processes caused by the changes in the environment, whether by natural or artificial causes. The sediment is suspended and accumulated in the environment and contains major and minor elements, such as O_2, CO_2, N_2, H_2, CH_4, N, NO_3, and P (Golterman, 2004; Schwarzenbach *et al.,* 2006).

Nutrients play an essential role in the ecosystem to enrich life and provide essential components, such as a food source for another organism, in this case, phytoplankton. Phosphate and nitrate are indicators to evaluate the quality of the water (Fachrul *et al.,* 2005). Major natural sources of phosphate and nitrate mostly come from the water body itself through decomposition, weathering, dead organism artifacts, and land-organic waste (domestic, industrial, agricultural, farming, and animal feed), which degrades by bacteria and is converted to a nutrient (Ruttenberg K.C, 2004; Paytan and McLaughlin, 2007).

Nitrate and phosphate are defined as nutrients that have key roles for phytoplankton growth and metabolism. The growth of phytoplankton is also considered an indicator to evaluate the condition and quality of the water (Fachrul *et al.,* 2005). Continuous organic matter supplied to the river body increases the amount of nutrients in the coastal area, causing eutrophication, which disturbs the ecological balance (Costa *et al.,* 2008; Faizal *et al.,* 2011).

Nitrate (NO_3) is the main form of nitrogen in a natural water body and is defined as a major nutrient for the growth of plants and algae. Nitrogen from nitrate is easily dissolved in the water, primarily in a stable form. This compound is produced by the complete oxidation of nitrogen compounds in the water. Thus, nitrification, which is the oxidation of ammonia into nitrite and nitrate with the aid of microorganisms, is an important process in the nitrogen cycle (Effendi, 2003).

Phosphorus in nature is mostly found in the form of ionic phosphate in organic or inorganic form. The appearance of this element in the soil layer was not stable, regarding to the reactive unstable mineral components that react with the water flow above (Golterman, 2004). This element easily degrades by erosion, weathering, and dilution. Along with these processes, the phosphate mineral decomposes to become phosphate ion, which plays a key role in the growth and metabolism of marine organisms (Paytan and McLaughin, 2007). In water and sediment, phosphorus is considered in the form of dissolved phosphate and particulate phosphate. In addition, the dissolved phosphate consists of organic phosphate (phosphate sugar, nucleoprotein, and phosphoprotein), while inorganic phosphate consists of orthophosphate and polyphosphate. The phosphate in the water degrades into an ionic form, such as H_2PO^{4-}, HPO_4^{2-}, and $PO4^{3-}$, which is then absorbed by phytoplankton and enters the food chain (Damar, 2004; Schulz, 2006).

Hence, it is necessary to conduct research to monitor the quality of nitrate and phosphate in the water and sediment environments. Research on Pangkep runoff is necessary to evaluate and identify the quality of the ecosystem.

2. Materials and Method

The sampling location was determined using a GPS (Table 1) and was carried out in February 2018. The sampling location along the Pangkep coastal area was chosen by measuring the area located next to the mainland, which was known to have dominant agricultural and fish-farming activity. Water and sediment samples were taken from five different stations.

Table 1. Coordinate of sampling station

Sampling Location	Latitude	Longitude
Pangkep River Estuary (MSP)	04.49.47.3	119.29.23.5
Laiya Island (P.LY)	04.48.31.9	119.24.30.4
Sarappo Keke Island (P.SKK)	04.48.20.8	119.13.31.2
Kondong Bali Island (P.KB)	04.43.24.0	119.02.34.4
Kapoposang Island (P.KPPS)	04.41.13.6	118.57.09.5

2.1. Water physico-chemical parameters

Seawater was collected using a 1-L bottle. The temperature, pH, salinity, and dissolved oxygen parameters were measured *in situ*, whereas the nitrate and phosphate concentrations were measured using spectrophotometry, using wavelength 543 nm for nitrate and 885 nm for phosphate.

2.2. Sedimental chemical parameters

The samples were collected using a grab sampler. About 1 kg of total sediment weight was sampled in each sampling location. The visual observation of the sediment in the Tallo and Pangkep River estuary showed it was mostly dominated by muddy smooth fraction, while sediment from the seawater formed mud with white granules and sand-like sediment. The samples were collected in plastic bags and transferred for laboratory analysis and preparation. The sediment was sifted using a 63-mesh filter with seawater. The sediment granules were mixed with water and deposited for a day. The filtering results were dried in a 60 °C oven. The dried samples were prepared for the nitrate and phosphate analysis using an atomic absorption spectrophotometer.

3. Results and Discussion

3.1 Determination of seawater physico-chemical parameters

The result of the water quality parameter analysis of the nitrate and phosphate concentrations in the water and sediment of Pangkep *runoff* are presented in Table 2. According to Table 2, the temperature of the seawater ranged from 29°C to 31°C. It was naturally occurring based on the physical position of the surface water, which is dominated by sun radiation in the daylight so that the temperature ranges in warm values. In addition, with the aid of the wind, the mixing of nutrients also naturally occurs in this surface water. The mixing event was located around 50–70 m in the surface to the inner water layer; however, this causes a homogenous temperature. Therefore, this layer is called the homogenous layer (Atmadipoera et al, 2004; Schwarzenbach et al., 2006). Furthermore, the pH values of the seawater show neutral values (7), and the pH values across the Indonesian seawater range from 6.0–8.5. In addition, high pH values will trigger the nitrification process. Effendi (2003) stated that the optimum pH values for nitrification are in the range from 8–9, which will produce a high nitrate concentration, whereas if the pH values are less than 6, the reaction will stop. Therefore, this information can be used as a consideration to conclude that the pH values of the sampling location are still in the normal state.

Table 2. Physico-chemical parameters in the water and sediment of Pangkep River

No.	Parameter of Water – Sediment Quality	Sampling Location				
		M.SP (I)	P. LY (II)	P. SKK (III)	P. KB (IV)	P. KPPS (V)
A	**Water physic**					
1.	Temperature (°C)	31	30	30	29	29
B	**Water**					
1.	pH	7	7	7	7	7
2.	DO (mg/L)	5	5	4	4	4,5
3.	Salinity (‰)	17	23	25	27	31
4.	Nitrate (mg/L)	0.057-0.063	0.034-0.057	0.034-0.049	0.025-0.037	0.018-0.022
5.	Phosphate (mg/L)	0.048-0.053	0.031-0.056	0.026-0.043	0.021-0.041	0.013-0.041
C	**Sediment**					
1.	Nitrate (mg/kg)	0.379-0.442	0.281-0.334	0.104-0.259	0.036-0.041	0.026-0.032
2.	Phosphate (mg/kg)	0.217-0.306	0.209-0.275	0.074-0.082	0.031-0.042	0.019-0.022

The optimum concentration of dissolved oxygen for organisms is around >5 mg/L (Wetzel, 2001). The result shows that, in the water environment in the Pangkep estuary, the dissolved oxygen concentration ranges from 4.5–5 g/L, while the salinity is around 17–31‰. The collected salinity concentration is categorized as low in the sampling location compared to other watery environments. The salinity concentration in the estuary is supposed to fluctuate based on the debit of fresh water that flows into the estuary, which dilutes the salinity. In addition, according to Yahia (2010) and Basit (2013), the values of salinity in the water environment are scattered and represent the water mass distribution from one area to another, for example, from the estuary to the coral reef ecosystem. High seawater salinity affects the nitrate concentration, and the nitrate concentration decreases with an increase of salinity (Lewi, 2000).

3.2. Nitrate Concentration on the Surface Water and Sediment

One abundant nutrient in the water body is nitrate. Nitrate in the form of nitrogen is a major important nutrient that is essential to the growth of plants and algae. Nitrate is defined as a soluble compound and has a stable form in water (Koike et al., 2001; Qu et al., 2012; Testa et al., 2013). A major known source for nitrate enrichment is runoff, erosion, leachate from fertile agricultural land, and residential waste. Most nitrate in the seawater surface comes from river runoff, which contains all of the activity derived from agriculture, farming, industry, and waste (Dzialowski et al., 2008; Mukerjee, 2009). This known condition also applies in the Pangkep River runoff and occurs all year. Furthermore, activities from agriculture or fish farming, which intensely use organic fertilizers, such as TSP, urea, or organic fertilizer, cause excess waste in the water, and the excess also flows to the sea. This event was a major cause of the variability of nitrate concentration in the water along the river.

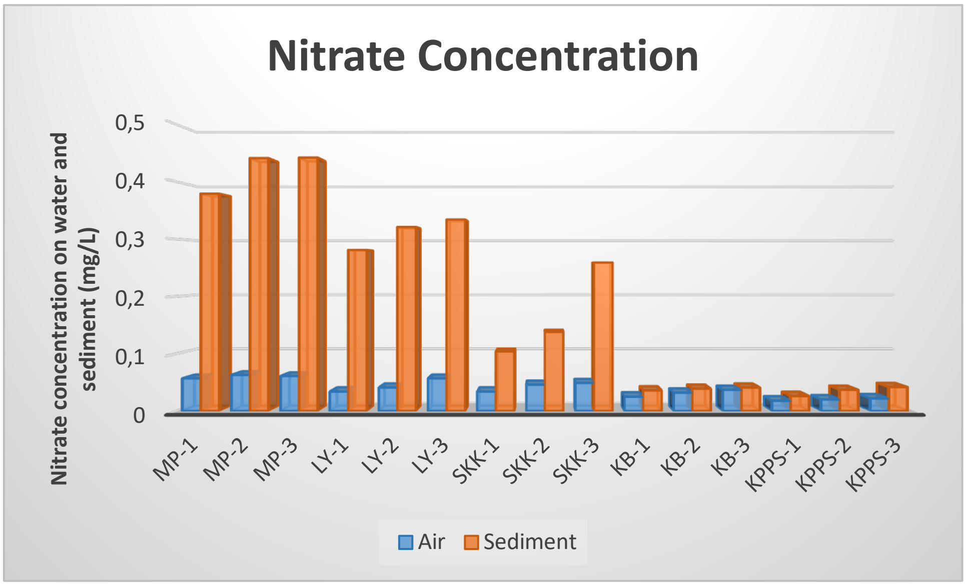

Figure 1. Nitrate concentration in the water and sediment of the Pangkep river

However, the natural nitrate concentration in water should not be over 0.1 mg/L. A nitrate concentration above 0.2 mg/L has a major eutrophication effect, which enhances the growth of phytoplankton and algae. Anthropogenic contamination is considered one of the major causes for the increased nitrate concentration and could increase the concentration above 5 mg/L (Gliber et al., 2008; Garnier et al., 2010). Sharp (1983) stated that the nitrate concentration in the seawater for normal conditions ranges from 0-0.14 ppm. Generally, the nitrate concentration in uncontaminated water is undetectable or low (around 10 mg/L). In addition, nitrate can also be used to categorize the quality of the water: 0-1 mg/L nitrate concentration indicates oligotrophic water, 1-5 mg/L indicates mesotrophic water, and 5-50 mg/L indicates eutrophic water (Wetzel, 2001).

According to Figure 1, the results show that the highest nitrate concentration was located in the Pangkep estuary compared to the concentration in seawater. The nitrate concentration of the seawater represents a decreasing trend in both the water and sediment samples. This condition is highly affected by the current, weather, nutrient sources, characteristics of the sampling locations, and the physical oceanographic factors in the water. Pangkep estuary generally obtains nutrients from the mainland during the rainfall season and when floods occur. Our sampling was carried out in the wet season; therefore, the tidal intensity, current velocity, wave pressure, and wind speed primarily affect the nitrate distribution vertically and horizontally. In the river water, the collected sample is primarily mixed with substrates (such as mud, mud/sand, coral/sand, and coral/debris). The sediment analysis results showed that the river area represents the lowest phosphate concentration. In contrast, it also showed the highest nitrate concentration. Based on the categorization of the water quality, the water was categorized as oligotrophic with an average nitrate concentration in every sampling station at around 0.039 mg/L in the water sample and around 0.19 mg/L for the sediment sample.

3.3. Phosphate Concentration on the Surface Water and Sediment

The concentration of the phosphate in the sediment from the Pangkep River estuary and the seawater showed a higher concentration than the phosphate concentration in the surface water (Figure 2).

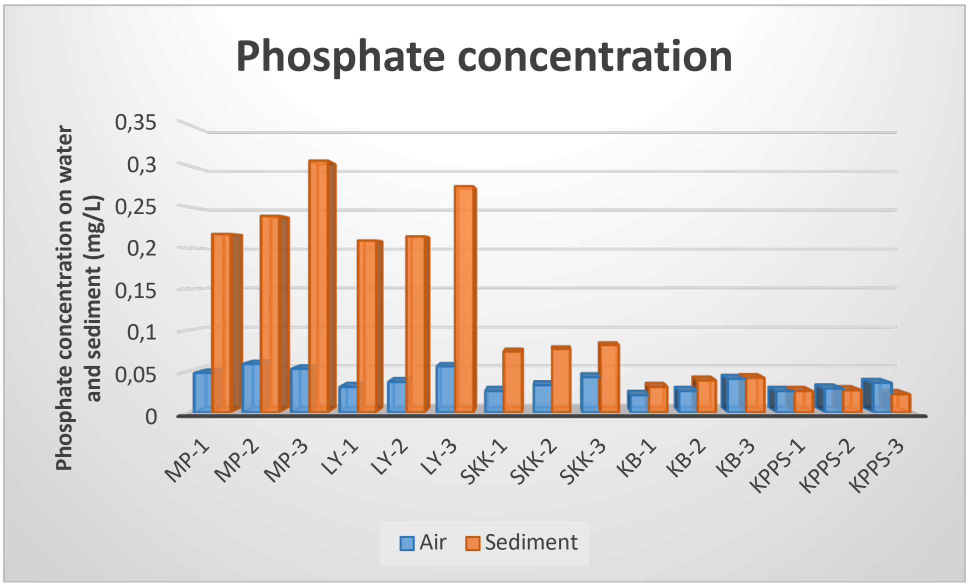

Figure 2. Phosphate concentration of the surface water and sediment in Pangkep river

The measured phosphate concentration in the sediment was found to be higher than the phosphate concentration in the surface water. This result hypothetically occurred because the sampling location received direct runoff from the mainland. Around the sampling location, there are many activities that can cause the increased concentration of phosphate, such as plywood industries, residences, fish farming, and markets. In addition, the phosphorus sources in the water and sediment predominantly come from phosphorus deposits, industries, domestic waste, agricultural activity, phosphate mining, and deforestation (Ruttenberg, 2004). These conditions act as the main trigger for eutrophication.

Furthermore, when the phosphate concentration excessively occurs in water, the phosphate is directly deposited to the sediment pore through sedimentation, adsorption, and precipitation. That is why sediment plays an essential role in eutrophication, primarily acting as a reservoir and source of phosphate (Williams and Mayer, 1972). The phosphorus/phosphate compound bound to the sediment can be decomposed with bacteria or through abiotic processes that can produce dissolved phosphate, which diffuses in the water column (Paytan and McLaughlin, 2007). In summary, based on the water quality categorized by Liaw (1969), a comparison of the phosphate concentration in each sampling location showed that the Pangkep water area is categorized as having a high level (rich) of phosphate. Liaw (1969) classified the richness of the water based on the phosphate level, which is 0–0.0002 mg/L (less rich), 0.0002–0.05 mg/L (average rich), 0.05–0.10 mg/L (rich), and > 0.10 mg/l (very rich).

4. Conclusion

The results showed that Pangkep *runoff* has nitrate and phosphate concentrations in the Pangkep estuary (near the mainland) that are categorized as eutrophic. The results also show a decreasing trend in the sea area. The nitrate concentration in the sediment ranged from 0.026–0.442 mg/L, and the nitrate concentration in the water ranged from 0.018–0.063 mg/L. Moreover, the phosphate concentration in the sediment ranged from 0.019–0.306 mg/L, and the phosphate concentration in the water ranged from 0.013–0.056 mg/L.

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