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Impact of increased Nutrient on the Variability of Chlorophyll-a in the West Coast of South Sulawesi, Indonesia

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Abstract- Increased nutrient runoff from land affect the level of productivity of waters and disrupt the balance of microalgae community. This study aimed to analyze nutrients (N, P; DIN/DIP; DSi/DIN; DSi/DIP) to the variability of chlorophyll-a concentrations in coastal waters of the west coast of South Sulawesi are experiencing eutrophication. Nutrient and chlorophyll-a samples collected in three seasons (transition season, dry season and rainy season), in the coastal waters of estuaries Tallo, Maros, and Pangkep. Samples were analyzed chlorophyll-a by the trichromatic method. Results showed the ratio of nutrients DSi/DIN and DIN/DIP parallel to the increase in the concentration of chlorophyll-a in the transition season and dry season, while the N parallel during the rainy season. Correlation molar N-P nutrient and ratio of DIN/DIP; DSi/DIN; DSi/DIP to the variability of chlorophyll-a concentration of less than 50%, unless the ratio DSi/DIP in Tallo estuary during the rainy season and in the Maros estuary during the dry season.

Index Terms- clorophyl a, coastal, nutrient, South Sulawesi, Indonesia

I. INTRODUCTION

Eutrophication strongly influenced the balance ratio of N/P and Si/N, as a result of excess N input relative to P and Si (Yin, et al., 2001; Trommer, et al., 2013). This nutrient ratio further changes will have an impact on the size and structure of the phytoplankton community (such as Smayda, 1990; Riegman et al., 1993; Yin et al., 2001; Maguer et al., 2009). In addition, it can also affect the production of biomass higher trophic levels are largely dependent on the size of the main producers (Goldman, 1988; Legendre, 1990; Tremblay et al., 2000; Butron et al., 2009).

The ratio of nutrients and their effects on the distribution of chlorophyll-a, showed an increase in the concentration of N will affect the increase in the concentration of chlorophyll-a, but not affected by the ratio of N/P (Stelzer and Lamberti, 2001). Trommer et al. (2013) states that, the ratio of dissolved nutrients are often not representative of the actual nutrient limitations that affect natural phytoplankton populations, where P remains significantly limiting nutrient when chlorophyll-a supreme value, despite the scarcity of Si. Si ratios for the N or P has particular relevance for diatoms, where Si is an essential nutrient, which limits phytoplankton in an environment dominated diatoms (Ragueneau et al., 2002). Increased input N is usually correlated with a decrease in the ratio of Si/N (Rabalais et al., 1996).

Coastal waters along the west coast of South Sulawesi classified as productive, in which there are mangrove, seagrass and coral reef Spermonde. Spermonde coral reef ecosystem is part of the Coral Triangle Initiative, which plays a crucial role in sustaining the economic life of coastal communities and food security. However, these waters also potentially experience a decrease in water quality due to the threat of sewage from the mainland, which is carried by large rivers. The mainland exiles mainly from (1) municipal waste or industrial-source material of organic and inorganic pollutants, and from (2) discharges agriculture or aquaculture-a source of nutrients and organic matter. The second major source of this has great potential to increase the levels of nutrients and organic matter in the waters of the west coast of South

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Sulawesi. Therefore, an examination of the potential productivity of the waters with the study of the variability of the concentration of chlorophyll-a in the spatial and temporal due to the influence of the mainland (ie of the major rivers on the west coast of South Sulawesi), which empties into the coast and the sea at coral reef Spermonde. Studies on this are needed to provide basic and comprehensive understanding of the impact of changes in the water quality of the coastal and marine environment.

II. MATERIALS AND METHODS

Study Area

Location of the study are in the southern part of the Makassar Strait or in the southwestern peninsula of South Sulawesi (*Spermonde Shelf*), especially the waters around the mouth of large rivers that Tallo estuaries 05°57 S, 119°26 E - 05°11 S, 119°25 E, 04°59 S, estuaries Maros 119°28 E, and estuaries Pangkep 04°52 S, 119°30 E - 04°49 S, 119°29 E (Figure 1). Water sampling is done in three seasons, the transition season (April 2013), dry season (June 2013), and the rainy season (February 2014).

Tallo estuaries is the estuary of the river that divides the city of Makassar, capital of South Sulawesi province and empties into the Makassar Strait. Tallo river has a length of 66 km with an area of 417 km^2 watershed. Around the mouth of the river there is a very dense settlement and several large industry. While the Maros estuary and Pangkep a lot of runoff from agricultural activities and fishing that also empties into the Makassar Strait.

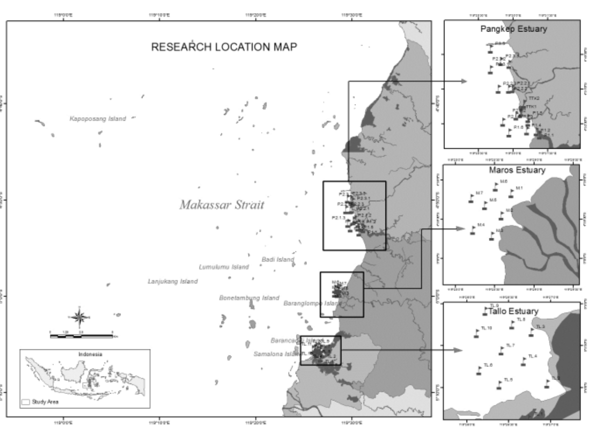

Figure 1. Map of study sites in waters off the west coast of South Sulawesi, the sampling locations are marked with a box. TL, Tallo estuary; M, Maros estuary; P, Pangkep estuary.

Sampling and Sample Preparation

Water sampling for chlorophyll-a and nutrients using a suction pump and bottle niskin with volume of 5 liters at a depth of 1-2 m below the surface of the river estuary and 5 m below sea level. Preparation of water samples for analysis of nutrients and chlorophyll-a done by filtering the water in the filter GF F (0.7 μm) by using a vacuum pump (pressure of 200 mm Hg), each filter for analysis of chlorophyll-a input in the bottle centrifuges then wrapped with aluminum foil and stored in a cool box. Results filter for nutrients then the toxification using $HgCl_2$ (400 mL/100 ml sample). Water samples are then stored at 4°C for further analysis. Contamination of the sample with the environment are concerned with avoiding direct contact with free air.

Analysis

The extraction of chlorophyll-a done using acetone (90% pa) and stored in a dark room for 24 hours at 4°C (Welschmeyer, 1994), then centrifuged at 4000 rpm for 10 minutes. Measurements of chlorophyll-a was conducted trichromatic method by using a spectrophotometer UV A1800-Simadzu at wavelengths of 630, 647, 664 and 750 nm (Aminot and Rey, 2001). Methods and analysis of the levels of nitrate (reducing cadmium), nitrite (sulfanilamide), ammonia (amonimum molibat), phosphate (stanous chloride), and silicates (molybdosilicate) with a Shimadzu spectrophotometer UV-A1800, with sample preparation and measurement based method of Grasshoff et al. (1983).

Student t-test performed to determine significant differences ($\rho<0.05$) between the molar and ratio of nutrient the temporal with a concentration of chlorophyll-a, and to determine the correlation at each location and season observations Person's correlation analysis was used with the SPSS v. 16.0 software program.

III. RESULTS AND DISCUSSION

Comparison of the concentration of chlorophyll-a in the waters of the west coast of South Sulawesi shows

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the spatial and temporal variability (Table 1; Figure 2). Nutrient supply from the mainland indirectly affect the variability of the concentration of chlorophyll-a, with the influence and the molar ratio of nutrients. If you view the phosphate concentrations in estuarine Tallo and Maros, including large, indicating phosphate rather than as limiting the growth of phytoplankton, but after normalized with nitrogen changed, with the composition of the enrichment of nitrogen and phosphate restriction. The maximum concentration of chlorophyll-a in the coastal Tallo, the transition season and dry season with a range of 1.86 to 11.93 mg m^{-3} and 0.38 to 7.68 mg m^{-3} (Table 1). While the maximum in Pangkep estuary during the rainy season with the range of 0.19 to 6.99 mg m^{-3}, although in estuaries Pengkap, the value of the ratio DIN/DIP minimum during the rainy season but the relationship to the concentration of chlorophyll-a is inversely proportional, ie an increase in chlorophyll-a was not followed by the high value of the ratio, indicating that the ratio of DIN/DIP in the estuaries Pengkep not correlate directly with the chlorophyll-a (Stelzer and Lamberti, 2001) but correlated with phytoplankton (Trommer et al., 2013). The concentration of chlorophyll a minimum is found in estuaries Maros in all seasons observations ranged 0.21 to 1.58 mg m^{-3} (transition season), 0.20 to 4.08 mg m^{-3} (dry season) and 1.13 to 2.56 mg m^{-3} (rainy season).

Table 1. Mean (M), standard deviation (SD) N nutrient concentration (NH_3^--N); P (PO_4^{3-}-P), nutrient ratio of DIN/DIP; DSi/DIN; DSi/DIP and Chl-a at the west coast of South Sulawesi, Indonesia.

Season	Location	NH_3^--N [μM]		PO_4^{3-}-P [μM]		DIN/DIP	DSi/DIN	DSi/DIP	Chl a (mg m^{-3})	
		M	SD	M	SD	M	M	M	M	SD
Transition (April 2013)	Tallo estuary	27.7	±8.46	0.20	±0.08	183.8	0.12	24.2	4.80	±3.35
	Maros estuary	19.3	±8.41	0.35	±0.16	82.3	0.85	67.0	0.74	±0.49
	Pangkep estuary	13.3	±5.50	0.25	±0.14	96.2	0.20	14.6	2.84	±2.85
Dry (June 2013)	Tallo estuary	13.6	±7.39	0.35	±0.13	43.3	0.40	15.4	4.64	±2.30
	Maros estuary	6.37	±1.74	0.31	±0.09	22.2	1.11	24.5	1.85	±1.58
	Pangkep estuary	6.86	±2.27	0.21	±0.06	37.1	0.78	32.5	2.15	±1.46
Rain (February 2014)	Tallo estuary	63.4	±6.71	0.56	±0.14	114.9	0.40	23.8	2.06	±0.44
	Maros estuary	25.9	±4.98	1.00	±0.23	28.1	0.90	24.5	1.60	±0.44
	Pangkep estuary	22.1	±8.57	0.82	±0.34	28.1	1.99	20.0	4.04	±2.27

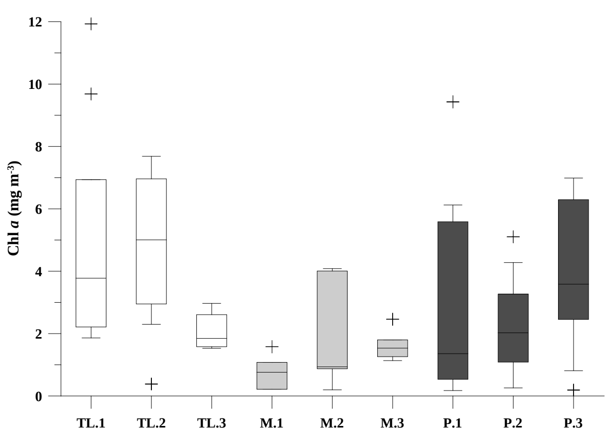

Figure 2. Comparison of chlorophyll-a concentration at each sampling location and season of observation in waters of the west coast of South Sulawesi, Indonesia; TL, Tallo estuary; M, Maros estuary; P, Pangkep estuary. 1, Transition season; 2, Dry season; 3, Rainy season.

The influence of the DIN/DIP ratio against the concentration of chlorophyll-a in estuaries Tallo, the maximum is found in the transition season (Table 1). The maximum concentration in the transition season is similar to the findings of Falco et al., (2010) at the Ebro estuary, Spain (April 1999), which is 17,59 mg m^{-3} which is the result of seasonal cycles of phytoplankton. In general, the concentration of chlorophyll a in the west coast of South Sulawesi in every season of observation is still lower than the Ebro estuary. Although, chlorophyll-a present in all types of phytoplankton, but also determines the size of phytoplankton (Goldman, 1988; Legendre, 1990; Tremblay et al., 2000; Butron et al., 2009) that contributes to the quantity of chlorophyll-a.

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Results of correlation analysis between chlorophyll a with a stoichiometry molar nutrients N, P and nutrient ratio of DIN/DIP; DSi/DIN; DSi/DIP on the west coast of South Sulawesi shows koefiesien determination (R^2) was very small with a dominant variations or changes in the concentration of chlorophyll-a < 50% (Table 2), but has indicated that nutrient contributes to the concentration of chlorophyll-a (e.g. Stelzer and Lamberti, 2001). Where, nutrient factors in the estuaries Tallo and Pangkep in the transition season showed negative correlation with chlorophyll-a, whereas in the estuaries Maros, nutrient molar N, P and the DIN/DIP ratio positively correlated. In the dry season, showed P is positively correlated with the concentration of chlorophyll-a was found only in the estuaries Pangkep location, otherwise N negatively correlated only in locations estuaries Maros. Meanwhile, the ratio of nutrient forms DIN/DIP; DSi/DIN; DSi/DIP correlated positively except DSi/DIP in estuaries Pangkep. Factors rainy season also gives effect to the variability of the concentration of chlorophyll-a, which in the estuaries Tallo and Maros shows the same correlation that nutrient N and P were positively correlated to the concentration of chlorophyll-a, and the nutrient ratio of DIN/DIP; DSi/DIN; DSi/DIP showed a negative correlation. Whereas in estuaries Pangkep, nutrient N, P and the DSi/DIN ratio negatively correlated to the concentration of chlorophyll-a, otherwise the ratio of DIN/DIP and DSi/DIP positively correlated.

Table 2. Correlation between chlorophyll-a with a stoichiometry molar nutrients and ratio of nutrients in the waters of the west coast of South Sulawesi. N (from N-NH_3^- µm); P (from P-PO_4^- µm), R^2, coefficient of determination. +, positive; -, negative.

Location **Season**		**N** **(R^2)**	**P** **(R^2)**	**DIN/DIP** **(R^2)**	**DSI/DIN** **(R^2)**	**DSI/DIP** **(R^2)**
Tallo estuary						
Transition		- (0.059)	- (0.039)	- (0.028)	- (0.000)	- (0.012)
Dry		+ (2E-06)	- (0.012)	+ (0.002)	+ (0.032)	+ (0.038)
Rain		+ (0.083)	+ (0.243)	- (0.225)	- (0.046)	- (0.51)
Maros estuary						
Transition		+ (0.314)	+ (0.018)	+ (0.039)	- (0.108)	- (0.096)
Dry	**Chl-*a***	- (0.197)	- (0.519)	+ (0.418)	+ (0.182)	+ (0.608)
Rain		+ (0.048)	+ (0.244)	- (0.150)	- (0.000)	- (0.131)
Pangkep estuary						
Transition		- (0.133)	- (0.015)	- (0.269)	- (0.029)	- (0.135)
Dry		+ (0.002)	+ (0.008)	+ (0.300)	- (0.275)	+ (0.005)
Rain		- (0.246)	- (0.072)	+ (0.214)	- (0.110)	+ (0.007)

Effect of nutrients in the form of DIN/DIP ratio against the concentration of chlorophyll-a in the coastal also showed varying patterns (Figure 3). In observation of the transition season, increasing the DIN/DIP ratio cause a decrease in the concentration of chlorophyll-a in estuaries Tallo and Pangkep. Whereas in the dry season tendency ratio change did not affect changes in the concentration of chlorophyll-a in the estuaries Tallo, except in the estuaries Maros increase in ratio causes a decrease in the concentration of chlorophyll-a and vice versa in estuaries Pangkep. In observation of the rainy season, increasing the DIN/DIP ratio cause a decrease in the concentration of chlorophyll-a, except in the estuaries Pangkep there is a trend increase in the

DIN/DIP ratio was followed by an increase in the concentration of chlorophyll-a.

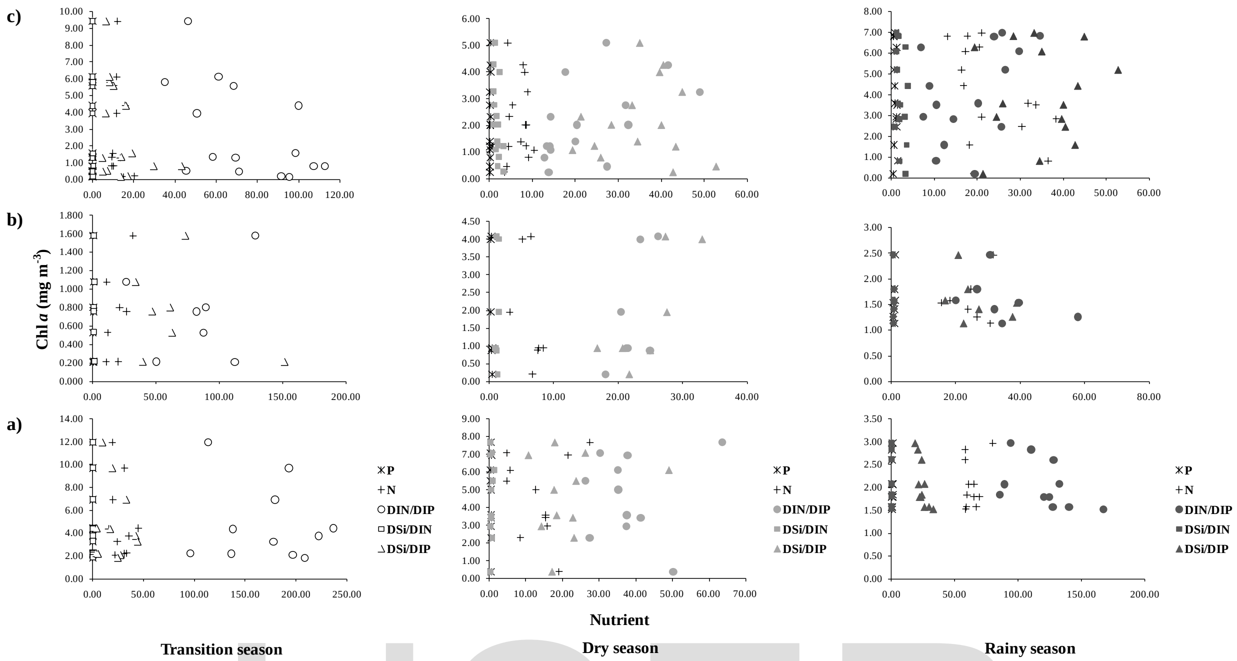

Figure 3. Stoichiometry molar nutrient N (N-NH_3^-); P (P-PO_4^-) and the ratio DIN/DIP; DSi/DIN; DSi/DIP against chlorophyll-a concentration variability in the west coast of South Sulawesi, Indonesia in the transition season, dry season and rainy season. a) Tallo estuary; b) Maros estuary; c) Pangkep estuary.

Factors DSi/DIN ratio has the same pattern with nutrient N, namely an increase in the concentration of chlorophyll-a was not followed by an increase in the value of the ratios and N concentration. DSi/DIN ratio is significantly affect the variability of chlorophyll-a concentrations ($p<0.05$), while, the model graph DSi/DIP ratio in Figure 3 shows the tendency of the ratio change is inversely proportional to the increase in the concentration of chlorophyll-a in the coast in the transition season and the rainy season. Meanwhile, the DIN/DIP ratio significant ($p<0.05$) in the dry season, is in contrast to the findings of Stelzer and Lamberti (2001), the changes tend to be proportional to the ratio of change in the concentration of chlorophyll-a. Although the value of the DIN/DIP ratio and chlorophyll-a minimum, but has a positive correlation (Table 2) which showed also that the concentration of P in the coastal high (Table 1), so that P is not limiting nutrient significantly. This positive correlation, due to the high concentration of ammonia included as a component of a dissolved inorganic nitrogen (DIN) in the dry season (Table 1), which is a kind of nitrogen which are generally more easily absorbed by phytoplankton (Millero and Sohn, 1991; Libels, 1992; Seeyave et al., 2013). Furthermore, increased N concentrations of ammonia in the rainy season (Table 1) significantly ($p<0.05$) influenced the increase in the concentration of chlorophyll-a (such as Stelzer and Lamberti, 2001). The high concentration of ammonia in the rainy season, due to the rainfall factor (Nedwell and Trimmer, 1996; Grizetti, et al., 2012) which accelerates runoff coming from the mainland to the coastal community activities.

IV. CONCLUSION

Nutrient enrichment in the waters of the west coast of South Sulawesi has led to variability of chlorophyll-a in the spatial and temporal. The maximum concentration of chlorophyll-a in the coastal Tallo in the transition season and dry season, while in the rainy season in the estuaries Pangkep maximum and minimum concentrations are found in estuaries Maros at all seasons of observation. Correlation nutrient stoichiometry N-P and nutrient ratios of DIN/DIP; DSi/DIN; DSi/DIP to the variability or changes in chlorophyll-a concentration of less than 50%, unless the ratio DSi/DIP in Tallo estuary during the rainy season and in the Maros estuary during the dry season. DSi/DIN ratio significantly affect the concentration of chlorophyll-a in the transition season, while the DIN/DIP ratio significant in the dry season and N significantly during the rainy season.

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