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RATIO OF CALCIUM CARBONAT WITH CADMIUM AND COPPER IN ALGAE *Halimeda* sp FROM DIFFERENT POLLUTED ENVIRONMENT

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ABSTRACT

Accumulated Cd, and Cu in the algae *Halimeda* sp at various levels of metal pollution has been done on the islands Laelae, Baranglompo and Karanrang. The aims of research to know accumulation Cd, Cu and their ratio with $CaCO_3$ in algae *Halimeda* sp at different level water pollution in Spermonde Archipelago. Sample algae *Halimeda* sp was collected in three location with different level of metal pollution within Spermonde Archipelago, namely Laelae, Barranglompo and Karanrang Islands. The highest concentrations Cd and Cu are found on the island Laelae, followed Baranglompo and Karanrang, showing anthropogenic influence on the level of metal in the algae *Halimeda* sp. There are differences in the pattern of ratio Cd/Ca and Cu/Ca among samples of algae *Halimeda* sp due to the influence of external input. Algae *Halimeda* sp sensitive to the accumulation of heavy metals Cd and Cu. These results prove that the algae *Halimeda* sp can be used as indicators of heavy metals pollution of Cd and Cu in marine waters

Keyword: $CaCO_3$, Cadmium, Copper, *Halimeda* sp, Spermonde Archipelago

INTRODUCTION

Coral Reef in Spermonde subjected to various pressures from the mainland. Sedimentation, nutrient enrichment, pollutants become a major contributor to reduced diversity of organisms in coral reefs (Rukminasari et al., 2014;). Various studies have been conducted on the effects of marine pollution coral reef ecosystems (Sawall, et al. 2011, 2013; Polonia et al., 2015). Research on metal accumulation in the skeleton of the coral as environmental monitoring efforts to the influence of anthropogenic (Samawi, 2012; Chan et al, 2014).

Conditions in the marine waters Spermonde Archipelago in general are still natural and unspoiled. However, studies conducted showed that the sea waters near the mainland have experienced contamination (Mallongi,

2014). The use of coral and algae as bioindicator organisms have been carried out monitoring (Fytianos et al , 1999; Neff, 2004; Chan et al., 2014). Algae *Halimeda* sp do calcification in its growth and assimilate metals from sea water and accumulate in skeleton $CaCO_3$. Thus *Halimeda* sp algae can be used to determine anthropogenic influences heavy metal Cadmium and Copper on coral reefs. However, the use of *Halimeda* sp type of algae that live in marine waters, especially coral reef area of interest to be studied as an organism to monitor metal pollution. This study aimed to determine the concentration of metals Cd and Cu in sea water, to determine the accumulation of metals Cd and Cu on the skeleton algae *Halimeda* sp from three locations, determine, and to determine Ratio of $CaCO_3$ to Cd and Cu in the algae *Halimeda* sp of the three locations

MATERIALS AND METHODS

Sampling Location

Sampling algae *Halimeda* sp were collected from three location Islands waters with different length from mainland South Celebes Province (Fig 1). Laelae Island water, on west of Makassar City, in influenced by input from domestic waste contained metals Cd and Cu.

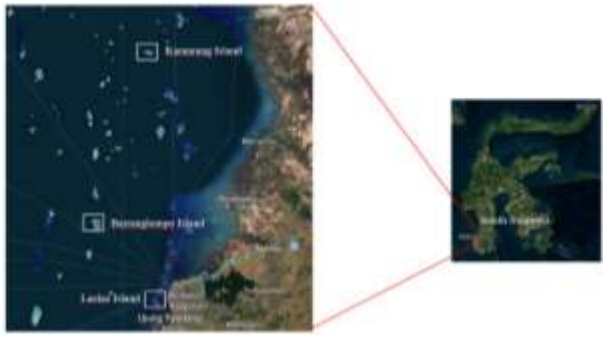

Fig. 1. Sampling locations of Laelae, Barranglompo, and Karanrang Islands

Baranglompo Island water, is about three miles from Makassar City and the location are fishermen dense settlements. Karanrang Island Water, is about ten miles from Makassar City, and the location of fishermen

settlement . In addition to algae *Halimeda* sp sample collection, measurement of temperature, salinity and pH.

Determination of Dissolved Cd and Cu in Seawater

Seawater samples were collected by SCUBA divers with clean polyethylene (PE) bottles. All PE bottles were acid cleaned with nitric acid (analytical grade) for a period of 2 days and rinsed with distilled deionized water (DDW) thoroughly before use. When sampling, PE bottles were pre-rinsed further 3 times with in situ seawater before filling with seawater (APHA, 1992). The collected seawater samples were filtered through filter paper Whatman 0.45 µm pore size. Metals in the pre concentrated seawater samples were determined by Atomic Absorption Spectrophotometer (AAS) type AA-6200.

Determination of Cd and Cu in algae *Halimeda* sp samples

Algae *Halimeda* sp samples were collected by SCUBA divers from Laelae, Baranglompo and Karanrang at a depth of 1-2 m in coastal area. (Fig. 2). Three colonies of the algae *Halimeda* sp were collected from each location. After collection, the algae *Halimeda* sp samples were transferred to the laboratory and frozen at 20 ^{o}C until they were analyzed. Before digested, the algae *Halimeda* sp was carefully washed using DDW to remove residual organic material, and then ultrasonically cleaned to remove any materials adhered to its surface. All algae *Halimeda* sp samples were dried at 110 ^{o}C for 24 h, ground by using an agate mortar and pestle and then transferred quantitatively into a Teflon beaker, followed by adding 8 ml concentrated ultrapure HNO_3 for digestion for a period of 24 h. algae *Halimeda* sp solutions were analyzed with AAS Type AA-6200, The bioconcentration factor (BCF) of heavy metal was calculated as the ratio between metal concentration in algae *Halimeda* sp and metal concentration in seawater (Chan et al, 2014). The ratio Cd/Ca and Cu/Ca was calculated.

Statistical analyses

One-way ANOVA was used to compare statistically the metal concentrations in different samples from three sampling locations. Whenever significant differences were found among the skeleton and tissues samples, the pairs were compared further using Tukey's tests. Hence, the significance level was set at $p < 0.05$, according to procedures of Lindman (1992).

RESULTS AND DISCUSSION

Distributions of dissolved metals in sampling locations

Figure 3 shows the distributions of dissolved metal concentrations and water parameters in the three locations. Relatively high metal concentrations occurred in seawater samples at Laelae Island Waters location. The concentrations were 0.078 ± 0.010 ppm for Cd and , 0.032 ± 0.0016 ppm for Cu,. The concentrations of dissolved metals at Karanrang Island Water were generally lower than those found at Barranglompo Island waters location. The measured values of pH (7.16 ± 0.05), temperature (29 ± 0.00 ^{o}C) and salinity (34.3±0.58 ppt) were recorded at Laelae. The values of pH (7.15 ± 0.01), temperature (28.6 ± 0.3 ^{o}C) and salinity (33.7 ±0.58 ppt) were recorded at Barranglompo. The seawater conditions at Barranglompo generally displayed normal values for pH (7.2), temperature (28.6 ± 0.3 ^{o}C) and salinity (34.3 ±1.53 ppt). The Spermonde Archipelago waters contains low concentrations of heavy metals Cadmium and Copper.

The effluent from mainland discharged into the Laelae Island water resulted in highest concentrations of Cd and Cu in ambient seawater at the algae *Halimeda* sp sampling location. However, these concentrations were lower than those found in the seawater Karanrang Island waters because location far from mainland and not anthropogenic source. Thus, the seawater at Barranglompo Island Water exhibited the higher concentration for the Cadmium dan Copper metals than Karanrang locations. Therefore, the relatively high concentrations of dissolved metals in ambient seawater could have caused an increase in the bioaccumulation of metals in algae *Halimeda* sp.

Accumulation of heavy metals in $CaCO_3$ algae *Halimeda* sp

Figure 4 shows the concentrations of Cd, Cu and Ca metals in algae *Halimeda* sp. The highest and lowest concentrations of Cadmium were identified in algae *Halimeda* sp samples from Laelae, Barranglompo and Karanrang islands, respectively (Fig. 4a).

The highest and lowest values of Copper were recorded in algae *Halimeda* sp samples from Laelae, Barranglompo and Karanrang islands, respectively (Fig. 4b). Calcium concentration was highest in the Karanrang samples and lowest in Laelae samples (Fig. 4c).

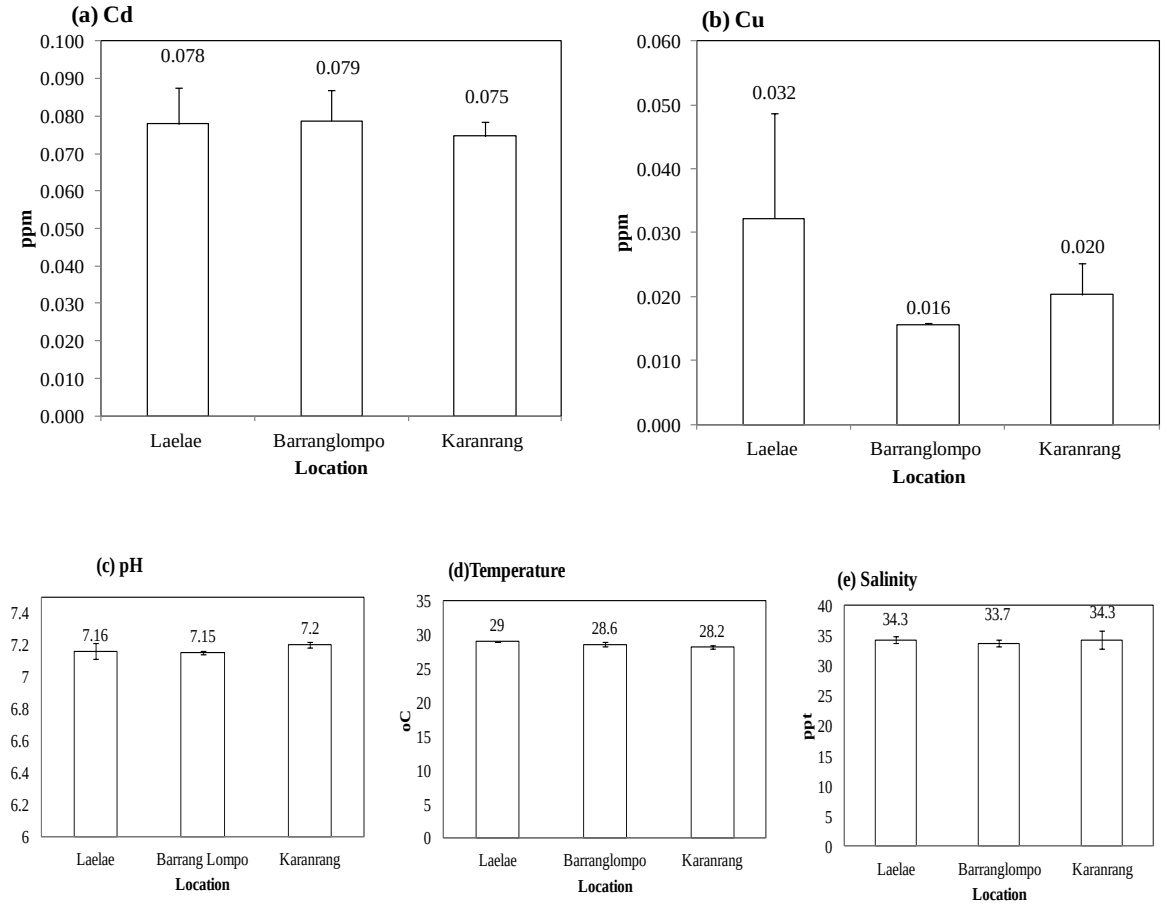

Fig. 3. Distributions of dissolved metals (a and b), pH (c), temperature (d) and salinity (e) in seawater collected from Laelae, Barranglompo and Karanrang alga *Halimeda* sp locations.

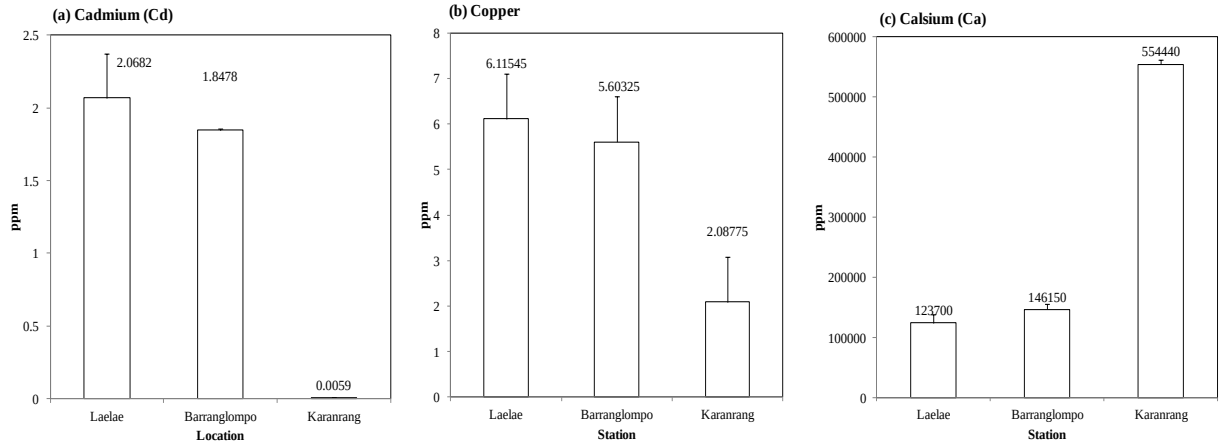

Fig. 4. Concentrations of heavy metals in $CaCO_3$ of the algae *Halimeda* sp from the three study sites.

Figure 5 shows the accumulation patterns of each heavy metal normalized with Ca in the algae *Halimeda* sp samples. The results of the statistical analysis show difference ($p < 0.05$) among three locations for Cd/Ca and Cu/Ca. However, metal Cd/Ca ratio was higher the samples from Laelae and Barranglompo, than in Karanrang. Similarly, metal Cu/Ca ratio was higher the samples from Laelae and Barranglompo than in Karanrang.

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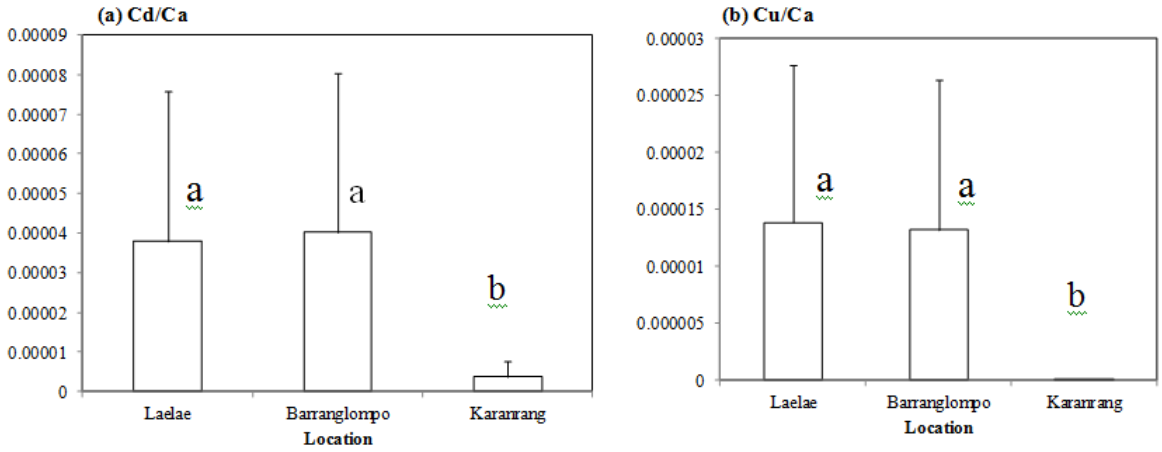

Fig. 5. Comparison of normalized conditions of metal/Ca in algae *Halimeda* sp collected from Laelae, Barranglompo and Karanrang sites. The superscripts (a, b) denote significant differences ($p < 0.05$, one-way ANOVA) among three sampling locations.

The application of algae *Halimeda* sp of specific areas influenced by terrestrial inputs and anthropogenic pollution enables researchers to monitor effects of metal enrichments in seawater. Our analysis of metal accumulation in the examined algae *Halimeda* sp samples could be indicative of the various degrees of metal pollution at Laelae, Barranglompo dan Karanrang locations. Meanwhile, the Ca-normalized metal concentrations (metal/Ca) in the algae *Halimeda* sp samples were significantly different for Cd/Ca and Cu/Ca, which corresponds with the condition of metal concentrations in the algae *Halimeda* sp samples. This could indicate that external inputs caused the elevated metal concentrations in the algae *Halimeda* sp samples. Several previous studies have reported the accumulation of metals in marine plant in numerous marine environments (Melawaty, et al, 2014, Ambo Rappe, 2014)

In this study, high concentrations of heavy metals in the algae *Halimeda* sp could be primarily attributable to the differential ability of metal incorporation into algae *Halimeda* sp, because we observed a significant difference in metal accumulation between the seawater and algae *Halimeda* sp samples. The ratio between the algae *Halimeda* sp and seawater concentrations ranged from 0.29 for Cu in the samples from Karanrang to 118.02 for Cu in the samples from Barranglompo. In addition, the environmental condition of karanrang Islnad waters was considered a relatively unpolluted ecosystem; thus, relatively low concentrations of heavy metals Cadmium and Copper were detected in the seawater, algae *Halimeda* sp. Thus, high concentrations of metals in algae *Halimeda* sp are the result of anthropogenic and natural inputs in the studied areas.

Bioconcentration factors of heavy metals

Table 1 lists the distributions of BCF in the seawater and algae *Halimeda* sp samples from the three locations. For the seawater and algae *Halimeda* sp samples from Laelae, the BCF was substantially higher than Barranglompo and Karanrang. Cu exhibited the highest BCF in the samples from Barranglompo, followed by those Laelae and Karanrang

Table 1. The bioconcentration factors of heavy metals in algae *Halimeda* sp from Laelae, Barranglompo and Karanrang Islands Waters.

Metals Location	Cadmium			Copper		
	Seawater	*Halimeda* sp	*Halimeda* sp / Seawater	Seawater	*Halimeda* sp	*Halimeda* sp / Seawater
Laelae	0.078	6.1155	78.4	0.0322	2.0682	64.16
Barranglompo	0.0787	5.6033	71.2	0.0156	1.8478	118.2
Karanrang	0.0747	2.0878	27.9	0.0203	0.0059	0.29

The BCF is substantially higher in algae *Halimeda* sp samples from Laelae than in the samples from Karanrang. (Table 1). Different BCFs identified among the three locations for the same metal could indicate different uptake processes when external metal inputs vary. Moreover, the sequence of magnitude among these metals differs between the BCF and dissolved concentration for a location. This could imply that algae *Halimeda* sp also uptake metals from directly from seawater.

CONCLUSION

The research has shown differential metal bioaccumulation in algae *Halimeda* sp from seawater in Laelae, Barranglompo, and Karanrang under various pollution conditions.

Relatively, high metal accumulation in the samples from Laelae and Barranglompo are associated with high metal concentrations in seawater derived from high metal loads.

Cu accumulation is substantially higher than Cd. Each metal yields different accumulated that such algae *Halimeda* sp has distinct selectivity for assimilating metals from seawater. This study supports the hypothesis that metal accumulation in algae *Halimeda* sp is suitable for monitoring in various polluted environments.

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