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HEAVY METALS CONTENT OF COPPER (CU) AND LEAD (PB) IN *CODIUM FRAGILE* SEAWEED

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ABSTRACT

This study aims to determine the concentration of copper (Cu) and lead (Pb) inseaweed *Codium fragile* and is expected to add information about copper (Cu) and lead (Pb) which accumulates inseaweed *C. fragile* in Puntondo waters. , Takalar Regency. This research was conducted from January to August 2021, located in Puntondo waters, Takalar Regency. This research method collects data in the form of seaweed samples from the field and seaweed obtained from seaweed sales. Data analysis was carried out using the One Way Anova test with a further test of LSD (Least Significant Difference). The results of this study indicate that the metal content of copper (Cu) at each research station in seawater and C. fragile samples has passed the threshold, while the content of lead (Pb) at each station in seawater and C. fragile samples has not passed the threshold based on PP No. 22 of 2021 (<0.008 mg/L) for sea water and BPOM Regulation No. 23 of 2017 (<0.2 mg/kg) for consumption materials. The metal content of copper (Cu) in seawater at each research station was significantly different and the metal content of copper (Cu) in C. fragile at each research station was not significantly different. The metal content of lead (Pb) in C. fragile seaweed at each research station was significantly different and the metal content of lead (Pb) in seawater at each station was below the detection limit of the instrument (<0.01 ppm). The highest content of copper (Cu) in seawater was found at stations near from the ships activity, that is 0.3625 mg/L, followed by stations close to settlements at 0.235 mg/L. The highest content of copper (Cu) in C. fragile was found at stations close to settlements at 6.63 mg/kg followed by stations at PPI Beba at 6.1575 mg/kg and stations close to ships activity at 4,965. mg/kg.

Keywords: Copper (Cu), Lead (Pb), seaweed, Codium fragile, Puntondo

INTRODUCTION

Metal pollution is a problem that often occurs in coastal waters. Heavy metals (now more commonly called metals) are metal elements that have a density greater than 5 gr/cm3 (Subowo et al., 1999). The presence of metals in seawater can come from human activities on land which then enter the sea via rivers, can also come from the atmosphere precipitating into the sea, or comes from volcanic activity (Hartati et al., 1993). Metal accumulation in waters can threaten the life of organisms, either directly or indirectly. The metal is difficult to degrade, causing it to easily accumulate in aquatic environments (Nontji, 1993).

Metals, including copper or Cuprum (symbolized by Cu) can naturally enter the waters through erosion or erosion of mineral rocks and through Cu compounds in the atmosphere which are carried down with rain (Palar, 2012). Apart from Cu, Pb metal is one of the main pollutant materials at present (Suhendrayatna, 2001). Lead metal (Pb) is a neurotoxin that is cumulative and damaging (Winarno, 1993). Motorized vehicles that produce waste in the form of Pb are the main source of lead pollution (Fardiaz, 1992). Pb metal enters the waters with the help of rainwater after going through the crystallization process. In addition, the corrosive process due to waves and wind is also the cause of the presence of lead in the waters (Palar, 2012).

South Sulawesi is one of the centers for seaweed production and is one of the leading commodities in this area (Mahatama & Farid, 2013). The largest seaweed producing area in South Sulawesi Province is Takalar Regency with production reaching 500 thousand tons (Rahadiati et al., 2018). The marine algae that are widely cultivated are Kappaphycus alvarezii, and Eucheuma spp. cultivated in the sea, and Gracilaria sp. which are generally cultivated in ponds (Anggadiredja et al., 2008).

*Codium fragil*e is a type of green macroalgae, with dichotomous branches with a very wide distribution (Trowbridge 1998). The collection location for *C. fragile* (Donge-donge) is close to settlements, so it is suspected that its waters are vulnerable to contamination by household waste which can cause contamination of copper metal (Cu). The existence of fishing boats is also suspected of influencing Cu and Pb levels in the waters, the fuel used by fishing boats (gasoline, diesel) is one of the main sources of Pb pollution that can enter the waters. Ships that are generally made from wood must be coated with paint containing Cuprum Chrome Arsenic (CCA) as an anti-fouling agent. The paint used to coat the wood will dissolve into the water column along with the ship's activities so that it can become a source of Cu pollution in the waters (Connel & Miller, 2006).

The large number of sources that have the potential as inputs for Cu and Pb metals in Puntondo waters, Takalar Regency, makes it necessary to conduct research on "Copper (Cu) and Lead (Pb) Metal Content in Codium fragile Seaweed in Puntondo Waters, Takalar Regency". The purpose of this study was to determine the concentration of Cu and Pb metals in C. fragile seaweed in Puntondo waters, Takalar Regency.

MATERIALS AND METHODS

This research was conducted in January - August 2021. Water and seaweed samples were taken from the waters of Puntondo Village, Mangara Bombang District, Takalar Regency, South Sulawesi Province (Figure 1). Sample analysis was carried out at the Marine Science Chemical Oceanography Laboratory, Faculty of Marine Science and Fisheries, Universitas Hasanuddin, Multitrophic Research Group Laboratory, Hasanuddin University LP2M Building and BBLK (Health Laboratory Center) Makassar City.

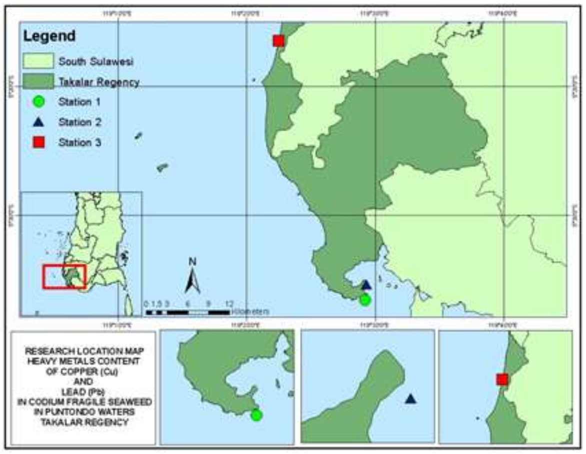

Figure 1. Map of research location

Data Collection

Samples of seawater and *C. fragile* were collected directly from the waters of Puntondo Villaget, Mangara Bombang District, Takalar Regency.

Sampling was carried out manually in areas suspected of receiving Cu and Pb metal pollutant sources. Seawater samples were taken at each station using a sample bottle. The samples that have been taken are then put into the coolbox for analysis in the laboratory

Measurement of physical chemical parameters of temperature was carried out in situ. Meanwhile, measurements of pH, turbidity and salinity were carried out ex situ. Each station is repeated four times.

The content of Cu and Pb metals in the samples was analyzed at the Makassar Health Laboratory using the Atomic Absorption Spectrophotometry (AAS) method.

Data Analysis

Data from measurements of Cu and Pb metal content in C. fragile and sea water from the laboratory were then analyzed descriptively. Data processing and analysis was carried out by comparing the results of the analysis with quality standards based on BPOM Number 23 of 2017 for consumption materials and Government Regulation Number 22 of 2021 concerning metal content in sea waters, then statistical analysis was carried out using One-way ANOVA to compare the concentration of Cu metal and Pb at each station.

Table 1. Quality standard for Cu and Pb in seawater (PP No. 22 of 2021)

Type of Metal	Unit	Quality Standard
Copper (Cu)	mg/L	0,008
Lead (Pb)	mg/L	0,008

Table 2. Quality standard for Cu and Pb in consumption materials (BPOM No. 23 of 2017)

Type of Metal	Unit	Quality Standard
Copper (Cu)	mg/kg	0,2
Lead (Pb)	mg/kg	0,2

RESULTS AND DISCUSSION

General Description of the Location

Geographically Takalar Regency is located in the southern part of South Sulawesi Province with a distance of 40 km from Makassar City. Part of the Takalar Regency area is a coastal area, including an area along the 74 km which includes the coastal area of Puntondo, Mangara Bombang District. Most of the Puntondo coastal communities utilize seaweed cultivation as a potential resource and have now become their main livelihood (Laikang Village Profile 2015). The use of coastal areas by the community sometimes has a negative effect on the environment. Communities that are generally only oriented towards economic value, often leave the waste from their activities just like that on the coast, which will eventually enter the waters and pollute the environment.

Environmental pollution is currently a concern because of the impact it causes. Pollution due to human activities (anthropogenic) becomes more dominant as a source of pollution compared to other sources of pollution (Harahap et al., 2019). Several sources of pollutant in the area around the study site which were declared as a result of anthropogenic activities included household waste, cultivation activities and transportation activities, especially sea transportation.

Heavy Metal Content of *C. fragile*:

Copper (Cu)

The results of the C. fragile sample analysis in Figure 2 show that the highest average value of Cu metal content was found in waters close to residential areas (6.63 mg/kg), the next highest was found at the third station, namely PPI Beba of 6.1575 mg/kg . and for the lowest average value at the first station, namely waters with ship activity of 4.965 mg/kg. The high concentration of metals is suspected because this area receives waste inputs, especially household waste. One source of Cu metal originating from household activities is waste from liquid floor cleaners containing CuO (Yanthy et al., 2013). Waste or residue from human activities in the form of metal which can eventually become a pollutant (Chandra et al., 2018), can be a source of Cu metal in addition to its natural sources such as erosion (Palar, 2012).

The station at PPI Beba also found a fairly high concentration of Cu metal. This is presumably because based on the seller's statement at PPI Beba where the C. fragile seaweed was collected, the seaweed sold at PPI Beba also came from Puntondo waters. Therefore, the concentration of Cu metal found at this station is almost the same as the concentration of metal found at the other two stations.

Stations that are in waters close to ship activities have the lowest concentrations of Cu metal. This is due to the nature of Cu metal which is easily dissolved and precipitated. Cu metal is the most easily dissolved and precipitated metal after mercury (Hutagalung, 1991). Therefore, although obtaining input from sources such as antifouling paint for fishing boats, the content of Cu metal in waters close to ship activities is lower than the other two stations. The results of the One way ANOVA statistical test showed that the copper metal content between research stations was not significantly different ($p>0.05$)

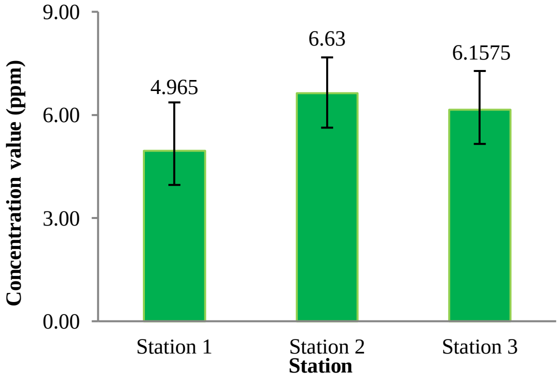

Figure 2. Average value of Cu metal content at the research station for *C. fragile*.

Lead (Pb)

The results of the analysis of C. fragile samples showed that the highest average value of Pb metal was at stations close to ship activities with a Pb content value of 0.1075 mg/kg, followed by stations not far from residential areas with a metal content of 0. 4 mg/kg and the lowest value was found in C. fragile which was traded at PPI Free (0.035 mg/kg). The high concentration of Pb metal content at stations close to ship activities is due to the fact that apart from using anti-fouling paint, fishing boats also use anti-corrosion paint containing Pb (Austin, 1984). The exhaust from fishing boats that interact directly with sea water results in the exhaust gases also directly contaminating the waters (Siaka, 2008). According to Sudarmaji et at., (2006) the results of burning vehicle fuel are one of the sources of the presence of Pb metal.

Stations that are not far from residential areas also found concentrations of Pb metal. This is because in addition to obtaining input from household waste from residents' settlements, the area also has cross roads that are traversed by various vehicles. In contrast to stations that are close to ship activities, the exhaust gas resulting from burning the fuel does not directly interact with sea water so that the Pb metal content found is not as high as stations that are close to ship activities. The results of the analysis of sample stations located at PPI Beba have the lowest concentrations of Pb metal, the results found are not much different from stations located near settlements. The results of the Oneway ANOVA test from the three stations (Figure 3) were significantly different ($P<0.05$), so further tests were needed to carry out Least Significant Difference (LSD). The BNT test results showed that station three was significantly different from station one, station two was significantly different from station one, while station three was not significantly different from station two. The highest Pb metal content was found in the waters of the ship activity area where the location is quite close to fishing nets (0.1075 mg/kg).

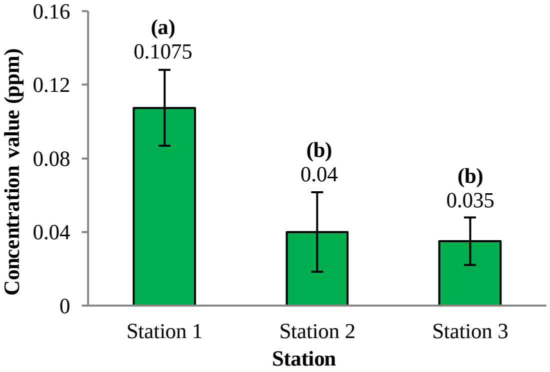

Figure 3. Average value of Pb metal content at the research station for *C. fragile*.

From the results of the analysis, Cu and Pb metals in the C. fragile sample found that based on BPOM regulations No. 23 of 2017, the content of copper (Cu) metal in C. fragile seaweed taken from all research stations was above the material quality standard. food, making it unfit for consumption. As for Pb metal, it shows that the metal content of each research station is still below the quality standards set by BPOM.

Metal Content at Seawater:

Copper (Cu)

The results of analysis of seawater samples showed that the highest average value of Cu metal was found at stations close to ship activities (0.3625 mg/L), stations close to residential areas had lower metal content (0.235 mg/L). Waters in areas close to ship activities have high concentrations of Cu metal presumably because they are close to ship activity areas. Ships made of wood are usually coated with anti-fouling paint which is one of the sources of entry of Cu metal into the waters (Austin, 1984).

Stations located in waters close to residential areas have lower concentrations of Cu metal. This is because the station which is close to residents' housing obtains metal input from household liquid waste. Stations that are close to residents' housing are also affected by tides. The tidal cycle causes the quantity of heavy metals in a certain unit of water mass to decrease (Moriarty, 1988).

Based on the results of the One Way ANOVA statistical test, it showed that there was a significant difference in the content of copper metal in the two research stations ($p < 0.05$), so the Independent-Samples T Test was carried out. The results of the Independent-Samples T Test showed that station one and station two differed significantly (Sig. (2-tailed) <0.05)

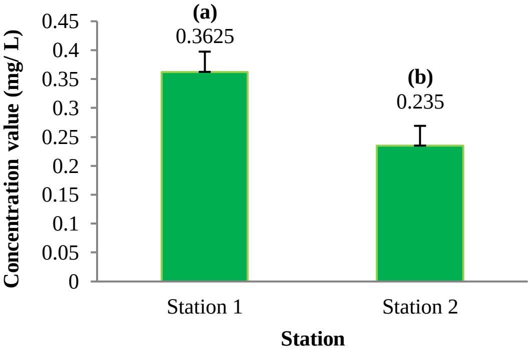

Figure 4. Average value of Cu metal content at the research station for seawater.

Lead (Pb)

The content of Pb metal was not detected down to the unit part per billion (ppb). The Pb metal content at both stations was less than 0.0001 ppm so that the calculation of the average value of Pb metal content and the oneway Anova statistical test could not be carried out. The Pb metal content in the waters was low because the metal that entered the waters was diluting due to the tide low tide. According to Wardani et al., (2014) currents and tides result in Pb metal entering the waters that can still move freely, causing dilution.

Table 3. Physical-chemical oceanographic parameters

Repetition	Physical and Chemical Oceanographic Parameters	Station 1	Station 2
1	Temperature (°C)	27	28
2		27	28
3		27	28
4		28	28
	Average	27,25	28
1	Salinity (‰)	33	34
2		34	34
3		34	34
4		34	33
	Average	33,75	33,75
1	Turbidity (NTU)	4,72	2,7
2		3,93	2,71
3		4,07	3,53
4		4,58	3,04
	Average	4,33	3,00
1	pH	7,59	7,63
2		7,57	7,63
3		7,58	7,59
4		7,63	7,63
	Average	7,59	7,62

Physico-Chemical Parameter

Temperature

The temperature at each station ranges from 27°C to 28°C. The temperature showed almost the same value at the two research stations, where the average temperature at stations that were close to ship activities was lower than the average temperature at stations that were close to settlements. Measurements were taken during cloudy weather and in the evening. The decrease in temperature affects the metal content in the waters. Temperature also affects the toxicity of metals to biota in the waters. An increase in temperature results in an increase in the process of incorporating metals into the body and the reaction of forming bonds between metals and proteins will be faster (Putri et al., 2016).

Salinity

Seawater salinity shows that each station has a uniform salinity value, which ranges from 33‰ to 34‰. The average salinity at the two research stations was the same, namely 33.75‰. Mance (1987) states that high salinity causes an increase in the formation of chloride ions, which results in a decrease in the concentration of heavy metal ions in waters caused by the reaction of these metal ions with chloride ions. Good salinity for seaweed growth ranges from 15‰ to 35‰ (Aslan, 1999). Salinity can also affect the presence of metals in waters.

pH

pH measurements at each station ranged from 7.57 to 7.63. The average pH value at stations that are close to ship activities is lower than the average pH value at stations that are close to residential areas. The increase in pH in the waters affects the biosorption ability of seaweed at the bottom of the waters, this is because heavy metals will precipitate and will not dissolve in seawater (Chandra et al., 2018). This is supported by Palar (2012), which states that an increase in pH results in a decrease in the solubility of metals in water.

Turbidity

Turbidity measurements show that each station has turbidity values ranging from 2.7 NTU to 4.72 NTU. The lowest level of turbidity is found at stations close to residential areas. Meanwhile, the highest level of turbidity was found at stations close to ship activities. According to Walhi (2006), the turbidity that meets the standards for seaweed environment is less than 20 NTU (Nephelometric Turbidity Units).

CONCLUSION

The content of copper metal (Cu) at each research station in seawater and C. fragile samples has exceeded the threshold, while the content of lead metal (Pb) at each station in seawater and C. fragile samples has not exceeded the threshold based on Government Regulation No. 22 of 2021 (<0.008 mg/L) for seawater and BPOM Regulation No. 23 of 2017 (<0.2 mg/kg) for consumption materials. The content of copper metal (Cu) in seawater at each research station was significantly different and the content of copper metal (Cu) in C. fragile at each research station was not significantly different. The content of lead metal (Pb) in *C. fragile* seaweed at each research station was significantly different and the content of lead metal (Pb) in seawater at each station was below the detection limit of the tool (<0.01 ppm). The highest content of copper (Cu) in seawater was found at stations near ship activities, namely 0.3625 mg/L, followed by stations close to settlements, 0.235 mg/L. The highest content of copper metal (Cu) in *C. fragile* was found at stations that were close to settlements, namely 6.63 mg/kg, followed by stations at PPI Beba, namely 6.1575 mg/kg and stations that were close to ship activities, 4.965 mg/kg.

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