Analysis of Lead (Pb) Value Comparison on Seaweed (Eucheuma cottonii) in Bluto and Saronggi Sumenep Marine, Madura, East Java

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Abstract. Metals and minerals are found in both freshwater and sea water. The inclusion of heavy metals, such as lead (Pb) and other heavy metals, in marine waters with excessive concentration can have a toxic effect on marine organisms, both animals and plants. Heavy metal such as lead (Pb) is a dangerous type of metal; if excessive concentration is found in seaweed it can lead to a decrease in the rate of growth. The purpose of this research is to prove the difference in lead levels accumulated in Eucheuma cottonii seaweed and compare the lead levels in seaweed Eucheuma cottonii with the provisions of Indonesian National Standard (SNI) in the Bluto and Saronggi Sumenep Marine, Madura. This research uses descriptive method and Mann Whitney U test. The results showed that lead level in seaweed in Bluto marine has an average of 0.018ppm and 0.023ppm and in Saronggi is equal to 0.256ppm and 0.0276ppm. The average content of lead accumulated in seaweed and seawater in both waters is still below the threshold value according to SNI 01-7387-2009 of 0.5mg/kg. However, the lead level in the sediments in both Bluto and Saronggi marine has exceeded the pre-determined lead limit level of 0.675ppm.

Keywords: Heavy metals, lead, Eucheuma cottonii.

1. Introduction
Madura marine waters are easily polluted because the water in Madura has a flow that connects Surabaya to Madura. The main source also comes from the river carried by fishing vessels and tanker ships coming from Surabaya directly carrying tin ore, accidently spilling into the waters nearby off Pamekasan and then ending up in Sumenep so that the lead metal rises in the Sumenep waters (Murtini et al., 2003). It can be seen from previous studies (Fransisca, 2012) that white shrimp and shellfish taken in Saronggi waters contain lead levels of 3.28mg/kg and 2.26 mg/kg. Preliminary studies have shown heavy metals of lead in Eucheuma cottonii, sediments and seawater; therefore, researchers decided to further investigate the heavy-metal content in E. cottonii seaweed.

Metals and minerals are almost always present in freshwater or seawater. The inclusion of heavy metals such as Pb (lead), Hg (mercury), Zn (zinc), Cd (cadmium) and other heavy metals in marine waters with excessive concentrations may have a toxic effect on marine or plant organisms. Sea clumps collect heavy metals from their aquatic environment (Lamai et al., 2005).
According to Soemirat (2003), in the world of commerce, contaminated food products will give the impression to the user that the market value will decrease. One of the polluted fisheries product stems is heavy metals. This circumstance, in addition to causing death of the organism, increases the heavy metals in the sea and may also cause a negative impression in people who eat seafood. According to Fransisca (2012), in the waters of Madura, especially the Saronggi Sumenep waters, which is also preserved by the Madura Strait, there is also fishery and transport activities and it is supported that the marine life of sea water has collected heavy metals.

Sahetapy (2011) says that this is caused through lead in the air with rain water and that dust containing containing lead from tetraethyl fuel-based lead also contributes to the presence of lead in water, the right of mineral rocks and the rest of the industry. In general, the majority of industry will eventually be discharged into the sea. Depending on the stem, the majority the industry may contain very large heavy metals. These heavy metals may enter food chains and potentially damage the plants and animals (Nursita et al., 2003) which are eventually eaten by humans. Heavy metals may be dangerous if the density exceeds the set limits.

2. Materials and methods

2.1. Place and time of research

This research was conducted in April 2017. The location of sampling of cultivated seaweed (E. cottonii) was in Bluto waters and the Saronggi Sumenep waters, Madura. The analysis of heavy metals on seaweed samples (E. cottonii) and sea water samples was conducted at Chemical Laboratory, Faculty of Mathematics and Natural Sciences, State University of Surabaya.

2.2. Tools and materials

The research equipment used for sampling was thermometer, refractometer, Ph-paper, secchi disk, five kilogram packing plastic, cool box, and scales. Equipment for heavy metal analysis included an Atomic Absorption Spectrometry (AAS), 50ml beaker, 10ml measuring flask, 5ml polyethylene vial, 10-100μL effendorf micropipette, and analytic balance. The materials used are seaweed (Eucheuma cottonii) taken directly from the waters of Bluto and Saronggi Sumenep Madura, H2SO4, concentrated HNO3, HCl solution, lead standard solution (Pb) and aquades.

2.3. Work procedures

Sampling in the form of seaweed, seawater and sediment was done directly in the waters of Bluto and Saronggi Sumenep, Madura. Samples taken were seaweed samples (Eucheuma cottonii) aged 17-20 days. Water quality measured included sea water temperature (°C), salinity, acidity degree (pH) using pH paper and brightness using secchi disk. Seawater sampling was one once at each station. Samples that were taken were then stored in a cool box to avoid any damage to the new samples and testing of lead levels was carried out in the laboratory and then data analysis performed.

The distance of sampling from the shoreline is about one kilometer. Sampling was done on two stations. At each station, sampling was done for three samples. Station 1 was located in a residential area. The second station was located in the area around the harbor for the fishing boats. Station 1 sampling at Bluto was located at 7°12' 36.6 south latitude and 113° 77' 64.57 east latitude, and station 2 was located at 7°12' 39.64 south latitude and 113° 77' 92.47 east latitude. At Saronggi Sumenep, station 1 was located at 7°12'59.25 south latitude and 113°89'29.17 east latitude, station 2 is located at 7°12'47.43 south latitude and 113° 89' 33.57 east latitude.

The method of measuring heavy metals was by using Atomic Absorption Spectrophotometry (AAS) which is a measurement based on the evaporation of the sample solution. Then the metal contained therein was converted to free atoms. The atoms absorbed the radiation from a light source emitted from a cathode lamp containing a heavy metal element of lead (Pb).
2.4. Measurement of heavy metal lead (Pb)
The metal element of Pb was released from the sample tissue by dry digestion (spraying) at 450°C. The metal in the ash was subsequently fastened with hydrochloric acid (HCl) 6M and nitric acid (HNO3) 0.1M, respectively. The resulting solution was then atomized using a graphite furnace. The elemental atoms interacted with light from the Pb lamp. The interaction was in the form of absorbance of the magnitude which could be seen in the display (monitor) of the atomic absorption spectrophotometer (Atomic Absorption Spectrophotometer). The amount of ray absorption was proportional to the concentration of the Pb metal element.

2.5. Data analysis
The data obtained are data of concentration of heavy metal of lead (Pb) in seaweed and water in Bluto and Saronggi Sumenep waters, Madura, then analyzed for heavy metal of lead (Pb) in seaweed and in the water where the organism is located. The accumulation of lead weight metal (Pb) in seaweed was analyzed by using Mann Whitney U test to determine the difference of two data groups (Sugiyono, 2009).

3. Results and discussion

| Sample        | Bluto Marine (ppm) | Saronggi Marine (ppm) |
|---------------|--------------------|-----------------------|
| Station 1     |                    |                       |
| Sample 1      | 0.017              | 0.026                 |
| Sample 2      | 0.018              | 0.026                 |
| Sample 3      | 0.019              | 0.025                 |
| Average       | 0.018              | 0.0256                |
| Station 2     |                    |                       |
| Sample 1      | 0.022              | 0.026                 |
| Sample 2      | 0.022              | 0.028                 |
| Sample 3      | 0.025              | 0.029                 |
| Average       | 0.023              | 0.0276                |

Source: Unesa Laboratory (2017).

From the results of lead testing on Bluto waters it shows average values obtained of 0.018ppm and 0.023ppm, while in Saronggi waters the average values obtained were 0.256 and 0.276ppm. This shows that the heavy metal content of lead in the waters of Saronggi is greater than the heavy metal content of lead in the waters of Bluto. The high lead factor in the waters of Saronggi can be due to several things, such as the number of fishing boats, ships used for domestic and non-domestic shipping as well as tankers carrying oil that often pass through the waters of Saronggi. Another factor that also affects this is offshore oil drilling; Saronggi’s own oil refinery is also starting to be established in the village of Tanjung subdistrict (Warta Sumenep, 2011). According to the Department of Fisheries and Marine Affairs of Sumenep Regency in 2012, the number of vessels in the vicinity of the port of Saronggi is a ship without its own engine as many as 276 units, 1,109 units with outboard motor, 1,011 GT motor boats as many as 4,111 units, and motor boats > 30 GT as many as 238 units.

Generally, oil fuel is given tetraetyl additives containing Pb to improve quality, decrease octane value, and corrosive resistant Pb properties, so that waste from these ships can cause Pb levels in these waters to be high. Another reason is the many agricultural lands and the number of settlements that produce waste from residents, such as wash water, cooking water, various oil, water baths, and so forth, and fishery and livestock activities.
Species that are filter feeders will more easily accumulate heavy metals. This is because the filter feeder organism has a low mobility that easily accumulates heavy metals in the body. Lead can be absorbed by filter feeder species from the water environment or through the water currents carrying the nutrients needed by seaweed. Seaweed acquires or absorbs its food through the cells in its thallus. Nutrition carried by the flow of water that hit the seaweed will be absorbed so that the seaweed can grow and multiply (Juneidi, 2004). Seaweed can absorb heavy metals because of its ability as a biofilter. The higher availability of toxic metals in the waters will spur high absorption by seaweed. Nevertheless, seaweed has a tolerance limit in the face of water conditions contaminated by toxic metals. Absorption of toxic metals in high concentrations and continuous conditions will lead to decreased absorption ability, which can lead to plant mortality (Yulianto et al., 2006). According to Fransisca (2012), the high pollution of heavy metal lead in the waters of Saronggi Sumenep is also possible due to seaweed cultivation along the coast, due to seaweed constituting an initial biota absorbing heavy metals dissolved in water and then distributing to other biota. Dead seaweed settles in the sediment which will then be decomposed so that the lead content in the sediment increases (Bontang, 2012). Based on the above test results it can be seen that seaweed is still within the safe limits for consumption.

Table 2. Lead levels in water and sediment.

|          | Average | Bluto Marine (ppm) | Saronggi Marine (ppm) |
|----------|---------|--------------------|-----------------------|
| Water    | 0.014   | 0.023              |                       |
| Sediment | 4.05    | 3.81               |                       |

Source: Unesa Laboratory (2017).

The table above shows that lead concentration in sea water tends to be high in Saronggi waters. However, lead levels in sediments tend to be higher in Bluto waters than in Saronggi waters. The lead level in the sediments in the Bluto waters is greater when compared with lead levels in seawater, but in seawater samples is still below the threshold of predetermined conditions. However, the lead level in the sediments at both sites has exceeded the specified threshold value.

Testing of heavy metals in lead sediment in Bluto waters obtained data of 4.05ppm and 3.81ppm in Sumenep waters; this figure shows that lead levels in sediments in the waters of Bluto are greater than Saronggi waters, but the value exceeds the threshold as the limit specified in the sediment is 0.675ppm. The test results of lead content in Bluto waters are 0.012 and 0.017 and 0.022 and 0.024 in the waters of Saronggi. This may indicate that water in the Saronggi has higher lead levels than the Bluto waters, but the value is still below the threshold according to KEPMEN Lingkungan No. 51 of 2004 regarding the Standard of Quality of Sea Water on Lead (Pb), which is equal to 0.05ppm.

The level of lead in seawater is lower than in the sediment, indicating the accumulation of heavy metals in sediments due to heavy metals in the water having a dilution process with the effect of tidal current patterns. The low levels of heavy metals in seawater does not mean that the heavy metal-containing contaminants have no negative impact on the waters, but, rather, the ability of these waters to dilute the high contaminants (Rochyatun et al., 2006). It is this turbulence and ocean currents that can also affect the fluctuations in lead weight in organisms (Karimah et al., 2002). The low levels of heavy metals in seawater does not mean that the heavy metal contaminants have no negative impact on the waters, but in the sediment they are quite high. Heavy metals have properties that easily bind organic materials and settle in the bottom of the waters and unite with the sediments, so that heavy metal content in the sediment is higher than in water (Harahap, 1991).

Table 3. Water quality results.

| Water Quality | Bluto Marine | Saronggi Marine |
|---------------|--------------|-----------------|
| Station 1     |              |                 |
| Temperature   | 29°C         | 30°C            |
| pH            | 7            | 7               |
Salinity 27 ppt 28 ppt  
Brightness 2 meter 3 meter  
DO 5mg/l 4mg/l  
Station 2  
Temperature 30°C 30°C  
PH 7 8  
Salinity 28 ppt 28 ppt  
Brightness 2.5 meter 3 meter  
DO 4mg/l 4mg/l  

Source: (Personal Documentation (2017)).

Water quality measurements (Table 3) show that sea water temperature at two observation stations ranges from 29-30°C. According to Setiyanto et al. (2008), the normal temperature for seaweed cultivation ranges from 24-30°C. According to Moerniati (2003), causes of extreme changes in water temperature can occur due to the disposal of waste heat in a body of water. But, in this research, the water temperature is relatively stable. According to Fransisca (2012), increasing the temperature of waters tends to increase the accumulation and toxicity of heavy metals; this is due to the increasing rate of metabolism of aquatic organisms. Ghurfran et al. (2005) said changes in water temperature can affect the organism's body's metabolism.

Salinity in both waters ranges from 27-28ppt (Table 3) and, according to Gazali (2013), the salinity suitable for seaweed farming ranges from 22-34ppt, this means that the salinity range in Bluto waters and the waters of Saronggi can still be said to be within the natural range of salinity. Salinity changes can affect heavy metals in waters, this is in accordance with the proposal by Bangun (2005) that increase in salinity value has a negative effect on heavy metal concentration; the higher the salinity; the lower will be the heavy metal concentration and the lower the salinity, the higher the heavy metals.

The degree of acidity (pH) at the two observation stations in the Bluto waters and the waters of Saronggi is 7-8 (Table 3). According to Gazali (2013), the pH of seaweed cultivation ranges from 6.5 to 8.5; this means that the pH range of both waters can be said to be in the range of natural pH values in nature. This value is a normal pH for aquatic commodities as habitat of marine biota. Water pH values can affect the type and structure of substances in aquatic environments and affect nutrient content and toxicity of micro elements (Moerniati, 2003). The solubility of the metal in water is controlled by the pH of the water. The increase in pH decreases the solubility of metals in water, because the increase in pH changes the stability of the carbonate form into hydroxides, which form bonds with particles in the body of water, thus settling to form mud (Fransisca, 2012). Waters containing heavy metals will be acidic rather than water free of heavy metals, so the change in acidity in acidic conditions in the waters will result in greater lead metal content (Darmono, 1995).

3.1. Relation of heavy metal content to water quality

To determine the water quality to the concentration of metals in water is very difficult, because it deals with suspended particles that dissolve inside. Metals in aquatic environments are generally in ionic form. These ions are free ions, organic ion pairs, complex ions and other ionic forms (Erlangga, 2007).

Temperature in the ocean is one of the important factors for the life of ocean organisms as it affects the metabolic activity and the development of an organism. Water temperatures are also influenced by solar radiation, sun position, geographic location, seasons, cloud conditions and the process of interaction between water and air. An increase in temperature can also lead to an increase in the accumulation of lead in heavy metals in tissues. Heavy metals that enter the waters can accumulate in the body of aquatic biota and accumulate in the sediment. Heavy metals in the water are easily absorbed and accumulated in the phytoplankton/aquatic plants, which are the starting point of the food chain, further through the food chain to other organisms (Fardiaz, 1992). From the observed temperature range in the two locations between 28-30°C, both locations are still considered feasible for
growth. High temperature rise will cause the pale thallus to yellow and become unhealthy (Ditjenkanbud, 2005).

Salinity in both waters ranged from 27-28ppt (Table 3). The salinity range in both waters can still be said to be within the natural range of salinity. Water salinity changes can affect heavy metal in a waters, this is in accordance with Erlangga (2007) who said salinity can also affect the existence of heavy metals in the waters; if there is a decrease in salinity, it will lead to increased heavy metal toxicity and heavy metal biakumulasi the greater. Bangun (2005) said the increase in salinity value has a negative effect on heavy metal concentration; the higher the salinity, the lower the heavy metal concentration, and vice versa.

The degree of acidity (pH) will affect the concentration of heavy metals in the water. According to Darmono (1995), waters containing heavy metals will be more acidic than water free of heavy metals. The increase in pH will decrease the solubility of heavy metals in water because the increase in pH changes the stability of the carbonate form into hydroxides, which form bonds with particles in water bodies so that it will settle to form mud (Palar, 2004). The pH values in the waters of Bluto and Saronggi Sumenep tend to be stable. That is, the increase in metal compounds tends to be small in biota.

The dissolved oxygen content can be used to express the degree of contamination in waters; high DO shows in low dirt excrement (Mahida, 1992). The DO concentration with Pb concentration in water is opposite (-). This shows that. with the increase of DO, the concentration of Pb in water decreases; Pb concentration in sediment will always increase because Pb is accumulative, although the correlation form is negative (Sunarto, 2005).

4. Conclusions and recommendations
The conclusion of this research is that lead level in seaweed in Bluto and Saronggi Sumenep waters shows different results (p <0.05). Lead level in seaweed in Bluto waters has an average of 0.018ppm and 0.023ppm and in waters of Saronggi is equal to 0.256ppm and 0.0276ppm. The average content of lead accumulated in seaweed and seawater in both waters is still below the threshold value according to SNI 01-7387-2009 of 0.5mg/kg. However, the lead level in the sediments in both waters. Bluto and Saronggi, has exceeded the level of lead limits established by Minister of Health Decree no. 416/Menkes/Per IX/1990 that is equal to 0.675ppm. There is need for stricter regulation of ships and waste from factories in the waters of Bluto and Saronggi Sumenep to reduce the impact of heavy metal pollution in the seaweed so that the value of heavy metal lead does not exceed the threshold value.

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