Effectiveness testing of attitude (*Enhalus acoroides*) on lead (Pb) and copper (Cu) metals

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Abstract. Increased human activity in all sectors due to rapid development, often resulting in pollutants such as heavy metals that have an impact on the environment and one alternative is phytotechnology. This study aims to (1) Determine the seagrass's capacity to absorb lead (Pb) and copper (Cu), (2) Determine the optimization of seagrass, sediment, and seawater in absorbing Pb and Cu. This study was an experimental study carried out at the Hasanuddin University hatchery unit, Barrang Lompo Island, then analysis of Pb and Cu metal content in the Analytical Chemistry Laboratory of the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University using the Atomic Absorption Spectrophotometer (AAS). The results showed that *Enhalus acoroides* seagrass had capacity to absorb Pb of 0.08 mg/kg at a concentration of 120 ppm, while it absorbed Cu of 0.65 mg/kg at a concentration of 2 ppm, so that this seagrass is more effective at absorbing Cu than Pb. The Pb optimum results in seawater at a concentration of 120 ppm at 3.04 mg / L and sediment at a concentration of 80 ppm at 29.30 mg/kg, while the optimum yield of Cu content in seawater and sediments, obtained at concentrations of 1 ppm and 2 ppm, namely 0.56 mg/L in seawater and at a concentration of 4 ppm is 29.67 mg / kg in sediment. While the optimal absorption of Pb by seagrass occurs at low concentrations of 40 ppm and 80 ppm of 0.07 mg/kg. The same result was obtained in sediments, 29.22 mg/kg at a concentration of 40 ppm. While the optimum Pb content in seawater is at a concentration of 40 ppm of 1.26 mg / L.

1. Introduction

Seawater is a component that interacts with the terrestrial environment, where waste discharges from land will flow into the sea. Waste containing pollutants will enter the coastal and marine ecosystems. Some are soluble in water, some are submerged to the bottom and are concentrated in sediments, and some enter the body tissues of marine organisms [1].

The increase in human activity in all sectors due to rapid development is directly proportional to the increase in the number of pollutants entering the environmental media. One of the pollutants that enter the environment and is toxic is heavy metal. Heavy metal pollution is a very serious problem to deal with because it harms the environment and ecosystems in general. Research of heavy metals has been carried out by utilizing marine life as a bioindicator [2,3].
Heavy metals in the waters will be absorbed by living organisms through biological processes and eventually accumulated. The content of heavy metals that accumulate in seawater and sediments will enter the food chain system and affect the life of organisms [4].

Heavy metal contamination that often occurs in open water is related to industrial activities, agriculture, plantations, and domestic waste. Heavy metals are dangerous pollutants because they are poisonous and difficult to decompose. In addition, if the marine organisms contaminated by heavy metals can cause the metal to move into the higher trophic levels and can enter the human food chain through seafood has contamination.

The decrease in water quality is caused by the presence of pollutants, both in the form of organic and inorganic components. Inorganic components, including dangerous heavy metals [5].

The presence of heavy metals in dangerous waters both directly on the life of organisms, and their effects indirectly on human health. This relates to the properties of heavy metals that are difficult to decompose so that they are easily accumulated in the aquatic environment and their existence is naturally difficult to decompose.

The way to determine the level of contamination in marine waters is to use macroalgae. Seagrass (seagrass) is a flowering aquatic plant (antophyta) and has the ability to adapt to live and grow in the marine environment. Seagrass has a large ecological function and is a primary producer in the sea which is quite large when compared to other ecosystems. One of the heavy metals is Pb (lead) and Cu (copper) [6,7]

The concept of concentrating on the role of plants as a natural technology to solve environmental problems known as phytotechnology. In a review of technology and processes clarifying phytotechnology as a natural-based approach to solving environmental problems [8].

Plants have the ability to absorb heavy metals from environmental media. Experiments in natural plant absorption to the concentration of Pb and Cu are 8 mg /L. However, the types of plants used in environmental phytotechnology are still very few. So that the types of local and wild plants in nature need to be conserved and explored their abilities against heavy metal pollution. Plant species l Amun (seagrass) selected for the type of original, local plant, found growing wild in nature and has not cultivated [9].

Seagrass is a marker of the capacity of metal accumulation because it interacts directly with water bodies and groundwater (substrate) through the leaves and roots to uptake ions so that seagrasses can reflect the overall health status of waters. Therefore, this study aims to determine the ability of plants l Amun (seagrass) against exposure to heavy metals Pb and Cu, as well as the concentrations found on the plants as fitoforensik approach.

This research is interesting to do and in line with plant conservation efforts. The information generated is expected to be the basis in phytotechnology research and the development of plant conservation in the future and increase knowledge about the potential of Indonesian plant diversity.

2. Materials and Methods
2.1 Research location and design
The study was conducted from September 2017 to January 2018. The research location was at the Hasanuddin University hatchery unit, Barrang Lompo Island and at the analytical chemistry laboratory at the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University.

This type of research is an experimental study using seagrass (Enhalus acoroides) for the absorption of lead (Pb) and Copper (Cu).

2.2 Population and sample
The population used in this study was the Seagrass Enhalus acoroides. While the sample is Seagrass seeds Enhalus acoroides which are grown for approximately 2 (two) months.
2.3 Research implementation stage
In the early stage of seagrass grow for 2 (two) months at the start in September until November 2017. Seagrass grown performed in laboratories Hery Hasanuddin University, Barrang Lompo island. The next treatment, which has been growing seagrass was brought to the chemical laboratory an Analytic Affairs Chemistry Faculty of Science, the University of Hasanuddin to be analyzed. The parameters observed were heavy metal content in plant media (sand and water) and plant parts (roots, stems, and leaves). Experiments were carried out with concentrations of exposure to Pb (40 ppm, 80 ppm, 120 ppm) and Cu (1 ppm, 2 ppm, 4 ppm), then analysis of the metal content of Pb and Cd.

2.4 Data analysis
Data obtained for each parameter (survival, color change) were analyzed using one-way ANOVA (Analysis of Variance)

3. Results

3.1 Pb addition test in sediments, seawater, and seagrass
Based on the results of research on the variation of Pb metal content, the higher the concentration of Pb in water the higher the absorption or accumulation of seagrass, as in table 3, the Pb concentration of 120 ppm, obtained in water by 3.04 mg/L and those found in seagrass are 0.08 mg/kg. while the 80-ppm sediment was 30.30 mg/kg Pb metal is toxic and its exposure effects on seagrass plants that can inhibit growth causing depigmentation and provide anatomically specific responses or abnormalities.

The measurement of Pb metal in *Enhalus acoroides* seagrass revealed the highest accumulation of Cu and Pb in the leaf. This is indicated by changes in leaves that have begun to wilt on observations day 4 to day 15. Laboratory test results show that with the addition of Pb levels in seagrass, the rate of Cu absorption is very low in contrast to the addition of Cu in seagrass which shows the absorption capacity of seagrass against Cu is very high.

3.2 Test addition of Cu to sediments, seawater, and seagrass
Based on the results of research the highest Cu content in seagrass is at 120 ppm concentration of 0.65 mg/kg. This shows the optimal levels of Cu that can be absorbed by seagrasses at the highest concentration. It differs from Cu levels found in seawater and sediments, because the optimum results obtained at the concentration of 2 ppm, is 0.56 mg/kg in seawater and 4 ppm in sediment 29.67 mg/kg, as in table 4.

Leaf aging also occurs in *Enhalus acoroides* on days 4 through 15, after Cu has been added, with more than 50% of leaves after exposure to higher Cu concentrations (2 to 4 mg/L). The effect of Cu exposure on leaf aging found in this study is consistent with previous studies by Malea (1994), namely this phenomenon is suggested to be associated with stimulation of phytochrome activity, which causes an increase in abscisic acid and ethylene production, a compound which is a precursor to leaf absorption and easing cell wall.

Based on the results of AAS analysis on *Enhalus acoroides* seagrass samples, it shows the accumulation of heavy metal Cu in the leaves, so it can be said that this plant can absorb and accumulate heavy metal Cu. Therefore, seagrass plants can be used as biological indicators of Cu heavy metal pollution.

3.3 Test addition of Pb (Cu + Pb) to sediments, sea water and seagrass
Based on observations of metal content with a combined treatment between Pb and Cu with the results of a special concentration of Pb metal. higher in sediment is 26.85 mg/kg and in water which has a lower content of 3.72 mg/L, in seagrass *Enhalus acoroides* is 0.66 mg/L as shown in table 5. This is related to the nature of heavy metals that are more likely to precipitate. So that it can be explained
from the pollutant waste which is described in the form of a solution (liquid), then experiencing precipitation in the planting medium (sand).

3.4 Test addition of Cu (Cu + Pb) to sediments, sea water and seagrass

Based on observations of metal content with a combined treatment of Pb and Cu with special results of Cu metal, it is higher in sediments which are 14.28 mg/L and in water that has a lower content of 0.40 ml/L, in seagrass *Enhalus acoroides* of 0.66 mg/L as in table 6. This is related to the nature of heavy metals that are more likely to precipitate. So that it can be explained from the pollutant waste which is described in the form of a solution (liquid), then experiencing precipitation in the planting medium (sand).

Based on the results of research the concentration of heavy metals Pb is much higher than the concentration of heavy metals Cu. The high content of Pb heavy metals in waters is thought to be caused by the volume of community activity waste in the port around the sampling location mainly resulting from industrial activities in the production process or activities using heavy metals.

### Table 1. Pb addition test results for sediments, seawater, and seagrasses

|                | Pb 40 ppm | Pb 80 ppm | Pb 120 ppm | Pb Kontrol |
|----------------|-----------|-----------|------------|------------|
|                | mg/L      | mg/kg     | mg/L       | mg/kg      | mg/L       | mg/kg      |
| Sediment       | -         | 29.22     | -          | 30.30      | -          | 29.69      | 31.53      |
| Seawater       | 1.26      | -         | 2.29       | -          | 3.04       | -          | 0.03       |
| Seagrass       | -         | 0.07      | -          | 0.07       | -          | 0.08       | -          |

### Table 2. Test results of Cu addition in sediments, seawater, and seagrasses

|                | Cu 1 ppm | Cu 2 ppm | Cu 4 ppm | Cu Kontrol |
|----------------|----------|----------|----------|------------|
|                | mg/L     | mg/kg    | mg/L     | mg/kg      | mg/L       | mg/kg      | mg/L       | mg/kg      |
| Sediment       | -        | 23.22    | -        | 29.07      | -          | 29.67      | -          | 28.55      |
| Seawater       | 0.56     | -        | 0.56     | -          | 0.51       | -          | 0.09       | -          |
| Seagrass       | -        | 0.31     | -        | 0.65       | -          | 0.64       | -          | 0.06       |

### Table 3. Optimization of sediments, seawater, and seagrasses in absorbing Cu mixture with Pb produces Pb

|                | Cu 1 ppm+Pb 40 ppm Pb | Cu 2 ppm+Pb 80 ppm Pb | Cu 4 ppm+Pb 120 ppm Pb | Cu+Pb Kontrol Pb |
|----------------|-----------------------|-----------------------|------------------------|------------------|
|                | mg/L                  | mg/kg                 | mg/L                   | mg/kg            | mg/L             | mg/kg      |
| Sediment       | -                      | 26.85                 | -                      | 26.79            | -                | 28.18      | -          | 26.46      |
| Seawater       | 1.86                   | -                     | 3.72                   | -                | 3.67             | -          | 0.52       | -          |
| Seagrass       | -                      | 0.66                  | -                      | 0.66             | -                | 0.60       | -          | 0.07       |

### Table 4. Optimization of sediments, seawater, and seagrasses in absorbing Cu mixture with Pb to produce Cu

|                | Cu 1 ppm+Pb 40 ppm Cu | Cu 2 ppm+Pb 80 ppm Cu | Cu 4 ppm+Pb 120 ppm Cu | Cu+Pb Kontrol Cu |
|----------------|-----------------------|-----------------------|------------------------|------------------|
|                | mg/L                  | mg/kg                 | mg/L                   | mg/kg            | mg/L             | mg/kg      |
| Sediment       | -                      | 13.06                 | -                      | 14.28            | -                | 13.57      | -          | 18.22      |
| Seawater       | 0.22                   | -                     | 0.40                   | -                | 0.17             | -          | 0.18       | -          |
| Seagrass       | -                      | 0.66                  | -                      | 0.66             | -                | 0.60       | -          | 0.07       |
4. Discussion
This study shows the results that Amun Enhalus have the capacity to absorb Pb of 0.08 mg/kg at a concentration of 120 ppm, while Amun absorbed Cu of 0.56 mg/kg at a concentration of 1 ppm and 2 ppm, so that these seagrass more effective in Pb Cu than absorb, because the capacity to absorb higher Cu acyl optimum levels of Pb in sediments obtained in concentrate 80 ppm, is 29.30 mg/kg and in seawater concentration of 120 ppm is 3.04 mg/L. While the optimal absorption of Cu metal content in sediments is obtained at a concentration of 4 ppm which is 29.67 mg/kg and in seawater concentrations of 1 ppm and 2 ppm which is 0.56 mg/L.

Waste that contains a lot of Pb element generally comes from a large number of ships leaning near the pier, in addition to domestic activities, and industries around the study site with various activities such as ship painting, ship repair, loading and unloading of goods, use of fuel and transportation flows also have the potential to produce Pb heavy metal waste.

The use of Pb heavy metals in various industries due to the heavy metal Pb has a low melting point making it easy and inexpensive to operate and has active chemical properties so that it can be used to coat metals for corrosion or rust protection because of its low water solubility.

In addition, intensive marine transportation activities also have the potential to produce exhaust emissions from ship engines into the air. Exhaust emissions resulting from the burning of fossil fuels containing heavy metals Pb. Pb heavy metal concentrations in the air can re-enter the waters through the water cycle (rain) so that it can cause an increase in Pb heavy metal pollutants into the sea.

The low content of heavy metal Cu in water can also be due to the absorption of heavy metal Cu by aquatic plants because this metal Cu is an essential heavy metal that is needed by organisms but in small amounts. Metal Cu required by the organism in the process of action of the enzyme. If the levels or concentrations of heavy metals that are too low in water can cause organisms to experience deficiency or nutritional deficiencies, but if the heavy metal elements are in excessive amounts can be toxic.

High and low concentrations of heavy metals in waters can also be influenced by several parameters of water quality, including water salinity. Salinity can affect the presence of heavy metals in water, if there is a decrease in salinity, the higher the concentration of heavy metals will be. The decrease will lead to lower salinity waters complexing compounds (Cl) so that the heavy metals will be more in the form of free ions and more easily absorbed by marine life.

The concentration of heavy metals Pb and Cu in these sediments is much higher than the concentrations of heavy metals Pb and Cu in seawater. This is due to the nature of heavy metals that are nonbiodegradable (difficult to decompose) so that they are easily accumulated in sediments so that the concentration is always higher than the concentration of metals in water. In addition, sediments are easily suspended because of the mass movement of water which will dissolve the metals they contain in the water so that the sediment becomes a potential source of pollutants on a certain time scale which will certainly settle to the sediment.

In addition, the high concentration of heavy metals at every second iteration in each concentration is thought to be related to the sediment type of each iteration. The concentration of heavy metals in sediments is also influenced by the size of sediment particles. The smaller the particle size, the greater the heavy metal content. This is because fine sediment particles have a large surface area with more stable ion density to bind heavy metals to larger sediment particles.

Fine sediments have the ability to pass water (permeability) to store/hold water better. Indirectly, nutrients and nutrients that are dissolved in water can be stored properly so that fine sediments generally have a relatively higher absorption ability. The high water content retained in fine sediments causes the ability of fine sediments to absorb to be lower than sediments with larger grain size.

Therefore, the concentration of heavy metals in sediments is increasing, but it is different with the concentration of heavy metals in water which tends to be still influenced by various hydrodynamic factors such as flow patterns that can spread heavy metals dissolved in seawater in all directions so that heavy metals in water the sea is lower than in sediment.
Based on the results of the analysis of AAS on seagrass samples, *Enhalus acoroides* showed the accumulation of heavy metals Cu and Pb in seagrasses, so it can be said that this plant can absorb and accumulate heavy metals Cu and Pb. Therefore, seagrass plants can be used as biological indicators of heavy metals pollution of Cu and Pb. The difference in the content of Cu and Pb in water, sediments, and seagrasses *Enhalus acoroides* can show the differences in the weight of heavy metals Cu and Pb in water.

This condition is thought to be related to the influence of the environmental conditions of the waters and the morphological-physiological conditions of the seagrass plant *Enhalus acoroides*. The level of absorption of toxic substances by plants is influenced by the environment and morphology and hormonal status of these plants.

When viewed in more detail in seagrass plants *Enhalus acoroides* the highest concentration, this is due to the seagrass absorption mechanism. The mechanism of absorption of heavy metals in plants through roots can be divided into three continuous stages, namely first absorption by roots, translocation of metals from roots to other plant organs and localization of metals in certain cell parts to keep from inhibiting the metabolism of these plants. Furthermore, in the process of nutrient transpiration also into the leaves so that the heavy metals are absorbed more in the leaves.

Pb metal content that is not essential for plants is generally higher in the rhizome because it is located closer in contact with sediment compared to leaves which allows the rhizome to have a system of stopping metal transport to the leaves, especially non-essential metals, so there is a buildup of metal in the roots. This is indicated by the physical observation of seagrass leaves that are exposed to Pb in the wilted state, in contrast to leaves that are exposed to blackish-colored Cu.

Each part of the seagrass has different metal content according to increasing leaf age, influenced by its concentration in sediment and in water. The difference in the size of seagrass plants can indicate differences in age and duration of seagrass in contact with metals.

5. Conclusions and Suggestions

*Enhalus acoroides* seagrass has a capacity to absorb Pb of 0.08 mg/kg at a concentration of 120 ppm, whereas in am absorbs Cu of 0.56 mg/kg at concentrations of 1 ppm and 2 ppm, so this seagrass is more effective at absorbing Cu than Pb, because the capacity to absorb Cu is higher. The optimum results of Pb content in sediments were obtained at 80 ppm concentration, which was 29.30 mg/kg and at seawater, the concentration of 120 ppm was 3.04 mg/L. Whereas the optimal absorption of Cu metal content in sediments was obtained at 4 ppm concentration which was 29.67 mg/kg and in seawater concentrations of 1 ppm and 2 ppm which was 0.56 mg/L.

References

[1] Amin B, Afriyani E and Saputra M A 2011 Distribusi spasial logam Pb dan Cu pada sedimen dan air laut permukaan di perairan Tanjung Buton Kabupaten Siak Provinsi Riau J. Teknobiologi 2

[2] Arifin 2001 *Ekosistem Padang Lamun* (Makassar)

[3] Alfionita S, Pursetyo K and Sahidu A 2018 Study of copper (Cu) contents in blood cockles (Anadara sp.) at Surabaya coastal waters *IOP Conference Series: Earth and Environmental Science PAPER* vol 137 (IOP Publishing) pp 1–5

[4] Said I, Jalaluddin M N, Upe A and Wahad A W 2009 Akumulasi logam berat krom dan timbal dalam sedimen estuaria Sungai Matangponto Palu *Media Eksakta* 5

[5] Siaka I M 2008 Korelasi antara kedalaman sedimen di Pelabuhan Benoa dan konsentrasi logam berat Pb dan Cu *J. Chem.*

[6] Effendi H 2003 *Telesah kualitas air, bagi pengelolaan sumber daya dan lingkungan perairan* (Kanisius)

[7] Darmokoesoemo H, Maghdhalena, Putranto T W L C and Kusuma H S 2016 Telescope snail (Telescopium sp) and mangrove crab (Seylla sp) as adsorbent for the removal of Pb2+ from aqueous solutions *Rasayan J. Chem* 9 680–5
[8] Mangkoedihardjo S and Samudro G 2009 Ekotoksikologi Teknosfer Surabaya Guna Widya

[9] Irawanto R 2014 Phytomedicine of Acanthus ilicifolius dan Coix lacryma-jobi. Prosiding 2nd International Biology Conference-ITS Surabaya