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Copper Accumulation on *Avicennia Marina* In Tapak, Tugurejo, Semarang, Indonesia

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Abstract- *Mangroves are good hyperaccumulators, they are not only able to grow on highly poisonous land, but also accumulate the poisonous substances in the branches and leaves. The aim of the research was to evaluate the bioaccumulation of Cu on Avicennia marina in Tapak Semarang. Tapak Semarang is selected as the research site because the mangrove ecosystem is surrounded by milkfish ponds.The research used ecological approach. Bioaccumulation data and heavy metal translocation in plants, sediment and water were analyzed using pre-determined formulation. Results showed that Cu was found in water (0.0069 mg/l), sediment (26.760-37.889 mg/Kg), roots (2.336-7.997 mg/Kg), young leaves (2.367-6.604 mg/Kg) and old leaves (1.080-6.748 mg/Kg) of A. marina. Sediment have the highest ability to accumulate Cu compared to water with concentration factors of ranging from 3878.26 to 5491.16. The Bioconcentration Factor (BCF) of roots and sediment was ranging from 0.09 to 0.211, and the Translocation Factors (TF) for young leaves was ranging from 0.83 to 1.54 and for old leaves was ranging from 0.46 to 0.94. It was found that the concentration of Cu in the pond tended to increase towards the sea. It was concluded that there was an accumulation of Cu in the sediment, roots and leaves of A. marina in Tapak, Tugurejo Semarang. The sediment have the highest ability to accumulate Cu from the environment*

Keywords – accumulation, *Avicennia marina, BCF,* Cu,*TF*

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1. Introduction

Mangrove forest is a type of forests typically found along the sea coasts or the estuaries, and this forest is commonly influenced by the tidal waves. Mangroves grow well in the sheltered coasts or in the shallow coasts protected from wind, or behind the coral reefs in the sheltered coasts [1]. Mangroves comprise the plant communities or a group of plant individuals that form a community in the intertidal zones, and the mangrove forest becomes the part of the coastal ecosystem with unique and distinctive characteristics which is rich of biological potential. Mangrove ecosystem consists of biotic and abiotic environments that interact each other in the mangrove habitat.

Mangrove ecosystem could not stand alone, and the ecosystem will have interconnection with other ecosystems. The ecosystem interconnection will form a larger system, i.e. the watershed. Mangroves that are growing in the downstream end of the river may act as the final destination of industrial sewage in the municipal and residential areas in the upstream areas. The solid and liquid wastes in the river water are brought by the stream toward the estuary and the open sea. The mangrove area will become the deposit area of the wastes, especially when the pollutants that enter the estuary overburden the natural capability of the area to cleanse the water [2,3].

Mangroves in the downstream end of the river may act as the final destination of industrial sewage in the municipal and residential areas in the upstream areas. The solid and liquid wastes in the river water are brought by the stream toward the estuary and the open sea. The mangrove forest area will become the deposit area of the wastes, especially when the pollutants that enter the estuary overburden the natural capability of the area to cleanse the water. The natural mangroves are effective in protecting the coasts from from natural stresses and erosion [3]. The decreasing rate of nutrients, heavy metals, and even organic pollutants in the mangrove forest has been attributable to the intricate interaction between soil, plants, microorganisms, and water components in the wetland areas.

The ability of mangroves in accumulating heavy metals is different for each species, and the heavy metal concentration in the different plant organs such as roots, branches and leaves is also different for each species. The heavy metal concentration difference on certain plant organs closely related to the physiological process of the plant [4,5]. [6]showed that the accumulation of Cr and Pb in roots, branches, and leaves of *A. marina* was different. The accumulation of Cr on roots > branches > leaves, whereas for Pb the accumulation was roots > (branches < leaves).

[7] utilized mangrove plant organs (roots, branches, leaves) and sediment to analyze the metal accumulation. It was suggested that in *A. marina*the accumulation of all heavy metals (except Cd) in the roots was higher than in the branches, leaves and sediment.

The conversion of the mangrove conservation area into fish/shrimp ponds has been the major cause of the destruction of mangrove ecosystem. The pond establishment around the estuaries and coastal zones along the North Coast of Java had been believed to have caused the real vegetation changes in those areas. The mangrove ecosystem is now found patchily in isolated areas or were planted along the pond dikes to prevent abrasion [8]. The mangrove area in Semarang has reduced from 52.4 Ha in (2002) to only 28.74 Ha (2007), and to 9.96 Ha (2009) which consists of mangrove forest in Sub-District of Tugu with an area of 7.74 Ha and in Sub-District of West Semarang with an area of 2.22 Ha (10).

2. Materials and Methods

2.1 Materials

The research was conducted in Tapak Area, Tugurejo Village, Semarang City.The samples were taken purposively, based on the pond distribution from the land to the sea. Primary and secondary data were collected in the first year of the research. The primary data consisted of microclimate data (i.e. temperature, pH, salinity), and Cu heavy metal concentration in the water and the sediment of milkfish ponds, as well as in the roots and the leaves of *A. marina.* The secondary data consisted of regional climate data; rainfall. The equipment used in the research were thermometer, refractometer, DO meter, pH meter. Meanwhile, AAS device was used to analyze the heavy metal concentration in the water, sediment, and mangrove plants.

Figure 1. Map of the research site, the mangrove ecosystem in Tapak Area, Tugurejo Village, Semarang City

The primary data collected from the field were environmental factors of mangrove ecosystem (temperature, pH, salinity, DO), and the sampling of water, sediment as well as roots and leaves of *Avicennia marina.* The secondary data were obtained from several relevant institutions such as Meteorological and Geophysics Agency and Environmental Agency, and the data were rainfall, temperature, tide, COD, BOD.

To understand the occurrence of heavy metal accumulation in mangrove plants, the metal concentration was calculated from sediment, roots and leaves.The metal concentration in the mangrove plant organs (roots and leaves) and in the sediment were measured and compared using Bioconcentration Factor (BCF).The BCF in the leaves and roots was measured to know the concentration of the metals in those plant organs that were originated from the environment. In addition to BCF, the Translocation Factors (TF) were also measured to compare the concentration of metals in the leaves and the roots of mangroves.The TF value was measured to know the accumulation of metals from the roots to the leaves [10].

3. Results and discussion

3.1 Cu Concentration

Laboratory analysis in the water and sediment, as well as in the roots and leaves of *A. marina* in four research Stations was summarized on Table 1. The laboratory result presented in Table 1 showed that the concentrations of Cu in the water in all Stations were less than 0.0069 mg/l, whereas in the sediment ranged from 26.76 to 37.889 mg/Kg. In the roots, the value ranged from 2.336 to 7.997 mg/Kg, in the young leaves from 2.367 to 6.604 mg/Kg, and in the old leaves from 1.08 to 6.748 mg/Kg. Figure 1 shows the laboratory result of Cu concentration in each research parameter.

Table 1. The mean concentration of Cu in the water and sediment, and in the roots and leaves of *Avicenni marina* in Tapak Area

	Water	Sediment	Roots	Young Leaves	Old Leaves
Station 1	0.0069	26.76	2.512	2.942	2.354
Station 2	0.0069	28.368	2.336	2.367	1.08
Station 3	0.0069	29.797	4.4	6.76	4.108
Station 4	0.0069	37.889	7.997	6.604	6.748

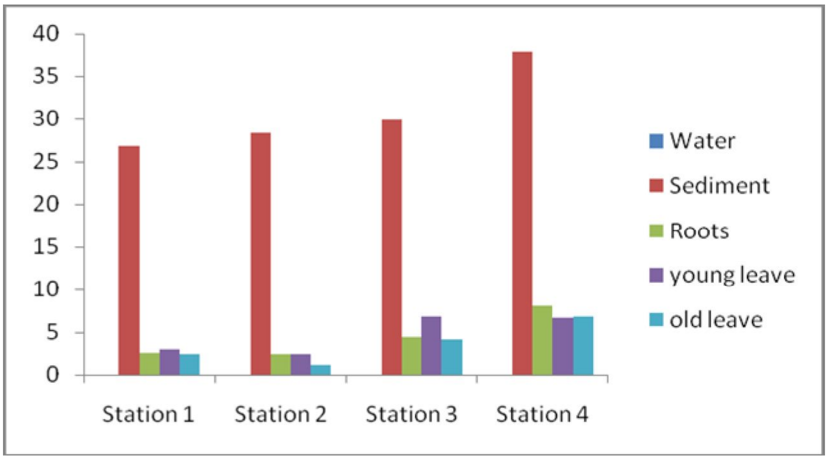

Figure 1. Graph of Cu in the water and sediment, and in the roots and leaves of *Avicennia marina*

Both graphs (Figure 1) show the trend of the increasing concentration of heavy metals from Station 1 to Station 4. These graphs also show the significant increase of heavy metals in the sediment and in the plant *A. marina* located in the research site.

This result was obtained because the sampling sites were different, in which Station 1 was the pond closest to the land and Station 4 was the pond closest to the sea. The estuaries are the place for the pollutants to settle, and therefore typically the sedimentation of Cu in the estuaries was higher than in the inland ponds. As mentioned by [3], the solid and liquid wastes in the river water are brought by the stream toward the estuary and the open sea. The mangrove forest area will become the deposit area of the wastes, especially when the pollutants that enter the estuary overburden the natural capability of the area to cleanse the water.

The concentration of Cu in the sediment was the highest (26.76 to 37.889 mg/Kg) compared to the other parameters (roots and leaves), due to the high ability of the sediment in absorbing metals. The physical and chemical properties of the sediment in the mangrove forest are the ability to accumulate the materials in the coastal areas. Further, the rooting system of mangroves plays role in retaining heavy metals to reside in the sediment [11]. [7, 12] stated that mangrove ecosystem plays important role as the filter and the natural control of pollution thanks to the rooting system that is able to control the water quality and to trap the sediment as well as the particles transported by stream from the estuaries to the sea.

The Cu concentration in the roots (2.336 to 7.997 mg/Kg); young leaves (2.367 to 6.604 mg/Kg), and old leaves (1.08 to 6.748 mg/Kg), showed the ability of the reoots and leaves of *A. marina* to accumulate Cu. One function of mangrove ecosystem is to absorp or bind heavy metals. Research by [7,12,13] showed that mangrove plays role as good bioaccumulator of heavy metals. [7] utilized mangrove plant organs (roots, branches, leaves) and sediment to analyze the metal accumulation.[10.14], found strong linear relationship between all heavy metals in the sediment and those in the mangrove tissues (i.e. roots). This means that there was tolerance and capacity to accumulate metaloids and metals through the concept of remediation of contaminated soil, in a process of phytoremediation or, more precisely, phytoextraction[13].

Figure 1 presents a graph that shows the increase of Cu concentration in the sediment that impacted on the increase of Cu concentration in the mangrove plant organs (roots and leaves). This increase showed the ability of the roots and leaves of *A. marina* to accumulate metals from the sediment they live. The metals tended to accumulate in the roots at the same concentration of the adjacent sediment, whereas the concentration of metals in the leaves was half of the roots or even lower. The concentration of metals in the leaves was one tenth or less compared to the concentration of metals in the sediment, with Cu and Zn showed the higher concentration compared to Pb [10,14].

This has proven that mangroves were the good hyper accumulator. Not only do mangroves capable of growing on the soil with high concentration of poisonous substances, but also accumulate the substances in the branches and leaves at higher level that is probably lethal to other living organisms. Some plants (i.e. metallophytes) can grow in the substrates containing very high concentration of metals [13].

3.2. Concentration Factor of Cu Heavy Metal in the Water and Sediment

The laboratory analysis of Cu concentration in the water and sediment of Tapak Area, Tugurejo Village, Semarang City, showed the Concentration Factor of each research site, as seen on Table 2.

Table 2. Concentration factor of Cu in the water and sediment

	Sediment	Water	Concentration factor
Station 1	26.76	0.0069	3878.26
Station 2	28.368	0.0069	4111.30
Station 3	29.797	0.0069	4318.41
Station 4	37.889	0.0069	5491.16

With the Cu concentration in the water of 0.0069 mg/l and in the sediment of 26.76 to 37,889 mg/Kg, the Concentration Factor would be 3878.26 to 5491.16. The location of the research, i.e. the estuary of Tapak River, allowed the accumulation of various metals. The high concentration of Cu in the sediment showed the ability of the pond sediment to accumulate Cu from the water in the environment.

The presence of Cu in the ponds in Tapak was in accordance with [15] who sttaed that Cu concentration in the pond waters in Tapak Area was 0.007 mg/l and Pb concentration was 0.003 mg/l, whereas the water of Tapak River contained Cuat0.013 to 0.037 mg/l and Pb was < 0,030 mg/l. Meanwhile, [17] showed that the values of the heavy metals Cu, Cd, Pb, and Ni were beyond the allowed limit of Sea Water Quality Standard for Tirangcawang Island in Tapak Area, Semarang.

Some research showed that mangrove ecosystem has ability to reduce pollutants from the urban areas [5, 17, 18]. The high concentration of heavy metals in mangrove ecosystem has been attributable to the anthropogenic input, including wastes from domestic, industry and agriculture, both from the tide inflow and the fresh water outflow from the river [2, 19, 20]. Similar to other natural and artificial wetlands, mangrove ecosystem may be considered as the alternative method that is inexpensive, easy to maintain, and simple to manage the wastes from the domestic, industry, agriculture and even mining [5]. This was due to the larger capacity of mangrove sediment in storing the heavy metals. However, the capacity to store heavy metals was depended upon the age of the plants and the biomass [21].

The type of soil of Tapak Area is mud which enables the sediment to absorp Cu from the water in the environment. Thus the plants absorp the metals accumulated in the sediment of the research sites. In their research [18, 19, 22], suggested that the heavy metal concentration was higher in the fine granules than in the sand of the sediment fractions; this was seen from the high concentration of Mn, Cu, Zn and organic carbons in the fine granule fractions (<63 μm). The metals were mainly found on the soil surface and accumulated in the 0-1 cm and 1-2 cm layers. The column that received wastewater had the concentration of Cu, Cd, Mn, and Zn that were significantly higher than the control, and Cu seemed to have been absorbed stronger by mangrove soil than other heavy metals. The concentration of the metal reduced significantly based on the soil depth [19, 22]. [23] found that mangrove soil has larger capacity to store Cu. In the end of the research, the Cu concentration has reduced by >40%.

3.3. Bio Concentration Factor (BCF) of Cu in mangrove roots

The Bio Concentration Factor (BCF) of Cu can be seen by comparing the concentration of Cu in the roots compared to the concentration of Cu in the sediment from each Station (Table 3).

Table 3.*Bio Concentration Factor* (BCF) of Cu in the roots and sediment

	Root	Sediment	BCF
Station 1	2.512	26.76	0.09
Station 2	2.336	28.368	0.08
Station 3	4.4	29.797	0.15
Station 4	7.997	37.889	0.211

The calculation of BCF showed the ability of roots to accumulate Cu from the sediment in the environment (0.09 to 0.211). The higher the metal concentration in the sediment, the higher the the metal concentration in the roots. On the Station 1 where BCF was the lowest (0.09), it was possible because the concentration of Cu in the sediment was 26.76 mg/Kg and the concentration of Cu in the roots was 2.512 mg/Kg. The highest value of BCF was obtained in Station 4 (0,211), with the concentration of Cu in the sediment was 37.889 mg/Kg and in the roots was 7.997 mg/Kg. The result of this research showed the capability of the roots of *A. marina* to accumulate Cu. In addition to accumulation, apparently *A. marina* was also able to prevent other toxic substances. Among others is by weakening the poisonous effect through dilution, that is by storing much water to dilute the concentration of heavy metals in the tissues so that the toxicity of the heavy metals is reduced [3]. The mangrove plants accumulate heavy metals mostly in their roots. However, other factors such as the mobility and the dilution of metals also play role in the heavy metal accumulation in the plants [5].

[14] said, that the roots of *A. marina*may be used as bioindicator of the Cu, Pb and Zn exposure in the environment. This shows the potential of *A. marina* phytoremediation species in the mangrove ecosystem**.** The growth of *A. marina* could be healthier than other mangrovespecies, and this suggests the adaptive capability of this plant in the polluted areas [7]. [10]asserted that the metals tended to accumulate in the roots at the same concentration of the adjacent sediment, whereas the concentration of metals in the leaves was half of the roots or even lower.The concentration of metals in the leaves was one tenth or less compared to the concentration of metals in the sediment, with Cuand Znshowed the higher concentration compared to Pb[14].

Although the BCF concentration of the roots of *A. marina*and the sediment was very small (0.008 to 0.211), this can be used as the indicator for the ability of the roots to accumulate Cu from the environment.This differs from [10] who stated that the metals tended to accumulate in the roots at the same concentration of the adjacent sediment, whereas the concentration of metals in the leaves was half of the roots or even lower.However, [14] said that the roots of *A. marina* may be used as bioindicator of the Cu, Pb and Zn exposure in the environment.This shows the potential of *A. marina*as phytoremediation species in the mangrove ecosystem**.** The growth of *A. marina* could be healthier than other mangrovespecies, and this suggests the adaptive capability of this plant in the polluted areas [7].

3.4. Translocation Factors (TF) of Cu in the leaves

The Cu concentration in the leaves compared to the roots of mangroves was calculated using *Translocation Factors* (TF) as seen on Table 4.

Table 4.*Translocation Factors* (TF) of Cu in the leaves and roots of mangroves

	Young Leaves	Old Leaves
Station 1	1.17	0.94
Station 2	1.01	0.46
Station 3	1.54	0.93
Station 4	0.83	0.84
Average	1.1375	0.7925

Table 4 shows that young leaves of *A. marina* has higher value of TF (0.83 to 1.54) compared the old leaves (0.46 to 0.94).This is possible because you leaves had higher capability to accumulate Cu (2.367 to 6.604 mg/Kg) than old leaves (1.08 to 6.748 mg/Kg). In addition to accumulating, it was suggested that *A. marina* has ability to cope with toxic substances, among others, by weakening the poisonous effect through dilution, that is by storing much water to dilute the concentration of heavy metals in the tissues so that the toxicity of the heavy metals is reduced.The dilution ability by storing water in the tissue is commonly found in the leaves, and the leaves normally undergo succulency. Excretion is also possible, i.e. by storing the toxic substances in the old tissues such as old leaves or easily stripped barks, to reduce the concentration of heavy metals in the tissues [3].

[7] showed the potential of *A. marina* as heavy metal phyto remediation species in many mangrove ecosystems. Whereas[24] asserted the domination of *A. marina* and the poor abundance and diversity of mangrove indicated the stress against the environment.

[7, 12] stated that mangrove ecosystem plays important role as the filter and the natural control of pollution thanks to the rooting system that is able to control the water quality and to trap the sediment as well as the particles transported by stream from the estuaries to the sea. This was supported by [10] who stated that mangrove ecosystem plays important role as phytostabilizer, and potential to help retain the poisonous metals, and therefore can reduce the transportation to the adjacent estuary zone and to the sea. Hence the removal of mangrove forest would not only remove the pollutant trappers that can effectively protect the environment, but also might release some pollutants trapped in the mangrove forest [25]. [26] stated that mangrove ecosystem could retain and probably reduce the remobilization of metals in the sediment, that would eventually reduce the transfer of metals to the waters due to the physical displacement of sediment-bound metals and biogeochemistry. This environment seems to be potentially utilized as the barrier for metal transportation. In Colombia, the mangrove wetlands were used to remove hydrocarbon and heavy metals in oil refineries and tanning wastes [12].

According to [27, the absorption and accumulation mechanism of heavy metals by plants can be broken down in three serial steps:

1. Absorption by roots. In order to absorp metals, the metals must be dissolved in the solution around the roots in various ways, depending on the plant species. These dissolved substances are then normally absorbed along with the water, whereas the hydrophobic substances will be absorbed by the root surface.
2. Metal translocation from roots to other organs. After the metals penetrate the root endoderm, these and other foreign substances will follow the transpiration flow to the other parts of the plant in the transportation tissues (xylem and phloem).
3. Metal localization in the cells and tissues. This happens in order to keep away the metals from disturbing the metabolism. Plants normally utilize detoxification mechanism to prevent poisoning, e.g. by

accumulating the metals in certain organs such as roots.

4. Conclusions

It was concluded that Cu accumulation happened in the sediment, as well as in the roots and leaves of *A. marina* in Tapak pond area, Tugurejo Semarang. The sediments have the highest ability to accumulate Cu from the environment.

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