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Concentration of Heavy Metal (Pb And Cu) in Sediment and Mangrove Avicennia marina at Porong River Estuary, Sidoarjo, East Java

Ledhyane Ika Harlyan, Dwi Retnowati, Syarifah Hikmah Julinda Sari, Feni Iranawati*)
*) Faculty of Fisheries and Marine Science, University of Brawijaya, Indonesia
Corresponding Email: ledhyane@ub.ac.id

ABSTRACT

The ability of mangrove (Avicennia) to absorb heavy metal has been known. This study aims to determine whether there are differences of absorption level of non-essential (Pb) essential (Cu) heavy metals in *Avicennia marina* from different location, based on distance of pollutants sources (downstream) toward to the mouth of Porong River Estuary at Sidoarjo. Results showed that accumulation of Pb in the roots and leaves was ranged from 0.0044 to 0.139 ppm and from 0.004 to 0.019 ppm respectively, while in sediment was ranged from 0.0560 to 0.0660 ppm. The accumulation of Cu in the roots and leaves was ranged from 0.07 to 0.415 ppm and 0.0318 to 0.2520 ppm while in sediments was from 0.2930 to 0.381 ppm. The highest concentration of Pb and Cu were found from sediments followed by roots and leaves. The high concentration of heavy metal (Pb and Cu) in the root is likely due to sediment size. The high concentration of heavy metal (Pb and Cu) in the root is likely due to sediment size. When the size is finer, heavy metal accumulation will be higher, although there was no significantly different from different location.

Keywords: Phytoremediation, coastal sediment, mangrove, heavy metal pollution.

INTRODUCTION

It is undoubted that porong is developing industrial area and this may have impact on the environment of costal area. There is indication that household waste and industrial waste is discarded in the porong river while the quality control of this waste was limited. Accumulation of this waste toward downstream will eventually effect on estuary area as final waste disposal. Mangrove is distributed in coastal area, especially in estuary. As such, the mangrove ecosystem is vulnerable to water pollution in particular with heavy metal.

Mangrove ecosystem have biogeochemical potential as a barrier for various pollutants such as heavy metal that result from anthropogenic activities, agricultural runoff and industrial waste (Nath *et al.*, 2014). Heavy metals can accumulate in the body of organisms and will remains inside the body for long period as poison. In addition, heavy metals can also accumulate in solids form as water sediment. Concentrations of heavy metals will cause environmental damage and increase toxicity, and bioaccumulation persistan metal itself (Lindsey et al., 2004).

Previous studies have shown that some mangrove species are able to accumulate heavy metals and in particular, species Avicennia marina, can accumulate heavy metals Pb and Cu greater than other mangrove species (Kamaruzzaman et al., 2011 and Heriyanto and Subiandono, 2011) The accumulation of heavy metals by mangrove species found in the roots are growing, stems and leaves (MacFarlane and Burchett, 2002).

This study aims was to measure the concentrations of heavy metals Pb and Cu in sediments, roots and leaves of mangrove A. marina and to evaluate whether the distance from the source of pollutants will

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affect the accumulation of heavy metals on *A. marina* or not.

LITERATURE REVIEW

1. Heavy Metal Pb.

Pb is classified as a soft textured metal with a bluish-white color or a dull grayish color when it containssulfide sedimentation mixed with other minerals such as zinc and copper (Sunu, 2001). Moreover, Pb is known as non essensial element which is malleablity and weak electrical conductivity. Belong to group IV-A with atomic number 82 and weight number 207,2, this heavy metal resits to corrosion (Lenntech, 2005). Pure Pb exits in scarce concentration naturally. It might be found in minerals which contain 10-20 mg/kg of Pb. In soil, Pb concentration is influenced by organic matter content in soil, pH, texture of soil, ion exchange and temperature. An average concentration of Pb in soil enviroment is ranged from 5-25 mg/kg.

Pb also exits in water in form of hydroxide compound, oxide compound, carbonate and sulfide compound. According to Goldstein and Kipen (1994), Pb in water occurs in dissolved and suspended form in low concentration. In addition, Pb in atmosphere forms particulate matter. The sources of Pb in atmosphere origin from vulcanic eruption and erosion (Palar, 2012). In the environment, Pb mostly comes from anthropogenic activities such as telephone cable, electricity cable, explosion materials, paint, power plants, and emission gas from vehicles.

Pb is determined as one of the most toxic metals for human health. Pb is uptaked by human body by foods/ingestion (65%), water (20%) and air (15%). Ones Pb containing in human body, it will be accumulated as the process of food chain (Hutabarat and Evans, 1985). Consequently, there will be adverse impact to human health such as bio-syhtheses distruption, anemia, neuron disease, brain distruption, and behaviour changing in children namely impulsive and hyperactive condition.

2. Heavy metal Cu

Cu is an essensial element that naturally occurs in low concentration. Forming in reddish crystal, Cu has atomic number 29 and atomic weight 63,456. In the environment, Cu found in free compound as well as bounded with solid particle to form minerals. Generally, Cu produces from mine activities (Palar, 2012). Entering the aquatic environment, Cu forms salts such as $CuCl_2$ and $CuSO_4$ that dissolve easily in water. In natural waters with alkaline condition, Cu is precipitated and sedimented as hydroxide Cu and carbonate Cu (Effendi, 2003).

Cu Concentration naturally in earth crust is approximately 50 mg/kg and in the aquatic environment is around less than 0,02 mg/L. In groundwater, Cu is about 12 mg/L while in seawater, concentration Cu is ranged between 0,001 - 0,125 mg/L. Moreover, natural sources of Cu are *chalcopyrite,* coopersulfida, malachite and azurite. Cu is applied in metal industries, textile, electronic, and antifouling paint. Cu is also applied to kill algae in the waters by absorp silicate inside diatomes so that flustule forming is disturbed (Effendi, 2003).

The presence of Cu in low concentration is beneficial for biota, while in high concentration it will induce toxicity to them. Toxicity of Cu (EC_{50}) in microalgae is ranged from 0,1 - 0,3 mg/L. In addition, LC_{50} of Cu in freshwater invetebrate is less than 0,5 mg/L, while in fish is between 0,02 - 1,0 mg/L (Moore, 1991). The high concentration of Cualso might cause corossion. Increasing of toxicity of Cu is in line with increasing of hard water and decreasing of alkalinity.

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3. Mangrove *Avicennia marina*

A. marina is recognized as grey mangrove that commnly found in coastal areas of Indonesia. This mangrove owns an unique adaptation strategy that may live in mud sediment and high salts content. The roots of *A. marina* poses breath roots that look line long and dense nail coming up from sediments. The leaves are elipcle shape with size between 9 x 4,5 cm with grannular in lower parts. The fruits shape is round and the color of flower is green greyish (Noor *et al*., 2006).

Avicennia marina is found to live in tidal areas. They also lie in soft mud to sand substrate (IUCN, 2014). The hight of this plant reaches 2 - 5 m. They commonly found from upstream to downstream of river. The salinity for *A.marina* growth range from 0 - 30 ppt (Robertson dan Alongi, 1992).

4. Mechanisms of Heavy Metal Absorption in Mangrove.

Heavy metal including Cu and Pb can be absorbed into mangrove plant by difussion or translocation mechanisms. Absorption of heavy metals is conducted by root, leaves and stomata of mangrove. The roots of mangrove more absorp organic matter and hydrophilic materials than its leaves. However, the leaves of mangrove tend to absorp lipophilic materials, while stomata prefer to absorp gas materials.

The mechanisms of plants to face the toxic materials are as follow. First, amelioration can be determined as if concentration of toxic materials is high inside the organ, it may relocate to intracelular or extracellular layer that is carried out by roots or old leaves excretion. Second, toleration can be descreabed as development of metabolic system to adapt in high concentration of toxic materials (Fittendan Hay, 1991 *in* Panjaitan, 2009).

Mangrove has capability to receive pollutant discharge without distruct their own growth rate. Nutrient concentration and primary productivity in mangrove ecosystem cause them to own capability in handling heavy metals. Heavy metals in mangrove is accumulated dan distributed dominantly in root parts. Concentration of heavy metals increase according to prensence of heave metals in their sediment. However, the capability to endure heavy metals depend on the age of plant and biomass production (Tam *et al.,*1997 *in* Kusumastuti, 2009).

Anggoro (2006) said that mangrove plant can absorb heavy metals in the polluted waterso that they will decrese the pollutant concentration in the environment. Mangrove actively absorp heavy metals in limited concentration when they lie in high concentration in sediment. Endoderm cells in mangrove's roots act as filters in absorption process, and then translocated them into other organs such as steams and leaves. They will undergo complexation with other subtances such as ficocelatin (Baker and Walker 1990 *in* MacFarlane *et al*., 2003). Hence, mangrove plant can be determined as a plant to phytoremediation process for heavy metal pollution.

METHODS

1. Sampling Sites.

Sampling was conducted in September 2014 at mangrove area in the Porong River Estuary, Sidoarjo, East Java, Indonesia (Figure 1). Samples were taken at three different locations, from the estuary toward the downstream area. Samples were collected from water, sediment, roots and leaves of mangrove *Avicennia marina*. Heavy metals assessed were non-essential (Pb) and essential heavy metals (Cu) using Shimadzu AA-6800 Flame Atomic Absorbance

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Spectrophotometer. Sediment type analysis, physical and chemical assessment of water such as temperature, DO, salinity, and pH were also carried out.

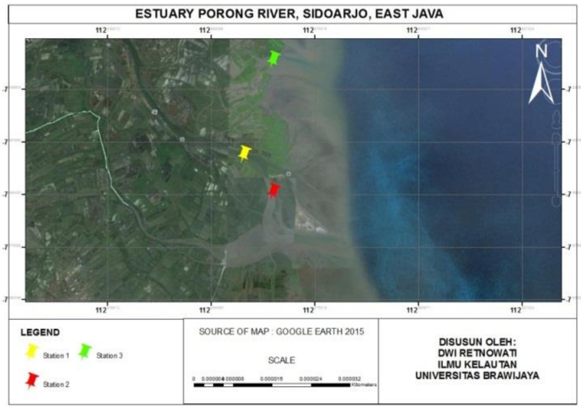

Figure 1 : Sampling Site Estuary Porong River, Sidoarjo, East Java, Indonesia.

2. Water Quality Measurements.

Water quality measurement was carried out in situ with three repetitions at each site. The tools applied for water quality measurements such as pH, DO, salinity and temperature were pHmeter, Winkler titration, salinometer and digital thermo-meter, respectively.

3. Heavy Metal Analysis of Mangrove Sample.

The sediment was taken from around the mangrove tree sample, two trees from each site respectively. Sediments were taken using PVC pipe that have a diameter of 15 cm with a length of 1 m and then put into plastic sample.

All samples collected were kept in an ice box and transferred back to the laboratory and preserved at 4°C for further analysis. Analysis of sediment carried at Jasatirta 1 Laboratory using Shimadzu AA-6800 AAS Flame to evaluate the concentration of heavy metals Pb and Cu. Hydrometer analysis was also applied to determine the composition of the sediment types.

4. Heavy Metal Analysis of Mangrove Sample.

Samples of mangrove were collected from the roots and leaves using scissors. Mangrove with 3 - 5 meters tall and 15 - 20 cm of trunk diameter were selected, two threes at each sites respectively. The roots were of which resides in the sediment while the leaves were of that are not too old and not too young as many as 30 leaves. All roots, leaves and sediment samples were clean up before kept in the plastic clip. The collected samples were transferred back to the laboratory in an ice box and refrigerated at 4° C for further analysis. Samples of leaves and roots of the mangrove *Avicennia marina* was dried using an oven at 105^0C for 24 hours. The extraction of dried samples was carried out by adding HNO3 and HClO4. The measurement of these heavy metals (Pb and Cu) were performed by using Shimadzu AA-6800 Atomic Absorbance Spectrophotometer (MacFarlane and Burchett, 2002).

5. Data Analysis.

Concentrations of Pb and Cu in the roots, leaves and sediment are known. Statistical analysis to determine whether there are significant differences in the uptake of heavy metals Pb and Cu interaction between the two by mangrove *Avicennia marina* be analyzed with factorial ANOVA.

RESULTS AND DISCUSSIONS

1. Physical and Chemical Parameters of Water and Sediment Compositions.

Result of physical and chemical parameters of water showed that average temperature at the Porong River estuary was $31,56^0$C while the average of salinity, pH and DO were 28.89‰, 7.89 and 8.53 mg/L, respectively. Based on the physical and chemical water results, this indicated that the waters are still able to support the life of living organism (Kep.Men. LH No. 51, 2004). The composition of the sediment in Porong estuaries were silt and clay and dominated by clay. Substrate conditions, in particular mud fraction will affect the metal concentrations in sediments (Hogarth, Peter J., 1999).

2. Concentration of Heavy Metals Pb and Cu.

2.1. Sediment.

According to Arifin *et al.* (2012), sediments are a good indicator in the environment to assess heavy metal because they are relatively stable. The results analysis of heavy metals concentration for Pb and Cu in Mangrove Ecosystem of Porong River Estuary is listed in Figure 2. Pb concentration was ranged from 0,0605 ppm - 0,0650 ppm. Cu concentration was found between 0,3185 ppm - 0,3755 ppm.

In details, Pb concentration in sediments of Porong River Estuary was 0,0650 ppm, 0,0615 and 0,0605 ppm for station 1,2 and 3, respectively. The average concentration of Pb was 0,0622 ± 0,0256 ppm. Station 3 was confirmed as the location which has the lowest heavy metal concentration in sedimen. It is because station 3 is located close to open sea and own high turbulence compared to other station. This situation was assumed to influence the concentration of heavy metals in the sediment. According to Agustanto (2007) in Juniawan (2012) heavy metals in the sediment was induced by turbulences condition and temperature of water. Station 3 had the highest temperature compared to other stations. Increase in temperature will decline particulate absorption so that sedimentation of heavy metals may reduce (Palar, 2012).

The highest concentration of Pb was found in station 1 because this station was located in dowstream areas. The downstream area was near the river that act as medium to recieve and accumulate discharging. There are several industries near Porong River such as metals and household industries that might contain Pb in their wastewater. Pb sources in aquatic environment come from sedimentation and atmospheric sources from fuel, erosion and industrial waste that flow into river's estuary, so that this location may potential to Pb pollution (Murtini dan Peranginangin (2006).

Cu concentration in sediment from Porong River Estuary was ranged from 0,3186 - 0,3755 ppm with the average values of 0,3547 ± 0,031 ppm. Station 1 contained Cu 0,3755 ppm, staion 2 had Cu 0,3700 ppm, and stasion 3 owned Cu 0,3185 ppm.

The highest concentration of Cu found in station 1 because this location closed to harbor and residential areas. According to Juniawan *et al.* (2013) Cu might be originated from anthropogenic activities. This waste presented in the rivers, then it would accumulate in estuary areas. The lowest Cu concentration found in station 3. In this area, there is more turbulence condition compared to other station. This situation would result less sedimentation of heavy metal (Amin *et al*, 2011).

The average concentration of Cu in sediments was higher than of Pb in sediments. It might occur because there were more sources of Cu compared to Pb in Porong River areas. According Palar (2012) concentration of Pb was less available in the environments.

Environmental quality standards in sediment base on CCME (Canadian Council of Minister of The Environment, 1987) are 30,2 - 112 mg/kg for Pb and 18,7 - 108 mg/kg for Cu. Therefore, it can be concluded that heavy metal Pb and Cu in sediment of mangrove ecosystem in Porong River Estuary were in safe level.

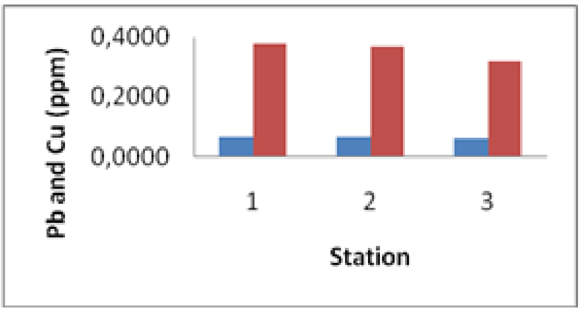

Figure 2. : Pb and Cu concentration in sediments of Porong River Estuary.

2.2. Roots.

Pb concentration in roots of A.marina lied from 0,0044 ppm - 0,0800 ppm. In station 1, the concentration of Pb in mangrove's roots 0,0044 ppm, while in station 2 was 0,0480 ppm. Mangrove roots from station 3 owned 0,800 ppm of Pb. Cu in mangrove A.marina's roots in Porong River Estuary was ranged from 0,208 ppm - 0,34 ppm. In details, Cu in roots from station 1 found 0,208 ppm, station 2 was 0,327 ppm and station 3 was 0,34 ppm. The concentration of Pb and Cu in roots of A.marina in Porong River Estuary is presented in Figure 3.

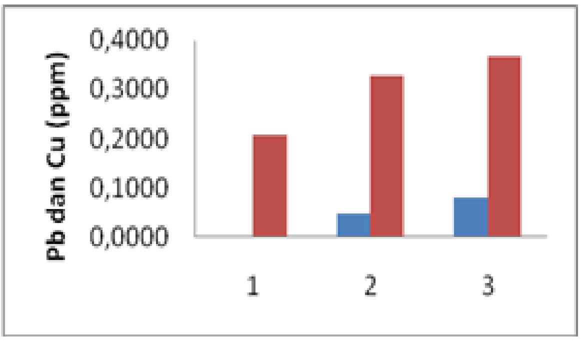

Figure 3. : Pb and Cu concentration in roots of *A.marina* in Porong River Estuary.

As can be seen in Figure 3, heavy metal Pb and Cu in Mangrove roots from station 1 had the lowest concentration, while in station 3 was confirmed as the highest concentration of Pb and Cu in mangrove roots of *A. marina*. Each station was dominated by different kinds of sediments fraction. This situation might cause different concentration of heavy metal in mangrove roots for each station. Heavy metals in sediments is easier to difuse in mangrove roots if the sediment fraction is in fine size (Nath *et al*., 2014).

The average of Cu in *A. marina* roots was six times higher compared to Pb concentration. Cu is defined as essensial elements. Moreover, the roots of *A. marina* is highly selective medium to absorp Pb as the non essensial elements (MacFarlane *et al*., 2003).

The roots of *A. marina* is able to absorp heavy metals from the environment because the roots immerse in the sediment for long period. Based on its physiological mechanism, mangrove may reduce pollutant in the sediments. The absorption of heavy metals through the roots may translocate the heavy metals from sediment to roots, and finally accumulate in the roots. However, this capability is only for limited concentration of heavy metals (Hamzah dan Setiawan, 2010).

2.3. Leaves.

The results of measurements of heavy metals Pb and Cu in leaves of *A. marina* were 0,0042 ppm - 0,0130 ppm for Pb and 0,1480 ppm – 0,2455 ppm for Cu.

Pb in leaves of *A. Marina* from station 1,2 and 3 were 0,0042 ppm, 0,0130 ppm and 0,0044 ppm, respectively. However, Cu in leaves of *A. marina* in each station were 0,1790 ppm for station 1, 0,2455 ppm for station 2, and 0,1480 ppm for station 3. Concentration of Pb and Cu in leaves of *A. marina* from Porong River Estuary is illustrated in Figure 4.

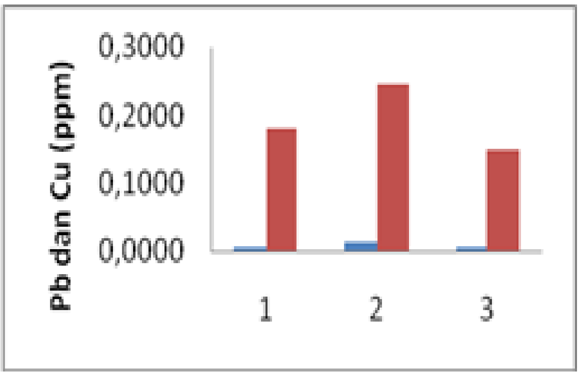

Figure 4. : Pb and Cu concentration in leaves A.marina in Porong River Estuary.

As can be seen in Figure 4, the lowest concentration of Pn di leaves of *A. marina* found in station 1 (0,0042 ppm). It was predicted that heavy metals in roots in this station was tranlocated to leaves, so that the Pb was more accumulated in leaves of *A. marina*. Dedy *et al.*, (2013) reported that roots of mangrove have a higher capability to transfer the heavy metals compare to other organ.

Concentration of Cu in leaves of mangrove *A. marina* in station 3 was confirmed as the lowest value. This is assumed that concentration of Cu was stored in roots and only little concentration passed into leaves parts. The mangrove which live in low concentration of essensial elements in their environment tend to accumulate the elements in particular organs such as the roots (Dedy *et al.*, 2013). According to Purwiyanto, (2013) in Cu-non polluted sediment, the mangrove on purpose absorp this elements from their environment.

The highest concentration of Pb and Cu di leaves of *A. marina* was belonged to station 2 (0,0130 ppm and 0,2455 ppm). Station 2 which is located in estuary areas owns low turbulence waters because this areas are blocked by Sarinah Island. This condition will influence absorption rate of heavy metals. Barutu et al., (2011) revealed that water turbulence affects the heavy metals absorption in mangrove plant.

2.4. Comparison between Concentration of Heavy Metals Pb and Cuin Roots, Leaves and Sediments.

The results showed that the difference of Pb accumulation capability of roots and leaves as well as sediments in the three sampling sites. There was significant difference of Pb uptake in sediments and leaves over three sampling sites (Sig 0.027). However, Pb concentration in sediment and leaves did not show any differences from those in roots.

It can be seen from Figure 5 that Pb concentration in sediments in three different sites revealed the relatively similar concentration. This might be happened due to distribution of pollutant through river stream. On the other sides, the Pb concentration in the roots of *A. marina* indicated different pattern in each station.

Comparison between Cu concentration in sediment, roots and leaves of *A. marina* in Porong River Estuary is presented in Figure 6. These Cu concentration in sediments from the three sampling sites showed that there was no significant difference seitherin the roots, leaves and sediment (Sig 0. 218).

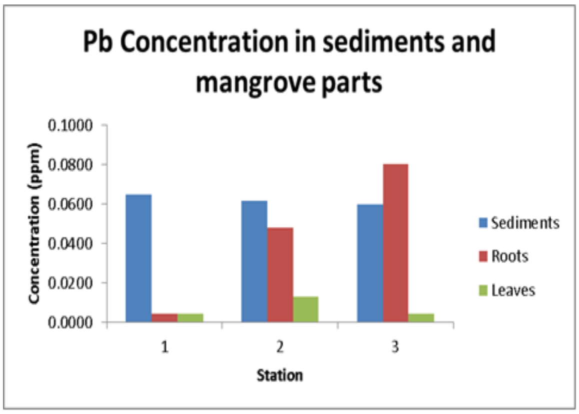

Figure 5. : Concentration Pb in Mangrove *Avicennia marina* (roots and leaves) and Sediments.

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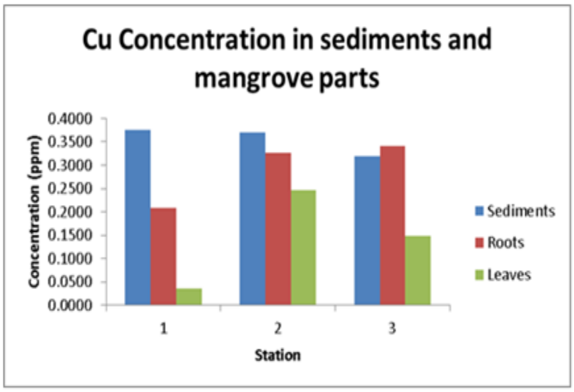

Figure 6. **:** Concentration Cu in Mangrove *Avicennia marina* (roots and leaves) and Sediments.

CONCLUSIONS

The results showed that the mangrove *Avicennia marina* has the ability to accumulate heavy metals Pb and Cu. The concentration of both of heavy metal Pb and Cu in sediment is greater than in the mangrove (roots and leaves). Based on a statistical test, there was no significant difference level of accumulation of heavy metals Pb and Cu in different locations from downstrean to estuary on the mangrove *avicennia marina*.

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