Copper Accumulation by *Avicennia marina* at Mangrove Eco-forest in Wonorejo, Surabaya

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Abstract. Large quantities of wastewater from industries and households were released to Wonorejo river in Surabaya East Coast area. The concentration of Cu at the Wonorejo Estuary reached 3.186 mg/L at brackish water in 2009 One of the inorganic pollutants that can be removed by mangrove is copper (Cu). The purpose of this research was to determine the potency of Cu accumulation by *Avicennia marina* that was grown for ten years at Wonorejo Estuary. The sampling activities were conducted using a transect quadrat sampling method with a 10x10 m dimension. There were ten points of location sampling, the sediment and root of *A. marina* samples were collected in those location sampling. All samples of sediment and root were extracted before those samples were analyzed using an atomic absorption spectrophotometer (AAS). The calculation of the Bioconcentration Factor (BCF) was conducted using a equation formulation. The results showed that concentration Cu in sediment was 27 mg/kg until to 150 mg/kg. The Cu accumulation by roots of *A. marina* reached 53 mg/kg until to 128 mg/kg. The BCF value in *A. marina* were 0.91 to 3.22 In conclusion, *A. marina* showed potential as a hyperaccumulator for Cu.

Keywords. Bioconcentration, Cu, estuary, heavy metal, mangrove, uptake

1 Introduction

Surabaya East Coast region has a ecosystem mangrove forest. The Many species of mangrove can grow well at the mangrove forest. This area has high levels of salinity [1]. Mangroves are perennial woody plants grown in tropical and sub-tropical inter-tidal zones [2]. The distance of Wonorejo forest was 10 - 20 meters from the estuary [2]. River mouth area Wonorejo has various types of mangroves. Type mangroves that are around the Wonorejo River, among others types of *Avicennia marina, Avicennia alba, Excoecaria*

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agalocha, Avicennia officinallis [3]. Mangroves have a tolerance high against heavy metals. Heavy metal accumulation occurs on the roots, stems and leaves of mangroves [4]. Generally, heavy metal pollution in mangrove areas can be caused from urban waste, agricultural waste, effluent Wastewater Treatment Plants (WWTP), industrial effluent waste, use of ships and chemical spills [5].

According to Mulyadi et al., (2009) [6], Cu concentration was 3,186 mg/L at Wonorejo River estuary in 2009. Based on sampling that was conducted in 2016, the Cu concentration was 22 mg/kg in sediment at the Wonorejo River estuary. It indicated that Cu concentration increased. Cu is included in the essential metal group. Cu is needed by organisms as a coenzyme in the body's metabolic processes in low levels. However, it can be toxic if the Cu concentration in high levels [7].

The aim of this research was to determine the potency of Cu accumulation by *Avicennia marina* that was grown for ten years at Eco-forest at Wonorejo Estuary.

2 Materials and Methods

2.1 Sampling Location

Sampling locations were shown in Fig 1 at Eco-forst at Wonorejo Estuary, Surabaya. The sampling activities were carried using a Transect quadrat sampling method due to the Transect quadrat sampling method was suitable. The dimension of one quadrant was 10m x 10m. Sampling point determinations were conducted using a GPSmap 76CSx (Garmin, USA).

Fig. 1. Sampling Location.

There were ten points of location sampling, namely M11A, M12A, M11B, M12B, M13A, M13B, M11D, M12D, M11E dan M12E. Sampling activities were conducted at the morning time due to sea water level was low enough at that time for sediment sampling. According to Usman & Mohamed's (2009) methods [8], sediment samplings were carried out by random sampling with a depth of 0–30 cm. Root samplings were carried out using a manual drill. All samples were stored in an icebox at 4°C. After then, all samples were taken to the Environmental Remediation Laboratory, Department of Environmental Engineering, Institut Teknologi Sepuluh Nopember (ITS) for further analysis.

2.2 Parameter Analysis

Sediment and mangrove root samples were first prepared before being analyzed using an atomic absorption spectrophotometer (AAS). The AAS was used to measure the concentration of Cu in sediment and *A. marina* roots. The model of AAS was a Rayleigh WFX 210 (China) at Department of Chemical Engineering, ITS.

First, samples of *A. marina* roots were dried at 105^{O}C for 24 h. After that, the dried root samples, were extracted using a modified wet digestion method procedure based on Titah et al. (2013) [9]. Meanwhile, the sediment extraction was conducted using EPA method 3050B (1996) [10].

2.3 Determination of Bioconcentration Factor (BCF)

The Bioconcentration Factor (BCF) or Biological Accumulation Coefficient (BAC) calculation [11] was used to determine the ability of the plants to uptake and accumulate some heavy metal from the media [12]. The determination for BAC was based on the following equation [8]. The results of the determination of BCF were matched with categories of plants (Table 1) to classify which plants are hyperaccumulator plants or otherwise [11].

$$BCF = \frac{C_{roots}}{C_{media}} \quad (1)$$

Table 1. Category of BCF

Category	Range
High accumulator plants	1-10
Moderate accumulator plants	0.1 – 1
Low accumulator plants	0.01 – 0.1
Non accumulator plants	< 0.01

3 Results and Discussions

Fig. 2 showed the concentration of Cu in sediment were 27 mg/kg until to 150 mg/kg. Based on *Interim sediment quality guidelines* (ISQGs) [13], the limit of Cu concentration for Cu contaminated area was 18.7 mg/kg. Meanwhile, according to EPA sediment quality standard [14], a non polluted area was below 25 mg/kg, a range for Cu slightly polluted area were 25 – 50 mg/kg and concentration value for Cu severely polluted area was upper than 50 mg/kg. According to Pollution Control Department of Thailand, the limit of Cu concentration for Cu polluted area was below 16 mg/kg [15].

Based on those standard, Cu concentration of sediment at 10 points of sampling location was shown variation of results. However, according to three standards that were not applied in this country, the condition was categorized as polluted area.

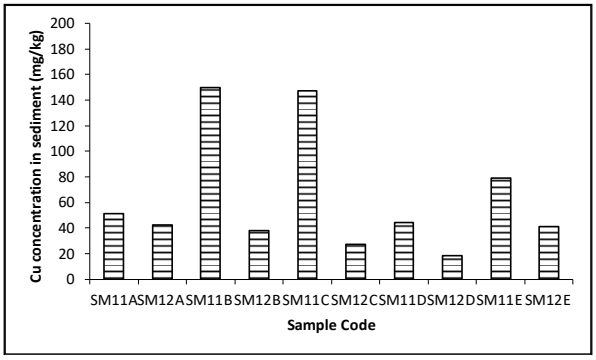

Fig. 2. Concentration of Cu in sediment at all points of sampling locations

Fig.3 showed the concentration of Cu in roots of *A. marina* was 53 mg/kg until to 128 mg/kg. It indicating that *A. marina* could uptake Cu and accumulate it in their roots. Overall, the concentrations of heavy metals were higher in plant roots as compared to sediment samples. According to Almahasheer et. al (2014) [16], grey mangrove or *A. Marina* could absorb and accumulate higher quantities of many heavy metals such as Cu, Fe, Mn, Zn, B, Ni, Pb and Cd. *Avicennia marina* was found to be highly tolerant to the metals applied. Copper was accumulated in root tissue in a linear relationship at lower sediment concentrations, but at concentrations of 200 µg/g and higher, no further increases in root Cu levels occurred [17].

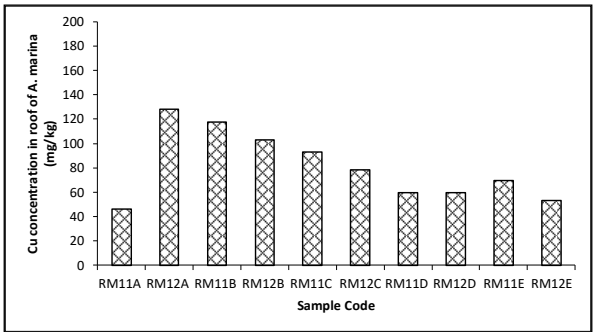

Fig. 3. Concentration of Cu in roof of *A. marina* at all points of sampling locations

Fig. 4 depicted the value of BCF were calculated based on equation 1. Based on Fig. 4, the BCF value of *A. marina* on Cu were 0.91 to 3.22 in sediment. However, 90% of those BCF value showed the BCF value > 1. It indicated that *A marina* can uptake, accumulate and has potential as a hypercummulator Cu plant. According to Usman et al. (2013) [18], BCF on *A. marina* for heavy metals (Cu, Cd, Ni, Pb, Zn and Cr) in the mangrove for surface sediments obtained values were too high (>1).

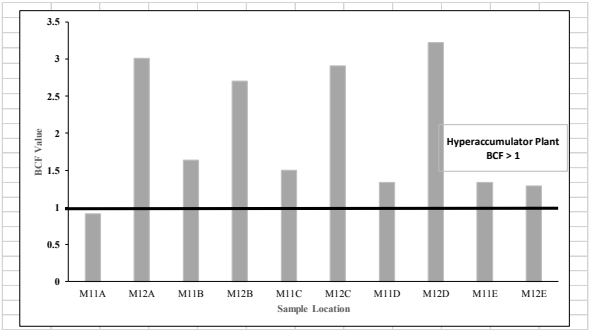

Fig. 4. BCF value of A. marina on Cu accumulation in sediment

4 Conclusions

Based on data, the range of Cu concentration at sediment of Wonorejo coastal were 27 mg/kg until to 150 mg/kg. The concentration of Cu in roots of *A. marina* were 53 mg/kg until to 128 mg/kg. The BCF values on *A. marina* in sediment were 0.91 to 3.22. Meanwhile, all of BCF value in sediment showed value > 1. Based on the BCF value, it indicated that *A. marina* was a hyperacumulator species for heavy metals of Cu. Mangrove *A. marina* has potentially to be used in Cu phytoremediation at coastal area.

Acknowledgement

The author would like to thank Kementerian Riset dan Teknologi/ Badan Riset dan Inovasi Nasional through scheme of Penelitian Dasar Unggulan Perguruan Tinggi – first year research, PDUPT 2020 for funding this research with No of contract, 3/E1/KP.PTNBH/2020, and No of amendment contract, 3/AMD/E1/KP.PTNBH/2020, and No. 1172/PKS/ITS/2020.

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