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Accumulation and Distribution of Lead and Copper in *Avicennia marina* and *Rhizophora apiculata* from Balok Mangrove Forest, Pahang, Malaysia

(Akumulasi Plumbum and Kuprum di dalam *Avicennia marina* and *Rhizophora apiculata* di Hutan Paya Bakau Balok, Pahang, Malaysia)

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ABSTRACT

Bioaccumulation of lead and Copper in Avicennia marina *and* Rhizophora apiculata *was studied. Samples of leaves, barks and roots were collected from Balok mangrove forest, Pahang. Pb and Cu accumulation was higher in* Avicennia marina *root tissue compared to bark and leaf but lower than surrounding sediment level. The average concentration of Pb in* A. marina *leaf, bark, root and sediment was observed to be 5.39 ppm, 3.63 ppm, 18.21 ppm and 23.13 ppm, and average Cu concentration was 4.13 ppm, 4.27 ppm, 4.81 ppm and 12.33 ppm, respectively.* R. apiculata *also showed higher concentration of Pb and Cu in root tissue compared to bark and leaf tissues but lower than surrounding sediment. The average concentration of Pb in* R. apiculata *leaf, bark, root and sediment was observed to be 4.30 ppm, 2.97 ppm, 22.45 ppm and 31.23 ppm, respectively. The average Cu concentration was 2.93 ppm, 4.71 ppm, 4.81 ppm and 15.52 ppm, respectively. Results of concentration factors (CF) showed that the accumulation of Pb and Cu was higher in* A. marina *than in* R. apiculata.

Keywords: Concentration factor; copper, lead; mangrove forest

ABSTRAK

Bioakumulasi plumbum (Pb) dan kuprum (Cu) dalam Avicennia marina *dan* Rhizhophora apiculata *telah dikaji. Sampel daun, kulit pokok, akar dan sedimen telah diambil dari kawasan hutan paya bakau Balok, Pahang. Kepekatan Pb dan Cu telah menunjukkan kadar akumulasi yang lebih tinggi di dalam akar* Avicennia marina *berbanding kulit pokok dan daun namun nilainya lebih rendah berbanding kepekatan Pb dan Cu di dalam sedimen persekitaran. Purata kepekatan Pb di dalam daun, kulit pokok, akar dan sedimen Avicennia marina adalah seperti berikut; 5.39 ppm, 3.63 ppm, 18.21 ppm dan 23.13 ppm manakala purata kepekatan Cu pula adalah 4.13 ppm, 4.27 ppm, 4.81 ppm dan 12.33 ppm.* Rhizhophora apiculata *juga telah menunjukkan nilai kepekatan Pb dan Cu yang lebih tinggi di dalam akar berbanding daun, kulit pokok dan sedimen persekitaran. Purata kepekatan Pb di dalam daun, kulit pokok, akar dan sedimen adalah seperti berikut; 4.30 ppm, 2.97 ppm, 22.45 ppm dan 31.23 ppm. Didapati purata kepekatan Cu pula adalah seperti berikut; 2.93 ppm, 4.71 ppm, 4.81 ppm dan 15.52 ppm. Keputusan daripada kiraan faktor kepekatan (CF) telah membuktikan bahawa kadar akumulasi Pb dan Cu adalah lebih tinggi di dalam* Avicennia marina *berbanding* Rhizophora apiculata.

Kata kunci: Faktor kepekatan; Hutan paya bakau; Kuprum; Plumbum

INTRODUCTION

Mangroves are one of the most productive and unique ecosystem in the world. Being located at the inter-tidal zones, this ecosystems is highly exposed to pollutants. Mangrove species such as *Avicennia marina* and *Rhizophora apiculata* are woody, seed-bearing and highly specialized plants and are found along sheltered intertidal coastlines of estuaries and lagoons. Because of their unique adaptations, mangroves thrive well in the environment where other plants cannot grow. It has been observed that the major pollutants in the mangrove ecosystems are heavy metals originating from urban runoff, sewage treatment plants, industrial effluents, mining operations, boating activities, domestic garbage dumps, and agricultural fungicides which dramatically increase the heavy metal concentration in intertidal sediments. In addition, specific properties of non-biodegradable trace metal which has high affinity towards anoxic sediments due to presence of fine clay, silt and detritial particles, high pH and sulphate reduction in mangrove ecosystem will lead to the accumulation of metals in the mangrove (Harbison 1986). It is apparent that significant increase in accumulation might have potential biological consequences for the plants. Laboratory research had proven that high concentration of Cu, Pb and Zn contributes to significant reductions in seedling height, leaf number and rooth growth of some mangrove plants (MacFarlane & Burchett 2002).

Generally, accumulation does occur at the root level, with restricted transport to aerial portions of the plants. This indicates that plants actively avoid the uptake of trace metals. Studies had been carried out on various terrestrial plants of Malaysia to determine their heavy metal accumulation capability. However, research related to mangroves is not well documented and only little information is known concerning the sedimentation of the mangrove forest. They are known to be a poor metal accumulators (Ogunwenmo et al. 2004).

In view of the importance of the mangrove to various aspects of the environment, a study was conducted to determine the ability of *Avicennia marina* and *Rhizophora apiculata* to accumulate Pb and Cu and to investigate the extent of accumulation and distribution of Pb and Cu in leaf, bark and root, and finally to determine the difference in the accumulation ability among both the mangrove species.

MATERIALS AND METHODS

SAMPLING SITES

Sampels were collected at Balok mangrove forest, which is located 8 km to north of Kuantan, Malaysia and facing the South China Sea (Figure 1). The study area has diverse ecosystems, with utilizable natural resources, vast array of biological diversity and coastal and riverine fishing activities. High rainfall was recorded in the monsoon season which normally begins from the month of November and ends in January at the study area. According to the twenty years (1968 to 1987) accumulated data obtained from the Malaysian Meteorological Service, the monsoon seasons with strong winds and long frequency periods with mean annual rainfall of 3064 mm occurred from November to January. Meanwhile the non-monsoon seasons with low rainfall occurred during April, May and June.

Root, bark and leave samples of both the species were collected and washed with mili-Q grade water before storage. Sediments between the roots of the sampled mangrove plants were also collected. All samples were packed into plastic bags, label and kept frozen until analysis.

HEAVY METAL ANALYSIS OF PLANT SAMPLES

Samples of roots, barks and leaves were dried at 105°C to constant weight and homogenised. The plant parts were then ground to a fine powder using porcelain mortar and pestle. Digestion and analytical procedures for elements Pb and Cu were performed using the published methods (Cioni

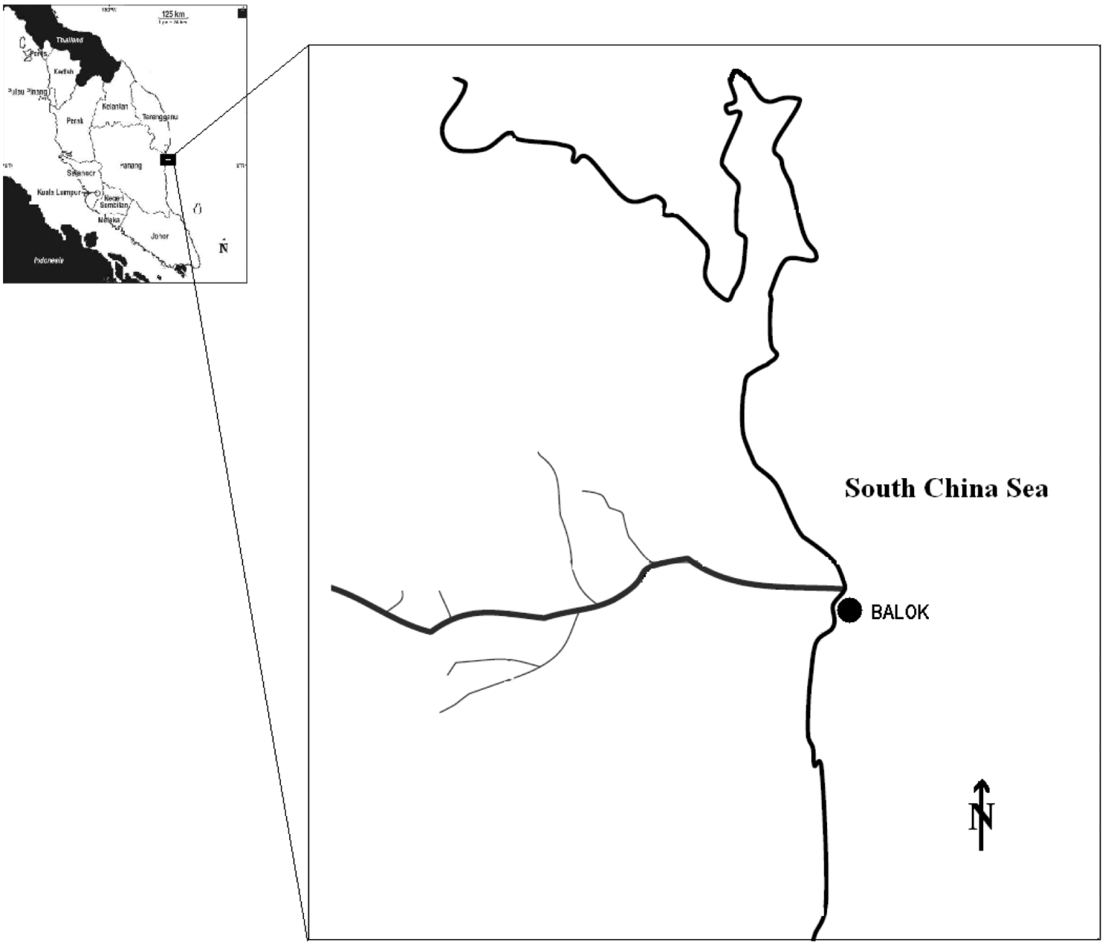

FIGURE 1. Location of the study area of Balok mangrove (●) from where leaves, barks, roots and sediment were collected randomly from *Avicennia marina* and *Rhizophora apiculata*

et al. 1976; Noriki et al. 1980). Two replicates of 200 mg of each tissue sample were ashed at 450°C for 3 h and the samples were then dissolved in 5 mL of 5 M hydrochloric acid and 1 mL of concentrated nitric acid. A clear solution with no residue was obtained. The heavy metal detection was carried out in Inductive Couple Plasma- Mass Spectrometry (ICP-MS). Blank and Laboratory standard samples (SRM 1547/peach leaves) were also subjected to the same procedure. The recovery test for plants was done using standard analysis and the percentage of recovery ranged from 95% to 105%.

HEAVY METAL ANALYSIS OF SEDIMENT SAMPLES

The sediment samples were digested according to the published methods (Sarmani 1989), with some modifications. An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the quick and precise determinations of Pb in the digested marine sediment. Briefly, the digestion method involved the heating of 50 mg of a < 63 µm size sample in a sealed teflon bomb with a mixed concentrated acids of HF, HNO_3 and HCl in the ratio of 2.5 : 3.5 : 3.5. The teflon bomb was then kept at 150°C for 3-5 hours. After cooling, a mixed solution of boric acid and ethylene diamine tetraacetic acid (EDTA) was added, and the vessel was again heated at 150°C for about 5 h. After cooling the sample to the room temperature, the content of the vessel was thoroughly transferred into a 10 mL polypropylene test tube and diluted to 10 mL with deionized water. A clear solution with no residue was obtained at this stage. Blank sample (sample without sediment) and laboratory standard sample (SRM 1646) were also subjected to same procedure and the precision was assessed by replicate analyses. The observed accuracy (3%) was also examined by analyzing in duplicate a Canadian Certified Reference Materials Project standard (DL-1a) and the recovery test ranged from 95% to 105%.

STATISTICAL ANALYSIS

In order to compare the degree of storage of the metal, concentration factors (CF) were calculated as concentration of metal g^{-1} tissue over the concentration of metal g^{-1} sediment (Ogunwenmo et al. 2004). Statistically significant differences in accumulating heavy metals by the two species were assesed using the one-way ANOVA. Pearson product correlation coefficients between heavy metal in plants tissue and in sediments were also computed.

RESULTS AND DISCUSSION

Heavy metal accumulation was detected in both *Avicennia marina* and *Rhizopora apiculata* varied in the study area of Balok, Kuantan. It is proved that Pb and Cu were distributed in all parts of the mangroves. *A. marina* showed higher Pb accumulation in root tissues compared to bark and leaf tissue but lower than surrounding sediment level. The average concentration of Pb in leaf, bark, root and sediment were 5.39 ppm, 3.63 ppm, 18.21 ppm and 23.13 ppm, respectively. Meanwhile, the results from analysis of *R. apiculata* also showed higher concentration in root tissues compared to bark and leaf tissue but lower than surrounding sediment level. It might be due to the fact that root system has direct connection with surrounding sediment than the other parts of the plant. The average concentration of Pb in *R. apiculata* leaf, bark, root and sediment were 4.30 ppm, 2.97 ppm, 22.45 ppm and 31.23 ppm, respectively. Average concentration of Cu in leaf, bark and root of *A. marina* was 4.13 ppm, 4.27 ppm and 4.81 ppm, respectively while in *R. apiculata* the accumulations were 2.97 ppm, 4.71 ppm and 4.81 ppm in leaf, bark and root respectively. The concentrations of Pb and Cu in each part of the plant are shown in Figure 2.

Positive correlation between grain size of sediment and the concentrations of Pb and Cu in the plant parts

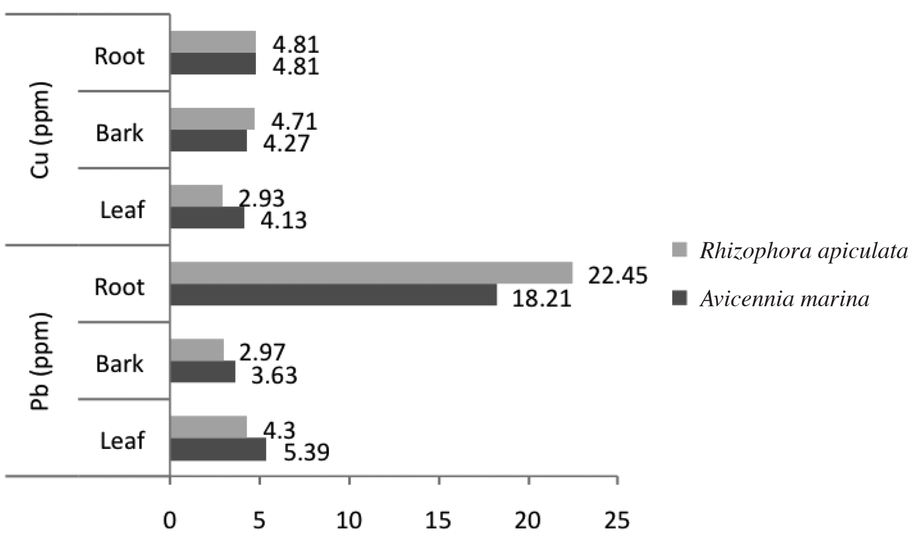

FIGURE 2. Concentration of Pb and Cu (ppm) in *Avicennia marina* and *Rizhophora apiculata*

was observed (Figures 3a & 3b), suggesting that when the sediment grain size becomes smaller, the heavy metal accumulative capacity of mangrove roots increases and they ultimately leads to high accumulation of Pb and Cu in other parts of the plant. However, the concentration distribution in plant parts like leaves, bark and roots may vary depending on the concentration of heavy metals in the sediment, the types of heavy metals and also the tolerance of the species and its parts towards the heavy metals (Kamaruzzaman et al. 2009).

Overall, in Balok mangrove area, Pb and Cu were found to be in higher concentration in the sediments. The increasing trend in their concentrations especially near the estuary reflects their predominant lithogenous origin. Furthermore, fine-grained sediments in the mangrove and nearby area are characterized by higher concentrations of these heavy metals compared to the coarse-grained sediments of the inner part of the rivers. Harbison (1986) reported that, there is a positive correlation between grain size and the concentrations of Pb and Cu, hence suggesting the influence of the fine fraction on their incorporation into the sediments. Sediments that are away from the estuary are characterized by the lower ratio of Pb and Cu, with the higher mean sediment size. Kamaruzzaman et al. (2002) also reported that there is a positive correlation between grain size and heavy metals, suggesting the influence of the fine fraction in their incorporation into the sediments.

It was also observed that the amount of organic matter found in the soils also affects the bioavailability of Pb and Cu in the sediments (Bar-Tal et al. 1988; Kamaruzzaman et al. 2008). The strongly correlation of Pb and Cu, with that of organic carbon suggested its association with heavy metals. The accumulation of organic material in the area not only provided the adsorbing surfaces but the reducing environment of the area prevented their possible remobilization. Besides sediment, salinity also influences levels of metals accumulated in surface

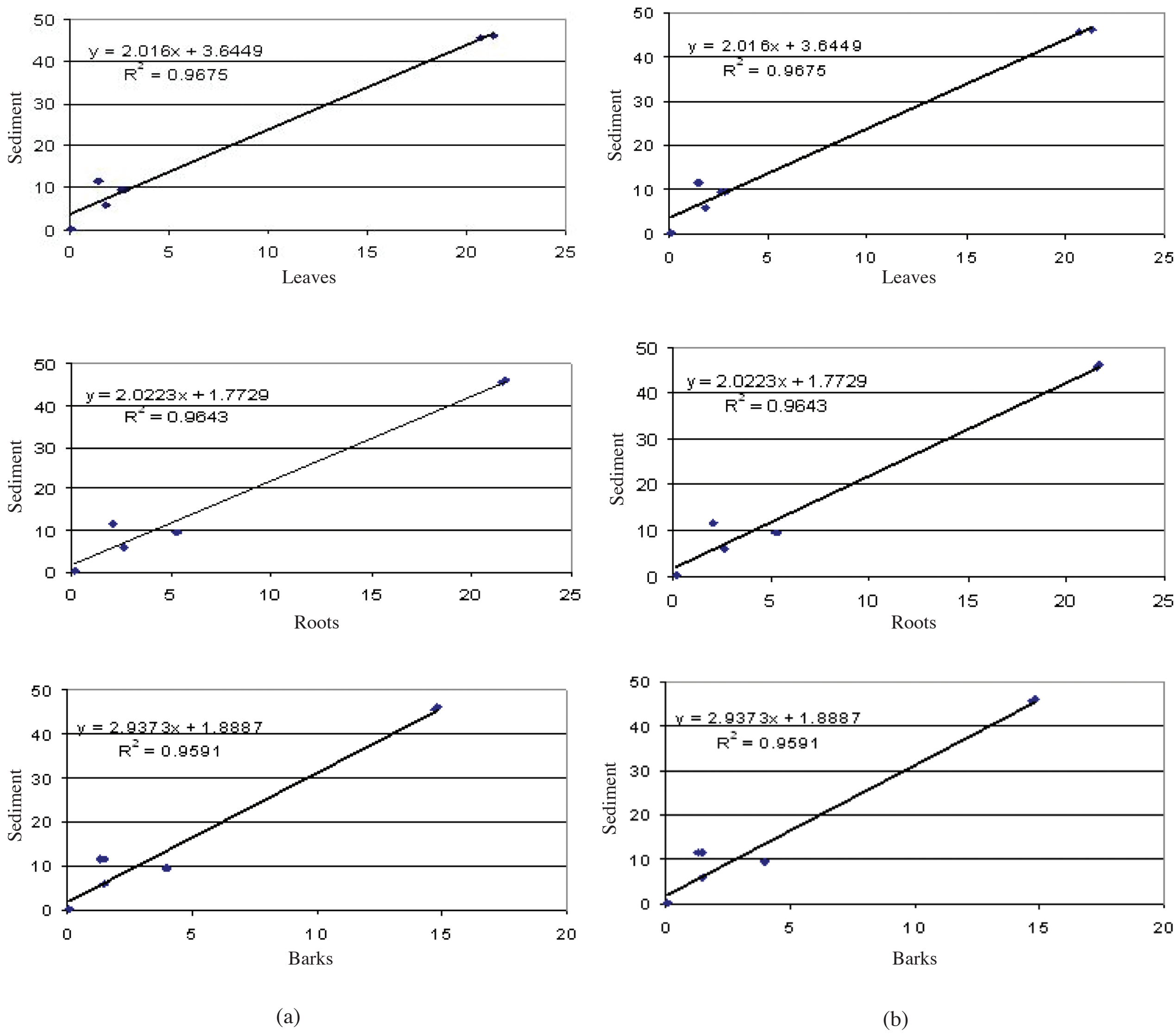

FIGURE 3. A positive correlation between sediment with leaves, barks and roots in (a) *Avicennia marina* and (b) *Rizhophora apiculata*

sediments. Du Laing et al. (2008) reported that increased salinity impedes the oxidation process and some heavy metals like Cr, Cu, Pb and Zn are able to cross the oxic layer and return to the water column, leading to lower concentrations at sites nearer to the sea. However, the overall average concentrations of Cr, Cu, Pb and Zn recorded in this study were generally comparable to and/or below the values reported by other scientists at other mangrove sediments (Sarmani 2004; Tam & Wong 1995)

Results of concentration factors (CF) showed that *A. marina* accumulates Pb 1.18 times greater than sediment levels (Table 1). Meanwhile, *R. apiculata* contained significantly lower Pb (containing only 0.96 times sediment Pb levels). Earlier, Kamaruzzaman et al. (2009) observed the less accumulation of Pb and Cu in *R. apiculata* sampled from Setiu mangrove forest.

TABLE 1. Concentration factor (CF) value for each plant organs in both *Avicennia marina* and *Rhizophora apiculata*

Plant organ	*Avicennia marina*	*Rhizophora apiculata*
Leaf	0.23	0.14
Bark	0.16	0.10
Root	0.79	0.71
Total CF	1.18	0.96

The increased accumulation of metals in plant tissues in a species is thought to be achieved through the translocation of air absorbed through lenticels in pneumatophores in underground roots. This creates oxidized rhizospheres within the anaerobic soil environment, a reduction in sulphides, a lowered stability of iron plaques, and a consequent higher trace metal concentration in the exchangeable form (Alex et al. 2007). ANOVA test showed no significant differences in accumulation of Pb and Cu between the two plants (p>0.05). Pearson product correlation coefficients showed the increases in Pb and Cu in the sediment may increase the accumulation of Pb and Cu level in the plant tissues ($R^2 = 0.81$).

Conclusion

Both the *Avicennia marina* and *Rhizophora apiculata* accumulate Pb and Cu in their tissues. Roots accumulate more Pb and Cu than other parts of the plant body (followed by leaf and bark) in the both species. Increasing concentrations of Pb and Cu in sediments resulted in a greater accumulation of Pb and Cu to root tissues. *A. marina* accumulates Pb higher than *R. apiculata*. Since the results of the present study clearly shows the bioaccumulative properties of selected species of mangroves, it is suggested that steps be taken to plant the mangrove trees in areas contaminated with heavy metals like Pb and Cu.

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