Comparison of metals levels in two mangrove species (*Rhizophora stylosa* and *Sonneratia hainanensis*) from Hainan Island, South China

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Abstract. Trace metals in mangrove tissues (leaf, branch and root) of two species (*Rhizophora stylosa* and *Sonneratia hainanensis*) from Dongzhai Harbor and Sanya Bay of Hainan Island were studied. The total average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As in the two mamgrove species were 2.4±1.3, 1.1±0.7, 7.8±8.0, 0.03±0.05, 1.4±1.6, 0.03±0.01 and 0.2±0.2 µg g-1 dw, respectively. Metals concentrations among different tissues of mangroves showed different pattern. In general, Zn, Cd and Hg were slightly enriched in leaf, Cu, Pb and As was enriched in root, and Cr were enriched in branch. Metals levels in *R. stylosa* and *S. hainanensis* from both Dongzhai Harbor and Sanya Bay were compared, which suggested that different mangrove species have their unique mechanism to bioaccumulate metals and TOC in the mangrove sediment could be one of the important factors for regulating metals in mangrove tissues. The biota-sediment accumulation factors (BSAF) of metals in mangrove tissues were calculated. The distribution of metals concentrations in mangrove tissues against metals levels in sediment demonstrated that mangrove leaves could be employed as a bio-indicator for some metals (Cu, Zn, Cd and Hg) with temporal monitoring.

1. Introduction

Mangroves are specific intertidal ecosystems, covering between 160,000 and 200,000 km^2 along more than 70% of tropical and subtropical coastlines [1]. This ecosystem is highly rich in biodiversity, and acts as a habitat for many species. It is estimated that almost 80% of global fish catches are directly or indirectly dependant on mangroves [2]. Mangroves can protect inland human communities from damage caused by coastal erosion and storms, provide critical habitat for a variety of terrestrial, estuarine and marine species, and serve as both a source and sink for nutrients/contaminants and sediment for other inshore marine habitats including seagrass bed and coral reef [3-5]. Mangroves can sequester up to 25.5 million tonnes of carbon per year, and provide more than 10% of essential organic carbon to the global oceans [6]. Mangrove forest is an efficient biogeochemical barrier to the transport of heavy metals to coastal areas [7]. However, mangrove areas are declining rapidly in the past several decades as they are cleared for coastal development and aquaculture and logged for timber and fuel production, and eleven of the 70 mangrove species (16%) are at elevated threat of extinction [5]. Currently, mangroves are also increasingly threatened due to anthropogenic chemicals sourced from uncontrolled agricultural runoff, urban and industrial effluent and wastewaters, as well as with urbanization and population growth [8-10]. Further, trace metals taken up by mangroves and concentrated in exported leaf detritus could be reintroduced to the adjacent deeper waters [11]. The biomass, productivity and litter of mangrove forests varied with the age of mangrove, dominant species, and locality. The bioaccumulation and/or fixation of trace metals in the mangrove tissues may prevent release of metals to the water column and limit entry of these contaminants to the food chain. The knowledge of bioaccumulation of trace metals in different mangrove species is important to understand the fates of these pollutants and, can alert coastal managers of possible impacts upon the detritus driven food web which can potentially lead to the bioaccumulation of contaminants in organisms.

Hainan Island, the second largest Island of China, has mangrove areas of 4772 hm^2, accounting for one third of the total mangrove forest areas of China. There are 26 mangrove plant species distributing in Hainan while 27 species in China [12]. Hainan Dongzhai harbor mangrove protection zone, as the first national mangrove reserve of China, was established in 1986 and was listed as the International Important Wetland in 1992. While Hainan Sanya mangrove protection zone, as the southmost mangrove reserve of China with the typical tropical features, was established in 1990. Since 1978 when China started the reform and opening up policy, the development of coastal zones throughout Hainan Island has put immense pressures on biological communities including mangrove ecosystem. More than 60% mangrove forest has disappeared since 1950s [13], and many mangrove forest areas were developed as culturing ponds and constructing sites. As an international important wetland, a few information is available on the status of trace metals in mangrove ecosystem of Hainan Island [9, 14], though many studies on trace metal pollution in mangrove wetlands around the world have been reported [15-16]. Further, there are very few data on mercury and arsenic concentrations in mangrove tissues around the world so far. Based on the concentrations of trace metals (Cu, Pb, Zn, Cd, Cr, Hg and As) in two mangrove species (including in root, branch and leaf) and sediments from two typical mangrove areas of Hainan Island, the present work aimed to compare metals levels in *R. stylosa* and *S. hainanensis* between Dongzhai Harbor and Sanya Bay; and to assess the biotic response of metals contamination in mangrove ecosystem, e.g., the relationship of metal concentrations between mangrove tissues and sediment.

2. Materials and methods

2.1. Study areas

Dongzhai Harbor, located in the northern Hainan Island, is the most well-preserved mangrove forest in China and suffers agricultural stress; Sanya Bay, situated in the center of Sanya city of the southern Hainan Island, is subjected to both sewage discharge and agricultural pollution. The two studied areas were predominantly colonized by mangrove species including *Rhizophora stylosa*, *Rhizophora apiculata*, *Bruguiera sexangula*, *Ceriops taga1*, *Aegiceras corniculatum*, *Avicennia marina*, and *Sonneratia hainanensis* [14, 17].

2.2. Sample collection and processing

Mangrove tissues at six sites of Dongzhai Harbor (DZ1, DZ2, DZ3, DZ4, DZ5 and DZ6) and three sites of Saya Bay (SY1, SY2 and SY3) (Figure 1), were collected in October 2008 using pre-determined GPS co-ordinates to accurately locate each station. Sampling sites were selected based on the spatial and the mangrove species community distribution and can be accessible. Mangrove tissues, including root, perennial branch (diameter about 5-8 cm) and leaf of two species (*R. stylosa* and *S. hainanensis*), were simultaneously collected. Mangrove samples were washed by deionized water in laboratory to remove the possible dust, and naturally dried, and were then sampled with a thin stainless steel blade.

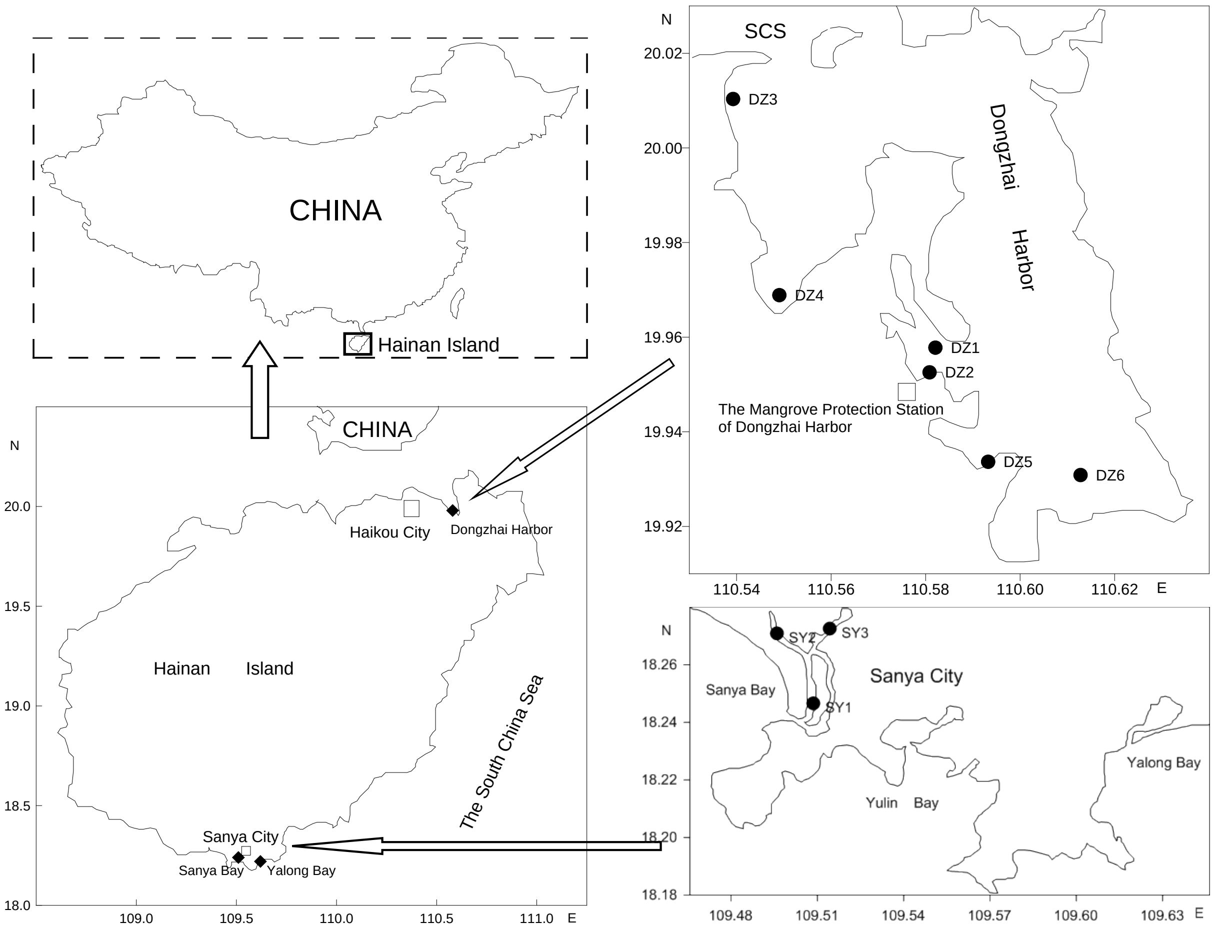

Figure 1. Sampling locations in two mangrove wetlands (Dongzhai Harbor and Sanya Bay) of Hainan Island, South China.

2.3. Chemical analysis

Measurements of trace metals followed the procedures described previously [14, 18]. 100.0 mg mangrove tissue sample was placed into Teflon pot pre-cleaned with high purity nitric acid; then 2.0 ml concentrated nitric acid (HNO_3) was added into the pot lasting for 2 h; and then heated in an electric board at 150 ^{o}C for 24 h. After cooling, the solution was diluted by high pure water to 40 g and the concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As were measured using ICP-MS (model DRC II, Perkin Elmer, USA). Measurements of trace metals in sediment followed the procedures in Qiu et al [14].

2.4. Quality assurance and quality control

All glass- and plastic-ware were soaked in 10% nitric acid overnight and rinsed thoroughly with deionized water before use. For quality control, reagent blanks, the Chinese national standard samples of GBW08571, GBW08517 and GBW010016 (reference materials for mussel, kelp, tea, respectively) were used to monitor the analytical quality. The results were consistent with the reference values with relative differences within 10% (mostly within 5%). Blank determinations were carried out for each set of analysis. The determination limits of Cu, Pb, Zn, Cd, Cr, Hg and As in mangrove tissues were 0.02, 0.002, 0.02, 0.02, 0.02, 0.002 and 0.02 μg g^{-1} dry wt., respectively. Statistical analysis was conducted using SPSS 18.0.

3. Results and discussion

3.1. Metal levels in mangrove tissues and sediment

The total average concentrations of Cu, Pb, Zn, Cd, Cr, Hg and As both in *R. stylosa* and *S. hainanensis* (n=23) from Dongzhai Harbor and Sanya Bay of Hainan Island were 2.4±1.3, 1.1±0.7, 7.8±8.0, 0.03±0.05, 1.4±1.6, 0.03±0.01 and 0.2±0.2 μg g^{-1} dw, while in sediment were 12.2±8.4, 23.9±10.6, 55.6±32.8, 0.14±0.06, 20.3±11.4, 0.07±0.04 and 9.2±4.4 μg g^{-1} dw, respectively. Previous study [19] showed that the metal concentrations in trunk of *Rhizophora apiculata* from Leizhou Peninsula, south China were 10.89, 0.51, 14.73, 0.15 and 26.64 μg g^{-1} for Cu, Pb, Zn, Cd and Cr, respectively, which all the target metals except for Pb were higher than those in the present study. The concentrations of Cu, Pb, Zn, Cd and Cr in roots of three mangrove species *(Acanthus ilicifolius*, *Aegicerus corniculatum* and *Kandelia candel*) in Mai Po, Hong Kong were 32.6, 34.4, 137.5, 0.4 and 3.5 μg g^{-1}, respectively [20], which were much higher than the present results. The concentrations of Cu, Pb, Zn, Cd and Cr in tissues (leaf, branch and root) of *Rhizophora mangle* in Natal, Brazil [7] were also higher than those in mangrove (*Avicennia marina*) leaves were 3.2, 1.7 and 14.3 μg g^{-1} [21], which were slightly higher than those in Hainan Island. Nath et al [22] recently reported the concentrations of Cu, Pb, Zn, Cd, Cr and As in *Avicennia marina* leaves in Sydney Estuary (Australia) of 10, 0.74, 14, 0.01, 0.49 and 0.48 μg g^{-1}, respectively, which were comparable to those in Hainan Island. Mercury concentrations in the present nine mangrove species (0.03±0.01μg g^{-1}) was lower than those in eight mangrove species from Tamil Nadu of India (0.06±0.03 μg g^{-1}; [23]). All above results suggested that Hainan mangrove was in a relatively unpolluted status.

In the present study, trace metals concentrations among different tissues of two mangrove species were not very significantly different, as shown in Figure 2. Comparatively, Zn, Cd and Hg were slightly enriched in leaf, Cu, Pb and As was enriched in root, and Cr were enriched in branch. The highest average concentrations for Cu (3.3 μg g^{-1}), Pb (1.3 μg g^{-1}), and As (0.34 μg g^{-1}) were detected in the belowground roots. It is well known that metal-rich deposits on roots of aquatic plants may moderate the uptake of potentially toxic metals [7, 24]. In the present study, the highest average concentrations for Zn (11.4 μg g^{-1}), Cd (0.05 μg g^{-1}), and Hg (0.04 μg g^{-1}) were in the leaf, while the branch presented the highest average concentrations for Cr (2.0μg g^{-1}). As the essential elements for the growth of plants, Zn tended to accumulate in leaf, while Hg, a semi-volatile metal, was deposited and accumulated in leaf. It was reported that *A. marina* mangroves of Sydney estuary selectively excluded non-essential elements (As, Cd, Co, Cr and Pb), while regulating essential elements (Cu, Ni, Mn and Zn) and limiting toxicity to plants [22]. Except for the pollution level in the local mangrove ecosystem, several factors (e.g., time of collection, tissue age and tissue type) may also influence the concentrations of tissue accumulated chemicals and their order of accumulation.

3.2. Comparision of trace metals levels in different mangrove species

Trace metals levels in *R. stylosa* and *S. hainanensis* (leaf, branch and root) from Dongzhai Harbor and Sanya Bay were shown in Figure 2. Generally, targeted metals levels in mangrove tissues of *R. stylosa* were lower than those in *S. hainanensis* from Dongzhai Harbor and Sanya Bay. According to the annual National Marine Pollution Bullet in China, pollution status went worse only in the recent decades in Hainan Island. As *R. stylosa* grows much slower than *S. hainanensis*, we may expect that *R. stylosa* grows in relative low level of metals for the longer period and will accumulate less metals, while *S. hainanensis* grows in the recent polluted years and will accumulate more metals. Many studies have showed that concentrations for the same trace metal and tissue can differ within a population of the same species and between different species [7, 15]. Interspecific differences have also been commonly reported and attributed to differences in physiology [23]. This is mainly due to physiological differences, variable translocation and excretion mechanisms of different plant organs. The present results suggested that different mangrove species have their unique mechanism to bioaccumulate metals.

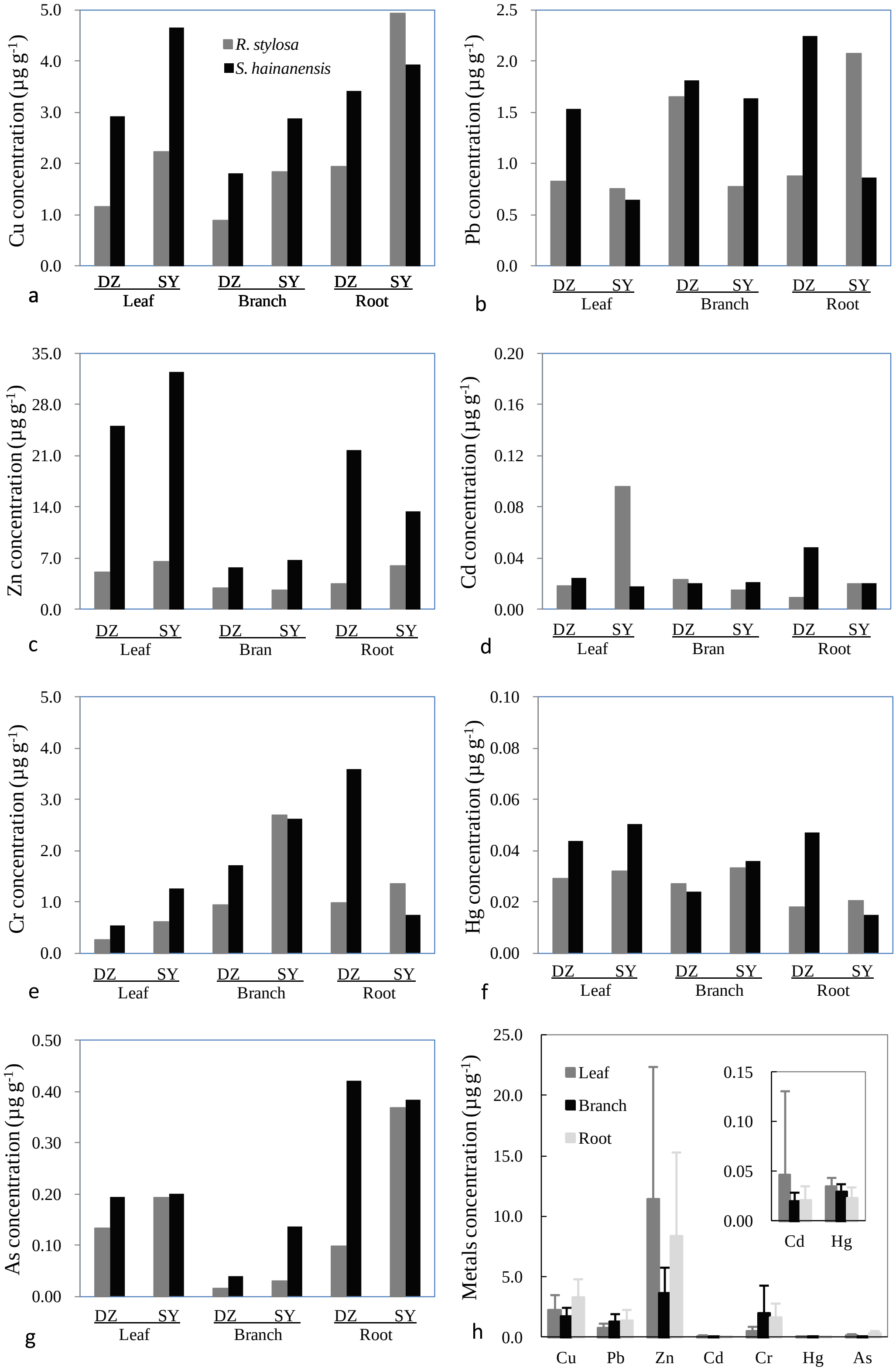

Figure 2. Comparision of metals levels in two mangrove species (*R. stylosa* and *S. hainanensis*) from Dongzhai Harbor (DZ) and Sanya Bay (SY) of Hainan Island.

From the Figure 2, we also can see that targeted metals levels in mangrove tissues of *R. stylosa* and *S. hainanensis* were generally lower from Dongzhai Harbor than those from Sanya Bay. Our previous results showed that the vertical profiles of trace metals concentrations in mangrove sediment cores of Dongzhai Harbor were elevated compared to those in Sanya Bay, but TOC contents in mangrove sediment cores had different patterns, with the higher TOC contents in sediment from *R. stylosa* zones in Dongzhai Harbor than those in Sanya Bay, and the similar TOC contents in sediment from *S. hainanensis* zones in Dongzhai Harbor and Sanya Bay [14]. Positive correlations between TOCs in mangrove sediments and the levels of metals in Hainan Island were also observed [14]. The profiles of TOC in Dongzahi Harbor appear not be different from the profiles of trace metals comparing with Sanya Bay. The present studies showed that TOC in the mangrove sediment could be one of the important factors for regulating metals in mangrove tissues. There were reports that organic matter from leaf fall contributes to the depletion of dissolved oxygen in the sediment with a consequent influence on the mobility of heavy metals [7, 25]. Organic matter is also known to chelate with trace metals, therefore affecting their mobility and bioavailability [16]. The present results further confirm the hypothesis that bioaccumulation of metal in organism depends on the biological availability of metal and not the total metal concentration in the natural environment.

Apart from the metals levels in the media of mangroves, the uptake of metals is primarily influenced by mangrove plant metabolic requirements (e. g., Cu and Zn, which are essential micro-nutrients) are more mobile than non-essential elements (such as Pb) resulting in variable metal accumulation in plant tissues [8, 22, 26-27]. Oxidation of the upper rhizosphere leads to precipitation of Fe-oxyhydroxides and formation of iron plaques around root surfaces and ultimately results in significant accumulation of trace metals in these zones [10, 28-29]. The formation of Fe plaque on the root surface not only reduced the metal bioavailability toward roots and plant metal uptake, it may also play a key role in the removal and detoxification of pollutants and protect plants against pollutants in constructed wetlands [30]. Recent reports showed that metal-tolerant mangrove species often exhibited a thick exodermis with high lignification and suberization which could delay the entry of metals into the roots, and thereby could contribute to a higher tolerance to heavy metals [31].

3.3. The biota-sediment accumulation factors (BSAF) of metals

Trace metals may enter the mangrove through transport by local rivers, marine waters intrusion or through atmospheric deposition. Plants could uptake contaminants from a polluted atmosphere by the deposition of the particle-phase contaminants on the waxy leaf cuticle or by uptake in the gas phase through stomata, plants could also take up contaminants from contaminated sediments or soils by roots, transferred to shoots and leaves [32]. Aquatic organism can absorb contaminants from sediment, and its ability can be expressed by the biota-sediment accumulation factors (BSAF). In the present study, the BSAFs (defined as the ratio of metal concentration in mangrove tissues to metal concentration in underlying sediment) based on all trace metals data both in sediment and mangroves were calculated and shown in Figure 3. Target metals with descending values of BSAFs (in parentheses) for leaves of all studied mangrove species in Hainan Island were all less than 0.5 (<1 unit) and followed the sequence of Hg (0.49) > Cu (0.26) > Cd (0.21) > Zn (0.17)> Cr (0.10) > Pb (0.06) > As (0.02). Mercury exhibited the highest BSAFs values because of its physical property, a semi-volatile metal. The essential metals such as Cu and Zn showed a greater mobility than the non-essential metals such as Pb, Cr and As. As for cadmium, which atomic structure being similar to Ca, also exhibited a high BSAF value. This may be explained by its similar chemical behavior as Cu and Zn [33], but the exact reasons still need further study. Our results were generally similar to those in Sydney Estuary of Australia, with BSAFs of Cu (0.38), Zn (0.25), As (0.09), Cr (0.05), Cd (0.04) and Pb (0.02) in leaves of *Avicennia marina* [22].

The distribution of metals concentrations in mangrove tissues (leaf, branch and root) against metals levels in sediment was shown in Figure 3. Overall, the data did not show a clear positive linear trend in targeted metals accumulations in mangrove tissues (branch and root) with increasing sediment concentrations. However, the slightly positive relationships for trace metals (Cu, Zn, Cd and Hg) concentrations between leaf tissues and sediment were observed, with the relative coefficients (R) of 0.51, 0.32, 0.40 and 0.24, respectively. The results suggested that mangrove leaves could be employed as a bio-indicator for these metals with temporal monitoring. Previous study also showed a restricted mobility of Cu and Zn and a strong exclusion mechanism of Pb in *A.marina* leaf tissues and concluded that *A. marina* leaves could be employed as a bio-indicator for Zn [27].

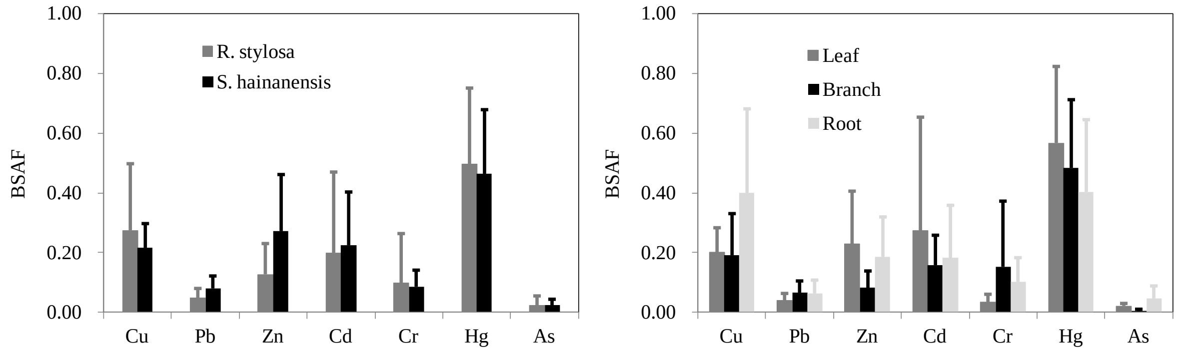

Figure 3. The average BSAF of metals in mangrove tissues (leaf, branch and root) from Dongzhai Harbor and Sanya Bay of Hainan Island.

4. Conclusions

Concentrations of trace metals (Cu, Pb, Zn, Cd, Cr, Hg and As) in mangrove tissues (leaf, branch and root) in Hainan Island, were analyzed. Trace metals levels in *R. stylosa* and *S. hainanensis* from Dongzhai Harbor and Sanya Bay were compared and the results showed that metals concentrations among different tissues of mangroves were different and different mangrove species have their unique mechanism to bioaccumulate metals. TOC in the mangrove sediment could be one of the important factors for regulating metals in mangrove tissues. Mangrove leaves could be employed as a bio-indicator for some metals (Cu, Zn, Cd and Hg) with temporal monitoring.

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