Abstract: Sepang mangrove forest ecosystem in Malaysia has become environmentally sensitive due to untreated waste disposal from several oil palm industries, pig farms and sewages into the Sepang Besar mangrove river. Very high zinc concentrations were found throughout the study area. High concentrations of zinc were also found in soil (1192.20 µg/g) and river water (11.18 mg/l) at the waste discharge point. Among the seedling (Rhizophora mucronata) parts, roots contained the highest (67.33 µg/g) zinc concentration followed by stems and leaves. Results of this study indicated that mangrove plants are adapted to high metal concentrations in soil.

Key words: Heavy metal; Micronutrient; Organic waste; Pollution; Zinc

Introduction

Heavy metal pollution to the terrestrial environment is not a recent topic. Presence of heavy metals in the industrial and farm wastes and its hazard to the environment are well recognized. Mangrove forest is a very complex ecosystem in the tropical and sub-tropical regions and serves as a transition area among the aquatic and terrestrial ecosystems (Aksornkoae, 1993).

Reducing condition and high organic matter content of wetland soil favour the accumulation of heavy metals in soil and exhibit little mobilization or bioavailability (Orson et al., 1992). Mangrove forests show the capacity to hold heavy metals (Chen and Lin, 1988; Tam and Wong, 1993) and play an important role in the biogeochemistry of trace metal contamination either as sinks or sources (Harbison, 1986; Silva et al., 1990; Lacerda et al., 1993).

Rhizophora mangla usually uptake 5% of the soil zinc and most of the absorbed metal is stored in roots. Roots contain the highest concentration of zinc (19.90 ppm) after iron (Silva et al., 1990). Metal concentrations in leaves of mangrove plants usually vary little
even though soil is enriched with high metal levels, due to lesser mobility of metals within plant parts (Lacerda et al., 1991).

Mangrove forest floors are generally flooded by tides and show seasonal fluctuations in salinity and hence altered the aerobic and anaerobic conditions. Mobility of metals in mangrove ecosystems depend on their physical, chemical and biological conditions (Lacerda et al., 1993). The absorption and desorption of metals in wetland soils depend on soil properties like pH, cation exchange capacity, organic matter content, clay content, redox potential, salinity, iron, manganese oxide and quantity of accumulated heavy metals (Harter, 1992; Kerner and Wallmann, 1992; Orson et al., 1992).

Zinc is one of the essential micro-nutrients for normal growth and development of plants but it is required only in small amounts (Adriano, 1986). High accumulation of zinc and it’s phytotoxicity cause death or prevent growth of natural forests (Beyer, 1988; Oyler, 1988). pH is the most important variable of soils that can influence zinc phytotoxicity and solubility. Zinc phytotoxicity is more severe in light textured soil than heavy textured soil. In strongly acidic soils, most of the species become chlorotic when they are exposed to excessive soil zinc (Chaney, 1993). The present study aims to determine the distribution of zinc in soil, water and different parts of Rhizophora mucronata seedlings in Sepang mangrove forest ecosystem in Malaysia.

Materials and Methods

Site Description: This study was conducted at the Sepang mangrove reserve forest in Selangor, Malaysia. Sepang mangrove reserve is situated on both the sides of the Sepang Besar river which is the state boundary of Selangor and Negri Sembilan. This mangrove forest is located in between latitudes 2° 36’ - 2° 41’ N and longitudes 101° 42’ - 101° 46’ E (Figure 1). A limited number of plant species is found of which Rhizophora mucronata, Rhizophora apiculata, Avicennia alba, Sonneratia alba, Bruguiera gymnorrhiz, Ceriops tagal and Xylocarpus granatum are most available. Of these species, Rhizophora mucronata has a wide distribution and the highest density (350 trees per ha) (Saberi, 1993).

Sampling Procedure: Six stations, each every 2 km from waste discharge points of pig farms towards the sea, were chosen (Figure 1). Two plots (each of 3 m X 3 m) were taken from each station and each was divided into three sub plots of 3 m X 1 m size. Total and available soil zinc and zinc concentration in infiltration water were measured for each station. Rhizophora mucronata seedlings were not found at Station 1, 2 and 3 hence zinc concentration was also measured in river water adjacent to each station. Zinc concentration in leaves, stems and roots of Rhizophora mucronata seedlings were measured in the last three stations toward the sea.

Soil analysis: Topsoil was collected by digging a hole of 10 X 10 X 10 cm sized in 3 sub plots of each main plot. One soil sample was taken from each sub plot. Samples were air-
Fig. 1. Map of the Sepang mangrove reserved forest area showing the location of Sepang Besar river with sampling stations.
dried at room temperature and thoroughly mixed before crushing and sieving. Total soil zinc was extracted by using concentrated HNO₃ and 60% HClO₄ in the proportion 2:1 (Hesse 1971) and 0.1M HCl was used for determining the available soil zinc (Wear and Sommer 1948).

**Water Analysis:** After taking a soil sample, accumulation of infiltration water can usually be observed at the bottom of the hole. Once the column reached equilibrium, the water in the hole was rapidly displaced with suction bulb and transferred to the bottle. Infiltration water samples were collected from all sub plots of all stations. River surface water was collected at mid width of the river adjacent to the plots of each station. Two river water samples were collected from each station. Total (dissolved and suspended) substances of river and infiltration water were brought into solution by using concentrated H₂SO₄, 60% HClO₄ and HNO₃ in the proportions 1:2:10 (Allen, 1974).

**Plant Analysis:** Three seedlings of *Rhizophora mucronata* having 4 leaves were collected from sub plots of Stations 4, 5 and 6. Samples were separated into different parts (i.e. leaves, stems and roots) and then oven-dried at 80°C. The dried material was then ground and sieved. Concentrated HNO₃ and 60% HClO₄ in the proportions 1:1 were used for plant sample extraction (Jones et al., 1991). Atomic Absorption Spectrophotometer (AAS) PERKIN ELMER 4100, Germany was used for measuring zinc ion concentration in the extract.

**Soil and Water Parameters other than Zinc:** Texture of soil samples was measured with the pipette method (Black, 1965). Fresh moisture content was measured by weight loss method and cation exchange capacity of soil was measured by distillation and titration method (Allen, 1974). Soil organic matter content was determined by the ignition method (Allen, 1974) where oven dried (at 105°C) soil sample was ignited at 450°C for burning out the organic matter. A pH meter with an automatic temperature compensator (Ciba-Corning Diagnostic Ltd. France) with accuracy of ± 0.05 was used to measure soil pH *in situ* from slurries of the samples in water (Peech, 1964). The pH of river water samples was measured in the field by following the same principle as described for soil samples. A conductivity and TDS cell (Ciba-Corning Diagnostic Ltd. France) were used for determining the conductivity and the total dissolved solid of river water in the field. River water salinity was measured directly in the field using a salinity meter (YSI model 33 manufactured by Yellow Springs Instrument Co. USA). Dissolved oxygen (mg/l) was measured by HI 9142 oxygen meter (HANNA Instrument, USA).

**Results and Discussion**

**Zinc in soil:** Very high concentration of zinc was found in soils of stations near to the discharge point. In stations 1, 2 and 3 (near to the discharge point), total soil zinc content varied from 1192.20 to 460.60 µg/g (Table 1). Available form of zinc in soil was also very high all over the study area. Stations 1, 2 and 3 contained 645.37 to 180.60 µg/g zinc in plant available form (Table 1). The availability, solubility and mobility of soil zinc
Table 1. The mean values with SE of soil and water parameters measured at different Stations.

| Parameters                      | Obs. No. | Station 1          | Station 2          | Station 3          | Station 4          | Station 5          | Station 6          |
|---------------------------------|----------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Soil Parameters                 |          |                    |                    |                    |                    |                    |                    |
| pH in situ                      | 6        | 7.08±0.17          | 6.98±0.07          | 6.92±0.02          | 6.36±0.02          | 6.44±0.06          | 5.60±0.28          |
| pH after treatment with H$_2$O$_2$| 6        | 4.24±0.07          | 3.73±0.03          | 3.72±0.05          | 3.59±0.15          | 2.63±0.07          | 1.77±0.04          |
| Fresh moisture content (%)      | 6        | 71.91±0.64         | 69.01±0.93         | 63.03±1.07         | 49.82±0.91         | 34.33±1.43         | 27.94±0.58         |
| Organic matter content (%)      | 6        | 20.46±0.32         | 15.21±0.52         | 14.49±0.18         | 11.17±0.40         | 6.22±0.35          | 4.71±0.36          |
| CEC (m.e./100 g)                | 6        | 1192.20±65.49      | 825.57±29.8        | 460.60±21.93       | 195.5±15.25        | 39.41±1.26         | 18.15±1.24         |
| Zinc (µg/g)                     | 6        | 645.37±18.45       | 366.13±7.00        | 180.60±5.79        | 72.13±4.99         | 16.63±2.36         | 4.16±0.37          |
| Available zinc (µg/g)           | 6        | 5.78±0.02          | 6.23±0.07          | 6.20               | 6.71               | 6.92±0.02          | 6.94               |
| Water Parameters                |          |                    |                    |                    |                    |                    |                    |
| pH                              | 3        | 21.50±0.50         | 23.00              | 24.00              | 26.00              | 26.75±0.75         | 32.50±0.50         |
| Salinity (ppt)                  | 3        | 1.45±0.05          | 2.25±0.15          | 3.90               | 5.80               | 6.65±0.35          | 7.10±0.10          |
| Dissolved oxygen (mg/l)         | 3        | 11.18±0.53         | 7.75±0.50          | 4.55±0.15          | 3.35±0.05          | 2.15±0.05          | 1.68±0.13          |
| Zinc in water (mg/l)            | 3        | 1.25±0.02          | 1.11±0.01          | 0.98±0.01          | 0.83±0.10          | 0.57±0.11          | 0.31±0.12          |

largely depend on soil pH and it becomes more available at acidic soil (Williams, 1980). Neutral to acidic (pH 7.08 to 5.6) soils were found at the study area and the total soil zinc showed a positive correlation (r= 0.74, p<0.05) with in situ soil pH. The total and available soil zinc were also positively correlated (r= 0.84 and 0.84, p<0.05) with soil organic matter. Higher zinc availability was observed in stations possessing high organic matter and high percentages of clay content. Zinc may have higher affinity for soil organic matter and for clay content. Total and available soil zinc also showed positive correlation (r= 0.70 and 0.71, p<0.05) with cation exchange capacity of soil. According to Mathur and Levesque (1983), metal levels in soil become phytotoxic when metal contents exceed 5% of the soil CEC value. From the result of this study, it was found that total and available form of zinc in soil exceeded the 5% of the cation exchange capacity value. The absorption of heavy metal depends on many soil properties such as clay-silt, organic matter and cation exchange capacity (Harbison, 1986; Dunbabin and Bowmer, 1992; Modak et al., 1992).

Mangrove soil may possess certain characteristics for accumulating high zinc contents or may act as a natural sink of heavy metals (Banus et al., 1975; Simpson et al., 1983). Total soil zinc content at the study area was 3 times higher than Red mangrove forest, Brazil (Silva et al., 1990), Shenzhen mangrove forest soil, Hong Kong and 10 times higher than Sai Keng mangrove forest soil, Hong Kong (Tam and Wong, 1996).
Zinc in Water: Zinc concentrations were highest in the river and infiltration water samples at station 1 and decreased towards Station 6. This descending order was found to be statistically significant (p<0.05). Waste in the river water may get additional scope to disperse comparatively the wider environment during traveling long distance from waste discharge point (Station 1) towards the sea (Station 6). High zinc concentrations were measured which were 11.18 mg/l and 1.25 mg/l respectively at station 1.

The acceptable concentration of zinc in water was 5.00 mg/l for domestic use (Miettinen, 1977). In this respect the study area was more enriched with zinc than normal level due to the discharge of untreated wastes from the nearby industries and farms. A highly positive correlation (r=0.89, p<0.05) was found between infiltration water and the river water zinc contents. During the high tides, the river water floods the forest floor and percolates into the soil profile. This could be the reason for positive correlation with river water zinc content. Moreover, it seems that the soil of the study area accumulates very high level of zinc from the river water. Acidity (5.78 to 6.94) was observed in river water at the study area (Table 1) and the acidic water may be possible for the metal ions to be released from water body and absorbed afterwards by sediment (Smith, 1990).

Zinc in Rhizophora mucronata: Seedling of Rhizophora mucronata was not found in Stations 1, 2 and 3. Seedling roots at station 4 contained the highest (67.33 µg/g) and those at the station 6 contained the lowest (15.5 µg/g) zinc concentrations (Table 2). The zinc concentrations in the roots of seedling were highest followed by stems and leaves at stations 4 and 5. On the other hand, the concentrations of zinc were highest in the leaves followed by stems and roots at the station 6 (Table 2).

Table 2. Zinc concentration with SE in different parts of seedlings in individual stations.

| Station | Number of observation | Soil Texture | Mean ± SE value for leaves (µg/g) | Mean ± SE value for stems (µg/g) | Mean ± SE value for roots (µg/g) |
|---------|-----------------------|--------------|----------------------------------|---------------------------------|---------------------------------|
| 4       | 18                    | Silty clay   | 33.67±1.03                       | 40.33±1.9                       | 67.33±4.09                      |
| 5       | 18                    | Sandy clay loam | 25.17±0.61                    | 27.33±0.02                      | 36.5±1.04                       |
| 6       | 18                    | Sandy        | 24.28±0.54                       | 21.17±1.01                      | 15.5±0.57                       |

Low concentrations of zinc detected in seedling parts at the station 6 may be due to the lower concentration of zinc in the soil compared with the stations 4 and 5 or longer distance from the discharge point. Concentrations of zinc in the different seedling parts were increased with increasing zinc level in the soil. The availability of metals and its uptake by plants depend on the metal concentrations in soil (Fleming, 1965) and metal content in plant tissue significantly correlate with the metal concentrations in the soil (Sloan et al., 1997). This concept is in support with the results of the present work.

On the other hand, Rhizophora mucronata may have the ability to tolerate high zinc level in soil or could have the characteristic of selective ion transport. The characteristic of oxygen release by mangrove roots create an oxidant geochemical microenvironment (Silva et al., 1990) and after oxidization, oxides and hydroxides of Fe and Mn strongly co-precipitates other metals (Barlett, 1961). The presence of an ‘ion plate’ is frequent in
salt marsh plants and is responsible for the precipitation of various metals at the root's surface (Otte et al., 1987). High zinc concentration in roots could be due to the process involving the release of oxygen by mangrove roots.

Zinc in soil is not readily available to the plant for uptake. The availability of metals to plants largely depend on the complex form of metals in the soil, and in marsh soils, metals usually occur in many forms (Tagwira et al., 1992). Slower reactions are observed when metals are entrapped. Metals are permanently bound to the soils and become unavailable to the biota due to the formation of primary and secondary minerals (Tessier et al., 1979). From the present study, it was found that *Rhizophora mucronata* seedlings at stations 4 and 5 uptake comparatively less zinc than the zinc in the soil (Tables 1 and 2). Moreover, soil pH could be another important factor for zinc availability to plants. At pH 7.00, the availability of zinc becomes bw and severe deficiency is associated with high soil pH (Adriano, 1986).

**Conclusion**

The present study showed that mangrove forest soil is the main reservoir or natural sink of zinc. Waste disposal to the river water mainly took part in the dispersion of pollutants in the studied forest area. However, a lower bioavailability of zinc to *Rhizophora mucronata* seedlings was observed. But in the long run, the effect of this pollution may severely affect the physical environment of the Sepang mangrove forest and may threaten its existence. Increased metal concentrations can affect biological processes in soils, including the rates of litter decomposition, soil respiration and activity of key soil enzymes and may result in the failure of nutrient recycling owing to adverse effects on microorganism population.

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