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# The dynamics of heavy metals through litterfall and decomposition in a red mangrove forest

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## Abstract

The cycling of Zn, Mn and Fe through production, decomposition, and export of litter was studied at the Itacurussá Experimental Forest, a red mangrove forest in Southeast Brazil. The total litterfall was 8.69 t ha$^{-1}$ yr$^{-1}$. The heaf litter represented 56% to 100% of the total litterfall. The metal concentrations in the fallen leaves were: Mn = 230 ± 50 $\mu$g g$^{-1}$; Fe = 116 ± 44 $\mu$g g$^{-1}$ and Zn = 5.5 ± 1.0 $\mu$g g$^{-1}$ (n = 15). The average transfer rates of heavy metals from canopy to sediment through leaf fall were: 1.39 kg ha$^{-1}$ yr$^{-1}$ for Mn, 0.70 kg ha$^{-1}$ yr$^{-1}$ for Fe, and 0.03 kg ha$^{-1}$ yr$^{-1}$ for Zn. These rates represent 4.5%, 4.0%, and 57.0% of the total forest biomass reservoir for Zn, Fe and Mn, respectively. There was no accumulation of the metals in the first 10 days of decomposition, and since the residence time of leaves in the sediments was less than 6 days, litter exported from the forest had relatively low metal concentrations. Since 7% of the leaf fall (0.42 t ha$^{-1}$ yr$^{-1}$) is exported to the sea, we estimated an average export of heavy metals throught leaf detritus as: Mn = 0.097 kg ha$^{-1}$ yr$^{-1}$, Fe = 0.049 kg ha$^{-1}$ yr$^{-1}$ and Zn = 0.002 kg ha$^{-1}$ yr$^{-1}$. The export of metals through leaf fall represents less than 0.01% of the total sediment reservoir. We conclude that mangrove ecosystems are probably efficient biogeochemical barriers to the transport of metal contaminants in tropical coastal areas.

## Introduction

Mangrove ecosystems play an important role in nutrient cycling and energy flow in most tropical coasts (Odum and Heald, 1974; Cintrón and Schaeffer-Novelli, 1983; Camilleri and Ribi, 1986; Flores-Verdugo et al., 1987; Lacerda et al., 1993; Silva, 1996; Silva and Mozeto, 1997). The recent industrialization of various tropical regions has resulted in a significant input of pollutants into mangroves (Lacerda, 1993; Tam and Wong, 1993; Rezende, 1988). Among these pollutants heavy metals have received special attention, due to their long term effects on the environment and their property of accumulating in protected depositional environments, where mangroves are also best developed (Harbison, 1981; Harbison, 1986b; Lacerda and Rezende, 1987; Silva, 1988; Silva et al., 1990).

Previous studies have proposed that mangroves are long-term sinks for most heavy metal pollutants by accumulation in organic rich sediments with high concentrations of sulfide compounds (Harbinson, 1981; Harbinson, 1986a; Silva, 1996; Lacerda, 1997). Field and laboratory experiments showed that the trapping of heavy metals in mangrove ecosystems is a very efficient and fast phenomenon (Montgomery and Price, 1979; Harbison, 1981; Harbison, 1986a; Harbison, 1986b; Tam and Wong, 1993). However, no quantitative study has been carried out on the role of litter production, decomposition and export in the heavy metal cycling in mangrove ecosystems.

The cycling of organic matter through litter production, decomposition and tidal transport, may eventually export a fraction of the accumulated heavy metals, and therefore convey it to detritus food chains in adjacent coastal waters (Silva, 1988; Murray, 1985). The aim of this research was to quantify the cycling of heavy metals through litter in a red mangrove (*Rhizophora mangle* L.) forest in Sepetiba Bay, city of Rio de Janeiro, a moderately polluted area where mangroves support important fisheries resources (Lacerda, 1983) and play an important role in the heavy metals cycling in the coastal region (Lacerda et al., 1991b; Lacerda, 1993).

## Study site

The study was carried out in the Itacurussá Experimental Forest, located along the North shore of Sepetiba Bay in the Itacurussá municipality, approximately 100 km from the city of Rio de Janeiro (23° S and 44° W), Brazil (Figure 1). The forest has an area of approximately 4 ha, and is limited by two tidal creeks running almost perpendicular to the shore and into the land, by a transitional vegetation of non-mangrove species. The average temperature ranges between 18°C in the winter and 23°C in the summer. Annual rainfall is about 2,300 mm, with a rainy season from December to March and a dry season from July to October. The dominant species is *Rhizophora mangle* L. although isolated trees of the black mangrove (*Avicennia schaueriana* Stpaf and Leech) and of the white mangrove (*Laguncularia racemosa* Gaerth) occur throughout the forest. Average *R. mangle* trees plant density is 4,510 trees ha$^{-1}$, with an average height of 6.1 m and an average diameter of 7.8 cm. The basal area is 21.6 m$^2$ha$^{-1}$ and the total biomass is 81.7 t ha$^{-1}$ distributed between above ground (65.4 tha$^{-1}$) and below ground (16.3 t ha$^{-1}$) biomass (Silva et al., 1991).

Fresh water inputs to the forest are groundwater and rainfall. The inundation pattern is determined by the tide which reaches 2.0 m in the spring. The pH and the redox potential (Eh) in the interstitial water of the mangrove mud are in the range 6.4 to 7.5 and –410 to –110 mV respectively (Ovalle, 1992). This area is a fringe forest following Lugo and Snedaker (1974).

## Material and methods

### *Litterfall and standing crop*

Litterfall was collected in eleven 0.30 m$^2$ baskets supported approximately 1.5 m above the ground, constructed of fiberglass nets (1 mm nylon mesh). Litterfall was collected at 11–19 day intervals from October 1986 to October 1987. The material from each basket was dried at 80°C up to constant weight and separated into leaves, reproductive parts and thin branches (lesser than 2 cm of diameter).

The standing crop of leaf litter was measured during 3 months (January, February and March) by collecting 15 arbitrarily chosen 0.25 m$^2$ (0.5 m x 0.5 m) samples of litter from the surface of the forest floor in the vicinity of the litter fall collectors. Surface leaf samples were processed in the same manner as litterfall samples.

In the laboratory the sediment was removed from the leaves by gently rubbing the leaves in running tap water and the samples were dried at 80°C. After these procedures, the samples were prepared for heavy metal analysis.

### *Leaf decomposition*

Senescent *R. mangle* leaves, yellow in color and ready to fall, were picked from the trees and allocated in the field on June 1987. The leaves were split into 16 samples, each one weighting 15 g. Each sample was placed in a separate nylon mesh bag of 16 cm x 21 cm and 1.0 mm mesh size, large enough to permit the entry of small invertebrates, but preventing large consumers, such as crabs, which actually cut the leaves. Sixteen bags were attached to *R. mangle* roots and subjected to intertidal conditions. Average conversion factors for subsequent comparison with the dry mass of field results were evaluated from four fresh samples of 15 g, dried untill to reach a constant mass at 80°C.

Two bags were retrieved from the site, on each of the subsequent days after the begnning of the experiment: days 7, 30, 60, 90, 120 and 140. In the laboratory the sediment was removed from the leaves by gently rubbing the leaves in running tap water and the samples were dried to a constant mass at 80°C. After these procedures, the samples were prepared for heavy metal analysis.

Percentage mass loss was plotted against time, in order to evaluate the decomposition half-time for *R. mangle* leaves. The rate at which mass was lost was calculated using a single exponential model, $Wt = Wo.e^{-k.t}$, where $Wt$ is the remaining mass at time ($t$), $Wo$ is the initial leaf mass, $k$ is the decay constant and $e$ is the base of natural logarithm (Olson, 1963). This model has been frequently used in mangrove de-

*Figure 1.* Location of the Itacurussá Experimental Forest (IEF) in Baía de Sepetiba, Rio de Janeiro State, SE Brazil.

composition studies (Cintrón and Schaeffer-Novelli, 1983).

*Transport of heavy metals from R. mangle to the sediment*

Silva (1988) found an average total litter fall rate of 8.69 t.ha$^{-1}$yr$^{-1}$ in our studied forest where the mean leaf fall rate (6.06 ± 4.60 t ha$^{-1}$ yr$^{-1}$) represented 69.74% of the total. Leaf fall was assumed to be the single output of heavy metals from *R. mangle* to the sediment throughout the year.

The transport of heavy metals through *R. mangle* leaf fall to the sediment was calculated by multiplying the mean concentration of heavy metals into leaf fall (Mn = 230 ± 50 $\mu$g g$^{-1}$, Fe = –116 ± 44 $\mu$g g$^{-1}$ and Zn = 5.5 ± 1.0 $\mu$g g$^{-1}$) by the mean of leaf fall rate. This estimate was a maximum value since it neglected possible export at spring tides of floating leaves.

### Exportation of heavy metals through leaf litter

The amount of *R. mangle* leaves exported in the form of macrodetritus in the studied area was estimated to be 7% (0.42 t ha$^{-1}$ yr$^{-1}$) of the total leaf fall (Silva, 1988). Silva et al. (1993) measured leaf export at this site (including others species than *R. mangle* trees) to be 0.47 t ha$^{-1}$ yr$^{-1}$ which correspond to 7.8% of the *R. mangle* leaf fall. A estimative of heavy metals exportation through the leaves was calculated by multiplying the average concentration of heavy metals in *R. mangle* leaf fall by the amount of *R. mangle* leaves exported by tides (0.42 t $ha^{-1}$ $yr^{-1}$).

### *Analysis of heavy metals*

Leaf litter samples (2 g) were oven dried (80°C, 24 h) and ashed (450°C, 12 h). The ashes were digested with aqua regia (HCl + $HNO_3$, 3 + 1) at 80°C on a hot plate till dryness and then dissolved in 30 mL of 0.1 N HCl. Trace metals were determined in these extracts through conventional flame atomic absorption spectrophotometry. All samples were run in duplicate, differences among duplicates were always less than 3%, and all digestion procedures were tested in reference material (NBS "Tomato Leaves" for plants). Differences between certified and measured results were always less than 10%. Details of chemical procedures and analytical errors can be found in Silva (1988) and Silva et al. (1990).

## Results and discussion

### *Litterfall mass and transport of heavy metals from R. mangle to the sediment*

Litterfall is an important factor in the cycling of heavy metals in mangrove ecosystem. Through litterfall, metals are transfered to sediments, incorporated into organic matter and eventually released by litter decomposition.The seazonal variation of litterfall rates in the forest is attributed to variations of leaf fall which represents 56% to 100% of the total *R. mangle* litter fall during the experiment (Figure 2). The highest values of litterfall of the *R.* mangle trees recorded occurred in late winter (September – 0.069 t $ha^{-1}$ $day^{-1}$) and summer (November and January – 0.042 t $ha^{-1}$ $day^{-1}$ and 0.039 t $ha^{-1}$ $day^{-1}$) and may be due to the strong winds and rain fall prevailing during these periods (Silva, 1988). The annual leaf fall rates year were 6.06 ± 4.60 t $ha^{-1}$ $yr^{-1}$; fine branches were 2.01 ± 2.12 t $ha^{-1}$ $yr^{-1}$ and reproductive structures were 0.62 ± 0.69 t $ha^{-1}$ $yr^{-1}$; with an average total litter fall of 8.69 t $ha^{-1}$ $yr^{-1}$.

The average total litterfall rate (8.69 t $ha^{-1}$ $yr^{-1}$) in the studied forest is similar to those of Duke et al. (1981) who also found 9.60 t $ha^{-1}$ $yr^{-1}$, and Odum and Heald (1974) who found 8.80 t $ha^{-1}$ $yr^{-1}$, both studies were also done in tropical fringe forests. This average however is much higher than the one reported by Golley et al. (1962) in an arid Puerto Rican mangrove forest (4.82 t $ha^{-1}$ $yr^{-1}$) and much lower than those reported by Bunt (1978), 28.11 t $ha^{-1}$ $yr^{-1}$, and Duke et al. (1981), 17.70 t $ha^{-1}$ $yr^{-1}$, for large tropical *R. mangle* forests in Australia. The measured litterfall rate however, is typical of tropical, New World fringe red mangrove forests (Lacerda et al., 1993).

*Table 1.* A comparison of the concentration of Mn, Fe and Zn ($\mu$g $g^{-1}$, dry weight) in the leaves of *R. mangle* trees in various mangrove forests.

| Area | Heavy metals | | | Author |
|---|---|---|---|---|
| | Mn | Fe | Zn | |
| Malaysia | – | 49–67 | 6–7 | Peterson et al (1979) |
| Chine | – | – | 9–32 | Chiu and Chou (1991) |
| India | – | 32.2 | 11.5 | Bhosale (1979) |
| Brazil | 20–882 | 68–943 | 10–34 | Lacerda et al. (1986) |
| Study area | 230 | 116 | 5.5 | This study |

The average concentrations of metals in leaves which fall from the trees were: Mn = 230 ± 50 $\mu$g $g^{-1}$ and Fe = 116 ± 44 $\mu$g $g^{-1}$. These concentrations are within the range of the previous data reported by Lacerda et al. (1986) for *R. mangle* leaves of Sepetiba Bay area (Mn – 38 to 473 $\mu$g $g^{-1}$ and Fe – 71 to 706 $\mu$g $g^{-1}$). On the other hand, our Zn values (5.5 ± 1.0 $\mu$g $g^{-1}$) are similar to those found by Peterson et al. (1979) in Malaysia (6 to 7 $\mu$g $g^{-1}$), see Table 1. Therefore, the estimated average input rates of heavy metals from the trees to the sediment through leaf fall were: Mn 1.39 kg $ha^{-1}$ $yr^{-1}$; Fe 0.70 kg $ha^{-1}$ $yr^{-1}$ and Zn 0.03 kg $ha^{-1}$ $yr^{-1}$.

### *Leaf litter decomposition and metals release*

The leaves of *R. mangle* in the litter bags lost 50% of their dry weight in 77 days. The initial rate of mass loss was more rapid within the first 7 days when the leaves lost 1.8% of their weight per day (Figure 3). After 84 days in the sediment the leaves lost 0.7% of their initial mass per day. A total of 70% of the dry mass was lost in a period of 133 days (Figure 3). Although based on only two samples collected per date, these rates of weight loss is in the range reported for other studies in mangroves, which recorded losses in field studies ranging from 13% to 44% during the first 10 days of decomposition (Cintrón and Schaeffer-Novelli, 1983; Van der Valk and Attwill, 1984).

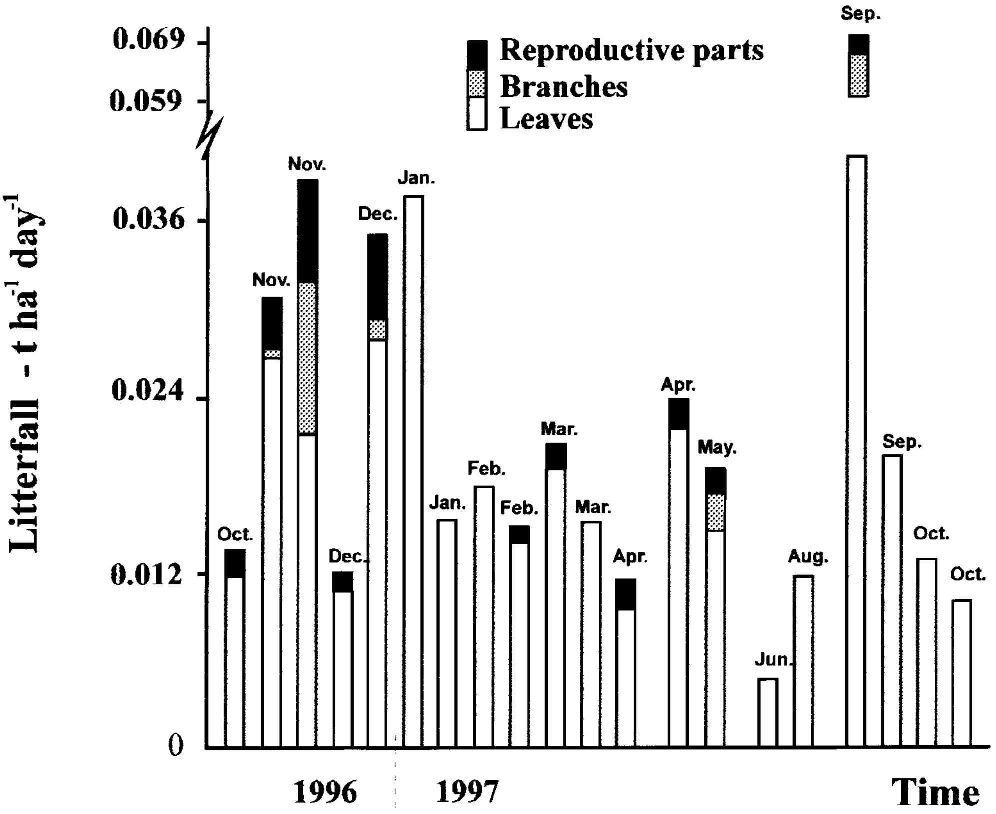

*Figure 2.* Instantaneous annual litter fall rate (kg ha$^{-1}$ day$^{-1}$, dry mass) of *R. mangle* from October, 1986 to October, 1987 in the Itacurussá Experimental Forest, SE Brazil.

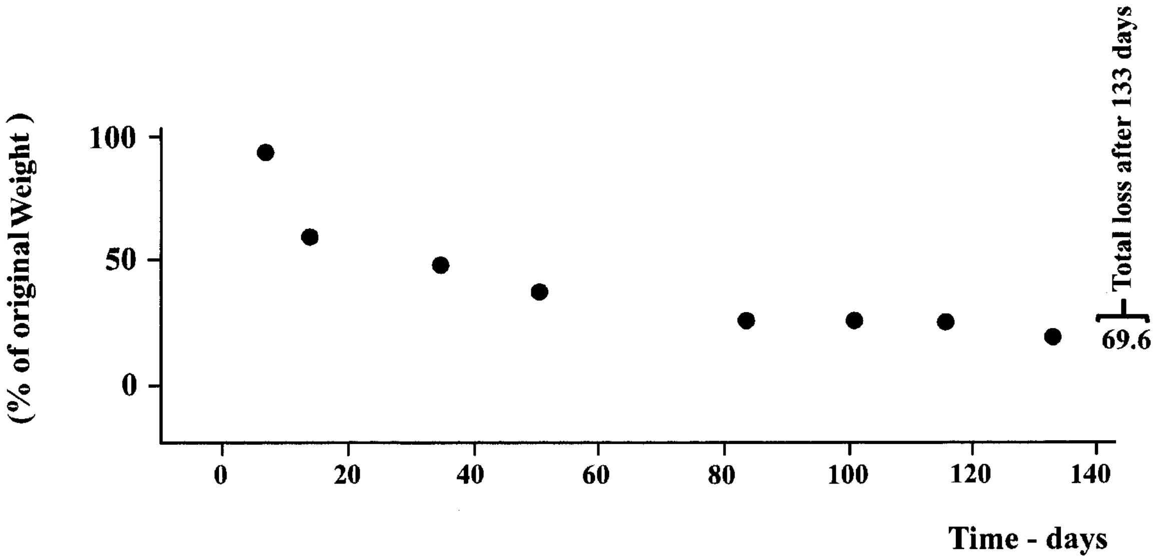

*Figure 3.* Decay (percentage of dry weight remaining) of the leaves of *R. mangle*. Each data point is a mean of two measurements.

The concentrations of Fe and Zn in the decomposing leaves increased rapidly in the first 84 days (Fe = –110 to 4,282 $\mu$g g$^{-1}$; Zn – 3.1 to 73 $\mu$g g$^{-1}$; see Figure 4). After this period up to the end of the experiment there was little change in their concentrations (Fe = 4,282–3,609 $\mu$g g$^{-1}$; Zn = 73–58 $\mu$g g$^{-1}$) (Figures 4 a and b, respectively). Mn concentrations decreaed from 150 to 18 $\mu$g g$^{-1}$ in the first 40 days of the experiment, and thereafter increased to 92 $\mu$g g$^{-1}$ (Figure 4c). The increase in manganese concentration is probably due to precipitation and adsorption of $Mn^{4+}$, when reduced $Mn^{2+}$ liberated from anoxic porewaters meet oxidizing conditons of the incoming tide and may be adsorbed to litter particles (Lacerda et al., 1988; Lacerda, 1993).

These changes of heavy metal concentrations during the decomposition of the *R. mangle* leaf tissues resulted from the combined effect of leaching losses and accumulative process of adsortion and microbial immobilisation (Larsen and Schierup, 1981).

Working with litter deposited in a prairie stream, Killingbek et al. (1982) reported an increase in the concentrations of Fe, Mn and Cu in decaying leaves. Similarly, Larsen and Schierup (1981) reported an increase of Pb in freshwater macrophyte litter. Lindberg and Harris (1974) studied the behaviour of Hg during the decomposition of *R. mangle* leaves in Florida. They found a 3.2-fold enrichment in Hg concentrations in leaf litter relative to undecomposed leaves, and a 10.4-fold enrichment in suspended detritus collected in a river draining the mangroves.

Rice and Windon (1982) also working with *R. mangle* litter, found similar results to our study. They reported a steady increase in Fe concentrations in decomposing leaves, from 35 ± 3 $\mu$g g$^{-1}$ at day zero of their experiment, to 700 ± 80 $\mu$g g$^{-1}$ at day 150. The behavior of Mn showed a sharp decrease in concentration during the first 10 days of the decomposition process (from 52 ± 1 to 2.0 ± 0.6 $\mu$g g$^{-1}$).

The difference between Fe, Mn and Zn release from *R. mangle* leaf litter to sediments may also be due to differences in the biochemistry and physiological functions of these inorganic constituents. For example, Mn is involved in reactions with nitrogen and with organic acidics and the metabolism of photosynthesis (Ferri, 1979; Ochiai, 1977). Mn is also more susceptible to leaching than Fe and Zn, which are frequently associated with more refractory structural compounds.

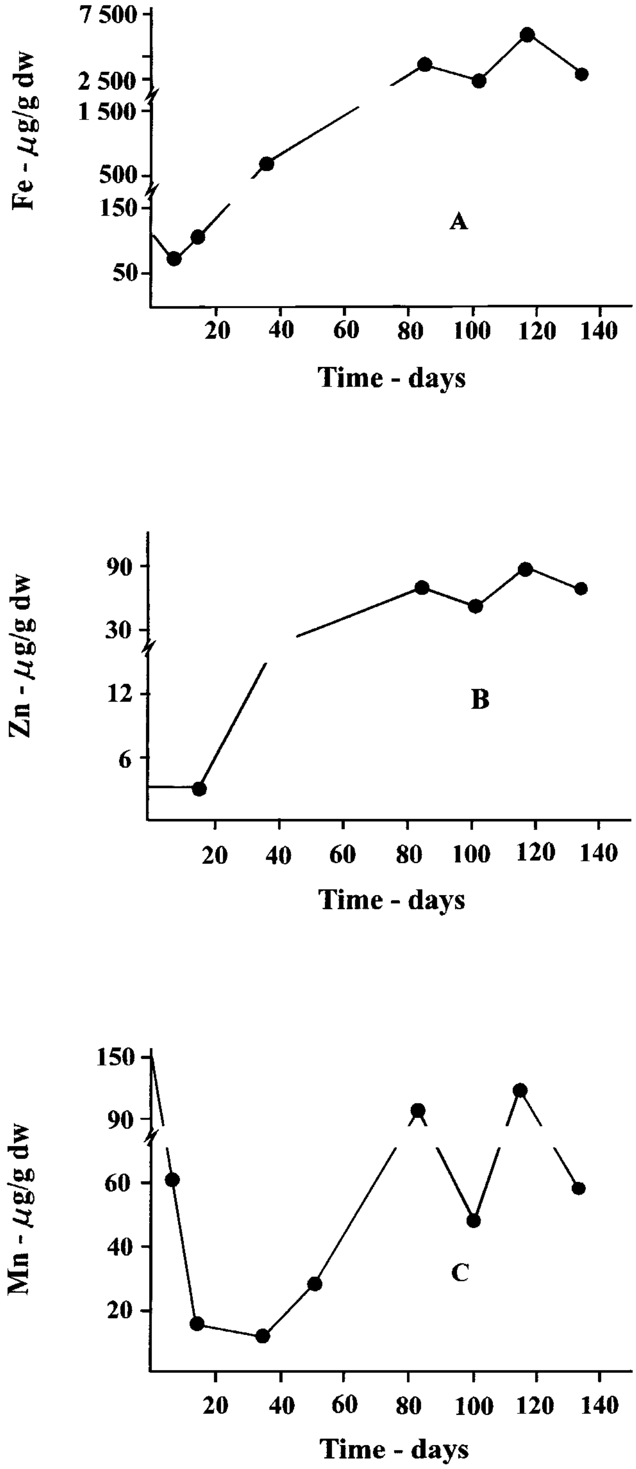

*Figure 4.* Temporal changes in the mean concentrations of (A) Fe, (B) Zn and (C) Mn, during the leaf decomposition process of *R. mangle.*

### *Residence time of leaves in sediments*

The residence time of leaves in the sediment in the forest studied was estimated following Olson's (1963) model,

$$1/k = Xss/L$$

where $L$ is litter mass production, $Xss$ is the steady state accumulation of surface mass on the forest floor (standing crop) and $1/k$ is the residence time. The measured standing crop of leaf litter was 0.062 ± 0.032 t $ha^{-1}$ (n = 16). Therefore the estimated residence time mean was 4 days, assuming an average annual leaf litterfall rate of 6.06 t $ha^{-1}$ $yr^{-1}$.

Mangrove litter residence time is quite variable depending mostly on the tidal range (Twilley, 1985; Ong et al.,1982), the realtive elevation of the forest relative to inundation (Twilley et al., 1986) and the activity of litter-feeding organisms in particular of seasarmid crabs (Robertson, 1986). Twilley et al. (1986) reported a residence time of 2 to 6 months in a basin forest in Southern USA. This long residence time is due to infrequent flooding of a basin forest, while our forest is a fringe type which is flooded nearly twice every day. In riverine *Rhizophora* forests, Ong et al. (1982) found residence times of leaves of about 30 days. Robertson (1986) showed that crabs can bury over 75% of total litterfall at low tide, speeding the "exportation" of deposited leaves. In our study area, the activity of seasarmid crabs, evaluated visually, is very intense during low tide periods. Therefore they may also significantly contribute to the short residence time of leaves on the top of the sediment in the studied forest.

### *The exportat of metals associated with leaf litter*

The exportat of heavy metals from the mangrove forest to adjacent coastal waters through leaf litter is a function of the amount of litter exported and its metal concentrations. It depends on the residence time of litter on the forest floor and ton he enrichment of metals during litter decomposition. The short residence time (4 days) of deposited litter in our forest limits the enrichment of heavy metal concentrations in decomposing leaves, since the metals in this study increased in concentration only after at least 10 days of decomposition (Figure 4 a-c). Therefore the concentration of metals in leaf during export from the forest is equal or even lower than the concentrations in recently fallen leaves.

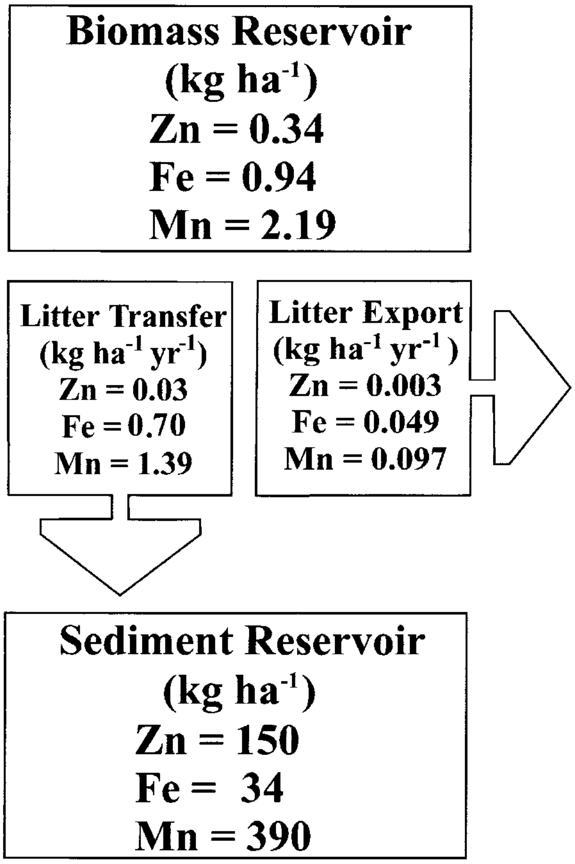

*Figure 5.* A schematic representation of the Zn, Mn and Fe dynamics through litter fall in the Itacurussá Experimental Forest.

The estimated average export at rates of heavy metals throught leaf detritus are 0.097 kg $ha^{-1}$ $yr^{-1}$ for Mn, 0.049 kg $ha^{-1}$ $yr^{-1}$ for Fe and 0.002 kg $ha^{-1}$ $yr^{-1}$ for Zn.

The variations of heavy metal concentrations during the decomposition of *Rhizophora* leaves support these small export rates. During first 7 days of decomposition, there was a loss of heavy metals from decomposing leaves on the mud sediment (Figure 4a-c). The enrichment of metals in the decomposing leaves occurred only after this initial stage. The meatls reached their highest concentrations at day 80 of the experiment. At this stage *R. mangle* leaves became less bouyant and were retained within the mangrove ecosystem, where a relatively fast sedimentation rate facilitated the burial of decomposed organic matter (Lacerda et al., 1991a).

## Conclusions

The internal cycling of Zn, Fe and Mn studied in the Itacurussá Experimental Forest is summarised in Figure 5. In this figure the data on the metal reservoirs in the forest biomass and in the sediments are from Silva et al. (1990). The main reservoir of the metals is the sediment. Decomposing litter do not contribute significantly with metal output to sediments because of the short residence time of leaf litter in the sediments and because the enrichment of metals only occurred later in the the decompositon process. The export of metals through *R. mangle* leaf fall is small, these fluxes represent only less than 0.01% of the total metal reservoir in the sediment. This reservoir is equivalent to 10,000 years of growth.

Our results show that mangrove leaf fall is of minor importance in metal cycling in our mangroves. Rather, mangrove ecosystems are probably efficient biogeochemical barriers to the transport of metal contaminants in tropical coastal areas. Hence mangroves could be used in the management of metal pollution in tropical coastal areas.

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