

TRACE METALS BIOGEOCHEMISTRY AND DIFFUSE POLLUTION IN MANGROVE ECOSYSTEMS

Luiz Drude de Lacerda



July 1998

International Society for Mangrove Ecosystems

ISME Mangrove Ecosystems Occasional Papers

Editorial Panel: invited reviewers who are specialists in different areas.

The International Society for Mangrove Ecosystems (ISME) was founded in August 1990. The aims of the Society are to promote research and surveys and to associate with other organisations with the purpose of promoting the conservation, rational management and sustainable utilization of mangroves. The Society also intends to serve as an international data-bank on mangrove ecosystems.

Prior to the foundation of ISME a number of mangrove ecosystems occasional papers had been published by the UNDP/UNESCO regional mangrove projects in Asia and the Pacific. ISME now intends to continue that series of publications and to extend their scope to accept papers from anywhere in the world. The ISME mangrove ecosystems occasional papers will accept completed papers on any aspect of mangroves and mangrove ecosystems. The responsibility for the opinions expressed in these papers rests with the authors and does not necessarily reflect the opinions of ISME or the Editor. The decision to publish a paper rests with the Editor.

Notice to Authors

Preparation of Manuscripts. Papers will be considered for publication if they add to the knowledge of mangrove ecosystems. Contributions concerned with general reviews, conservation issues and management strategies of mangroves will also be published. The criteria for publication are that the work should be presented concisely and clearly in English and introductory material should not exceed what is necessary to indicate the essential background. All papers are reviewed by the Editor who will also send individual papers to recognised specialists for review. To prevent delays in publication small editorial revisions may be made without reference to the author.

Manuscripts. The original and one copy of the manuscript must be submitted. The original must be typed with double spacing throughout, and with a margin of at least 4 cm on the left-hand side. All pages of the manuscript must be numbered consecutively, including those carrying references, tables and captions to illustrations, all of which are to be placed after the text. Illustrations, both line drawing and photographs, are to be numbered as figures in a common sequence, and each must be referred to in the text. A typed list of captions is required. Original illustrations will be returned if requested. Poorly prepared or unnecessarily lengthy manuscripts have less prospect of being accepted.

References. Are cited chronologically in the text by the author and date and are not numbered. All references in the text must be listed at the end of the paper, with the names of authors arranged alphabetically. Titles must be included for all references. Abbreviations should conform to those given in the latest issue of 'Serial Sources of the BIOSIS Data Base' (Bio Sciences Information Services, Philadelphia, Pa).

Unit of Measurement. The metric system is adopted as standard. The system of units known as SI should be used.

Tables. Tables should be numbered in Arabic numerals and each submitted on a separate sheet with an appropriate legend at the head. The preferred position in the text should be indicated. Tables should be kept as simple as possible.

Illustrations. Authors are encouraged to submit original line drawings and lettered and mounted photographs which are suitable for direct reproduction. If facilities are not available to the author for lettering of illustrations to a suitable standard, unlettered illustrations may be submitted. Original line drawing must be drawn with black ink on white board or on drawing or tracing paper; their dimensions should have regard for the size of the printed page. Photographs must be of high quality with a full range of tones and be trimmed squarely to exclude features not relevant to the paper. Intending authors should write to the editor:

International Society for Mangrove Ecosystems (ISME)

ISME was inaugurated on 23 August 1990 and the seat of the Society is Okinawa, Japan. ISME takes over from the UNDP/UNESCO Regional Mangrove Ecosystems projects. ISME is affiliated to ICSU (International Council of Scientific Unions) and is part of IUBS (International Union of Biological Sciences) through IABO (International Association of Biological Oceanography). The Society was certified as a Foundation on 23 October 1992 in Japan.

ISME Mangrove Ecosystems Occasional Papers No.2

Trace Metals Biogeochemistry
and
Diffuse Pollution
in Mangrove Ecosystems

Luiz Drude de Lacerda

Departamento de Geoquímica,
Universidade Federal Fluminense,
CEP-24020-007, Niterói, RJ, Brazil

Editor: M. Vannucci

July 1998

International Society for Mangrove Ecosystems

Contents

Abstract	1
1. Introduction	1
1.1 The relative importance of diffuse pollution in coastal environments	1
1.2 The chemical time bomb concept	2
1.3 Mangroves as chemical time bombs	2
1.4 Trace metals as key pollutants from diffuse sources	4
2. Environmental contamination by trace metals	4
2.1 Anthropogenic inputs of trace metals to the biosphere	4
2.2 Trace metals dynamics in coastal environments	5
2.3 The impact of trace metals on tropical coastal areas	11
3. The natural history of mangroves	13
3.1 Origin and worldwide distribution of mangroves	13
3.2 Biology of mangrove ecosystems	14
3.3 Structure and productivity of mangrove forests	15
3.4 The physical environment	17
3.5 Mangrove utilization	18
4. Trace metal dynamics in mangroves	19
4.1 Trace metals inputs and outputs from mangroves	20
5. Trace metals in mangrove sediments	28
5.1 Biogeochemistry of trace metals in mangrove sediments	28
5.2 Distribution and accumulation of trace metals in mangrove sediments	29
5.3 Geochemical partitioning of trace metals in mangrove sediments	31
5.4 The effect of plant cover on the distribution of trace metals in mangrove sediments	34
6. Trace metals in mangrove plants	35
6.1 Trace metals distribution in mangrove leaves	35
6.2 Factors controlling trace metal concentrations in mangrove plants	36
6.3 Trace metal distribution in mangrove plant organs	38
6.4 Trace metals mass balance in the biomass of mangrove forests	40
7. Trace metals concentration and distribution in mangrove animals	42
8. Diffuse pollutants interactions with global environmental impacts on mangroves	44
9. Summary and outlook	46
10. Acknowledgments	46
11. References	47

Trace Metals Biogeochemistry and Diffuse Pollution in Mangrove Ecosystems

L.D. Lacerda

Departamento de Geoquímica, Universidade Federal Fluminense, CEP-24020-007, Niterói, RJ, Brazil

Key words: Trace metals, biogeochemistry, cycling, mangroves, diffuse sources, sediments, plants

Abstract

Pollutants from diffuse sources are becoming a significant environmental issue after the increasing control of point-source effluents in the last two decades. In most coastal areas, mangroves are an important receptor of such pollutants, from atmospheric deposition, continental runoff and tidal currents. Among these pollutants, heavy metals due to their long lasting effects on ecosystems are of key importance. Heavy metals reach mangroves incorporated in suspended particles, brought in by tides and river flooding, mostly associated with oxidized substrates. Mangroves act as a physical barrier by trapping suspended matter from tidal and fluvial waters. Once deposited, these particles with their heavy metal load face reducing environments, due to anaerobic sulfate reduction, the dominant metabolism in mangrove environments. Under such conditions heavy metals precipitate as refractory sulfides and accumulate in mangrove sediments, but under a chemical form of very low bioavailability. The mangrove plants' physiology appears to cope with high salinity of the pore waters, to help in hampering heavy metal absorption. As a result, heavy metal concentrations are, in general, very low in mangrove plants and animals. However, this immobilization mechanism only works when the mangrove ecosystem is kept under its natural conditions, deforestation or degradation of mangrove forest will also result in the mobilization of the accumulated heavy metals, later conveying them to coastal food chains. Therefore, conservation of mangrove ecosystems is above and beyond the biodiversity issue, since it can also significantly contribute to maintenance of the environmental health of tropical coastal areas.

1. Introduction

1.1 The relative importance of diffuse pollution in coastal environments

In the process of conducting economic activities that cause chemical inputs into the environment, little forethought has been given to diffuse sources of chemicals and the potential for long-term, time delayed ecological impacts. Attention was focused on obvious point sources of pollutants and on major episodic chemical accidents, the impact of which is usually evident in the short term. The appreciation of polluting impacts on the environment resulted on the other hand on improvement of technological processes and on the other on enforcing policies of control over point sources of pollutants; this approach however, has failed to evaluate the long-term impact of diffuse pollutant sources.

The increasing control of potential polluting activities and the development of "clean" technologies, though resulting in a global decrease of pollutant emissions, has substantially increased the relative importance of diffuse pollution sources (Behrendt, 1993). Presently, diffuse sources of pollutants, such as disposal of urban solid wastes, sewage, intensive use of agro-chemicals, burning of fossil fuels and of solid wastes, have become the major sources of many pollutants, in particular of trace metals, organic micro-pollutants and excess nutrients. Some of these pollutants are extremely long-lived and may be the cause of environmental health problems lasting even after the control or ban of the present sources.

Coastal areas are typical integrators of different activities taking place along their basins. Notwithstanding their increasing social-economic value, which resulted in the enforcement of regulations on the use of

coastal areas and other *in situ* activities, they are permanently threatened by basin activities. For example, Hg contamination on most coastal areas of SE Brazil is due to diffuse inputs from the atmosphere, which has received Hg from a variety of sources located along river basins, in general very far from the coastal area (Marins *et al.*, 1996; 1997b). Copper contamination of Empress Augusta Bay and its mangrove forests, Papua New Guinea, is due to the fluvial transport of tailings from mining operations located 700 m above sea level in the central mountain range of the island, as far as 50 km inland (Jeffery *et al.*, 1988). Many other examples could be listed, suggesting that whatever control policies are applied to polluting activities located in the coastal area, basin activities can still contribute with a significant input of pollutants to coastal ecosystems and time-delayed effects can occur even many years after banning the pollutant source.

1.2 The chemical time bomb concept

Numerous studies refer to chemical sinks as the ultimate environmental deposition of man-made inputs of heavy metals and long-lived chemicals. Examples of such sinks often include well-buffered clayey soils, wetlands, including mangroves, and many types of aquatic sediments. The image suggested by the word "sink" is one of a bottomless hole into which chemicals may be wasted away never to be encountered again. However, increasing evidence suggests that such sinks are in reality more like "sponges" than like "bottomless pits", meaning that those chemicals are out of sight but certainly should not be out of mind. This view is critical to make a quantitative estimate of the impacts of chemical inputs into the environment (Salomons & Stigliani, 1995).

Just as a sopping-wet sponge loses its capacity for absorbing more liquid, the "sink-as-sponge" image suggests that while environmental systems often have large capacities for adsorbing and immobilizing toxic and environmentally harmful chemicals, they can eventually become saturated with accumulated chemical inputs. Moreover, during the time over which the system is capable of immobilizing toxic chemicals, clear environmental effects may not be evident. When the effects are finally manifested, they are usually displaced in time from the activities causing the problem in the first place. In addition the effects may also be spatially-displaced. This occurs when the chemicals

are transported by rivers, groundwater or the atmosphere to environments where they become more mobile and/or bioavailable. Saturation of sinks is defined in respect of the impact on the ecosystem or human health, therefore a slow but increasing release of the chemical with time will affect the system until when certain threshold is reached and detrimental effects occur. The thresholds may result from changes in the ecosystem functioning or may be more "down to earth" surpassing the criteria for pollutant concentrations in environmental compartments, as defined by law in most countries (Stigliani, 1995). The time delayed and the spatially-displaced effects should be taken into account where chemicals are used and are disposed off into the environment.

1.3 Mangroves as chemical time bombs

Some recent studies have strongly suggested that mangroves, the dominant ecosystem of over 75% of the tropical coastline, have some biogeochemical characteristics which may result in a chemical time-bomb type response to environmental pollutants. For example; DDT was found to be still accumulating in mangrove sediments in SE Brazil even 10 years after banning their agricultural use of in the region. Biogeochemical processes involving the burial of undegraded organic matter were related to low degradation rates of these pollutants in the mangrove environment (Japenga *et al.*, 1988). Thus, increasing the threat of contamination from a substance considered an environmental issue of the past. A typical time-delayed, chemical time-bomb phenomenon.

Another example of peculiar behavior of mangroves in relation to pollutants was observed in the speciation of Hg in mangrove sediments. Quevauviller *et al.* (1992) showed accumulation of dimethyl-Hg, a highly toxic compound, in mangrove sediment cores. This compound is in general volatile and unstable under oxic conditions, however, these authors have shown that binding to abundant polysulfides in mangrove sediments may result in decreasing decomposition rates of dimethyl-Hg in mangrove sediments, which then accumulate.

After many years of research on the fate of trace metals in mangrove ecosystems in Australia, Harbinson (1981, 1984, 1986a) concluded that although mangroves act as a sink of many trace metals,

changing physical-chemical conditions can turn the ecosystem into a net source of these pollutants, conveying them to local food chains. Similar results have been found in mangroves of the southeastern Brazilian coast (Lacerda *et al.*, 1991a,b; Lacerda 1993; Silva *et al.*, 1990), as well as in mangroves along the Arabian Gulf (Sadiq & Zaidi, 1994), Taiwan (Chiu & Chou, 1991) and India (Bhosale, 1979; Ramadhas *et al.*, 1975; Rao *et al.*, 1991).

Although there are many examples scattered in the literature, no attempt has been made to consolidate the available data and generalize upon the role displayed by mangroves in the biogeochemical cycle of long-living pollutants in coastal environments, no attempts were made on the potential impact of such substances on mangrove functioning or on mangrove resources and uses.

The behavior of a functioning mangrove ecosystem in relation to the immobilization and mobilization of pollutants is described in figure 1.1, modified from Stigliani (1995). For any given point on the curve, the vertical axis shows the quantity of a given pollutant immobilized by a mangrove ecosystem, i.e. the bulk accumulation in forest compartments, particularly in mangrove soils. The horizontal axis shows pollutant amount in mobilized phases, in the case of mangroves,

mobilized phases are mostly dissolved species in soil pore waters and tidal waters. The slope of the line at a given point ($\Delta Q/\Delta C$) gives the accumulation capacity of the mangrove ecosystem to a particular pollutant.

At the beginning of the contamination process the immobilization capacity is higher (see $\Delta Q_1/\Delta C_1$), as the contamination proceeds, immobilization capacity decreases as in $\Delta Q_2/\Delta C_2$, until maximum accumulation capacity is reached where the level of immobilization tends to zero, meaning that the mangrove ecosystem is saturated and no more pollutant can be immobilized. At this point any extra load of a given pollutant will be rapidly mobilized through soil pore water and tidal waters. However, it is quite possible that even before reaching this threshold, pollutant concentrations would already be higher than standard values for the protection of wildlife.

Since the processes involved in the immobilization of a pollutant and, therefore of the maximum accumulation capacity of a given mangrove, forest will be dependent on the biogeochemical properties of a given site, mangroves under different environmental conditions will show different maximum accumulation capacity. Also, it seems that the immobilization of pollutants in mangroves is tightly linked to the ecosystem health. Once the typical conditions of mangroves

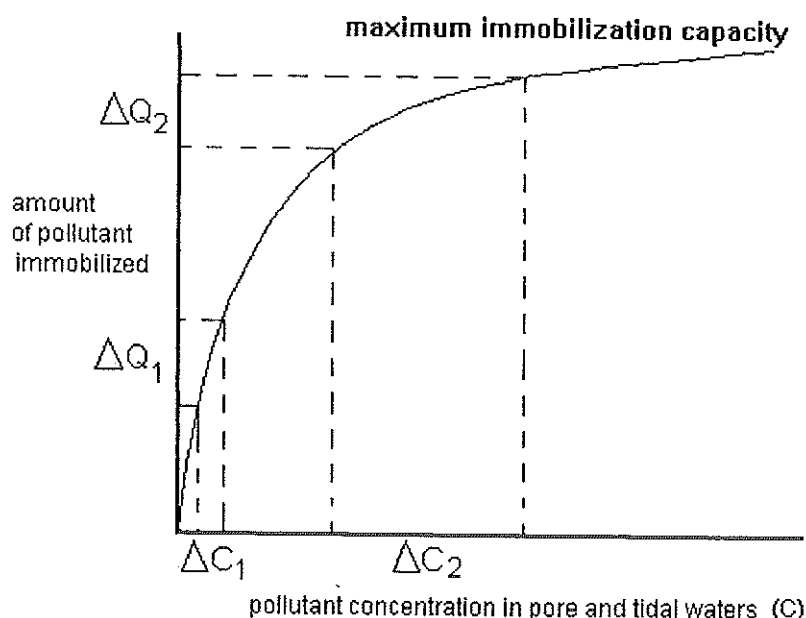


Fig. 1.1. General curve describing the hypothetical behavior of pollutants in mangrove ecosystems, modified from Stigliani (1995).

are changed (e.g. through deforestation, erosion, fish farming), they shift from long term sinks into sources of the accumulated pollutants.

1.4 Trace metals as key pollutants from diffuse sources

Trace metals are natural occurring and non-degradable. They are ubiquitous by-products mostly of urban, industrial and agricultural activities and are present in significant quantities in their effluents into soils, waters and the atmosphere. At least 13 trace metals are considered harmful to human health and to the preservation of natural ecosystems (Novotny, 1995). Today modern civilization mobilizes more metals than their natural weathering cycles.

Diffuse sources have mobilized trace metal contamination globally. Increasing concentrations of Pb and Cu have been measured in Arctic ice over the last 2,000 years due to atmospheric deposition of trace metals generated by pyrometallurgical processes and more recently due to the burning of fossil fuels (Hong *et al.*, 1996; Nriagu, 1996). Mercury, originated from the industrial revolution in the northern hemisphere, has been recently measured in lake sediments from the Amazon region (Lacerda & Salomons, 1997). The widespread use of trace metals by modern civilization makes anthropogenic structures a potential source of these pollutants, to a point that the washout of urban and agriculture surfaces are presently the most important sources of many trace metals. For example, Zn roof materials are excellent buffer surfaces for acid rain. However, Zn concentration in the runoff from Zn roofs is 450 times higher than in rainfall, when pH is below 4.0 (Novotny, 1995). Diffuse loads of trace metals in the Rhine basin in Germany, increased from 18%, 42% and 40%, of the total load of Cd, Pb and Zn respectively, in the 1970's; to 58%, 66% and 56% (for Cd, Pb and Zn respectively), in the late 1980's (Behrendt, 1993).

The long residence time of trace metals in surface compartments of the biosphere, and in particular in soils and sediments, allows for great accumulation. This accumulation process may result in a very high concentration increase with time. Therefore, even considering diffuse sources, with low input to area ratio, trace metals can become a serious environmental risk.

2. Environmental contamination by trace metals

2.1 Anthropogenic inputs of trace metals to the biosphere

Trace metals are ubiquitous by-products of industrialization and urbanization. Although used by humans since pre-historic times, the large quantities of these elements presently mobilized by modern civilization, has resulted in increased concentration in many natural environments, submitting the biota to toxic levels of these pollutants and leading to reduction in biodiversity and in the quality of many natural renewable resources. Also in many areas, significant effects on human health have been reported.

Table 2.1 summarizes the most recent estimates of the quantities of selected trace metals mobilized annually by industrial processes and natural weathering and their respective anthropogenic mobilization factors, defined as the ratio between these two variables.

The industrial mobilization of trace metals is by far the most important pathway of their transfer to the biosphere, being in specific cases such as for Hg, Cd and Pb, over 11, 4 and 3 times higher than the mobilization of these metals through natural intemperism. Only naturally abundant metals such as Mn, and Fe and Al (not shown in table 2.1), present a greater mobilization through weathering.

Among the many industrial sources of trace metals, the most important are pyrometallurgical processes in mining and smelting (Nriagu, 1989;1990). Burning of fossil fuels, incineration of wastes and release of non-treated domestic and urban sewage are also important sources of trace metals to the environment. Historically, most sources of trace metals were associated with large urban centers which, throughout the world are preferably located along the seashore, and this is particularly true for tropical regions. Recently, many countries in the tropics have witnessed rapid industrialization and urbanization, generally lacking proper environmental care. Most of this developmental process takes place along protected coasts where water and harbor facilities and cheap land, are more favorable for this development. Also, internal migration has driven more than half of these countries' populations to the coast (World Resources Institute, 1992). In Brazil, the largest population in tropical

Americas, over 75% of the country's population lives on the coast, roughly 110 million people. In India, domestic wastes reaching the east coast of the country, amount to 18 million cubic meters per day, whereas industrial wastewater amounts to 700 million cubic meters per day and is much larger than the natural freshwater flux in many regions (Ramachandran, 1996). Therefore, contamination of coastal environments with trace metals is becoming a permanent threat in most of the tropical world.

Among the trace metals reaching the coastal zone, many are of environmental concern. Some like Cu, are highly phytotoxic affecting the phytoplankton and consequently primary production (Fowler, 1982; Bryan, 1984). Others, like Pb and Cd present a generalized toxicity to marine biota, leading to changes in natural communities structure by causing local extinction of more sensitive species (Bowen, 1979). Some like As and Hg may form metal-organic complexes and accumulate progressively through the food chain to very high concentrations, eventually reaching humans and causing serious health problems including death (Mitra, 1986). Whichever the metal involved, all present high concentration factors in the marine biota, are virtually non-degradable, thus producing long lasting effects on the environment and that may cause environmental health problems even after the major sources are stopped or controlled.

2.2 Trace metals dynamics in coastal environments

Coastal environments such as estuaries, bays and lagoons are transitional littoral zones between the sea and the mainland, having developed during changes in sea level during the Holocene. Coastal zones cover only 8% of the ocean surface and less than 5% of the ocean volume but are responsible for 18 to 33% of the total ocean production (Gomes, 1996). They also play an important role in the ecology of the seas, by supporting many indigenous biocoenosis, and providing spawning and nursery grounds for migratory species. These environmental characteristics have turned most coastal environments into ideal sites for fisheries, aquaculture and tourism, eventually followed by accelerated urbanization and inevitable conflicts among their many uses, to a point where anthropogenic fluxes of materials are higher than the natural flux in many coastal areas.

Many coastal areas act as intermediate steps in the transport of water and substances from land to sea. Once these reach the coastal areas, fluvial conditions change drastically both in physical and chemical characteristics. Decreasing river topography gradients towards the sea results in decreasing water velocity and transport capability, which in turn affects the deposition of particles by gravity. As a result of these changes, most of the suspended particulate load, including trace metals and other long-lasting pollutants, are trapped and deposited, and only a minor fraction of the continental load is exported to the open ocean (Salomons *et al.*, 1988; Kremling, 1988). It is estimated that from 75% to 90% of the total flux of continental materials to the oceans is trapped in coastal environments (Berner, 1982; Gomes, 1996). Therefore coastal areas are, in general, deposition environments and function as filters by retaining materials supplied by rivers, the atmosphere and the oceans for relatively long periods of time (Kjerfve & Magill, 1989; Berner, 1984).

Most coastal areas have recently been affected by human activities other than traditional fisheries and tourism, they receive an increasing load of contaminants from diverse urban, industrial and agricultural sources, which can accumulate to dangerous levels in these typically deposition environments. However, far from being static sinks of these substances, the complex coastal biogeochemical processes affect the physical-chemical and environmental properties of most contaminants, altering their bioavailability and in consequence, their associated environmental risks (Krumbein, 1982; Postma, 1982; Salomons *et al.*, 1988; Kremling, 1988; Lacerda, 1994; Förstner, 1995).

2.2.1 Sources of trace metals to coastal environments

Trace metals reach coastal environments through atmospheric deposition, fluvial inputs and direct discharges of solid and liquid wastes and from *in situ* activities producing metal containing effluents, such as shipping and other harbor activities. Erosion of inland watersheds due to deforestation may also represent a significant source of trace metals, in particular in tropical areas (Lacerda *et al.*, 1985a; Carvalho, 1992). Fluvial inputs are generally the most important route of trace metals entering the coastal environment. They characteristically have a high input to area ratio

Table 2.1. Global mobilization of selected trace metals, in thousands of tons per year, due to industrial processes and natural weathering and respective anthropogenic mobilization factors (AMF), based on Bowen (1979); Salomons & Förstner (1984) and Nriagu (1990).

Metal	Hg	Cd	As	Cr	Cu	Pb	Mn	Zn
Industrial mobilization	11	24	105	1,010	1,048	565	1,894	1,427
Natural weathering	1	5	90	810	375	180	4,800	540
AMF's	11	4.8	1.2	1.2	2.8	3.1	0.4	2.6

and, therefore, generally have high environmental impacts (Norton *et al.*, 1981; Irion & Muller, 1988). Fluvial inputs of trace metals are mainly associated with suspended particles (Bourg, 1988).

The major sources of trace metals to coastal environments (table 2.2) are; fuel combustion, mostly of Pb, Hg and As; non-ferrous metal smelters and iron and steel plants, for Cd, Ni, Pb, Zn, and Cu and the dumping of sewage sludge, for Cr, Cu, Ni and Zn (Nriagu & Pacyna, 1988; Nriagu, 1989; 1990, Brown, 1988). Major access pathways of heavy metals to the coastal zone are fluvial and atmospheric inputs which can be very high, for both highly industrialized and developing countries. For example, in Sepetiba Bay, a mangrove dominated area South of Rio de Janeiro city, Brazil, annual inputs of trace metals reach 389, 768 and 55 tons of Zn, Mn and Cu respectively and of 534 kg of Hg. Fluvial inputs alone account for over 90% of these yearly inputs, whereas atmospheric inputs account for 27.8 tons per year of Zn (7.4%) and only 0.2% and 0.7% of Cu and Mn (Pedlovski *et al.*, 1990, 1991a,b). But reaches over 35% of the total Hg input (Marins *et al.*, 1997b).

Atmospheric inputs however, can be the major source of certain elements, as those typically enriched in fly ash from thermal plants such as Bo, Ge, V. In Lake Macquarie, New South Wales, fly ash from local power plants is an important source of Bo, Ge, V, Zn and Cu to superficial sediments, and can reach at localized sites up to 40% of the total input of such elements (Crawford *et al.*, 1976). Similar results have been reported in mangrove areas of Todos os Santos Bay, NE Brazil by Paredes *et al.* (1995). In the Coroa Grande mangroves, in SE Brazil, Pachineclam & Bezerra (1987) showed that dust generated by rail traffic transporting ores to local harbors was the major source of Cd, Zn and Pb to surface sediments. Atmospheric inputs can otherwise affect areas far from

direct pollutant sources (Botello & Menelewicz 1988) and account for the majority of metal fluxes. At Lover's Lake, Bermuda, for example they can be significantly high and range from 3 to 14, to $43\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{year}^{-1}$, for Cd, Cu, Pb and Zn; and Cr respectively (Lyons *et al.*, 1983).

Sewage, depending on treatment, may be greatly enriched in trace metals, in particular Pb, Zn, Cr and Cu. Emission rates for these metals can vary from $\text{ng}\cdot\text{l}^{-1}$ in treated sludge to $\mu\text{g}\cdot\text{l}^{-1}$ in untreated sludge (Nriagu & Pacyna, 1988; Salomons & Förstner, 1984). Along tropical coasts, urban, untreated sewage is frequently the principal source of trace metals to coastal areas (Garcia, 1989). As sewage is normally associated with high biological oxygen demand (BOD), reducing conditions are favored and may affect trace solubility in the water column, resulting in a synergistic interaction between the two types of contamination and therefore augmenting trace metal toxicity in the entire ecosystem (Souza *et al.*, 1986). Direct effluents released into coastal areas may also be important, and are mostly due to metals associated with shipping and harbor activities and urban wastes from pipelines, but since these activities are considered typical point sources of trace metals, they will not be discussed further.

These observations suggest that most coastal areas worldwide are far from pristine conditions in relation to trace metal contamination. Even where direct metal inputs are very low, they may present higher concentrations of trace metals than pristine marine or fluvial environments, since diffuse pathways such as atmospheric deposition and continental runoff can be major sources of trace metals to coastal areas.

2.2.2 Fate of trace metals in coastal environments

Figure 2.1 presents an oversimplified scheme of the transport of trace metals through the coastal zone,

Table 2.2. Major anthropogenic sources and transport pathways of heavy metals to coastal environments. Most important major sources and pathways appears first in each line, as well as most toxic metals.

Metal	Major sources	Input pathways	Toxicity
Hg, As	Fuel combustion, Chlor-alkali plants (Hg), fungicides, metal smelters, gold mining	Atmosphere, rivers, direct discharges	High to humans and to high trophic level aquatic species
Cd	Electro-electronic industry, pyrometallurgy, fertilizer and plastic production	Rivers, atmosphere, direct discharges	High to fish and man, low to other aquatic biota
Pb	Fossil fuel combustion, pyrometallurgy	Atmosphere, rivers, direct discharges	High to most aquatic biota and to man
Cu	Pyrometallurgy, anti-fouling paints, sewage sludge	Rivers, atmosphere, direct discharges	High to phytoplankton and benthic algae, low to other aquatic biota
Zn, Cr, Ni	Pyrometallurgy, sewage sludge, mining, electronics	Rivers, atmosphere, direct effluents	Low to all aquatic biota and to man

which will be discussed further on. Apart from specific situations, trace metals reach coastal areas mostly by fluvial inputs (Figure 2.1). Suspended particles are by far the most important metal carriers from rivers to coastal areas (Barcellos *et al.*, 1988; Barcellos & Lacerda, 1994). When entering brackish waters, deposition of fine particles, due to decrease in current velocity, flocculation of negatively charged clay particles, and general decrease of metal species solubility occurs, leading to a gradual accumulation of trace metals in sediments (Salomons & Förstner 1984).

The accumulation process varies in magnitude depending on the specific adsorption constant between metal and particle and the solubility constant of the new metal complexes formed with the species present in the coastal waters. For instance the high specificity of Cu for carboxyl and polyphenolic functional groups (Whitfield & Turner, 1986) and the high stability constant of Cd chloro-complexes (Comans & van Dijk, 1988), will favor the permanence of these metals in solution in respect to metals like Fe and Cr with high affinities for inorganic particles with fast settling velocities (Santschi, 1988). Therefore, different accumulation rates of metals will depend not only on the loads input, but also on the specific chemical characteristics of each metal (Salomons, 1983; Souza *et al.*, 1986).

Deposited metals will be strongly affected by sediment characteristics. One of the most important parameters is grain size (Lucas *et al.*, 1986; Horowitz & Elrick, 1987). Fine sediments with high surface area scavenge much higher amounts of metals than sands.

Therefore metal accumulation in coastal bottom sediments will also be a function of fine sediment distribution and movement (Osuma *et al.*, 1986). In general the accumulation of trace metals in protected coastal areas also corresponds to an increase in fine, pelitic particles, organic matter and cation exchange capacity of their bottom sediments in relation to fluvial and marine ones (Krumbein, 1982; Lacerda & Abrão 1984). This implies that coastal ecosystems such as mangroves, which typically accumulate fine sediments, will also accumulate relatively higher amounts of trace metals compared to other coastal environments.

Although there are very few trace metal balance studies in coastal areas, they all indicate that coastal areas accumulate trace metals. The retention rates however, vary. In the Gironde estuary, France, retention rates of Zn, Cu, Pb and Ni were reported to be 17%, 3%, 13% and 17% respectively of the total input (Jouaneau, 1982); in the Scheldt estuary, Holland retention rates were reported much higher, reaching 59% for Ni, 77% to 90% for Zn (Kerdijk & Salomons, 1982; Wollast & Peters, 1978). In Narraganset Bay, USA, retention rates were more variable, from only 15% to 30% for Cd, to 70% to 90% for Cu and from 80% to 100% for Pb (Nixon *et al.*, 1987). Lacerda *et al.*, (1987) have also found high (>75%) retention rates of heavy metals in Sepetiba Bay, Brazil.

2.2.3 Trace metal remobilization from bottom sediments

Although accumulation of trace metals in bottom sediments of the coastal zone seems to be the general

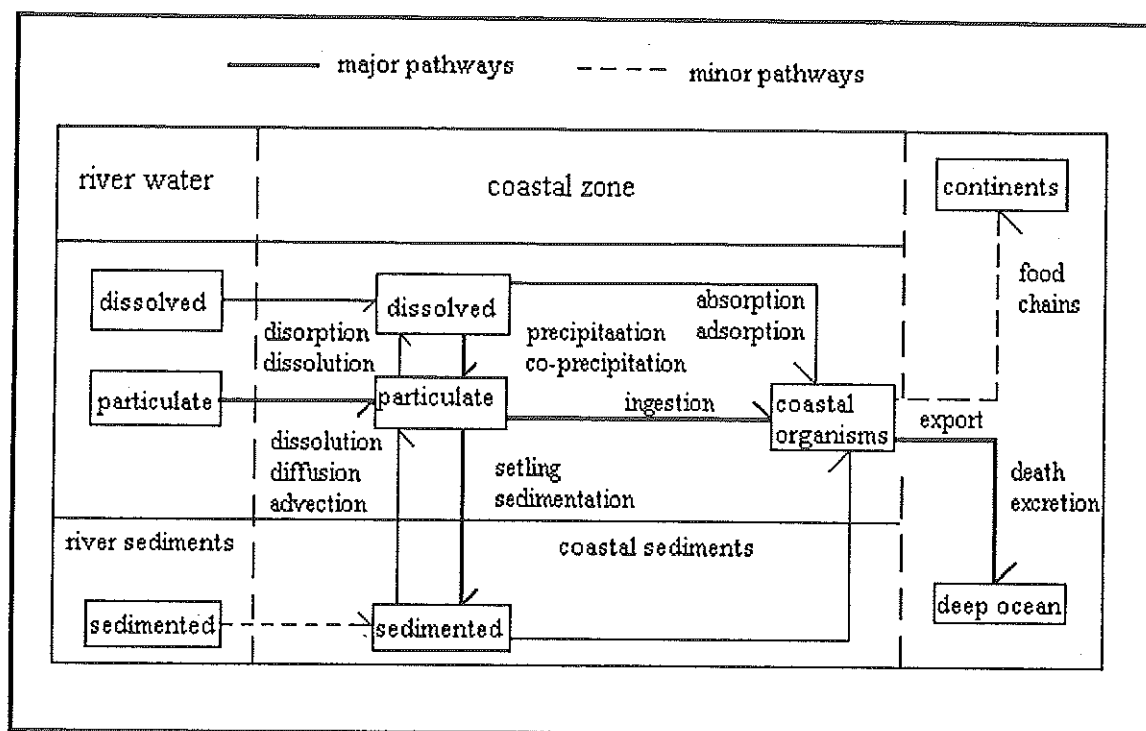


Figure 2.1. Simplified scheme of the transport of trace metals through the coastal zone, showing major and minor pathways.

rule, this system is far from being a general sink of these substances. Coastal bottom sediments are moved and reworked much more frequently than deep sea sediments. Forces such as winds, tides, biota, fluvial inputs and some anthropogenic activities such as dredging, induce patching of the sediments, where residence time of pore waters and their associated trace metals may be very short and variable, resulting in high metal remobilization to the water column (Postma, 1982; Camacho-Ibar & Alvarez Borrego, 1988; Hall *et al.*, 1987a, b). Also, the biogeochemical processes occurring at the water-sediment interface will keep trace metals constantly cycling among the many coastal compartments, resulting in comparatively higher concentrations of trace metals in coastal waters as compared to adjacent sea or river waters. Figure 2.2 shows a schematic representation of the major physical-chemical processes involving trace metal post-deposition mobilization in coastal sediments. The enrichment of pore water metal concentrations occurs due to solubilization of substances and metal complexes subject to redox processes, in particular oxidized compounds of Fe and Mn, and most probably of As; to desorption processes as consequence of the lower pH typical of pore waters; and to

the partial mineralization of organic matter and subsequent solubilization of metal complexes with dissolved organic species, which readily react with free aminoacids and aminosugars and polyphenols of low to medium molecular weight (Salomons & Förstner, 1984; Lacerda & Rezende, 1987; Henrichs & Farrington, 1979; Mopper *et al.*, 1980; Lindberg & Harris, 1974).

An extreme example of trace metal remobilization is found in Bikini Atoll, where nuclear tests resulted in an increase in artificial nuclides in the atoll environment. Nevissi & Schell (1975), studying the fate of Pu and Am in the Atoll lagoon, found that 16 years after the last nuclear test on the atoll, these radionuclides were neither buried totally in the lagoon sediments nor were totally discharged into the ocean. They concluded that remobilization at the water-sediment interface by currents, winds and storms, would enhance the complexation of the released ions with suspended particles. Coagulation with organic detritus and incorporation within the plankton, would cause metal containing suspended particles to increase in size, allowing settling, remineralization and therefore recycling within the atoll ecosystem.

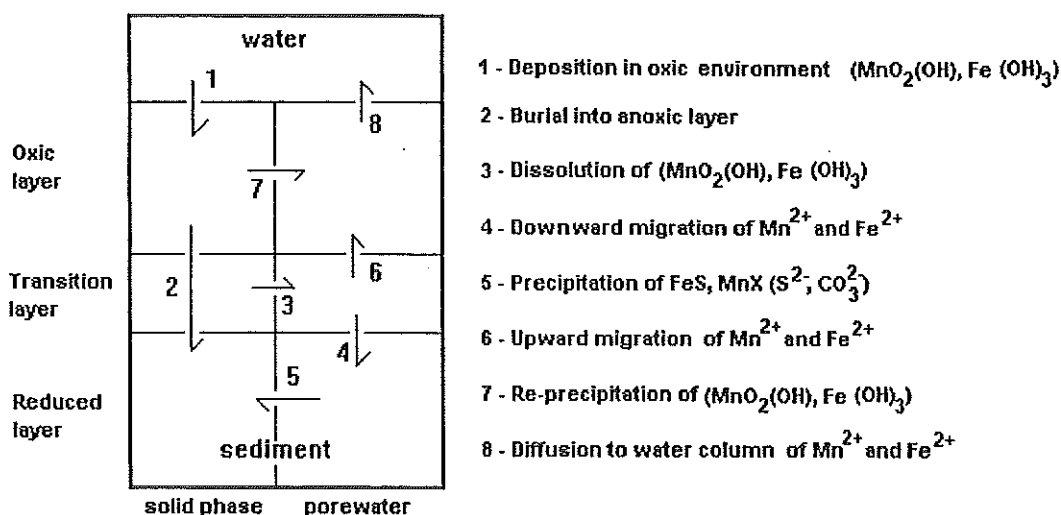


Figure 2.2. Schematic representation of post-deposition mobilization of trace metals in coastal sediments.

Biological processes at the sediment-water interface are also a major force affecting metal release from sediments to the overlying water column. Lacerda (1993) proposed that diurnal variation of Zn concentration in pore waters inside a mangrove forest of Sepetiba Bay was due to dissolution of Zn-polysulfides by oxygen produced by algal photosynthesis. Photosynthesis by algae is also reported as the main cause for the observed seasonal variation of dissolved Zn concentration in many other coastal areas (Salomons, 1983; Salomons & Förstner, 1984). In some tropical coastal areas, mangrove forests have also been reported to strongly affect water pH. In Taqueriga Lagoon, Venezuela, a reduction in water pH from 9.2 to 7.3 due to mangrove organic matter partial degradation was reported. Although no data exist for metals in the system, the observed variability in water pH could cause variability in dissolved metal species.

Seagrass and other marine macrophytes may alter physico-chemical parameters of sediments such as grain size, cation exchange capacity, organic matter content and redox potentials (Pulich, 1982). This can cause spatial variability in pore water composition on a scale from centimeters to meters (Camacho-Ibar & Alvarez-Borrego, 1988). Lacerda & Rezende (1985) found a two-fold Cu and Zn increase in bottom sediments under the seagrass *Halodule wrightii* Arschers, due to a ten-fold increase in fine particles and organic matter content in comparison with sediments outside

the seagrass beds. The same macrophyte has been reported to increase Mn dissolved concentration in selected areas of Corpus Christi Bay, Texas, by decreasing redox potential of sediments under colonization of bare areas by the macrophyte, which increases microbial activity on the deposited organic debris (Pulich, 1982).

Release of oxygen by the roots of salt marsh and mangrove plants significantly affects the post-deposition mobilization of trace metals in coastal sediments. Figure 2.3 shows the effect of roots from *Spartina alterniflora* plants in a mangrove area in Sepetiba Bay, on the Hg distribution in sediment cores. The oxygen released by the roots dissolves deposited Hg-sulfides, resulting in mobilization to pore waters and eventual export from the sediments (Marins *et al.*, 1997a).

The above examples indicate that liberation of metals from pore waters can be regarded as the major internal source of metals into the coastal zone (Salomons, 1983) keeping them in permanent cycling from sediment to pore water, then to the water column and again to the sediments with high efficiency.

2.2.4 Fate of trace metals in the water column

Some physical and chemical parameters of coastal areas have a direct relationship with the concentration and variability of dissolved metal species in the water column (Santschi, 1988) (Table 2.3). A closed

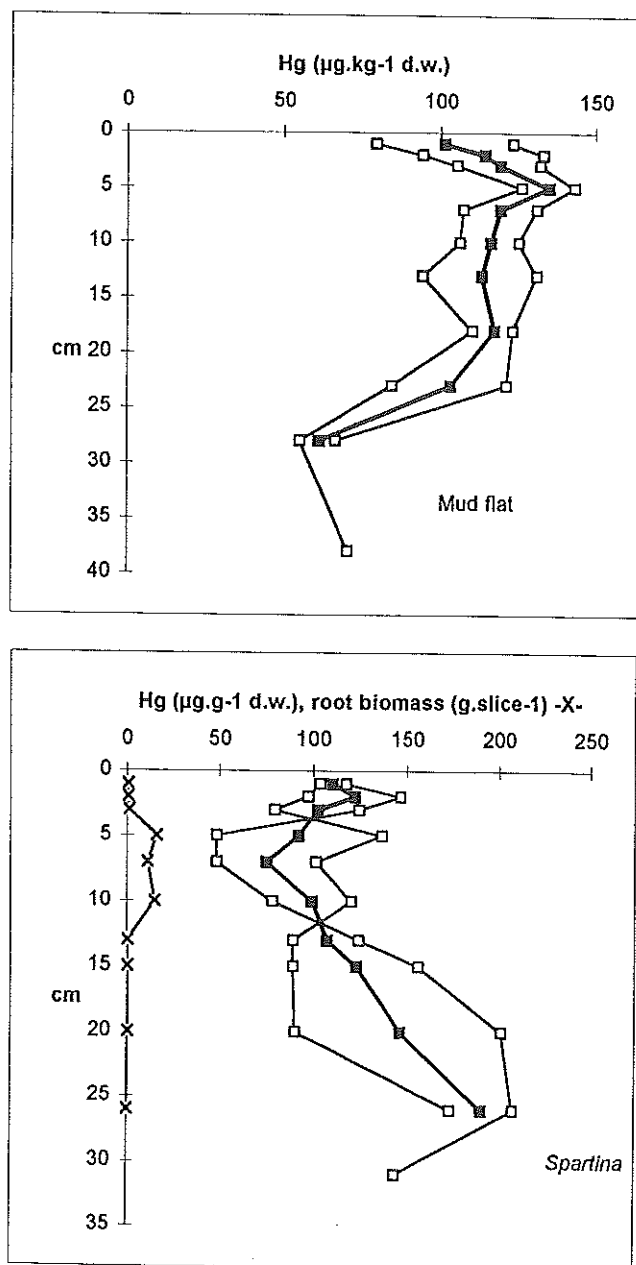


Fig. 2.3. Mercury distribution in mangrove sediment cores colonized by *Spartina alterniflora* and a control without vegetation. Modified after Marins *et al.* (1997a).

hydrography and, to a certain extent, a limited exchange with the sea, result in relatively long residence time of waters, which are frequently of the order of weeks to months (Kjerfve & Magill, 1989). The shallow depth of most coastal areas will promote intimate contact between water and sediments, which are frequently enhanced by resuspension due to winds and waves, facilitating the release of dissolved metals from

pore waters to the overlying water by diffusion transport and also avoiding the development of stratified thermal layers and thus oxygenate the entire water column. This allows for the continuous decomposition of organic matter and consequently the release of incorporated metals (Cossu *et al.*, 1987). As a result, differently from the open ocean, metal inputs will tend to concentrate rather than become diluted during longer residence time and with an almost permanent contribution from the sediments.

The permanence of most metals in solution will depend on the possibility of complex formation with organic and inorganic ligands. Again, coastal waters are characteristically enriched in such substances. First of all because autigenic organic production is high in coastal waters as compared to most waters of the continental shelf, as land derived nutrients and those regenerated in bottom sediments sustain a continuous growth of phytoplankton. Also, shallow depth facilitates the colonization by macrophytes such as seagrasses, saltmarshes and mangrove species which contribute to the supply of organic matter. The high organic production therefore will supply a large quantity of highly diverse organic ligands to the water column.

Frequently dissolved organic carbon (DOC) can reach concentration orders of magnitude higher than in the open sea. Dissolved DOC is generally refractory to further degradation and metals forming complexes with such substances may be kept in solution almost permanently (Lindberg & Harris, 1974).

Dissolved organic matter from different origins however, present different metal complex capacity. Mackey & Szymezak (1988) found that Cu complex capacity of waters in Port Hac King, Australia, was not correlated with terrestrial organic matter export, but increased by a factor of 10 due to a phytoplankton bloom that resulted from intrusion of nutrient rich waters. Jones & Thomas (1988) and Jones *et al.* (1982) showed that "red tide" algae on reaching low salinity waters, release humic substances which can chelate Fe from water to a level of 5%, and actively influence the cycle of most metals. These substances, mostly monocarboxylic acids, would facilitate any reaction with metal ions adsorbed onto particulate material by promoting a dissolution process whereby colloidal-bound metal ions are converted to labile metal ions.

Table 2.3. Major biogeochemical factors affecting trace metals in the water column of coastal environments, based on Santschi (1988).

Factor	Processes	Effects
Salinity	Chloro-complexion Desorption	Cd^{2+} to CdCl_2 Pb -particle to Pb^{2+} ; Cu -particle to $\text{Cu}(\text{OH})_2$
Plankton synthesis	Bio-incorporation of soluble forms of nutrient-like metals (Ni, As, Cu and Zn)	Generation of organic-bound metals, transport through food-chains
Dissolved organic Carbon	Complexion and coagulation	Converting dissolved forms of Hg, Pb, Cu and Fe to metal-organic complexes
Particle setting	Scavenging	Deposition of geogenic metals (Cr, Pb, Th, Co, Mn, Fe, U)
Bacterial activity	Degradation of organic matter Organification	Solubilization of incorporated metals. Formation of organo-complexes of larger biological residence times. (e.g Co in vitamin B12 and Hg in alkyl-mercurials).
Sediment resuspension	Changing redox potential	Oxidation of reduced forms, e.g. metal sulfides, or reduction of oxidized forms of Mn and Fe. Both processes may liberate metals to solution.

Complexion and coagulation may also affect other metals such as Pb, Cu and Hg and regulate their concentrations in a time scale of hours to days (Santschi, 1988).

Concentrations of dissolved metal complexes therefore, will increase in the presence of marine humic substances. As eutrophication or at least periodic algal blooms are characteristic of most coastal areas, and the sediments are a continuous source of metals to the water column, high concentrations of dissolved metal complexes are expected to be present. These metal-organic species, will in general decrease metal availability to the biota. However, most organic-metal complexes can easily release adsorbed metals when other more abundant ions, such as Ca, out-compete them for the organic binding sites (Campbell & Evans, 1987). These will cause frequent, temporary situations of concentration peaks of metals in the water column enhancing the potential toxicity to the biota.

Apart from DOC, dissolved metal species will also be highly dependent on the variability of some physical-chemical parameters, among them redox potential and salinity are of major importance. In most coastal areas, salinity and redox potential are highly variable. Redox potential can reach negative values (up to -500mV) due to consumption of dissolved

oxygen during decaying organic matter or after strong resuspension of reduced sediments, metals such as Fe, Mn and As and any other complexes with Fe and Mn oxo-hydroxides, will have their dissolved concentration increased during such occasions. Salinity also varies both spatially and temporally from values <1‰ to sea water concentration. Metals forming stable chloro complexes such as Cd and Hg will be highly soluble at intermediate salinity (Table 2.3).

Therefore, it is expected that the concentration of dissolved metal species will frequently reach high values in the water column of coastal areas. These concentration peaks may be important sources of metals to organisms, and eventually become a toxicological threat to some of them.

2.3 The impact of trace metals on tropical coastal areas

Tropical coastal areas present some environmental characteristics that may maximize the impact of trace metal pollution more intensively than in temperate coasts. Table 2.4 compares selected characteristics of tropical and temperate coasts which may affect trace metal fate and bioavailability, as well as their impact on local human populations.

Table 2.4. Selected characteristics of temperate and tropical coasts which may affect the fate and availability of trace metals.

Environmental characteristics	Temperate coasts	Tropical coasts
Hydrochemistry	Highly seasonal	Low season dependent
Terrestrial inputs of materials	Low, season dependent	Very high, event dependent
Biological oxygen demand and ecosystem metabolism	Medium to low	Very high
Primary production	Phytoplankton, salt marshes; highly seasonal	Bacterioplankton(?), mangroves, seagrasses, phytoplankton, non-seasonal
Biodiversity	Medium to low	Medium to high
Urban sewage	Medium, treated	High, untreated
Industrial effluents	High, monitored	Medium to high, non-monitored

The first major difference between tropical and temperate coasts is the much larger fresh water and sediment discharge from the continents to the sea. Rivers of tropical Southeast Asia alone are responsible for about 70% of the total terrigenous sediment discharge to the oceans. Whereas South American rivers alone contribute nearly 60% of the global freshwater inputs to the oceans (Milliman & Meade, 1983; Degens & Ittekkot, 1985). Also, tropical rivers contribute with over 75% of the global terrestrial carbon flux to the oceans (Ittekkot, 1988). Sediment discharges from tropical rivers reach over $120 \times 10^6 \text{ t.yr}^{-1}$. Since rivers account for the major inputs of trace metals to the coastal zone, this enormous load of terrestrial materials brings in very large amounts of trace metals from weathering to the tropical seas. Carvalho (1992) and Carvalho *et al.* (1993) showed anomalous high trace metal content in shelf sediments off the NE and SE Brazilian coast close to river estuaries. For example, Hg from anthropogenic sources associated with suspended matter, was detected as far as 70 miles offshore and over 200 m deep sediments in the SE Atlantic under the influence of the Paraíba do Sul River, Brazil (Lacerda *et al.*, 1993b).

The large freshwater input and small seasonal variation of most hydrochemical parameters, frequently expand estuarine conditions offshore and along continental margins. Extreme examples are the northern coast of South America from the Amazon River delta to the Orinoco River delta, where the coastal marine waters are in estuarine conditions the year round, and the coast-line is colonized by a nearly continuous belt of mangroves. The Ganges-

Brahmaputra delta in the Indian Ocean shows similar characteristics.

High BOD and ecosystem metabolism of tropical coastal areas the year-round, promote permanent recycling of trace metals and nutrients, whereas in temperate coasts this is frequently restricted to short periods of the year. Primary production is dominated by evergreen mangroves, phytoplankton, algae, sea grasses and symbiotic algae in corals. Temporal fluctuations are due to climatic events rather than seasons. This variety of primary producers results in a large biodiversity in tropical coasts. The increasing complexity of food chains maximizes the effect of pollutants at the ecosystem level, since the elimination or the decrease in the metabolism of more sensitive species, may result in imbalances of the complex interactions between components of the system.

The last major difference between tropical and temperate coastal areas relates to the utilization and impacts due to human occupation. Whereas most temperate coasts border developed nations, with strong control policies regulating the emission of industrial and urban effluents, most tropical developing countries lack such policies. Accelerated urbanization of tropical coasts is a worldwide phenomenon, due mainly to the colonial status of most of the tropics, which lasted to the middle of this century and required harbor facilities for the commerce with the colonial powers. Later, socio-economic imbalance in the distribution of agricultural areas, resulted in intense internal migration to the coastal area. Finally, the more recent phenomenon of tourism, which regards tropical coasts

as the number one tourist attraction worldwide, resulting in seasonal migration of millions .

The coastal areas in the tropics are in general occupied by mangrove forests. Therefore, in many places, mangroves may already be submitted to abnormally high concentrations of contaminants. These ecosystems are probably playing a key role in the fate of contaminants in coastal systems in the tropics. Due to their high biomass and productivity rates, mangroves may accumulate trace metals in large quantities sequestering them from their cycling in coastal waters for a certain period of time. However, they can also export trace metals incorporated into organic detritus, which is the basis for many food chains in areas close to mangrove forests. Therefore, the increasing anthropogenic pressure upon these ecosystems may cause a rapid increase in the environmental toxicity of heavy metals leading to decreasing water quality and damage for the exploitation of their natural biological resources.

3. The natural history of mangroves

3.1 Origin and worldwide distribution of mangroves

3.1.1 The pollen record

The mangrove flora is believed to have evolved from the tropical flora of the Indo-Pacific region approximately 65 million years ago. Mephram (1983), proposed a broader Tethyan region as the place where angiosperms first acquired the mangrove habit, and where most contemporary mangrove genera originated. The ubiquitous genera *Rhizophora* and *Avicennia* are thought to have evolved earlier and therefore were able to spread through the Tethys Sea into what is presently the Mediterranean and thence to the east coast of the Americas and the West coast of Africa. They may have reached the Caribbean by the early Eocene (some 55-50 million years BP), when the distance from the Tethys Sea was considerably smaller. This route is believed to be confirmed by the widespread pollen of *Nypa*, an Asian mangrove palm, in late Eocene deposits (c.a. 40 million years BP) along the present Mediterranean coast, England, North America, West Africa and Northeastern Brazil (Muller, 1980; Macnae, 1968; Dolianiti, 1955).

Mangrove pollen of *Rhizophora*, *Avicennia* and *Pelliciera* (a restricted mangrove species from the Caribbean) have been reported from the Gatuncillo Formation, Panama, of the middle to late Eocene (c.a. 40Ma BP) (Graham, 1989). Around the same time extensive *Rhizophora* and *Avicennia* forests covered northern South America (Wijmstra, 1969). Later pollen records along the Americas show abundant mangrove pollen (Graham, 1989; 1992), that confirm the early Eocene as the probable date of mangrove arrival to the New World. By the time of the arrival of the first mangrove genera to the American continent, the Panama isthmus was still open, making possible the colonization of the western coast of the Americas. The closure of the Tethys Sea route and the decrease of temperature of the South African coast due the Benguela Current would have prevented the migration of more recent mangrove genera. As a result, whereas Asian mangroves evolved over 70 species of plants, New World mangroves species are restricted to 11. For details on mangrove origins and migration routes see Lacerda *et al.* (1993c).

3.1.2 Present day distribution of mangroves

Mangrove forests presently occur over 75% of the tropical and subtropical coasts between latitude 30° N and 30° S. Small, dwarf mangroves occur as north as Bermuda (32°) and as south as New Zealand (33°). the best developed and largest forests however are roughly restricted between 10° N and 10° S (Twilley *et al.*, 1992).

Recent estimates of world mangrove cover vary, and range from 15 to 30 million ha, most recent estimates however give figures close to the lower end of this range (Lacerda *et al.*, 1993c; Twilley *et al.*, 1992; Lugo *et al.*, 1990; Saenger *et al.*, 1983). A summary of the most recent published values is shown in table 3.1. Worldwide distribution of mangrove forests shows that Latin American and Caribbean mangroves represent approximately 29% of the total. African mangroves cover about the same area, whereas mangrove cover in the Indo-Pacific region, represents nearly half of the world's mangroves, with over 6.8 million hectares of area.

Table 3.1. Mangrove forests cover in the Atlantic and Pacific coasts of Latin America, including the Caribbean Islands, Africa, Asia and world total.

Continent	Mangrove area (ha)	Fraction of world mangrove area (%)	Author
Americas	4,062,335	(28.6)	Lacerda <i>et al.</i> (1993c)
Africa	3,257,700	(22.9)	Diop (1993)
Asia	6,877,600	(48.5)	Saenger <i>et al.</i> (1983)
World total	14,197,635	(100)	

3.2 Biology of mangrove ecosystems

3.2.1 Flora composition and distribution

The mangrove flora is composed of nearly one hundred taxa of true mangrove plant species, those which are either restricted or mostly abundant in this environment (Rao, 1987; Mephram & Mephram, 1985; Duke, 1992). Highest species diversity occurs in Asia with over 70 species, followed by Africa (20-30 species) and the New World mangroves which are very poor in number of tree species, including only 11 species and one variety. Old World mangroves are dominated by *Rhizophora*, *Bruguiera* and *Kandelia* (Rhizophoraceae), and the palm *Nypa fruticans*, while *Rhizophora* (Rhizophoraceae) and *Avicennia* (Avicenniaceae) are the dominant trees in New world mangroves (Hong & San, 1993; Lacerda *et al.*, 1993c). Other widespread genera are *Laguncularia* and *Conocarpus* (Combretaceae).

Along the very humid coasts some tropical forest species "invade" mangroves, mainly vines and lianas. In the New World epiphyte bromeliads and orchids are also common. Along large river estuaries such as along the Amazon and Congo rivers, where mangroves are seldom exposed to high or even moderate salinity, typical freshwater macrophytes and palms occur among true mangrove species (Lacerda *et al.*, 1993c).

Salt marsh and seagrass species also occur in mangroves, though they are in general restricted to pioneer formations at the seaward fringe of the mangrove forest, to natural gaps under the canopy and occasionally along tidal creeks and channels. Common species are *Spartina alterniflora* Loisel and the seagrasses, *Halodule wrightii* Aschers, *Thalassia testudinum* König, and *Ruppia maritima* L. (Phillips, 1992; D'Croz, 1993). Salt marshes and sea grasses may play an important role in the hydrochemistry and

environmental conditions of mangroves (Costa & Davy, 1992; Lacerda & Abrão, 1984), they promote sediment fixation and trapping of chemical elements, including trace metals, in the mangrove environment.

Macroalgae are mostly found on the roots of mangrove trees (over 50% of the species). Other hard substrates like rocks, stones and large shell fragments, account for nearly 30% of the species, while soft mud and sandy substrates account for the other 20% of the species (Cordeiro-Marino *et al.*, 1992). The macroalgal community of trunks and aerial roots, is dominated by the Bostrichietum association, which includes species of *Bostrichia*, *Caloglossa* and *Catenella*. Another typical association is in the sediment, the Rhizoclonietum association, formed by over 10 species of green algae of the genera *Rhizoclonium*, *Enteromorpha* and *Cladophora*. The metabolism of these algae may affect the chemistry of mangrove porewaters and sediments. Algal photosynthesis results in the release of oxygen into the sediment, changing pH and redox potential thus influencing the dynamics of dissolved trace metals.

Marine fungi of mangroves belong to all groups of higher fungi of warm waters. They infest submersed roots, stems and twigs, as well as sessile animals and algae. Over 30 species of marine fungi occur in mangroves. However, only a few seem to be host-specific (Kohlmeyer & Kohlmeyer, 1979). The distribution and species composition of the mycoflora is determined by the duration of submergence of the parts of the tree infested by the fungus and of its physiology. Submersed parts have a different mycoflora from the non-submersed parts. However, at high tide level, marine and terrestrial fungi overlap. Marine fungi play a key role in litter decomposition processes and nutrient and trace metal cycling in mangrove ecosystems.

3.2.2 Mangrove fauna composition

The mangrove fauna is large and diversified, whether transient or permanent. However, few animal species are exclusive inhabitants of mangroves, hence the difficulty of characterizing a "true" mangrove fauna (Bacon, 1970). Over 300 species of birds and 500 species of fish and hundreds of species of terrestrial and marine invertebrates, create high faunal diversity environments along otherwise low biodiversity mud flats. Due to the accelerated destruction of inland forests in many tropical countries, mangrove areas have become important sanctuaries and migratory routes of various species, which otherwise would be threatened by extinction. For example the manatee *Trichechus manatus*, the scarlet ibis *Eudocimus ruber* and the American crocodile *Crocodylus acutus*, once widespread throughout the Caribbean are presently restricted to the remnant mangrove areas in the Caribbean and Northern South America. The Bengal Tiger finds its last refuge in the immense mangroves of the Sunderbans. Therefore, additional impacts on mangroves, such as industrial pollution, may have a significant impact on the global biodiversity.

Crustaceans are among the most noteworthy taxa related to the mangrove swamps. The most common crabs are members of the Grapsidae, Sesamididae and Portunidae, with many species of high economic importance. Some of these decapods feed on detritus material from the mangrove's litterfall, as reported for *Uca*, *Sesarma*, *Cardisoma* and *Ucides*. Other species are filter feeders (*Petrolisthes*), predators and scavengers (*Callinectes*) and some include living mangrove leaves in their diet. Several species of penaeid shrimps are related to mangroves using the mangrove swamps as nursery area (D'Croz & Kwiecinski, 1980). These shrimps enter the mangrove swamps as small post-larvae seeking protection and food in this brackish water habitat and move offshore as juveniles. These penaeids are the major component of the coastal shrimp fisheries in most tropical regions. Also of high economic importance are many mollusc species, including oysters, clams and mussels.

Over 500 fish species have been reported to occur in mangrove areas. Most of these fishes are found as juveniles in the mangrove channels. In coral reefs areas such as the Australian Barrier Reef and the Caribbean, a great diversity of typical coral reef fishes are frequently found in mangroves (Alvarez-León, 1993).

Over 260 species of fish have been reported for the mangroves of Vietnam alone (Hong & San, 1993).

In addition to the aquatic fauna, some birds, reptiles and mammals are inhabitants of mangrove forests. Birds such as the pelicans *Pelecanus erythrorhynchus* and *P. occidentalis*, the spoonbill *Ajaia ajaia*, the kingfisher *Chloroceryle americana*, and the egret *Bubulcus idis*. Among the reptiles are: the *Iguana iguana*, the alligator (*Alligator* spp), the caiman (*Corocodylus fuscus*) and the crocodile (*Crocodylus acutus*). Mammals, as the opossum *Didelphis marsupialis*, the crab-eating raccoon *Procyon lotor*, the otter *Lutra annectens*, and the weasel *Mustela frenata* (Aveline, 1980; Alvarez-León, 1993).

All the fauna depends on the quality of the mangrove resources. Some important shellfish are natural accumulators of environmental pollutants and can efficiently convey pollutants to food chains (Lacerda *et al.* 1983). Therefore, contamination of these ecosystems can represent a significant drawback of major economic activities along tropical coasts and their biodiversity.

3.3 Structure and productivity of mangrove forests

3.3.1 Physiognomy of mangrove forests

Mangrove forests are best developed under tropical climates, where the coldest winter temperature is above 20°C and temperatures are fairly constant throughout the year (< 5°C of variation). Highly developed forests are also associated with low energy, protected shorelines, with abundant freshwater supply, allowing the deposition and accumulation of fine organic mud, and keeping the salinity range between 5 and 30‰. Large tidal amplitude will allow the migration of mangrove forests farther inland, forming large forest belts which can extend over 60 km landward from the sea (Walsh, 1974; Lugo & Snedaker, 1974).

In the tropics the conditions described above are more common along equatorial coasts influenced by intense convective activity in the intertropical convergence zone, which generates annual rainfall higher than 2,000 mm. At these latitudes, coasts are subjected to mesotidal or macrotidal regimes (up to 8m of tidal amplitude), which generate extensive tidal plains. These conditions are to be found roughly restricted to

within 10o of the Equator. Along this belt the largest mangrove forests are located. In the Americas these optimal conditions occur South of the Amazon River Estuary to São Luís, in North Brazil where nearly continuous 700,000 ha of mangroves are located. In Asia, the Sunderbans with nearly 800,000 ha mangroves along the Ganges Brahmaputra delta are probably the largest continuous mangrove forest in the world.

Under optimal environmental conditions, mangrove forests attain their maximum growth. Red mangrove (*Rhizophora*) forests 40 to 50m in height and more than 1.0m in diameter have been reported in Ecuador and Colombia (West, 1977). At the Southern coast of Costa Rica and several areas of the Panamanian coast, where seasonality is less pronounced and annual rainfall ranges from 2,100 to 6,400mm, mangrove trees exceed 35 m in height and a biomass of 280 tons.ha⁻¹. Well developed black mangrove forests, with trees up to 30 m in height and 0.7 m in diameter, occur on the coasts of Suriname, French Guyana and Northern Brazil, frequently with biomass of about 200ton.ha⁻¹ (Lacerda *et al.*, 1993c).

Structure of mangrove forests has been classified by Lugo & Snedaker (1975) who recognized six different mangrove forest types: Fringe, Riverine, Basin, Overwash, Dwarf and Hammock forests. The last three types are supposed to be specific cases of the first three types. This classification is based on the functioning of the ecosystems rather than on physiographic characteristics. Therefore it is of great importance in the study of the fate of contaminants in mangrove ecosystems. Briefly the major characteristics of these forest types are:

Basin forests occur inland in drainage depressions channeling terrestrial runoff toward the coast. Water flow is slow, laminar and floods extensive areas of low topography. These forests are particularly sensitive to inundation and export of mangrove litterfall to coastal areas is minimal, most exported Carbon is in the dissolved form (Twilley, 1985).

Fringe forests occur along the borders of protected shorelines and islands and are periodically flooded by tides. Due to their greater exposure to waves and tides and their greatly developed root system, they are particularly sensitive to erosion and marine

contamination. Nutrient cycling and litterfall dynamics are dependent on episodic climatic events rather than on the ecophysiology of the forest itself. Variable and important amounts of nutrients and Carbon from marine origin participate in nutrient cycling processes of these forests (Lacerda *et al.*, 1988a; Ovalle *et al.*, 1990; Silva *et al.*, 1991; Rezende *et al.*, 1990).

Riverine forests occur along rivers and creeks and are flooded daily by tides. They generally consist of tall straight-trunked trees and the low surface water-flow velocity precludes redistribution of ground litter. Fluvial nutrients and constant freshwater supply often support high productivity rates of these forests.

3.3.2 Primary production, biomass distribution and allocation

Net aboveground primary productivity of mangroves is the sum of wood growth and total litterfall. While litterfall has been studied by many authors, wood growth has rarely been monitored. Therefore, estimates of total net primary productivity of mangroves are very scarce. Wood growth seems to be highly influenced by the availability of freshwater and nutrients. Fringe and riverine mangrove stands in Laguna de Términos, Mexico, under humid conditions (1,680 mm of rainfall) showed very different values (Day *et al.*, 1988). Fringe forest wood growth was significantly smaller (772 g.m⁻².yr⁻¹) than riverine forest (1,206 g.m⁻².yr⁻¹). Under the more arid conditions found in Puerto Rico (810mm rainfall), Golley *et al.* (1962), estimated a smaller wood growth rate of 307g.m⁻².yr⁻¹.

Based on these values and on litterfall rates, net primary productivity for these forests was estimated to be 2,457, 1,606 and 781 g.m⁻².yr⁻¹, for the Mexican riverine, fringe and Puerto Rican forests respectively. Other estimates for mangrove primary productivity were provided through gas exchange experiments in various mature south Florida mangroves (Twilley *et al.*, 1992; Carter *et al.*, 1973). These studies found much higher values ranging from 2,044 to 5,475g.m⁻².yr⁻¹ probably due to the method used.

Leaf litter is the major component of total litterfall of mangrove forests, regardless of forest type, latitude or climate. In general it sums up to over 70% of the total litterfall. From the available data no clear relationship is found between rainfall and litterfall.

However, the data suggest that the lower the latitude the higher the annual litterfall. Notwithstanding this, local site specific differences seem to be very important in determining litterfall rates, sites very close to each other may show different litterfall values.

Total litterfall typically average $1.0 \text{ kg.m}^{-2}.\text{yr}^{-1}$, but can be as low as $0.1 \text{ kg.m}^{-2}.\text{yr}^{-1}$ in arid mangroves of Florida (Lugo & Snedaker 1975) and as high as $5.6 \text{ kg.m}^{-2}.\text{yr}^{-1}$, in the highly productive forests of Vietnam (Hong & San, 1993). Highest aboveground biomass is found roughly between 10° North and 10° South. For example the mangroves of Darien, Panama ($8^\circ 00' \text{N}$) under annual rainfall of 2,200 mm show 279 and 190 t.ha^{-1} of above and below ground biomass respectively (Golley *et al.*, 1978). However, average values are of the order of 100 t.ha^{-1} of aboveground biomass and approximately 30% of it as belowground biomass.

3.4 The physical environment

3.4.1 Hydrology

Mangroves are subject to regular or occasional inundation by water of riverine, estuarine, or oceanic origin. Waters inundating mangroves regularly can have salinity up to 37‰ without adversely impacting the function of mangroves, as long as the trees are protected from wave action and strong currents. The area flooded during each tidal cycle increases with increasing tidal range along deposition, low-lying tropical coasts. Along the seaward margin of mangroves, strong tidal currents can prevent mangroves from settling and can export seedlings to other areas. Along the landward margin, stunted and dying mangrove trees are often occur adjacent to an extensive zone of non-vegetated bare sand, where high evapo-transpiration has lead to hyper-saline interstitial conditions which do not support even mangrove trees (Galloway, 1982; Blasco, 1984).

Hydrology of mangroves is highly dependent on mangrove forest type. The hydroperiod in most mangroves lasts only hours and occurs daily as a result of high tide wash, which is the only water input to this type of wetland. Riverine mangroves have an hydroperiod which may last from hours to days. The frequency of the hydroperiod however, may be daily or seasonal due to changes in river discharges. Stream flow and tides represent the major water fluxes of this

type of mangrove forest. Basin mangroves have hydroperiod of perennial duration, continuous frequency, and shallow waters. Fresh ground-water discharge, overland runoff, and superficial and underground salt-water intrusion are the water inputs to these mangroves (Zack & Roman-Mas, 1988).

In general major rates of water transport in mangrove systems occur during short periods (1-2 hours) of the tidal cycle, immediately before and after high water standstill, when the flow direction also changes. Although stream velocities can be substantial, the flow within the mangrove vegetation is slow and sluggish and seldom exceeds 5 cms^{-1} . Major hydrochemical water and soil changes can occur during these short periods (Lacerda *et al.*, 1988a; Rezende *et al.*, 1990; Kjerfve, 1990), as well as exchanges of dissolved and particulate material (Ovalle *et al.*, 1990).

3.4.2 Mangrove soils

Mangroves are salt-tolerant trees and grow most prolifically along low-lying depositional coasts and deltas, where the substrate is predominately made of clay and silt rather than sand. This suggests the importance of river-borne nutrients in fueling the productivity of mangrove wetlands, since nutrients often are adsorbed onto sediment particles. Rains and subsequent river floods carry alluvial sands and mud to tidal flats, creating a substrate for mangrove colonization. Although some mangrove specimens may grow on sand, gravel, or rocky shores, these substrates are abrasive and cause considerable damage to mangrove seedlings. Thus, mangroves ideally colonize fine-grained alluvial mud and sand flats deposited by river runoff, particularly in deltas, and along protected shorelines of bays, estuaries, and lagoons (Thom, 1984). During flash floods, large quantities of alluvium can be deposited rapidly and may cause initial destruction to mangroves before rebuilding commences.

The ratio of rainfall to evapo-transpiration exerts a critical control on mangrove production. Differences in rainfall leads to leaching, which can cause substantial nutrient export from mangroves as a function of plant type, season, and rainfall periodicity (Twilley *et al.*, 1992). In climates that remain humid throughout the year, soils are continuously leached of salts by heavy but evenly distributed rainfall, which yields constantly low and stable salinity levels. In arid

climates with marked seasonal rainfall distribution, in contrast, the drought periods lead to high evapotranspiration rates, and consequently high soil salinity. During the rainy season, this situation reverses, and the soil salinity drops. As a consequence, mangrove species diversity in arid regions is substantially lower than in humid regions.

Mangrove soils are generally of fine granulometry, rich in organic matter and periodically waterlogged. Dominant soils in continental mangroves are mostly entisols, sometimes followed by istosols. Riverine mangroves generally grow on immature clay soils (clay hydraqcents). On tidal flats mangrove grow on mineral (sulfaquents) and organic (sulfahemists) soils. Seaward fringe mangroves grow on acid sulfate soils whereas in many coral reefs areas such as in most Caribbean islands mangroves grow on bioclastic, coralline sands (Alvarez-León, 1993), however, on such soils mangroves are very poorly developed.

A detailed study of mangrove soils was performed on the Guyanas coast (Brinkman & Pons, 1968; Augustinus, 1978), where extensive mangroves have grown on the young coastal plains. Marine clays of the Comowine phase (later than 1,000 BP) are found in a band along most of the Guyanas with their surface at about high tide level. The sediments are saline with brown or reddish-brown mottles when leached at the surface. Original pyrite content is low to medium, but thin layers of pyrite clay occur in places. On these clays pioneer *Avicennia* forests develop along lines which alternate with ridges of coarses of shelly sand. Soils of river and estuary levees in areas dominated by *Rhizophora* show less variation in soil depth and degree of soil formation than marine clays. Rapid accretion of mud and sand characterizes the coast of the Guyanas, the dominant mud type being a reduced olive gray pelite. In Guadeloupe, mangrove soils were found similarly under reducing conditions, with Redox potential of -300 mV indicating strong anaerobiosis (Febvay & Kermarrec, 1978).

Recent studies by Thibodeau & Nickerson (1986); Nickerson & Thibodeau (1985) and Lacerda *et al.* (1993a) showed that, at least close to the rizosphere of mangrove plants, mangrove soils are highly influenced by the physiological activity of the roots which is different depending on plant species. For example, consistently lower redox potential have been reported for

Rhizophora soils when compared to *Avicennia* soils. Also the organic content and composition of mangrove soils are directly related to the above vegetation. Carbon isotopic studies showed that over 95% of the Carbon present in mangrove soils originate in mangrove litter (Lacerda *et al.*, 1986b; 1995).

3.5 Mangrove utilization

Mangroves play an important role in tropical coastal economies providing many goods and services for the human population. These include: coastline protection and stabilization, nursery for a variety of economically important molluscs, crustaceans and fish, and are source of important products to coastal human populations in the form of timber, firewood and charcoal, chemicals, medicine and waterways for transport, enrichment of marine coastal waters by nutrients, and an environment for aquaculture, although some of these benefits are presently poorly understood or unrecognized. Examples of the importance of such direct and indirect benefits provided by mangrove are significant for the rational management of the tropical coastal belt.

Protection of along-shore structures using mangroves are common in Ecuador and Colombia. In Brazil, USA and in the Ryukyus islands in Japan, mangroves have recently been included in the management plans of marinas, roads, breakwaters and coastal condominiums. In Panama, up to 60% of the total shrimp fisheries is based on 5 species which depend on mangroves for completing their life cycle. Along the Maranhão coast, North Brazil, the huge shrimp production includes two species of shrimps which develop in the local mangroves. The same occurs in most southeastern Asian countries.

Firewood and charcoal seems to be the major uses of mangroves in Central America and Africa. In countries like Nicaragua, where nearly 80% of households uses wood for cooking, mangroves provide a significant percentage of firewood. In Brazil, mangroves are a regular source of firewood for bakeries and potteries, even along the most developed areas of the South-eastern coast (Araújo & Maciel, 1979). In Tanzania, the use of mangroves to produce wood has a history of over 1,000 years, and had been an important trade between Africa and Asia (Semesi, 1993). Charcoal production is another major use of mangrove wood,

although only a fraction of the total yield is collected due to inefficient extraction techniques. Mangrove bark is still a source of tannin in many tropical countries.

Despite their importance for most coastal tropical countries, mangrove ecosystems have been witnessing an accelerated rush for their resources, mostly without the necessary care to maintain their integrity while threatening their sustainable utilization. Estimates of deforestation are, however, scarce. In Central America for example, annual cover losses reach over 10,000ha, mostly for conversion into rice fields, salt pans and aquaculture. In Ecuador nearly half of the total mangrove area (ca. 80,000 ha) has been deforested for shrimp ponds construction, during the last two decades. In the Ilha Grande Bay, southeastern Brazil, which harbored nearly 2,000 ha of mangrove forests in the early 80's, nearly 80% of it have been reclaimed to build condominiums and marinas. African, Asian and Caribbean mangroves are also threatened by deforestation.

Apart from deforestation itself, degradation of large mangrove areas is taking place in many countries due to misuse of coastal resources. Diversion of freshwater for irrigation and land reclamation purposes has been one of the major actions leading to mangrove degradation (Conde & Alarcón, 1993). The mangroves of Guanabara Bay, Rio de Janeiro, which reached nearly 80 km² at the beginning of the century, are presently nearly totally degraded with less than 15km² of pristine forests, mostly due to clearcutting of creek and river banks, oil spills, solid wastes dumping and decreased freshwater inputs. In French Guyana over 20,000 ha of mangroves have been cut for rice culture and large amounts of fungicides, pesticides and fertilizers are being used. In the insular Caribbean and the Caribbean coast of Venezuela, tourism development in coastal regions has been the major destroyer of mangrove areas (Bacon, 1993).

World wide mangroves are being clear cut or affected by many non-sustainable uses. The consequences of these impacts upon mangrove dominated coastal areas are, however, still un-assessed.

4. Trace metal dynamics in mangroves

Mangroves have been considered by Harbinson (1981) to be a sink for certain trace metals but also a source of these same metals depending on major physical-chemical parameters such as pH, Eh, dissolved oxygen, salinity and the quality and quantity of suspended matter (e.g. organic and inorganic). These variables are dependent on tidal amplitude and flooding characteristics, season and meteorological conditions.

Figure 4.1 shows the schematic view of trace metal dynamics in mangrove ecosystems. Trace metals reach the mangrove environment through many routes (e.g. dry and wet atmospheric deposition, river inputs and tides). In heavily industrialized areas or in mining districts, trace metals can be released directly into mangroves from effluent pipes or leaching of tailings (Aksornkoae & Saraya, 1987). In general, rivers are the major route of trace metals to coastal areas (Salomons & Förstner, 1984; Harbinson, 1986b). However, Lacerda *et al.* (1988a) suggested that metals carried by the rivers are first distributed in the coastal zone, and are then transported to mangroves by tides, or through overbank flooding when tides partially block the river flow.

Trace metals are transported mostly associated with suspended particles, in coastal waters (Wollast & Peters, 1978; Lacerda *et al.*, 1988a) and this is the major form under which trace metals reach mangrove areas (Harbinson, 1986a). Once inside the mangrove forest, trace metals will suffer a series of processes typical of the mangrove water and sediment conditions, which are different from those occurring in the marine and riverine environments. The dominant direction of these reactions is, in general, the deposition and accumulation of trace metals associated with suspended particles into mangrove sediments, which frequently present high sedimentation rates.

Mangrove sediments present certain characteristics which may favor metal accumulation. Sheltered, slack water conditions allow deposition of fine particles normally enriched with trace metals. High organic matter and sulfide content helps in fixing trace metals as insoluble sulfides and precipitated organic-metal complexes. Finally, high sedimentation rates contribute to a permanent burial of locally formed metal

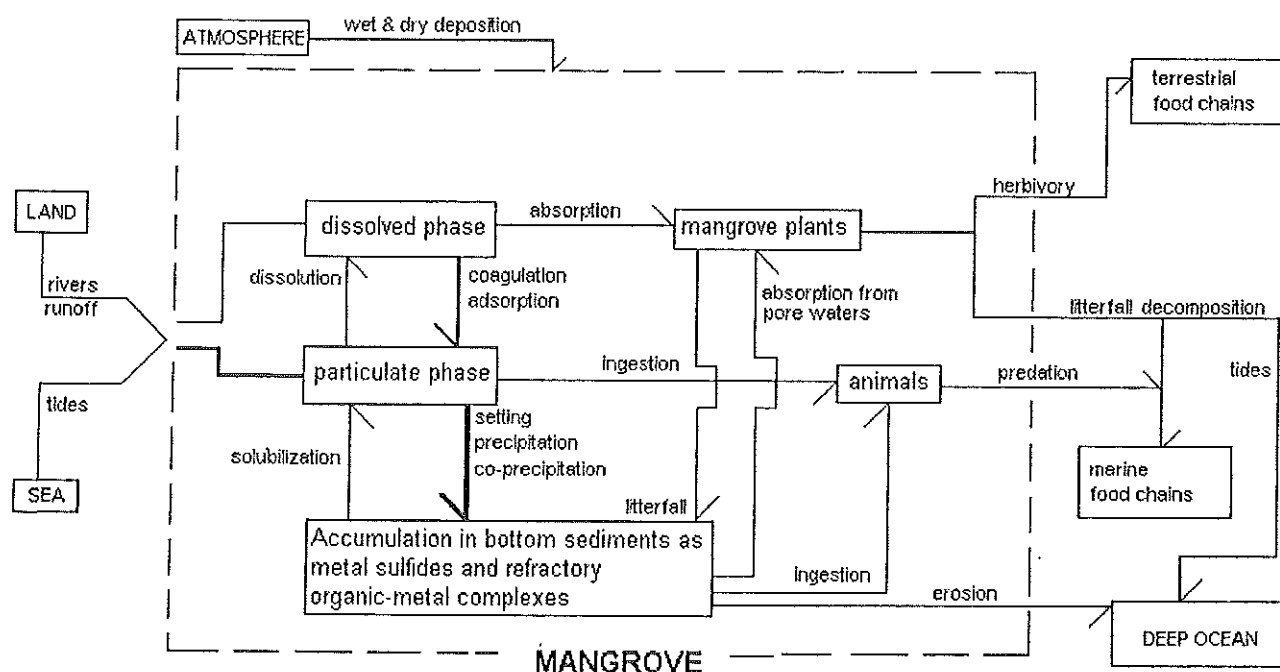


Fig. 4.1. Schematic representation of trace metal dynamics through a mangrove ecosystems, after Lacerda (1993).

sulfides and refractory metal organic complexes (Lacerda & Abrão, 1984; Harbinson, 1981; Aragon *et al.*, 1986; González-Farías *et al.*, 1997).

After reaching equilibrium under the physical-chemical conditions prevailing into mangroves, trace metals may be incorporated by the mangrove biota. Eventually they can be transferred through food chains to terrestrial and marine ecosystems and be exported to the continental shelf associated with dissolved and particulate detritus. Most studies to now however, suggest that these pathways are of minor importance compared to the deposition and accumulation of trace metals in the sediments. In this chapter, the major mechanisms of trace metal exchange between mangroves and adjacent coastal systems, as well as the mechanisms involved in trace metal accumulation in mangroves, will be discussed.

4.1 Trace metals inputs and outputs from mangroves

The balance between inputs and outputs of trace metals in estuarine areas is mostly dependent on the balance of suspended particulate matter (SPM) load and its trace metal content (Jouaneau, 1982; Salomons & Förstner, 1984; Wollast & Peters, 1978), and

this is also true in estuaries dominated by mangrove ecosystems (Rezende, 1988; Lacerda *et al.*, 1988a). Contrary to most estuaries however, mangrove dominated areas also have peculiar hydrochemistry, which may affect trace metal chemistry. The characterization of SPM during tidal cycles is essential for the understanding of trace metal balances in mangrove ecosystems. This characterization must include not only the trace metal concentration in the SPM and the causes of their variability, but the sources of SPM to and from mangrove ecosystem, since different origins (e.g. terrestrial and marine borne SPM) may result in completely different assemblages and concentrations of trace metals. Also hydrochemical changes, since they can alter trace metal composition and concentration in the SPM itself (Woodroffe, 1985a, b, c), must be characterized.

4.1.1 Water balance and tidal hydrochemistry in mangroves

Tidal amplitude and weather can affect hydrochemistry of mangrove waters and therefore the SPM load and trace metal composition (Ovalle *et al.*, 1987; 1990). Hydrology of mangrove ecosystems has been recently reviewed by Kjerfve (1990). Also, hydrology of mangroves are very site specific and a complete description is not the scope of the present work.

However, some hydrological characteristics of importance to the understanding of trace metal dynamics in mangrove ecosystems will be mentioned.

Typical hydrological cycles in mangroves show that water flow is, in general, not evenly distributed through the tidal cycle. Maximum water flux occurs during short periods (1 to 2 hours) at the inflection of tides, characterizing water flow pulses of incoming and outwelling waters. These pulses are efficient in eroding and transporting materials between the mangrove and the adjacent coastal and terrestrial systems. During low tide periods pore water drains into mangrove channels, having a large influence on the waters fluxing out of mangroves (Ovalle *et al.*, 1990; Kjerfve, 1990; Kjerfve *et al.*, 1997).

The variations of major physical-chemical parameters in mangrove creek waters during typical tidal cycles have been studied in many mangrove areas. One of the best studied variables is oxygenation of tidal waters, either through the direct measurements of dissolved oxygen or through the determination of the water redox potential. Figure 4.2 shows the typical variation of dissolved oxygen concentrations, pH and redox potential (Eh) of tidal waters in a southeastern

Brazilian mangrove creek during tidal cycles. At the peak of low tide, pH and Eh and dissolved oxygen are at a minimum. Redox potential, dissolved oxygen and pH reach their maximum values at the peak of the high tide, coincident with the increasing current velocity, and remain constant during the entire flood period (Ovalle, 1992; Lacerda *et al.*, 1988a; Harbinson, 1986b). Therefore, more oxidizing waters at high tide and less oxidizing at low tide seems to be a general rule in mangroves. This large variability in Eh, pH and dissolved oxygen, may significantly affect trace metal behavior in mangrove tidal creeks. In particular those associated with Fe and Mn oxy-hydroxides, which may be dissociated due to these changes in redox potential and pH.

4.1.2 Nature of suspended matter during tidal cycles

Suspended particulate matter (SPM) flowing in and out of mangroves are of different nature. It may include alloctonous materials derived from the adjacent terrestrial and marine environments, and may also include autoctonous materials produced in the mangrove itself. Therefore, SPM can convey trace metals from polluted marine and fluvial areas to mangroves and/or *vice versa*. It is fundamental to establish the

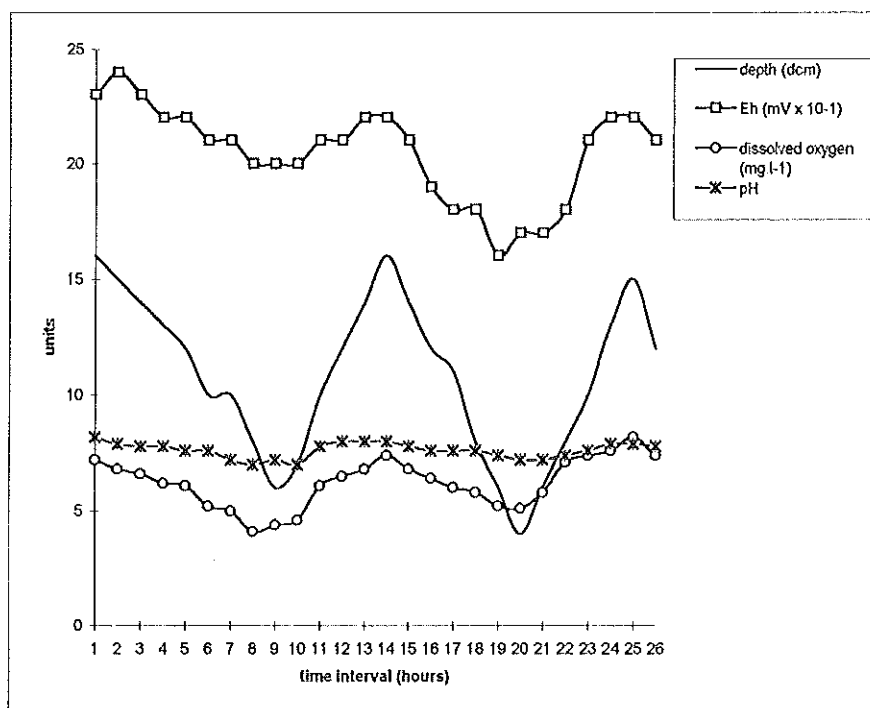


Fig. 4.2. Hydrochemistry variations (pH, Eh and dissolved oxygen) during tidal cycles in a mangrove creek in SE Brazil, after Rezende (1988).

origin of the SPM to understand trace metal sources to mangroves.

The ratio between stable isotopes of Carbon, has been successfully used as a tracer of SPM origins in mangroves. Mangroves are typical terrestrial plants in terms of the $^{13}\text{C}/^{12}\text{C}$ ratios, normally expressed as $\delta^{13}\text{C}$, in parts per thousand (‰) of this ratio in a standard carbonate of *Permitella americana* (PDB). Mangrove organic matter presents very constant and consistent $\delta^{13}\text{C}$, independent of location. For example, *Rhizophora mangle* L. collected from latitude 22°S, in Brazil, to latitude 30°N in Florida, showed $\delta^{13}\text{C}$ values ranging from -26 ‰ to -29 ‰ only (Raz-guzman *et al.*, 1993; Lacerda *et al.*, 1986b; Zieman *et al.*, 1984). Table 4.1. compares $\delta^{13}\text{C}$ from different mangrove species in South America and Africa, and values reported for mangrove sediments and suspended particles at the same sites. In general, mangrove leaf material worldwide, shows $\delta^{13}\text{C}$ ranging from -24 ‰ to -29 ‰. The same range of values is found in mangrove suspended matter and in mangrove sediments (Raz-guzman *et al.*, 1993; Lacerda *et al.*, 1986b; Zieman *et al.*, 1984). However, these values are very different from those observed in mangrove green algae and marine suspended matter, including phytoplankton. This difference allows to quantify by means of a simple two-end-member model, the relative importance of mangrove and marine sources of SPM during the tidal cycle in mangrove ecosystems (Rezende *et al.*, 1990); in association with trace metal concentrations, and to suggest possible sources and pathways of these pollutants in the mangrove ecosystem.

Table 4.1 shows that the $\delta^{13}\text{C}$ signatures of mangrove bottom sediments and SPM indicate that the

production of mangrove organic matter accumulated in sediments or as part of the SPM is almost entirely originated by the mangrove productivity itself. Studies of the organic matter composition in mangrove soils showed that sugars, amino sugars and amino acid composition found is the same as that found in mangrove plants (Lacerda *et al.*, 1995).

Figure 4.3 shows the variation of $\delta^{13}\text{C}$ during tidal cycles in a mangrove ecosystem in Sepetiba Bay, SE Brazil, based on the studies of Lacerda *et al.* (1988a) and Rezende *et al.* (1990). In general, flood periods are characterized by SPM mostly of marine origin ($\delta^{13}\text{C} < -22$ ‰), whereas during ebb periods mangrove SPM ($\delta^{13}\text{C} > -25$ ‰) dominates the flux. This result suggests that mangroves efficiently trap most of the marine borne SPM brought into the forest by tides. Since most contaminants from diffuse sources will reach mangroves through tides, it is expected that marine borne SPM will have higher trace metal content than mangrove SPM in contaminated sites, and therefore, they will also be efficiently trapped by mangroves.

4.1.3 Mass balances of suspended solids

The variations of suspended particulate matter (SPM) and particulate organic carbon (POC) during tidal cycles typically show minimum and maximum values of SPM ranging from about 10.0 to 100.0mg.l⁻¹ and for POC from less than 0.5 to 10.0mg.l⁻¹ (Rezende, 1988; Woodroffe, 1985 b,c). The highest content of SPM and POC were associated with high discharge periods either at flood or ebb tides. However, the maximum peaks of POC occurred in general during ebb tides (Rezende *et al.*, 1990), when mangrove POC is exported to coastal areas. POC export

Table 4.1. Carbon isotopic composition $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$ ‰ PDB) of diverse mangrove ecosystem compartments, in South America, SE Brazil (Lacerda *et al.*, 1986b) and Africa, Kenya (Rao *et al.*, 1993).

South America, SE Brazil	($\delta^{13}\text{C}$ ‰ PDB)	East Africa, Kenya	($\delta^{13}\text{C}$ ‰ PDB)
<i>Rhizophora mangle</i> ,	-27.6	<i>Rhizophora mucronata</i>	-26.09
<i>Laguncularia racemosa</i>	-27.41	<i>Bruguiera gymnorrhiza</i>	-28.58
<i>Avicennia schaueriana</i>	-25.15	<i>Ceriops tagal</i>	-24.28
Mangrove green algae	-18.34 to -17.28	<i>Xylocarpus granatum</i>	-25.87
Mangrove bottom sediments	-27.56 to -25.61	<i>Sonneratia alba</i>	-26.7
Mangrove suspended particles	-26.70 to -25.53	<i>Avicennia marina</i>	-26.62
Marine suspended particles	-20.75 to -20.50	<i>Lumnitzera racemosa</i>	-27.17

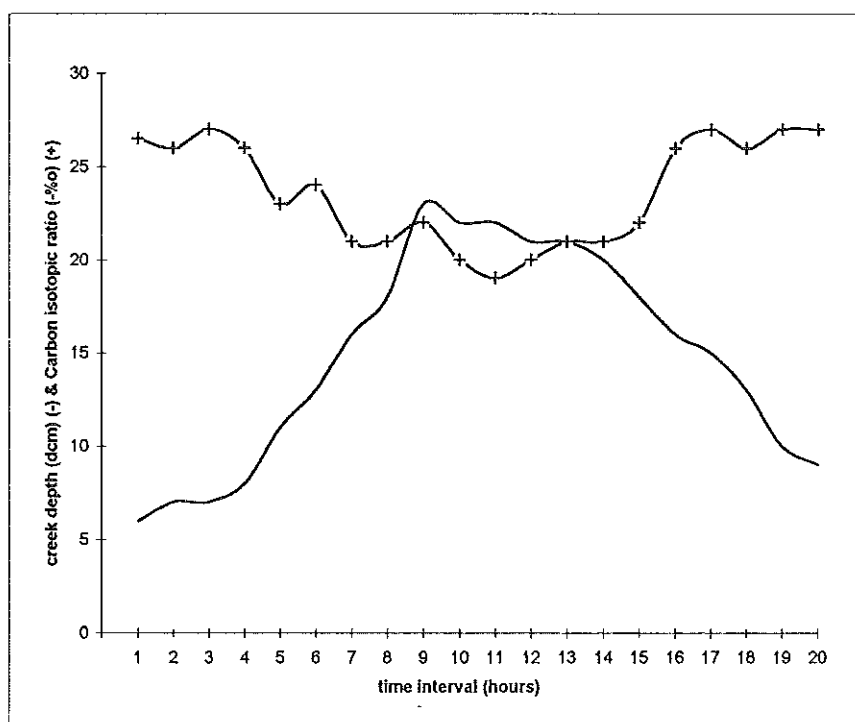


Figure 4.3. Carbon isotopic composition variations in suspended particulate matter during tidal cycles in a mangrove creek in SE Brazil, after Rezende (1988).

can range from 20% to over 70% of the total mangrove Carbon production (Heald, 1969; Snedaker, 1984; Twilley, 1985; Lacerda, 1992). The tidal variability of SPM and POC transport is in general, of the same amplitude as the seasonal variability, and sometimes even higher. For example, González-Faria *et al.* (1997), working in Baja California mangroves, Mexico, a region with strongly marked rainy season, found SPM seasonal variation from 5 mg.l⁻¹ in May to 158 mg.l⁻¹ in December, a 31-times difference. Particulate organic carbon (POC) in the same site however, ranged from 0.7 mg.l⁻¹ in early winter to 4.6 mg.l⁻¹ in early summer, a 6.5-times difference. Similar ranges have been reported to occur during one tidal cycle, in particular during spring tides in other mangrove areas (Rezende, 1988; Ovalle *et al.*, 1990), mostly associated with erosion of mangrove and creek sediments.

4.1.4 Metal concentrations and variability in suspended particles

Trace metal concentrations in SPM will be a function of the origin of the suspended particles. In general, trace metals present higher concentrations during the changes in the tidal flow, since during these periods of the tidal cycle maximum flow velocity occurs

promoting some remobilization of metal-rich fine, pelitic, bottom sediments from mud flats adjacent to the forest (flood periods) and of mangrove sediments themselves (ebb periods), that may contribute to a fraction of the suspended matter in mangrove creeks (Rezende *et al.*, 1990). The enrichment of creek water with suspended matter derived from remobilization of bottom sediments has been shown to occur in salt-marsh creeks and to change the SPM composition (Ward, 1981; Ward & Twilley, 1986).

Heavy metal concentrations may vary greatly between different tidal cycles and even between sampling intervals within a given cycle, reflecting the overall high variability of mangrove ecosystems. Notwithstanding the large fluctuations, in general during ebb tides the metal concentrations are lower when compared with the material transported during flood tide (Rezende, 1988; Lacerda *et al.*, 1988a), suggesting that most of the marine borne SPM is trapped inside the mangrove and that trace metal-poor SPM from the mangrove itself dominates the export during ebb tide, as shown by the lighter $\delta^{13}\text{C}$ values of POC during ebb tides (Figure 4.3).

In Sepetiba Bay, SE Brazil, where most earlier work on the dynamics of trace metals in mangroves was done, long term monitoring showed that SPM moving in and out through the major creek draining the forest is of different origin (Figure 4.3). During flood periods the SPM entering the mangrove forest is almost totally of marine origin while during ebb periods SPM leaving the system is of mangrove origin (Ovalle *et al.*, 1987; Lacerda *et al.*, 1988a). Figure 4.4 shows trace metals concentrations during those tidal cycles. As trace metal concentrations are higher in marine borne SPM and lower in mangrove borne SPM (Lacerda *et al.*, 1988a; Rezende, 1988; Rezende *et al.*, 1990), the shift in the origin of SPM seems to be the major source of heavy metal variability in these mangroves. The behavior of trace metals during tidal cycles shown in figure 4.4, strongly suggests that

mangroves are efficient traps in trace metal transport associated with SPM. The mechanisms involved are the fast setting of SPM at the peak of high tide, when flow velocity is nearly zero for at least a few hours (Ovalle *et al.*, 1990), and trapping of the deposited SPM by the entangled mat of mangrove roots and pneumatophores (Harbinson, 1986a). Some chemical mechanisms, such as trace metal co-precipitation, may increase trace metals transfer from dissolved to particulate forms, speeding up their deposition. Oxy-hydroxides of Fe and, in particular, Mn, may play an important role in this process.

4.1.5 The manganese cycle

Korte *et al.* (1975) showed the importance of the behavior of Fe and particularly of Mn oxy-hydroxides in releasing associated trace metals upon dissolution

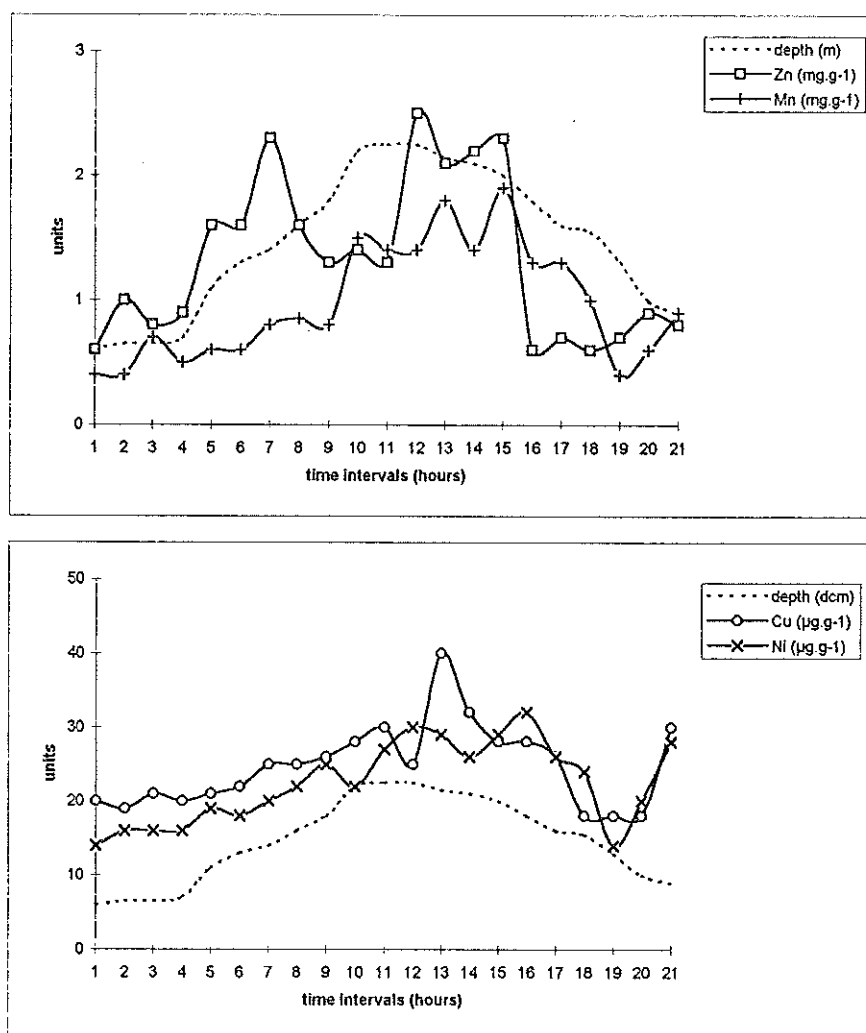


Figure 4.4. Trace metals concentrations in suspended particulate matter during tidal cycles in a mangrove creek in SE Brazil, after Rezende (1988).

due to changing physical-chemical conditions, particularly the redox potential. In mangrove ecosystems, Mn oxy-hydroxides may play an important role in trace metal fluxes into and out of mangroves. The range of redox-potential frequently found in waters during a tidal cycle is sufficient to change Mn species equilibrium (Mn (II) Mn (IV)), resulting in dissolution or precipitation of Mn oxy-hydroxides and consequently of any trace metal associated with them. The range of redox potential of tidal waters, however, is not sufficiently great to affect Fe species. Iron is a key element under sedimentary conditions (Howarth, 1979). However, the range of Eh found during tidal cycles (see figure 4.1), is sufficient to alter the equilibrium between dissolved and particulate Mn (Figure 4.5.) (Krauskopf, 1979; Vorjak *et al.*, 1985).

The relationship between redox potential (Eh), dissolved oxygen and the different species of Mn (dissolved Mn (II) and particulate Mn (IV), during tidal cycles of a mangrove creek water, in a mangrove forest in Sepetiba Bay, SE Brazil, is shown in figure 4.5. It is clear that high tide waters are more oxygenated and have higher Eh than low tide waters as had been previously shown. High tide waters are basically sea water whereas low tide is rightly influenced by the export of mangrove waters. As discussed, mangroves consume oxygen from tidal waters in the process of organic matter oxidation.

Particulate Mn (IV) is the dominant Mn species during high tide periods. However, when less oxygenated waters flow through the creek Mn (IV) dissolves and Mn (II) dominates the flow. When open bay waters dominates the tidal cycle again, Mn (II) is oxidized and precipitates on the suspended matter present in the water (Lacerda *et al.*, 1988a).

The precipitation of Mn (IV) onto particles is probably of colloidal species (Balikungeri *et al.*, 1985) and involves biological mediation, accelerated by the frequently high temperature found in mangroves. This precipitation scavenges trace metals present in solution and is responsible for a significant enrichment of trace metals in the incoming suspended particles (Lacerda *et al.* 1988a), as has been shown for many aquatic systems (Salomons & Förstner, 1984). Figure 4.6 illustrates this phenomenon for a mangrove area in SE Brazil. It is clear that all trace metals show an enrichment peak simultaneous with the

Mn maximum onto SPM, suggesting that scavenging of trace metals by Mn oxidation is occurring. However, the enrichment due to Mn precipitation is smaller than that due to changing in the origin of the SPM, as discussed earlier (Rezende, 1988; Lacerda *et al.*, 1988a; Lacerda, 1993; Ribeiro, 1994).

4.1.6 Metal mass balances

Mangrove ecosystems present an alternating behavior with net import and net export of trace metals occurring in different cycles, depending mostly on the local oceanographic conditions. For example, spring tides associated with cold fronts may result in intensive erosion of mangrove sediments, resulting in active transport of SPM with associated trace metals out of the mangrove. However, the final balance after long periods of time, seems to be a net import of trace metals, as a result of the physical and chemical processes described above. Table 4.2 summarizes the results of long term monitoring of trace metals transfer from a 4-hectare mangrove forest to adjacent ecosystems in Sepetiba Bay, SE Brazil. Large quantities of SPM are accumulated inside mangroves, as well as most metals carried into the mangroves by tides. The importance of SPM load in controlling the balance of trace metals transport in wetland ecosystems has been demonstrated in other similar situations (Woodroffe, 1985a, b, c; Rezende, 1988).

One important result shown in table 4.2 is the large variability of the mass of trace metals transported through the mangrove creek, as confirmed by the large standard deviation of the averages. This suggests that at short intervals, net import and export of trace metals can occur. On the other hand, the mass balance results show that on a long term trace metals are eventually being accumulated in mangroves. The effect of tidal forcing associated with tide type can explain some of the variability. Table 4.3 compares the mass balance of selected trace metals between mangroves and the adjacent marine system, during spring and neap tides. It is clearly shown that spring tides are able to erode accumulated sediments from mangroves, carrying back some of the accumulated trace metals during neap tides.

There is a great variability in physical-chemical parameters during tidal cycles in mangrove ecosystems, including significant changes in suspended matter load and composition, and trace metal

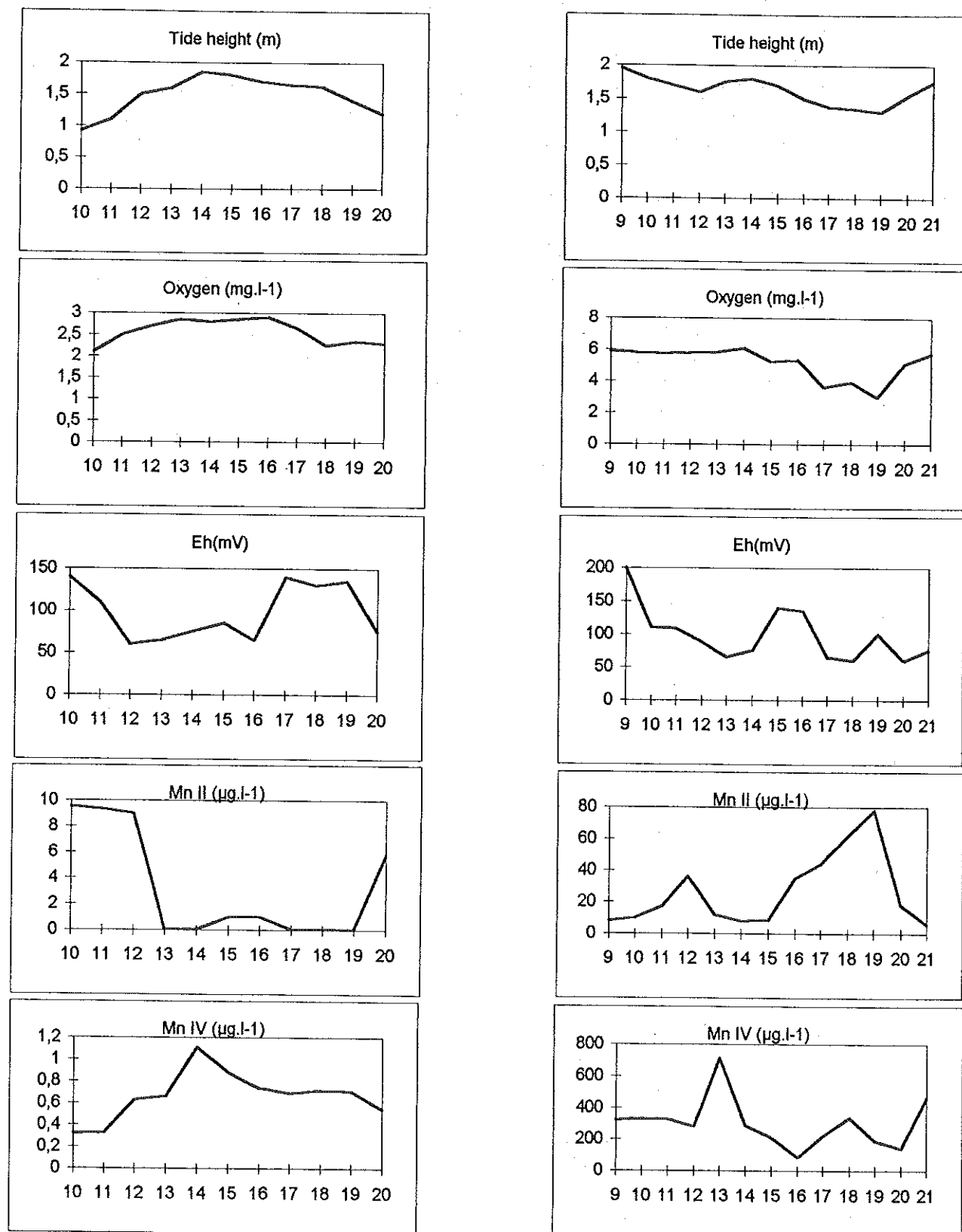


Figure 4.5. Dissolved (MnII) and particulate (MnIV) manganese concentrations, dissolved oxygen and redox potential during tidal cycles in a mangrove creek in SE Brazil, after Ribeiro (1994).

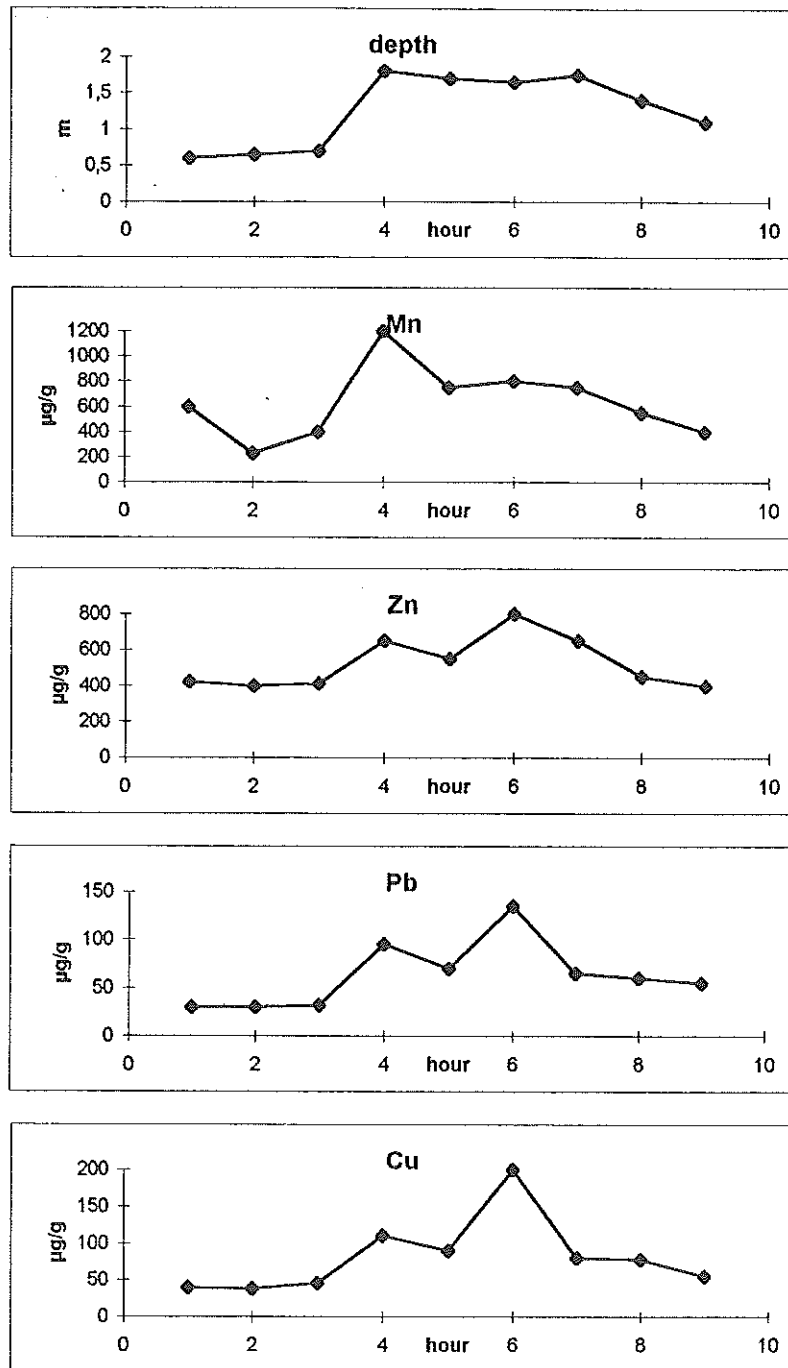


Figure 4.6. Manganese and trace metal concentrations in suspended particulate matter in a mangrove tidal creek in SE Brazil, after Lacerda *et al.* (1988a) and Rezende (1988).

concentrations. Some variability has been shown to occur also in other coastal wetlands (Nixon *et al.*, 1987; Woodroffe 1985a, b, c). However, significant differences between sources of suspended matter during the tidal cycle have been poorly documented, though this is now proved to be of great importance

for the understanding of trace metal behavior in the mangrove forest.

The results discussed above strongly suggest that mangrove ecosystems can act as active sinks of trace metals in coastal waters, in the long term. The high input of these metals in the system is due to a net import

Table 4.2. Mass balance of trace metals in a Sepetiba Bay mangrove, after 28 tidal cycles Lacerda *et al.* (1991b); Rezende (1988), in kg.ano⁻¹. (+) Export. (-) Import. SPM = Suspended Particulate Matter.

Metal	Mn	Zn	Cu	Cd	Fe	Pb	SPM
Mean	+ 8.2	- 5.7	+ 0.3	- 0.2	+ 227	+ 0.2	+ 1,808
Standard deviation	34.8	35.9	2.3	0.7	1,225	1.9	39,640

Table 4.3. Comparison between trace metal masses transported during spring and neap tides in a 4-hectare SE Brazilian mangrove forest in kg.ano⁻¹. After Rezende (1988). SPM = Suspended Particulate Matter.

Metal	Mn	Zn	Cu	Ni	Fe	Pb	SPM
Spring tide	- 2.5	- 12.4	- 0.4	- 0.1	- 127	- 0.2	- 7,200
Neap tide	+ 9.3	+ 3.0	+ 0.5	+ 0.2	+ 274	+ 0.3	+ 6,100
Difference	+ 6.8	- 9.4	+ 0.1	+ 0.1	+ 147	+ 0.1	- 1,100

of suspended particulate matter enriched in metals from adjacent estuarine areas, and a small export of accumulated trace metals due to internal mechanisms of the mangrove ecosystem. There are no data on trace metals balance in areas where major trace metal fluxes come from river waters. However, one can see no reason why the mechanisms described above would not take place also under this situation. Accumulation mechanisms may include anaerobic decomposition of organic matter in mangrove sediments through sulfate reduction, resulting in a net accumulation of sulfides, which can precipitate trace metals, and of refractory organic compounds, which can complex trace metals. These mechanisms will be discussed in detail in the next chapter.

5. Trace metals in mangrove sediments

5.1 Biogeochemistry of trace metals in mangrove sediments

In strongly reducing environments, metals distribution in sediments would be controlled primarily by the formation of highly insoluble sulfides. This is the case of the so called type B metals which form stable sulfides under natural anoxic conditions (Berner, 1984). Stability constants of such metals are, in general very high, reaching from $K = -56$ for Hg and $K = -27$ for Cd, for example (Kersten, 1988). Also, organic-metal complexes are more stable under reducing conditions. For example, the formation of

polysulfides and their interaction with refractory organic compounds, may form extremely high molecular weight compounds, which are very resistant to oxidation, thus accumulating trace metals in strong refractory positions (Casagrande, 1977; Boulegue *et al.*, 1982; Altschuler, 1983).

Trace metals associated with Fe and Mn oxihydroxides, are released from these complexes when reaching a transition zone between oxic and anoxic layers. This transition zone is called post-oxic or sub-oxic (Korte *et al.*, 1975; Berner, 1982), and extends for a few millimeters to a few centimeters in most coastal areas, but may reach a few meters in areas of large physical forcing over the sediments, such as in the Amazon river estuary (Aller *et al.*, 1994; Alongi *et al.*, 1996). Upon reaching this post-oxic layer, oxihydroxides of Fe and Mn solubilize and release their trace metal load. Dissolved trace metals may thus migrate to permanently anoxic layers through sulfide-rich pore waters, and precipitate as insoluble sulfides. Again, the presence of refractory dissolved organic compounds in pore waters will facilitate and accelerate the accumulation process (Boulegue *et al.*, 1982). Therefore, if a given coastal area presents high sedimentation rates, these stable trace metal compounds may accumulate relative to surface sediment concentrations. For example, Lyons *et al.* (1983) studying Mangrove Lake sediments in Bermuda, found a significant increase in trace metal concentrations in deeper mangrove mud layers, in relation to surface carbonate sediments (Figure 5.1). This finding is even

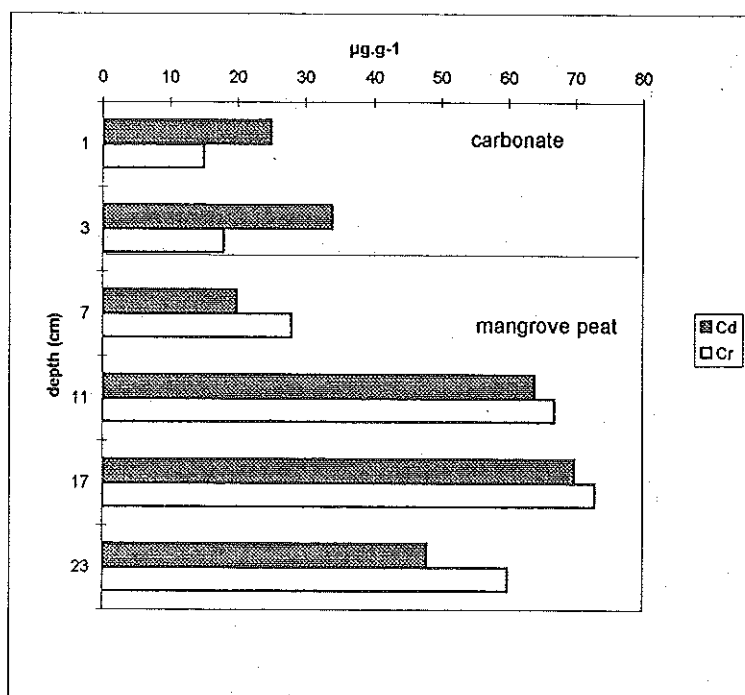


Figure 5.1. Distribution of Cd and Cr in Mangrove Lake sediments, Bermuda, modified from Lyons *et al.* (1983).

more significant if one considers that this remote Atlantic Ocean Island is free from any direct contamination source, suggesting that accumulation of trace metals in this type of sediment is a natural phenomenon, capable of concentrating trace metals even from very low ocean water concentrations.

Annexes 5. 5. 1a, b show trace metal concentrations in surficial mangrove sediments from different parts of the world. Contrary to biological compartments or water, these data are very difficult to compare, since they depend on some physical properties of sediments, in particular grain size, organic matter content and redox conditions. However, as expected, trace metals forming stable sulfides such as Fe, Zn, and Cu, among the essential elements, and Pb, Cd and Hg, among the non-essential, generally present relatively higher concentrations. Unfortunately many more data are necessary in order to make a proper comparison between mangroves themselves, and between mangroves and adjacent marine and fluvial sediments, regarding trace metal concentrations.

Although accumulation of trace metals in anoxic sediments of coastal areas has been reported

worldwide, a certain degree of post-deposition mobilization is possible (Förster, 1989). Upon oxidation, some metals such as Cd may be released from sulfur and organic matter compounds and associate with chlorine or dissolved organic matter and be kept in solution. However metals such as Cu and Pb are released much slower (Hunt & Smith, 1983). Some studies were reported on the export of trace metals from mangrove sediments associated with dissolved organic carbon and chlorine (Lindberg *et al.*, 1977; Tripp & Harris, 1979). Figure 5.2 shows the major mechanisms influencing trace metal dynamics in mangrove sediments.

5.2 Distribution and accumulation of trace metals in mangrove sediments

Mangrove sediments are of fine grain size, rich in organic matter and flooded daily by tides. Under such conditions, sediments become reducing because of microbial decomposition of organic matter, and by consumption of oxygen in the process. Most of mangrove sediments metabolism is through sulfate reduction, which releases high quantities of HS^- and $\text{HCO}_3^{3=}$ to pore waters and even to waters overlying the

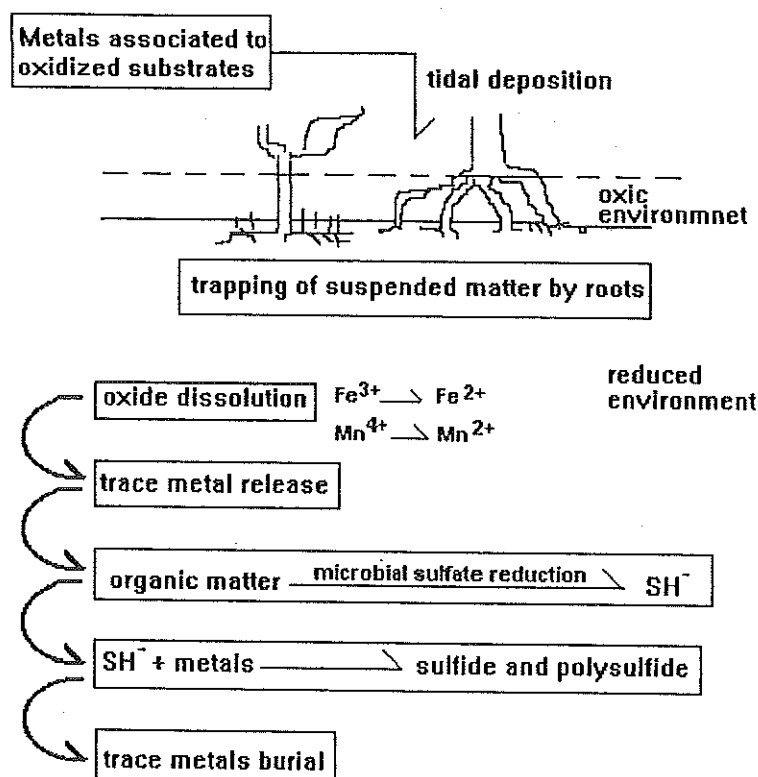


Figure 5.2. Summary of major metabolic processes in anoxic mangrove sediments.

sediments. Sulfide concentration derived from this process may reach 10mg.l^{-1} in water overlying the sediments (Harbinson, 1986a). Under these physical-chemical conditions the formation of sulfide minerals is favored, precipitating dissolved trace metals, in particular the "soft" B type metals which includes most heavy metal pollutants such as Zn, Hg, Ni, Cu and Cd (Berner, 1984; Harris *et al.*, 1993).

Trace metals are enriched in clay sediments compared to typical marine carbonate sediments. The accumulation process is highly enhanced by high organic matter content. The strength of the association between the metal and the mangrove soil components, is a function of the specificity of a given metal for the substrate and the stability of recently formed compounds. For example in the presence of humic substances, that are particularly rich in mangroves, trace metals like Cd, Ni and Pb have very low mobility in soils, probably due to complexation of the metals which hampers leaching by solutions (Kersten, 1988). The high affinity of Hg for sulfur groups, results in strong immobilization and therefore, accumulation in mangrove sediments. Quevauviller *et al.*, (1992), working

in Sepetiba Bay, SE Brazil, showed that mangrove sediments are able to immobilize and accumulate Hg, even the volatile dimethyl-Hg through complexation with sulfide groups. Therefore, three major aspects are involved in the accumulation and distribution of trace metals in mangrove sediments: a- preferential accumulation of sediments of fine granulometry; b- accumulation of high organic matter content, and c- precipitation of metal sulfides present as a by-product of the sulfate reduction based metabolism.

Figure 5.3 shows trace metal accumulation and organic matter content in sediments from a fringe mangrove forest compared to adjacent mud flats, in Sepetiba Bay, SE Brazil (Lacerda & Abrão, 1984). Higher accumulation of trace metals in mangrove sediments relative to adjacent mud flats occurs by a factor of 2 to 4 depending on the element, following the increase in organic matter content by a factor of 3. In a study of the mangroves of Botafogo River, NE, Brazil, Meyer (1996) also found strong correlation between Hg concentrations in sediments and the content of organic matter and fine particles.

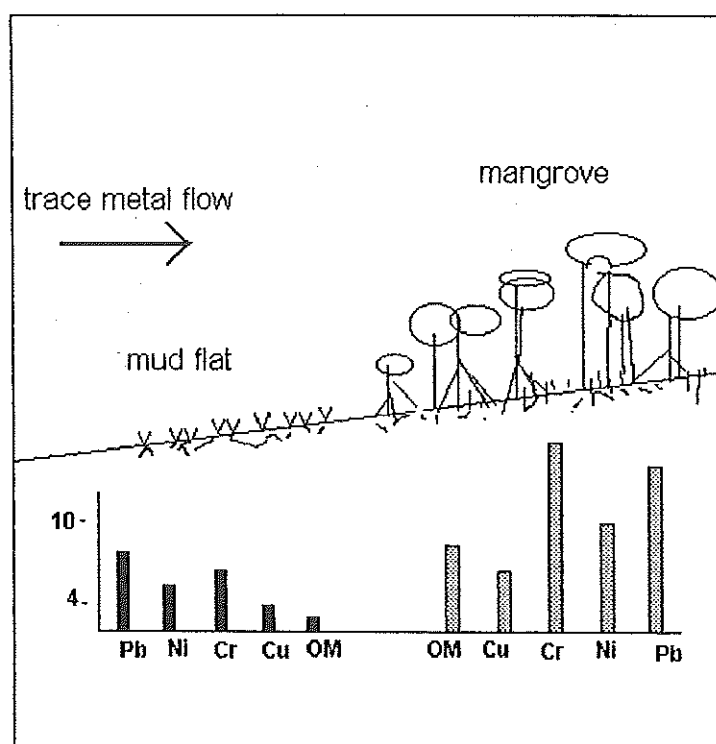


Figure 5.3. Trace metal concentrations and organic matter content in sediments of a mud flat-mangrove environment in Sepetiba Bay, SE Brazil, modified from Lacerda & Abrão (1984).

Trace metals reach the mangrove environment associated with fine particles of marine and terrestrial origin brought into the forest by rivers and tides (Rezende, 1988). Terrestrial materials are frequently enriched in trace metals content (see chapter 1) and also have fine granulometry and are rich in organic matter (Rezende, 1988). Therefore, events enhancing runoff from mangrove basins will result in higher trace metal contents of suspended particles. During monsoon periods in Thailand, for example, runoff particles are enriched in trace metals from smelter wastes located in the basin, relatively far from mangroves (Brown, 1988). In Papua New Guinea, the same phenomenon is observed when tailings from mining operations are transported to the coast (Jeffery *et al.*, 1988).

The redox potential of mangrove sediments is another significant parameter controlling trace metal concentrations in mangrove sediments. Changing redox potential can affect the solubility of certain elements, the so called redox sensitive elements, such as Mn and Fe, or indirectly by making metal-precipitates unstable (e.g. metal sulfides). Figure 5.4 shows the variability of dissolved oxygen in pore waters and leachable Fe concentrations in sediments across a

mud flat-mangrove-salt flat gradient in Sepetiba bay, SE Brazil. The different physiography of the areas, which occur as fringes parallel to the shore, creates redox boundaries between the different sub-habitats. This is clearly seen from the dissolved oxygen concentrations. Dissolved oxygen reaches high (up to 8.2 mg.l^{-1}) at the seaward mud flats decreasing to less than 5.0 mg.l^{-1} at the two mangrove fringes and again increasing at the salt flat area. Leachable Fe concentrations respond sharply to changing oxygen content of pore waters. At the boundaries between sub-habitats leachable Fe reach maximum concentrations ($> 40 \text{ } \mu\text{g.g}^{-1}$), probably as a result of increasing solubility due to reduction of Fe^{3+} to Fe^{2+} , made possible by decreasing oxygenation. At higher oxygen levels, resistant Fe oxides precipitate, decreasing its leachability (Aragon *et al.*, 1986).

5.3 Geochemical partitioning of trace metals in mangrove sediments

When trace metals are dissociated from oxic suspended matter and are eventually fixed in reducing substrates of the mangrove soil, they will have their geochemical partitioning altered. Figure 5.5 shows Cu

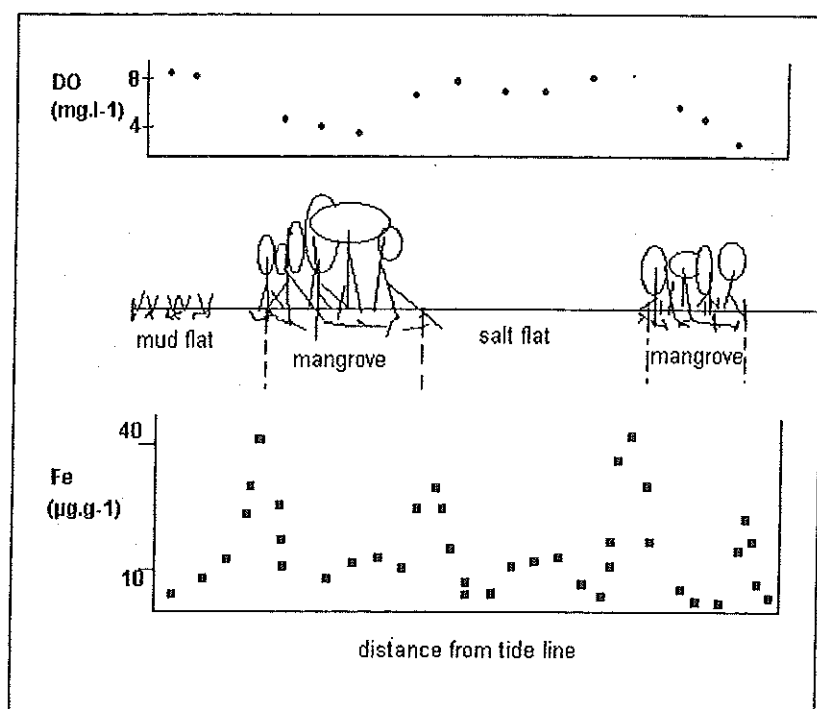


Figure 5.4. Variation in leacheable Fe concentrations in sediments and pore water dissolved oxygen concentration, across a mud flat-mangrove-salt flat gradient in Sepetiba Bay, SE Brazil, modified from Aragon *et al.* (1986).

and Zn geochemical partitioning in Zaire River, Africa, and its adjacent mangrove sediments (Salomons *et al.*, 1988), and in Sepetiba Bay, SE Brazil bottom sediments and the adjacent mangroves (Lacerda, 1993).

The results show a sharp difference between the two mangrove sediments and their fluvial or marine counterparts. In river sediments at the Zaire estuary, Cu and Zn concentrations are associated with reducible fractions (hydro-oxides of Fe and Mn) and inert positions, with oxidizable fractions, which includes organic matter and sulfides, responsible for only 15% and 8% of the total concentrations of Cu and Zn respectively. In the mangrove sediments in the same area, Cu and Zn concentrations shift to oxidizable fractions (organic matter and sulfides), which accounts for 85% and 40% of the Cu and Zn concentrations respectively. In Sepetiba Bay, the same behavior occurs, with the oxidizable fraction of Cu and Zn total concentrations increasing from approximately 10% for both metals in the bay's sediments to 77% and 60% in mangrove sediments, for Cu and Zn respectively. This has also been shown to occur for other trace metals

such as Fe, Pb and Cr (Lacerda, 1993). Similar results have also been reported by Chiu & Chou (1991) when comparing trace metals geochemical partitioning in mangroves and bamboo forest soils, along the Tamshi River, Taiwan.

The above data indicate that increasing organic matter and fine particles content, create reducing conditions, leading to a redistribution of deposited trace metals in sediments (Salomons *et al.*, 1988). This shift in trace metal partitioning has been observed also in other mangrove areas in Africa (Salomons & Förstner, 1984). The chemical reactions involved in this process have not been described in detail yet. However, the formation of framboidal pyrites, mediated by microorganisms, may be a clue to the geochemical processes undergoing the change of the major substrate of trace metals present in sediments. Pyrites (Figure 5.6), are deposited by sulfate reducing bacteria that coprecipitate trace metals in the process. Relatively enrichment of Cu and Au has been reported in recently precipitate framboidal pyrites in mangroves (Aragon, 1997; Pires, 1997).

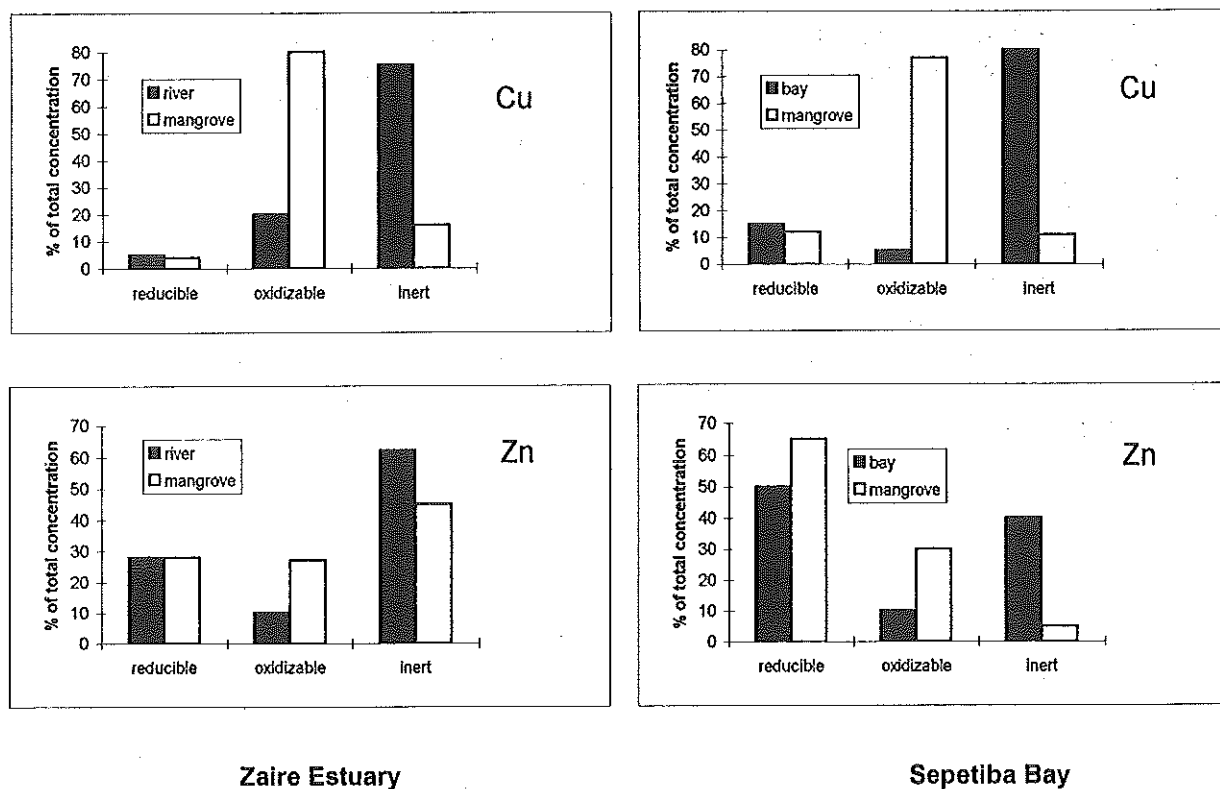


Figure 5.5. Copper and zinc geochemical partitioning in bottom sediments from the main river and adjacent mangroves at the Zaire River estuary, Africa, after Salomons *et al.* (1988); and from open bay bottom sediments and mangrove sediments at Sepetiba Bay, SE Brazil, after Lacerda (1993).

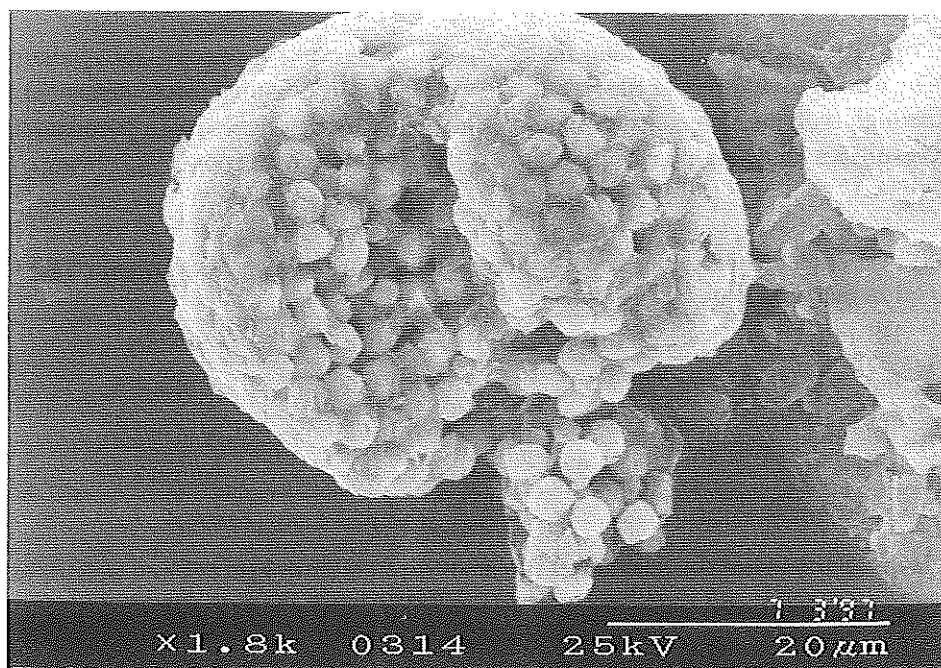


Figure 5.6. Framboidal pyrite photographed from biofilms collected in mangrove sediments from a fringe mangrove forest in Sepetiba Bay, SE Brazil.

5.4 The effect of plant cover on the distribution of trace metals in mangrove sediments

Trace metals accumulation in mangrove sediments is due to the formation of precipitated metal sulfides, which are buried fast by the high sedimentation rates generally found in the mangrove environment. However, although the metal-sulfide complex is highly stable under the reducing conditions found in mangrove sediments, they can be dissociated upon oxidation of the sediment. Mangrove plants are able to oxidize the rhizosphere by exuding oxygen through their roots into the sediment. This phenomenon has been well described for salt marsh environments (see chapter 2), and has recently also been described for mangrove environments. The mangrove genera *Avicennia* and *Rhizophora*, can efficiently oxidize their rhizospheres, creating conditions where metal sulfides can be dissociated (Carlson *et al.*, 1983; Nickerson & Thibodeaux, 1985; Thibodeaux & Nickerson, 1986; Lacerda *et al.*, 1993a). The oxidation capacity of *Avicennia*, for example, is such that virtually no sulfide is detected in its rhizosphere pore waters (Nickerson & Thibodeaux, 1985).

Table 5.1 shows the major physical-chemical characteristics of mangrove rhizosphere pore waters under *Avicennia* and *Rhizophora*, and from mud flats without plant cover in a mangrove forest in SE Brazil. The data confirm the high oxidation capacity of mangrove roots. Whereas sulfides show high concentration

in mud flat pore waters, this decreases by a factor of 3 under *Rhizophora* and sulfides are virtually absent under *Avicennia*. Also, redox potential, an indirect measurement of oxidation level, shows very negative values in the mud flats, indicating permanent reducing conditions, whereas under mangrove plants it can reach positive values, indicating high oxidation. Interesting to note is the high standard deviations found, suggesting that rhizosphere pore waters shift constantly from reducing to oxidizing conditions, keeping various chemical species unstable, including trace metal sulfides.

Table 5.2. shows weakly bound trace metal concentrations in the same sediments. Although concentrations are very low, *Avicennia* rhizosphere sediments show significantly higher trace metal concentrations than mud flat sediments. The changing redox conditions and the possibility of periods of high oxidation, as shown in table 5.1, suggest a certain degree of trace metals remobilization, probably resulting from the dissociation of metal sulfides. The concentrations under *Rhizophora* are not significantly different from mud flat sediments, for some metals, in particular Fe and Zn. Therefore, although *Rhizophora* seems to be able to oxidize its rhizosphere, this is not sufficient to release all trace metals from precipitated sulfides.

The results discussed above show that at least under certain circumstances, deposited trace metals can eventually be released into pore waters by the metabolism of mangrove roots.

Table 5.1. Major physical-chemical variables of porewaters, and soil organic matter content (OM) in a fringe mangrove forest in Sepetiba Bay, Rio de Janeiro, Brazil.

Plant cover	HS ⁻ (mg.l ⁻¹)	Eh (mV)	pH	Salinity	OM(%)
<i>Avicennia</i>	0.33 ± 0.49	-63 ± 92	6.8 ± 0.6	32.8 ± 6.5	24.7 ± 11.8
<i>Rhizophora</i>	15.6 ± 4.6	-173 ± 125	6.8 ± 0.2	31.2 ± 4.9	12.5 ± 4.3
Mud Flat	47.1 ± 16.3	-204 ± 95	7.1 ± 0.3	26.4 ± 2.7	20.5 ± 7.9

Table 5.2. Weakly bound trace metal concentrations (µg.g⁻¹ dry weight) and iron (% dry weight) in mangrove soils compared to salt marsh and mud flats in Sepetiba Bay, Rio de Janeiro, Brazil. Trace metal fraction extracted with 0.5N HCl.

Plant cover	Fe	Zn	Pb	Cu	Cd
<i>Avicennia</i>	3.6 ± 0.7	387 ± 189	23 ± 3.6	12 ± 5.6	3.4 ± 1.5
<i>Rhizophora</i>	3.6 ± 0.3	529 ± 641	22 ± 2.6	13 ± 4.4	3.5 ± 0.4
Mud Flat	4.5 ± 0.4	823 ± 26	39 ± 1.8	24 ± 1.4	6.9 ± 0.4

6. Trace metals in mangrove plants

6.1 Trace metals distribution in mangrove leaves

The location of mangroves in protected coastal sites adjacent to large industrial and urban areas prompted studies aiming at the use of mangrove plants as biological monitors of trace metal pollution (Sadiq & Zaidi, 1994; Peterson *et al.*, 1976; 1979; Lacerda *et al.*, 1986a). Nearly all these studies concluded that mangrove trees are not suitable for heavy metal monitoring, since they fail to show any correlation between concentrations of trace metals in sediments and in mangrove plant leaves. Nevertheless, these studies, though reporting only metal concentrations in leaves, are the only source of information on the distribution of trace metals in mangrove plants.

Reports show that mangrove plants have present very low concentration factors (CF) for trace metals (CF = ratio between the concentration of trace metals in leaves and the concentration in soil). Mangrove CF's are in general much lower than 1.0. Rao *et al.* (1991) for example, found As CF's ranging from <0.02 in *Rhizophora mucronata* to 0.09 in *Avicennia marina* in India, whereas in the same area 7 species of marine benthic brown algae showed CF's ranging from 1,510 to 6,980. Jayasekera (1991) also compared CF's of *R. mangle* with brown algae and found that mangrove CF's are in general from 1 to 1,000 times smaller than the algae CF's, for most trace metals of environmental significance. Lacerda *et al.* (1986a), found CF's lower than 1.0, for Fe, Cu, Zn, Pb, Cd and Cr, in mangrove plants from 18 forests along the SE Brazilian coast, including sites heavily contaminated by trace metals. Their study also found higher CF's in *Avicennia* species than in *Rhizophora*.

Peterson *et al.* (1976; 1979), studied the concentrations of Sn, Fe, Zn and Cu in mangroves of Malaysia submitted to mining effluents and found much lower CF's in these plants than in other local marine organisms. They also found no correlation between trace metal concentrations in mangrove leaves and in the sediment.

Sadiq & Zaidi (1994) studied the concentrations of various metals in mangroves along the Persian Gulf coast of Saudi Arabia, finding the following order of

trace metals concentrations: $\text{Fe} \gg \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Co}$. Along 1,000 km of the SE Brazilian coast, Lacerda *et al.* (1986a) found the same concentration order in trees collected from 18 forests. Both studies reported no significant correlation between trace metal concentrations in soils and in leaves, with the exception of Mn, which presented highly significant correlation.

Bhosale (1979) studied the concentrations of five metals in 9 mangrove species from the Indian coast which presented clear zonation pattern and thus were submitted to different soil conditions. Notwithstanding this, no correlation was found between soil and plant metal concentrations of Cu, Zn, Mo, Co, Mn and Fe. As for Co the plants showed sub-optimal concentrations although relatively high levels were found in the soil. The author suggested that "the specificity of the plant for each metal" was responsible for the lack of correlation found. Soto (1992) also found sub-optimal concentrations of selected trace metals in mangrove species from the Pacific coast of Costa Rica. Peterson *et al.* (1979) reported lack of correlation between metal concentrations in plants and soil as due to the "complex interactions between plants and soils typical of mangroves". Unfortunately these terms are obviously not an explanation for the lack of correlation between plants and soils but a statement of the phenomenon and the inability to explain it so far.

Chiu & Chou (1991) showed that mangrove plants display high resistance to trace metals. They showed that seedlings of *Kandelia candel* from pristine areas can adapt to areas polluted by trace metals, due to high tolerance mechanisms. In laboratory experiments with *Rhizophora mangle* seedlings, Walsh *et al.* (1979) showed that metal sulfides are deposited close to mangrove roots, avoiding the uptake of Pb, and to a lesser extent, of Cd and Hg which were translocated to the plant. No effect on the seedlings was observed up to 500 $\mu\text{g.g}^{-1}$ of metals in soils. The only metal to affect the growth of mangrove seedlings at this concentration level was Hg, but even for this element, seedlings showed resistance to up to 100 $\mu\text{g.g}^{-1}$ of Hg in soils. Mechanisms of trace metals tolerance hypothesized by these authors to explain the lack of toxicity of the translocated metals involve chelation on cell walls or segregation in the well developed hypodermis of the leaf.

Annex 6. 6. 1a, b show trace metal concentrations in leaves of mangrove plants in many areas of the tropics. Concentrations are in general higher among the essential trace metals, decreasing in the following order: $Mn > Fe > Zn > Cu$, and vary among the non-essentials according to site, depending on the contamination status of each site, in particular for some metalloids. For example, Peterson *et al.* (1979) found very high Sn concentration in mangrove leaves growing close to mining operations in Malaysia. Relatively high concentrations were also found among some other metalloids (not shown in the tables). Fluoride concentrations in mangrove species from Australia close to emission sources were up to 100 times higher than background values (Murray, 1985). Concentrations of Ba in mangrove sites receiving oil from production waters in Colombia also showed to be from 10 to 100 times higher than background concentrations (Grosso *et al.*, 1996). It is interesting to note that some of these metalloids (e.g. F) show significant leaf uptake from atmospheric deposition. However, other non-essential heavy metals such as Pb, Hg and Cd (Table Annex 6. 6. 1b) show relatively constant concentrations regardless of the area studied.

Most trace metal concentrations in mangrove leaves are similar or lower than the average concentration found in leaves from temperate and other tropical tree leaves, which generally occur in soils much poorer in trace metals than mangrove soils (Golley *et al.*, 1978; Silva *et al.*, 1990; Whittaker *et al.*, 1979). However, as can be clearly deduced from the tables, data on trace metal concentrations in mangrove plants are still scarce and incomplete. Therefore, it is impossible to analyze inter-specific differences on trace metal accumulation by mangrove species or make comparisons with better studied vegetation forms, at present.

The concentrations of selected trace metals in two of the most studied mangrove genera, with relatively well known physiology, *Avicennia* and *Rhizophora* are shown on table 6.1. The two species show different physiological adaptations to cope with the high salinity of mangrove soils. Whereas *Rhizophora* species are typical salt-excluding plants, *Avicennia* are typical salt-excreting species (Chapman, 1976). Lacerda *et al.* (1985b) showed that these mechanisms of salt uptake control affect trace metals uptake. These authors showed that *Avicennia* consistently showed higher

concentrations of trace metals than *Rhizophora*. Table 6.1, shows data from pair of plants from these genera analyzed in the same site worldwide. The results confirm that at least for essential trace metals, for which enough data are available, it is clear that salt-excluding mechanisms may be very efficient in avoiding the uptake of trace metals, as expressed by the consistently lower concentrations in *Rhizophora* than in *Avicennia* plants.

Apart from differences among species, leaf trace metal content also depends on age of the leaf. Younger leaves, show in general, higher concentrations of trace metals than older leaves. Rao *et al.* (1991) showed this for the high mobile ion As in 7 species of mangroves along the Goa coast, India. Chiu & Chou (1991) however, found no significant difference in the concentrations of the less mobile metals Cu, Zn, Pb, Cd and Ni, between young and old leaves of *Kandelia candel* in Taiwan. Peterson *et al.* (1979) found higher concentrations of Sn in old leaves of *R. mucronata* and *A. illicifolius*, but lower concentrations of Fe, Zn and Cu. It seems that less mobile elements are translocated more slowly, if ever, than the leaf growth rate, resulting in the dilution of young leaf concentration due to accumulation of biomass as the leaf grows. Lacerda *et al.* (1988b) showed this phenomenon to occur in *R. mangle* seedlings during development. Concentrations of Fe, Zn, Mn and Cu decrease consistently with the growing of the seedling. At least for Zn, concentrations drop to sub-optimal levels, requiring further translocation from the mother plant when the seedlings are ready to fall.

6.2 Factors controlling trace metal concentrations in mangrove plants

Concentration factors calculated from a complete set of data from SE Brazil (Silva *et al.*, 1990) for *R. mangle* and the trace metals concentrations bioavailable in the soil (Table 6.2), show that for the majority of metals CF's are up to two orders of magnitude lower than 1.0, the only exception being Mn with CF's of about 2.0. These concentration factors suggest that either mangrove plants actually avoid metal uptake and/or that most metals present very low bioavailability in mangrove soils, notwithstanding the relatively high concentrations found in mangrove sediments.

Table 6.1. Essential trace metal concentrations in species of *Rhizophora* and *Avicennia* from different parts of the world.

Species	Site	Fe	Zn	Cu	Mn	Author
<i>R. mangle</i>	St. Catarina,	99	69	1.6	260	Panitz (1997)
<i>A. schaueriana</i>	South Brazil	127	145	2.1	195	
<i>R. conjugata</i>	Penang,	50-69	6.2-7.1	2.6-3.0	—	Peterson <i>et al.</i> (1979)
<i>A. alba</i>	Malaysia	139-185	15-19	2.8-6.0	—	
<i>A. officinalis</i>		88	12	4.5	—	
<i>R. mucronata</i>	Ganapatipule,	—	11.5	4.1	32.2	Bhosale (1979)
<i>A. officinalis</i>	India	—	17.5	9.2	158.7	
<i>R. mangle</i>	Pacific coast	80-420	6.0-19	3.5-16	—	Soto (1992)
<i>R. harrisonii</i>	of Costa Rica	100-440	8.0-17	4.8-17	—	
<i>A. germinans</i>		80-380	17-22	8.0-21	—	
<i>R. mangle</i>	São Paulo,	208	12	4.5	254	Lamberti (1969)
<i>A. schaueriana</i>	South Brazil	175	28	7	63	
<i>R. mangle</i>	Sepetiba Bay,	68-943	10-34	3.0-34	20-882	Lacerda <i>et al.</i> (1986b)
<i>A. schaueriana</i>	SE Brazil	71-606	20-66	3.0-19	38-473	

The bioavailability of trace metals to plant uptake is a function of their geochemical partitioning in the mangrove soil. Metals are precipitated in mangrove sediments as sulfides (Lacerda & Rezende, 1987) which are stable under the anoxic conditions of mangrove soils and unavailable to plant uptake. Other data that suggest that sulfide is responsible for the low availability of trace metals in mangrove soils is the high concentration factors found for Mn, which do not form stable sulfides and is soluble under the redox conditions found in mangroves (Aragon *et al.*, 1986; Lacerda *et al.*, 1988a). For example, Mn consistently shows higher exchangeable contents in sediments than most other trace metals. This has been reported for mangroves as far apart as South America, China and Australia (Lacerda *et al.*, 1986a; Tam *et al.*, 1995; Mackey *et al.*, 1992). The importance of sulfides in controlling the availability of trace metals to various organisms inhabiting aquatic sediments has been often demonstrated and sulfide concentration actually controls the concentrations of trace metals in pore waters

of reduced sediments (Di Toro, 1990). Chiu & Chou (1991) suggested that the low concentrations of trace metals found in *Kandelia candel* forests in Taiwan was due to sulfide precipitation. In this study they also showed that this was not the case for Mn.

Apart from sulfide precipitation, organic matter complexation may also decrease the availability of some trace metals to plant uptake in mangroves. Lacerda *et al.* (1991b) showed that at least for Cr, which does not form sulfide minerals, refractory organic compounds were responsible for Cr fixation and accumulation in mangrove sediments. Table 6.3 shows the total and bioavailable concentrations of trace metals in mangrove soils under *R. mangle* in the Itacuruçá Experimental Forest, SE Brazil (Lacerda *et al.*, 1993a). These results show that less than 1% of the total metal content is available for root uptake, confirming the low bioavailability of trace metals in mangrove soils. Similar results have been found for mangroves in Asia (Tam *et al.*, 1995; Chiu & Chou, 1991).

Table 6.2. Trace metals concentrations in leaves of *Rhizophora mangle* and bioavailable metal concentrations in sediments of a mangrove forest in Southeastern Brazil. ($\mu\text{g.g}^{-1}$ dw).

Compartment	Mn	Fe	Zn	Cu	Pb	Cr
Leaves	101 \pm 39	37 \pm 9	7.2 \pm 0.8	<0.05	<0.06	<0.2
Sediment	52 \pm 11	4,856 \pm 247	18 \pm 5	2.8 \pm 0.8	0.6 \pm 0.2	9.4 \pm 4.3
Concentration factor	2	<0.01	<0.5	<0.01	<0.01	<0.1

Table 6.3. Total and weakly bound trace metal concentrations in sediments under *R. mangle* in a mangrove in SE Brazil (Lacerda *et al.*, 1993a) ($\mu\text{g.g}^{-1}$ dw).

Metal	Fe	Zn	Pb	Cu	Cd
Total metal concentration	3,600 \pm 300	191 \pm 140	21.5 \pm 2.4	12.5 \pm 1.2	3.1 \pm 1.1
Weakly bound concentration	35 \pm 6.7	1.1 \pm 0.7	0.1 \pm 0.01	0.01 \pm 0.01	0.01 \pm 0.01

Apart from low bioavailability however, other factors may be responsible for the low trace metal concentrations found in mangrove leaves and for the lack of correlation between the concentrations of most trace metals in soils and in the plants. Mangrove species present physiological adaptations aimed at controlling the uptake of ions present in large quantities in the saline and frequently reduced soil porewater. For example, the higher trace metals concentrations found in *Avicennia* when compared to *Rhizophora* (Table 6.1) may be a result of salt-excluding mechanism in the latter, although no study so far has addressed this subject (Lacerda *et al.*, 1985b; Walsh *et al.*, 1979; Werner & Stelzer, 1990; Scholander *et al.*, 1955; 1962). Some of these adaptations may act as a tolerance mechanism, reducing trace metal uptake. Among them, the formation of redox barriers such as iron and manganese plaques may be particularly efficient in trace metal uptake. Immobilization of trace metals on the cell wall and complexation with root exudates may also reduce trace metal uptake particularly under the organic rich conditions of mangrove soils (Walsh *et al.*, 1979; Taylor, 1987; Otte *et al.*, 1987; Tanizaki, 1993). Also, high salinity itself may reduce trace metal uptake (Soto, 1992).

Few studies have dealt with the tolerance of trace metals to mangrove plants. Walsh *et al.* (1979) showed that mangrove (*R. mangle*) seedlings are particularly resistant to Cd, Pb and Hg, due to the precipitation of insoluble metal compounds on the external surfaces of roots induced by the seedling me-

tabolism. However, these authors did not characterize the chemistry of these precipitates.

Seedlings of *Kandelia candel* also showed high tolerance to trace metals, 20 to 80 times higher than salt marsh plants in China (Chiu & Chou, 1991). The mechanism(s) responsible for the high tolerance presented by this species, however, was not identified.

6.3 Trace metal distribution in mangrove plant organs

The distribution of trace metals in different organs of *R. mangle* is shown on tables 6.4 and 6.5, and suggests some possible mechanisms involved in decreased metal uptake by mangrove plants, with the exception of Mn, all other trace metals showed highest concentration in below-ground roots. Highest concentrations of Mn were found in leaves.

Jayasekera (1991) grew *R. mangle* under controlled conditions for one year. His results, given on table 6.5, also show that with the exception of Mn, with highest concentrations in leaves, all other trace metals had their highest concentration in below-ground roots which are responsible for the nutrient uptake and all plant-sediment interactions. Similar results have been reported by other authors and other mangroves.

Chiu & Chou (1991) found the same relative distribution in *Kandelia candel* in China. Montgomery & Price (1979) showed by *in vitro* experiments using a continuous flow of effluent containing metals, that the

Table 6.4. Trace metal concentrations in different organs of *R. mangle* in a mangrove forest in SE Brazil according to Silva (1988) ($\mu\text{g.g}^{-1}$ dw).

Organ	Mn	Fe	Zn	Cu
Fruits	18 \pm 6	3.2 \pm 0.6	1.2 \pm 0.1	--
Flowers	59	67	9	--
Leaves	101 \pm 39	37.2 \pm 8.9	7.2 \pm 0.8	--
Stems	67	19.4	6.2	0.6
Trunks	20.4 \pm 5.8	12.4 \pm 7.3	3.4 \pm 0.8	0.5 \pm 0.3
Aerial roots	15.5 \pm 3.2	8.2 \pm 3.2	7.2 \pm 2.4	0.4 \pm 0.2
Below-ground roots	15.3 \pm 5.9	1,011 \pm 637	19.9 \pm 7.8	5.1 \pm 3.0

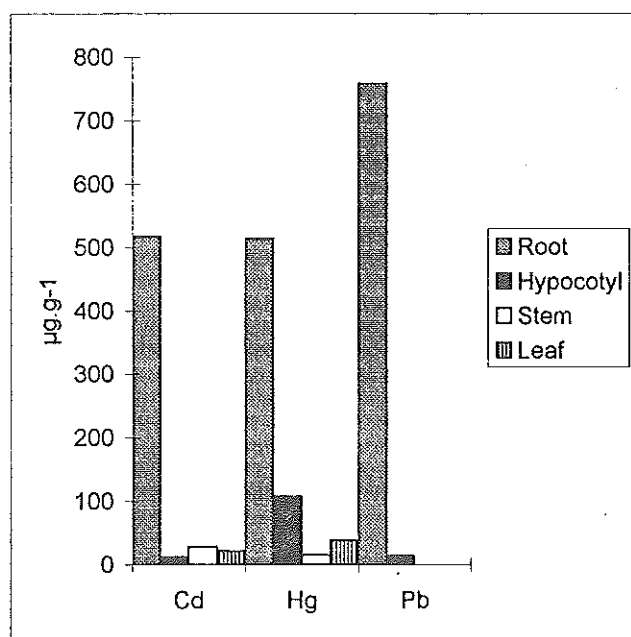
Table 6.5. Trace metal concentrations in different organs of *R. mangle* after one year growth in artificial media according to Jayasekera (1991) ($\mu\text{g.g}^{-1}$ dw) and percentage of the total content weight averaged in parenthesis).

Metal	Leaves (%)	Stem (%)	Roots (%)
Co	7.1 (10.4)	7.4 (32.5)	13 (57.4)
Cu	11.1 (7.3)	12.0 (23.2)	36.2 (69.5)
Fe	52.9 (1.6)	37.3 (3.2)	1,100 (95.2)
Mn	298 (36.9)	117.8 (43.0)	55.4 (20.1)
Zn	15.6 (3.0)	9.4 (5.4)	159 (91.5)

underground fine roots of *R. mangle* accumulated high trace metals concentrations, but not the other plant parts submitted to the same treatment. Walsh *et al.* (1979) growing *R. mangle* seedlings under controlled laboratory conditions, showed that most of the metals added to the culture medium are accumulated by the roots. Only a small proportion is translocated to the rest of the plant (Figure 6.1).

The gradient of high trace metal concentrations in roots and low in leaves and the absence of significant correlation between trace metal concentrations in soils and plants, although not characterizing the mechanism involved, clearly indicates that these plants actively avoid uptake of trace metals, even where their concentration in the soil are high (Taylor, 1987).

The dominant redox conditions of mangrove soils make it particularly enriched in phyto-toxins. Trace metals such as Fe and Mn are soluble under these conditions and may reach very high concentrations. Also,

**Figure 6.1.** Distribution of selected trace metals after 240 days culture under controlled laboratory conditions, after Walsh *et al.* (1979).

the microbial metabolism based on the dissimilatory reduction of sulfate, generates large amounts of sulfides. Therefore, the roots are frequently submitted to toxins under reduced forms. The most efficient mechanism to neutralize such substances is the exudation of oxygen translocated through the aerenchyma to the root surface (Scholander *et al.*, 1955), creating an oxidized rhizosphere. Soluble Fe and Mn are precipitated as oxides forming iron-plaques on the root surface while sulfides are oxidized to harmless sulfate (Ponnamperuma, 1972; Taylor, 1987; Armstrong, 1978). This oxidized rhizosphere can affect the mangrove soil

adjacent to the roots (Nickerson & Thibodeau, 1985; Carlson *et al.*, 1983; St-Cyr & Crowder, 1990).

Otte *et al.* (1987) and Mendelsshon & Postek (1982), studied in detail the formation, morphology and composition of iron-plaques in salt-marsh plants and showed their efficiency as geochemical barriers to the uptake of trace metals by the root cells of these marsh plants. Thibodeau & Nickerson (1986) and Nickerson & Thibodeau (1985) studied the release of oxygen by mangrove roots and showed the formation of oxydized micro-environments in the rhizosphere. The release of oxygen in the soil adjacent to the root will favor the precipitation of iron originated in the reduced pore-waters of mangrove soils forming typical iron-plaques at the rhizosphere (Tanizaki, 1993). The high concentration of iron in the fine, underground roots of *R. mangle* measured in most studies suggest that they are also efficient as barriers of trace metals in mangrove plants.

At the Itacuruçá Experimental Forest Lacerda *et al.* (1993a) studied the importance of iron plaques as biogeochemical barriers to trace metal uptake. In table 6.2 it was shown that the weakly-bound fraction of trace metals in mangrove soils were less than 1% of the total trace metal concentration in the soil adjacent to the roots of *R. mangle*. Paradoxically, trace metals concentrations in mangrove roots are in general very high (Montgomery & Price, 1979; Silva *et al.*, 1990; Chiu & Chou, 1991). When analysis of root plaque concentration are shown however, (Table 6.6) it is clear that the majority of the trace metals present in the roots are fixed on the iron plaques deposited on the external cortex of the roots rather than in internal root tissues. Similar results have also been found for other estuarine plants (St-Cyr & Crowder, 1990) and for *A. schaueriana* (Tanizaki, 1993).

Table 6.6. Trace metal concentrations in roots and iron-plaques of *R. mangle* ($\mu\text{g.g}^{-1}\text{dw}$), after Tanizaki (1993).

Compartment	Fe	Mn	Zn	Cu
Root (total)	25,000	730	140	23
iron-plaques	24,000	670	90	12
% in iron-plaques	96	92	62	52

The low trace metals concentrations generally found in mangrove plants and the lack of correlation between trace metal concentrations in soils and plants can be explained by the extremely low bioavailability of trace metals in mangrove soils and by the presence of efficient tolerance mechanisms involving the precipitation of iron-plaques on the root surfaces.

6.4 Trace metals mass balance in the biomass of mangrove forests

The accumulation of trace metals in mangrove soils occurs through the precipitation of stable sulfides under the anoxic conditions prevailing in such soils. This results in extremely low bioavailability of trace metals and the presence of tolerance mechanisms at the root level makes even more difficult the uptake of trace metals by mangrove plants. As a result, mangrove trees show low trace metal concentrations and do not respond to changes in soil concentrations, typically they have concentration factors lower than 1.0. However, since mangrove production is high, even with low concentrations of trace metals, mangrove leaves would be an important component in their cycling (Ramadhas *et al.*, 1975).

In order to understand the mass distribution of trace metals in mangroves Silva *et al.* (1990) studied the mass contribution of trace metals in the first 50 cm of the sediments and on the biomass of the major plant compartments of the Itacuruçá Experimental Forest, SE Brazil. The resultant mass balance is shown on table 6.7.

The results of such estimate show that the mass distribution of trace metals is not proportional to the mass distribution of the different compartments in the forest. While the relationship between the mass of sediment and the total biomass is only 58, the mass relationship between the mass of trace metals in the sediments and in the biomass of mangroves ranged from a minimum of 110 and 165 for Cu and Mn respectively and a maximum of 200 to 1,000 for Fe and Zn respectively.

These results clearly demonstrate that mangrove forests do not accumulate nor reflect the trace metal concentrations of mangrove soils, although in other tropical forests the biomass is the major reservoir of

nutrients and of trace metals, rather than the soil (Golley *et al.*, 1978).

Table 6.8 gives the mass distribution of trace metals in different compartments of *Rhizophora mangle* biomass. The results clearly show the importance of below-ground roots in trace metal accumulation. For Fe for example, although below-ground root biomass is only 20% of the total biomass, 94% of the Fe mass were accumulated in the roots. This result is a clear indication of the presence of iron-plaques in mangrove roots which correspond to 66.7% of the total Cu and 49.3 % of the total Zn concentrations. On the other hand, the retention of Mn in the roots is very inefficient since only 10% of the Mn mass is stored in the total root biomass which represents *circa* 20% of the total tree biomass. Manganese, however, was the only metal showing significant accumulation in leaves reaching over three times the mass expected taking into account only the biomass ratio for this compartment. Similar results were reported for *R. mangle* growing in a Puerto Rico forest (Table 6.9) by Ragsdale & Thorhaug (1980).

For all other metals, mangrove leaves had very low contents as expected, in particular for Fe and Cu with total metal mass at least one order of magnitude lower than the respective biomass of these compart-

ments. Since leaves are the compartment with faster cycling rates and the major route for trace metals transfer from plants to soil, and eventually to adjacent coastal waters, it is clear that a minor proportion of metals incorporated in mangrove trees will cycle through the ecosystem. The preferential incorporation of trace metals takes place in perennial tissues of mangrove trees, and makes these compartments semi-permanent sinks of trace metals. Therefore, both at the abiotic level (stable, low-bioavailable compounds in soils) and biological (through fixation in root iron-plaques and perennial tissues), trace metals are efficiently trapped in mangroves, suggesting that these ecosystems are efficient biogeochemical barriers for trace metals in tropical coastal areas.

The data discussed here strongly suggest that mangrove plants are inefficient accumulators of trace metals and therefore are poor biological monitors for trace metals contamination. However, the mangrove ecosystem as a whole may play an important role as a biogeochemical barrier to trace metal transport in coastal areas. At the soil level, mangroves keep trace metals unavailable to plant uptake. At the plant level they display physiological mechanisms which make trace metals uptake extremely difficult, fixing them on the outer surface of roots. By preferentially accumulating trace metals in perennial tissues, and keeping

Table 6.7. Mass distribution of trace metals in sediments and biomass of a fringe mangrove forest in SE Brazil (Silva *et al.*, 1990). (kg.ha⁻¹).

Compartment	Mass	Mn	Fe	Zn	Cu
Sediment	4,799,604	390	33,492	150	13
(% of total)	(98.3)	(99.4)	(99.9)	(99.5)	(99.1)
Biomass	81,707	2.4	17.5	0.7	0.12
(% of total)	(1.7)	(0.6)	(0.1)	(0.5)	(0.9)
Sediment/biomass	58	165	1,000	200	110

Table 6.8. Mass distribution of biomass and trace metals in different compartments of a *R. mangle* forest in SE Brazil, after Silva *et al.* (1990) (kg.ha⁻¹).

Compartment	Mass (%)	Mn (%)	Fe (%)	Zn (%)	Cu (%)
Below-ground roots	16,334 (20.0)	0.25 (10.2)	16.51 (94.6)	0.33 (49.3)	0.08 (66.7)
Aerial roots	16,762 (20.1)	0.26 (10.7)	0.14 (0.8)	0.12 (17.9)	0.01 (8.3)
Trunks	31,422 (38.6)	0.64 (26.2)	0.39 (2.2)	0.11 (16.4)	0.02 (16.6)
Branches	12,912 (15.9)	0.87 (35.7)	0.25 (1.4)	0.08 (11.9)	0.01 (8.3)
Leaves	4,202 (5.2)	0.42 (17.2)	0.16 (0.9)	0.03 (4.5)	<0.01 (<0.1)

Table 6.9. Mass distribution of biomass and trace metals in different compartments of a *R. mangle* forest in Puerto Rico, after Ragsdale & Thorhaug (1980) (kg.ha⁻¹).

Compartment	Mass (%)	Fe (%)	Zn (%)	Cu (%)
Below-ground roots	55,500 (43.7)	45.1 (71.1)	0.70 (68.1)	0.89 (82.3)
Aerial roots	17,700 (13.6)	49.5 (24.9)	0.19 (5.9)	0.21 (6.2)
Trunks	50,200 (38.6)	1.91 (2.7)	0.29 (25.6)	0.13 (10.8)
Leaves	6,600 (5.1)	(0.01)	0.03 (0.4)	0.04 (0.5)

leaf concentrations low, mangrove trees also act as a long term sink these pollutants. Therefore, mangrove ecosystems have a significant role in trace metal contamination control in tropical coastal areas.

7. Trace metals concentration and distribution in mangrove animals

Trace metal contamination of mangrove animals has been poorly studied. A generalized pattern of their distribution cannot be described at present. Mercury has been one of the most studied elements, and since its major sources are diffuse, its behavior may be typical of this type of contaminant. In general, most studies have dealt with the contamination of molluscs, due to the facility of collecting these organisms and their high concentration factors. For example, in the mangroves of the Botafogo River, northeastern Brazil, mangrove oysters show concentration factors (CF) for Hg, ranging from 750 to 1,500, relative to the water total Hg concentrations (CF = Hg concentration in oyster/Hg concentrations in water and/or sediments) (Meyer, 1996).

The high concentration factors frequently found in filter feeding organisms, are due to a multiple exposure of the oyster to many environmental compartments containing trace metals. As filter feeding organisms, they incorporate their trace metal load through direct absorption of dissolved metals from the water and from the ingestion of contaminated suspended particles and resuspended bottom sediments. Although dissolved trace metals are more bioavailable than other forms, sediments can also be a significant source of contaminants in the changing tidal estuarine environment (Bryan, 1986; King & Davies, 1987).

Evidence from temperate studies suggests that suspended matter is more important as a source of trace metals to invertebrates than seawater. The availability of trace metals in suspended particles will depend on the chemical bond and on the stability of the metal-particle interaction, facing digestion. Studies by Bryan (1984, 1986) have shown that trace metals bound to biogenic carbonates and organic matter are incorporated more efficiently by bivalves than those bound to Fe and Mn precipitates. Di Toro (1990) showed that trace metals precipitated as sulfides are practically non available to filter feeding organisms. In the mangrove environment, conditions are generally reducing, and there is abundance of organic matter and fine sediments that may complex trace metals as stable organic-metal compounds, or by strong adsorption onto clays and/or precipitation as sulfides, thus decreasing their bioavailability to particle-feeding animals (Harbinson, 1986a; Lacerda, 1993; Carvalho & Lacerda, 1992). This may result in a lower trace metal content in animals living in mangroves as compared to those living in adjacent coastal waters.

Lacerda *et al.* (1983) and Pfeiffer *et al.* (1985) found concentrations of Zn, Cd, Cu, Cr and Pb in the mangrove oyster *Crassostreaa (rhizophorae) brasili-ana*, one order of magnitude lower in animals collected inside mangroves than in animals collected in adjacent coastal waters, in SE Brazil. These animals were submitted to the same trace metal sources. Therefore, the only explanation of these results is the lower bioavailability of trace metals in mangrove environments relative to coastal waters. However, due to the scarcity of data, no generalization of this preliminary information is possible.

Mangrove animals, particularly molluscs, have been used in some studies mostly for monitoring purposes. Contrary to the macroalgae, other typical

monitoring organisms, with very low biomass and small size in mangrove ecosystems that frequently occur mixed with fine sediments, molluscs are abundant, have a relatively large size and large biomass. Therefore, these animals are ideal for monitoring purposes.

Crassostraea (rhizophorae) brasiliiana for example, was used in the monitoring of the spatial and temporal distribution of Zn, Cd, Cr and Fe along the SE coast of Rio de Janeiro, an area dominated by mangroves. The results showed that this oyster species responds well to the spatial distribution of environmental concentrations of these pollutants. A certain amount of seasonal variation was reported, causing difficulty for a proper monitoring of the temporal variability of the pollutant concentrations (Lima *et al.*, 1986). In a study with the same objective, Meyer (1996) found no seasonal variation in the Hg content of *Crassostraea (rhizophorae) brasiliiana* along the Canal de Santa Cruz mangroves in northeastern Brazil, but found significant positive correlation between Hg content in oysters and the concentrations in suspended and bottom sediments.

A summary of the data on the trace metal concentrations in mangrove animals is shown on table 7.1. Contrary to concentrations in plants, the results for animals are always given in wet weight. The data clearly show that no conclusion whatsoever can be drawn because of shortage of data.

Even fewer studies have dealt with the factors affecting trace metal concentrations in mangrove animals. Lacerda *et al.*, (1983) found decreasing trace metal concentrations with size in the mangrove mussel *Mytella guyanensis*, a relationship frequently reported for temperate mussels, due to faster metabolic rates of younger organisms. However, Cd showed an inverse relationship with size, suggesting a net accumulation of this toxic metal with increasing animal size (figure 7.1). For essential elements such as Cu, the concentrations were nearly constant regardless of body size, suggesting that essential trace metals may be physiologically controlled to an optimum necessary for the functioning of the animal's metabolism.

Unfortunately many more studies are necessary to draw a general picture of the fate of trace metals in mangrove animals. This, however, is a crucial and urgent step, due to the socio-economic importance of

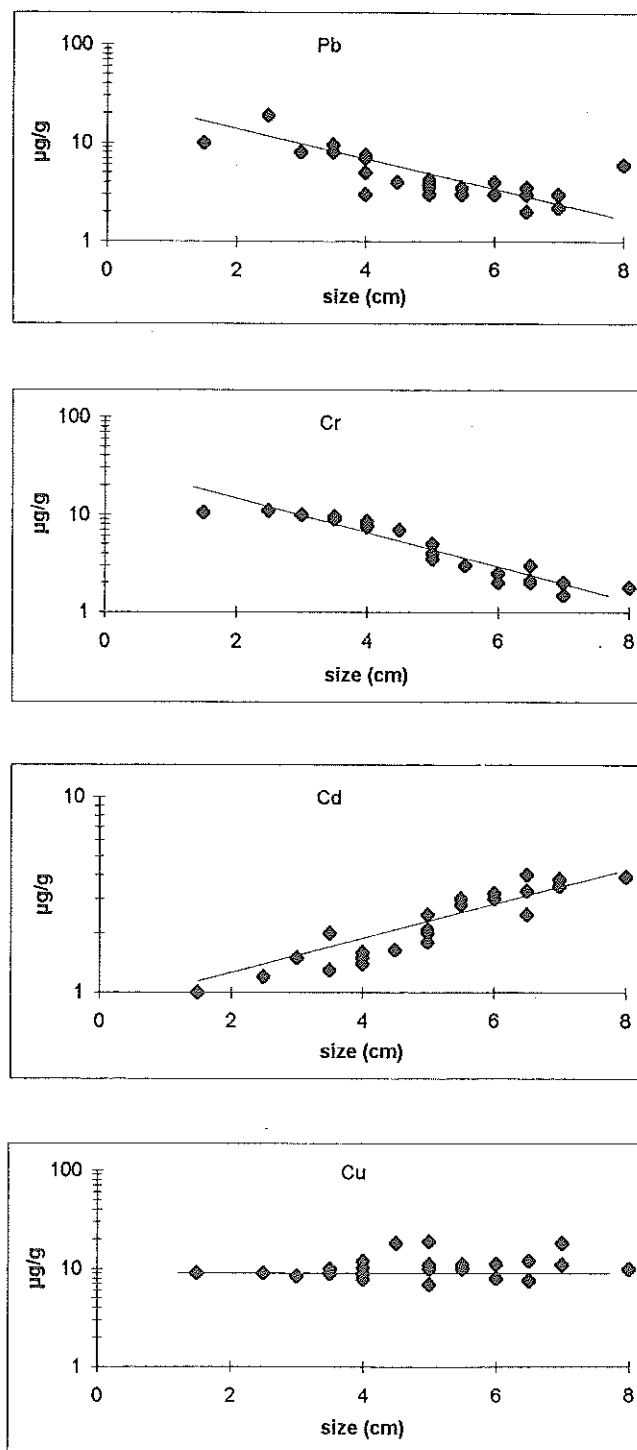


Figure 7.1. Size and trace metal concentration in the mangrove mussel *Mytella guyanensis* from SE Brazil (Lacerda *et al.* (1983)).

mangrove animals for many coastal populations, and the fact that animals are the potential pathway to the transfer of pollutants to humans in coastal environments.

Table 7.1. Concentrations of selected trace metals in mangrove animals ($\mu\text{g}\cdot\text{g}^{-1}$ wet weight).

Animal	Site	Cd	Hg	Zn	Author
<i>Lile piquitinga</i>	Recife, NE Brazil	-	0.09	-	Meyer (1996)
<i>Anchovia clupei</i>	Recife, NE Brazil	-	0.08	-	Meyer (1996)
<i>Crassostraea rhizophorae</i>	Recife, NE Brazil	-	0.2-0.4	-	Meyer (1996)
<i>Crassostraea rhizophorae</i>	Sepetiba, SE Brazil	0.3-0.7	-	430-650	Pfeiffer <i>et al.</i> (1985)
<i>Mytella guyanensis</i>	Sepetiba, SE Brazil	<0.1-0.2	-	5.6-18	Feema (1997)
<i>Mytella guyanensis</i>	Sepetiba, SE Brazil	0.2-0.9	-	4.5-84	Lacerda <i>et al.</i> (1983)
<i>Cardisoma sp.</i>	SE Brazil	<0.1-1.4	-	14-106	FEEMA (1997)

8. Diffuse pollutants interactions with global environmental impacts on mangroves

The biogeodynamics of pollutants originated from diffuse sources, contrary to most of those derived from direct, point sources, may be affected by anthropogenic impacts which cause changes in ecological, physical and chemical conditions of mangrove ecosystems. The interactions between the biogeodynamics of pollutants from diffuse sources and other environmental impacts on mangroves may act at two levels. First, impacts can affect the mobilization of the pollutant proper and second, a given impact can alter the capacity of a mangrove ecosystem to immobilize pollutants. Among the many anthropogenic impacts on mangroves which may affect pollutant biogeodynamics, the most important is changing hydrological patterns and salinity regime due to engineering works at mangrove watersheds, dredging of waterways, and the disposal of aquaculture, agriculture and urban wastes in mangrove basins. Also, "natural" impacts can influence pollutant biogeochemistry in mangroves, in particular storms and hurricanes and relative sea level rise (table 8.1).

Hydrological changes in mangrove basins, mostly caused by canalization, increases the flux of particle-bound trace metals as well as organic micropollutants, leached from soils. However, it also results in increasing sedimentation rates and consequently increasing pollutant burial rates. For example, in Sepetiba Bay, SE Brazil, canalization of the São Francisco canal, resulted in an increase by a factor of 10 of the fluvial load. As a result, sedimentation rates in mangrove dominated sites increased from $0.12 \text{ cm}\cdot\text{yr}^{-1}$ to $0.54 \text{ cm}\cdot\text{yr}^{-1}$ and $0.78 \text{ cm}\cdot\text{yr}^{-1}$ (Barcellos, 1995). This

increased sedimentation reduces surface trace metal concentrations in the Bay's bottom sediments due to dilution and increased trace metal burial rates (Barcellos *et al.*, 1997). Decrease in porewater salinity can also be induced by increasing fresh water supply and may augment mangrove productivity in saline stressed areas leading to enhanced mangrove accumulation capacity for pollutants.

Dredging of navigation canals is the adjacent open waters and construction of breakwaters have an opposite effect on sedimentation rates. Here increase in erosion rates is expected, resulting in the removal of buried pollutants from mangrove sediments. For example, the construction of the protection moles for the Lagos harbor, Nigeria, resulted in intense erosion of coastal sediments and a regression of the coast line at a rate of 25 to 30 meters per year (Adegbe, 1996). Mobilization of buried pollutants occur not only through the physical transport by stronger tidal currents, but also by putting pollutants into a different chemical environment from the one found in the sediment column, changing the equilibrium between dissolved and particulate phases. Similar results are also expected due to construction of dams upstream, with the consequent decrease in freshwater supply to mangroves.

Building of aquaculture ponds in mangrove areas is a major issue at present for mangrove conservation strategies. For example, shrimp ponds are reported to have substituted nearly 200,000 ha of mangroves in Ecuador (Bodero, 1993). In India aquaculture farms release nearly 3 million m^3 per day of effluents to coastal areas (Ramachandran, 1996). The construction of ponds results in rapid changes in sediment chemical conditions, in particular on the redox

Table 8.1. Interactions between pollutant biogeochemicals and other environmental impacts on mangrove ecosystems.

Impact	Effects
1. Canalization of basin fluvial systems	<ul style="list-style-type: none"> - increased particle-bound pollutant flux due to increasing suspended sediment load to coastal waters - increased pollutant burial rates due to increasing sedimentation
2. Dredging of navigation canals	<ul style="list-style-type: none"> - enhanced pollutant removal from sediments and export to the sea due to increasing erosion from stronger tidal currents - increasing wash out of deposited litter and its metal load
3. Pond aquaculture	<ul style="list-style-type: none"> - dissolution of precipitated metal sulfides due to increasing redox potential of pore waters
4. Increasing sewage input	<ul style="list-style-type: none"> - increased metal sulfide precipitation due to increasing oxygen consumption
5. Relative sea level rise	<ul style="list-style-type: none"> - increased particle-bound pollutant flux to the sea due to increasing erosion - increased heavy metals mobilization due to more efficient leaching of deposited metals by saline pore waters - increased heavy metals uptake by plants due to decreasing efficiency of physiological barriers at the root level - speed up of metal cycling through accelerating leaf turnover.

potential of sediment porewater. During the construction and infill up of ponds, fast oxidation of anoxic sediment layers occurs. Under this newly created oxidizing environment, precipitated metal sulfides are dissolved and mobilization of metals to pore waters and tidal currents take place, resulting in high dissolved metal concentrations and contamination of the species under culture. This is particularly serious for shrimp aquaculture, since shrimp larvae are particularly sensitive to high concentration of dissolved heavy metals.

As a result from fast urbanization of coastal areas, increasing loads of urban sewage takes place in many mangrove areas. Oxidation of organic matter from sewage results in strong anoxia of mangrove waters. At first instance, decreasing redox conditions will favor metal precipitation as sulfides. However, in the long term, permanent anoxia may affect mangrove plant's metabolism, decreasing their capacity for immobilizing heavy metals and for decreasing iron plaque production, or reducing filtration capacity as for the Rhizophoraceae.

The impacts of relative sea level rise upon mangrove biogeochemistry have been recently reviewed (UNEP, 1994). It may result in increasing erosion of mangrove sediments causing a larger flux of particulate heavy metals to the ocean. Also, washout of deposited litter may increase, accelerating the transfer of pollutants associated with mangrove leaf litter to

coastal food chains. Saline intrusion may efficiently leach heavy metals deposited in the basin soils. Also, more saline pore waters are able to enhance heavy metals mobilization in the sediments. For example metals deposited in bottom sediments from coastal lagoons of different salinity show different availability, regardless of the total amount present in sediments (Lacerda, 1993).

Apart from enhancing heavy metal mobilization in the sediments, increasing salinity leads to stress conditions of mangrove trees which results in lowered efficiency in blocking metal uptake, such as decreasing of iron plaque formation and imbalance of salt uptake control mechanisms. Heavy metals concentrations in leaves of mangrove plants are significantly correlated with sediment salinity (Lacerda *et al.*, 1985b), rather than with sediment trace metal concentrations, meaning that salinity may effectively control at least part of the trace metal uptake by mangrove plants. Since higher salinity also accelerates leaf turnover rates, the cycling of heavy metals in mangroves may be accelerated, resulting in a larger supply of pollutants to marine food chains.

The short discussion above intends to put forward an issue which may be of high significance to the conservation of mangrove forests. Since direct effluents of pollutants released directly into mangroves are being extensively controlled by governmental authorities in

most countries, the remobilization of existing pollutants due to unrelated anthropogenic impacts, may become the major threat to these ecosystems. This may result in time-delayed and spatially displaced effects, difficult to forecast and nearly impossible to prevent.

9. Summary and outlook

Trace metals reach mangrove ecosystems mostly from diffuse sources, such as atmospheric deposition, tidal transfer, flooding of rivers and continental runoff. Although direct inputs can be important in selected sites, as in mining districts, they are being controlled in most countries. The biogeochemical processes dominating the mangrove sediments result in a natural accumulation mechanism and relatively high trace metal concentrations, even when the anthropogenic influence is small. However, under pristine conditions, these same mechanisms (sulfate reduction/sulfide precipitation and organic matter complexation) keep most trace metals under chemical forms of very low availability to the biota. Therefore, mangrove ecosystems are a natural sink for trace metals.

Mangrove plants incidentally use their mechanisms of salt uptake control and of oxidation of their rhizospheres to make trace metal uptake difficult. Even when some trace metals are incorporated into plants, they are preferentially accumulated in perennial tissues, in particular trunks, which augments their residence time in the forest biomass. This also results in relatively low trace metal concentrations in mangrove detritus, when compared to the trace metal concentrations in suspended particulate matter from adjacent coastal waters.

Unfortunately, very few data exist on trace metal contamination of mangrove animals. Although the low bioavailability of trace metals in the mangrove environment will result in low trace metal concentrations in animals, the great socio-economic importance of the mangrove fauna to coastal human populations, requires that intensive research should be dedicated to this subject.

The resistance of mangroves to trace metal pollution and its character of long term sinks, may allow these ecosystems to be used as an economically

interesting alternative for treating some urban and industrial effluents, after a proper evaluation of each specific situation. Notwithstanding this, the sink capacity of mangroves to trace metals will be limited, but the threshold of the accumulation process, without significantly affecting the mangrove organisms, is probably very site specific and still unknown. Since the processes responsible for the sink character of mangroves are biologically mediated and are dependent on the maintenance of the mangroves natural physical and chemical conditions, time delayed effects of trace metal contamination can occur, following disturbances of the mangrove environment. Of greater significance are those anthropogenic activities which result in erosion and oxidation of mangrove sediments, such as deforestation, dredging and canalization. In the long term, relative sea level rise and changes in land use, may also trigger deleterious effects of the accumulated trace metals.

The general scarcity of data on a global basis on the impacts of trace metals and diffuse pollution on mangroves, calls for an urgent extensive survey on the situation, in particular in rapid developing tropical countries, both to evaluate mangrove utilization as a natural defense against pollutants and as a potential source of such substances in areas where mangroves are threatened by impacting anthropogenic activities.

10. Acknowledgments

This report is part of the project "Trace Metal Biogeochemistry and Diffuse Pollution in Mangrove Ecosystems", supported by the International Society for Mangrove Ecosystems (ISME), Japan, with funds from the Japan International Forest Promotion Cooperation Centre. The author is indebted to the Secretariat of ISME for helping with final editing of the manuscript.

Figure 5.6 of this report is a courtesy of Mr. Luiz Carlos Pires, and was taken at the University of Kobe, Japan, with support from the Japan International Cooperation Agency (JICA).

I am also indebted to the Universidade Federal Fluminense (UFF) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq),

Brazil, for the continuous support of my work on the subject.

11. References

- Adegbie, A.T. 1996. The Nigerian coastal zone: Problems and response measures. *Proceedings of the International Symposium on Socio-economic Benefits of Integrated Coastal Zone Management*. CDG/GKSS, Bremen, pp. 111-113.
- Aksornkoae, A & Saraya, A. 1987. Effects of tin mining on mangrove ecosystem in Ranong, Thailand. *In: Mangroves of Asia and the Pacific: Status and Management*. UNESCO-UNDP, Quezon City, pp. 367-382.
- Aller, R.C.; Blair, N.E.; Xia, Q. & Rude, P.D. 1994. Remineralization rates, recycling and storage of carbon in Amazon shelf sediments. *Continental Shelf Research* (in press).
- Alongi, D.M.; Boyle, S.G.; Tirendi, F. & Payn, C. 1996. Comparison and behavior of trace metals in post-oxic sediments of the Gulf of Papua, Papua New Guinea, *Estuarine Coastal & Shelf Science* 42: 197-211.
- Altschuler, Z.S. 1983. Sulfur diagenesis in Everglades peat and origin of pyrite in coal. *Science* 221:221-227.
- AlvarezLeón, R. 1993. Mangrove ecosystems of Colombia. *In: Lacerda L.D. (ed.) Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions*. International Society for Mangrove Ecosystems, Okinawa, pp.75-114.
- Aragon, G.T. 1997. *Formação de Pirita em Ecossistemas de Manguezal*. PhD Thesis. Dept. Geoquímica, Univ. Federal Fluminense, Niteroi, 165p.
- Aragon, G.T.; Pires, V.S.; Lacerda L.D. & Patchineelam, S.R. 1986. Distribuição espacial de nutrientes e metais pesados em sedimentos e águas superficiais em um ecossistema de manguezal. *Acta Limnologica Brasiliensia*, 1: 365-385.
- Araújo, D.S.D. & Maciel, N.C. 1979. *Os Manguezais do Recôncavo da Baía de Guanabara*. Fundação Estadual de Engenharia do Meio Ambiente, Rio de Janeiro, 114p.
- Armstrong, Y. 1978. Root aeration in the wetland condition. *In: D.E. Hook & R.M. Crawford (eds.), Plant Life in Anaerobic Environments*. Ann Arbor Sci. Publ., Michigan, pp: 269-298.
- Augustinus, P.G.E.F. 1978. The changing shoreline of Suriname (South America). *Uitgaven Natuurwetenschappelijke Studierkring vor Suriname en de Nederlandse Antillen* 95:1232.
- Aveline, L.C. 1980. Fauna dos manguezais Brasileiros. *Revista Brasileira de Geografia* 42:786-821.
- Bacon, P.R. 1970. *The Ecology of Caroni Swamp*. Trinidad. Spec. Publ. Central Statistics Office, Port of Spain, Trinidad, 68p.
- Bacon, P.R. 1993. Conservation and Utilization of mangroves in the Lesser Antilles, Jamaica and Trinidad and Tobago. *In: Lacerda L.D. (ed.) Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions*. International Society for Mangrove Ecosystems, Okinawa, pp.155-210.
- Badanedeem, A.; Damodaram, K.T.; Sajan, K. & Padmalal, D. 1986. Texture and geochemistry of the sediment of a tropical mangrove ecosystem, Southwestern coast of India. *Environmental Geology* 27:164-169.
- Balikungeri, A.; Robin, D. & Haerdi, W. 1985. Manganese in natural waters. Evidence for microbial oxidation of Mn(II). *Toxicology & Environmental Chemistry* 9: 309-325.
- Barcellos, C. 1995. *Biogeoquímica de Cd e Zn na Baía de Sepetiba, Rio de Janeiro*. PhD Thesis, Universidade Federal Fluminense, Niteroi, 184p.
- Barcellos, C. & Lacerda, L.D. 1994. Cadmium and zinc source assessment in Sepetiba Bay, SE Brazil. *Environmental Monitoring and Assessment* 29: 183-199.

- Barcellos, C.C.; Fernandes, H.M. & Azevedo, H.L.P. 1988. The role of the Arroio Pavuna river in the transport of particulate heavy metals to Jacarepaguá lagoon, Brazil. *The Science of the Total Environment* 75: 211-223.
- Barcellos, C.; Censi, R.C. & Lacerda, L.D. 1997. Sediment budget in a tropical bay, Sepetiba Bay, Brazil. *Environmental Geology* (in press).
- Batley, G.E. 1987. Heavy metal speciation in waters, sediments and biota from Lake Macquarie, New South Wales. *Australian Journal of Marine and Freshwater Research* 38: 591-606.
- Behrendt, H. 1993. Separation of point and diffuse loads of pollutants using monitoring data of rivers. *Water Science & Technology* 28: 165-175.
- Berner, R.A. 1982. Burial of organic Carbon and pyrite sulfur in the modern oceans: its geochemical and environmental significance. *American Journal of Science* 282: 451-473.
- Berner, R.A. 1984. Sedimentary pyrite formation: An update. *Geochimica Cosmochimica Acta*, 48: 605-615.
- Bhosale, L.J. 1979. Distribution of trace elements in the leaves of mangroves. *Indian Journal of Marine Sciences* 8: 58-59.
- Blasco, F. 1984. Climatic factors and the biology of mangrove plants. In: *The Mangrove Ecosystem: Research Methods*. UNESCO. Paris, pp:18-35.
- Bodero, A. 1993. Mangrove swamp ecosystems of Ecuador. In: L.D. Lacerda (ed.), *Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions. Part I. Latin America*. International Society for Mangrove Ecosystems, Okinawa, pp: 88-103.
- Botello, A.V. & Mendelewicz, M. 1988. Pollution and pollutants in the Terminos Lagoon region. In: A. Yañez-Arancibia & J.W. Day Jr. (eds.), *Ecology of Coastal Ecosystems in the Southern Gulf of Mexico: The Terminos Lagoon Region*. Univ. Nac. Autonoma de México, México, DF, pp:415-430.
- Boulegue, J.; Lord, C.J. & Church, T.M. 1982. Sulfur speciation and associated trace metals (Fe and Cu) in pore water of Great Marsh, Delaware. *Geochimica Cosmochimica Acta* 46: 453-464.
- Bourg, A.C.M. 1988. Metals in aquatic and terrestrial systems: Sorption, speciation and mobilization. In: *Chemistry and Biology of Solid Wastes*. Salomons, W. & Förstner, U. (eds.), Springer Verlag, Berlin, pp: 3-32.
- Bowen, H.J.M. 1979. *Environmental Chemistry of the Elements*. Academic Press, London, 333p.
- Breteler, R.J.; Valiela, I. & Teal, J.M. 1981. Bioavailability of mercury in several northeastern U.S. *Spartina* ecosystems. *Estuarine Coastal & Shelf Science* 12: 155-166.
- Brinkman, R. & Pons, L.J. 1968. *A PedoGeomorphological Classification and Map of the Holocene Sediments in the Coastal Plain of the Three Guyanas*. Netherlands Soil Survey Institute, Wageningen, 40p.
- Brown, B.E. 1988. Fate of metals in biota and biological interactions in the tropical coastal zone. In: U. Seeliger; L.D. Lacerda, & S.R. Patchineelan (eds.) *Metals in Coastal Environments of Latin America*. Springer-Verlag, Berlin, pp: 109-121.
- Bryan, G.W. 1984. Pollution due to heavy metals and their compounds. *Marine Ecology* 5: 1289-1431.
- Bryan, G.W. 1986. Copper, zinc and organotin as long-term factors governing the distribution of organisms in the Fal Estuary in south-west England. *Estuaries* 10: 208-219.
- Camacho-Ibar, V.F. & Alvarez-Borrego, S. 1988. Nutrient concentrations in pore waters of intertidal sediments in a coastal lagoon: patchiness and temporal variations. *The Science of the Total Environment* 75: 325-339.
- Campbell, J.H. & Evans, R.D. 1987. Inorganic and organic ligands binding of lead and cadmium and resultant implications for bioavailability. *The Science of the Total Environment* 62: 219-227.

- Carlson, P.R.; Yarbro, L.A.; Zimmermann, C.F. & Montgomery, J.R. 1983. Pore water chemistry of an overwash mangrove island. *Florida Scientist* 46: 239-249.
- Carter, M.R.; Burns, L.A.; Cavinder, T.R.; Dugger, K.R.; Fares, P.L.; Hicks, D.B.; Revells, H.T. & Schmidt, T.W. 1973. *Ecosystem Analysis of the Big Cypress Swamp and Estuaries*. USEPA, Region IV, Atlanta, Georgia. USEPA 904/1974002.
- Carvalho, C.E.V. 1992. *Distribuição de Metais Pesados em Sedimentos da Plataforma Continental Nordeste e Sudeste do Brasil*. MSc Thesis. Universidade Federal Fluminense, Niteroi, 91p.
- Carvalho, C.E. V. & Lacerda, L.D. 1992. Heavy metals in the biota of Guanabara Bay, why such low concentrations. *Ciencia & Cultura* 44: 184-186.
- Carvalho, C.E.V.; Lacerda, L.D.; Rezende, C.E.; Ovalle, A.R.C. & Abrão, J.J. 1993. The fate of heavy metals in sediments of the northeastern and southeastern Brazilian continental shelf. *Proceedings of the 9th International Conference on Heavy Metals in the Environment*, Toronto, CEP Consultants, Edinburgh, pp: 153-156.
- Casagrande, C.S. 1977. Sulfur in peat forming system of the Okefenokee swamp and Florida Everglades: Origin of sulfur in coal. *Geochimica Cosmochimica Acta* 41: 161-167.
- Chapman, V.J. 1976. *Mangrove Vegetation*. Cramer, Vaduz, 447p.
- Chiu, C.Y. & Chou, C.H. 1991. The distribution and influence of heavy metals in mangrove forests of the Tamshui Estuary in Taiwan. *Soil Science and Plant Nutrition* 37: 659-669.
- Comans, R.N.J. & van Dijk, C.P.J. 1988. Role of complexation processes in cadmium mobilization during estuarine mixing. *Nature* 336: 151-154.
- Conde, J.E. & Alarcón, C. 1993. A review of current knowledge and status of Venezuelan mangroves. In: L.D. Lacerda (ed.), *Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions. Part I. Latin America*. International Society for Mangrove Ecosystems, Okinawa, pp: 211-243.
- Cordeiro-Marino, M.; Braga, M.R.A.; Eston, V.R.; Fujii, M.T. & Yokoya, N.S. 1992. Mangrove macroalgal communities of Latin America: The state of the art and perspectives. In: Seeliger, U. (ed.), *Coastal Plant Communities of Latin America*, Academic Press, San Diego, p:5164.
- Cossu, R., Fraja Frangipane, E.; Degobbis, D.; Orio, A.A. & Andreottola, G. 1987. Pollution and eutrophication in the Venice Lagoon. *Water Science & Technology* 19: 813-822.
- Costa, C.S.B. & Davy, A.J. 1992. Coastal salt marsh communities of Latin America. In: Seeliger, U. (ed.), *Coastal Plant Communities of Latin America*, Academic Press, San Diego, p:179199.
- Crawford, E.A., Roy, P.S.; Brooks, K.; Zamberlain, A.; Scott, T.; MacKay, N.J. & Chrojka, R. 1976. *Heavy Metals in Bottom Sediments and Fish from Lake Macquarie*. Report, Geological Survey of NSW, GS 1976/283.
- Day, J.W.; Conner, W.H.; Day, R.H.; LeyLou, F. & Navarra, A.M. 1988. Productivity and composition of mangrove forests at Boca Chica and Estero Pargo. In: Yañez-Arancibia, A. & Day, J.W. (eds.) *Ecology of Coastal Ecosystems in the Southern Gulf of Mexico: The Términos Lagoon Region*. Ed. Universitaria, Mexico, DF, pp:237258.
- D'Croz, L. 1993. Mangrove uses and conservation in Panama. In: L.D. Lacerda (ed.), *Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions. Part I. Latin America*. International Society for Mangrove Ecosystems, Okinawa, pp:115-128.
- D'Croz, L. & B. Kwiecinski. 1980. Contribución de los Manglares a las Pesquerías de la Bahía de Panamá. *Revista de Biología Tropical* 28: 1329.
- Degens, E.T. & Ittekkot, V. 1985. Particulate organic carbon. An overview. *Mitt. Geologische Paläontologische Institut Universität Hamburg* 58: 7-27.

- Diop, E.S. 1993. Status of mangrove ecosystems in Africa: In: Lacerda, L.D. & C.D. Field (eds.). *Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa*. International Society for Mangrove Ecosystems (ISME), Okinawa, pp:2122.
- Di Toro, D.M. 1990. Toxicity of the cadmium in sediments: the role of acid volatile sulfides. *Environmental Toxicological Chemistry* 9: 1487-1502.
- Dolianiti, E. 1955. Frutos de *Nypa* no Paleoceno de Pernambuco, Brasil. *Boletim da Divisão de Geologia DNPM* 158:136.
- Duke, N. 1992. Mangrove Floristics and Biogeography. In: A.I. Robertson and D.M. Alongi (eds.) *Tropical Mangrove Ecosystems*. American Geophysical Union, Washington, pp: 43100.
- Febvay, G. & Kermarrec, A. 1978. Quelques paramètres physicochimiques de la forêt littorale (mangrovê et forêt palustre) et leur évolution. *Bulletin Liaison du Groupe de Travail Mangrove et Zone Côtière*, 4:7073.
- FEEMA, 1997. *Mapeamento de Sedimentos da Baía de Sepetiba. Contaminação por Metais Pesados*. Relatório Técnico Abril/97. Fundação Estadual de Engenharia do Meio Ambiente, Rio de Janeiro, 39 p.
- Förstner, U. 1989. *Contaminated Sediments*. Lecture Notes in Earth Sciences No. 21. Springer Verlag, Berlin, 138p.
- Förstner, U. 1995. Contaminated aquatic sediments and waste sites: Geochemical engineering solution. In: W. Salomons, U. Förstner & Madsen, P. (eds.), *Heavy Metals: Problems and Solutions*. Springer Verlag, Berlin, pp: 237-258.
- Fowler, S.W. 1982. Biological transfer and transport processes. In: Kullenberg, G. (ed.) *Pollutant Transfer and Transport in the Sea*. CRC Press. Florida, pp: 1-65
- Galloway, R.W. 1982. Distribution and physiographic patterns of Australian mangroves. In: B.F. Clough (ed.). *Mangrove Ecosystems in Australia: Structure, Function and Management*. Australian National University Press. Canberra. pp. 31-54.
- Garcia, H.G. 1989. *Estudio de la contaminación marina por metales pesados en algunas áreas cubanas*. PhD Thesis, Centr. Nac. Investigaciones Científicas, La Habana, Cuba, 68p.
- Golley, F.B.; Odum, H.T. & Wilson, R. 1962. A synoptic study of the structure and metabolism of a red mangrove forest in Southern Puerto Rico in May. *Ecology* 43:918.
- Golley, F.B.; McGinnis, J.T.; Clements, R.G.; Child, G.I. & Duever, H.J. 1978. *Ciclagem mineral en un ecossistema de floresta tropical húmeda*. EPU/EDUSP, São Paulo, 238p
- Gomes, E.D. 1996. Pressures on the coastal zone in developing countries: A recent Phillipine challenge (1994-1996). In: *Proceedings of the International Symposium on Socio-economic Benefits of Integrated Coastal Zone Management*. CDG/GKSS, Bremen, pp: 192-197.
- González-Faria, F.; Flores-Verdugo, F.F. & Hernández-Gaza, M. 1997. Annual variation of particulate organic carbon and mangrove detritus in Agua Brava lagoon, Nayarit, México. In: Kjerfve, B.; Lacerda, L.D. & Diop, E.S. (eds.), *Mangrove Ecosystem Studies in Latin America and Africa*. UNESCO/ISME, Paris, pp. 47-63.
- Graham, A. 1989. Paleofloristic and paleoclimatic changes in the tertiary of northern Latin America. *Reviews of Palaeobotany & Palynology* 60:283293.
- Graham, A. 1992. Utilization of the isthmian land bridge during the Cenozoic: Paleobotanical evidence for timing, and the selective influence of altitude and climate. *Reviews of Palaeobotany & Palynology* 72:119:128.
- Grasshof, K.; Ehrhardt, M. & Kremling, K. 1983. *Methods for Sea Water Analysis*. Verlag Chemie, Nürnberg, 389p.
- Grosso, J.L.; Restrepo, R.; Sanchez, L.E.; Avendaño, D. & Mantilla, I. 1996. Evaluación preliminar de

- la participación de especies de mangle en el control de Bario en aguas de producción. *Ciência, Tecnologia y Futuro* 1:55-65.
- Hall, A.; Duarte, A.C.; Caldeira, M.T.M. & Lucas, M.F.B. 1987a. Sources and sinks of mercury in the coastal lagoon of Aveiro, Portugal. *The Science of the Total Environment* 64: 75-87.
- Hall, A.; Duarte, A.C.; Oliveira, J.P. & Pereira, M.E. 1987b. Release of mercury from polluted sediments under a salinity gradient. In: *Proceedings of the 6th International Conference on Heavy Metals in the Environment*, New Orleans, CEP Consultants Edinburg, 2: 224-226.
- Harbinson, P. 1981. The case for the protection of mangrove swamps: Geochemical considerations. *Search* 12: 273-276.
- Harbinson, P. 1984. Regional variation in the distribution of trace metals in modern intertidal sediments of Northern Spencer Gulf, South Australia. *Marine Geology* 61:221-247.
- Harbinson, P. 1986a. Mangrove mud: a sink and a source for trace metals. *Marine Pollution Bulletin* 17: 246-250.
- Harbinson, P. 1986b. Diurnal variations in the chemical environment of a shallow tidal inlet, Gulf St. Vincent, South Australia: Implications for water quality and trace metal migration. *Marine Environmental Research* 20: 161-195.
- Harris, R.C.; McMahon, J.; Snodgrass, W.J. & Hilemans, O.E. 1993. Sulfide control on methyl mercury and other metals in aquatic systems. In: *Proceedings of the 9th International Conference on Heavy Metals in the Environment*, Toronto, CEP Consultants, Edinburgh, 2: 313-316.
- Heald, E.J. 1969. *The Production of Organic Detritus in a South Florida Estuary*. University of Miami Sea Grant Program, Miami, Florida, 110p.
- Henrichs, S.M. & Farrington, J.W. 1979. Amino acids in interstitial waters of marine sediments. *Nature* 279: 319-322.
- Hong, P.N. & San, H.T. 1993. *Mangroves of Vietnam*. IUCN Wetland Program. International Union for the Conservation of Nature and Natural Resources. Gland, 173p.
- Hong, S.; Candelone, J.P.; Patterson, C.C. & Boutron, C.F. 1996. History of ancient copper smelting pollution during roman and medieval times recorded in Greenland ice. *Science* 272: 246-248.
- Horowitz, A.N. & Elrick, K.A. 1987. Sediment trace element chemistry: Interrelation with surface area, grain size and geochemical substrate. In: *Proceedings of the 6th International Conference on Heavy Metals in the Environment*, New Orleans, CEP Consultants, Edinburgh, 2: 227-229.
- Howarth, R.W. 1979. Pyrite: Its rapid formation in a salt marsh and its importance in the ecosystem metabolism. *Science* 203: 49-50.
- Hunt, C.D. & Smith, D.L. 1983. Remobilization of metals from polluted marine sediments. *Canadian Journal of Fisheries and Aquatic Sciences* 40: 132-142.
- Irion, G. & Muller, G. 1988. Lateral distribution and sources of sediment-associated heavy metals in the North Sea. In: Ittekkot, V.; Kempe, S.; Michaelis, W. & Spitz, A. (eds.). *Facets of Modern Biogeochemistry*. Springer Verlag, Berlin, pp:175-203.
- Ittekkot, V. 1988. Global trends in the nature of organic matter in river suspensions. *Nature* 332: 436-438.
- Japenga, J.; Wagennar, W.J.; Salomons, W.; Lacerda, L.D.; Patchineelam, S.R. & Leitão, C.M. 1988. Organic micropollutants in the Rio de Janeiro coastal region, Brazil. *The Science of the Total Environment* 75: 169-180.
- Jayasekera, R. 1991. Chemical composition of the mangrove *Rhizophora mangle* L. *Journal of Plant Physiology* 138: 119-121.
- Jeffery, J.; Marshman, N. & Salomons, W. 1988. Behaviour of trace metals in a tropical river basin affected by mining. In: W. Salomons & U. Förstner

- (eds.), *Chemistry and Biology of Solid Wastes*. Springer Verlag, Berlin, pp: 259-274.
- Jones, G.B. & Thomas, F.G. 1988. Effect of terrestrial and marine humics on copper speciation in an estuary in the Great Barrier Reef Lagoon. *Australian Journal of Marine & Freshwater Research* 39: 19-31.
- Jones, G.B.; Burdon-Jones, C. & Thomas, F.G. 1982. Influence of *Trichodesmium* red tides on trace metal cycling at a coastal station in the Great Barrier Reef lagoon. *Oceanologica Acta* sp.: 319-326.
- Jouaneau, J.M. 1982. Matières en Suspension et Oligo Eléments Métalliques dans le Système Estuarien Girondin: Comportement et Flux. T. Dout., Univ. Bordeaux, 242p.
- Kerdijk, H.N. & Salomons, W. 1982. *Heavy Metal Cycling in the Scheldt Estuary*. Delft Hydraulics Report M1640/M1736, Haren, 112p.
- Kersten, M. 1988. Geochemistry of priority pollutants in anoxic sludge, Cadmium, Arsenic, Methylmercury and chlorinated organics. In: *Chemistry and Biology of Solid Wastes*. Salomons, W. & Förstner, U. (eds.), Springer Verlag, Berlin, pp:170-213.
- Kjerfve, B. 1990. *Manual for Investigation of Hydrological Processes in Mangrove Ecosystems*. UNESCO/UNDP. New Delhi, India. 79p.
- Kjerfve, B. & Magill, K.E. 1989. Geographic and hydrodynamic characteristics of shallow coastal lagoons. *Marine Geology* 88: 187-199.
- Kjerfve, B.; Lacerda, L.D.; Rezende, C.E. & Ovalle, A.R.C. 1997. Hydrological and hydrochemical variations in mangrove ecosystems. In: A. Yáñez-Arancibia (ed.). *Mangrove Ecosystems in Tropical America: Structure, Function and Management*. IUCN-EPOMEX, Campeche, p: (in press).
- Kohlmeyer, J. & Kohlmeyer, E. 1979. *Marine Mycology. The Higher Fungi*. Academic Press, New York, 690p.
- Korte, N.E.; Skopp, J.; Niebla, E.E. & Fuller, W.H. 1975. A baseline study on trace metal elution from diverse soil types. *Water, Air & Soil Pollution* 5: 149-156.
- Krauskopf, K.B. 1979. *Introduction to Geochemistry*. 2nd ed., McGraw-Hill Kogakusha, Tokyo, 423p.
- Kremling, K. 1988. Metal cycles in coastal environments. In: U. Seeliger; Lacerda, L.D. & S.R. Patchineelan, (eds.). *Metals in Coastal Environments of Latin America*. Springer-Verlag, Berlin, pp: 199-214.
- King, D.G. & Davies, I.M. 1987. Laboratory and field studies of the accumulation of inorganic mercury by the mussel *Mytilus edulis* (L.). *Marine Pollution Bulletin* 18: 40-45.
- Krumbein, W.E. 1982. Biogeochemistry and geomicrobiology of lagoons and lagoonary environments. In: *Coastal Lagoon Research, Present and Future*. UNESCO Technical Papers in Marine Sciences no. 33, Paris. pp. 97-110.
- Lacerda, L.D. 1992. Carbon burial in mangrove sediments: a potential source of Carbon during events of sea level change. In: L.D. Lacerda, B. Turcq, B.A. Knoppers & B. Kjerfve (eds.), *Paleoclimatic Changes and the Carbon Cycle*. Soc. Bras. Geoquímica-Univ. Estado do Rio de Janeiro-Dept. Geoquímica-UFF, Rio de Janeiro. pp: 107-114.
- Lacerda, L.D. 1993. *Biogeoquímica de Metais Pesados em Ecossistemas de Manguezal*. Prof. Titular Thesis, Universidade Federal Fluminense, Niteroi, 72p.
- Lacerda, L.D. 1994. Biogeochemistry of heavy metals in coastal lagoons. In: B. Kjerfve (ed.), *Coastal Lagoon Processes*. Elsevier Oceanographic Series n° 60. Elsevier Sci. Publ. Amsterdam, pp:221-241.
- Lacerda, L.D.; Lima, N.R.W.; Pfeiffer, W.C. & Fizman, M. 1983. Size and metal concentration in the mangrove mussel *Mytella guyanensis* from Sepetiba Bay, Brazil. *Revista de Biologia Tropical* 31: 333-335.

- Lacerda, L.D. & Abrão, J.J. 1984. Heavy metal accumulation by mangrove and saltmarsh intertidal sediments. *Revista Brasileira de Botânica* 7: 49-52.
- Lacerda, L.D. & Rezende, C.E. 1985. The effect of *Halodule wrightii* Archers. on the geochemical partitioning of Mn, Zn and Cu in coastal sediments. *5th International Conference on Heavy Metals in the Environment*, Athens, CEP Consultants, Edinburgh, 2: 292-294.
- Lacerda, L.D.; Rezende, C.E.; Jose, D.M.V.; Wasserman, J.C.; Francisco, M.C.F. & Martins, J.C. 1985b. Mineral concentrations in leaves of mangrove trees. *Biotropica* 17: 260-262.
- Lacerda, L.D.; Rezende, C.E.; José, D.M.V. & Francisco, M.C.F. 1986a. Metallic composition of mangrove leaves from the Southeastern Brazilian coast. *Revista Brasileira de Biologia* 46: 385-399.
- Lacerda, L.D.; Rezende, C.E.; Martinelli, L.A.; Ovalle, A.R.C.; Mozetto, A.A.; Nogueira, F.B.; Victoria, R.A.; Aragon, G.T.; Cunha, C.T. & Silva, C.A.R. 1986b. Composição isotópica de carbono em componentes de um manguezal na Baía de Sepetiba, RJ. *Ciência & Cultura* 38: 1714-1717.
- Lacerda, L.D. & Rezende, C.E. 1987. Heavy metal geochemistry in mangrove sediments. In: *Anais do I Simpósio sobre Ecossistemas da Costa Sudeste do Brasil*. São Paulo, 3: 123-131.
- Lacerda, L.D.; Pfeiffer, W.C. & Fiszman, M. 1987. Heavy metals distribution, availability and fate in the Sepetiba Bay, SE-Brazil. *The Science of the Total Environment* 65: 163-173.
- Lacerda, L.D.; Martinelli, L.A.; Rezende, C.A.; Mozetto, A.A.; Ovalle, A.R.C.; Victoria, R.L.; Silva, C.A.R. & Nogueira, F.B. 1988a. The fate of trace metals in suspended matter in a mangrove creek during a tidal cycle. *The Science of the Total Environment* 75: 249-259.
- Lacerda, L.D.; José, D.M.V. & Francisco, M.C.F. 1988b. Nutritional status and chemical composition of mangrove seedlings during development. *Revista Brasileira de Biologia* 48: 401-405.
- Lacerda, L.D.; Rezende, C.E.; Ovalle, A.R.C.; Silva, C.A.R. & Carvalho, C.E.V. 1991a. Annual balance of heavy metals in a mangrove ecosystem in Southeastern Brazil. In: *Proceedings of the 8th International Conference on Heavy Metals in the Environment*. Edinburgh, CEP Consultants, Edinburgh, 1: 539-542.
- Lacerda, L.D.; Aragon, G.T.; Ovalle, A.R.C. & Rezende, C.E. 1991b. Iron and chromium distribution and accumulation in a mangrove ecosystem. *Water, Air, & Soil Pollution*, 57/58: 513-520.
- Lacerda, L.D.; Carvalho, C.E.V.; Tanizaki, K.F.; Ovalle, A.R. & Rezende, C.E. 1993a. The biogeochemistry and trace metals distribution of mangrove rhizospheres. *Biotropica* 25: 252-257.
- Lacerda, L.D.; Pfeiffer, W.C.; Rezende, C.E. & Carvalho, C.E.V. 1993b. Mercury in sediments from the Paraíba do Sul river continental shelf, SE-Brazil. *Marine Pollution Bulletin* 26: 220-222.
- Lacerda, L.D.; Conde, J.E.; Alarcon, C.; Alvarez-León, R.; Bacon, P.R.; D'Croz, L.; Kjerfve, B.; Polania, J. & M. Vannucci. 1993c. *Mangrove Ecosystems of Latin America and the Caribbean: a Summary*. In Lacerda, L.D. (coord.) *Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions, Part I. Latin America*. International Society for Mangrove Ecosystems, ISME, Okinawa, pp.1-72.
- Lacerda, L.D.; Ittekkot, V. & Patchineelam, S.R. 1995. Biogeochemistry of mangrove soil organic matter: A comparison between *Rhizophora* and *Avicennia* soils in southeastern Brazil. *Estuarine Coastal & Shelf Science* 40:713-720.
- Lacerda, L.D. & Salomons, W. 1997. *Mercury from Gold and Silver Mining. A Chemical Time Bomb*. Springer Verlag, Berlin, 210p.
- Lamberti, A. 1969. Contribuição ao conhecimento da ecologia das plantas do manguezal de Itanhaém.

- Boletim da Faculdade de Filosofia Ciências e Letras da Universidade de São Paulo, Serie Botânica* 23: 1-217
- Langstron, W.J., Burt, G.R. & Mingjiang, Z. 1987. Tin and organotin in water, sediments, and benthic organisms of Poole Harbour. *Marine Pollution Bulletin* 18: 634-639.
- Lima, N.R.W.; Lacerda, L.D.; Pfeiffer, W.C. & Fiszman, M. 1986. Temporal and spatial variability studies of Zn, Cr, Cd and Fe concentrations in oyster tissues (*Crassostrea brasiliensis* Lamarck, 1819) from Sepetiba bay, Brazil. *Environmental Technology Letters* 7: 453-460.
- Lindberg, S.E. & Harris, R.C. 1974. Hg-organic matter associations in estuarine sediments and interstitial water. *Environmental Science Technology* 8: 459-462.
- Lindberg, S.E.; Andren, A. & Harriss, R. 1977. Geochemistry of mercury in the estuarine environment. In: *Estuarine Research*, Academic Press, New York, pp: 64-97.
- Lu, J.C.S. & Chen, K.Y. 1977. Migration of trace metals in interfaces of sea water and polluted sediments. *Environmental Science & Technology* 11: 174-182.
- Lucas, M.F.; Caldeira, M.T., Hall, A.; Duarte, A.C. & Lima, C. 1986. Distribution of mercury in the sediments and fishes of the Lagoon of Aveiro, Portugal. *Water Science & Technology* 18: 141-148.
- Lugo, A.E. & Snedaker, S.C. 1974. The ecology of mangroves. *Annual Review of Ecology & Systematics* 5: 39-64.
- Lugo, A.E.; Brown, S. & Brinson, M.M. 1990. Concepts in wetland ecology. In: Lugo, A.E.; Brinson, M.M. & Brown, S. (eds.), *Forest Wetlands. Ecosystems of the World*, Nº15. Elsevier Sci. Publ. Comp., Amsterdam, pp:53-85.
- Lyons, W.B.; Armstrong, P.B. & Gaudette, H.E. 1983. Trace metal concentrations and fluxes in Bermuda sediments. *Marine Pollution Bulletin* 14: 65-68.
- Mackey, A.P.; Hodgkinson, M. & Nardella, R. 1992. Nutrient levels and heavy metals in mangrove sediments from Brisbane River, Australia. *Marine Pollution Bulletin* 24: 418-420.
- Mackey, D.J. & Szymezak, R. 1988. Seasonal variations in the copper complexity capacity of Port Hacking. *Australian Journal Marine & Freshwater Research* 39: 125-132.
- Macnae, W. 1968. A general account on the fauna and flora of mangrove swamps and forests in the Indo-West Pacific region. *Advances in Marine Biology* 6:732-70.
- Marins, R.V.; Lacerda, L.D. & Silva-Filho, E.V. 1996. Atmospheric mercury deposition over Sepetiba Bay, SE Brazil. *Journal of the Brazilian Chemical Society* 9: 77-88.
- Marins, R.V.; Lacerda, L.D.; Paiva, E.C. & Gonçalves, G. 1997a. Effects of *Spartina alterniflora* on the post-depositional mobilization of mercury in salt marsh soils. *Bulletin of environmental Contamination and Toxicology* 58:733-738.
- Marins, R.V.; Lacerda, L.D. & VillasBoas, R.C. 1997b. Mercury inputs to Sepetiba Bay and Basin. *Ciência & Cultura* (in press).
- Mendelsshon, I.A. & Postek, M.T. 1982. Elemental analysis of deposits on the roots of *Spartina alterniflora* Loisel. *American Journal of Botany* 69: 904-912.
- Mephram, R.H. 1983. Mangrove floras of the southern continents. Part 1. The geographical origin of the Indo Pacific mangrove genera and the development and present status of the Australian mangroves. *South African Journal of Botany* 2:18.
- Mephram, R.H and Mephram, J.S. 1985. The flora of tidal forests a rationalization of the use of the term "mangroves". *South African Journal of Botany* 51:7799.
- Meyer, U. 1996. *On the Fate of Mercury in the Northeastern Brazilian Mangrove System, Canal de Santa Cruz, Pernambuco*. Zentrum für Marine

- Tropeökologie, ZMT Contribution No. 3, Bremen, 105 p.
- Milliman, J.D. & Meade, R.H. 1983. Worldwide delivery of river sediments to the ocean. *Journal of Geology* 91: 1-21.
- Mitra, S. 1986. *Mercury in the Environment*. Trans. Tech. Publ. Switzerland, 327p.
- Montgomery, J.R. & Price, M.T. 1979. Release of trace metals by sewage sludge and the subsequent uptake by members of a turtle grass mangrove ecosystem. *Environmental Science & Technology* 13: 546-549.
- Mopper, K.; Dawson, R.; Leibezelt, G. & Ittekkot, V. 1980. The monosaccharid spectra of natural waters. *Marine Chemistry* 10: 55-66.
- Muller, J. 1980. Palynological evidence for Paleogene climatic changes. *Mémoires du Musée National d'Histoire Naturelle de Paris* n.s. 27:211-218.
- Murray, F. 1985. Cycling of fluoride in a mangrove community near a fluoride emission source. *Journal of Applied Ecology* 22: 277-285.
- Nevissi, A. & Schell, W.R. 1975. Distribution of plutonium and americium in Bikini Atoll Lagoon. *Health Physics* 28: 539-547.
- Nickerson, N.H. & Thibodeau, F.R. 1985. Association between porewater sulfide concentrations and the distribution of mangroves. *Biogeochemistry* 1: 183-192.
- Nixon, S.W.; Hunt, C.D. & Nowicki, B.L. 1987. The retention of nutrients (C,N,P), heavy metals (Mn,Cd,Pb,Cu), and petroleum hydrocarbons in Narragansett Bay. In: P. Laner & J.M. Martin (eds.) *Biogeochemical Processes at the Land-sea Boundary*. Elsevier Publ. Co., Netherlands. pp: 99-122.
- Norton, M.G.; Eagle, R.A.; Nunny, R.S.; Rolfe, M.S.; Hardiman, P.A. & Hampson, B.L. 1981. The field assessment of effects of dumping wastes at sea. *Fisheries Research Technical Report* 62: 1- 62.
- Novotny, V. 1995. Diffuse source of pollution by toxic metals and impact on receiving waters. In: W.Salomons; U. Förstner & P. Mader (eds.) *Heavy Metals: Problems and Solutions*, Springer Verlag, Berlin, pp: 33-52.
- Nriagu, J.O. 1989. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279: 409-411.
- Nriagu, J.O. 1990. Global metals pollution: Poisoning the biosphere? *Environment* 32: 7-33.
- Nriagu, J.O. 1996. A history of global metal pollution. *Science* 272: 223-224.
- Nriagu, J.O. & Pacyna, J.M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333: 134-139.
- Osuma, F.P.; Botello, A.V. & Villanueva, J. 1986. Heavy metals in Coatzacoalcos estuary and Ostion lagoon, México. *Marine Pollution Bulletin* 17: 516-519.
- Otte, M.L.; Buijs, E.P.; Riemer, L.; Rozema, J. & Broekman, R.A. 1987. The iron-plaque on the roots of salt marsh plants: a barrier to heavy metal uptake? In: *Proceedings of the 6th International Conference on Heavy Metals in the Environment*, New Orleans, CEP Consultants Ltda., Edinburgh, p: 407-409.
- Ovalle, A.R.C. 1992. Hidroquímica de um Canal de Maré em um Manguezal de Itacuruçá, Baía de Sepetiba, RJ. PhD Thesis. Universidade Federal de São Carlos. São Carlos, 182p.
- Ovalle, A.R.C.; Carmouze, J.P.; Rezende, C.E.; Lacerda, L.D.; Barros, K.M.; Silva, C.A.R. & Silva, L.F.F. 1987. Hidrogeoquímica de um canal de maré em um sistema de manguezal, Baía de Sepetiba, Rio de Janeiro. *Anais do I Congresso Brasileiro de Geoquímica*, Porto Alegre. 2: 225-232.
- Ovalle, A.R.C.; Rezende, C.E.; Lacerda, L.D. & Silva, C.A.R. 1990. Hydrochemistry of a mangrove tidal creek in Sepetiba Bay, Rio de Janeiro,

- Brazil. *Estuarine, Coastal & Shelf Science* 31: 639-650.
- Panitz, C.M.N. 1997. Ecological description of the Itacorubi mangroves, Ilha de Santa Catarina, Brazil. In: Kjerfve, B.; Lacerda, L.D. & Diop, E.S. (eds.), *Mangrove Ecosystem Studies in Latin America and Africa*. UNESCO, Paris, pp. 204-225.
- Paredes, J.F.; Queiroz, A.F.S.; Carvalho, I.G.; Ramos, M.A.S.B.; Santos, A.L.F. Santos & Mosser C. 1995. *Heavy metals in sediments: Mangrove swamps of the Subaé and Paraguaçu tributary rivers of Todos os Santos Bay, Bahia, Brazil*. Serie Tecnologia ambiental No. 9, Centro de Tecnologia Mineral, rio de Janeiro, 15p.
- Patchineelam, S.R. & Bezerra, H.C. 1987. Distribution of heavy metals in Coroa Grande mangrove deposits, Rio de Janeiro, Brazil. In: *Proceedings 6th International Conference on Heavy Metals in the Environment*, New Orleans. CEP Consultants Ltda., Edinburgh, Vol. 1: 497-499.
- Pedlovski, M.A. 1990. *Entradas Atmosféricas de Metais Pesados, Nutrientes e Acidez Livre para a Baía de Sepetiba*. MSc Thesis, Inst. Geociências, UFRJ, Rio de Janeiro, 127p.
- Pedlovski, M.A.; Lacerda, L.D.; Ovalle, A.R.C.; Watts, P.P.R. & Vieira, E. 1991a. Atmospheric inputs of Fe, Zn, Mn to Sepetiba Bay, RJ. *Ciência & Cultura* 43: 380-382.
- Pedlovski, M.A.; Rezende, C.E.; Lacerda, L.D. & Ovalle, A.R.C. 1991b. Atmospheric inputs of heavy metals to Sepetiba Bay, Rio de Janeiro, Brazil. In: *Proceedings 8th International Conference on Heavy Metals in the Environment*, Edinburgh, CEP Consultants Ltda., Edinburgh, Vol. 1: 254-257.
- Peerzada, N. & Rohoza, W. 1989. Some heavy metals in sediments from Darwin Harbour, Australia. *Marine Pollution Bulletin* 20: 91-92.
- Peterson, P.J.; Burton, M.A.S.; Gregson, M.; Nye, S.M. & Porter, E.K. 1976. Tin in plants and surface waters in Malaysian ecosystems. In: D.D. Hemphill (ed.), *Trace Substances in Environmental Health*. Univ. Missouri, pp: 123-132.
- Peterson, P.J.; Burton, M.A.S.; Gregson, M.; Nye, S.M. & Porter, E.K. 1979. Accumulation of tin by mangrove species in West Malaysia. *The Science of the Total Environment* 11: 213-221.
- Pfeiffer, W.C.; L.D. Lacerda, L.D.; Fiszman, M. & Lima, N.R.W. 1985. Metais pesados no pescado da Baía de Sepetiba, Rio de Janeiro. *Ciência & Cultura* 37: 297-302.
- Phillips, R.C. 1992. The seagrass ecosystems and resources in Latin America. In: Seeliger, U. (ed.), *Coastal Plant Communities of Latin America*. Academic Press, San Diego, p:259-267.
- Pires, L.C. 1997. *Biogeoquímica de Pirita em um Manguezal da Baía de Sepetiba, Rio de Janeiro*. PhD Thesis, Dept. Geoquímica, Univ. Federal Fluminense, Niteroi, (in press).
- Ponnamperuma, F.N. 1972. Chemistry of waterlogged soils. *Advances in Agronomy* 24: 29-96.
- Postma, H. 1982. Processes in the sediment and in the water-sediment interface. Coastal Lagoon Research, Present and Future. *UNESCO Tech. Papers on Marine Sciences* 33: 111-118.
- Pulich, W.M. 1982. Edaphic factors related to shoal-grass (*Halodule wrightii* Aschers.) production. *Botanica Marina* 25: 467-475.
- Queiroz, A.F.S.; Mosser, C. & Santos, A.L.F. 1993. Heavy metal concentrations in sediments of mangrove swamps of Todos os Santos Bay. In: *Proceedings of the 1st International Symposium on Environmental Geochemistry in Tropical Countries*, Niteroi, Universidade Federal Fluminense, Niteroi, pp. 123-126.
- Quevauviller, P.; Donard, O.F.X.; Wasserman, J.C.; Martin, F.M. & Schneider, J. 1992. Occurrence of methylated tin and dimethyl mercury compounds in a mangrove core from Sepetiba Bay, Brazil. *Applied Organometallic Chemistry* 6: 221-228.

- Ragsdale, H.L. & Thorhaug, A. 1980. Trace metal cycling in the U.S. coastal zone: Synthesis. *American Journal of Botany* 67: 1102-1112.
- Ramadhass, V.; Rajendran, A. & Venugopalan, V.K. 1975. Studies on trace elements in Pichavaram mangroves (South India). In: W.E. Walsh; S.C. Snedaker & H. Teas (eds.), *Proceedings of the International Symposium on Biology and Management of Mangrove Ecosystems*, University of Florida, Miami. pp: 96-114.
- Ramachandran, S. 1996. Socio-economic impacts of coastal environmental degradation and need for integrated coastal zone management in India. In: *Proceedings of the International Symposium on Socio-economic Benefits of Integrated Coastal Zone Management*. CDG/GKSS, Bremen, pp. 77-79
- Rao, A.N. 1987. Mangrove ecosystems of Asia and the Pacific. In: *Mangrove Ecosystems of Asia and the Pacific: Status and Management*. Tech. Rep., UNDP/UNESCO Research and Training Pilot Programme on Mangrove Ecosystems in Asia and the Pacific. UNESCO-UNDP, Philippines, p:133.
- Rao, C.K.; Chinnaraj, S.; Inamdar, S.N. & Untawale, A.G. 1991. Arsenic content in certain marine brown algae and mangroves from Goa coast. *Indian Journal of Marine Sciences* 20: 283-285.
- Rao, R.G.; Woitchik, A. F.; Goeyens, L.; van Riet, A.; Kazungu, J. & Dehairs, F. 1993. Carbon, nitrogen contents and stable carbon isotope abundance in mangrove leaves from an east African coastal lagoon (Kenya). *Aquatic Botany* 47: 175-183.
- Raz-guzman, A.; Lanza, G. & Soto, L.A. 1993. Caracterización isotópica ($\delta^{13}\text{C}$) de la carcino-fauna del sistema lagunar de Alando, Vera Cruz, Mexico. *Revista de Biología Tropical* 41: 73-79.
- Ray, P.S. & Crawford, E.A. 1984. Heavy metals in a contaminated Australian estuary - dispersion and accumulation trend. *Estuarine Coastal & Shelf Sciences* 19: 341-358.
- Rezende, C.E. 1988. *Balanço de Matéria Orgânica e Metais Pesados em um Ecossistema de Mangue, Baía de Sepetiba, RJ*. MSc Thesis, Univ. Fed. Fluminense, Niteroi, 86p.
- Rezende, C.E.; Lacerda, L.D.; Ovalle, A.R.C.; Silva, C.A.R. & Martinelli, L.A. 1990. Nature of POC transport in a mangrove ecosystem: A carbon-isotopic study. *Estuarine, Coastal & Shelf Science* 30: 641-645.
- Ribeiro, M.G. 1994. Dinâmica de manganês em um canal de maré de um manguezal da Baía de Sepetiba - RJ. MSc Thesis, Univ. Fed. Fluminense, Niteroi, 71p.
- Robertson, A.I. 1986. Leaf burying crabs: Their Influence on energy flow and export from mixed mangrove forest (*Rhizophora* spp.) in Northeastern Australia. *Journal of Experimental Marine Biology and Ecology* 102: 237-248.
- Sadiq, M. & Zaidi, T.H. 1994. Sediment composition and metal concentrations in mangrove leaves from the Saudi coast of the Arabian Gulf. *The Science of the Total Environment* 155: 1-8.
- Saenger, P.; Hegerl, E.J. & Davie, J.D.S. 1983. Global status of mangrove ecosystems. *The Environmentalist* 3: 1-88.
- Salomons, W. 1983. *Trace Metal Cycling in a Polluted Lake* (Ijsselmeer, the Netherlands). Delft Hydraulics Lab. Rep. S 357/EEC contr. no. 199-7-1 ENV N. 50p.
- Salomons, W. & Förstner, U. 1984. *Metals in the Hydrocycle*. Springer Verlag, Berlin.
- Salomons, W.; Kerdijk, H; van Pagee, H.; Klomp, R. & Schreur, A. 1988. Behaviour and impact assessment of heavy metals in estuarine and coastal zone. In: U. Seeliger; L.D. Lacerda & S.R. Patchineelan (eds.). *Metals in Coastal Environments of Latin America*. Springer-Verlag, Berlin, pp. 157-198.
- Salomons, W. & Stigliani, W.M. 1995. *Biogeochemistry of Pollutants in Soils and Sediments*. Springer Verlag, Berlin, 352 p.

- Santschi, P.H. 1988. Factors controlling the biogeochemical cycles of trace metals in fresh and coastal marine waters as revealed by artificial radioisotopes. *Limnology & Oceanography* 33: 848-866.
- Scholander, P.F.; L. van Dam & S.I. Scholander. 1955. Gas exchange in the roots of mangroves. *American Journal of Botany* 42: 92-98.
- Scholander, P.F.; Hammel, H.T.; Hemmingsen, E. & Garey, W. 1962. Salt balance in mangroves. *Plant Physiology* 37: 722-729.
- Semesi, A. 1993. Mangrove Ecosystems of Tanzania. In: Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions. pp. 211-227. ISME/ITTO Techn. Rep. 2, Okinawa. Japan.
- Silva, C.A.R. 1988. Distribuição e Ciclagem Interna de Metais Pesados em um Ecossistema de Manguezal Dominado por *Rhizophora mangle*, Baía de Sepetiba, Rio de Janeiro. MSc Thesis, Dept. Geoquímica, Univ. Fed. Fluminense, Niteroi. 78p.
- Silva, C.A.R.; Lacerda, L.D. & Rezende, C.E. 1990. Heavy metal reservoirs in a red mangrove forest. *Biotropica* 22: 339-345.
- Silva, C.A.R.; Lacerda, L.D. & Rezende, C.E. 1991. Forest structure and biomass distribution in a red mangrove stand in Sepetiba Bay, RJ. *Revista Brasileira de Botânica* 14: 23-28.
- Silva, M.R.; Lamotte, M.; Donard, O.F.X.; Soriano-Sierra, E.J. & Robert, M. 1996. Metal contamination in surface sediments of mangroves, lagoons and Southern Bay in Florianopolis Island. *Environmental Technology* 17: 1035-1046.
- Snedaker, S.C. 1984. Mangroves: A summary of knowledge with emphasis on Pakistan. In: B.U. Haq & J.D. Milliman. (eds.). *Marine Geology and Oceanography of Arabian Sea and Coastal Pakistan*. Van Nostrand Reinhold Co., New York. pp. 255-262.
- Snedaker, S.C. & Brown, M.S. 1981. *Water Quality and Mangrove Ecosystem Dynamics*. USEPA, publ. EPA-600/481-022, Gulf Breeze, Florida, 80p.
- Soto, R. 1992. Nutrient concentration and retranslocation in coastal vegetation and mangroves from the Pacific coast of Costa Rica. *Brenesia* 37: 33-50.
- Souza, C.M.M.; Pestana, M.H.D. & Lacerda, L.D. 1986. Geochemical partitioning of heavy metals in sediments of three estuaries along the coast of Rio de Janeiro (Brazil). *The Science of the Total Environment*, 58: 63-72.
- Srivastava, P.B.L.; Majid, N.M. & Shariff, A.H. 1980. Foliage and soil nutrients in *Rhizophora apiculata* Bl. Stands. *Tropical Ecology* 21: 113-124.
- St-Cyr, L. & Crowder, A.A. 1990. Manganese and copper in the root plaque of *Phragmites australis* (Cav.) Trin ex Stendel. *Soil Science* 149: 191-198.
- Stigliani, W.M. 1995. Global perspectives and risk assessment. In: W. Salomons & W.M. Stigliani (eds.), *Biogeochemistry of Pollutants in Soils and Sediments*, Springer Verlag, Berlin, pp: 331-344.
- Tam, N.F.Y. & Wong, Y.S. 1993. Retention of nutrients and heavy metals in mangrove sediments receiving wastewater of different strengths. *Environmental Technology* 14: 719-729.
- Tam, N.F.Y.; Li, S.H.; Lan, C.Y.; Chen, G.Z.; Li, M.S. & Wong, Y.S. 1995. Nutrients and heavy metal concentrations of plants and sediments in Futian mangrove forest. *Hydrobiologia* 295: 149-158.
- Tanizaki, K.F. 1993. *Biogeoquímica da Rizosfera de Plantas de Mangue*. MSc Thesis, Univ. Federal Fluminense, Niteroi. 68p.
- Taylor, G.J. 1987. Exclusion of metals from the symplast: a possible mechanism of metal tolerance in higher plants. *Journal of Plant Nutrition* 10: 213-222.
- Thibodeau, F.R. & Nickerson, N.H. 1986. Differential oxidation of mangrove substrate by *Avicennia*

- germinans* and *Rhizophora mangle*. *American Journal of Botany* 73: 512-516.
- Thom, B.G. 1984. Mangrove ecology and deltaic geomorphology, Tabasco, Mexico. *Journal of Ecology* 55:301-343.
- Tripp M. & Harris, R.C. 1979. Role of mangrove vegetation in mercury cycling in the Florida Everglades. In: J.O. Nriagu (ed.) *Environmental Biogeochemistry. Volume 2. Metal Transfer and Ecological Mass Balances*. Ann Arbor Science Publ, Ann Harbor, pp: 489-497.
- Twilley, R.R. 1985. The exchange of organic Carbon in basin mangrove forests in Southwest Florida estuaries. *Estuarine, Coastal & Shelf Science* 20: 543-557.
- Twilley, R.R.; Zimmerman, R.; Solorzano, L.; Rivera-Monroy, V.; Boderio, A.; Zambrano, R.; Pozo, M.; Garcia, V.; Loo, K.; Garcia, R.; Cardenas, W.; Gaibor, N.; Espinoza, J. & Lynch, J. 1990. *The Importance of Mangroves in Sustaining Fisheries and Controlling Water Quality in Coastal Ecosystems*. Interim Report, USAID, Program on Science and Technology Cooperation, Washington, DC. 213p.
- Twilley, R.R.; Chen, R.H. & Hargis, T. 1992. Carbon sinks in mangroves and their implications to carbon budget of tropical coastal ecosystems. *Water, Air & Soil Pollution* 64: 265-288.
- UNEP, 1994. *Assessment and Monitoring of Climatic Change Impacts on Mangrove Ecosystems*. UNEP Regional Seas Report and Studies No. 154, United Nations Environmental Program, Nairobi, 62 p.
- Vorjak, P.W.L.; Edwards, C. & Jones, M.V. 1985. Evidence for microbiological manganese oxidation in the River Tamar Estuary, south-west England. *Estuarine Coastal & Shelf Science* 20: 661-671.
- Walsh, G.E. 1974. Mangroves: A review. In: R.J. Reimold & W.A. Queen (eds.), *Ecology of Halophytes*. Academic Press, Inc., New York. pp: 51-174.
- Walsh, G.E.; Ainsworth, F.A. & Rigby, R. 1979. Resistance of the red mangrove (*Rhizophora mangle* L.) seedlings to lead, cadmium, and mercury. *Biotropica* 11: 22-27.
- Ward, L.G. 1981. Suspended material transport in marsh tidal channels, Kiawah Island, S.C. *Marine Geology* 59: 85-103.
- Ward, L.G. & Twilley, R.R. 1986. Seasonal distribution of suspended particulate material and dissolved nutrients in a coastal plain estuary. *Estuaries* 9: 156-168.
- Werner, A. & Stelzer, J. 1990. Physiological responses of the mangrove *Rhizophora mangle* grown in the absence and presence of NaCl. *Plant, Cell & Environment* 13: 243-255.
- West, R.C. 1977. Tidal saltmarsh and mangal formations of Middle and South America. In: Chapman, V.J. (ed.), *Wet Coastal Ecosystems*. Ecosystems of the World N° 1. Elsevier Science Publ. Comp., Amsterdam, pp:193-213.
- Whitfield, M. & Turner, D.R. 1986. Chemical speciation in tropical waters - A cautionary tale. *The Science of the Total Environment* 58: 9-36.
- Whittaker, R.H.; Likens, G.E.; Bormann, F.H.; Eaton, J.S. & Siccama, T.G. 1979. The Hubbard Brook ecosystem study: forest nutrient cycling and element behavior. *Ecology* 60: 203-220.
- Wijmstra, T.A. 1969. Palynology of the Alliance Well. *Geologie Mijnbouw* 48: 125-133.
- Wollast, R. & Peters, J.J. 1978. Biogeochemical properties of an estuarine system: The River Scheldt. In: *Biogeochemistry of Estuarine Sediments*. UNESCO, Paris, pp: 279-293.
- Woodroffe, C.D. 1985a. Studies of a mangrove basin, Tuff Crater, New Zealand, I: Mangrove biomass and production of detritus. *Estuarine, Coastal & Shelf Science* 20: 265-280.
- Woodroffe, C.D. 1985b. Studies of a mangrove basin, Tuff Crater, New Zealand, II: Comparison of volumetric and velocity area method of estimating

- tidal flux. *Estuarine, Coastal & Shelf Science* 20: 431-445.
- Woodroffe, C.D. 1985c. Studies of a mangrove basin, Tuff Crater, New Zealand, III: The flux of organic and inorganic particulate matter. *Estuarine, Coastal & Shelf Science* 20: 447-461.
- World Resources Institute. 1992. *World Resources 1992-1993*. Oxford University Press, New York. pp:195.
- Zack, A. & Roman-Mas, A. 1988. Hydrology of the Caribbean Island wetlands. *Acta Científica* 2: 65-73.
- Zieman, J.C.; Macka, S.A. & Mills, A.L. 1984. Role of seagrasses and mangroves in estuarine food webs: Temporal and spatial changes in stable isotope composition and amino acid content during decomposition. *Bulletin of Marine Sciences* 35: 380-372.

Annex 5.5.1a. Trace metal concentrations in mangrove sediments from different parts of the world. a- essential trace metals ($\mu\text{g.g}^{-1}$)

Site	Cu	Zn	Fe	Mn	Mo	Co	Author
Sepetiba Bay, SE Brazil	5.4-8.3	58-280	1700-3700	147-256	-	1.7-5.3	Lacerda & Abrão (1984)
Spencer Gulf, Australia	7.0-8.0	4.0-25	1600-7600	30-78	-	-	Harbinson (1984)
Gulf St. Vincent, Australia	27-31	28-34	14900-20900	90-123	-	-	Harbinson (1984)
Brisbane River, Australia	7.0-30.2	41-144	-	-	11.2-82.6	-	Mackey <i>et al.</i> (1992)
Darwin Harbour, Australia	3.7-32.3	15.9-270	-	-	-	-	Peerzade & Rohoza (1989)
St. Catarina, S Brazil	14.5-36.5	26.9-101.1	-	-	-	-	Silva <i>et al.</i> (1996)
Tamshui Estuary, Taiwan	5.6-68.2	13-150	-	-	-	-	Chiu & Chou (1991)
Coroa Grande, SE Brazil	-	155	27,800	377	-	34	Patchineelam & Bezerra (1987)
Sai keng, Hong Kong	10.7	34.1	-	37.1	-	-	Tam & Wong (1993)
Salvador, NE Brazil	4.3-74.4	15.3-102	-	-	-	-	Queiroz <i>et al.</i> (1993)
Shenzen, China	16-308	53-423	-	125-789	-	-	Tam <i>et al.</i> (1995)
SW India coast	19-92	112-466	13300-61200	305-465	-	-	Badarudeen <i>et al.</i> (1996)
Puerto Rico, USA	45-94	69-160	39000-46000	420-1100	-	-	Ragsdale & Thorhaug (1980)
Arabia Gulf, Saudi Arabia	0.14-3.83	2.2-17.1	645-3600	2-69.3	<0.01-3.9	0.81-3.25	Sadiq & Zaidi (1994)
Subaé River, NE Brazil	6.8-31.9	15.3-78.9	500-7090	78.1-487	-	-	Paredes <i>et al.</i> (1995)

Annex 5.5.1b - non-essential trace metals ($\mu\text{g.g}^{-1}$)

Site	Cd	Pb	Pd	Sb	Sr	Ag	V
Sepetiba Bay, SE Brazil	0.9-2.8	13.8-16.8	-	-	-	-	-
Spencer Gulf, Australia	-	20	-	-	-	-	-
Gulf St. Vincent, Australia	-	4.0-7.0	-	-	-	-	-
St. Catarina, S Brazil	0.05-0.13	11-51.3	0.14-1.06	1.0-3.9	70-349	0.17-0.86	-
Darwin Harbour, Australia	0.9-3.0	22-96	-	-	-	-	-
Brisbane River, Australia	<0.1-1.9	20-82	-	-	-	<0.6-2.8	20-49
Tamshui Estuary, Taiwan	0.2-1.0	9.0-35	-	-	-	-	-
Puerto Rico, USA	<0.3-<0.9	-	-	-	-	-	-
Arabia Gulf, Saudi Arabia	0.17-3.0	6.13-18.7	-	-	-	-	3.4-12.2
Subaé River, NE Brazil	<0.1-0.16	4.0-19.0	-	-	-	-	-
Corao Grande, SE Brazil	5.8	226	-	-	-	-	-
Sai Keng, Hong Kong	0.25	-	-	-	-	-	-
Salvador, NE Brazil	<0.01-12.8	2.5-156	-	-	-	-	-
Shenzen, China	0.3-7.9	0.1-63	-	-	-	-	-

Site	Hg	Se	Sn	U	Ni	Cr	As
Sepetiba Bay, SE Brazil	-	-	-	-	7.7-13.9	12.6-42.8	-
St. Catarina, S Brazil	0.01-0.22	0-2.9	1.4-5.0	0.7-5.1	1.1-30	0-15.9	3.5-24.8
Spencer Gulf, Australia	-	-	-	-	-	15-24	-
Gulf St. Vincent, Australia	-	-	-	-	-	27-31	-
Tamshui Estuary, Taiwan	-	-	-	-	2.1-12.5	-	-
Puerto Rico, USA	0.2-0.4	-	-	-	47-75	70	-
Arabia Gulf, Saudi Arabia	-	-	-	-	21.96-18.1	2.5-12.7	-
Subaé River, NE Brazil	<0.5-0.3	-	-	-	-	23.3-112	-
Cora Grande, SE Brazil	-	-	-	-	-	44	-
Evergaldes Florida, USA	0.07-0.23	-	-	-	-	-	-
Florida, USA	1.02	-	-	-	-	-	-
Sai Keng, Hong Kong	-	-	-	-	4.2	-	-
Salvador, NE Brazil	-	-	-	-	-	22-334	-
Shenzen, China	-	-	-	-	-	6.8-56.7	-
SW India coast	-	-	-	-	59-207	71-388	-

Annex 6.6.1a. Trace metal concentrations in leaves of mangrove from different sites in the world ($\mu\text{g g}^{-1}$) d.w. a. Essential trace metals

Species	Site	Fe	Zn	Cu	Mn	Co	Mo	Author
<i>Rhizophora conjugata</i> L.	Penang, Malaysia	50-69	6.2-7.1	2.6-3.0	—	—	—	Peterson <i>et al.</i> (1979)
<i>Acanthus ilicifolius</i> L.	"	47-63	29-42	7.2-12	—	—	—	"
<i>Bruguiera caryophyllodes</i> Blume	"	41-42	9.0-11	2.2-4.4	—	—	—	"
<i>Carapa moluccensis</i> Lam.	"	52-102	7.0-7.4	3.3-3.9	—	—	—	"
<i>Scyphiphora hydrophyllacea</i> Gaertn	"	68	18	10	—	—	—	"
<i>Excoecaria agallocha</i> L.	"	150	42	6.5	—	—	—	"
<i>Avicennia alba</i> Blume	"	139-185	15-19	2.8-6.0	—	—	—	"
<i>Avicennia officinalis</i> L.	"	88	12	4.5	—	—	—	"
<i>Kandelia candel</i> L. (Drude)	Tamshui, Taiwan	—	9.2-21.8	1.8-7.4	—	—	—	Chiu & Chou (1991)
<i>Rhizophora mucronata</i> Lam.	Ganapatipule, India	—	11.5	4.1	32.2	2.3	11.5	Bhosale (1979)
<i>Bruguiera gymnorhiza</i>	"	—	12.8	6	46.5	2.3	11.5	"
<i>Ceriops tagal</i>	"	—	11.1	5.3	82.2	2.2	11.1	"
<i>Avicennia officinalis</i> L.	"	—	17.5	9.2	158.7	3.2	15.9	"
<i>Lumnitzera racemosa</i>	"	—	29.4	4.1	29.4	5.9	29.4	"
<i>Aegiceras corniculatum</i>	"	—	8.3	4.3	25.8	1.7	8.3	"
<i>Acanthus ilicifolius</i> L.	"	—	24.7	9	96.7	3.3	16.7	"
<i>Aeluropus lagopoides</i>	"	—	107.1	6.6	54.3	1.4	7.1	"
<i>Clerodendro inerme</i>	"	—	36.5	10.8	133.3	3.2	15.9	"
<i>Avicennia marina</i> (Forsk)	Tarut Bay, Saudi Arabia	52.4	280.2	0.5-23.3	4.5-66.6	<0.1-3.7	<0.3-4.3	Sadiq & Zaidi (1994)
<i>Rhizophora mangle</i> L.	Pacific coast, Costa Rica	80-420	6.0-19	3.5-16	—	—	—	Soto (1992)
<i>Rhizophora harrisonii</i>	"	100-440	8.0-17	4.8-17	—	—	—	"
<i>Avicennia germinans</i> L.	"	80-380	17-22	8.0-21	—	—	—	"
<i>Pelliciera rhizophoreae</i>	"	210-360	21-24	7.5-19.5	—	—	—	"
<i>Laguncularia racemosa</i> R. Gertn.	"	160-790	21-23	10.2-17	—	—	—	"
<i>Conocarpus erectus</i> L.	"	170-230	24-42	8.0-16	—	—	—	"
<i>Rhizophora apiculata</i> Blume	Matang, Malaysia	64-167	7.3-12.8	2.7-3.4	210-330	—	—	Srivastava <i>et al.</i> (1980)

Annex 6.6.1a cont.

Species	Site	Fe	Zn	Cu	Mn	Co	Mo	Author
<i>Aegiceras corniculatum</i> (L.) Blanco	Shenzhen, China	—	85.2	4.1	166	—	—	Tam <i>et al.</i> (1995)
<i>Kandelia candel</i> (L.) Druce	"	—	69.7	4.1	1,048.0	—	—	"
<i>Rhizophora mangle</i> L.	São Paulo, South Brazil	208	12	4.5	254	—	—	Lamberti (1969)
<i>Laguncularia racemosa</i> R. Gertn.	"	129	23	6	22	—	—	"
<i>Avicennia schaueriana</i> Stapf. & Leech.	"	175	28	7	63	—	—	"
<i>Rhizophora mangle</i> L.	Darién, Panama	82	11	6	387	46-56	1.6-6.5	Golley <i>et al.</i> (1978)
<i>Rhizophora mangle</i> L.	Sepetiba, SE Brazil	68-943	10.0-34	3.0-34	20-882	—	—	Lacerda <i>et al.</i> (1986)
<i>Laguncularia racemosa</i> R. Gertn.	"	84-603	17-53	5.0-37	16-336	—	—	"
<i>Avicennia schaueriana</i> Stapf. & Leech.	"	71-606	20-66	3.0-19	38-473	—	—	
<i>Rhizophora mangle</i> L.	Puerto Rico	60	4.5	5.2	561	—	—	Ragsdale & Thorhaug (1980)
<i>Rhizophora mangle</i> L.	Florida, USA	52	10	7	146	—	—	Snedaker & Brown (1981)
<i>Laguncularia racemosa</i> R. Gertn.	"	60	63	6	27	—	—	"
<i>Rhizophora mangle</i> L.	Florida, USA	152	43	—	30	—	—	Morton (1965)
<i>Rhizophora mangle</i> L.	Florida, USA	82	11	—	370	—	—	Walsh (1974)
<i>Rhizophora mangle</i> L.	St. Catarina, S. Brazil	99	69	1.6	260	—	—	Panitz (1997)
<i>Laguncularia racemosa</i> R. Gertn.	"	127	145	2.1	195	—	—	"
<i>Avicennia schaueriana</i> Stapf. & Leech.	"	113	97	3.9	270	—	—	"

Annex 6.6.1b- non-essential elements ($\mu\text{g g}^{-1}$)

Species	Site	Pb	Cd	Ni	Hg	Sn	Cr	Author
<i>Kandelia candel</i> (L.) Druce	Tamshui, Taiwan	<1.0-7.0	0.2-0.9	0.7-2.6	-	-	-	Chiu & Chou (1991)
<i>Rhizophora mucronata</i> Lam.	Ganapatipule, India	-	-	-	-	-	-	Bhosale (1979)
<i>Bruguiera gymnorhiza</i>	"	-	-	-	-	-	-	"
<i>Ceriops tagal</i>	"	-	-	-	-	-	-	"
<i>Avicennia officinalis</i> L.	"	-	-	-	-	-	-	"
<i>Lumnitzera racemosa</i>	"	-	-	-	-	-	-	"
<i>Aegiceras corniculatum</i>	"	-	-	-	-	-	-	"
<i>Acanthus ilicifolius</i> L.	"	-	-	-	-	-	-	"
<i>Aeluropus lagopoides</i>	"	-	-	-	-	-	-	"
<i>Clerodendro inerme</i>	"	-	-	-	-	-	-	"
<i>Avicennia marina</i> (Forsk.)	Tarut Bay, Saudi Arabia	<0.3-23	<0.4-3.1	<0.2-7.5	-	-	<0.2-9.2	Sadiq & Zaidi (1994)
<i>Rhizophora mangle</i> L.	Florida	-	-	-	0.2-0.3	-	-	Tripp & Harriss (1979)
<i>Rhizophora mangle</i> L.	Florida	-	-	-	0.2-0.3	-	-	Lindberg <i>et al.</i> (1977)
<i>Rhizophora mangle</i> L.	Puerto Rico	-	<6.0	2.6	0.12	-	<1.0	Ragsdale & Thorhaug (1980)
<i>Rhizophora conjugata</i> L.	Penang, Malaysia	-	-	-	-	5.8-6.9	-	Peterson <i>et al.</i> (1979)
<i>Acanthus ilicifolius</i> L.	"	-	-	-	-	3.8-5.4	-	"
<i>Bruguiera caryophyllioides</i> Blume	"	-	-	-	-	1.1-4.8	-	"
<i>Carapa moluccensis</i> Lam.	"	-	-	-	-	1.3-4.6	-	"
<i>Scyphiphora hydrophyllacea</i> Gaertn	"	-	-	-	-	3.7	-	"
<i>Excoecaria agallocha</i> L.	"	-	-	-	-	3.5	-	"
<i>Avicennia alba</i> Blume	"	-	-	-	-	1.8-4.0	-	"
<i>Avicennia officinalis</i> L.	"	-	-	-	-	1.6	-	"
<i>Rhizophora mangle</i> L.	St. Catarina, S. Brazil	2.7	0.1	-	-	-	0.8	Panitz (1997)
<i>Loguncularia racemosa</i> R. Gertn.	"	2.9	0.4	-	-	-	0.8	"
<i>Avicennia schaueriana</i> Stapf. & Leech.	"	0.8	0.6	-	-	-	0.8	"

ACTIVITIES OF THE INTERNATIONAL SOCIETY FOR MANGROVE ECOSYSTEMS (ISME)

ISME was founded in 1990 as a society to promote study and research concerning mangrove ecosystems, with the ultimate goal of laying the bases for rational, sustainable use and management of these resources. A non-governmental and non-profit-making organization, ISME brings together interested scientists, professionals and institutions working for the conservation and better use of the mangroves of the world.

The Society is affiliated to the ICSU family of organizations as a constituent part of the International Union of Biological Science (IUBS) through the International Association of Biological Oceanography (IABO), and has observer status with several organizations of the United Nations.

ISME organizes and cosponsor conferences, seminars, symposia and working group meetings; to organize lectures and courses; to publish both scientific and popular articles. ISME promote mangrove ecosystems research and extension activities for sustainable management, rational utilization, rehabilitation and conservation of mangrove ecosystems. Since 1995, ISME has been implementing a two month mangrove training course, financed by JICA. The number of participants for the last three years sums up to 20 from 17 countries. As of March 1998, ISME has 667 individual members and 34 institutional members from 73 countries.

While its Secretariat is located in Okinawa (Japan), ISME undertakes to implement projects anywhere in the world where the expertise of its members can be of service. Through its newsletter, the Society provides an open forum for discussion leading to the optimum modalities of attaining its objectives. In addition, ISME has co-operated with the International Tropical Timber Organization (ITTO) to promote mangrove research.

As well, ISME organizes annual training courses, sponsored by the Japan International Cooperation Agency, and publishes educational and professionals papers as well as videos. Thus far, the following have been produced:

ISME Mangrove Ecosystems Occasional Papers

- No. 1. 1993. Mangrove Nurseries in Bangladesh, by N.A. Siddiqi, M.R. Kslam, M.S.S. Kahn, and M. Shahidullah;
- No. 2. 1998. Trace Metals Biogeochemistry and Diffuse Pollution in Mangrove Ecosystems, by Luiz Drude de Lacerda.

ISME Mangrove Ecosystems Proceedings

- No. 1. 1993. Proceedings of a Workshop on Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions, Niteroi, Brazil 28-30 May 1993;
- No. 2. 1993. Proceedings of a Workshop on Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions, Dakar, Senegal, 20-22 January 1993;
- No. 3. 1994. Proceedings of VII Pacific Science Inter-Congress Mangrove Session, Okinawa, Japan, 1-2 July 1993.

ISME Mangrove Ecosystems Technical Reports

- No. 1. 1993. The Economic and Environmental Values of Mangrove Forests and their Present State of Conservation in the South-east Asia/Pacific Region. (an ITTO/ISME Project);
- No. 2. 1993. Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions, Part I - Latin America. (an ITTO/ISME Project);
- No. 3. 1993. Conservation and Sustainable Utilization of Mangrove Forests in Latin America and Africa Regions, Part II - Africa. (an ITTO/ISME Project);
- No. 4. 1994. Study of Chokoria Sundarbans Using Remote Sensing Techniques, by A.M. Choudhury, D.A. Quadir, and Md. Jinnahatul Islam. (with the support of AEON Foundation).

Slide Set Programme for Children

- 1994 - A Slide Programme of Environmental Education for Vietnamese Children, entitled "Know Your Mangroves", 73 slides and textbook;
- 1995 - A Slide Programme of Environmental Education for Children, entitled "Know Your Mangroves", 2nd edition, 76 colour slides and textbook;
- 1996 - Video on mangroves of Fiji, entitled "What the Tides Bring";
- 1997 - Video on mangroves of Thailand, entitled "Living with Mangroves".

Outputs of ITTO/ISME Project:

"Manual and a world natural mangrove atlas for mangrove ecosystem restoration"

- Non-technical publication: Journey Amongst Mangroves;
- Technical manual: Restoration of Mangrove Ecosystems;
- Atlas: World Mangrove Atlas.

For more information and purchase, contact:

ISME Secretariat
c/o College of Agriculture,
University of the Ryukyus
Okinawa 903-0129 Japan

Telephone: (81-98) 895-6601;
Facsimile: (81-98) 895-6602.