Chapter

Effect of Trace Elements Accumulation on Mangrove Ecosystem and Their Interaction with Humic Substances: The Case of Nickel and Iron

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Abstract

Mangroves are areas of permanent preservation, but anthropogenic interference in this ecosystem (for example the launching of pollutants from industrial, mining, fertilizer by farmers, sewage) is increasing startlingly. Preserve and look for ways to bioremediate mangroves is fundamental, since these maintain the productivity of coastal ecosystems and is thus regarded as a natural nursery. The need to study the mangroves has been growing in recent years, particularly in respect to the environmental characteristics of this ecosystem. This chapter aimed to draw a parallel between the damage that can be caused by the trace elements nickel and iron on the mangrove ecosystem, more specifically affecting the nutrition of mangrove plants, in addition to showing possible effects of the interaction of these metals with humic substances of organic matter acting on the mitigation of stresses caused to the ecosystem under study. Through surveys of the information covered in this chapter, it can be observed that the presence of trace elements such as Iron and Nickel at high levels can cause eminent stress to the plant structure within the scope of its sedimentary physiology and biochemistry. It is necessary to subsidize further studies so that it is explicit and approved by the scientific community that, this environment, which is sensitive and important, the basis for various trophic levels, needs greater attention from government officials for its preservation, as well as the restoration of those many mangroves that are polluted by being close to urban places, receiving an exacerbated supply of pollutants.

Keywords: mineral stress, biostimulant, mangrove, plant mineral nutrition

1. Introduction

The Mangrove is a coastal ecosystem, in transition between terrestrial and marine environments, characteristic of tropical and subtropical regions [1]. Despite being considered an ecosystem associated with the Atlantic Forest, the Mangrove is made up of areas of little biological diversity, but of great functional diversity [2].

It is composed of highly specialized halophyte vegetation, adapted to fluctuations in salinity, subject to the tidal regime and characterized by colonizing muddy sediments with low oxygen levels, on poorly consolidated substrates [3].

It suffers from water input from both the continent and the marine environment, the Mangrove ecosystem is of recognized importance, having primary primary productivity, filtering, storing and making available organic matter and nutrients, with a fertilizing influence on the adjacent coastal waters [4]. The "tangle" of Mangrove roots captures, traps and stabilizes interstitial sediments, forming a natural physical barrier against the erosion mechanisms generated by waves, tides and currents, promoting stabilization of the coastline [5]. In addition, canopies of vegetation protect adjacent terrestrial environments from strong ocean storms and winds [6].

Underestimated in the past, the Mangrove was considered an inhospitable environment for a long time [7]. Until the mid-1970s, the progress of the coast was equivalent to clean beaches, sanitary landfills, ports and cultivation to take advantage of the land of the old mangroves, which would have future consequences [8]. Regarding the economic and social importance of this ecosystem, this approach was partly responsible for the construction of ports, spas, coastal highways, urban expansion and the release of raw sewage into its channels, considerably reducing its extent [9].

In more recent times, the mangroves were cut and grounded for the expansion of cities and the implementation of various enterprises [10]. Most of the vegetation of the Mangroves in the city of Vitória has been destroyed in the last decades due to several factors, among which the occurrence of landfills, real estate speculation, urban projects, slums, sewage disposal and deforestation stand out [11]. In different parts of the world and in an increasingly present way, in parallel with the degradation process, ways are developed to recover the impacted environments and even provide conditions necessary for the creation of new areas [12].

Due to this phase of expansion of recovery, there are now several techniques that may or may not include planting and the recovery of an ecosystem can be defined as the act of returning it, as far as possible, to a condition close to the original [13]. This management method is based on knowledge of the processes essential to the development and sustainability of the productivity of the system as a whole and not of its parts, therefore, it is necessary to acquire specialized knowledge about plants and animals, that is, it is necessary to know, first of all, the structure and functioning of the ecosystem [14].

Several Brazilian municipalities are already working with replanting, recovery and restoration of mangroves, however, there is still a need to investigate which factors interfere in the growth and development of these plants. One of these factors is probably the accumulation of heavy metals in the substrate, which combined with the massive presence of organic matter and its main component, humic substances, which is recognized as a potential plant biostimulant [15, 16], may be causing a greater accumulation of these elements, which in high concentrations become harmful to plants, leading to death [17]. Therefore, according to the above, studies on the interaction of the mangrove with other biotic and abiotic components of this ecosystem are necessary. Data of this nature will be essential when adapting restoration and recovery methods. In addition, municipal, state and federal public authorities will be able to more safely base possible interventions in this ecosystem, since the law states that it is their obligation to recover degraded areas.

The purpose of this chapter is to carry out a consistent approach to mangroves and the intrinsic effects of trace elements on the specie *Rhizophora mangle* L. in order to subsidize the understanding in the treated area for the scientific community.

2. Mangroves

2.1 Characterization, location and importance of mangroves

Mangroves are present on about 60–75% of the planet's tropical coast. These ecosystems play an important role in the carbon balance of coastal systems, with an export of terrestrial carbon [C] to the oceans (11%) about 15% of the total carbon that is deposited in current marine sediments [18]. Mangroves contribute about 10% of the terrestrial dissolved organic carbon when compared to other habitats and this large export of organic matter directly interferes with the food webs of coastal systems [19–22]. Recently, coastal ecosystems are being strongly impacted by natural climate change and human activities that affect their structure and food web, resulting in broad economic consequences. In addition, adjacent oceans provide considerable amounts of nutrients to coastal ecosystems and regulate nutrient dynamics [22, 23].

The mangrove can reach high levels of primary production. Mangrove litter provides trophic subsidy in adjacent coastal waters (the "outwelling hypothesis"), through a food web the debris is converted into a more palatable microbial biomass, which in turn acts as a dominant food source for the higher trophic levels [24]. In view of the economic importance of fishing in mangrove systems and adjacent waters, trophic dependence is a widely publicized function on mangroves and an important argument for their conservation [25].

The mangrove is an ecosystem that occurs in tropical coastal areas related to low, flat and estuarine regions, bordering lagoons, rivers or channels, waterlogged, brackish areas, being influenced by the tidal regime, but absent from direct wave actions [26]. All of these aspects influence the large deposition of sediments and organic matter. It is considered a link, as it is a transition area between marine, terrestrial and freshwater environments and is characterized by the high variation that occurs between these areas due to the regimes of both aquatic and terrestrial environments. The substrate has a pasty consistency, little compacted, swampy, rich in organic matter, little oxygen and subject to tidal regime [27]. These systems are generally young, as their dynamics produce constant changes in these lands, the result of constant advances and retreats of the tides [28–30].

Regarding their origin, the characteristic species of mangroves have records from the Eocene (period when angiosperm species began to occupy the land-sea transition areas) about 60 million years ago [31]. In order to have all this adaptation on the part of the plants in the system as currently, there was at that time an adaptive evolution of angiosperms from the end of the Cretaceous and beginning of the Eocene in such a way that the plant species started to adapt and tolerate high concentrations of salts in the sediment, whose first species were the genus Rhizophora and Avicennia resulting from continental drift. These species occur in practically all latitudes where there are mangroves [30, 32].

From the mangroves that have disappeared, it is possible to point out the formation of terraces of marine construction where beach sandstone and raised sandbank occur, dehydrated and consolidated by clay and humid cement. Mangroves are systems in constant dynamics, with some of them still in full expansion, with a constant movement of the horizon or superficial layer of the mangrove due to the withdrawal and sedimentary deposition [33–35].

The penetration of mangrove roots in deep regions allows the reduction of tidal currents leading to the accumulation of clay and sludge, components of the nutrient cycling process that sustains the high productivity in the mangrove system [36]. Sediments are characterized by being native or alien, accumulating fine fractions due to their low energy in the environment, justifying fluid retention [37].

Mangrove vegetation provides habitat for a variety of wildlife. A large number of mammals frequently visit these habitats, but few live permanently. Also a wide variety of birds and fish inhabit the mangroves, as well as shrimp, which use the mangroves as a nursery [38]. The mangrove oyster is found on the aerial roots of Rhizophora species (red mangrove). Dead leaves and branches of mangroves serve as a food source for microorganisms, which in turn form the food base for juvenile fish and shrimp [39].

The mangrove ecosystem constitutes a large portion, equivalent to 60–70% of the coastline in the tropical and subtropical regions of planet Earth [40]. However, it is found in 118 countries and its area reaches more than 137,760 km^2 [41]. The largest extension of mangroves is found in Asia (42%) followed by Africa (20%), North and Central America (15%), Oceania (12%) and South America (11%). About 75% of mangroves are concentrated in only 15 countries [41]. In the Americas, mangroves cover about 4.1 million hectares [40, 42].

Brazil is currently the third country with the largest extension of mangroves in the world with 968,963 ha, 7% of the world area, behind only Indonesia and Australia [41], occupying approximately 51% of the area in South America [2]. Brazil has several Environmental Physiographic Units along its coastline, which were classified by their similar characteristics of each environment taking into geomorphological aspects, sea currents, climate, etc. [43].

The mangroves in the State of Espírito Santo are distributed from the mouth of the Rio Doce in the extreme north to the Itabapoana River, bordering the State of Rio de Janeiro, occupying approximately 70 km^2 [44]. Some mangroves are poorly anthropized like that of the São Mateus River, others are considerably anthropized like that of Vitória Bay [45].

Among the six typical species of Brazilian mangroves, four are found in Espírito Santo: *Rhizophora mangle* (red mangrove), *Laguncularia racemosa*, (white mangrove), *Avicennia schaueriana* and *Avicennia germinans* (black mangrove). In addition, associated species are found, such as: *Conocarpus erectus* (button mangrove); *Acrostichum aureum* and *Acrostichum danaeifoliun* (mangrove fern) and *Hibiscus pernambucensis* (cotton-beach) [46].

2.2 *Rhizophora mangle* L

For this species to develop in unstable environments it has adaptations such as the so-called root-anchor, allowing its support in swampy environments influenced by the variation of tides. The specie *R. mangle* L. also known as red mangrove, belongs to the family Rhizhophoraceae which includes 16 genera and about 150 species [47]. In Rhizophora, the seed still germinates within the fruit attached to the mother plant and remains attached to it by the cotyledons that form a necklace within which the primordial bud of the seedling is included (**Figure 1A**). When the seedling (propagule = "pen") detaches from the mother plant, the cotyledons remain attached to it, thus, the structure that reaches the substrate consists of a large hypocotyl and the seedling [48].

One of the most striking features in *R. mangle* is the presence of structures that project in various directions around its stem towards the ground, called "aerial roots" or support, which are in fact special branches with positive geotropism, which form large number of roots when in contact with the soil, these special branches are rhizophores, that is, branches bearing roots, with negative geotropism (**Figure 1B**) [49]. *R. mangle* has opposite leaves, elliptical, glabrous, without glands; apopetal flowers, diclamids; glabrous, dark brown fruit; it blooms and bears fruit all year round and has the geographic distribution of America, West Africa and some islands of the Pacific [50].

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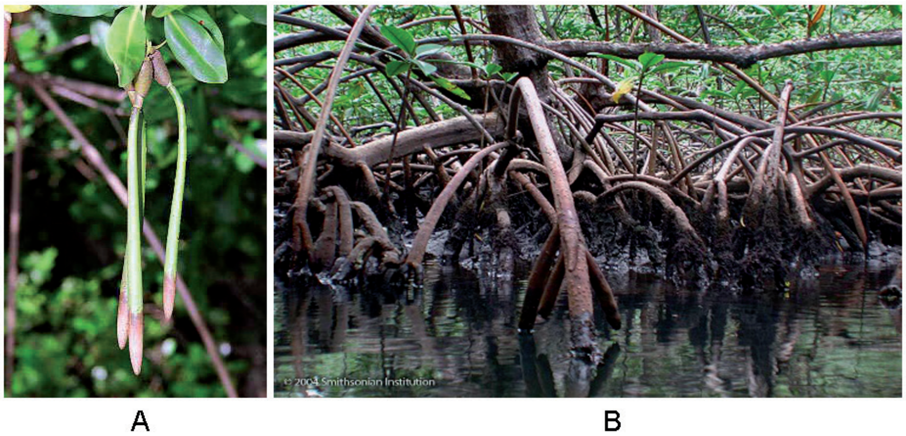

Figure 1.
*Characteristics of red mangrove plants (*R. mangle*) - (A) Propagule with a well-defined abscission band; (B) Aspect of the rhizophore.*

2.3 Ecophysiology of mangrove plants

Mangroves are systems that generate interest for researchers in the field of plant ecophysiology, due to their peculiarities and adaptations, such as, for example, high rates of salinity, temperature, tidal variation, nutritional deficiency, unconsolidated sediment and physical–chemical factors [48, 51], adaptations with which were possible through different morphological, anatomical, physiological and biochemical mechanisms presented by these plant species and which increase their productivity [51].

In general, the mangrove develops optimally with low salinity, however, some species tolerate higher salinity than others. Excessive Na^+ and Cl^- ions can lead to imbalances in several plant organs, however these responses vary between species. Mangrove plants generally decrease the water potential of their tissues in relation to sediment, thus allowing water absorption, which is one of the first adaptive mechanisms to excess salts. With the increase in the concentration of salts in the sediment, the concentration of Na^+ and Cl^- also increases, but this same occurrence is not seen for K^+ [51].

The accumulation of ions leads to the destabilization of cell membranes and even induces oxidative stress through the formation of ROS (reactive oxygen species), there is partial loss of the granal cell, cytochrome B6f and dissociation of polypeptides directly related to photosystem II. These peculiarities affect the absorption of carbon, and the increase of biomass. Hypersalinity can still cause disintegration of chloroplasts and mitochondria, alter (reduce) the chlorophyll concentration, which reduces photosynthetic capacity, due to chronic photoinhibition, however in *L. racemosa* plants it was observed at 30 ppm salinity, an increase in the concentration of chlorophyll a and b. It also reduces stomatal conductance and mesophilic conduction, limiting photosynthesis by low CO_2 diffusion [51].

Plants that grow in a saline environment have two problems, osmotic regulation and ion toxicity [52]. Mangrove plants need to restrict water loss and keep their potential low in the leaf interior through adaptations such as leaf thickening, increased nitrogen retention and water use efficiency. Mangrove plants are considered to have the highest water use efficiency rates of all C3 plants, because they have low rates of stomatal conductance and low transpiration [51, 53, 54].

2.4 Adaptive mechanisms

Halophyte species are naturally more tolerant to salinity, increase photochemical efficiency and promote greater CO_2 assimilation when compared to other plants not tolerant to salinity. *L. racemosa* when compared to *R. mangle*, has a higher assimilation of carbon for being more tolerant to salinity [54, 55].

When it comes to adaptations due to the fact that they are subject to flooding, in the mangrove species the circulation of water eliminates the possibility of absorbing toxic substances such as hydrogen sulfide from the degradation of sedimentary organic matter. When flooded, the species deal with hypoxia (complete or partial) leading to a decrease in the rate of growth and root death in *L. racemosa*, for example. However, its biomass is mainly allocated in the aerial part due to the flooding and flooding conditions that affect the gas exchange system and nutrient absorption by the plants in the long term. However, floods may have little effect on mangrove plants, due to their capacity to store oxygen in their root aerenchyma while the tide is low [48, 51].

Increase was observed in the content of chlorophyll a and b and carotenoid pigments at the points of greatest environmental pollution in both *R. mangle* and *L. racemosa* plants [56]. Chlorophyll b and carotenoids act as photoprotective pigments, therefore, an increase in their content constitutes a response by plants to environmental stressors. Since the chlorophyll a fluorescence is almost exclusively originated from chlorophyll a molecules associated with photosystem II, it reflects the primary photosynthetic reactions in the thylakoid membranes [57]. Variations in chlorophyll a fluorescence emission are indications of changes in photosynthetic activity and reflect the effects of environmental stress on the photosynthetic apparatus [51, 56].

3. Mineral nutrition

The study of plant nutrition establishes the essential elements for the life cycle of plants, how they are absorbed, translocated and accumulated, their functions, requirements and disturbances when in deficient or excessive quantities. As for the nutrient, it is defined as a chemical element essential to plants, that is, without it the plant does not live. For a chemical element to be considered a nutrient, it is necessary to meet the essentiality criteria (direct, indirect or both) [58].

Mineral nutrition is considered a determining factor for rooting, considering its involvement in the determination of plant morphogenic responses, such as the formation of adventitious roots, as well as the modulation of length and density. In this way, it is necessary to consider the influence of the various nutrients in the adventitious rooting, therefore, it is necessary to analyze the role of each nutrient, particularly in each phase of the process [59]. Although these nutrients are equally important for plant production, there is a classification, based on the proportion in which they appear in the dry matter of the vegetables. Therefore, there are two major groups of plant nutrients (not considering carbon [C], hydrogen [H] and oxygen [O]): 1) macronutrients which are the nutrients absorbed or required by plants in greater quantities [nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and sulfur (S) (expressed in g kg^{-1} of dry matter)]. This class can be further divided into primary macronutrients that are N, P and K and secondary macronutrients that are Ca, Mg and S. 2) micronutrients that are the nutrients that are absorbed or required by plants in smaller quantities [Iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), chlorine (Cl) and molybdenum (Mo) (expressed in mg kg^{-1} dry matter)] [60].

Most essential elements are absorbed in ionic form, from the soil solution. The way in which these ions are displaced depends on a number of factors such as the flow of water in the plant, density of the roots, in addition to the genetic characteristics of the species. In addition, this process undergoes abiotic interference, in which each species will respond in a different way. Minerals are absorbed from the capacity of ionic selectivity, and this selectivity is limited by osmotic factors and interactions with ions present in the soil. Another important point when talking about nutritional absorption is that it can occur under a concentration gradient. The absorption of an element also depends on the availability in the soil, for this reason, the assimilation of these elements is related to biogeochemical cycles [61].

In addition to the elements said to be essential to plant life, there are others considered beneficial and also the group of toxic elements. As for the beneficial element, it is defined as that which stimulates the growth of vegetables, but which are not essential or which are essential only for certain species or under certain conditions [61]. Silicon (Si) and cobalt (Co) are considered beneficial to the growth of certain plants, as well as Sodium (Na), nickel (Ni) and Selenium (Se). It should be noted that even a nutrient or beneficial element, when present in high concentrations in the soil solution, can be toxic to plants. However, it is considered a toxic element, which does not qualify as a nutrient or beneficial element. Thus, the toxic elements, even in low concentrations in the environment, can present a high potential for harm, accumulating in the trophic chain and slowing the growth and leading to the death of the plant. As an example of potentially toxic elements, we have aluminum (Al), cadmium (Cd), lead (Pb), mercury (Hg) and etc. [62].

4. Mineral stress

Mineral stress is defined as the sub-optimal availability of essential nutrients or the toxicity of nutrients or other elements (especially Al, Na, Cl, Mn, and other heavy metals), it is a primary restriction on plant growth in a large portion of the land surface [63].

Excessive intake of minerals can also have harmful effects on physiology, which has led researchers in recent years to acquire accurate data on the minimum requirements and toxic dosages of minerals present in food. The level of mineral content in vegetables depends on a number of factors including the genetic properties of the species, climatic conditions, the characteristics of the soil and the degree of maturity of the plant at the time of harvest. Thus, some nutrients essential to vegetables are involved in the response of plants to stress [64].

5. Responses of halophytic plants to stress of trace element

Halophyte plants are a great example of evolved species and adapted to hyperosmotic environments. These vegetables have evolved to adapt to adverse conditions, such as: high salinity, xerothermic environments, cold at seasonal temperatures and tolerance to the presence of toxic ions, mainly in the form of sodium and chloride [65].

Starting with the sediment, in the mangrove, the sediment acts as a deposit of nutrients arising, in part, from the release of domestic and industrial sewage and the use of agricultural fertilizers and pesticides [66]. In addition, considerable amounts of nutrients reach the mangrove ecosystems dissolved in seawater through the movement of the tides. Every characteristic present in that sediment can affect the physiological characteristics of a plant, such as the concentration of photosynthetic pigments, whose characteristics of the plant that can be altered by a variety of environmental factors, such as: salinity, irradiance, flooding, heavy metals, state nutritional, pollutants and therefore a potential indicator of adverse environmental conditions [51, 56, 67].

It has also been suggested that plants tolerant to salinity would be better adapted to deal with environmental stresses, including heavy metals. This performance is notably due to the plant's ability to accumulate metals in its tissues, triggering toxic metal detoxification mechanisms [68, 69].

Three distinct phases between plant responses to stress [70], in which a fourth was added after [71]:

- Response Phase (beginning of stress): alarm reaction or general alarm syndrome (SGA) (deviation from functional normality, decline in vitality and catabolic processes exceeding anabolism);

- Restitution phase (continuation of stress): resistance stage (adaptation, repair and reactivation processes);

- Final Phase (long-term stress): stage of exhaustion (very high stress intensity, overloading the capacity for adaptation, leading to chronic disease or cell death);

- Regeneration Phase: partial or complete regeneration of physiological functions when the stressor is removed and the damage is not very high.

The heavy metals released into the terrestrial environment tend to be concentrated in the soil and sediments, which become a large reservoir available for the roots of plants, which are very vulnerable to variations in concentrations of these elements. In aquatic environments these elements are available for both roots and shoots [72].

5.1 Iron stress conditions

Iron is an essential micronutrient for plants, involved in several fundamental processes such as photosynthesis, respiration, nitrogen fixation, DNA and hormone synthesis [73]. However, at high levels, this element can be toxic to plants [74].

This element is abundant in nature, reaching about 5% of the earth's crust. Despite this, iron toxicity is not normally a problem for plants, since most of this nutrient in soils is unavailable to plants [75]. In acidic and/or flooded soils, or in areas where Fe ore is being mined or being processed, increasing the concentration of Fe can lead to the excessive absorption of this metal, which quickly accumulates in the leaves and often reaching levels of toxicity [76].

Iron, when free and in excess within the cell, is capable of generating free radicals, such as the hydroxyl radical, through the Fenton reaction [77]. This radical is extremely toxic for cellular metabolism, being responsible for the oxidation of biological macromolecules such as proteins, nucleic acids and membrane lipids [78].

Studies [69], demonstrated that mangrove species that were evaluated, presented low iron bioconcentration factor in the leaf tissue. The redox environment and the high content of organic matter decrease the bioavailability of this element. In addition, the retention of this metal in the root suppresses its translocation to the leaves [69].

Plants, when they are under high levels of Fe and, or under reducing conditions, often form on the root surface the so-called "iron plate" in aquatic plants and in some terrestrial plants subject to flooding. The formation of these plaques is closely related to the oxidation of Fe^{2+} to Fe^{3+} and the consequent precipitation of iron oxides on the root surface [38, 79].

Due to the high adsorption capacity of the functional groups of Fe oxides and hydroxides, the iron plate can act as a barrier to the absorption of nutrients and toxic metals by adsorption and, or co-precipitation, interfering in the availability of these elements in the rhizosphere and its subsequent absorption and translocation to the aerial part [79].

Fe, although abundant in nature, normally does not reach toxic levels for most plants, since most of this nutrient in soils is unavailable, especially in neutral and, or alkaline soils [76]. In acidic and or flooded soils, or in mining or mineralization areas, there may be an increase in the concentration of available Fe, resulting in excessive absorption of this metal, often reaching levels of toxicity [76].

In the leaves, in high doses of iron, the appearance of yellow/brownish spots was observed, followed by the appearance of necrotic lesions, decreased leaf area and leaf abscission, probably resulting from the formation of oxidizing agents in the intercellular spaces that react with the components of the cell wall and plasma membranes [80]. The roots became darkened, indicative of Fe oxide deposition [81]. Less root formation was also observed and the roots became short, thin, rigid and brittle. The visible chlorosis observed in some leaves was proven by the decrease in the content of chlorophyll a. The reduction of chloroplast pigments has been associated with oxidative damage caused by the accumulation of reactive oxygen species (ROS) induced by toxic levels of Fe in leaf tissues [82].

In general, the excess of Fe induces P, K, Ca, Mg and Zn deficiency causing multiple nutritional disorders [83]. This interference of excess Fe may be associated with the precipitation of iron oxides on the root surface and the consequent formation of a ferric oxide crust (iron plate). The ability of plants to form these iron plates on the root surface is considered part of the mechanism used by plants to tolerate high levels of Fe^{2+} [84]. The formation of iron plaque, however, can lead to nutritional imbalance due to the high capacity of iron hydroxide functional groups to immobilize nutrients and metals by adsorption and / or co-precipitation inhibiting absorption, transport and/or use of other nutrients such as P, K and Zn [85].

The presence of organic matter can promote the availability of Fe, presumably through the supply of soluble complexing agents that interfere with fixation. When Fe is added to the soil in the form of a chelate, or when chelation occurs by soluble organic compounds, the concentration and gradient in the soil solution is generally higher than the concentration of Fe and non-chelated gradient and diffusion transfer is much larger [86].

The phenomenon of oxy-reduction is the most important chemical change on plants that are in flood areas, and oxidation–reduction or redox potential, which is a quantitative measure of the intensity of this change. The most drastic changes that occur when a soil is submerged and its Eh falls, reducing NO to nitrogen oxides, and Fe III to Fe II [87].

In an attempt to prevent iron deficiency, the plants developed two ways for its absorption: I - reduction of Fe^{3+} in Fe^{2+} through the acidification of the rhizosphere, caused by the proton extrusion by plasma membrane H^+-ATPases. This reduction of Fe^{3+} in Fe^{2+} is promoted by a specific protein, Ferro Chelate Reductase (FRO). After reduction, Fe^{2+} is transported by specific membrane transporters (IRT) into the cells [88]. II - Phytosiderophores (compounds that have a high affinity for iron) are secreted into the rhizosphere, where they join Fe^{3+} forming a chelate complex (Fe^{3+} -FS). This complex is transported by specific carriers known as Yellow Stripe (YS) into cells [89].

The ionic strength can influence the electrical potential and spatial structure of organic matter (OM) and, thus, affect its complexation with Fe. The complexation of Fe and Humic Acid (HA) is influenced by the ionic strength. From known values of ionic strength of freshwater, estuaries and marine environments, it is predicted that the complexation of Fe and HA occurs mainly in freshwater bodies, such as rivers and lakes. PH is one of the most important factors in the complexation of Fe and OM. The peak intensity of the Fe-HA complex was improved by increasing the pH from 4 to 6 and reached a maximum at pH 6. When the pH exceeded 6, the intensity of the complex of Fe-AH gradually decreased. The complexation of Fe and HA is strongly pH dependent due to the deprotonation of HA and hydrolysis of Fe. This can be assumed that Fe-HA complexes are formed mainly in freshwater bodies, where pH and ionic strength favor complexation. The Fe-HA complex in most freshwater bodies would eventually migrate to the estuary, and dissociate to release Fe at a higher pH. Within the estuary, the released Fe would be recomplexed with other strong binders from coastal water. HA, as an important dissolved iron transporter, can transport Fe from fresh water to estuaries [90].

5.2 Nickel stress conditions

Some researchers consider Ni to be an essential micronutrient in certain plant species, especially when grown in urea media, since Ni is a constituent of the urease enzyme [91], and its deficiency it leads to a reduction in urease activity in plant tissues such as soy, rice and tobacco, leading to an accumulation of excessive urea, making it phytotoxic [92]. Although the mechanisms of its phytotoxicity are still poorly studied, it is known that high levels of Ni in plant tissues inhibit photosynthesis and respiration. Symptoms of toxic effects are related to tissue damage, growth retardation, chlorosis and other symptoms specific to plant species [93].

Industrialization and urbanism are responsible for the increasing contamination of soils and water resources, with different toxic substances that represent a potential risk to human health and agriculture [94]. Heavy metals and metalloids constitute a special group of two pollutants due to their non-biodegradability, as well as rapid transport to the food chain. Ni is a significant environmental pollutant. In 2008, Ni was classified as "the allergen of the year" [95]. Generally, the majority of Ni released to the environment by human activities, especially those related to the raw material, is used in electroplating and metallurgy industries, as well as the application of mineral fertilizers that contain this metal [69, 96].

During the last decades, studies that discuss Ni toxicity have gained notoriety mainly due to their concentration in contaminated soil reaching 20 to 30 times (200–26,000 mg kg^{-1}) higher than the average (10–1000 mg kg^{-1}) found in natural soil [85]. Ni is unique among heavy metals, unlike Cd, Pb, Hg, Ag, and several other metals that have no known physiological function in plants. It is a constituent of a large number of enzymes, including ureases, which play an important role in seed germination and is necessary for the nitrogen metabolism of plants. Therefore, Ni maintains the appropriate cellular redox state and participates in several important metabolic processes [69].

Ni toxicity to plants has become a worldwide problem that also threatens sustainable agriculture. Ni can affect the transport of nutrients to the cells of the roots and consequently change the entire plant physiology, such as reducing the levels of chlorophyll, the photosynthetic activity of the leaf, leading to tissue damage and strongly reducing the production of plant biomass. At the biochemical level, Ni has a deleterious effect on the function of the membrane [70, 96, 97]. In chloroplasts, for example, it affects the light capture complex (CCL) and carotenoid values. It can also interfere with the electron transport chain and its intermediates (such as cytochromes b6f and b559) in leaves. By inhibiting key enzyme activities in the Calvin Cycle, Ni can also slow the dark reactions of photosynthesis. Additionally, there is growing evidence that Ni toxicity in plants is associated with oxidative stress as reflected by the increased concentration of hydroxyl, superoxide, nitric oxide and hydrogen peroxide radicals [67, 98, 99].

The excess of Ni induces leaf iron deficiency [100]. It was suggested that Ni could reduce the amount of Fe via competition with Fe^{2+} through the mechanism of absorption of the root cell membrane and the inhibition of its translocation from the root to the formation of the diaspore, causing over-accumulation of Fe in the roots. This situation may be responsible for the production of chlorotic leaves, especially between the veins [67, 101]. Another effect generated by the presence of Ni is its competition for binding sites, as they have ionic rays similar to Ca and Mg, and through this competition they can decrease the absorption of these macronutrients. This possible decline in the absorption of nutrients can also result in metabolic diseases and reduce the activity of the proton pump, thus reducing the energy required for the absorption of K [101].

Thus, the decline induced by Ni in photosynthetic activity and the deficiency of photosystem II can be explained by the adverse effect of excess of this metal on the electron transport chain, as a consequence of a decrease in chlorophyll synthesis. This is consistent with other studies that show that through the stress generated by excess Ni, the plant reduces photosynthetic activity, as this element is linked to the inhibition of primary photochemical processes [101].

Ni induces a reduction in total fresh weight without the concomitant effect on dry mass, suggesting a change in plant water status, which may be the result of decreased water absorption or increased water loss, both of which may occur due to damage to cellular structures [102]. In addition, Ni can promote a decrease in succulence and leaf density, which indicate real water deficiency [103]. However, in low concentrations, Ni is considered an essential element mainly due to its function as an irreplaceable component of urease [104].

An important point is the "browning" of the roots of mangrove seedlings treated with Ni, as also observed in roots of *Z. mays*. The darkening of root cells may indicate the oxidation of phenolic compounds to cytotoxic quinones, which is believed to be mediated by the reduction of an electron to semiquinone radicals that self-oxidize to form ROS [96, 105].

Works with *R. mangle* exposed to trace elements such as Ni are hardly found, due to little study in this area. The sensitivity of this plant to Ni is still poorly known, however, a study with *R. mangle* in an impacted environment and an non-impacted one comparing the results of both, it was concluded that the in spite of the morpho-anatomical changes observed, it is possible to state that this species survives without the considerable impairment of its leaf structure, in areas subjected to environmental impacts, differently from the results found in the present study, which allows us to consider our results to be positive [81].

Reduced growth and reduced biomass production are general responses of plants superior to the toxicity of heavy metals, which can be linked to loss in cell turgor, resulting in decreased mitotic activity and / or inhibition of cell elongation. Thus, the toxicity of Ni can cause growth inhibition of the aerial part and/or roots, as observed in several tested plant species, such as roots, and aerial part [106].

The symptoms of toxic effects are related to tissue damage, growth retardation, chlorosis and other symptoms [107]. The phytotoxicity of Ni is the result of its action on the photosystem, causing disturbances in the Calvin cycle and inhibition of electrical transport because of the excessive amounts of ATP and NADPH accumulated by the inefficiency of the biochemical phase of photosynthesis [108, 109].

6. Dynamics of organic matter in mangroves

In mangrove sediments, because of the intrusion carried out by the flood, there is a decrease in gas exchange between the soil and the air, since the rate of oxygen diffusion in water is slower than in the air, creating a reducing environment. Thus, the decomposition of organic matter will occur by organisms that do not use O_2 with a receptor, but NO^{3-}, Fe^{3+}, organic acids, SO_4^{2-} and SO_3^{2-}. Therefore, microorganisms more slowly decompose organic matter, which accumulates in the soil [110].

The organic matter accumulated in the soil is a source of nutrients in the mangrove, since the decomposition and mineralization of plant material is important in the nutrient cycling that occurs in the soil–plant-atmosphere system, allowing part of the carbon incorporated by biomass through the process of photosynthesis return to the atmosphere as CO_2 and the nutrients absorbed by the plants are again usable [111]. The mineralization of organic matter is influenced by factors such as soil redox potential, microbial activity, plant species, litter production, litter C/N ratio and tidal flooding [112].

The mangrove sediments are classified as Organosols and Gleisols, depending on drainage conditions. Organosols have an accumulation of plant remains with varying degrees of decomposition and restricted drainage conditions [113]. The Gleisols present an intense reduction of the iron compound in the presence of organic matter, with or without oxidation alternation and are permanently or periodically saturated with water [114]. The water saturation is due to the influence of the tides, which is considered as the main mechanism of entry of saline waters in the mangroves [115]. Tides are responsible for important characteristics of these soils, such as reduced redox potential, existence of high pH values and dynamics of elements such as sulfur and iron [116].

Because of the effects of flooding on mangrove sediments, there is a decrease in gas exchange between soil and air, as the rate of oxygen diffusion in water is slower than in air. This interference in the diffusion of oxygen generates a reducing environment, causing the microorganisms to have their metabolism slowed down, since O_2 acts as an electron receptor promoting the maximum efficiency of decomposition of organic matter. With this, the microorganisms start to use electron acceptors other than O_2 for the decomposition of organic matter, following the following thermodynamic sequence: NO^{3-}, Mn^{4+}, Fe^{3+}, $SO4^{2-}$, CO_2 (methanogenesis), N_2 and H^+ in a way slower and less efficient, resulting in the accumulation of organic matter in the soil [110].

In regions where mangroves predominate, it is common to see a combination of high levels of organic matter, arising from the greater supply of plant biomass, anaerobic conditions, source of reactive Fe and sources of $SO4^{2-}$, from sea water, both readily available, making mangrove soil an environment conducive to the occurrence of bacterial sulfate reduction (RBS) [117]. This RBS is the dominant form of breathing in mangrove soils, with iron and sulfur compounds being important elements in the biochemical cycles of these environments [118].

The dynamics of Fe and S in these environments are affected by the amplitude of the tides, which sometimes cause oxidative conditions and sometimes reduce the mangrove soils [119]. Vegetation also influences, as it oxidizes the rhizosphere region by translocating the oxygen absorbed on the soil surface to the root structures located on the subsurface [116]. Therefore, elements such as iron and sulfur, which are sensitive to changes in redox conditions, have their dynamics altered and may suffer an increase or decrease in the solid fractions of the soil and interstitial waters [116].

In the mangrove, the rate of denitrification and ammonification can be high, due to factors such as anaerobic condition combined with high levels of organic matter [116]. Under flood conditions, high levels of ammonium can accumulate, since this ion is relatively stable in anoxic conditions, predominating in most soils [120]. The levels of inorganic nitrogen in the mangrove soil are usually low because of the low addition of N to the soil, losses by tide, reduced transformation processes and efficient microbial assimilation [116].

The decomposition of organic matter in the mangrove is determined by the quality of the litter present in the soil [116], and the chemical composition of the leaves can accelerate or delay the decomposition [116]. The leaves of the genus Rhizophora have constituents that are more difficult to degrade than the leaves of Avicennia, due to their large amount of polyphenols [121].

The mineralization of organic matter in mangrove soils is carried out by aerobic and anaerobic microbial processes. In anaerobic mineralization, microorganisms use other electron acceptors to replace O_2, e.g. NO_3 - → Mn (IV) → Fe (III) → $SO4^{2-}$ → CO_2. According to this sequence, there is a gradual decrease in the redox potential and in the free energy of oxidizing agents for respiration. Thus, the use of acceptors other than O_2, causes the decomposition of organic compounds to be slower, accumulating in the soil [116]. Anaerobic mineralization in mangrove soils, associated with the high capacity for biomass production, makes this area an accumulator of carbon and, therefore, important in the global cycle of this element and in the context of climate change [122].

The process of decomposition of organic matter through aerobics occurs on the soil surface and in the small aerobic zones around the roots where there is oxygen and a few centimeters from the water column [123]. In addition to aerobic and anaerobic respiration, suboxide respiration can also occur in the degradation of organic matter in the mangrove soil [116]. Under sub-toxic conditions, iron oxides and hydroxides are reduced in the decomposition of organic matter, generating high levels of Fe^{2+}, which can precipitate in the formation of carbonates, sulfides, phosphate or new oxidation, promoting the synthesis of ferrihydrite, lepidocrocyte and goetite [116].

Because seawater has high concentrations of sulfate, the decomposition of organic matter in mangrove soils is predominantly attributed to the process of bacterial sulfate reduction (RBS) [124], resulting in the formation of sulfide. The sulfide generated in the RBS process can have several destinations, such as precipitation in the form of iron sulfides - example: Pyrite (FeS_2) was considered as the final product, and more stable in the RBS process and participate in redox reactions [125]. Consequently, most mangrove soils contain high levels of inorganic sulfur in the form, mainly, of FeS_2 and elemental sulfur (S_0) [126]. In iron-rich environments, the oxidation of iron in the decomposition of organic matter can be comparable, or even greater, than the reduction of sulfate as this can be impaired in the presence of other electron receptors such as O_2 and Fe^{3+} [116].

The presence of functional groups of organic matter in the soil can complex trace metals present in the soil solution, and thus decrease the toxic capacity of the metals [127]. However, to explain the effects of the possible decrease in toxicity caused by nickel in *R. mangle* seedlings, which was observed in the vast majority of parameters analyzed, one should not only take into account the role of SH on plant growth and plant development as a whole, but also taking into account the complexing capacity of SH, since organic matter is considered an important mitigator of the toxic effects of heavy metals because it has the ability to form insoluble complexes with these metals and other elements, making plants less available, enabling the cultivation of plants in areas with high levels of contamination [128, 129].

6.1 Organic matter; humic substances and their possible interactions with trace elements

Soil is the basis of the entire production process on the planet. It is an important and well-organized component of nature, adjusted to multiple functions of dynamic balance. Its composition is varied and dependent on factors and formation processes (biogeochemical), as well as on the handling and use to which it is submitted [130]. The organic matter content (OM) of the soil is dependent on many factors that exert its influence individually and together, such as: climate, soil texture, topography, drainage, vegetation cover and land use [131]. The process of formation of organic matter in the soil is initially a biological process and almost all the flora and fauna existing in the soil has a direct or indirect effect [132].

OM is a complex matrix formed during the microbial decomposition of plant and animal waste that exists in soil, groundwater and rivers and plays a vital role in the global carbon cycle [133]. This OM can be divided into two fractions. The hydrophobic (non-humic) group that contains aliphatic chains of C and N, including carboxylic acids, carbohydrates, tannic acids (TA) and proteins and a hydrophilic one, composed of humic substances (HS), aromatic carbon, phenolic structures, and conjugated double bonds.

HS can be classified in terms of its solubility in different pH ranges: humic acids (HA) comprise the fraction that is insoluble at a low pH; fulvic acids (FA) are low molecular weight compounds that are soluble in a larger pH range and humine is the fraction that is insoluble at any pH.

The greater the amount of C and N, the greater the degree of evolution of humic materials. Atomic C / N, H / C and O / C ratios are often used to monitor structural changes in humic fractions and to elucidate the structural formulas of humic substances from different sources [134, 135]. The C/N ratio indicates the degree of incorporation of N and the degree of humification in the structure of SH [136, 137]. The O/ C ratio is normally used to estimate the abundance of oxygen contained in functional groups [138] and the H/C ratio is used as an index of aromaticity and aliphaticity of organic matter [136].

The root architecture of *R. mangle* seedlings was altered by adding SH to the culture solution. The number of lateral roots (NRL) of *R. mangle* seedlings was changed by the presence of the best dose of SH (6.25% HS) in relation to the control treatment [139–141].

SH and metals have interactions that are influenced by several variables, such as chemical load and heterogeneity of the humic material. These interactions of metals with SH are closely linked to ionic strength and not only to concentration that are also bound to their binding functions [142].

Mangrove sediments are known to have a great capacity to accumulate metallic elements, which is attributed in part to their high content of organic matter, which can act as an agent for complexing trace elements. In addition, the mangrove sediments are subjected to sulfate reduction processes, which leads to the precipitation of sulfide minerals that are capable of retaining, for example, Co and Ni in marine sediments. In mangrove sediments, the complexation processes of trace elements, however, depend on biogeochemical gradients, salinity, redox potential and organic matter contents that are moved by the distance to the seashore, the magnitude of the tide, and the types of mangrove tree species. In addition, diagenetic reactions can operate on sediments as a function of time, due to tidal cycles, flooding seawater, as well as freshwater intakes. The redox cycle in mangrove sediments can thus have a significant impact on speciation of trace elements [143, 144].

On the other hand, the humate's ability to leach minerals and mobilize metals is well known, and is assumed to be an important pedogenic process. With this there is a reconstitution of organic complexes and stabilization of metals initially released silicates and oxides. Several metals, including Cu, Zn, Co, Ni and Fe, are mobilized in soils and lead to reducing conditions [145].

Oxygen atoms in HS are mainly present in the form of carboxylic and phenolic groups [146] that can play an important role in creating binding sites for certain inorganic species (such as polarizable metal cations) and tracking organic compounds (including pesticides and endocrine disrupters) present in the environment [147].

HS are defined as supramolecular associations of organic molecules of small molecular mass that hold together because of the hydrophobic bonding forces of van der Waals, dipole–dipole and hydrogen bonds [148]. HS can play an important role in the bioavailability of metals in soils and, thus, contribute to the mitigation of toxicity to plants. Assessing the influence of HS on the mobility of Cu and Zn during aerobic composting of sewage sludge, a study [149] was observed an increase in the distribution coefficient of humic acids (HA)-Cu and HA-Zn of 27.5 and 3.33%, respectively, suggesting that there was a reduction in the mobility and availability of these metals.

The interest in the chemical characterization of HS is based on its marked influence on the solubility and mobility of trace elements in the soil and on the complexation of nutrients [150]. The ability of HS to interact with metals is normally attributed to the high content of functional groups containing O, such as carboxyls (CO_2H), carbonyls (CO) and hydroxyls (OH) [151]. The main chemical elements affected by redox reactions are: C, N, O, S, Mn and Fe. In contaminated soils, arsenic (As), Se, Cr, Hg and Pb can also be added.

In anaerobic conditions, resulting from O_2 depletion, after flooding the soil, or even in anoxic microsites, such as inside water-saturated micropores, aerobic microorganisms drastically decrease their activity, become quiescent or die [152]. Optional and anaerobic microorganisms then proliferate, using carbon compounds as a substrate and compounds of N, Mn, Fe and S, to transfer their electrons from respiration. In flooded systems, the decomposition of organic matter occurs almost entirely through the work of anaerobic and/or facultative microorganisms [152]. As anaerobic bacteria operate at a much lower energy level than aerobic ones, both decomposition and assimilation are slower in submerged systems. This fact is illustrated by the accumulation of plant residues in swamps and submerged sediments [153].

Humic acids (present in humic substances) have functional groups, such as carboxylic groups that can form metal salts, treatment with humic acids is likely to remove metals. Some of the metals can be associated with carbohydrates or amino acids. It is possible, however, that humic acid behaves like a macrocyclic compound for metals. These compounds have unusual ion-binding abilities. Its ability to form stable compounds with the alkali and alkali metal ions. In fact, alkaline and alkaline earth hydroxide solutions make up the bulk of the inorganic portion of humic acids. Part of heavy metals can also be associated with humic acids by the same mechanism that allows the complexation of metal ions by natural polyelectrolytes, such as polygalaturonic acid, or other polyacids. The addition of metals of such polymers forms insoluble complexes in the form of a "sandwich" [154].

7. Conclusions

Related evidence in the literature shows that attributes related to the growth and development of mangrove plants are negatively affected by their exposure to stress conditions by iron and nickel. However, organic matter, governed by its main component (such as humic substances) can, at least in part, assist recovery due to the damage caused by the aforementioned trace elements, showing the potential of humid organic matter to recover degraded environments and/or anthropized, such as the various mangroves located around the world.

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Conflict of interest

The authors declare no conflict of interest.

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