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The partitioning of transitional metals (Fe, Mn, Ni, Cr) in mangrove sediments downstream of a ferralitized ultramafic watershed (New Caledonia)

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Abstract

In New Caledonia, one third of the Island is composed of ultramafic rocks, and lateritic soils enriched in Fe, Ni and Cr. Open-cast mining occurs all around the Island, and processes of erosion and sedimentation, which occur naturally along the coastline, are strongly amplified by mining activities. Due to their position, at the interface between land and sea, mangroves receive extensive amounts of particles emanating from rivers through estuaries. The purpose of this study is to understand the distribution and partitioning of some transitional metals (Fe, Mn, Ni, Cr) in sediments and pore-waters in a mangrove swamp, which is situated downstream of a catchment characterized by lateritic soils that were exploited a century ago. Quantitative analyses on bulk and after selective extraction, were carried out on cores collected along a transect within the intertidal zone, i.e. beneath a *Rhizophora stylosa* stand, an *Avicennia marina* stand, and within a salt flat. Mean metal concentrations were ($\mu\text{mol g}^{-1}$): Fe (1997) > Ni (44.2) > Cr (31.9) > Mn (8.8). Thus, Ni, Cr and Fe concentrations in this study are substantially higher than mangrove world average. In addition, Ni concentrations are 10 to 100 times higher than in other New Caledonian mangrove developing downstream of a catchment not composed of ultramafic rocks. The studied mangrove is characterized by gradients of water and organic contents with depth and along the intertidal zone, which induced different redox conditions, and thus different metals partitioning. Transitional metals are deposited in the mangrove mainly as oxides and/or oxy-hydroxides, that are subsequently dissolved by bacteria for the decomposition of organic matter, and which leads to a strong increase of metals in the dissolved phase. Then, dissolved metals were precipitated with organic and sulfide compounds. To conclude, organic diagenesis in mangrove sediments leads to the transfer of transitional metals from oxide form to organic and sulfide forms.

Keywords : Mangrove; Transitional metals; Organic matter; Redox conditions; New Caledonia

1. Introduction

Mangrove forests play a key role in the conservation of tropical and subtropical coastlines. They support a wide variety of ecosystem services (Walters et al., 2008) and provide critical nurseries and habitats for fish and crustacean (Nagelkerken et al., 2008). Mangroves act as a natural barrier against cyclones, flooding, and coastal erosion. These forests are highly productive, with a NPP estimated to $\sim 218 \pm 72 \text{ Tg C a}^{-1}$ ([Bouillon et al., 2008] and [Kristensen et al., 2008]). Cumulating all the services provided by mangroves, the ecosystem value can reach up to several thousand US\$ $\text{yr}^{-1} \text{ ha}^{-1}$ (Walters et al., 2008). Mangrove ecosystems once covered almost 200,000 km^2 (Spalding et al., 1997). However despite their value, mangroves are threatened ecosystems, disappearing worldwide at the rate of 1 to 2% per year, as a result of over-exploitation, pollution, and conversion ([Valiela et al., 2001], [FAO, 2003] and [Duke et al., 2007]). Due to their position, at the interface between land and sea, mangroves receive extensive amounts of sewage emanating from rivers through estuaries. In emerging countries, where 90% of the mangroves are located, demographic pressure combined with industrial development, has led to the release of metals and metaloids into the environment. Because of their toxicity, bio-accumulation capacity and persistence, transitional metals represent a major threat to mangrove biodiversity and also for human health. In contrast with organic pollutants, metals cannot be biologically or chemically degraded, and thus may either accumulate locally or be transported over long distances. Due to the capacity of mangroves to efficiently trap suspended material from the water column (Furukawa et al., 1997), and the high affinity of organic matter (OM) for metals (Nissenbaum and Swaine, 1976), mangrove sediments have a large capacity to accumulate these pollutants. The cycling of trace metals in mangrove ecosystems is thus a serious question addressed by many authors during the last few decades ([Harbison, 1986], [Lacerda et al., 1988], [Clark et al., 1998] and [Tam and Wong, 2000]).

In New Caledonia, extensive mangroves are fringing 80% of the western coastline of the Island and 20% of the eastern side. These mangroves act as a buffer between a lagoon of more than 20,000 km^2 , delimited by an almost continuous coral barrier reef of over 1500 km in total length and recently registered as an UNESCO World Heritage site, and a land that is characterized by mining activities (Ni-ore) exploiting mainly lateritic soils. New Caledonia is currently the third largest nickel producing country in the world. Processes of erosion and sedimentation, which occur naturally along the coastline, are strongly amplified by mining activities (Fernandez et al., 2006). The mangrove flora of New Caledonia includes more than 20 species (Duke, 2006). *Rhizophora* spp. are predominant in 50% of mangrove areas, colonizing the seashore, and *Avicennia marina* in more than 15%, developing at the edge of salt flats (Virly, 2006). Throughout the world, the existence of different zones parallel to the coastline, each dominated by a different botanical species, is commonly observed in mangrove swamps. In a previous study (Marchand et al., 2011a), we suggested that in New Caledonia the main factor controlling the distribution of mangrove species is the soil salinity, which in turn is controlled by the duration of tidal immersion and thus by soil elevation (Baltzer, 1982). This distribution in the tidal area may be responsible for differences in sediment geochemistry, principally speciation and metal bioavailability between the different parts of mangrove forests. The purpose of this study is to understand the distribution and partitioning of some transitional metals (Fe, Mn, Ni, Cr) in sediments and pore-waters in a mangrove swamp, which is situated downstream of a watershed characterized by lateritic soils that was exploited a century ago. In this context, we were interested in the relationships between mangrove species, sedimentary organic content, pore-water properties, and metals concentrations. To reach our goal, quantitative analyses, e.g. Rock-Eval, ICP-OES on bulk

and after selective extraction, were carried out on cores collected along a transect within the intertidal zone, i.e. beneath a *Rhizophora stylosa* stand, an *A. marina* stand, and within a salt flat. These data would also provide some baseline information on the variability of transitional metal concentrations in New Caledonian mangrove substrate, and will be useful for further studies on mangroves that are situated downstream current Ni exploitation areas. This study was undertaken as part of a larger investigation of metal cycling in the mangrove of New Caledonia, the main objective being to understand the impact of Ni exploitation on the ecosystem.

2. Materials and methods

2.1. Study site and sampling

New Caledonia, which is situated in the South-West Pacific Ocean, is orientated along a northwest–southeast axis, and is almost 500 km in length and about 50 km in width (Fig. 1). The main island (20°S–23°S) is characterized by a tropical climate, strongly influenced by the Intertropical Convergence Zone (ITCZ) cycling, with a mean annual rainfall close to 1100 mm, and average monthly air temperatures fluctuating between 20 and 27 °C. However, the west coast of the main island, on which the studied mangroves develop, is characterized by a semi-arid tropical climate. Work was carried out at the end of the rainy season in May 2008. The studied mangrove is located at the mouth of the Dumbea River. The catchment of this river is composed of ultramafic rocks and lateritic soils (BRGM, 1965), enriched in Ni and Cr, which were exploited from the end of the 19th century to the middle of the 20th century. Mining is no longer occurring in this catchment; however because of the old mines, processes of erosion are intense during heavy rain, and sediments are deposited along the shoreline, and more specifically in the mangrove.

Cores (70 cm deep) were collected at low tide with an Eijkelkamp gouge auger along a transect within the intertidal zone: in the *R. stylosa* stand, in the *A. marina* stand, in the salt flat. One core was collected in each mangrove stand. In the *R. stylosa* forest, core was collected under prop roots. In the *A. marina* forest, core location was chosen equidistant from trees, in consideration of the large extension of the radial cable roots. After being collected, cores were wrapped in plastic film and aluminum foil in order to limit gaseous exchanges. Back at the lab (less than 1 h after core collection), the cores were cut into 2 cm sections from 0 to 20 cm depth, every 5 cm sections from 20 to 70 cm depth. Subsamples for trace metals analysis were collected at the center of core throughout the length. Until drying, samples were kept frozen. After drying the core sections were ground with an agate pestle and mortar. At least, 10 samples per core were chosen for analyses as a function of physico-chemical parameters depth trend (redox, pH, salinity).

Dissolved metals in pore waters were extracted, at the lab, on the day of coring with soil moisture samplers Rhizon® (Song et al., 2003), which were directly inserted into a piece of core. The sampler is connected to a syringe using luer-lock fittings and PVC tubing. The syringe piston was drawn back thereby creating a vacuum and allowing the collection of pore-water from the sediments. All samples were then immediately filtered through 0.45 µm Sartorius® filters and acidified to pH 2 with Suprapur® HNO₃ (Merck). Samples were stored in cleaned 14 ml polypropylene tubes, in a cold room (T = 4 °C) until analysis.

2.2. Analytical methods

2.2.1. Salinity, pH, and redox

Physico-chemical parameters were determined in an air-conditioned laboratory a couple of hours after coring. Salinities were determined using an Atago refractometer after extracting a drop of interstitial water from the core (through filter paper in a hand press). pH was measured using a glass electrode and a pH meter (WTW). The pH electrode was calibrated using pH 4 and 7 standards (NIST scale). Redox potential was measured, using a combined Pt and Ag/AgCl (reference) electrode connected to a pH/mV/T meter (WTW). The redox electrode was periodically checked using a 0.43 V standard solution and demineralized water. Probes were carefully inserted into the mud until stable measurements were reached, then were thoroughly washed. Redox data are reported relative to a standard hydrogen electrode, i.e., after adding 202 mV to the original mV values obtained with an Ag/AgCl reference electrode (at 25 °C). Redox conditions were defined as follows in this study:

–Oxic > 400 mV, presence of measurable dissolved oxygen.

–100 mV < Suboxic < 400 mV, lack of measurable oxygen or sulfide, presence of dissolved iron or manganese, and no reduction of sulfate.

–Anoxic < 100 mV, sulfate reduction.

2.2.2. TOC and TS

Total Organic Carbon (TOC) was determined using a Rock-Eval 6 pyrolysis on powdered sediment samples ([Lafargue et al., 1998] and [Marchand et al., 2008]). In the R-E 6, samples are first pyrolysed under inert nitrogen atmosphere, and the residual carbon is subsequently burnt in an oxidation oven. The pyrolysis program was: 200 °C (2 min), then to 650 °C at 30 °C min⁻¹ (hold 3 min). The oxidation phase starts with an isothermal stage at 400 °C, followed by an increase to 850 °C at 30 °C min⁻¹ (hold 5 min). TOC is determined as the sum of residual and pyrolysed organic carbon contents.

Total sulfur (TS) concentrations were measured by combustion at 1100 °C with a CNS-2000 LECO apparatus.

2.2.3. Transitional metals/selective extractions

To highlight the geochemical behavior of the metals (Cr, Fe, Mn and Ni), a sequential extraction protocol was used. Despite some criticism associated with sequential extraction techniques in the literature (e.g., [Jouanneau et al., 1983] and [Nirel and Morel, 1990]), this type of protocol makes it possible to understand the phenomena which occur in the different mangrove deposits. The protocol used was based on the technique developed for river sediments ([Tessier et al., 1979] and [Meguelatti, 1982]), and subsequently adapted to lateritic environments. Briefly, two grams of fine dry sediment were subjected to a 4 phase chemical extraction protocol to obtain metal concentrations associated with 4 geochemical fractions. The various extractions were completed as follows:

•Oxidizable forms — this fraction represents the metals linked to the organic matter in the sediment. This extraction was completed using strong oxidants in acidic medium (HNO₃);

- Acid-soluble forms — these are relatively easily extracted using a weakly buffered acidic solution (CH₃COOH/CH₃COONa). The forms either occur in the carbonate matrix of the sediment, or are adsorbed on the particle surfaces or coprecipitated (e.g., [Chester and Hugues, 1967] and [Gupta and Chen, 1975]). In lagoonal deposits, these metals originate from the aragonitic skeleton of organisms which, when alive, ingest or assimilate metals (Brocero, 1998). Due to a lack in the chemical selectivity of the reactants, this extraction step also potentially includes the easily leachable metal, initially bound by adsorption on the poorly crystallized manganese and iron oxides (Förstner et al., 1986) and clays (Posselt et al., 1968).

- Reducible forms — these forms are associated with oxyhydroxides of manganese, aluminum and iron, and are extracted using reducing conditions such as hydroxylammonium chloride in an acidic medium.

- Refractory forms — these are the metals that are strongly held by the particle matrix, e.g., in silicates, aluminosilicates and mainly oxides as the result of the peridotite weathering. These were extracted using alkaline fusion technique.

The reagents and chemicals used were Merck, ProAnalysis grade. The containers used for the sequential extractions were made of HDPE, Teflon or platinum. All containers were decontaminated by soaking in nitric acid (5%) for 24 h and rinsed in ultra-pure water (Milli-Q).

The quantification of Cr, Fe, Mn and Ni in each geochemical phase was carried out by ICP-OES (Optima 3300 VD, Perkin Elmer). Analyses were carried out on certified reference materials (SD-M-2/TM, NRCC-BCSS-1) for total elements content. In addition, samples of two certified reference materials (TM-26.3 and TMDA-61, Environment Canada, Table 1) were intercalated during the analytical series.

3. Results and discussion

3.1. Characteristics of mangrove sediments

Mangrove sediments geochemistry strongly differs from that of marine sediments because of the continuous inputs of fresh higher plant debris. As a consequence, physico-chemical characteristics of mangrove sediments are highly variable, mangrove tree species being one of the controlling factors (McKee, 1993). Results concerning the physico-chemical properties of the studied sites, i.e. salt flat, *A. marina* stand, and *R. stylosa* stand, are presented in Fig. 2. The measured parameters, i.e. Eh, pH, water content, salinity, total sulfur (TS), and total organic content (TOC), strongly varied between sampling sites, and with depth. In New Caledonia, the same species distribution within mangroves can be observed over the whole island. *Rhizophora* trees develop mainly in zones swept daily by tides, while *Avicennia* trees develop, at higher elevations, at the borders of the salt flat, which occupies the higher area in the intertidal zone. This topographic zonation induces differences in the length of immersion by tides, and thus differences in the water content of the sediments, which may influence diagenetic processes. At low tide, within the *Rhizophora* forest, the water content varied between 60 and 80%, without any specific trend, while in the *Avicennia* stand, it increased from 45%, at the top of the core, to 65% at 20 cm deep, where it stabilized. Finally, within the salt flat the water content varied around 40% throughout the length of the core. At the time of coring, i.e. at the end of the rainy season, salinity values increased with depth in the 3 stands, reaching up to 60, but no clear differences between sites can be highlighted. However in

previous studies in mangroves of New Caledonia carried out during different seasons ([Marchand et al., 2011a] and [Marchand et al., 2011b]), we measured an increase in salinity values from the seaside to the landside of the mangrove, with values higher than 100 in a salt flat. We thus suggested that surface ground elevation indirectly controlled zonation, by controlling the length of immersion, the amount of evaporation, and thus the salinity of pore-water. Salinity is recognized as a key factor in mangrove zonation (Walsh, 1974), along with flood tolerance ([Naidoo, 1985] and [McKee, 1993]), and specific properties of propagules ([Rabinowitz, 1978] and [Smith et al., 1989]). Within the present transect, from the *Rhizophora* stand to the salt flat, there were not only a water content gradient, but also a gradient of organic matter content. TOC values ranged between 8 and 17% in the *Rhizophora* stand, 2 and 9% in the *Avicennia* stand, and around 1% in the salt flat. Mangrove forests are highly productive ecosystems, with a net primary productivity estimated at $149 \text{ mol C m}^{-2} \text{ y}^{-1}$ (Bouillon et al., 2008). Kristensen et al. (2008) showed that median TOC is around 2.2% in mangrove sediments, with strong variations existing between sites. The fact that the organic enrichment of sediments beneath *Rhizophora* is higher than the *Avicennia* is consistent with previous observations in Australia (Alongi et al., 2000). This enrichment reflects the more developed root-system of *Rhizophora* (Hesse, 1961), compared to the radial cable root system of *Avicennia* that develops predominantly in the subsurface zone (de Granville, 1974). In the core collected in the *Avicennia* forest, TOC increased with depth, from 2% in the upper 25 cm to 8% at 40 cm depth. This result is consistent with our visual observations of the core, since at this depth, the core was characterized by an increased proportion of red tissues, characteristic of *Rhizophora* wood. We also made this observation in other mangroves developing on the west coast of New Caledonia ([Marchand et al., 2011a] and [Marchand et al., 2011b]), implying that the *Avicennia* forests develop on sediments that were previously colonized by *Rhizophora*. The gradients of water and organic contents with depth and along the intertidal zone induced different redox conditions. Beneath *Rhizophora* stand, the upper sediment was characterized by a sharp decrease of redox values, from 360 mV at the top of the core down to 60 mV at 18 cm, with TS concentrations increasing from 3 to 12%. pH values decreased from 6.5 at the top of the core to 5.8 at 18 cm deep, and then slightly increased without being higher than 6. Beneath the *Avicennia* stand, TS concentrations were nearly close to the limit of detection in the upper 30 cm of the core, and then started to increase, reaching 12% at 60 cm depth. Redox and pH values decreased with depth on the whole core, from 320 mV to 30 mV, and from 6.8 to 6.2, respectively. In the core collected in the salt flat, TS was less than the limit of detection in the upper 20 cm, and was around 3% below this depth. Redox values ranged between 300 and 400 mV over the whole profile, while pH values ranged between 6.2 and 6.8. Sulfate reduction is the main organic matter decomposition pathways in mangrove sediments. Nevertheless aerobic respiration, and in to lesser extent denitrification, manganese and iron respirations, can develop (Kristensen et al., 2008). Suboxic to oxic conditions may be explained by biological or physical factors. First, crab burrows may induce such condition, by allowing the renewal of electron acceptors during high tide (Kristensen, 2008). Bioturbation can also be created by the root system of mangrove trees. In addition, the physiological activities of the root system can lead to increased O_2 concentrations in sediments. Since Scholander et al. (1955), it is known that pneumatophores constitute a pathway for the exchange of oxygen between the atmosphere and sediments. In addition, this cable root system has the capacity to diffuse oxygen into the sediment, creating oxidized rhizosphere (Thibodeau and Nickerson, 1986). In French Guiana, we demonstrated that the older the *Avicennia* forest, the higher the redox values, providing the sedimentary organic content was low, highlighting the key role of root growth on redox conditions (Marchand et al., 2004). Thus, oxic to suboxic decomposition pathways can characterize sediments below *Avicennia* stands, while beneath *Rhizophora*,

sediments are known to be highly anoxic and sulfidic (Hesse, 1961), which is consistent with our redox and TS measurements. With the present results, we suggest that redox conditions found within mangrove sediments are directly linked with the position of the forest in the intertidal zone. On the one hand, this position induces various lengths of immersion, and thus sediments contain different amounts of water. Low water content, associated with mud cracks like in the salt flat, allows higher oxygen diffusion from the atmosphere towards the sediment, inducing oxic to suboxic conditions. On the other hand, mangrove zonation influences the sedimentary organic content. Firstly, because the root system of *Avicennia* is less developed and induces lower organic enrichment of the sediment. Increasingly smaller trees are observed with increasing distance from the water inputs. *Avicennia* trees, being at the edge of the salt flat, develop at the price of energy consumption, which is incompatible with a certain growth. They rarely exceed the shrub stage in New Caledonia. This is likely to result in low productivity, lower organic accumulation in the sediment, and thus less oxygen consumption. Consequently, there is a decreasing gradient of sediment oxygenation from the salt flat to the *Rhizophora* stand.

3.2. Accumulation of transitional metals in sediments

Due to of the high rate of organic accumulation and the fact that fine particles can be trapped in mangroves, this ecosystem can act as a sink for trace metals flowing down rivers from catchments (Harbison, 1986). The average concentrations of some metals (Ni, Cr, Fe and Mn) from the studied mangroves and salt flat sediments in Dumbea are given in Table 2 along with their respective ranges. Mean trace metal concentrations were ($\mu\text{mol g}^{-1}$): Fe (1997) > Ni (44.2) > Cr (31.9) > Mn (8.8). Mn concentrations are in the range of those measured in other mangroves all around the world. On the contrary, Ni, Cr and Fe concentrations in this study are substantially higher than world average. For example, in mangroves sediments of the Godavari estuary (Ray et al., 2006), of the Pearl River estuary (Li et al., 2007), and in Panama (Defew et al., 2005), Ni concentrations were lower than $1 \mu\text{mol g}^{-1}$. Cr concentrations in mangrove sediments are also usually lower than $1 \mu\text{mol g}^{-1}$ ([Perdomo et al., 1998], [Tam and Yao, 1998] and [Jingchun et al., 2006]). Recently, Lewis et al. (2011), in their review concerning contaminants in mangrove ecosystems, confirmed that Ni and Cr concentrations higher than $1 \mu\text{mol g}^{-1}$ were not described worldwide. Concerning Fe, concentrations ranging from 100 to $1000 \mu\text{mol g}^{-1}$ were measured recently in Brazilian mangroves ([Ferreira et al., 2007] and [Otero et al., 2009]). The mean sediment metals concentrations measured in the present study are substantially elevated, with metals concentrations similar to those measured in soils close to a FeCr smelter, where mean concentrations reached $25 \mu\text{mol g}^{-1}$ for Ni, $1160 \mu\text{mol g}^{-1}$ for Fe, and $96 \mu\text{mol g}^{-1}$ for Cr (Shtiza et al., 2005). Similarly, mean Ni concentrations close to $15 \mu\text{mol g}^{-1}$ are reported from the vicinity of a Ni smelter (Nicolaidou and Nott, 1998). In New Caledonia, one third of the Island is composed of ultramafic rocks, and lateritic soils enriched in Fe, Ni and Cr. Open-cast mining occurs all around the Island. A large part of the Ni and Cr in these soils are associated with Fe-oxides (Becquer et al., 2003). The catchment of the Dumbea River is composed of lateritic soils, exploited only up to 1927. The richness of these mangrove sediments in metals reflects the mineralogical and elemental composition of this catchment area. In addition, it highlights the fact that even if mining has stopped, natural erosion can lead to the deposit of huge quantities of metals in mangroves. In other mangroves of New Caledonia, we measured Fe concentrations ranging from 600 to $900 \mu\text{mol g}^{-1}$, Ni concentrations ranging from 0.5 to $3 \mu\text{mol g}^{-1}$, and Cr concentrations around $1 \mu\text{mol g}^{-1}$ ([Marchand et al., 2011a] and [Marchand et al., 2011b]). Thus in the present study, Ni concentrations are 10 to 100 times higher than in a mangrove developing downstream of a catchment not composed of ultramafic rocks.

3.3. Fe partitioning in mangrove swamp sediments

Highly weathered ferralsols occur extensively in New Caledonia (Latham et al., 1978). Becquer et al. (2001) showed that total Fe_2O_3 content represented always more than 50% of the mineral composition, and could reach up to 65% in the upper part of a toposequence developing on peridotites in the south of New Caledonia. The mineralogical composition of this toposequence is dominated by goethite, whereas hematite, magnetite, and maghemite were present at lower concentrations. Coastal sediments of the Dumbea River, on which the studied mangrove develops, derived for 95% of peridotitic parts of the watershed (Baltzer, 1982). As a consequence, one can imagine that Fe partitioning in mangrove sediments is dominated by oxide forms, and mainly goethite. However, the selective extraction method used (Tessier et al., 1979) in this study does not allow for the separation of highly crystallized oxides and iron oxyhydroxides in the oxide-bound form. In fact, hydroxylammonium chloride only extracted poorly crystallized forms (or neoformed forms), ferrihydrite iron and lepidocrocite iron (Ferreira et al., 2007). Consequently, with the method used, we considered that highly crystallized forms of iron oxides were associated with the residual phase and not with the oxide phase. The selective extraction data are used in this study only to reveal trends in trace metal partitioning in sediments beneath different mangrove stands. Within the core collected in the salt flat, Fe was distributed as follows: the residual phase represented between 60 and 90%, the oxide phase between 7 and 20%, the carbonate phase was below 5%, and the organic and exchangeable phase was less than 1% (Fig. 3a, b). Within the core collected in the *A. marina* stand, Fe was distributed as follows: the residual phase represented between 45 and 95%, the oxide phase between 3 and 45%, the carbonate phase was less than 2%, and the organic and exchangeable phase ranged between 1 and 15% (Fig. 3d, e). Within the core collected in the *Rhizophora* stand, Fe was distributed as follows: the residual phase represented between 20 and 85%, the oxide phase between 10 and 50%, the carbonate phase between 2 and 6%, and the organic and exchangeable phase between 2 and 30% (Fig. 3g, h). There are thus great variations of composition between stands. Considering the nature of the catchment and the literature, we suggest that sediments that are deposited in the Dumbea mangrove are mainly composed of goethite, explaining the high metal content in residual phase, up to $1900 \mu\text{mol g}^{-1}$ of Fe in the salt flat. We demonstrated in a previous chapter that the development of the mangrove towards the seaside resulted in increased concentrations of organic matter, reaching up to 20% in the *Rhizophora* forest. This high organic content and the associated processes of decomposition may have induced alteration of iron minerals, mainly oxides, associated with the residual phase, resulting in increased concentrations in the dissolved phase. Dissolved Fe in pore waters reached more than $50 \mu\text{mol l}^{-1}$ under *Rhizophora*, and up to $100 \mu\text{mol l}^{-1}$ under *Avicennia*, while mean value in the salt flat was only $7 \mu\text{mol l}^{-1}$ (Fig. 3c, f, i). In fact, dissolved Fe increased from the top of the core to an intermediate layer, where iron respiration is the dominant organic matter (OM) decay process. Below this layer, dissolved iron decreased probably due to its precipitation as less crystallized oxide forms including, ferrihydrite iron and/or lepidocrocite iron, as highlighted by the increased oxide-bound iron. For example in the *Avicennia* stand, oxide-bound iron increased from $60 \mu\text{mol g}^{-1}$, at the top of the core, to $860 \mu\text{mol g}^{-1}$ at 60 cm depth. Part of the dissolved iron may also have been precipitated with OM. Organic bound and exchangeable iron was less than 5% within the salt flat, ranged between 1 and 15% in the *Avicennia* stand, and between 2 and 30% in the *Rhizophora* stand, while TOC mean concentrations were 1, 5 and 13%, respectively. In a previous study (Marchand et al., 2008), we suggested that the decomposition of OM in mangrove sediments lead to the production of dissolved inorganic carbon (DIC) that can precipitate as carbonates in anoxic layers. In the current study, we suggest that carbonate can also precipitate, and that iron can be included in these carbonate

minerals, explaining the increased proportion of carbonate-bound iron from the salt flat to the *Rhizophora* stand, and with depth. Carbonate-bound iron reached up to $140 \mu\text{mol g}^{-1}$, within *Rhizophora* sediments, which was also the sediment containing the highest concentrations of organic carbon. Finally, mangrove sediments are also characterized by high rate of sulfate-reduction (Kristensen et al., 2008). Precipitation of iron as sulfides is commonly observed in mangrove sediments (Ferreira et al., 2007), with the presence of framboids of pyrite observed in mangrove sediments of French Guiana (Marchand et al., 2004). Considering the high TS content in the *Rhizophora* and *Avicennia* forests, we consider as certain that iron also precipitated as sulfides in our study sites. Concerning the layers enriched in dissolved Fe, the high concentrations measured can result from both sulfide oxidation and oxide dissolution. Sulfide oxidation also results in a lowering of pH. In fact, in layers where dissolved Fe peaked, pH was slightly acidic. In summary, we suggest that the increasing content of organic carbon from the landside to the seaside of the mangrove results in the dissolution of some iron oxide originating from the catchment. This dissolved iron can subsequently be complexed with OM, and precipitate as carbonates, poorly crystallized oxides, and sulfides that can form thanks to the different redox conditions that can develop in mangrove sediments.

3.4. Mn partitioning in mangrove swamp sediments

In the upper part of the core collected in the salt flat, the majority of the Mn was contained within the residual phase, followed by the oxide-bound phase, with close to 8 and $2 \mu\text{mol g}^{-1}$ of Mn, respectively. Considering the absence of vegetation in this zone, and the low organic content of the upper core, we considered that diagenetic processes linked to OM decomposition are fairly limited, and that the composition of the sediment reflects the original materials from the watershed. As explained earlier, soils of the catchment are mainly composed of oxides, which is consistent with these results obtained. In the three cores, Mn concentrations associated with the residual phase and oxide-bound phase, decreased sharply with depth, falling to $2 \mu\text{mol g}^{-1}$ and below the limit of detection, respectively (Fig. 4b, e, h). The dissolution of Mn oxides is also evidenced by the increased concentrations of dissolved Mn with depth, increasing, for instance, from undetectable concentrations at the top of the core to $20 \mu\text{mol l}^{-1}$ at a depth of 40 cm in the *Avicennia* zone (Fig. 4f). In contrast to dissolved Fe, dissolved Mn concentrations did not fall, below the suboxic zones, in layers characterized by high TS content. This was possibly because Mn-sulfides minerals (e.g. alabandite) were undersaturated or possibly that another phase, such as carbonate, is more stable. This assessment clearly shows that the use of manganese oxides in the decomposition of organic matter involves its transformation into reduced manganese Mn^{2+} , which becomes soluble below the oxic sediment layer. Manganese in solution is able to be incorporated by mangrove plants. Lacerda et al. (1999) observed relatively high Mn concentrations in mangrove leaves, correlated with Mn concentrations in pore waters. However, in our study site, we also observed that Mn concentrations associated with carbonate phase increased below the suboxic layer, reaching up to $0.8 \mu\text{mol g}^{-1}$ at a depth of 35 cm in the core collected in the *Rhizophora* forest (Fig. 4g). Precipitation of authigenic Mn carbonate is frequently described in coastal sediments. Along the mangrove fringed coast of French Guiana, sediments were supersaturated with respect to rhodochrosite a few centimeters below the sediment surface (Aller et al., 2004). In a Brazilian mangrove, Otero et al. (2009) described that a considerable portion of the free Mn was associated with carbonates, with concentrations up to $2.5 \mu\text{mol g}^{-1}$. In the present study, within the organic-rich layers, organic bound and exchangeable phase formed the dominant fraction representing at least 75% of total Mn concentrations, and up to 98% at 35 cm depth in the *Rhizophora* forest (Fig. 4g). Concentrations in this fraction reached up to $18 \mu\text{mol g}^{-1}$, which is even higher than the

maximum total Mn concentrations measured in the salt flat, $12 \mu\text{mol g}^{-1}$. This result implies that most of the Mn oxides that are deposited in the mangrove, and which are subsequently dissolved during Mn reduction processes, are then associated with this organic matter. In summary, the organic enrichment of mangrove sediments from the salt flat to the *Rhizophora* forest induced the transfer of Mn from the oxide forms to the organic-bound fraction and to a lesser extent to the carbonate-bound fraction.

3.5. Ni partitioning in mangrove swamp sediments

In mangrove sediments of Dumbea, the mean total Ni concentration in the solid phase was $44.2 \mu\text{mol g}^{-1}$, with a minimum value of $21.9 \mu\text{mol g}^{-1}$, and a maximum value of $65.4 \mu\text{mol g}^{-1}$ (Table 2). The highest values were measured in the organic-rich layers of the *Avicennia* and *Rhizophora* stands. In these layers, the organic-bound and exchangeable fractions represented up to 60% of the total Ni content (Fig. 5d, g). In freshwater sediments, Doig and Liber (2006) found that OM strongly influenced Ni partitioning, and demonstrated that organic-rich sediments may complex significant quantities of Ni under aerobic conditions. They also observed that Ni complexation, on carboxylic and phenolic functional groups, increased with increasing pH, from 6 to 8. In our organic-rich layers, pH is close to 6, so one can imagine that the organic-bound fraction may increase with increasing pH, for instance at high tide with the abundant supply of basic cations. Surprisingly, the proportion of Ni associated with the organic bound and exchangeable fractions also increased, from 10 to 60% (Fig. 5a) with depth in the salt flat, where the organic content slightly increased, never being higher than 3%. However, as explained earlier, the organic composition at depth was different, and characterized by the presence of degraded *Rhizophora* tissues. Within the three mangrove stands, total Ni concentrations decreased with depth in the upper part of the core, before increasing, mainly as organic bound fraction. This decrease mainly resulted from the fall of Ni concentrations associated with the residual phase. In fact this fraction represented nearly 80% of the total Ni at the top of cores, and only 20% in the organic rich layers of the *Avicennia* (from 48 to $12 \mu\text{mol g}^{-1}$) and *Rhizophora* stands. From the top of the core to the organic-rich layers, there was also an increase in dissolved Ni, with concentrations reaching up to $30 \mu\text{mol l}^{-1}$ (Fig. 5i). In mangroves developing downstream from non-ultrabasic catchments, mean dissolved Ni concentrations were close to $1 \mu\text{mol l}^{-1}$, with values never exceeding $5 \mu\text{mol l}^{-1}$ ([Marchand et al., 2011a] and [Marchand et al., 2011b]). The fall in the residual fraction associated with the increase of concentrations in the dissolved phase may indicate that Ni was mainly associated with oxides and/or oxy-hydroxides minerals when being deposited in the mangrove, and that the dissolution of these minerals in suboxic conditions, lead to the release of Ni in pore water. Such high dissolved Ni concentrations can cause acute toxicity to benthic organisms (Di Toro et al., 1992). However, Ni complexation with dissolved organic matter (DOM) in pore water, where concentrations can be really high in mangrove sediments (Marchand et al., 2006), can alter metal bioavailability and toxicity to aquatic organisms (Doig and Liber, 2007). As a consequence, in mangrove sediments Ni speciation and toxicity is intimately linked with organic matter cycling both in the solid and the dissolved phases. In fact, trends in the depth profiles of organic bound and exchangeable fraction and dissolved Ni concentrations are very similar. As explained earlier, OM decomposition induces DIC production that can precipitate in anoxic conditions. The Ni carbonate bound fraction depth trend follows that of the organic-bound fraction, but concentrations were never above $4 \mu\text{mol g}^{-1}$, representing only 6% of total Ni concentrations (Fig. 5a, d, g). Within anoxic and sulfidic conditions, Ni is thought to preferentially form insoluble sulfides (Di Toro et al., 1990). Nissenbaum and Swaine (1976) found that sulfides dominate the solid phase partitioning of Ni in recent sediments, being incorporated into iron

sulfides, or forming a pure Ni–S phase ([Boulègue, 1977], [Baltzer, 1982], [Burton et al., 2006] and [Doig and Liber, 2006]). At depth in the *Avicennia* and *Rhizophora* stands, sediments were characterized by high TS content, highlighting intense sulfato-reduction processes. We suggest that iron sulfides, mainly pyrite but also probably greigite, precipitated in these layers. Ni is also probably precipitated as sulfides, notably beneath *Rhizophora* stand where TS content increased from 1% at the top of the core to more than 10% below 15 cm depth (Fig. 2i). As a consequence, Ni was mainly present as components of sulfide minerals and organic complexes, which is consistent with the observations of Clark et al. (1998) in an Australian mangrove. Again, organic content distribution linked to mangrove stand zonation is a key parameter of Ni partitioning, and thus mobility and bioavailability in mangrove sediments.

3.6. Cr partitioning in mangrove swamp sediments

In New Caledonia, within the ferralsols deriving from ultramafic rocks, Cr is present in solid phases such as chromite and Cr-substituted goethite chromium, but also present in Fe-oxides ([Becquer et al., 2001] and [Becquer et al., 2003]). Since the Dumbea catchment is mainly composed of ultramafic rocks, most of the Cr being deposited in the mangrove may be in these forms, which are highly insoluble (Burton et al., 2006). As a consequence of the selective extraction used, it is possible that some of the solid Cr was not digested and that our total Cr concentrations are underestimated. Nevertheless, as shown in Section 3.2, we measured total Cr concentrations up to $40 \mu\text{mol g}^{-1}$, which is as high as soils developing close to a FeCr smelter (Shtiza et al., 2005). There were not great differences in total Cr concentrations with depth or between mangrove stands, but the partitioning between phases varied strongly. Within the core collected in the salt flat, Cr was distributed as follows: the residual phase represented between 80 and 93%, the oxide phase was below 5%, the carbonate phase was below 2%, and the organic and exchangeable phase ranged between 6 and 15% (Fig. 6a, b). Within the core collected in the *A. marina* stand, Cr was distributed as follows: the residual phase represented between 40 and 90%, the oxide phase was below 10%, the carbonate phase was less than 4%, and the organic and exchangeable phase ranged between 10 and 50% (Fig. 6d, e). Within the core collected in the *Rhizophora* stand, Cr was distributed as follows: the residual phase represented between 25 and 75%, the oxide phase was under 9%, the carbonate phase between 1 and 6%, and the organic and exchangeable phase between 20 and 60% (Fig. 6g, h). The main trends were: a decrease of the residual phase associated with an increase in the organic-bound and exchangeable phase from the salt flat to the *Rhizophora* stand, and with depth. Consequently, we suggest that the increase in organic-bound and exchangeable Cr resulted from the dissolution of oxides and/or oxy-hydroxides during diagenetic processes. Chromite crystals being liberated from goethite by such dissolution processes are documented in Baltzer (1982). As well as for Ni, the organic enrichment in sediments induced a modification of Cr partitioning, to forms that may be more bioavailable. Lacerda et al. (1991) observed, in a Brazilian mangrove, that Cr was immobilized in sediments as Cr-organic compounds. Cr has different degrees of toxicity depending on its oxidation state: the Cr (III), which is rather benign, and the Cr (VI), which is highly toxic and soluble (Fendorf, 1995). Different studies have shown the high toxicity of Cr (VI) to plants (Sharma et al., 1995). At the time of the sampling we were not able to perform measurements of dissolved Cr, and partitioning between the Cr (III) and Cr (VI) forms. Nonetheless, with our knowledge on Fe, Mn, S, and OC cycling, we can make some hypothesis. In the natural environment, Cr (III) can only be oxidized to Cr (VI) by Mn-oxides (Fendorf, 1995). Taking into account, the richness of the upper mangrove sediments in Mn associated with the oxide bound and residual phases, oxidation of Cr (III) to Cr (VI) is

thought to occur. Conversely, Fe (II) production can lead to the reduction of Cr (VI), and Cr precipitation with Fe oxide (Fendorf, 1995). In a waterlogged environment, Fe reduction due to ferri-reducing bacteria occurs, and Fe oxide can be solubilized (Quantin et al., 2001), which is the case in mangrove sediments, and therefore can increase Cr (VI) in pore waters. Nonetheless, within the anoxic and organic-rich layers, Cr (VI) can be reduced by organic matter and sulfides, inducing a lower bioavailability and toxicity of Cr. To conclude, mangrove sediments, developing downstream of an ultramafic watershed, are rich in Cr, and the various redox processes that occur can lead to the alternating production and reduction of Cr (VI).

4. Conclusions

This combined study of pore water parameters, sedimentary organic content and transitional metal partitioning in a mangrove developing downstream an ultramafic watershed evidenced the fact that mangroves act as a natural reactor, transforming the forms of metals during their transfer from watershed to coastal waters. In addition, it highlights the differences of distribution and partitioning of metals beneath various mangrove species, and the key role of the sedimentary organic content. The main conclusions of this study can be summarized as follow:

The erosion of highly weathered ferralsols induces relatively high concentrations of Fe, Ni, Cr in mangrove sediments. Concentrations in Ni are 10 to 100 times higher than in mangrove developing downstream a watershed that is not ultramafic.

In New Caledonia, mangrove distribution is mainly controlled by soil salinity, and thus by duration of tidal immersions. On the one hand, this zonation is translated by higher oxygen diffusion from the atmosphere to the sediment, from the *Rhizophora* stand towards the salt flat. On the other hand, this zonation induces an increasing sedimentary organic content from the landside to the seaside of the mangrove. The combined decreasing gradients of length of immersion and organic matter content induce that redox conditions evolve from anoxia beneath *Rhizophora* to oxic conditions in the salt flat. The different redox conditions characterizing the various stands and the various depths lead to different partitioning of metals in the sediment.

Metals are deposited in the mangrove mainly as oxides and/or oxy-hydroxides, that are subsequently dissolved by bacteria for the decomposition of organic matter, and which leads to a strong increase of metals in the dissolved phase. Concentrations of Fe and Ni associated with the organic and the oxide fractions increased with depth and from the salt flat to the *Rhizophora* stand. Consequently the organic enrichment of mangrove sediments from the salt flat to the *Rhizophora* forest induced the transfer of trace metals from oxide form to organic and sulfide forms. Within anoxic conditions, Fe and Mn also precipitated as carbonates. Finally, taking into account, the richness of the upper mangrove sediment in Mn associated with the oxide bound and residual phases, oxidation of Cr (III) to Cr (VI) is thought to occur. Nonetheless, within the anoxic and organic-rich layers, Cr (VI) can be reduced by organic matter and sulfides, inducing a lower bioavailability and toxicity of Cr.

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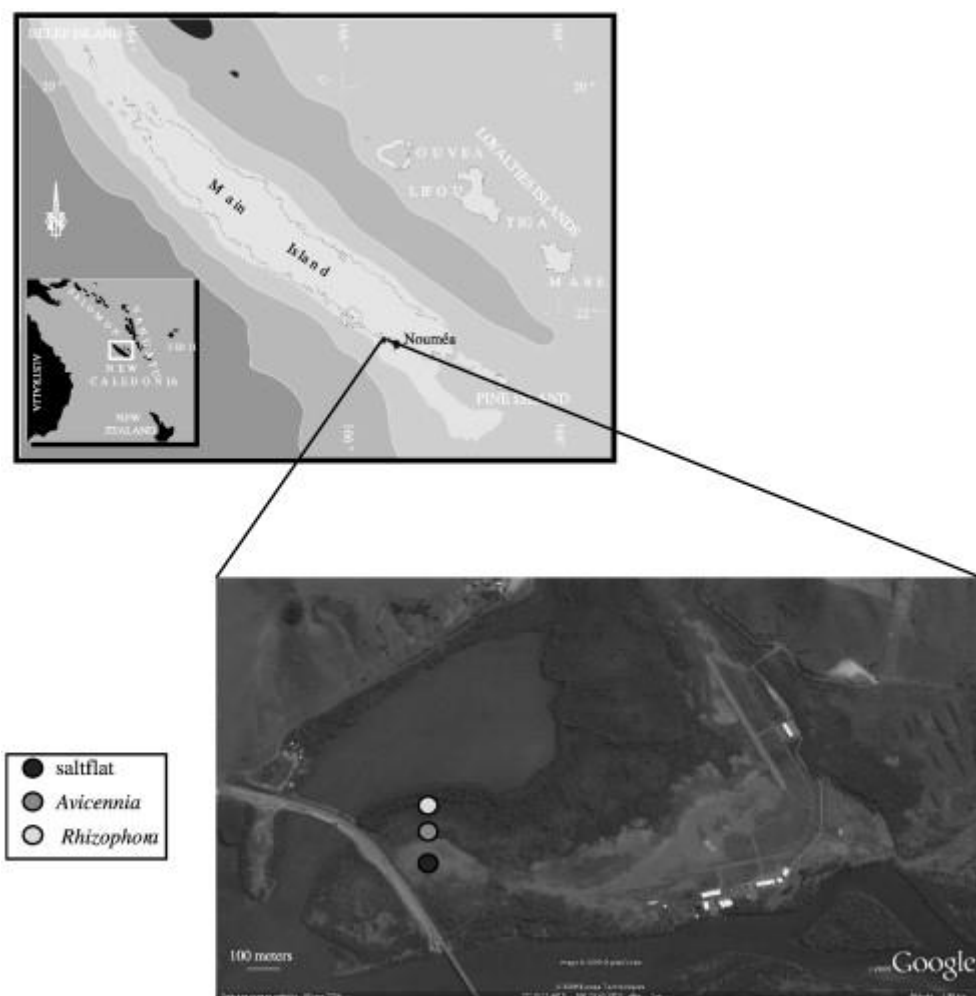


Fig. 1. Map of the studied area (Dumbea Bay, New-Caledonia) showing: i) the location of New-Caledonia in the Pacific Ocean; ii) the location of the collected cores in the mangrove.

Table 1. Accuracy precision. Analysis of reference materials.

Metal	TM-26.3 ($\mu\text{g l}^{-1}$)		TMDA-61 ($\mu\text{g l}^{-1}$)	
	Measured value	Certified value	Measured value	Certified value
Fe	23.2 ± 0.7	21 ± 3.6	84.9 ± 1.2	81.1 ± 10.1
Mn	18.2 ± 0.3	17 ± 1.4	82.4 ± 0.8	74.8 ± 7.3
Ni	8.7 ± 0.4	10.2 ± 1.3	62.1 ± 0.8	58.7 ± 6.4

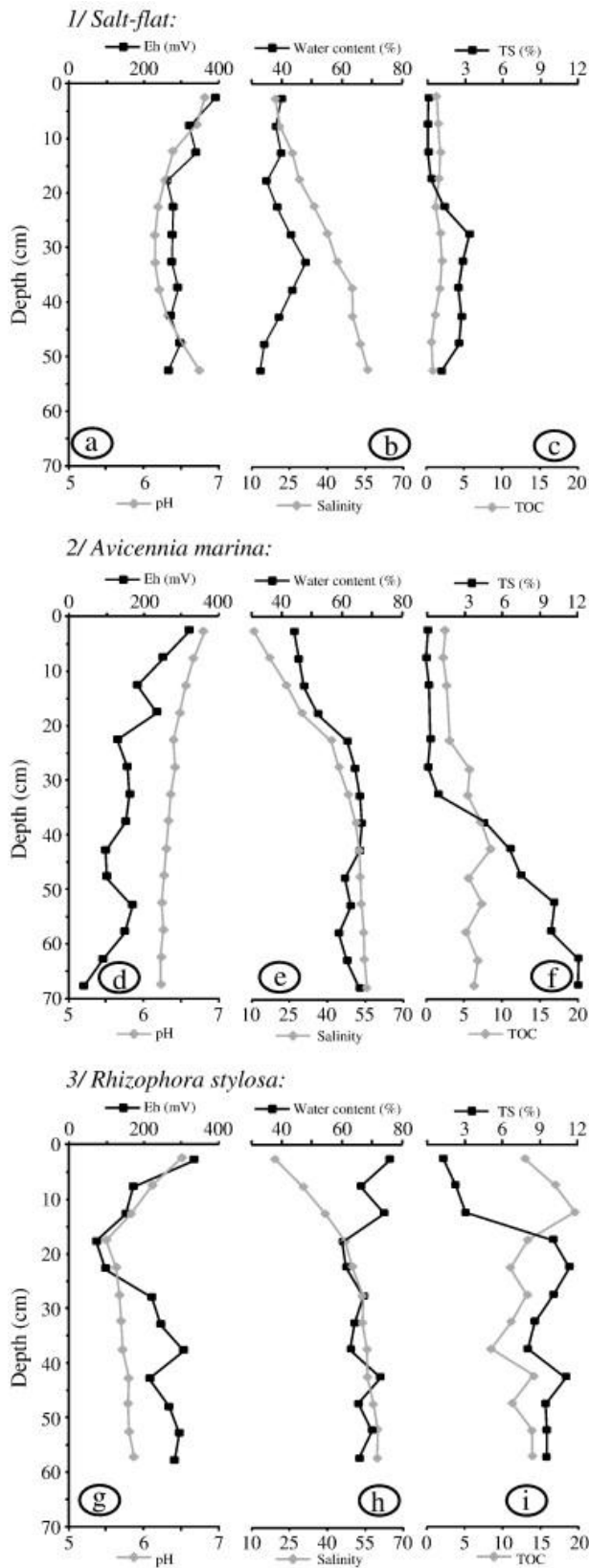


Fig. 2. Depth distribution of some parameters: 1) in the salt-flat: a) Eh, pH; b) water content salinity; c) TS, TOC; 2) in the *Avicennia marina* forest: d) Eh, pH; e) water content, salinity; f) TS, TOC; 3) in the *Rhizophora stylosa* forest: g) Eh, pH; h) water content salinity; i) TS, TOC.

Table 2. Heavy metals concentrations in sediments of the studied mangrove in Dumbea, New Caledonia (mean, S.D., max, min).

	Ni ($\mu\text{mol g}^{-1}$)	Cr ($\mu\text{mol g}^{-1}$)	Fe ($\mu\text{mol g}^{-1}$)	Mn ($\mu\text{mol g}^{-1}$)
Mean (n = 39)	44.19	31.91	1997.5	8.81
S.D.	10.29	6.06	359.94	4.41
Max.	65.37	40.22	2682.86	20.99
Min.	21.89	20.18	1003.34	2.21

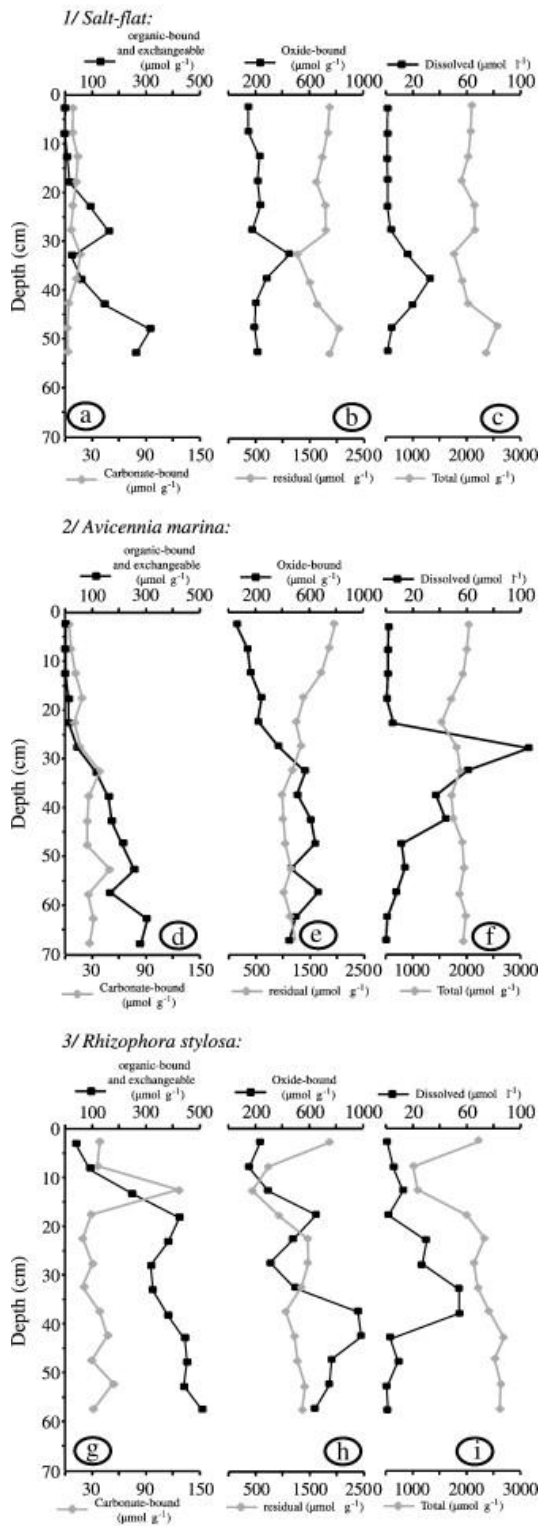


Fig. 3. Fe partitioning: 1) in the salt-flat: a) organic-bound and exchangeable, carbonate-bound; b) oxide-bound, residual; c) total in the dissolved phase, total in the solid phase; 2) in the *Avicennia marina* forest: d) organic-bound and exchangeable, carbonate-bound; e) oxide-bound, residual; f) total in the dissolved phase, total in the solid phase; 3) in the *Rhizophora stylosa* forest: g) organic-bound and exchangeable, carbonate-bound; h) oxide-bound, residual; i) total in the dissolved phase, total in the solid phase.

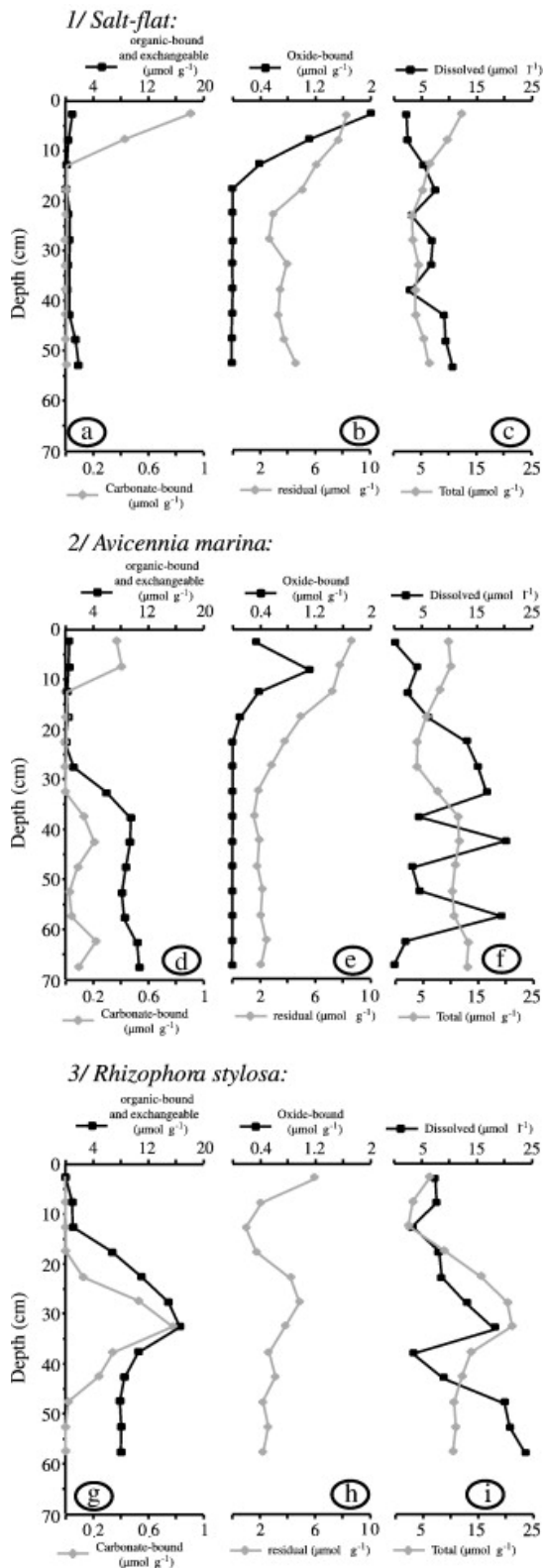


Fig. 4. Mn partitioning: 1) in the salt-flat: a) organic-bound and exchangeable, carbonate-bound; b) oxide-bound, residual; c) total in the dissolved phase, total in the solid phase; 2) in the *Avicennia marina* forest: d) organic-bound and exchangeable, carbonate-bound; e) oxide-bound, residual; f) total in the dissolved phase, total in the solid phase; 3) in the *Rhizophora stylosa* forest: g) organic-bound and exchangeable, carbonate-bound; h) oxide-bound, residual; i) total in the dissolved phase, total in the solid phase.

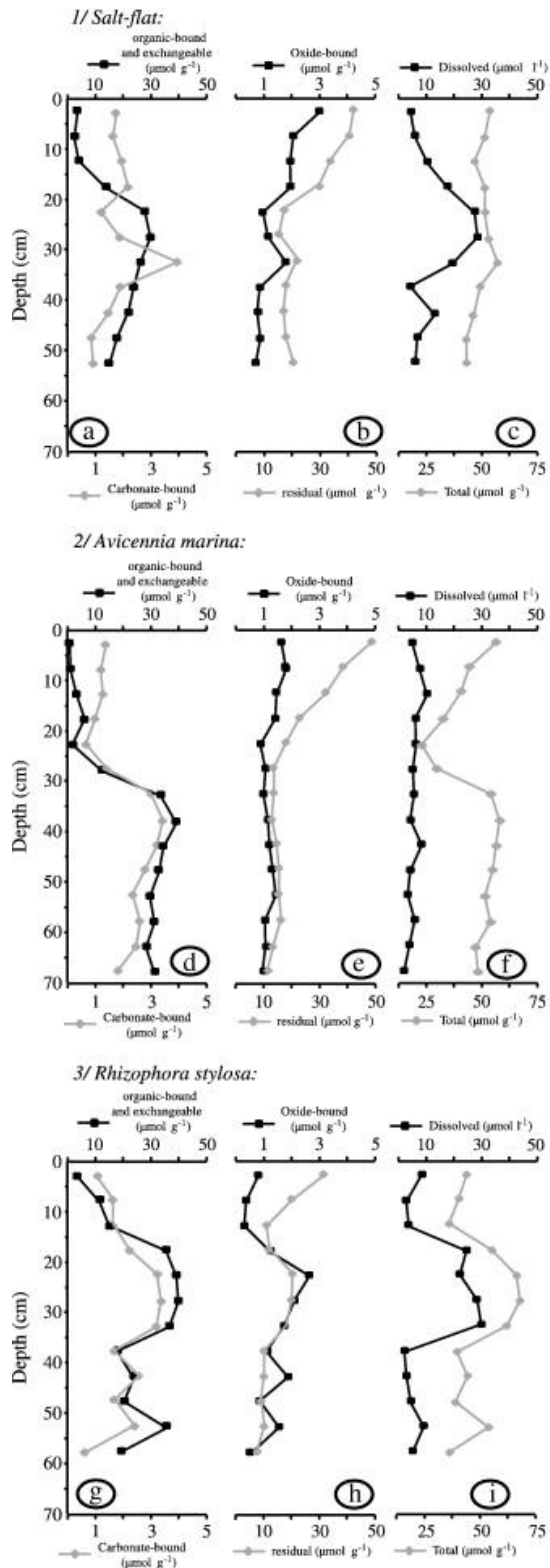


Fig. 5. Ni partitioning: 1) in the salt-flat: a) organic-bound and exchangeable, carbonate-bound; b) oxide-bound, residual; c) total in the dissolved phase, total in the solid phase; 2) in the *Avicennia marina* forest: d) organic-bound and exchangeable, carbonate-bound; e) oxide-bound, residual; f) total in the dissolved phase, total in the solid phase; 3) in the *Rhizophora stylosa* forest: g) organic-bound and exchangeable, carbonate-bound; h) oxide-bound, residual; i) total in the dissolved phase, total in the solid phase.

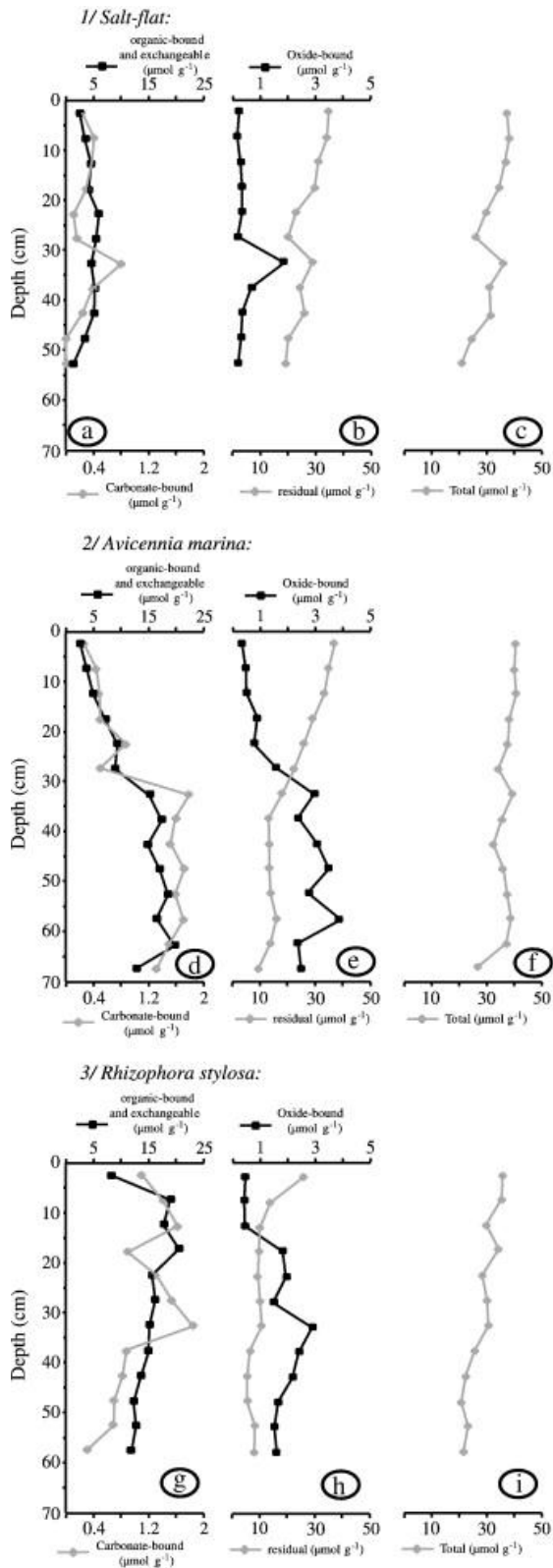


Fig. 6. Cr partitioning: 1) in the salt-flat: a) organic-bound and exchangeable, carbonate-bound; b) oxide-bound, residual; c) total in the solid phase; 2) in the *Avicennia marina* forest: d) organic-bound and exchangeable, carbonate-bound; e) oxide-bound, residual; f) total in the solid phase; 3) in the *Rhizophora stylosa* forest: g) organic-bound and exchangeable, carbonate-bound; h) oxide-bound, residual; i) total in the solid phase.