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Relationships between heavy metals distribution and organic matter cycling in mangrove sediments
(Conception Bay, New-Caledonia)

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Abstract

Mangroves of New-Caledonia act as a buffer between a lagoon of more than 20,000 km² and the Island, which suffers intense processes of erosion resulting from urbanization and natural resources exploitation. This preliminary study aims at determining how heavy metals are distributed in mangrove sediments and pore-waters in relationship with their organic content. To reach our goal, a series of 50-cm deep cores were collected in the mangrove of Conception Bay. The various coring sites are representative of live forests (*Avicennia marina*, *Rhizophora stylosa*), dead forest, and intertidal unvegetated area. The ranges of concentrations in sediments were the following ($\mu\text{mol g}^{-1}$): Cu (0.08 to 0.51), Co (0.01 to 0.38), Ni (0.03 to 3.55), Cr (0.36 to 3.11), Zn (0.68 to 2.36), Mn (1.13 to 5.0) and Fe (22.64 to 721.69). Heavy metals distribution within sediments and pore-water appear to result from diagenetic processes linked to OM decomposition. Beneath the dead *Avicennia* forest and in the *unvegetated* sediments, the higher the organic content, the higher the metal concentration in the solid phase. Beneath living mangrove stands, despite a higher organic content, as well as higher sulphur content, heavy metals concentrations were not higher than those measured in the other sampling sites. Beneath these forests, redox conditions were mainly controlled by the length of waterlogging and the activity of root-system. We suggest that, because of the specificity of the *Avicennia* root system and its position in the intertidal zone, heavy metals are more bioavailable and potentially more mobile than beneath *Rhizophora* stand.

Keywords: mangrove, heavy metals, organic matter, redox conditions, New-Caledonia

1 Introduction

Mangroves are specific intertidal ecosystems, covering between 160,000 and 200,000 km² along more than 70% of tropical and subtropical coastlines (Spalding et al., 1997; FAO, 2003). Mangroves comprise close to 80 species worldwide from around 20 families of vascular plants (Tomlinson, 1986). This ecosystem is highly rich in biodiversity, and act as a habitat for many species (Nagelkerken et al., 2008). Mangrove forests are among the most productive terrestrial ecosystems, with a NPP estimated at 149 mol C m⁻² y⁻¹, providing food sources for local faunal communities and also adjacent coastal foodwebs (Kristensen et al., 2008; Bouillon et al., 2008). Nevertheless, resulting from demographic increase, urbanization increase, expansion of industrial activities, natural resources prospecting and exploitation, mangroves are disappearing at an alarming rate (Duke et al., 2007). Due to their persistence, potential toxicity, and bioavailability, heavy metals represent a major threat for mangrove biodiversity and also for human health. Additionally to their anthropogenic origin (e.g. mining activities, industries, etc.), natural processes, such as geologic weathering of soils and rocks, increase their occurrence. Heavy metals are transported by water or wind to coastal areas, where they can be deposited as sediments. Because of 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 heavy metals (Nissenbaum and Swaine, 1976), mangrove sediments have a large capacity to accumulate these pollutants (Lacerda et al., 1988; Tam and Wong, 2000). Ramos et al. (2006) suggested that mangrove trees can be considered as a biochemical reactors, not only because of their physiological and biochemical processes but also due to their active role in organic matter decomposition within the sediments that greatly influence the mobility of heavy metals. Mangroves can act as a long term sink for heavy metals because of their precipitation with sulfides during diagenetic reactions and the relative stability of these minerals (Huerta-Diaz and Morse, 1992). However, mangrove organic-rich sediments are subjected to various diagenetic processes. Sulfate reduction is thought to be the dominant process, but aerobic respiration and also Fe and Mn respiration can be important OM decomposition pathways in mangrove sediments (Alongi et al., 1998; 2000; Kristensen, 2000). Decay processes vary spatially and temporally as a result of various factors, such as the ability of root system

to diffuse air into the sediment, intense faunal bioturbation, and seasonal alternation of water logging (Scholander et al., 1955; Clark et al., 1998; Marchand et al., 2004; Marchand et al., 2006). This variability may induce changes in heavy metals distribution between dissolved and particulate phases, and thus changes of their toxicity. As an example, metals in pore-waters are more bioavailable than ones adsorbed on mineral surfaces, and can be easier uptake by organisms, thus entering foodwebs. As a consequence, mangrove sediments may shift from a heavy metals sink to a heavy metals source for adjacent systems (Harbison, 1986). In New-Caledonia, mangroves are associated with a lagoon of more than 20,000 Km², delimited by an almost continuous coral barrier reef of over 1500 km in total length. Extensive mangrove are fringing 80% of the western coastline of the Island and 20% of the eastern's. As a consequence of their distribution, mangroves represent a major source of nutrients for the lagoon. Nevertheless, the economic development of the Island increases the pressure on mangrove environment. New-Caledonia is currently the 3rd nickel producing countries in the world. Anthropogenic pressure can be expressed following two main ways. The former corresponds to the construction of road and buildings, i.e. urbanization, and the latter is the mining activities (Ni-ore) occurring in lateritic soils located upstream mangrove areas. Processes of erosion and sedimentation along the coastline, and which occur naturally, are strongly amplified by mining activities and urbanization (Fernandez et al., 2006). The purpose of this preliminary study was to understand the distribution of some heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn) in sediments and pore-waters in an urban mangrove, where the catchment do not contain significant Ni occurrence, but had suffered erosion resulting from urbanization. In this context, we were interested in the relationships between mangrove stands, sedimentary organic matter, pore-water parameters and heavy metals concentrations. To reach our goal, quantitative analyses, e.g. Rock-Eval and HR-ICP-OES, were carried out on cores collected beneath 2 living mangrove stands (*Avicennia marina* and *Rhizophora stylosa*), a dead mangrove, and in intertidal unvegetated sediments. These data would also provide some baseline information on the variability of heavy metal concentrations in New-Caledonian mangrove substrate, and will be useful for further studies on mangroves that are situated downstream Ni exploitation areas.

2 Materials and Methods

2.1 Study site and sampling

New-Caledonia, which is situated in the South Pacific Ocean, is orientated along a northwest-southeast axis, and is almost 500 km in length and about 50 km in wide (Fig. 1). The main island (20°S–23°S) is characterized by a tropical climate, strongly influenced by the ITCZ cycling, with mean annual rainfall close to 1100 mm, and average monthly air temperatures fluctuating between 20 and 27°. Work was carried out during the dry season in September 2005. The studied mangrove is located in Conception Bay, which is close to Noumea, the main city of New-Caledonia.

Samples studied herein come from 5 mangrove areas defined in terms of vegetation composition: 2 *Avicennia marina* forests, 2 *Rhizophora stylosa* forests, and a dead *Avicennia* forest with standing dead trees. In addition, cores were collected in the intertidal unvegetated sediment.

Cores (50 cm deep) were performed at low tide with an Eijkelkamp gouge auger along 2 transects. Elevation related to mean sea level was measured on both transects, allowing determining elevation differences between sampling sites. This survey was realized using a theodolite with an electronic distance measurement device, and was started from a benchmark on the road crossing the mangrove (Fig. 1). Mean values of metals concentrations in sediments, presented in table 1, were calculated using all the samples, in order to make global comparison with other locations. To compare the various areas studied herein, results of one core per site for each parameter is presented; the redox profiles of the twin cores being very similar. In the *A. marina* forest, core locations were chosen equidistant from trees, in consideration of the large extension of the radial cable roots. In the *R. stylosa* forest, cores were collected under prop 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 hour after cores collection), samples were collected every 2 cm from 0 to 20 cm depth, every 5 cm from 20 to 50 cm depth. Subsamples for trace metals analyses were collected at the center of cores on the whole thickness. Until drying, samples were kept frozen. Then, they were grounded with an agate pestle and mortar.

Pore-waters were extracted, at the lab, on the day of coring with soil moisture sampler Rhizon[®] (Song et al., 2003), which were directly inserted into a piece of core from the gouge auger. The sampler is connected to a syringe using luer-lock fittings and PVC tubing. Evacuating the syringe by drawing the piston allows collecting pore-water from sediments. After 2 hours, the output was around 20 ml of pore-water for a piece of core of 150 cm³. All samples were then immediately filtered through 0.45 µm Sartorius[®] filters and acidified to pH 2 with Suprapur[®] HNO₃. 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 measurements

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 pore-water from the core. pH was measured using a glass electrode and a WTW pH meter. The pH electrode was calibrated using 4 and 7 standards (NIST scale). Redox potential was measured, using a combined Pt and Ag/AgCl (reference) electrode connected to a WTW pH/ mV/T meter. The redox electrode was periodically checked using a 0.43 V standard solution and demineralized water. Probes were directly inserted into the mud until stable values 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). The redox scale used in this study is:

- Oxic > 400 mV, contain measurable dissolved oxygen.
- 100 mV < Suboxic < 400 mV, lack measurable oxygen or sulfide, but contain dissolved iron or manganese, no reduction of sulfate.
- Anoxic < 100 mV, sulfate reduction.

2.2.2 Rock-Eval analyses

Total Organic Carbon (TOC) was determined using a Rock-Eval 6 pyrolysis on powdered rock samples (Lafargue et al., 1998). 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 programme is: 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 pyrolysed and residual organic carbon contents. In the present study, two others Rock-Eval parameters are used, the hydrogen index (HI) and the oxygen index (OIRE6). HI corresponds to the quantity of hydrocarbon (HC) released during pyrolysis relative to TOC, expressed in mg HC g⁻¹ TOC. It is correlated with H/C ratios. OIRE6, which is correlated with O/C ratios, corresponds to the quantity of oxygen released as CO and CO₂ during pyrolysis, relative to TOC. It is expressed in mg O₂ g⁻¹ TOC.

2.2.3 Total Nitrogen and Total sulfur

Total nitrogen and total sulfur (TS) concentrations were measured by combustion at 1100 °C with a CNS-2000 LECO apparatus. C/N ratios were then determined to characterize OM quality.

2.2.4 Major elements

Major elements (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, in % weight) were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after classical digestion. 100 mg of sample was fused at 1,000 °C with 1 g of LiBO₂ for about 30 minutes. The fusion residue was then dissolved with 5 % HCl. 4 samples per core were chosen for analyzes as a function of pH and redox depth trends. Si/Al ratios were then determined.

2.2.5 Trace elements

The concentrations of Fe, Mn, Cr, Co, Cu, Ni, and Zn, expressed in μmol g⁻¹, were determined on a Jobin-Yvon HR-ICP-AES after microwave digestion. A 10 ml volume of a mixture of Suprapur[®] HCl, HNO₃ and H₂O (1:1:1) was added to 100 mg of sample. The whole was placed in Teflon vessels,

previously washed with concentrated nitric acid. Samples were digested in a MDS 2000 (CEM Corp.®) microwave at 100% power with pressure set at 0.83 Mpa, temperature set at 165°C, and for 30 min. 6 to 7 samples per core were chosen for analyses as a function of pH and redox depth trends. At least 1 sample by redox conditions was analyzed. Blank acid mixtures were digested in the same way. Each sample was measured in triplicate with mean standard deviation for Fe, Mn, Cr, Cu, Co, Ni, Zn less than 2%, 1%, 2%, 5%, 5%, 5%, and 2% respectively. Accuracy of the measurements was checked by analysis of an estuarine sediment certified reference material (LGC 6137) (Tab. 2). Analytical results obtained for references materials differed by less than 15% from the certified values.

Dissolved Fe, Mn, Cr, and Ni concentrations, expressed in $\mu\text{mol l}^{-1}$, were also measured in triplicate on pore-water samples. 4 to 7 samples per core were chosen for analyses as a function of redox depth trends.

3 Results

3.1 Intertidal unvegetated area

Concerning the core collected in the unvegetated area, depth trends of the various parameters are presented in Fig. 2. Heavy metal concentrations ranged as follow (in $\mu\text{mol g}^{-1}$): Fe from 232 to 440; Mn from 2.7 to 5; Zn from 0.8 to 2.4; Cr from 0.4 to 2; Ni from 0.3 to 1.7; Cu from 0.1 to 0.5; Co from 0.1 to 0.2. Their distribution with depth as well the distribution of most of the various sediment characteristics indicated three distinctive layers developing from the top to 6 cm depth, from 6 to 26 cm depth, and below 26 cm depth. The highest heavy metals concentrations were measured in the intermediate layer. This layer was also characterized by the highest TOC and C/N values, reaching 3%, and 20, respectively. The upper and the deeper layers were characterized by mean TOC and C/N values close to 0.7 and 8, respectively (Fig. 2a). HI were low on the whole depth profile, with values lower than 150 mg HC g^{-1} TOC, while OIRE6 increased in the deeper layer, reaching 300 $\text{mg O}_2 \text{g}^{-1}$ TOC at 50 cm depth (Fig. 2b). pH values were stable on the whole depth profile, with a mean value close to 7.4. Conversely, redox conditions strongly varied between the three layers (Fig. 2e). In the

upper 6 cm, suboxic conditions were evidenced by Eh values close to 200 mV, dissolved Fe concentrations close to $10 \mu\text{mol l}^{-1}$ and total sulfur (TS) concentrations lower than $200 \mu\text{mol g}^{-1}$ (Fig. 2f). The intermediate layer was characterized by anoxic and slightly sulfidic conditions, with Eh values ranging between -200 mV and 100 mV, dissolved Fe concentrations lower than $0.5 \mu\text{mol l}^{-1}$, and TS concentrations reaching $400 \mu\text{mol g}^{-1}$. Finally at depth, redox values and TS concentrations were close to those of the upper 6 cm, but dissolved Fe concentrations were lower than $0.5 \mu\text{mol l}^{-1}$. Concerning major elements, Si/Al ratios increased with depth, from 6.5 at 2 cm to more than 9 at 38 cm depth (Fig. 2g). Concerning heavy metals in the dissolved phase, Cr concentrations were under the detection limit on the whole depth profile, while Ni concentrations increased with depth, being under the detection limit in the upper 5 cm and reaching $0.9 \mu\text{mol l}^{-1}$ between 30 and 35 cm depth (Tab. 3).

3.2 *Rhizophora stylosa* forest

Concerning the core collected beneath the *Rhizophora stylosa* forest, depth trends of the various parameters are presented in Fig. 3. Heavy metal concentrations ranged as follow (in $\mu\text{mol g}^{-1}$): Fe from 400 to 720; Mn from 2.4 to 3.7; Ni from 0.9 to 2.4; Cr from 1.2 to 2; Zn from 0.1 to 2.1; Cu from 0.2 to 0.5; Co from 0.1 to 0.3. Depth profiles were different for each metal, but there are some common trends for metals as Cu, Zn and Mn. The upper 20 cm of the core was enriched in organic carbon, with a mean TOC value close to 15%, whereas below this depth TOC rapidly decreased to reach values close to 3%. C/N values ranged between 20 and 30 on the whole depth profile without any specific trend (Fig. 3a). HI and OIRE6 values were stable with depth, with values close to $220 \text{ mg HC g}^{-1} \text{ TOC}$ and $90 \text{ mg O}_2 \text{ g}^{-1} \text{ TOC}$, respectively (Fig. 3b). Suboxic conditions characterized the upper 6 cm of the core, with Eh values higher than 150 mV, TS concentrations lower $200 \mu\text{mol g}^{-1}$ and dissolved Fe concentrations close to $10 \mu\text{mol l}^{-1}$. Below this depth, conditions became anoxic and sulfidic, with TS concentrations reaching $1300 \mu\text{mol g}^{-1}$ at 20 cm depth (Fig. 3e, f). Concerning major elements, Si/Al values increased with depth, from 3.58 to 7.42 (Fig. 3g). In the dissolved phase, Cr and Ni did not show any specific trend. Mean dissolved Cr and Ni concentrations were 0.2 and $0.3 \mu\text{mol l}^{-1}$, respectively (Tab. 3).

3.3 Dead *Avicennia marina* forest

Concerning the core collected beneath the dead *Avicennia marina* forest, depth trends of the various parameters are presented in Fig. 4. Heavy metal concentrations ranged as follow (in $\mu\text{mol g}^{-1}$): Fe from 63 to 530; Mn from 1.1 to 4.5; Ni from 0.1 to 3.6; Cr from 0.4 to 3.1; Zn from 0.7 to 1.7; Cu from 0.1 to 0.5; Co from 0.05 to 0.2. All heavy metals exhibited almost the same depth trend. Concentrations were highest at the top of the core, decreased to 35 cm depth, and then stabilized. TOC concentrations decreased on the whole depth profile, from 8 to 1% at 2 and 50 cm depth, respectively (Fig. 4a). However, C/N and HI values increased from 10 to 25, and from 340 to 520 mg HC g^{-1} TOC at 2 and 35 cm depth, respectively. Below this depth, C/N values decreased to 12 and HI values to 360 mg HC g^{-1} TOC (Fig. 4a, b). Anoxic conditions characterized the whole depth profile, with Eh values always lower than 0 mV and dissolved Fe concentrations lower than $0.5\mu\text{mol l}^{-1}$. However, TS concentrations ranged between 280 and 520 $\mu\text{mol g}^{-1}$ in the upper 35 cm. Whereas below this depth, concentrations were close to $100\mu\text{mol g}^{-1}$. pH values slightly decreased with depth, from 7.4 to 6.7 at 2 and 50 cm depth, respectively (Fig. 4e, f). Concerning major elements, Si/Al values increased with depth, from 4.26 to 8.25 (Fig. 4g). Ni concentrations in the dissolved phase were under the detection limit, while Cr concentrations did not show any specific trend with depth, with a mean value close to $0.7\mu\text{mol l}^{-1}$ (Tab. 3).

3.4 *Avicennia marina* forest

Concerning the core collected beneath the *Avicennia marina* forest, depth trends of the various parameters are presented in Fig. 5. Heavy metal concentrations ranged as follow (in $\mu\text{mol g}^{-1}$): Fe from 33 to 707; Mn from 2.2 to 4.7; Ni from 0.5 to 2.6; Cr from 0.5 to 2.1; Zn from 2 to 4; Cu from 0.2 to 0.4; Co from 0.1 to 0.4. Depth trends were different for each metal. Concerning the sedimentary organic content, two layers can be differentiated. In the upper 35 cm, TOC values decreased from 13 to 8 %, while C/N slightly increased from 15 to 25 (Fig. 5a). In this layer, HI values were stable and relatively high, close to 400 mg HC g^{-1} TOC, while OIRE6 were stable and low, close to $100\text{ mg O}_2\text{ g}^{-1}$ TOC (Fig. 5b). Below 35 cm, TOC, C/N, and HI values strongly decreased to 1%, 15, and 180 mg

HC g⁻¹ TOC, respectively. pH values slightly increased from 5.4 to 6.4 at 4 and 50 cm depth, respectively. However, three layers of redox conditions can be differentiated. The sediment of the upper 15 cm was characterized by suboxic conditions with Eh values close to 200 mV, mean dissolved Fe concentration higher than 10 μmol l⁻¹ and TS concentrations lower than 200 μmol g⁻¹. Between, 15 and 35 cm depth, TS concentrations strongly increased, reaching more than 800 μmol g⁻¹, while Eh values and dissolved Fe concentrations decreased to - 50mV and 0.9 μmol l⁻¹, respectively, thus highlighting anoxic and sulfidic conditions. Below 35 cm depth, TS concentrations decreased to 300 μmol g⁻¹, while dissolved Fe concentrations increased to 87 μmol l⁻¹, thus highlighting again suboxic conditions (Fig. 5e, f). Concerning major elements, Si/Al ratios increased with depth, from 3.5 to more than 10 at 2 cm and 45 cm depth, respectively (Fig. 5g). Cr and Ni in the dissolved phase ranged from 0.21 to 0.46 μmol l⁻¹, and from 0.19 to 1.88 μmol l⁻¹, respectively, without any specific trend with depth (Tab. 3).

4 Discussion

4.1 Mangrove zonation

The existence of more or less different zones parallel to the coastline, each dominated by a different botanical species, is commonly observed in mangrove swamps throughout the world. However, the zonation of mangrove swamps often corresponds to a mosaic which varies according to the physical, biological and chemical interactions which become established between plant and substratum in a given zone. Salinity is recognized as a factor influencing the zonation of species in many places (Walsh, 1974). Flood tolerance (Naidoo, 1985; McKee, 1993) and altitude of ground surface (Baltzer, 1969) also indirectly control zonation, by controlling the immersion length and thus the evaporation and the salinity of pore-water. The specific properties of propagules also help explain many features of mangrove zonation (Rabinowitz, 1978; Smith et al., 1989). In our previous studies in French Guiana, we suggested that the predominant development of *Avicennia germinans*, which represent more than 90% of mangrove plants along this coastline, was probably due to the ability of its seedlings to take

root into frequently reworked sediment (Marchand et al., 2004). Opposite to French Guiana, mangroves of New-Caledonia are composed of more than 20 species (Duke, 2006), *Rhizophora* spp. representing more than 50% of mangrove areas, and *Avicennia marina* more than 15% (Virily, 2006). As it is shown on Fig. 1, *Avicennia* develop at higher elevation than *Rhizophora*. In fact, *Rhizophora* develops mainly in zones daily swept by tides, the salinity of which is made homogeneous by the admixture of waters (Fig. 6). *Avicennia* trees develop in the borders of saltmarshes, and is thus less frequently immersed by tides, which induces higher pore-water salinities (Fig. 6). Consequently, *Avicennia* trees seem to be the best adapted to high situation in the intertidal zone, and to high pore-water salinities. However, they develop at the price of an energy consumption which is incompatible with a certain growth. *Avicennia* rarely exceeds the shrub stage in New Caledonia. In our study site, a dead *Avicennia* area is present between the *Rhizophora* and the *Avicennia* stands. This dead area was situated at a lower elevation than the living forests at the time of the coring (Fig. 1), and sea water stayed in this area that was like a basin. The origin of this erosion process, which led to the lower elevation, is unknown.

We thus suggest that in New-Caledonia the main factor controlling the distribution of mangrove species is the soil salinity, which is strongly influence by the soil elevation. This distribution in the tidal area, by inducing differences in tidal immersion length, may be responsible for differences in sediment geochemistry between the study sites (see next chapters).

4.2 Sediments characteristics

The catchment of this bay is mainly composed of volcanic and sedimentary rocks rich in silicium, mainly sandstone. The name of the geological formation is “Formation des schistes de Pilou”, it is of Senonian age (BRGM, 1965). Si/Al ratios are lower in the upper parts of the cores collected in mangrove sediments compare to the shoreface area and the bottom of the cores. This result indicate that the mineralogical composition of sediments is different between the upper and the deeper part of the core, the upper part being richer in clay, and the lower part in sand (Cojan and Renard, 1997; Duchauffour, 1997). This difference in mineralogical composition may induce differences in the

geochemical processes in mangrove sediments between the upper and the deeper parts of the cores (see next chapters).

4.3 Mangrove stands and sedimentary organic matter composition

Mangrove forests are known to be highly productive ecosystems, with a net primary productivity estimated at $149 \text{ mol C m}^{-2} \text{ y}^{-1}$ (Bouillon et al., 2008). In addition, they can store large amounts of organic carbon in their substrate over several meters depth (Lallier-Vergès et al., 1998). The quantitatively most important source of organic carbon (OC) to mangrove sediments is litter from trees deposited at the sediment surface and subsurface root growth (Alongi, 1998). Nevertheless, epiphytic and benthic microalgae, macroalgae, and a mixture of riverine and marine material, more or less oxidized, can also contribute to sediment enrichment in OC (Marchand et al., 2003; Bouillon et al., 2004; Marchand et al., 2005). Mangrove sediments of Conception Bay are highly enriched in OC compared to the unvegetated shoreface sediment, with maximum values up to 18% and 3%, respectively. Median total organic carbon (TOC) is of 2.2% in mangrove sediments, however, there are strong variations between sites, 44% of the available data having TOC less than 2% and 28% with values between 2 and 5% (Kristensen et al., 2008). In Conception Bay, mean TOC value within mangrove sediments is around 9%, which is relatively high, but close to the one measured by Alongi et al. (1998) in Malaysia for mangrove stands older than 15 years. In this study, beneath the *Rhizophora* stand, the organic content is higher than beneath the *Avicennia* stand, with TOC mean values in the upper 50 cm being 11.54 % and 7.83 %, respectively. This can be the result of the more developed root-system of *Rhizophora* (Hesse, 1961), compared to the radial cable root system of *Avicennia* that develop only in the subsurface (deGranville, 1974). This may also explain that beneath *Avicennia*, TOC values higher than 10% are only observed in the upper 10 cm of the core, whereas beneath *Rhizophora*, they are observed down to 20 cm deep. In French Guiana, TOC depth trends beneath *Avicennia* stands were totally different, with a rapid decrease with depth, whatever the forest developmental stage, highlighting that the root-system actually develop in the subsurface (Marchand et al., 2003). The organic content was also lower as a result of the highly dynamic feature of the

coastline, which induces a limited lifetime of the mangrove, and thus limited accumulation of OC (Marchand et al., 2003). Conversely, in New-Caledonia, mangroves have been stable for hundreds of years, allowing the accumulation of OC in their substrate. To identify the origin of the sedimentary organic pool, and its stage of decomposition, we used 3 proxies: C/N ratios, hydrogen index (HI) and oxygen index (OIRE6) derived from Rock-Eval 6 pyrolysis. These parameters evidenced that algae derived OM was the main organic source in the upper 2 cm of the core collected in the unvegetated shoreface sediment, with a C/N close to 7, which is typical of this kind of material (Meyers and Lallier-Vergès, 1999). This layer was also characterized by low HI's, indicating a rapid decomposition of this OM. An increase of TOC and C/N ratios below sediment surface indicates a mixing of higher plant and algae derived OM. Beneath both mangrove stands, C/N ratios varied between 15 and 35, reflecting the contribution of higher plant debris to the organic pool, and are in the range of ratios measured in mangrove sediments in Brazil (Lacerda et al., 1995), in India and Sri-Lanka (Bouillon et al., 2003). C/N ratios are higher beneath *Rhizophora* than beneath *Avicennia* probably resulting from three causes. First, C/N ratios of fresh tissues of *Rhizophora* are higher than those of *Avicennia* (Tab 4), e.g. 43 and 91 for their wood, respectively. Then, leaves are characterized by lower C/N ratios than wood. Yet, *Rhizophora* stand develops on the sea-side of the mangrove, and is continuously subjected to tidal flushing, and thus leaf litter cannot accumulate compared to the *Avicennia* stand that develops on the land-side of the mangrove. On the field, leaf litter was observed beneath *Avicennia* and not beneath *Rhizophora*. Finally, beneath *Avicennia* stand, decomposition rate may be more efficient than beneath *Rhizophora* because of more oxic conditions (see next chapter; Alongi et al., 2000; Marchand et al., 2004). This result may indicate that beneath *Rhizophora*, the sedimentary organic pool derives mainly from woody tissues, whereas beneath *Avicennia*, the pool can be a mixture of decomposing leaves and wood. HI values depth trend confirm these hypothesis. *Avicennia* fresh leaves and wood have HI's of 569 and 405 mg HC g⁻¹ TOC (Tab. 4), respectively, typical of fresh higher plant tissues. The fact that mangrove wood is characterized by slightly lowers HI's than leaves may be linked to a higher or even nearly exclusive ligno-cellulosic content (Marchand et al., 2005). OM decomposition induces its dehydrogenation, and thus a decrease of HI values, consequently in sediments, HI's are

lower than in fresh tissues (Marchand et al., 2008). Beneath *Avicennia*, they are close to 400 mg HC g⁻¹ TOC, highlighting a mixture of leaves and woody tissues. Conversely beneath *Rhizophora*, HI's were close to 200 mg HC g⁻¹ TOC. This result is consistent with the fact that beneath *Rhizophora*, OM mainly derived from woody tissues, since HI values of *Rhizophora* wood are low, around 300 mg HC g⁻¹ TOC, compared to the leaves, which have HI's higher than 500 mg HC g⁻¹ TOC (Tab. 4).

In the core collected in the *Avicennia* forest, C/N peaked at 35 cm depth, and at the same depth HI values decrease to 200 mg HC g⁻¹ TOC, which is the value measured beneath the *Rhizophora* forest. Actually, this result is consistent with our observations of the core since at this depth, the core was characterized by an increased proportion of red tissues, characteristic of *Rhizophora* wood. This result implies that the living *Avicennia* stand develop on sediments that were previously colonized by *Rhizophora*. This topic will be investigated in a further research effort concerning the evolution of the mangrove of New-Caledonia with climate change during the last millennium. Concerning OIRE6, values were relatively low, both beneath *Avicennia* and *Rhizophora* stands, close to 100 mg O₂ g⁻¹ TOC, which is characteristic of higher plant debris slightly oxidized. In French Guiana, OIRE6 values slightly increased, from 110 to 170 mg O₂ g⁻¹ TOC, in the upper 35 cm of a senescent forest, showing OM oxidation with decomposition (Marchand et al., 2008). Finally, beneath the *Avicennia* dead forest, depth trend are really specific. HI's are close to 400 mg HC g⁻¹ TOC on the whole core, which is consistent with values measured beneath *Avicennia* living trees. However, TOC values are lower than 8, and decrease with increasing depth, while the C/N ratios increased with depth. These results indicate a better preserved OM at depth, mainly derived from higher plant, while on the top of the core OM may derived both from higher plant and algae. This is consistent with the fact that no more fresh OM derived from higher plant is introduced into the sediment.

4.4 Influence of mangrove stands on redox conditions, Fe and S cycling

Although denitrification, manganese respiration and iron respiration are certainly underestimated, it is considered that aerobic respiration and sulfate reduction are the most important respiration processes in mangrove sediments (Alongi, 1998). In this present study, we thus decided to focus on Fe and S

cycling, and also because trace metals can be incorporated into FeS (pyrite or greigite) during sulfato-reduction processes (Boulègue et al., 1982; Huerta-Diaz and Morse, 1992). Within Conception Bay, redox conditions, Fe and S concentrations, both in the solid and the dissolved phase, are highly variable between sampling sites and with depth. Suboxic to anoxic and sulphidic conditions were evidenced. Within the intertidal unvegetated area, a stratification of 3 distinctive layers can be identified: an anoxic and slightly sulfidic zone under a suboxic zone, and below an anoxic but non-sulphidic one. This intertidal area is situated at the lowest elevation of our sampling sites, and is thus more frequently inundated by tides, which may explain that atmospheric O₂ did not penetrate deeply in the sediment. Aerobic degradation of labile materials near the surface is usually so rapid that O₂ rarely penetrates more than 2 mm into the sediment (Kristensen et al., 1994). However, redox conditions can be fully oxic below totally anoxic conditions within the surficial mm of algal mats (De Witt et al., 1989). When O₂ is consumed, OM is oxidized by a wide variety of anaerobic microorganisms using electron acceptors in the following sequence according to the energy yield: Mn⁴⁺, NO₃⁻, Fe³⁺ and SO₄²⁻. In the upper 6 cm of the core, the reduction of SO₄²⁻ was not reached probably because of the low organic content, the proximity of the surface, and possible infaunal burrowing. While below, the anoxic and sulphidic layer, with TS up to 300 μmol g⁻¹ dw, can be clearly associated with an increase of organic content, to more than 3% compared to the mean TOC value of the core, which is lower than 1%. The fact that below this layer, the sediment was anoxic but non-sulphidic may be linked to the lower OC content, which may be also less metabolizable as highlighted by the higher OIRE6 values. In addition, the fact that Si/Al ratios increased at depth may indicate a sandier feature of the sediment, and thus the fact that sediments may allow more lateral exchange. Thus, without vegetation, redox conditions within intertidal sediments seem to be mainly controlled by organic content, but also by depth. In mangrove sediments, redox conditions are dependent on the quantity and reactivity of organic matter, sediment grain size, bioturbation activity, like in marine sediments, but also on forest age, physiological activities of the root system, extent of water logging and crabs burrowing (Clark et al., 1998; Kristensen, 2000; Marchand et al., 2004; Marchand et al., 2006; Kristensen et al., 2008). Within mangrove sediments of Conception Bay, with the organic enrichment of sediment described

previously, resulting from plant development, one can imagine that redox conditions will be anoxic and sulphidic really close to sediment surface, but it is not the case. Beneath *Rhizophora* stand, suboxic conditions prevailed in the upper 5 cm, while the OC content is the highest. Below this depth, the sediment became anoxic and sulphidic. The suboxic condition 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. However this mangrove that is situated in an urban area is very poor in crabs. Bioturbation can also be created by the root system of *Rhizophora*, however it is known that this root system develop deeper than 5 cm. The roots of *Rhizophora* are at their most dense between 15 and 30 cm depth (Otero et al., 2006). In addition, *Rhizophora* root system is not known to diffuse O₂ into the sediment. We suggest that the suboxic conditions that prevailed in the upper sediment beneath the *Rhizophora* stand result from the fact that this mangrove develop at higher physiographic conditions, is thus less inundated by tides, and as a consequence exchange between atmosphere and sediment can be more efficient than in the unvegetated sediment. Below this suboxic layer, the lowest Eh and the highest TS concentrations were measured probably as a result of the high organic content. Since Hesse (1961), *Rhizophora* sediments are known to be highly sulphidic due to the fibrous and organic nature of its sediment. Consequently, the length of waterlogging of a mangrove stand, depending on its topographic situation in the intertidal zone, seems to be also a main factor controlling redox conditions. Opposite to *Rhizophora* sediments, in which TS increased from the top of the core to 20 cm depth, *Avicennia* sediments show suboxic to oxic conditions in the upper 15 cm, and only below this depth TS started to increase. *Avicennia* trees are known for their extensive cable root system developing close to sediment surface (deGranville, 1974). Otero et al. (2006) also demonstrated that their root system is concentrated in the upper 20 cm. Since Scholander et al. (1955), it is known that pneumatophores constitute a pathway for the exchange of oxygen between 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, 2003;

2004). In New-Caledonia, *Avicennia marina* develop behind *Rhizophora* spp., which colonize the seashore, and thus *Avicennia* develop at a higher elevation than *Rhizophora* (Fig. 1). As a consequence, sediments beneath *Avicennia* are less frequently inundated by tides, and exchange with atmosphere and sediment dessication can add their effect to the diffusion of oxygen via the root system. Between, 15 and 35 cm depth, below the living roots layer, redox conditions were anoxic and sulphidic, probably as a result of the high organic content. Below 40 cm depth, redox conditions became suboxic, with very high dissolved Fe concentrations ($80 \mu\text{mol l}^{-1}$). Like in the intertidal unvegetated sediment, the fact that this layer is less enriched in OC, that this OC is less metabolizable, as highlighted by the higher OIRE6, and that the Si/Al ratios indicated a sandier nature of the sediment, may explain these conditions. The role of the *Avicennia* root system in creating suboxic to oxic conditions in the upper sediment is also evidenced when having a look on the depth trend of the various parameters in the *Avicennia* dead forest. This dead forest develops at almost the same physiographic conditions than the living one, and the organic content is lower. Consequently, if waterlogging length would be the main factor controlling redox conditions, suboxic conditions should also prevail in the upper core. However the whole depth profile is anoxic, indicating that living *Avicennia* root system has a key role on the redox conditions of the upper sediments. In French Guiana, we also demonstrated that the redox conditions vary considerably between the dry and the rainy season, the water table being higher during the rainy season inducing anoxic conditions. In the present study, we only performed core during the dry season, but we are aware that results may be different during the rainy season (Marchand et al., 2004).

4.5 Distribution of heavy metals in mangrove sediments and pore-water

Heavy metal concentrations, in mangrove sediments, are usually quite high (Lacerda et al., 1988; Tam and Wong, 2000). On the one hand, this richness can derive from anthropogenic metal loadings carried by the upstream of tributary rivers. Many authors described high heavy metals concentrations in mangrove sediments as a result of anthropogenic input, proximity to harbor, landfill, industrial area, etc (Clark et al., 1998; Machado et al, 2002). On the other hand, this richness may result from

mangrove physico-chemical properties, e.g. efficiency to trap material from the water column, richness in OM, richness in clay, etc. Ray et al. (2006) observed that metal concentrations were higher in mangrove sediments compared to adjacent estuarine sediments, mainly as a result of higher organic content. Conversely, in French Guiana, concentrations in mangrove sediments and in unvegetated coastal sediment were similar, as a result of the dynamic feature of the coastline and the occurrence of oxic to suboxic processes in the earlier stages of mangrove development (Marchand et al., 2006). Nevertheless and despite the fact that no anthropogenic sources were identified, these sediments were also relatively rich in some metals, notably Hg, and this as a result of the nature of the Amazon watershed (Roulet et al., 1996, 2000). In New-Caledonia, highly weathered Ferralsols, enriched in heavy metals, occur extensively, deriving from ultramafic rocks and representing a third of the surface of the main island (Trescases, 1973; Lathal, 1985). In the present study, we were interested in determining concentrations and distribution of heavy metals in a mangrove developing downstream a watershed that is not enriched in heavy metals, in order to have some baseline data for further study. In fact, Fe, Zn, Mn, Co concentrations were lower than in the mangroves previously cited. Nevertheless, mean Ni concentration was close to $1.11 \mu\text{mol g}^{-1}$ (Tab. 1), which is twice the concentrations we measured in French Guiana ($0.54 \mu\text{mol g}^{-1}$), and also higher than those measured in Hong Kong (Tam and Wong, 2000), and in Colombia (Perdomo et al., 1998), where anthropogenic sources were identified. This result suggest that even if the catchment of the present study is not enriched in Ni, coastal sediments of the lagoon present relatively high Ni concentrations, probably as a result of the current that bring sediments originated from lateritic watershed. Fernandez et al. (2006) highlighted that natural and mining-related terrigenous inputs delivered to the lagoon by the small Coulée River catchment, composed of ultramafic rocks (BRGM, 1975), and which is close to our study site, are not limited to the closest bay, but partly exported mainly as a result of prevailing along-shore currents generated by the trade winds.

Heavy metals concentrations varied greatly between sampling sites and with depth. Many parameters may influence the distribution of heavy metals in mangrove sediments, among which the quality and quantity of sedimentary organic matter, and the redox driven Fe, S cycling. Beneath the dead

Avicennia forest and in the *unvegetated* sediments, heavy metals behaviors seem to be similar regarding the relationships with TOC. The cores collected within these study sites present clear heavy metals distribution, having all the same depth trend. The higher the organic content, the higher the metal concentrations. The dead forest, richer in OM, is also richer in heavy metals, highlighting the role of OM in metal accumulation in estuarine sediments. Taking into account its high specific surface area, OM can form complexes with heavy metals (Nissenbaum and Swain, 1976). In fact, Cr, Cu, and Ni are correlated with TOC (Tab. 5), as observed by Chen et al. (2007) in Taiwan estuarine sediments, and by Ray et al. (2006) in Indian mangrove sediments. The top of the core presents the highest concentrations of the whole samples set, with Ni concentration higher than $3 \mu\text{mol g}^{-1}$. Nevertheless, heavy metals are probably not only associated with OM. Within these sites, the higher the organic content, the higher the sulphur content, resulting from the precipitation of sulphur during processes of sulfato-reduction induced by OM decomposition. In anoxic conditions, heavy metals can precipitate with sulphide minerals, and being rapidly removed from the dissolved phase (Huerta-Diaz and Morse, 1992; Aragon and Miguens, 2001). These sulphide minerals are probably iron sulphide ones, like pyrite or greystone, as highlighted by the correlation between TS and Fe concentrations (Tab. 5). At the bottom of the core collected in the *unvegetated* sediments, concentrations in OC were lower, conditions were less anoxic and the pH slightly less basic. At this level, Ni concentration in the dissolved phase increased to $0.91 \mu\text{mol g}^{-1}$, probably as a result of their release in pore-water during sulphide oxidation, which may indicate that part of Ni was, actually, associated with sulphide. Burton et al. (2006) observed that nickel extractability was low, possibly due to formation of pure Ni-S phases or sequestration by pyrite. Consequently, within these sediments, in which oxygen supply only comes from the surface, OM richness is the main factor driving, first, the precipitation of sulphur via sulfato-reduction processes, and then, the concentrations of heavy metals, which may be associated both with OM or sulphur minerals. In Brazilian mangrove sediments, OM and sulphide seem to be the most important factors regulating the amount of free or biologically available metals (Kehrig et al., 2003). Beneath *Rhizophora* stand, despite a higher organic content, as well as higher sulphur content, heavy metals concentrations were not higher than those measured in the sediment collected beneath

the dead forest. In addition, no specific trend can be observed with depth except for Cu, Zn and Mn. Solid Fe concentrations depth trend follow the one of TS, probably highlighting the precipitation of iron sulphides (Berner, 1984), while Mn concentrations reached their maximum values at the bottom of the core. Mn depth trends are not correlated with TS ones since Mn sulphides are not stable, and in anoxic conditions Mn precipitate mostly as carbonate minerals such as rhodochrosite (Aller et al., 2004). In previous studies (Marchand et al., 2006; 2008), we suggested that the decomposition of OM in upper mangrove sediments leads to the production of DIC that can migrate to deeper layers with the percolation of pore-water, where carbonates can precipitate because of the marked anoxic conditions prevailing there. The higher the organic content in the suboxic upper layer, the higher the carbonate concentrations in the bottom anoxic layer. The fact that there are no specific trend with depth for most metals may be related to the fact that redox conditions are highly variable, conversely to the stable anoxic conditions of the dead forest and the unvegetated sediments, and that when sulphides minerals are dissolved in suboxic conditions, they can be incorporated into oxyhydroxide that precipitate in micro-oxic environment (Atkinson et al, 2007; Fereira et al., 2007). Either iron sulphide or iron oxide are believed to provide good adsorbing sites for heavy metals (Lee, 2006), explaining the low concentrations measured in pore-water. In Brazilian mangrove swamps, Otero et al. (2009) observed that there was a significant decrease with depth in all the types of Fe oxyhydroxides measured, particularly the poorly crystalline forms, in relationship with the decreasing Eh values. We suggest that these oxyhydroxides may be a sink for trace metals in the upper core of our studied mangrove. Beneath *Avicennia* trees, the scenario is very similar except that oxic to suboxic conditions prevail to 15 cm depth due to the cable root system that diffuses oxygen in the upper sediment. These conditions probably induced some sulphide minerals dissolution and thus the release of heavy metals in pore-water. The fact that Fe concentrations in pore water is relatively low, probably results to its rapid precipitation as oxyhydroxides. In fact, the upper sediment beneath *Avicennia* is characterized by the highest Ni concentration in the dissolved phase, up to $1.88 \mu\text{mol l}^{-1}$. This result suggest that because of the specificity of the *Avicennia* root system, heavy metals in the dissolved phase present higher concentrations than beneath *Rhizophora* stand, and thus that heavy metals are more bioavailable and

potentially more mobile beneath *Avicennia* stand. This specificity enhances the potential of some metals entering into the food chain beneath *Avicennia*. Nevertheless, during the rainy season, with a higher water table, results may have been different. In a previous study, we suggested that beneath *Avicennia*, metals precipitated with sulphides during the rainy season due the anoxic conditions prevailing, and resulting from the higher water table (Marchand et al., 2006).

5 Conclusions

This preliminary study, in the mangroves of New-Caledonia, allowed us to better understand heavy metal distribution in relationship with OM cycling and mangrove zonation, in a coastal area that is not affected by mining activities. The conclusion can be summarized as follow :

- Organic content is higher beneath the *Rhizophora* stand than beneath the *Avicennia* stand. We suggest that this can result from the more developed root-system of *Rhizophora* compared to the radial cable root system of *Avicennia* that develop only in the subsurface. The difference of extension of their root system may also explain that the OC enrichment is deeper beneath *Rhizophora* than *Avicennia*.
- Surprisingly at depth, beneath *Avicennia*, the sediment was characterized by an increased proportion of *Rhizophora* tissues. This result implies that the living *Avicennia* stand develop on sediments that were previously colonized by *Rhizophora*. This topic will be investigated in a further research effort concerning the evolution of the mangrove of New-Caledonia with climate change during the last millennium.
- Organic sources also differ beneath the two species, and as a result of their distribution. Beneath *Rhizophora*, the sedimentary organic pool derives mainly from woody tissues, whereas beneath *Avicennia*, the pool can be a mixture of decomposing leaves and wood. Actually, *Rhizophora* stand develops on the sea-side of the mangrove, and is continuously subjected to tidal flushing, and thus leaf litter cannot accumulate compared to the *Avicennia* stand that develops on the land-side of the mangrove.

- Mangrove zonation also induces differences in the redox conditions that occurred beneath the 2 species. We suggest that the suboxic conditions that prevailed in the upper sediment beneath the *Rhizophora* stand result from air diffusion from the atmosphere. This layer is not very deep because *Rhizophora* stand is frequently submerged by tides. Below this layer, and as a result of the high organic content, the conditions were anoxic and sulfidic. Conversely beneath *Avicennia*, suboxic conditions prevailed deeper. We suggest that oxygen diffusion from atmosphere is more important because of its higher position in the intertidal zone, and that this diffusion add its effect to the one via the root system, which is well known to create oxidized rhizosphere. Consequently, the present study confirms that the length of waterlogging of a mangrove stand, depending on its topographic situation in the intertidal zone, seems to be a main factor controlling redox conditions in the upper sediment, as well as the activity of the root system.

- Despite its high organic content, mangrove swamps of Conception Bay are not enriched in heavy metals, except Ni. We suggest that even if the catchment of the present study is not enriched in Ni, coastal sediments of the bay present relatively high Ni concentrations, probably as a result of the current that bring sediments originated from lateritic watershed.

- Heavy metals distribution within sediments and pore-water appear to result from diagenetic processes linked to OM decomposition. Beneath the dead *Avicennia* forest and in the *unvegetated* sediments, the higher the organic content, the higher the metal accumulation. The dead forest, richer in OM, is also richer in heavy metals, highlighting the role of OM in metal accumulation in estuarine sediments. Nevertheless, the higher the organic content, the higher the sulphur content too. As a consequence, with our data set, it is not possible to decipher between heavy metals complexation with humic acids or incorporation into sulphide minerals. Beneath living mangrove stand, despite a higher organic content, as well as higher sulphur content, heavy metals concentrations were not higher than those measured in the sediment collected beneath the dead forest. In addition, no specific trend were evidenced, probably resulting from the fact that when sulphides minerals are dissolved in suboxic conditions of the upper layers, they can be incorporated into oxyhydroxides that precipitate in micro-oxic environment.

- Concerning heavy metals in the dissolved phase, the higher concentrations were measured in the upper suboxic conditions of the *Avicennia* forests. We suggest that because of the specificity of the *Avicennia* root system and its position in the intertidal zone, heavy metals in the dissolved phase present higher concentrations than beneath *Rhizophora* stand, and thus that heavy metals are more bioavailable and potentially more mobile beneath *Avicennia* stand. This specificity enhances the potential of some metals entering into the food chain beneath *Avicennia*.

Now that we have some baseline information on heavy metals dynamics, we will work on this topic in mangrove that are situated downstream ultramafic soils, which are exploited or not, in order to assess the impact of extracting activities on the concentration and distribution of heavy metals in mangroves.

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Figures

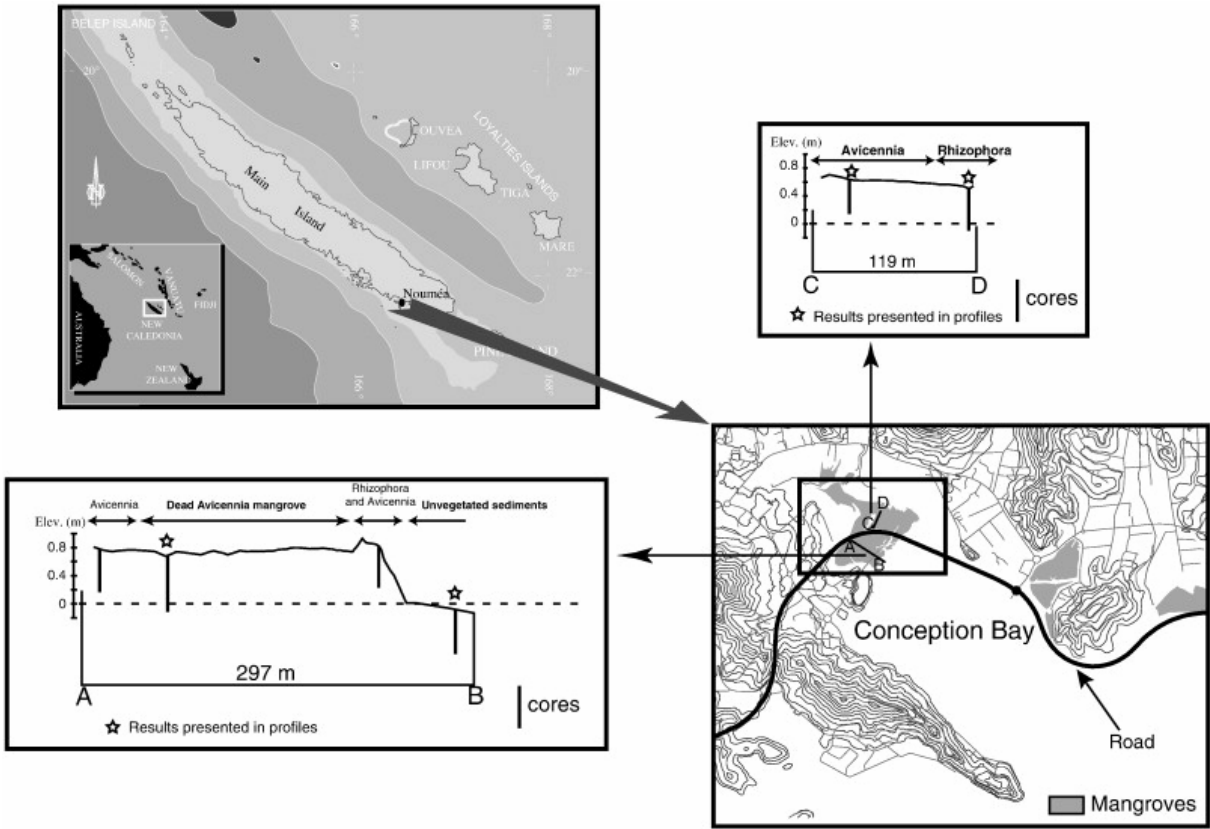


Fig. 1. Map of the studied area (Conception Bay, New Caledonia) showing: i) the localization of New Caledonia in the Pacific Ocean; ii) the localization of the 2 studied transects in the mangrove forest of Conception bay; iii) the position of the cores along transects and their differences of elevation.

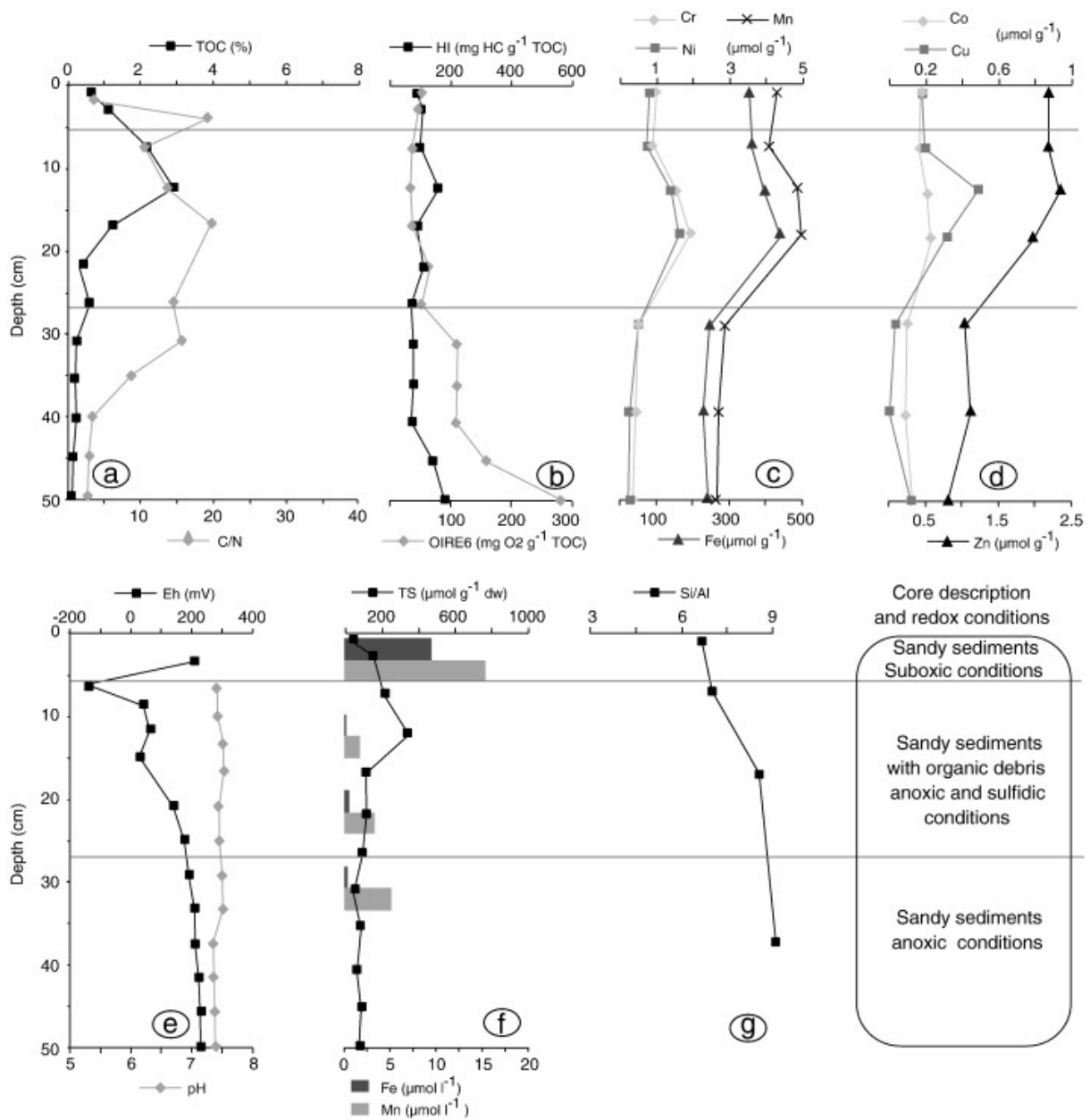


Fig. 2. Depth distribution of some parameters in the intertidal unvegetated sediment: a) TOC, C/N; b) HI, OIRE6; c) Fe, Mn, Cr, Ni in the solid phase; d) Co, Cu, and Zn, in the solid phase; e) pH, redox; f) TS, Fe and Mn in the dissolved phase, g) Si/Al atomic ratios, core description.

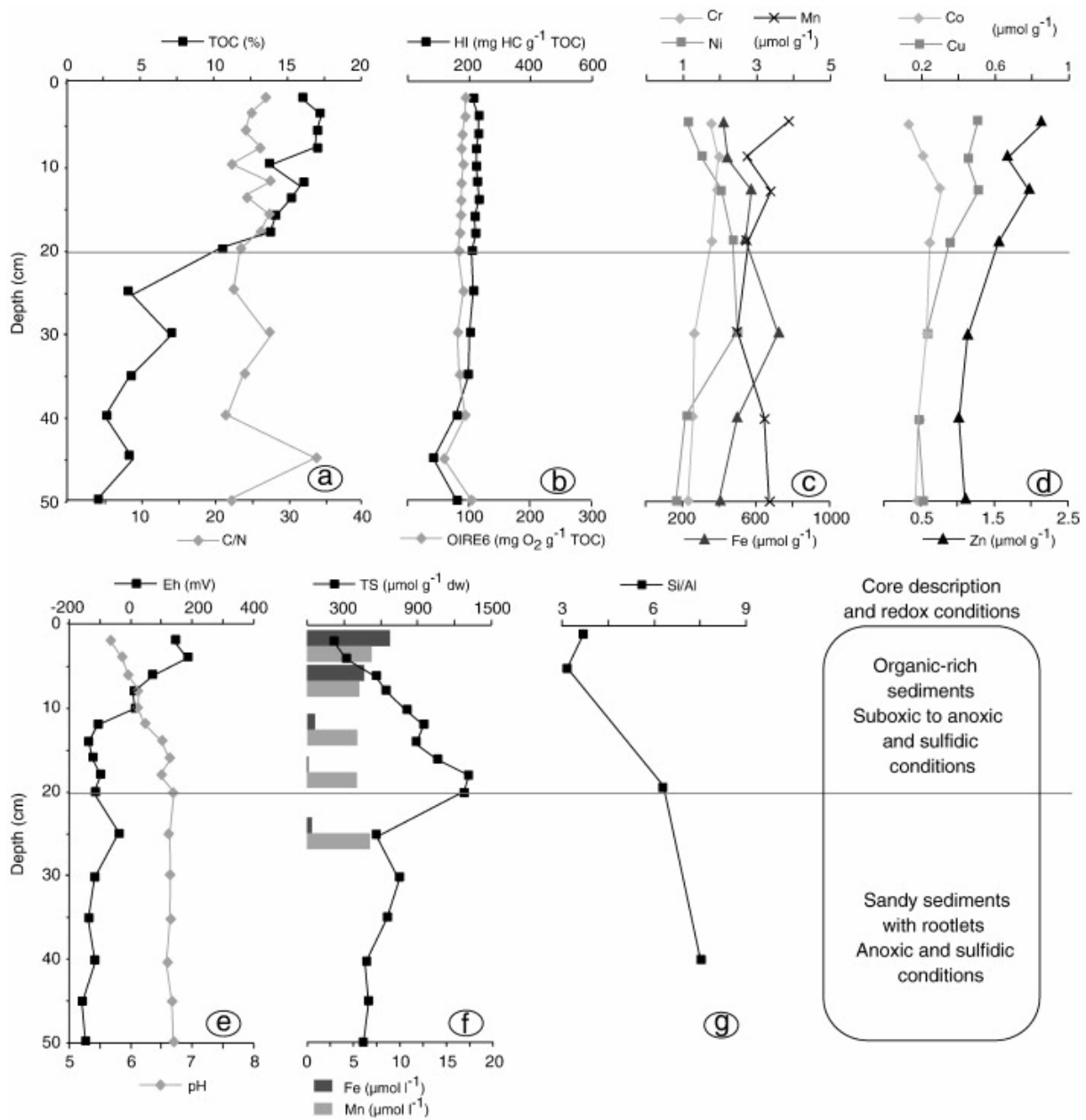


Fig. 3. Depth distribution of some parameters beneath the *Rhizophora stylosa* forest: a) TOC, C/N; b) HI, OIRE6; c) Fe, Mn, Cr, and Ni in the solid phase; d) Co, Cu, and Zn, in the solid phase; e) pH, redox; f) TS, Fe and Mn in the dissolved phase, g) Si/Al atomic ratios, core description.

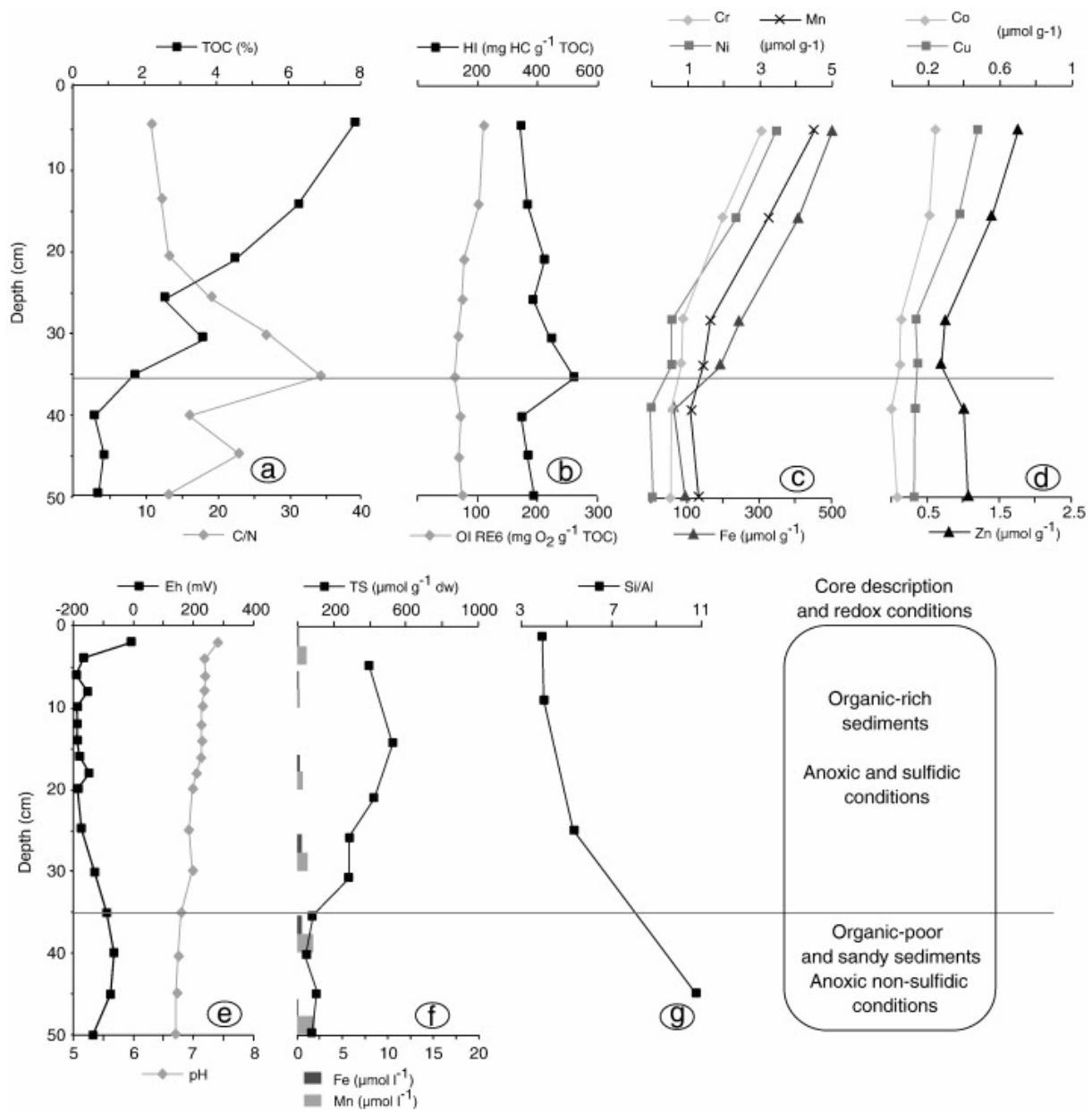


Fig. 4. Depth distribution of some parameters beneath the dead *Avicennia marina* forest: a) TOC, C/N; b) HI, OIRE6; c) Fe, Mn, Cr, and Ni in the solid phase; d) Co, Cu, and Zn, in the solid phase; e) pH, redox; f) TS, Fe and Mn in the dissolved phase, g) Si/Al atomic ratios, core description.

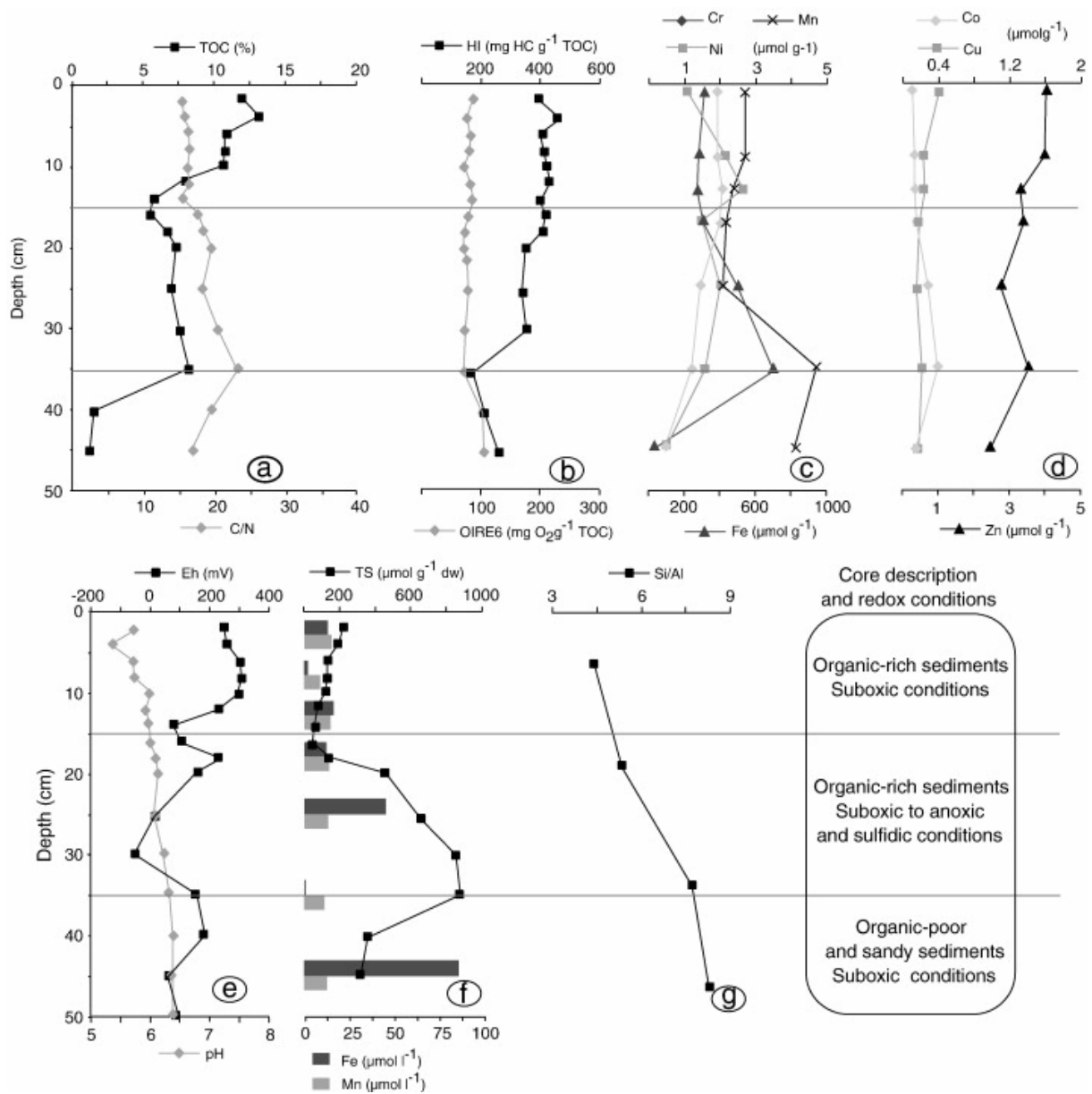


Fig. 5. Depth distribution of some parameters beneath the *Avicennia marina* forest: a) TOC, C/N; b) HI, OIRE6; c) Fe, Mn, Cr, and Ni in the solid phase; d) Co, Cu, and Zn, in the solid phase; e) pH, redox; f) TS, Fe and Mn in the dissolved phase, g) Si/Al atomic ratios, core description.

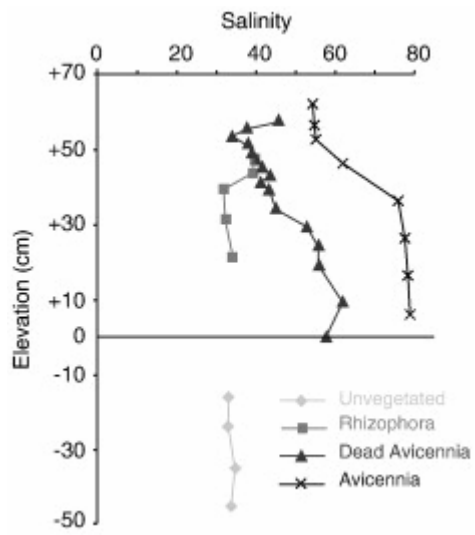


Fig. 6. Depth distribution of pore-water salinity in the various study sites.

Tables

Table 1. Concentrations of heavy metals, TS, and TOC in cores collected in Conception Bay. Average, standard deviation (S.D.), maximum, and minimum values.

	Cr ($\mu\text{mol g}^{-1}$)	Cu ($\mu\text{mol g}^{-1}$)	Ni ($\mu\text{mol g}^{-1}$)	Zn ($\mu\text{mol g}^{-1}$)	Fe ($\mu\text{mol g}^{-1}$)	Mn ($\mu\text{mol g}^{-1}$)	Co ($\mu\text{mol g}^{-1}$)	TS (%)	TOC (%)
Mean ($n = 45$)	1.22	0.22	1.11	1.35	331.85	2.90	0.14	0.96	4.99
S.D.	0.66	0.12	0.82	0.44	175.66	1.05	0.08	0.89	5.41
Max.	3.11	0.51	3.55	2.36	721.69	5.00	0.38	4.09	21.25
Min.	0.36	0.08	0.03	0.68	22.64	1.13	0.01	0.12	0.2

Table 2. Accuracy precision and detection limits (expressed as 3 times the standard deviation determined from numerous analyses).

	HR-ICP-AES detection limit (nmol g^{-1})	LGC 6137 certified values (nmol g^{-1})	Standard deviation	Measured concentrations (nmol g^{-1}) ($n = 6$)	Standard deviation
Cr	18	904	135	1164	121
Mn	16	665	27	742	33
Fe	291	30,700	1600	32,200	1200
Co	25	232	29	206	28
Ni	29	537	43	505	62
Cu	30	497	25	484	25
Zn	17	3538	245	3889	282

Table 3. Cr and Ni concentrations depth distribution in pore-waters. UD: under the detection limit.

Mangrove	Depth (cm)	Cr ($\mu\text{mol l}^{-1}$)	Ni ($\mu\text{mol l}^{-1}$)
Unvegetated	0–5	UD	UD
	10–15	UD	0.17
	20–25	UD	0.27
	30–35	UD	0.92
<i>Rhizophora</i>	0–5	0.19	0.59
	5–10	0.19	0.24
	10–15	0.21	0.47
	15–20	0.19	0.17
	25–30	0.21	0.2
<i>Avicennia</i>	0–5	0.38	1.88
	5–10	0.38	0.81
	10–15	0.46	0.8
	15–20	0.29	0.44
	20–25	0.33	0.19
	30–35	0.21	0.2
	40–45	0.38	0.98
Dead	0–5	0.56	UD
	5–10	0.56	UD
	10–20	0.81	UD
	20–30	0.81	UD
	30–40	0.87	UD
	40–50	0.69	UD

Table 4. Characteristics of fresh mangrove tissues (TOC, C/N, HI, and OIRE6).

Samples	TOC	C/N	HI	OIRE6
	(%)		(mg HC g ⁻¹ TOC)	(mg O ₂ g ⁻¹ TOC)
<i>A. marina</i> leaf	40	20	569	127
<i>A. marina</i> wood	37	43	405	152
<i>R. stylosa</i> leaf	38	40	529	92
<i>R. stylosa</i> wood	43	91	341	89

Table 5. Correlation half matrix ($n = 45$). Bold print indicate correlation higher than 0.5.

	Cr	Cu	Ni	Zn	Fe	Mn	TS	TOC
Cr	1.							
Cu	0.76	1.						
Ni	0.88	0.57	1.					
Zn	0.47	0.66	0.32	1.000				
Fe	0.54	0.49	0.68	0.29	1.			
Mn	0.31	0.46	0.27	0.60	0.43	1.		
TS	0.35	0.47	0.51	0.08	0.73	0.11	1.	
TOC	0.67	0.73	0.56	0.38	0.47	0.01	0.59	1.