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Redox conditions and heavy metals distribution in mangrove forests receiving shrimp farm effluents (Teremba bay, New Caledonia)

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Abstract

Purpose Mangroves of New-Caledonia act as a buffer between a lagoon of more than 20,000 km² and the Island, which is characterized by ultramafic rocks and lateritic soils that are exploited for their richness in some heavy metals. We will endeavour in this article to first bring out a better understanding of the redox conditions, and secondly to understand heavy metals distributions in mangroves receiving shrimp farm effluents.

Materials and methods Samples come from 4 areas defined in terms of vegetation composition: a salt-flat, an *Avicennia marina* forest, in which effluents are released, a *Rhizophora stylosa* forest, and a dead *Rhizophora* forest. They were collected during the maximum of effluent release. Some measurements on pore-water were also done during a period without effluent. Cores (70 cm deep) were performed at low tide with an Eijkelkamp gouge auger, and pore waters were extracted using soil moisture samplers. Physico-chemical parameters (pH, Eh, salinity) were measured by directly inserting the probes into cores. Total nitrogen and total sulphur were determined. The sedimentary organic content was studied using a Rock-Eval 6 pyrolysis. Finally, heavy metals concentrations were determined, both in the solid and the dissolved phases, using an HR-ICP-AES.

Results and discussion The distribution of heavy metals in the core collected in the salt-flat is mainly controlled, on the one hand, by the sedimentary organic content, on the other hand, by the elevation of the area, which induced dessication. The release of effluent within the *Avicennia* stand induced anoxic conditions on the whole depth profile, while these conditions are suboxic without effluent release, probably inducing different metal speciation. The *Rhizophora* forests, located at 100 m from the release point, do not seem to show any impact from the effluent phase, as indicated by the redox profiles which show similar results with and without effluents release. Beneath these two stands, conditions are mainly anoxic and sulphidic, as a result of the decomposition of high organic matter content.

Conclusions The release of effluent within the *Avicennia* stand, by modifying the length of water-logging, clearly modifies the redox conditions. We suggest that the differences of redox conditions between the two periods modify the carrier phase of heavy metals, being mainly associated with sulphides during effluent release. Metals are thus less mobile, and consequently when mangrove receives effluents, they act as a sink for trace metals.

Keywords Heavy metals • Mangrove • New-Caledonia • Organic carbon • Redox conditions • Shrimp farm effluent

1 Introduction

Mangrove ecosystem once covered almost 75% of the world's tropical and subtropical coastline (Spalding et al. 1997). However during the last decades, they disappeared worldwide at the rate of 1 to 2% per year, a rate greater than or equal to threatened ecosystems like coral reefs or tropical rainforests (Valiela et al. 2001; FAO 2003; 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. 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. 1995; Tam and Wong 2000).

Mangrove forests which develop within the intertidal zone, are considered as a very productive area with high rates of organic carbon accumulation (Kristensen et al. 2008; Bouillon et al. 2008). Many complex geochemical processes, with a great variability of major pore water parameters (pH, redox, salinity), take place in mangrove sediments. These processes vary considerably due to seasonal and spatial variations; moreover reciprocal effects exist between plant species and sediment geochemistry (McKee 1993; Marchand et al. 2004). As a result, mangroves may act as a sink or a source of heavy metals along tropical and subtropical coastal areas (Harbison 1986; Tam and Wong 2000), and are thus a natural laboratory to study metals distribution between the dissolved and the solid phases.

In New-Caledonia, mangroves are associated with the world's longest continuous barrier reef, a boundary to a lagoon of more than 20,000 km² in area, recently registered on the UNESCO World Heritage. Extensive mangrove swamps are fringing about 80% of the eastern and 20% of the western coast of this island. 24 mangrove species were identified, covering more than 25,000 ha (Duke 2006; Virly 2006). Shrimp farming in New-Caledonia is the second economic exporting activity, besides Nickel industry. 19 farms have been created on more than 700 ha on the west coast of the island. Conversely to many regions, ponds were not

created at the expense of mangrove forests. They were constructed on salt-flat, besides mangrove ecosystem, at higher physiographic conditions in the intertidal zone. The farming technique which is used is the flow-through semi-intensive system, at the rate of 20 to 30 animals per m⁻². The quantity as well as the quality of the water for this type of breeding is critical. In order to allow optimum growth, the water must be permanently renewed so as to balance water salinity and to respond to variations of parameters such as dissolved oxygen, turbidity, quality and quantity of phytoplankton (Della Patrona and Brun 2008).

In New Caledonia, the water is pumped from the lagoon, sometimes at the mouth of rivers or directly from mangrove swamps. The water is then directly drained back into the mangrove swamps, mainly into the *Avicennia* stand. In this article we will endeavour to first bring out a better understanding of the redox conditions with and without effluent release, and secondly to understand the heavy metals distributions during effluent release beneath various representative sites at increasing distance from the discharge point. Pore-water properties were determined, and quantitative analyses of organic carbon, major elements, and heavy metals contents were carried out on sedimentary cores collected in 4 areas: a salt-flat, an *Avicennia* stand, which develops very close to the discharge point, a dead *Rhizophora* forest, and a *Rhizophora* forest, which develop further from the discharge point.

2 Materials and methods

2.1 Study site and sampling

New-Caledonia which is located in the Pacific Ocean, is orientated along a northwest-southeast axis, and is almost 500 Km in its length and about 50 Km in its width (Fig. 1). The studied mangrove swamp is located in the municipality of Moindou, on the west coast of the island, at approximately 130 km north of Nouméa, the main city. This mangrove developed in the Teremba bay, close to the mouth of the La Foa River. The catchment of this river is not composed of ultramafic rocks, and is thus not enriched in heavy metals. The mangrove swamp receives the effluents of the shrimp farm Sodacal (see Fig. 1). This farm was built in 1983, and is the oldest in New Caledonia. The Sodacal farm is also the biggest of the territory with 132.7 ha of ponds. Work was carried out in March 2007, and some measurements of pore-water parameters were also done in July 2008, in a period of low activity at the farm, without effluent release into the mangroves.

Cores (70 cm deep) were performed at low tide with an Eijkelkamp gouge auger along a transect. Samples studied herein come from 4 areas defined in terms of vegetation composition: a salt-flat, an *Avicennia marina* forest in which the effluent are released, a *Rhizophora stylosa* forest which is located at 200 m from the discharge point, and a dead *Rhizophora* forest with standing dead trees located at 150 m from the discharge point (see Fig. 1). 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. Samples were collected every 2 cm from 0 to 20 cm depth, every 5 cm from 20 to 70 cm depth. Until drying time, samples were kept frozen. They were then grounded with an agate pestle and mortar.

Pore waters were extracted on the day of coring with soil moisture samplers 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 is around 20 ml of pore water for a piece of core of 150 cm³. All samples were 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, redox, and ΣH₂S 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 interstitial water from the core (through filter paper in a hand press). 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 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). 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.

The same WTW pH/mV/T meter connected with a WTW Ag/S 800 electrode was used to determine $\Sigma\text{H}_2\text{S}$. The calibration of the electrodes was performed by titration of sulphide solutions (prepared with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ PROLABO) by a standard AgNO_3 solution.

2.2.2 Rock-Eval analysis

Total Organic Carbon (TOC) was determined using a Rock-Eval 6 pyrolysis on powdered rock samples (Espitalié et al. 1985; Lafargue et al. 1998; 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 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 residual and pyrolysed organic carbon contents.

2.2.3 Total Nitrogen and Total sulfur

Total nitrogen and total sulfur (TS) concentrations were measured by combustion at 1,100°C with a CNS-2000 LECO apparatus. C/N ratios were then determined to characterize organic matter (OM) quality.

2.2.4 Heavy metals

The concentrations of Fe, Mn, Cr, and Ni expressed in $\mu\text{mol g}^{-1}$, 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 lot 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 analysis as a function of physico-chemical parameters depth trend. Blank acid mixtures were digested in the same way. Each sample was measured in triplicate with mean standard deviation for Fe, Mn, Cr, Ni, less than 2%, 1%, 2%, and 5%, respectively. Accuracy of the measurements was checked by analysis of an estuarine sediment certified reference material

(LGC 6137). Analytical results obtained for references materials differed by less than 15% from the certified values (Table 1).

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 physico-chemical parameters depth trend to have at least one sample per redox conditions.

2.2.5 Major elements

Major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 , in % weight) were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after classical digestion. 100 mg of sample was fused at $1,000^\circ\text{C}$ with 1 g of LiBO_2 for about 30 minutes. The fusion residue was then dissolved with 5% HCl. Only Si and Al are discussed in this article.

3 Results and discussion

3.1 Salt-flat

The salt-flat is located at the same tidal level as the ponds, and no effluents are released in this area (see Fig. 1). This zone presents a distribution contrasted of all the parameters with depth (Fig. 2). Two zones can be clearly distinguished, the limit of which is situated close to 25 cm deep. In the upper layer, total carbon organic (TOC) contents are close to 0.5%, which is very low, resulting from the almost absence of vegetation colonizing this area. Pore-water salinities were higher than 100 on the whole depth profile. *Avicennia* trees which are, in New Caledonia, the mangrove trees most adapted to the highest point in the tidal zone and thus to high salinities (Walsh 1974; Marchand et al. in press) seem not to be able to develop with such salinity values. On the field, we only observed algal mats developing at sediment surface. These high salinity values and the absence of higher plant result from the fact that this area is only reached during spring tides, and is thus highly subjected to evaporation processes that induce high pore-water salinities (Ridd and Sam 1996). Nevertheless, carbon over nitrogen ratios (C/N) vary between 5 and 20, indicating a mixture between highly degraded fragments deriving from upper plants and from materials deriving from algal mats. The latter which is present on the surface of salt-flat, have a C/N close to 8, whereas fresh tissues of the various mangroves have C/N varying between 20 and 120 (Table 2). When

higher plant tissues degrade, C/N values fall, on the one hand, because carbon mineralizes faster than nitrogen, and on the other hand, the bacteria, decomposing these materials produce some nitrogen (Meyers and Lallier-Vergès 1999; Marchand et al, 2005). These upper plant degraded fragments were probably brought during high tides from the mangrove that develops ten meters away. Under 25 cm deep, the TOC content increases strongly as well as the C/N values, until 16% and 60, respectively. The macroscopic observations of the core, with the presence of red tissues characteristic of *Rhizophora*, and the high C/N values indicate that this increase of carbon is linked to the presence of mangrove tissues in decomposition. The C/N are relatively high, on the one hand, because fresh *Rhizophora* woody tissues have high C/N, 115 (see Table 2), and on the other hand, anoxic conditions prevail at this depth, and thus the degradation rate is probably low. Consequently, the present salt-flat develops on a former mangrove swamp. In a mangrove located close to Noumea, we were able to observe this trend beneath an *Avicennia* stand (Marchand et al. in press). The processing method of a mangrove swamp zone in one salt-flat is made according to climate changes of the zone and/or to variations of hydrocirculation. We therefore suggest that a drained salt-flat can be recolonized by a mangrove swamp, and conversely a mangrove swamp dried up will convert into a salt-flat. This topic will be the subject of further research, i.e. the changing processes of the mangroves in New-Caledonia amidst climate variations during the last millennium. Correspondingly, the contents in mineral elements are higher in the top of the core, the average contents in Si and Al are, respectively, 9 and 2.5 mmol g⁻¹, while they are lower than 4 and than 1 mmol g⁻¹, respectively, in the inorganic matter enriched zone (OM). As regards to the physico-chemical parameters, similar profiles were measured during both field; i.e. with and without effluent release (Fig. 2 and Fig. 3). The upper zone oxidizes and the pH decreases regularly, the lower zone being close to the anoxia and the pH remaining stable, around 5.5.

The oxidation of the upper sediment results, on the one hand, from the almost entire absence of OM, its mineralization being the consumer of oxygen, and on the other hand, from the important desiccation of salt-flat, because of its high position in the tidal range zone. This position allows oxygen diffusion from the atmosphere towards the sediment. This desiccation is also highlighted by the water content measurement, which is lower than 30%. Conversely in the deep layer, the moisture content is higher, reaching 70%, probably because of subterranean hydrocirculations and because of the presence of OM which retains water. In the

upper sediment, the tidal supply of basic cations induces pH values close to 7. The acidic basal deposits may be the result of oxidation of reduced compounds (NH_3 , H_2S , FeS_2), and the decomposition of OM (Middelburg et al. 1996; Alongi et al. 1998).

The concentrations in dissolved sulphides are under the detection limit on the whole depth profile. The contents in total sulfur are lower than 0.5% in the upper part, whereas they increase until more than 4% in the zone enriched in OM, indicating sulphides precipitation during processes of sulfate-reduction which take place in conditions of anoxia, as indicated by the low Eh values (Otero et al. 2009).

The distribution of the metallic elements is also highly contrasted between the two zones, oxidizing on-surface, anoxic in-depth. The concentrations in Fe and Mn, in the solid phase, are raised in the upper zone, around $900 \mu\text{mol g}^{-1}$ and $12 \mu\text{mol g}^{-1}$, respectively. The fall of Fe concentrations between 15 and 30 cm, in the solid phase, is correlated with an increase in Fe in the dissolved phase, the concentrations rising from 0 to more than $300 \mu\text{mol l}^{-1}$. This phenomenon characterizes the zone of transition between the oxic zone and the anoxic zone (Marchand et al. 2006a). It is the suboxic zone, where mainly the oxygen of iron oxyhydroxides is used by bacteria to decompose the organic matter, thus inducing oxides dissolution and the liberation of the iron in the dissolved phase (Ferreira et al. 2007). Otero et al. (2009) observed that there was a significant depth decrease in all types of Fe oxyhydroxides measured, particularly in the poorly crystalline forms, compared to the decreasing Eh values. In previous studies (Marchand et al. 2006a), we indicated that the higher the oxidizing conditions in the upper zone, the higher the dissolved Fe concentrations in the transition zone.

Deeper, in the anoxic zone, the content in dissolved Fe probably falls as a result of their precipitation with sulphides to form iron sulphides, pyrite or greigite, as observed in French Guiana (Marchand et al. 2003). As regards Mn, the content in the solid phase also falls in the zone of transition thus indicating the use of the oxygen of MnO_2 for the decomposition of OM (Alongi et al. 2000), while increasing in the dissolved phase.

Unlike the iron, the content in dissolved Mn does not fall in the anoxic zone. Mn sulphides are unstable and are rarely observed as opposed to Fe sulphide. Concerning Cr and Ni in the solid phase, they have similar distributions. Their maximal concentration is observed in the oxidizing zone, with values close to $1.5 \mu\text{mol g}^{-1}$. They are probably incorporated into oxy-

hydroxides (Atkinson et al. 2007; Ferreira et al. 2007). Their concentration falls in the zone enriched in OM, with values lower than $0.5 \mu\text{mol g}^{-1}$. In the dissolved phase, the content in these two elements is relatively stable with the depth, raised for Ni, around $5 \mu\text{mol l}^{-1}$, and weak for Cr, around $0.1 \mu\text{mol l}^{-1}$. The high dissolved Ni concentration results probably from alternations between oxic and anoxic conditions, which induce the dissolution of certain oxides within which Ni were present.

3.2 *Avicennia* stand

In the *Avicennia* mangrove swamp, the content in organic carbon and the C/N ratios are relatively homogeneous in the upper 40 cm, around 5% and around 20%, respectively (Fig. 4). These results indicate enrichment relatively moderated in carbon probably resulting from the decomposition of leaves and woody tissues of *Avicennia*, with C/N values of 23 and 59 (see Table 2), respectively. The enrichment is moderated compared to other mangrove swamps (Kristensen et al. 2008). This is due, on the one hand, because the root system of *Avicennia* is less developed than other species like *Rhizophora*, and it is mainly a radial cable root system that develops close to sediment surface (de Granville 1974). This zone is, on the other hand, the closest to effluent release, and we suggest that leaf litter may be flushed with the effluent, thus limiting its accumulation as well as TOC values in the sediment. Under 40 cm deep, higher TOC values and increased C/N probably indicate a former mangrove swamp, like the one observed beneath the salt-flat.

In the top of the core, the contents in Si and Al is relatively stable around 8 and 2 mmol g^{-1} , respectively, while they fall slightly in the part enriched in OM, under 40 cm deep. Fe has the same behavior, with concentrations close to $900 \mu\text{mol g}^{-1}$ in the top of the core, falling to $600 \mu\text{mol g}^{-1}$ at the bottom.

As regards the physico-chemical parameters (Eh and pH), the vertical gradients are less marked than in the core taken in the salt-flat, probably because of a less important gradient of TOC. Close to sediment surface, redox values fall from -50 mV to -150 mV under 20 cm deep, whereas the pH slightly increases, from 6.2 to 6.5. The upper conditions may imply a more effective mineralization of OM, allowing a liberation of humic acids, thus of light acidity, compared with the deeper anoxic sediment. As regards dissolved Fe and Mn, their

concentration quickly falls from the surface to 12 cm deep passing from 20 to 0 $\mu\text{mol l}^{-1}$, and 8 to 0 $\mu\text{mol l}^{-1}$, respectively. The presence of dissolved Fe in the upper zone indicates suboxic conditions. Also, concentrations in dissolved sulphides were measured on the whole profile, and TS was detected from 15 cm with concentrations reaching 4%, marking phenomena of sulfate-reduction (Otero et al. 2006). Usually, beneath *Avicennia* trees, oxidizing conditions are observed in the upper sediment. On the one hand, pneumatophores constitute a pathway for the exchange of oxygen between atmosphere and sediments (Scholander et al. 1955). On the other hand, *Avicennia* cable root system has the capacity to diffuse oxygen into the sediment, creating oxidized rhizosphere (Thibodeau and Nickerson 1986; Clark et al, 1998). 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). Clark et al. (1998) attributed the “lower oxidation zone” of their redox stratification model to the activity of the radial cable roots of *Avicennia*; while the “upper oxidation zone” was attributed to animal bioturbation. Alongi et al. (2000) demonstrated that O_2 breathing accounted for nearly 80% of the total oxidation of carbon in the soil of a young *Avicennia* forest. In fact, during the period without effluent release, redox and pH profiles are totally different (see Fig. 3). In the upper core, where the root system develops, Eh values reach 400 mV, and pH decreases to 4, probably as a result of a more efficient OM degradation and sulphide oxidation. The fact that the conditions are not oxidizing in the upper core collected beneath *Avicennia*, during the period of effluent release, is most probably a direct impact of the disposal of effluents in this zone. Further, this forest being continuously submerged by the effluent, which modify the length of water-logging of the sediment, may indeed imply a more important O_2 consumption, and thus lower redox values in the upper core.

Regarding Cr and Ni in the solid phase during the phase of effluent release, it is observed that the concentration lightly increases with depth (except the first point for Cr). Further, the concentration in Cr increases from 0.8 to 1.5 $\mu\text{mol g}^{-1}$, whereas the Ni concentration increases from 0.5 to 0.8 $\mu\text{mol g}^{-1}$. Conversely, in the dissolved phase, the concentration decreases with depth, from 1.2 to 0.6 $\mu\text{mol l}^{-1}$ for Ni, and from 0.4 to 0.1 $\mu\text{mol g}^{-1}$ for Cr. These results are linked to the redox conditions; the upper 10 cm being suboxic thus implying dissolution of Mn oxides and certain iron oxides, releasing metals, formerly associated with them, under dissolved phase. In the anoxic conditions prevailing at the bottom of the core, trace metals can

be incorporated into FeS during the sulfate-reduction processes (Boulègue et al. 1982; Huerta-Diaz and Morse 1992).

3.3 Standing dead *Rhizophora* forest

In the dead *Rhizophora* zone, TOC distribution indicates 3 different layers. In the upper 8 cm, the contents are close to 10%, whereas they fall to 5% between 10 and 25 cm deep, before increasing to a maximum of 19% at 45 cm deep (Fig. 5). The C/N is low on-surface, oscillating between 20 and 30, whereas they reach more than 50 in the rich TOC zone, between 40 and 50 cm deep. The decomposition of dead wood at sediment surface, as observed in the field, is probably the main contributor to this OM. The lower TOC value measurement between 10 and 30 cm deep, are more intriguing. They correspond to a zone richer in Si and Al. The zone enriched in TOC at depth may correspond to the *Rhizophora* root system, but usually this root system develops between 15 and 35 cm depth (Otero et al. 2006). The zone with a weaker TOC content suggests that this forest would have been subjected to an important influx of sediments, which would have suffocated the forest by burying the root system. The origin of this influx is not well defined; however New-Caledonia is frequently subjected to cyclones. We suggest that heavy rains may have eroded zone without vegetation and rich in fine particles, which are situated close to big ponds, and that the sediment was deposited in some zones of the *Rhizophora* forest, killing the trees. Ellison (1998) showed that excess input of sediments to mangroves can cause death of trees owing to root smothering.

The contents in Fe are relatively stable with the depth, around $900 \mu\text{mol g}^{-1}$. The concentrations in Mn are stable in the upper 40 cm, around $4 \mu\text{mol g}^{-1}$, then increase abruptly to reach $12 \mu\text{mol g}^{-1}$. The increased Mn concentrations can result from their precipitation in the form of carbonates. Indeed, this zone is rich in TOC deriving from the root system and the decomposition phase produces mineral C in the form of dissolved carbonates. In anoxic conditions such dissolved carbonates can precipitate to form carbonated minerals, by incorporating certain elements as Mn (Zhu et al. 2002). In previous studies (Marchand et al. 2006b, 2008), we suggested that the decomposition of OM in upper mangrove sediments leads to the production of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) that can migrate to deeper layers with the percolation of pore-water. Thus, DOC can

accumulate and carbonates can precipitate because of the marked anoxic conditions that prevail there. As regards the redox conditions, they are similar during both periods, with and without effluent release. We would therefore suggest that the geochemistry of this area, which is located further from the discharge point than the *Avicennia* stand, is less influenced by effluent release. During the period of effluent release, redox conditions are slightly suboxic in the upper 5 cm, with redox values higher than 200 mV, concentrations in dissolved Fe close to 25 $\mu\text{mol l}^{-1}$, and concentrations in dissolved Mn close to 6 $\mu\text{mol l}^{-1}$. Below this depth, conditions evolve towards the anoxia, with Eh values lower than -100 mV, dissolved Fe concentrations being under the detection limit, concentrations in dissolved sulphides reaching 80 $\mu\text{mol l}^{-1}$, and S contents exceeding 6%. The suboxic conditions close to sediment surface probably result from oxygen diffused from the atmosphere. Below this depth, the conditions become quickly anoxic, as a result of the decomposition of the high organic content. As for the other sites, the upper suboxic layer contains concentrations relatively raised in dissolved metals. The concentrations in Fe, Mn, Ni, and Cr are 25, 6, 4, 0.2 $\mu\text{mol l}^{-1}$, respectively. These concentrations fall strongly in the anoxic zone probably because of precipitation of minerals either under the form of sulphides (Huerta-Diaz and Morse 1992), or under the form of carbonates (Zhu et al. 2002).

3.4 *Rhizophora* stand

The living *Rhizophora* forest may also have been subjected to sediment deposits that have induced the death of the zone next to it. However this deposit was probably less important and did not thus suffocate mangroves trees. This sedimentary deposit is translated by a zone less rich in TOC in the upper 5 cm, with values around 5% and C/N close to 20 (Fig. 6), while leaf litter was observed at sediment surface. These upper 5 cm are also richer in Si and Al compared to the rest of the core with concentrations of 8 and 3 mmol g^{-1} , respectively. From 15 cm deep, the contents in TOC are relatively stable, around 10%, and the C/N ratios are close to 40, indicating an OM, which probably mainly derives from the root system of the *Rhizophora* trees. In this zone enriched in TOC, the contents in Si and Al are respectively 6 and 2.5 mmol g^{-1} .

Similarly to the other sites, Fe concentrations are nearby 900 $\mu\text{mol g}^{-1}$, whereas the content in Mn increases with depth, from 3 $\mu\text{mol g}^{-1}$ at sediment surface to 7 $\mu\text{mol g}^{-1}$ at depth,

probably, as previously observed, as a result of the precipitation of carbonate minerals in anoxic conditions. The concentrations in Ni and in Cr, in the solid phase, also increase with the depth, from 0.6 to 1.2 $\mu\text{mol g}^{-1}$, and from 1 to 1.6 $\mu\text{mol g}^{-1}$, respectively.

The redox conditions are stratified in 3 layers, and are similar during both periods, with and without effluent release (see Figs. 3, 6). The upper 5 cm are characterized by oxic conditions, similar to those reigning on the surface of the salt-flat, with values of Eh close to 400 mV, also by an absence of dissolved sulphides and of solid S, and with very low dissolved Fe concentrations. These conditions result from the fact that the *Rhizophora* mangrove swamp seems to develop at a slightly higher elevation than the dead zones, and seems not to receive the effluent. This is also highlighted by the leaf litter that can accumulate. The top of the sediment is thus slightly dried out, as shown by the moisture contents, resulting in an increase of oxygen being diffused from the atmosphere. The deeper suboxic condition may be explained by numerous factors. Firstly, 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 *Rhizophora*, which is described to be thicker between 15 and 30 cm depth (Otero et al. 2006). However, the *Rhizophora* root system is not known to diffuse O_2 into the sediment, as in the case with *Avicennia*. Between 5 and 25 cm deep, redox values fall from 300 to 0 mV, and the concentrations in dissolved Fe reach about 900 $\mu\text{mol l}^{-1}$. Concentrations are exceptionally high in this case. It seems that the more the conditions are oxidizing in the upper sediment, the higher the concentrations in dissolved Fe in the suboxic underlying layer, as observed in the salt-flat. Under 25 cm deep, the conditions become anoxic, with Eh lower than 100 mV, an absence of dissolved Fe, because of its precipitation with dissolved sulphides in order to form iron sulphides (Ferreira et al. 2007), with TS concentrations reaching 6%. *Rhizophora* sediments are known to be highly sulphidic due to the fibrous and organic nature of its sediment (Hesse 1961). The concentrations in dissolved Mn increase slightly in the upper 25 cm, from 3 to 8 $\mu\text{mol l}^{-1}$, probably because of the dissolution of Mn oxides in suboxic conditions, then fall to 4 $\mu\text{mol l}^{-1}$, because of the likely precipitation with carbonates as observed beneath the dead *Rhizophora* forest. Ni and dissolved Cr present particular profile, with average concentrations of 0.5 and 0.1 $\mu\text{mol l}^{-1}$, respectively.

4 Conclusions

Our conclusions can be summarized as follows:

1/ Influence of shrimp farm effluent on mangrove geochemistry seems to be limited to the mangrove developing the closest from the discharge point, i.e., the *Avicennia marina* stand. The release of effluent within the *Avicennia* stand, by modifying the length of water-logging, clearly modifies the redox conditions, being anoxic almost on the whole depth profile during the period of effluent release, while oxidizing in the upper core during the period without effluent release, as a result of the physiological activity of the root-system. We suggest that the differences of redox conditions between the two periods modify the carrier phase of heavy metals, being mainly associated with sulphides during effluent release.

2/ Distribution of heavy metals in the core collected in the salt-flat, developing at the same tidal level as the ponds and not been subject to prolonged water-logging, is mainly controlled by the organic distribution, the salt-flat developing on a former mangrove swamp. The key role of the elevation of the zone is also highlighted, in fact the salt-flat develops in the highest zone of the tidal range and is thus subjected to dessication, inducing oxic conditions in the upper sediment.

3/ The conditions developing beneath the dead and the living *Rhizophora* forests seem not to be influenced by the effluent located at least at 100 m from the release point, as indicated by the redox profiles that are similar at the two periods. Beneath these two stands, conditions were mainly anoxic and sulphidic as a result of high organic matter content to be decomposed. However, this is not the case in the upper cm, where oxic to suboxic conditions prevailed probably as a result of air diffusion from the atmosphere, and also crab bioturbation.

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Figure captions

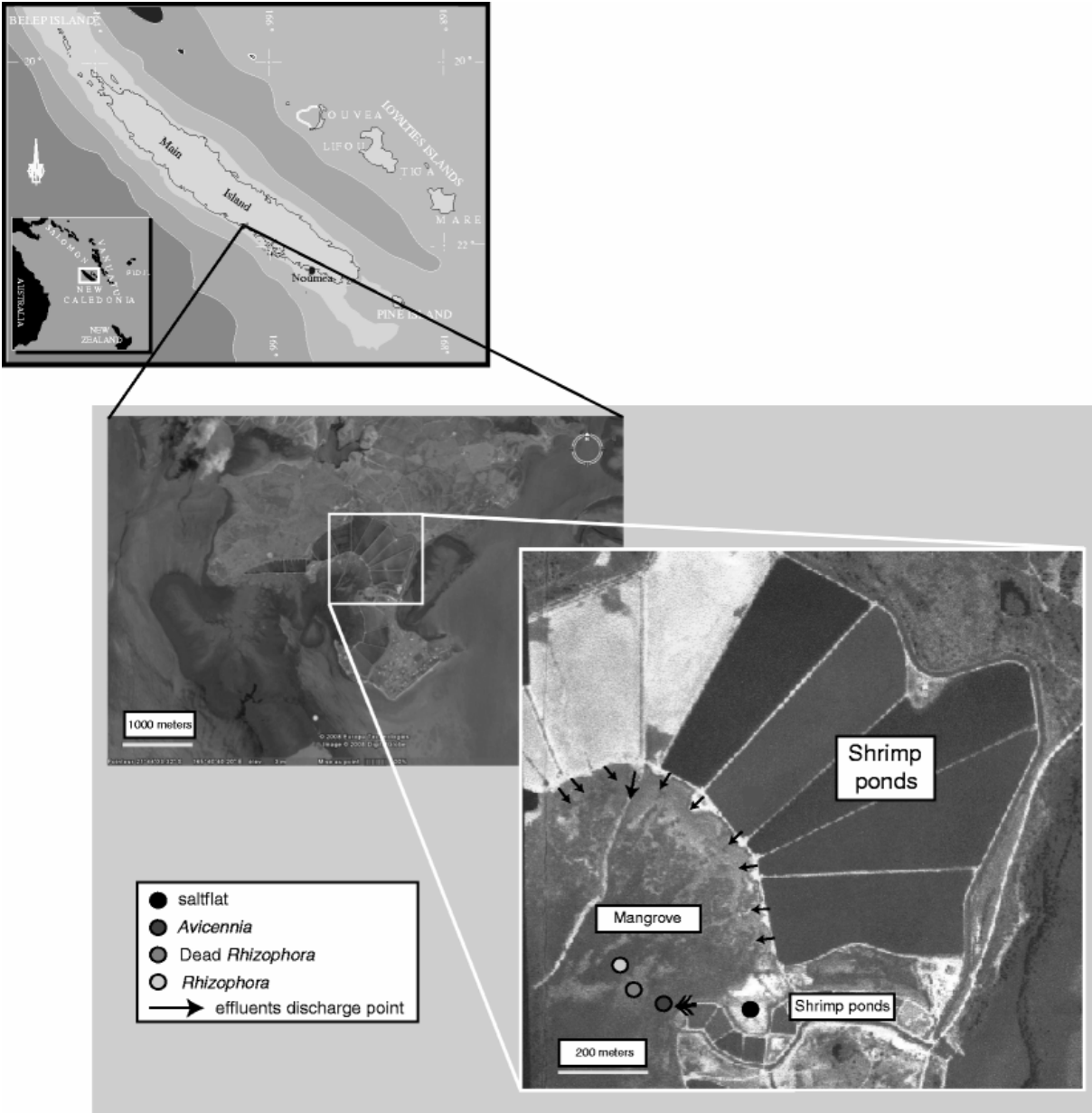


Fig. 1 Map of the studied area (Teremba Bay, New-Caledonia) showing: i) the location of New-Caledonia in the Pacific Ocean; ii) the location of the ponds and the mangrove in the bay; iii) the position of the cores

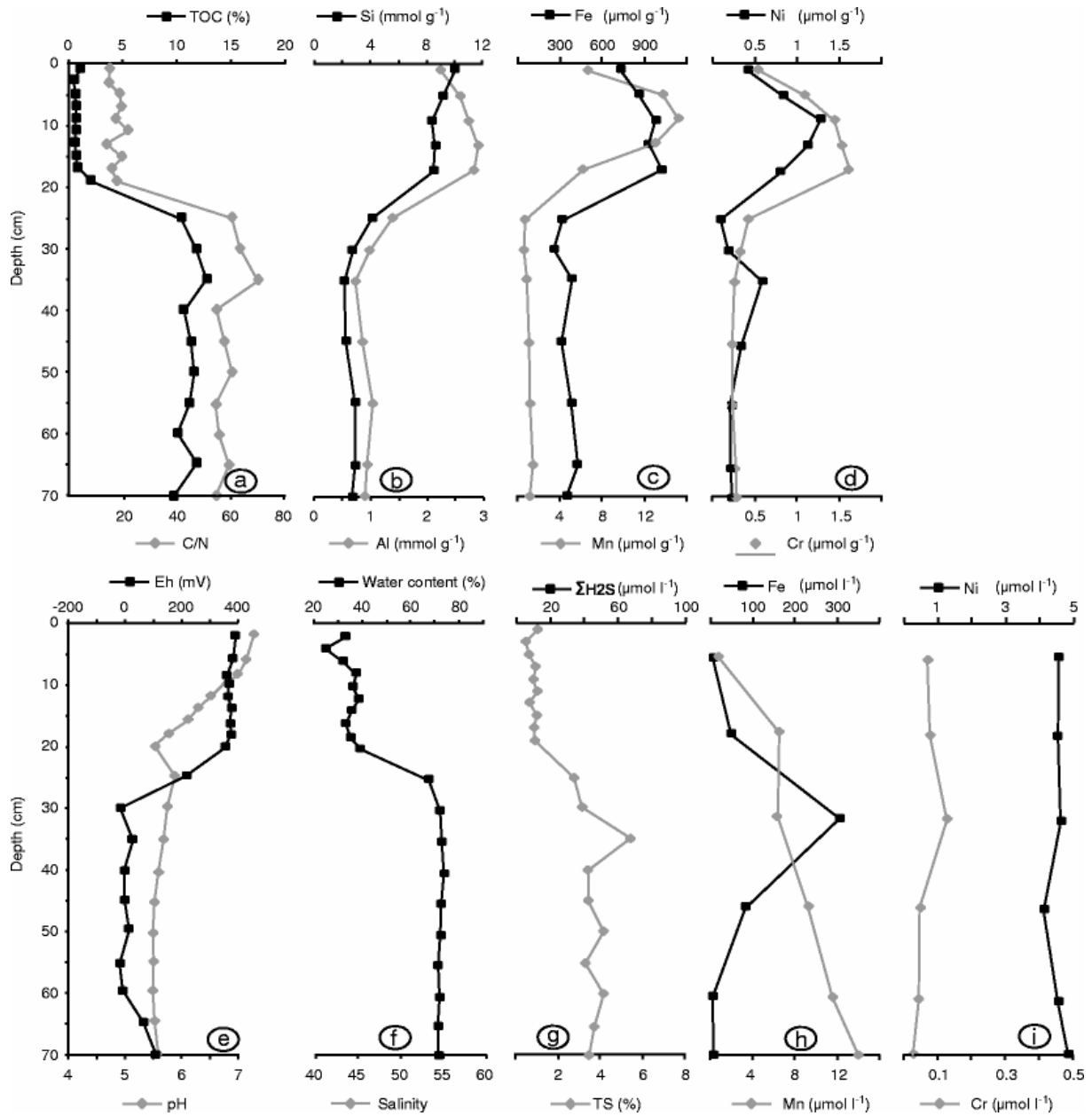


Fig. 2 Depth distribution of some parameters in the salt-flat: a) TOC, C/N; b) Si, Al in the solid phase; c) Fe, Mn in the solid phase; d) Cr, Ni in the solid phase; e) pH, redox; f) water content, salinity (higher than 100 on the whole depth profile); g) $\Sigma\text{H}_2\text{S}$ (Under the detection limit), TS; h) Fe Mn in the dissolved phase; i) Cr, Ni in the dissolved phase

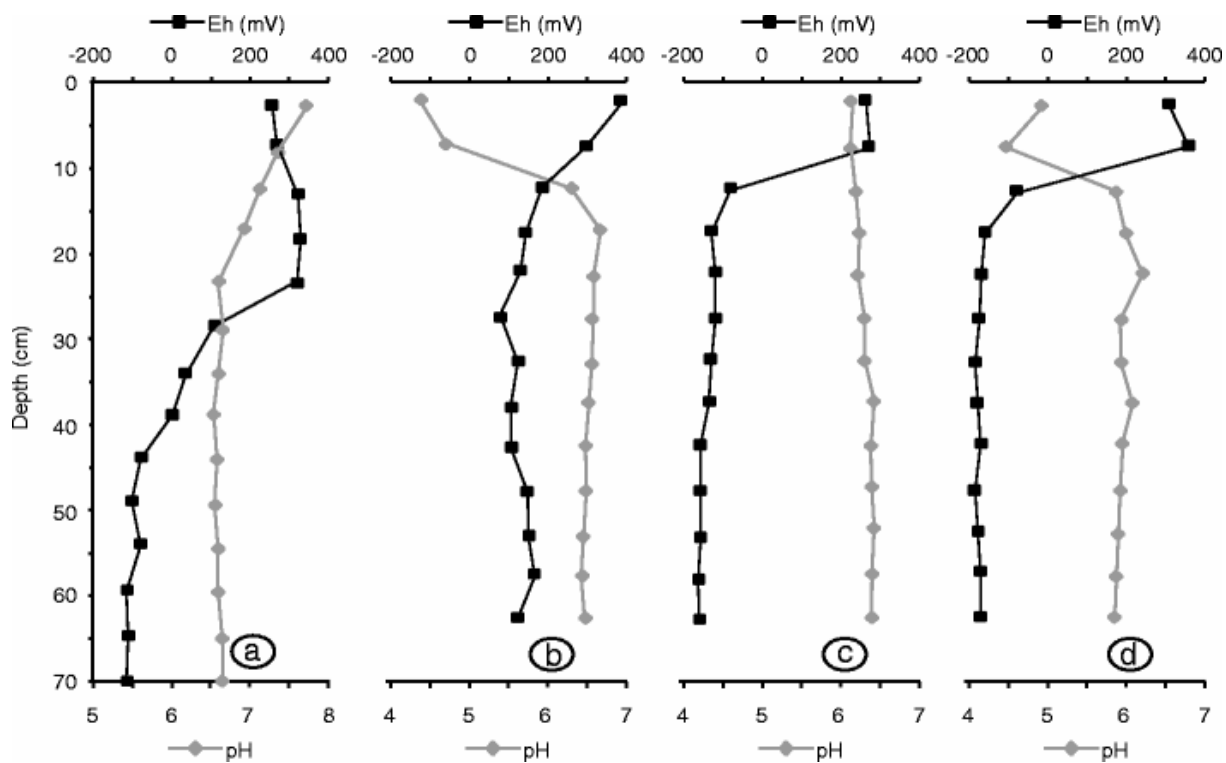


Fig. 3 Depth distribution of redox and pH without effluent in the various sites: a) salt-flat; b) *Avicennia marina* forest; c) dead *Rhizophora stylosa* forest; d) *Rhizophora stylosa* forest

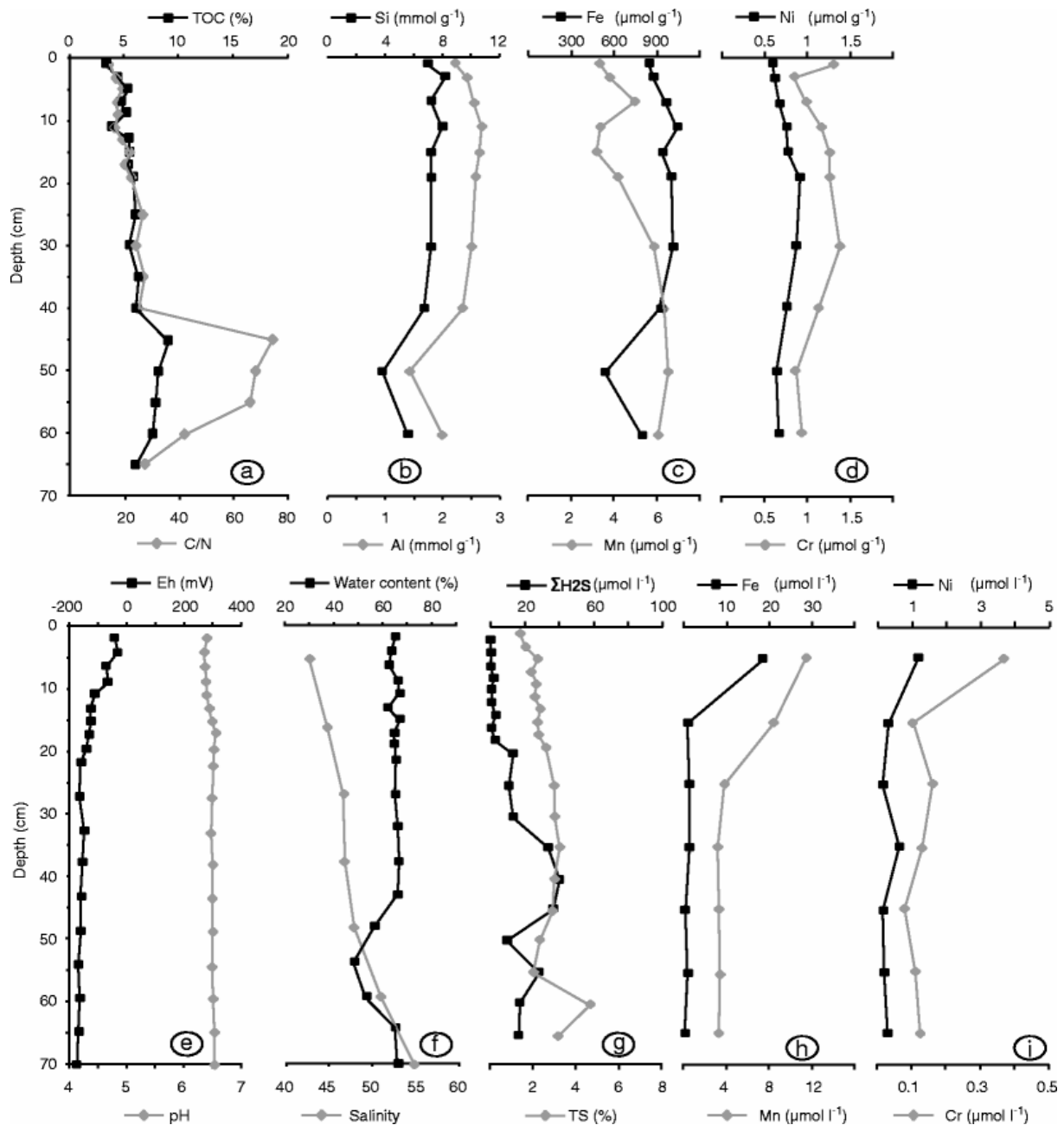


Fig. 4 Depth distribution of some parameters in the *Avicennia marina* forest: a) TOC, C/N; b) Si, Al in the solid phase; c) Fe, Mn in the solid phase; d) Cr, Ni in the solid phase; e) pH, redox; f) water content, salinity; g) $\Sigma\text{H}_2\text{S}$, TS; h) Fe Mn in the dissolved phase; i) Cr, Ni in the dissolved phase

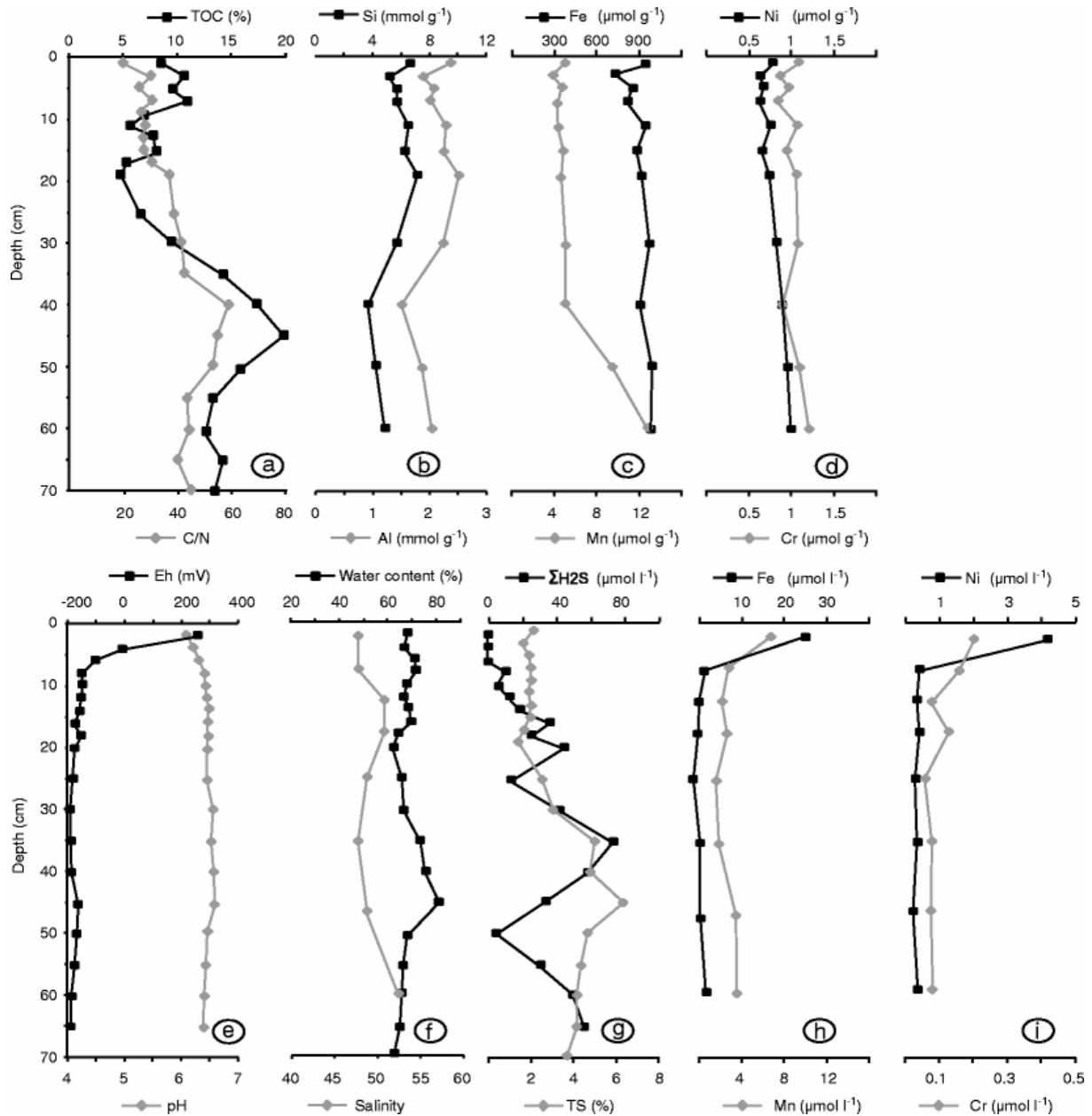


Fig. 5 Depth distribution of some parameters in the dead *Rhizophora stylosa* forest: a) TOC, C/N; b) Si, Al in the solid phase; c) Fe, Mn in the solid phase; d) Cr, Ni in the solid phase; e) pH, redox; f) water content, salinity; g) $\Sigma\text{H}_2\text{S}$, TS; h) Fe Mn in the dissolved phase; i) Cr, Ni in the dissolved phase

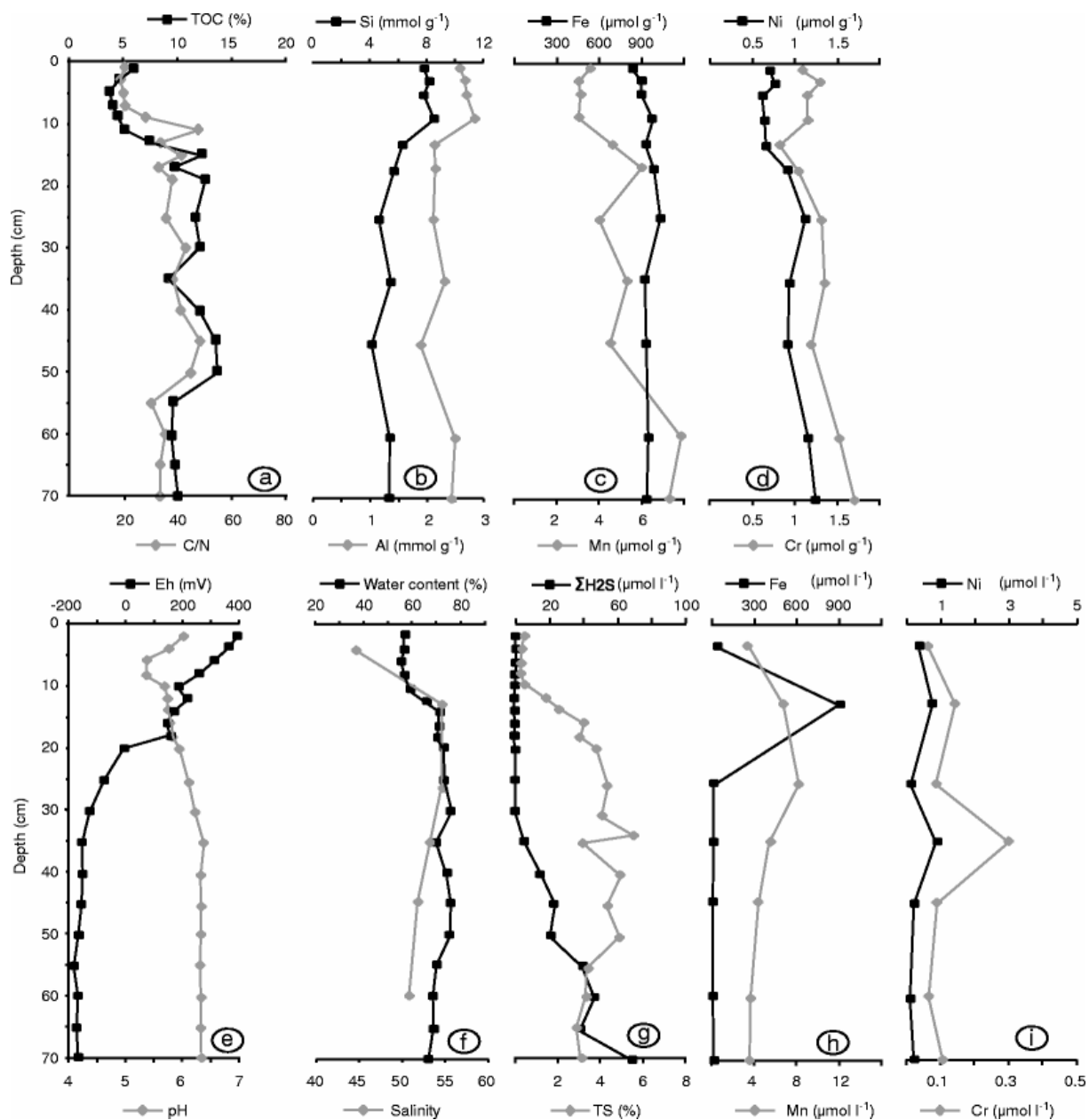


Fig. 6 Depth distribution of some parameters in the *Rhizophora stylosa* forest: a) TOC, C/N; b) Si, Al in the solid phase; c) Fe, Mn in the solid phase; d) Cr, Ni in the solid phase; e) pH, redox; f) water content, salinity; g) $\Sigma\text{H}_2\text{S}$, TS; h) Fe Mn in the dissolved phase; i) Cr, Ni in the dissolved phase

Table list:

Tab. 1 Accuracy precision and detection limits (expressed as 3 times the standard deviation determined from numerous analyses)

Table 1 Accuracy, precision, and detection limits (expressed as three times the standard deviation determined from replicate analyses)

| | HR-ICP-AES detection limit (nmol g⁻¹) | LGC 6137 certified values (nmol g⁻¹) | σ | Measured concentrations (nmol g⁻¹; n=6) | σ |
|----|---|--|----------|---|----------|
| Cr | 18 | 904 | 135 | 1,164 | 121 |
| Mn | 16 | 665 | 27 | 742 | 33 |
| Fe | 291 | 30,700 | 1,600 | 32,200 | 1,200 |
| Ni | 29 | 537 | 43 | 505 | 62 |

Tab. 2 Characteristics of fresh mangrove tissues (TOC, C/N)

| Samples | TOC (%) | C/N |
|------------------------|----------------|------------|
| <i>A. marina</i> leaf | 44 | 23 |
| <i>A. marina</i> wood | 44 | 59 |
| <i>R. stylosa</i> leaf | 45 | 48 |
| <i>R. stylosa</i> wood | 46 | 115 |
| Algae | 32 | 8 |