



## Trace metal geochemistry in mangrove sediments and their transfer to mangrove plants (New Caledonia)



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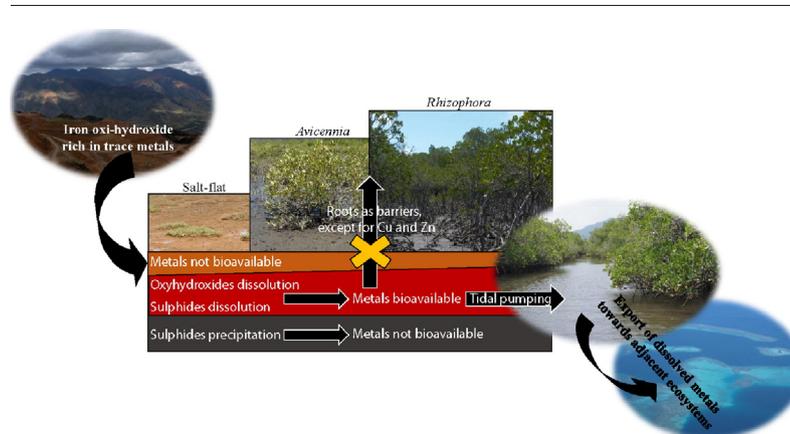
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### HIGHLIGHTS

- Unusual high concentrations of Fe and Ni were measured in mangrove tissues.
- Bioconcentration and translocation factors of Fe, Ni, Co and Mn were low.
- Low bioavailability can result from metal association with refractory bearing phase.
- Cu and Zn have greater mobility in mangrove sediments and plants.
- Metals stocks decreased towards the sea as a result of more reactive substrate.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 20 February 2016

Received in revised form 27 March 2016

Accepted 29 March 2016

Available online xxx

Editor: F.M. Tack

#### Keywords:

Mangrove

Trace metals

Partitioning

Bioaccumulation

New Caledonia

### ABSTRACT

Because of their physico-chemical inherent properties, mangrove sediments may act as a sink for pollutants coming from catchments. The main objective of this study was to assess the distribution of some trace metals in the tissues of various mangrove plants developing downstream highly weathered ferral soils, taking into account metals partitioning in the sediment. In New Caledonia, mangroves act as a buffer between open-cast mines and the world's largest lagoon. As a result of the erosion of lateritic soils, Ni and Fe concentrations in the sediment were substantially higher than the world average. Whatever the mangrove stand and despite low bioaccumulation and translocation factors, Fe and Ni were also the most abundant metals in the different plant tissues. This low bioaccumulation may be explained by: i) the low availability of metals, which were mainly present in the form of oxides or sulfur minerals, and ii) the root systems acting as barriers towards the transfer of metals to the plant. Conversely, Cu and Zn metals had a greater mobility in the plant, and were characterized by high bioconcentration and translocation factors compared to the other metals. Cu and Zn were also more mobile in the sediment as a result of their association with organic matter. Whatever the metal, a strong decrease of trace metal stock was observed from the landside to the seaside of the mangrove, probably as a result of the increased reactivity of the sediment due to OM enrichment. This reactivity led to higher dissolution of bearing phases, and thus to the export of dissolved trace metals through the tidal action. Cu and Zn were the less concerned by the phenomenon probably as a result of higher plant uptake and their restitution to the sediment with litter fall in stands where tidal flushing is limited.

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## 1. Introduction

Mangrove forests play a key role in the conservation of tropical and subtropical coastlines, notably acting as a buffer between land and coastal waters (Lee et al., 2014). They support a wide variety of ecosystem services and the ecosystem value can reach up to several thousand US\$ yr<sup>-1</sup> ha<sup>-1</sup> (Walters et al., 2008). Despite their value, mangroves are threatened ecosystems, disappearing worldwide at the rate of 1 to 2% per year, as a result of over-exploitation, pollution, and conversion (Valiela et al., 2001; FAO, 2003; Duke et al., 2007). Demographic pressure, combined with industrial development in emerging countries, has led to the release of metals and metalloids into the environment, and to their accumulation in specific ecosystem like mangroves because of their ability to trap suspended material from the water column (Furukawa et al., 1997), their richness in organic matter (OM) (Marchand et al., 2011a), and the various diagenetic processes that take place in mangrove sediments (Kristensen et al., 2008), which make them true natural biogeochemical reactors. The potential toxicity of these elements for human health and the fact that mangroves are a prime fishing area for the inhabitants of tropical coastlines, the cycling of metals in mangrove forests is a serious question that has been addressed by many authors since the end of the 1980s (Harbison, 1986). As a result, distribution, accumulation, and partitioning of trace metals in mangrove sediments have been studied in various places in the world; for instance in Australia (Clark et al., 1998), in Hong-Kong (Tam and Wong, 2000), in Brazil (Lacerda et al., 1988), in French Guiana (Marchand et al., 2006), etc. However, fewer studies were interested in the metal transfer and accumulation in mangrove plants; see the reviews of MacFarlane et al. (2007), Lewis et al. (2011) and the one of Bayen (2012). These authors notably highlighted that despite mangroves being a taxonomically diverse group, metal accumulation for all metals examined were broadly similar across genera and families.

New Caledonia is currently the third largest nickel producing country in the world, and extensive mangroves are fringing 80% of the western coastline of the Island. Processes of erosion and sedimentation along the coastline, and which occur naturally, are strongly amplified by open-cast mining activities (Fernandez et al., 2006). Large amount of trace metals can be deposited in mangrove sediments (Marchand et al., 2012; Noël et al., 2015), and thus the ecosystem can act as a buffer between open-cast mining on land and the world's largest lagoon (>20,000 km<sup>2</sup>) registered as an UNESCO World Heritage site. The mangrove flora of New Caledonia includes >20 species (Duke, 2006). *Rhizophora* spp. are predominant in 50% of mangrove areas, colonizing the seashore, and *Avicennia marina* in >15%, developing at the edge of salt-flats, on which *Salicornia* can develop. This is the typical mangrove zonation along semi-arid coastlines. Within this context, we developed several studies on trace metal, demonstrating the role of organic matter and mangrove zonation on redox processes and thus on the speciation and accumulation of trace metals in the mangrove sediment of New Caledonia (Marchand et al., 2011a,b, 2012; Noël et al., 2014, 2015; Deborde et al., 2015). However, transfer and accumulation of trace metals in mangrove tissues were never studied along this semi-arid coastline. Our hypothesis was that the bioavailability of trace metals, and their transfer to mangrove plants will differ between stands as a result of: i) different sediment properties related to the position of the stand along the tidal zone, and ii) different plant requirements. In a previous study on the same mangrove, we showed that organic diagenesis in mangrove sediments leads to the transfer of Fe and Ni from oxide form to organic and sulfide forms. Our objective was thus to determine the transfer of some trace metals, essential and not essential (Co, Cu, Fe, Mn, Ni, Zn), from mangrove sediments to plant tissues of various mangrove species (*Rhizophora*, *Avicennia*, *Salicornia*) that are representative of the mangrove zonation in semi-arid climate. In order to develop a better management of the ecosystem, we were also interested in determining which stand can act as a good sink for trace metals, by studying the trace metals stocks in the sediment. New Caledonia is a developing

country with more and more space needed on the shoreline, sometimes resulting in mangrove destruction. To reach our goals, we collected sediment cores, fine roots, main roots, and leaves of the various plants. For trace metals in the sediment, we determined their bulk concentrations and achieved selective extractions to determine their partitioning.

## 2. Materials and methods

### 2.1. Study site and sampling

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

Cores (between 60 and 70 cm deep) were collected at low tide with an Eijkelkamp gouge auger along a transect within the intertidal zone: in the *Rhizophora stylosa* stand, in the *A. marina* stand, in the salt-flat. In the *R. stylosa* forest, core was collected under prop roots. In the *A. marina* forest, core location was chosen equidistant from trees, in consideration of the large extension of the radial cable roots. After being collected, cores were wrapped in plastic film and aluminum foil in order to limit gaseous exchanges. Back at the lab (<1 h after core collection), the cores were cut into 5 cm sections. Subsamples for trace metals analysis were collected at the centre of cores on the throughout the length. Until drying, samples were kept frozen. After drying the core sections were ground with an agate pestle and mortar. At least, 10 samples per core were chosen for analyses as a function of physico-chemical parameters depth trend (redox, pH, salinity).

Dissolved metals in porewaters were extracted, at the lab, on the day of coring with soil moisture samplers Rhizon® (Song et al., 2003), which were directly inserted into a piece of core. The sampler is connected to a syringe using luer-lock fittings and PVC tubing. The syringe piston was drawn back thereby creating a vacuum and allowing the collection of pore-water from the sediments. All samples were then immediately filtered through 0.45 µm Sartorius® filters and acidified to pH 2 with Suprapur® HNO<sub>3</sub> (Merck). Samples were stored in cleaned 14 ml polypropylene tubes, in a cold room ( $T = 4$  °C) until analysis.

Biological tissues were collected for each stand: *R. stylosa*, *A. marina*, and the salt-flat, within a radius of approximately 20 m around the sediment cores. 3 leaf samples and 3 root samples were analyzed per stand. Each leaf sample consisted of 20 leaves from 5 trees. Each root sample corresponded to a sediment core in which the roots were sorted. Two sizes of root have been distinguished using a sieve, fine roots (<2 mm) and the main roots. Concerning *Salicornia* developing on the salt-flat, each sample of root and leaf stems correspond to five bunches, and 3 samples were analyzed.

### 2.2. Analytical methods

#### 2.2.1. Salinity, pH, and redox

Physico-chemical parameters were determined in an air-conditioned laboratory a couple of hours after coring. Salinities were

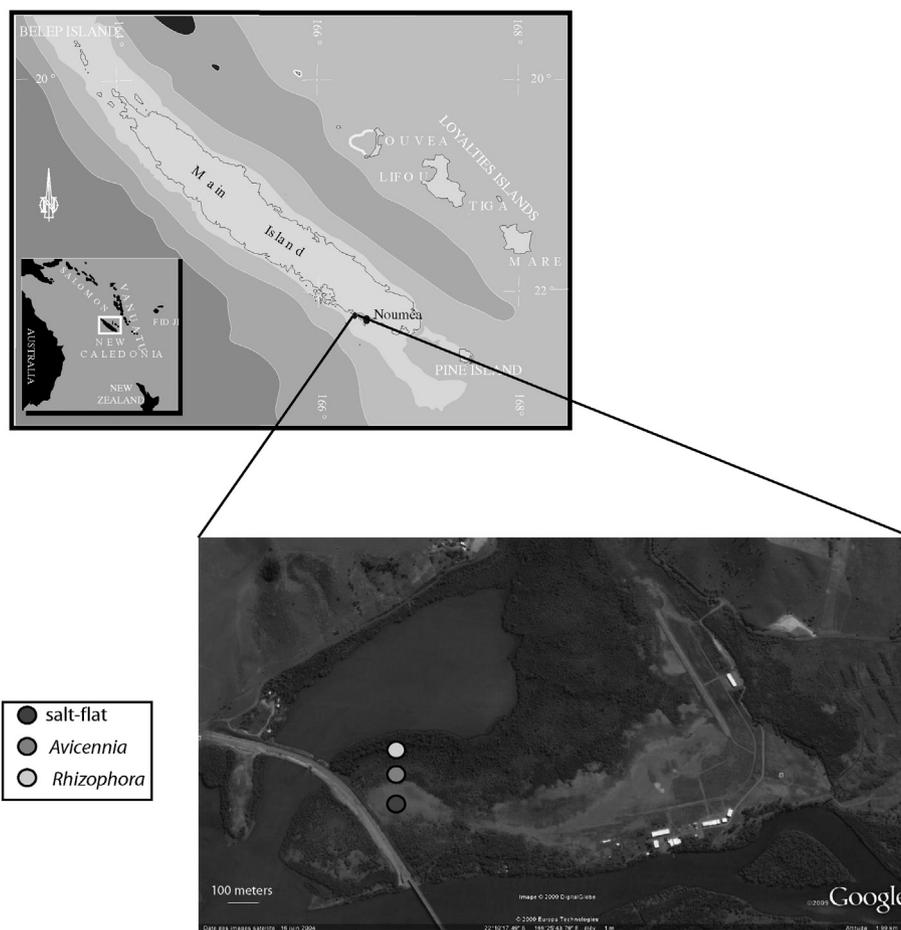


Fig. 1. Map of the studied area (Dumbea Bay, New Caledonia) showing: i) the location of New Caledonia in the Pacific Ocean; ii) the location of the collected cores in the mangrove.

determined using an Atago refractometer after extracting a drop of interstitial water from the core (through filter paper in a hand press). pH was measured using a glass electrode and a pH meter (WTW). The pH electrode was calibrated using pH 4 and 7 standards (NIST scale). Redox potential was measured, using a combined Pt and Ag/AgCl (reference) electrode connected to a pH/mV/T meter (WTW). The redox electrode was periodically checked using a 0.43 V standard solution and demineralized water. Probes were carefully inserted into the mud until stable measurements were reached, then were thoroughly washed. Redox data are reported relative to a standard hydrogen electrode, i.e., after adding 202 mV to the original mV values obtained with an Ag/AgCl reference electrode (at 25 °C). Mean values for each stand are presented in Table 1. Detailed results were discussed in Marchand et al. (2012).

### 2.2.2. TOC and TS

Total Organic Carbon (TOC) was determined using a Rock-Eval 6 pyrolysis on powdered sediment samples (Lafargue et al., 1998;

Marchand et al., 2008). In the R-E 6, samples are first pyrolysed under inert nitrogen atmosphere, and the refractory carbon is subsequently burnt in an oxidation oven. The pyrolysis programme was: 200 °C (2 min), then to 650 °C at 30 °C min<sup>-1</sup> (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<sup>-1</sup> (hold 5 min). TOC is determined as the sum of refractory and pyrolysed organic carbon contents. To discuss the influence of the quality of organic matter on trace metals dynamic in the sediment, HI and OI were also determined. HI corresponds to the quantity of hydrocarbon (HC) released during pyrolysis relative to TOC, expressed in mg HC · g<sup>-1</sup> TOC. It is correlated with H/C ratios. OI, which is correlated with O/C ratios, corresponds to the quantity of oxygen released as CO and CO<sub>2</sub> during pyrolysis, relative to TOC. It is expressed in mg O<sub>2</sub> · g<sup>-1</sup> TOC. Total sulfur (TS) concentrations were measured by combustion at 1100 °C with a CNS-2000 LECO apparatus. Mean values for each stand are presented in Table 1. Detailed results were discussed in Marchand et al. (2012).

**Table 1**  
Mean values (±SD) of Total Organic Carbon (TOC), Total Sulfur (TS), redox (Eh), pH, water content and bulk density in the sediment of the 3 studied mangrove stands in Dumbea, New Caledonia. n: number of samples used to calculate mean values.

	TOC (%)	TS (%)	Eh (mV)	pH	Water content (%)	Bulk density (g · cm <sup>-3</sup> )
Salt-flat (n = 6)	1.15 ± 0.17	0.1 ± 0.07	355 ± 49	6.76 ± 0.07	39 ± 1.57	0.79 ± 0.04
<i>Avicennia marina</i> (n = 10)	3.17 ± 1.48	0.22 ± 0.1	216 ± 69	6.55 ± 0.14	52 ± 8.54	0.55 ± 0.16
<i>Rhizophora stylosa</i> (n = 15)	13.03 ± 3.16	7.7 ± 3.85	195 ± 85	5.83 ± 0.29	68 ± 5.74	0.3 ± 0.07

### 2.2.3. Heavy metals/selective extractions

Results of Fe, Ni, and Mn partitioning in the sediment were already published in Marchand et al. (2012), and are used in this publication to compare their behavior with the one of the other metals (Cu, Zn, Co) and also to determine the bioconcentration factors and the translocation of metals to mangrove tissues. To highlight the geochemical behavior of the metals a sequential extraction protocol was used. Despite some criticism associated with sequential extraction techniques in the literature (e.g., Jouanneau et al., 1983; Nirel and Morel, 1990), this type of protocol makes it possible to understand the phenomena which occur in the different mangrove deposits. The protocol used was based on the technique developed for river sediments (Tessier et al., 1979; Meguelatti, 1982), and subsequently adapted to lateritic environments. Briefly, two grams of fine sediment were subjected to a 4 phase chemical extraction protocol to obtain metal concentrations associated with 4 geochemical fractions. The various extractions were completed as follows:

- Oxidisable forms – exchangeable – Phase 1 – this fraction represents the metals linked to the organic matter in the sediment. This extraction was completed using strong oxidants in acidic medium (HNO<sub>3</sub>);
- Acid-soluble forms – Phase 2 – these are relatively easily extracted using a weakly buffered acidic solution (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa). The forms either occur in the carbonate matrix of the sediment, or are adsorbed on the particle surfaces or coprecipitated. Due to a lack in the chemical selectivity of the reactants, this extraction step also potentially includes the easily leachable metal, initially bound by adsorption on the poorly crystallized manganese and iron oxides and clays.
- Reducible forms – Phase 3 – these forms are associated with oxyhydroxides of manganese, aluminum and iron, and are extracted using reducing conditions such as hydroxylammonium chloride in an acidic medium.
- Refractory forms – Phase 4 – these are the metals that are strongly held by the particle matrix, e.g., in silicates, aluminosilicates and mainly oxides as the result of the peridotite weathering. These were extracted using alkaline fusion technique.

The reagents and chemicals used were Merck, ProAnalysis grade. The containers used for the sequential extractions were made of HDPE, Teflon or platinum. All containers were decontaminated by soaking in nitric acid (5%) for 24 h and rinsed in ultra-pure water (Milli-Q). The quantification of trace metals in each geochemical phase was carried out by ICP-OES (Optima 3300 VD, Perkin Elmer). Analyses were carried out on certified reference materials (SD-M-2/TM, NRCC-BCSS-1) for total elements content. In addition, samples of two certified reference materials (TM-26.3 and TMDA-61, Environment Canada) were intercalated during the analytical series. For all metals, the differences between the certified values and the measured values were lower than 10%. Mean values for each stand are presented in Table 2, and depth profile is presented in Fig. 2 for Cu, Zn and Co, and in Fig. 3 for Fe, Mn, and Ni. Dissolved concentrations in porewaters are presented in Fig. 4.

**Table 2**

Trace metals concentrations in mangrove sediments of the 3 studied mangrove stands in Dumbea, New Caledonia (mean, SD). Fe, Ni, and Mn data from Marchand et al. (2012)).

		Co (μmol·g <sup>-1</sup> )	Cu (μmol·g <sup>-1</sup> )	Fe (μmol·g <sup>-1</sup> )	Mn (μmol·g <sup>-1</sup> )	Ni (μmol·g <sup>-1</sup> )	Zn (μmol·g <sup>-1</sup> )
Salt-flat (n = 6)	Mean	2.76	0.17	2018.79	11.00	48.05	0.73
	SD	0.45	0.03	232.93	2.83	5.34	0.06
<i>Avicennia marina</i> (n = 10)	Mean	2.08	0.14	1792.43	6.73	36.36	0.58
	SD	1.07	0.06	137.68	2.83	10.24	0.34
<i>Rhizophora stylosa</i> (n = 15)	Mean	3.89	0.27	2144.18	11.07	43.38	0.86
	SD	1.47	0.05	555.19	5.88	14.00	0.30

Trace metals stocks were determined for every sediment samples using the metal concentrations and the bulk density of the sample. Then, results were integrated per stand on 50 cm depth and converted to obtain values in t·ha<sup>-1</sup>. Values are presented in Table 3.

### 2.2.4. Plant tissues

First, the tissues were rinsed with ultra-pure (18.2 MΩ) water and then dried in an oven at 50 °C for >48 h to constant mass. They were then ground using an automatic agate mortar. The concentrations of trace metals in mangrove tissues, expressed in μmol·g<sup>-1</sup>, were determined with an ICP-OES (Optima 3300 VD, Perkin Elmer) after microwave digestion (Multiwave, Anton Paar). Briefly, 250 mg of tissues was attacked by adding 4 ml of HNO<sub>3</sub> and 2 ml of concentrated H<sub>2</sub>O<sub>2</sub>. Analyses were also carried out on certified reference materials (SD-M-2/TM, NRCC-BCSS-1). The reagents and chemicals used were Merck, ProAnalysis grade. The containers used were made of HDPE, Teflon or platinum. All containers were decontaminated by soaking in nitric acid (5%) for 24 h and rinsed in ultra-pure water (18.2 MΩ).

Average concentrations of metals in the different tissues were calculated by averaging the concentrations of the three samples collected. They are presented in Table 4. Bioconcentration factors of each metal (BCF = metal concentration in the tissue/metal concentration in sediments) were determined for each tissue. In the *A. marina* stand, the root systems being present only within the upper 30 cm of the soil (as observed in the field), BCFs were calculated from a mean total concentration in sediments corresponding to the average total concentrations determined over a 30 cm depth. Concerning the *R. stylosa* stand, these trees have an extensive root system; hence the BCFs were calculated from concentrations in sediment equal to the average concentration of the whole core, i.e. 60 cm depth. Regarding *Salicornia*, its root system is less developed, mainly in subsurface, therefore the BCFs were calculated from concentrations determined in the sediment equal to the average total concentrations of the top 10 cm. Translocation factors (TF = metal concentration in the leaves/metal concentration in roots) were also determined for each mangrove plant. BCFs are presented in Table 5, and TFs in Table 6.

### 2.2.5. Data analysis

In order to assess the relationships between trace metals concentrations in the sediment and co-variables (TOC, HI, OI, TS, Redox, pH) a Principal Components Analysis (PCA) was done on 32 samples (Fig. 5). To simplify the interpretation of the PCA projections, a Varimax (orthogonal) rotation was applied to the first three principal components (eigenvalues >1). Rotation of the factor axes is commonly used to improve the factor structure. A correlation matrix was also realized (Table 7).

## 3. Results and discussion

In the studied mangrove, developing downstream lateritic soils, mean trace metal concentrations in sediments were (μmol·g<sup>-1</sup>): Fe (1997) > Ni (44.2) > Cr (31.9) > Mn (8.8) > Co (2.91) > Zn (0.72) > Cu (0.19) (Table 2). These concentrations, notably for Fe and Ni, are substantially higher than world average (Table 8) (Lacerda et al., 1993;

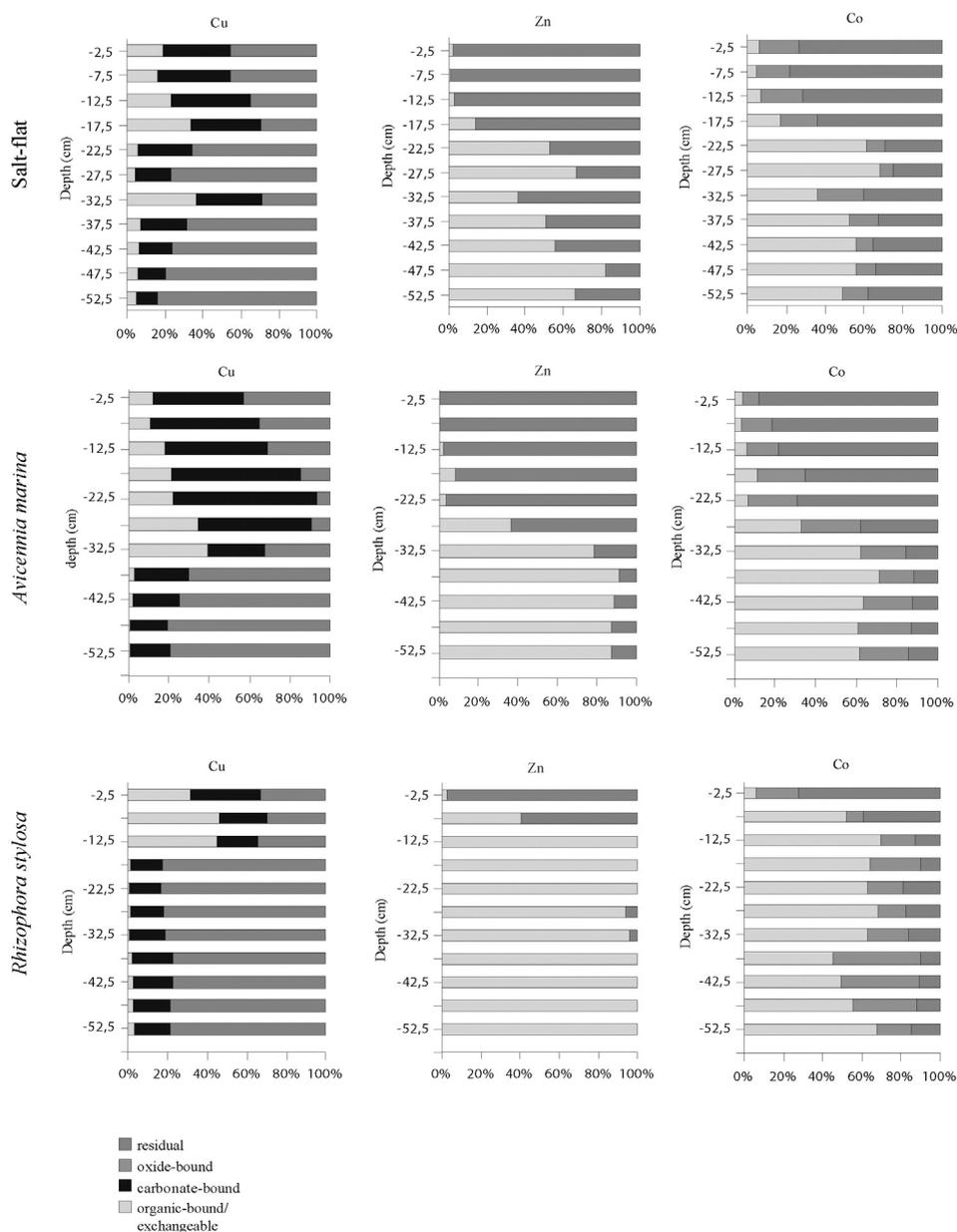


Fig. 2. Partitioning of Cu, Zn and Co in the sediment of the 3 studied mangrove stands.

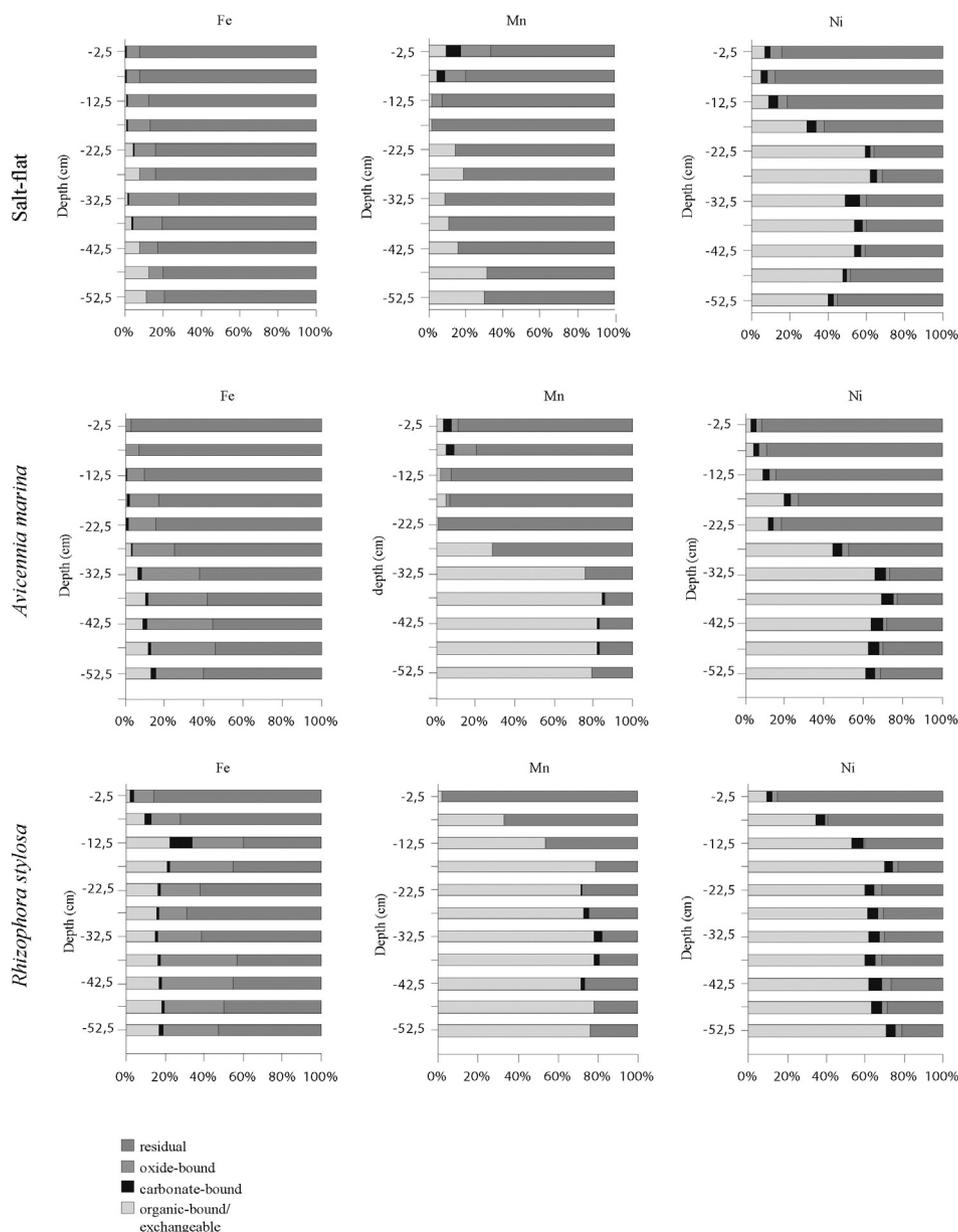
Ray et al., 2006; Li et al., 2007, Defew et al., 2005, Tam and Yao, 1998; Perdomo et al., 1998; Jingchun et al., 2006; Lewis et al., 2011; Bayen, 2012). We can thus legitimately wonder whether these high trace metals concentrations in the sediment can be partly incorporated into mangrove plants, taking into account that metal partitioning strongly varied between stands and with depth (Figs. 2; 3).

### 3.1. Partitioning and transfer of trace metals characterized by low bioconcentration factors: Fe, Ni, Mn, and Co

#### 3.1.1. Accumulation in mangrove tissues: unusual concentrations of Fe and Ni

Whatever the mangrove stand, Fe and Ni were the most abundant metals in the mangrove tissues (Table 4). Iron is as an essential element for plants, being notably involved in photosynthesis and chloroplast development. In the present study, iron bioconcentration factors (BCF) ranged from 0.06 to 0.13 (Table 5); and its translocation factors (TF) to the leaves ranged from 0.03 to 0.15 (Table 6). Despite these low factors, its concentrations in mangrove tissues reached up to

13,000  $\mu\text{g}\cdot\text{g}^{-1}$  (Table 8). Recently, Arrivabene et al. (2015) reported Fe concentrations in leaves of *Avicennia schaueriana* and *Rhizophora mangle* of 337 and 130  $\mu\text{g}\cdot\text{g}^{-1}$ , respectively, which is 2 orders of magnitude lower than in the present study. We suggest that these really high concentrations can result from the high concentrations of Fe both in the sediment (Table 2) and in the porewater (Fig. 4), where it can be easily bioavailable. In South America, the highest Fe concentrations in mangrove sediments reported was 5%, but with mean values usually close to 1% (Defew et al., 2005; Otero et al., 2006), which is far from the concentration measured herein, up to 12%. The high concentrations of dissolved Fe measured in the studied mangrove, up to 100 and 60  $\mu\text{mol}\cdot\text{l}^{-1}$  beneath *Avicennia* and *Rhizophora*, respectively (Fig. 4), resulted both from the dissolution of both iron oxides and iron sulphides during organic matter diagenetic processes (Marchand et al., 2006; Noël et al., 2014). In mangrove ecosystems, these iron bearing-phases dissolution can occur in suboxic conditions, which can be explained by biological or physical factors. On the one hand, crab burrow and root system may induce these conditions allowing the renewal of electron acceptors with tides; and on the other hand, physiological activities of



**Fig. 3.** Partitioning of Fe, Mn and Ni in the sediment of the 3 studied mangrove stands. Data from Marchand et al. (2012).

mangrove root system can lead to increased  $O_2$  concentrations in the sediment (Kristensen et al., 2008). Nagajyoti et al. (2010) suggested that in waterlogged conditions, like in mangroves, the presence of  $Fe^{2+}$  may induce an increased uptake by the root system, which may be toxic for the plant, notably by reducing photosynthesis, increasing oxidative stress, and damaging membrane, DNA, and proteins. Even if, iron cycling in mangrove sediments is highly studied (e.g. Ferreira et al., 2007; Otero et al., 2009; Noël et al., 2014); its transfer to mangrove plants has been rarely described. Arrivabene et al. (2015) did not measure any evident morphological or structural damage of the leaves, but the concentrations in the sediment were 1000 lower than in Dumbea. We thus suggest that studying a possible impact of iron on mangrove physiology would be relevant in this specific context. Like for iron, and despite the fact that nickel BCF and TF were relatively low, from 0.12 to 0.25 (Table 5) and from 0.11 to 0.23 (Table 6), respectively, Ni was the second most abundant metal in mangrove tissues, with values up to  $700 \mu\text{g}\cdot\text{g}^{-1}$  (Table 8), which is unusual, reported values in the literature never being higher than  $100 \mu\text{g}\cdot\text{g}^{-1}$  (Table 8; Lewis et al., 2011;

Bayen, 2012). We suggest that these high values are directly related to the richness of the sediment in Ni due to ferralsols erosion in the catchment. In fact, downstream ultrabasic watershed, Ni concentrations in mangrove sediments were 10 to 100 times higher than downstream non-ultrabasic ones in New Caledonia (Table 8), with concentrations reaching up to almost  $3000 \mu\text{g}\cdot\text{g}^{-1}$  for this study and 5000 for a companion study (Noël et al., 2015). In the literature, the highest concentrations reported in mangrove sediments never exceeded  $200 \mu\text{g}\cdot\text{g}^{-1}$  (review of Bayen, 2012). To our knowledge the influence of Ni on mangrove trees physiology was not studied yet. However for terrestrial plants, high Ni concentrations can result in disturbing membrane functionality and ion balance in the cytoplasm, as well as a decrease of water uptake (Seregin and Kozhevnikova, 2006; Nagajyoti et al., 2010). Maximum Co concentration in mangrove sediments and in tissues were 230 and  $46 \mu\text{g}\cdot\text{g}^{-1}$  (Tables 2, 4), respectively, with root BCF and TF ranging from 0.06 to 0.25 (Table 5), and TF ranging from 0.03 to 0.38 (Table 6). Very few information on Co dynamic in mangrove is available. Nath et al. (2014) observed that translocation of non-essential metals, like Co,

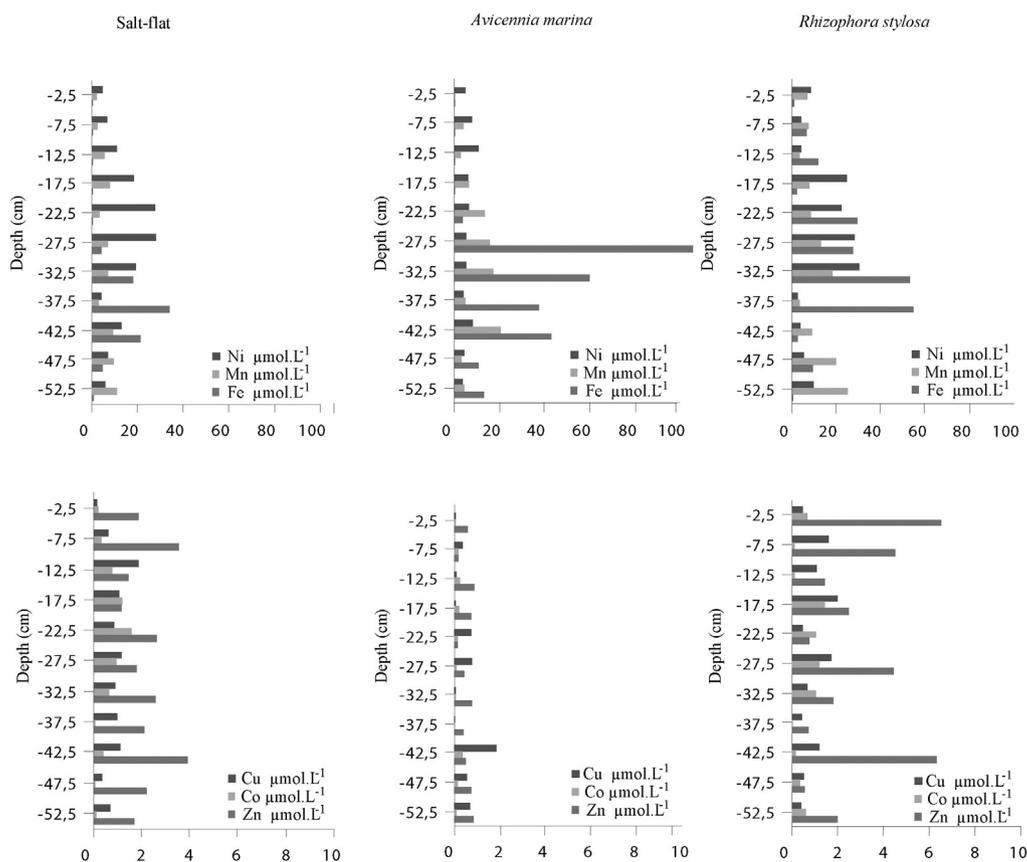


Fig. 4. Depth profile of dissolved concentrations of trace metals in the 3 studied mangrove stands.

were really limited to *Avicennia* leaves. They measured concentrations lower than  $23 \mu\text{g}\cdot\text{g}^{-1}$  and  $0.2 \mu\text{g}\cdot\text{g}^{-1}$  for mangrove sediments and *Avicennia* leaves, respectively, which correspond to the same BCF than in this study. Concerning manganese, its concentrations in the sediment downstream ultrabasic watershed was not higher than downstream non-ultrabasic watershed (Table 8) with maximum values not exceeding  $700 \mu\text{g}\cdot\text{g}^{-1}$ , and the maximum concentration in mangrove tissues being  $75 \mu\text{g}\cdot\text{g}^{-1}$ , which is far from being the highest values reported for mangrove tissues,  $>2000 \mu\text{g}\cdot\text{g}^{-1}$  (Lewis et al., 2011; Bayen, 2012). Consequently, we consider that its accumulation in the roots and its translocation to the leaves were low, except for *R. stylosa*, for which, translocation to the leaves was important (TF: 4.08), suggesting different metabolic requirements. Mn plays an important role in enzymes reactions and is also needed for water splitting at photosystem II (McEvoy and Brudvig, 2006). At the river Coochin in the Pumicestone region, Mn concentrations measured in roots of *A. marina* were slightly higher than herein, up to  $2.97 \mu\text{mol}\cdot\text{g}^{-1}$ , although concentrations in sediments ( $0.073$  to  $5.61 \mu\text{mol}\cdot\text{g}^{-1}$ ) were lower than in *Dumbea* ( $6.73 \mu\text{mol}\cdot\text{g}^{-1}$ ) (Preda and Cox, 2002).

### 3.1.2. Low BCF as a result of low bioavailability in the sediment

In the *Dumbea* mangrove, 90% of Mn at the root level was associated to the refractory phase of the sequential extraction developed, and was

therefore not bioavailable (Fig. 3; Marchand et al., 2012). This low bioavailability related to the refractor character of metals bearing phase may also explained the low BCF measured for Fe, Ni, and Co. The combined decreasing gradients of length of immersion and organic matter content along the zonation cause that redox conditions evolve from anoxia beneath *Rhizophora* to oxic conditions in the salt-flat (Table 1) (Marchand et al., 2012). In fact, the *Rhizophora* stand is almost always waterlogged and rich in OM, which led to anoxic conditions; while the salt-flat is subject to high air diffusion from the atmosphere (because of low tidal immersion) and characterized by a low organic content; free oxygen is thus rarely depleted. The different redox conditions characterizing the various stands and the various depths lead to different partitioning of metals in the sediment (Marchand et al., 2012). Metals are deposited in the mangrove mainly as oxides and/or oxyhydroxydes (Noël et al., 2014), that are subsequently dissolved by bacteria for the decomposition of organic matter, and which leads to a strong increase of metals in the dissolved phase, thus increasing their bioavailability. However, metals can rapidly be trapped by pyrite during sulphato-reduction processes (Marchand et al., 2006; Noël et al., 2014, 2015). In fact, the organic enrichment of mangrove sediments from the landside to the seaside of the mangrove induced the alteration of trace metals in the oxide form to organic and sulfide forms (Marchand et al., 2012; Noël et al., 2014). Chakraborty et al. (2015) showed that

**Table 3**  
Trace metals stocks in the sediment of the 3 studied mangrove stands in *Dumbea*, New Caledonia. n: number of samples used to calculate the stock. Values were obtained using metal concentration and bulk density of each sample, and then integrated on 50 cm depth.

	Co ( $\text{t}\cdot\text{ha}^{-1}$ )	Cu ( $\text{t}\cdot\text{ha}^{-1}$ )	Fe ( $\text{t}\cdot\text{ha}^{-1}$ )	Mn ( $\text{t}\cdot\text{ha}^{-1}$ )	Ni ( $\text{t}\cdot\text{ha}^{-1}$ )	Zn ( $\text{t}\cdot\text{ha}^{-1}$ )
Salt-flat (n = 6)	0.34	0.04	471.78	1.32	11.09	0.18
<i>Avicennia</i> (n = 10)	0.21	0.03	270.41	1.19	6.73	0.14
(% salt-flat)	61	75	57	90	61	78
<i>Rhizophora</i> (n = 15)	0.16	0.02	176.49	0.99	4.09	0.09
(% salt-flat)	47	50	37	75	37	50

**Table 4**

Trace metals concentrations in mangrove tissues of the 3 plants studied in the mangrove of Dumbea, New Caledonia (mean, SD).

	Mean heavy metals concentrations ( $\mu\text{mol}\cdot\text{g}^{-1}$ )					
	Co	Cu	Fe	Mn	Ni	Zn
<i>Avicennia marina</i>						
Leaves	0.16 ± 0.01	0.28 ± 0.08	5.59 ± 2	0.83 ± 0.13	0.61 ± 0.16	0.31 ± 0.07
Main roots	0.53 ± 0.08	0.19 ± 0.02	141.60 ± 49.32	1.36 ± 0.51	6.10 ± 3.04	0.50 ± 0.07
Fine roots	0.32 ± 0.15	0.14 ± 0.02	230.39 ± 71.02	1.06 ± 0.19	5.43 ± 3.06	0.43 ± 0.06
<i>Rhizophora stylosa</i>						
Leaves	0.02 ± 0.01	0.14 ± 0.01	9.76 ± 4.93	2.20 ± 0.19	1.08 ± 0.39	0.14 ± 0.02
Main roots	0.25 ± 0.06	0.22 ± 0.04	196.46 ± 51.96	0.58 ± 0.12	4.99 ± 0.56	0.41 ± 0.06
Fine roots	0.79 ± 0.61	0.26 ± 0.02	133.65 ± 37.84	0.50 ± 0.18	11.35 ± 7.27	0.40 ± 0.17
<i>Salicornia</i>						
Leaves	0.09 ± 0.03	0.20 ± 0.02	30.32 ± 13	0.89 ± 0.24	1.48 ± 0.76	0.28 ± 0.06
Roots	0.48 ± 0.14	0.14 ± 0.02	199.06 ± 85.07	3.07 ± 0.42	6.68 ± 2.45	0.76 ± 0.15

the non-refractory fractions of Ni ( $<10\%$  of  $80\ \mu\text{g}\cdot\text{g}^{-1}$ ) was mainly associated with Fe/Mn oxyhydroxide and organic phases in the sediments, controlling its bioavailability for mangrove plants. Nath et al. (2013) also suggested that the precipitation of reactive Fe-oxide phases in mangrove sediments has potentially contributed to low metal bioavailability in polluted sites. We consider that further studies should be focused on the transfer of trace metals to roots at the redox boundary, where oxides and/or sulphides are dissolved and metals released in the porewater. Regarding the stock of these metals in the upper 50 cm, a strong decrease was observed from the landside to the seaside of the mangrove for Fe and Ni, from  $471$  to  $176\ \text{t}\cdot\text{ha}^{-1}$  and from  $11$  to  $4\ \text{t}\cdot\text{ha}^{-1}$ , respectively (Table 3). The salt-flat being at the highest position in the intertidal zone, the sedimentation rate would probably be lower than in the *Rhizophora* stand, and then 50 cm of sediments may not represent the same duration of deposits. However, we suggest that this decreasing loss towards the sea is rather related to the increase amount of sedimentary organic matter. On the one hand, it induced a decrease of the bulk density of the sediment, and on the other hand it induced a more reactive substrate. On the PCA (Fig. 5), total Fe concentrations in the sediment and Hydrogen Index are almost along the second axis, but in opposite direction. HI is an indicator of the degree of hydrogenation of organic matter, and thus an indicator of its freshness. This PCA result indicates fresh OM introduced in the sediment induced a loss of iron. Noël et al. (2014) observed that the relative proportion of a newly formed and poorly ordered iron-oxyhydroxides increased towards the sea, suggesting that tidal fluctuations may lead to uninterrupted Fe reduction–oxidation cycles. They suggested that the amount of Fe released by the reductive dissolution of ferric oxyhydroxide minerals and by the oxidation of iron sulfide minerals may not be fully balanced by the amount of Fe immobilized via the formation of iron

**Table 5**

Bioconcentration factors (BCF = metal concentration in the tissue/metal concentration in sediments) of the various plants developing in the studied mangrove in Dumbea, New Caledonia.

	Bioconcentration factors					
	Co	Cu	Fe	Mn	Ni	Zn
<i>Avicennia marina</i>						
Leaves	0.08	2.03	0.01	0.12	0.02	0.54
Main roots	0.25	1.39	0.08	0.20	0.17	0.87
Fine roots	0.15	1.06	0.13	0.16	0.15	0.75
<i>Rhizophora stylosa</i>						
Leaves	0.01	0.52	0.01	0.20	0.02	0.16
Main roots	0.06	0.86	0.09	0.05	0.12	0.48
Fine roots	0.20	1.51	0.06	0.04	0.25	0.58
<i>Salicornia</i>						
Leaves	0.03	1.18	0.02	0.08	0.03	0.38
Roots	0.17	0.86	0.10	0.28	0.14	1.04

sulphides and by the precipitation of ferric oxyhydroxides. This process would lead to a loss of iron and of some other elements whose cycle are closely linked to the one of iron, like Ni. This loss is rather related to tidal action than plant uptake taking into account the low BCF, and it thus implied an export of trace metals towards adjacent ecosystem. The role of tidal pumping and porewater seepage were recently evidenced in the export of carbon from mangrove sediments to coastal waters (Maher et al., 2013). This loss of iron, as well as a loss of P, was confirmed by Deborde et al. (2015). The element for which the loss would be the lowest was Mn, probably as a result of less reactive bearing phase (90% was associated with the refractory phase).

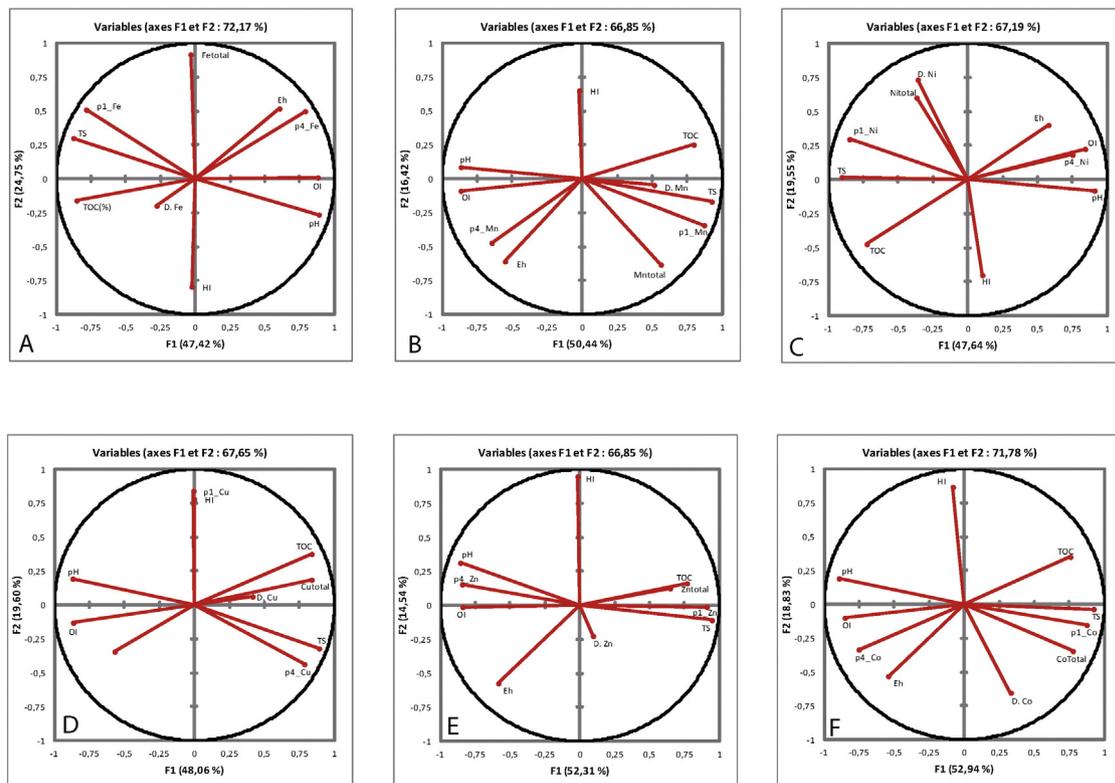
### 3.1.3. Low BCF as a result of biological processes

The low bioavailability may not be the only explanation of the low BCF of these metals in the mangrove. Even if the residence time of trace metals in porewaters can be low as a result of rapid re-precipitation or export with tide, this time would probably be sufficient for plant uptake. For instance, dissolved inorganic nitrogen and phosphorus are uptake by mangrove plants as soon as they are produced in the sediment (Alongi, 1996; Deborde et al., 2015). We thus suggest that physiological factors may be involved. The low BCFs may be explained by the fact that mangrove roots can act as barriers to metals translocation in the plant, as demonstrated by the low metals concentrations in the roots as well as the low TF to the leaves. Lacerda et al. (1993) suggested that mangrove plants can be extremely tolerant to metals, thanks to their root system, in which metals can accumulate, limiting physiological effects on mangroves. Souza et al. (2015) indicated that *A. schaueriana* can develop adaptive changes, leading to reduce the amount of metals–metalloids in roots, by reducing the uptake and/or increasing the translocation, or both. Fine roots may also have a strong influence on the transfer of elements to the plant (Helmisaari et al., 1999). Chaudhuri et al. (2014) observed a strong linear relationship between metal concentrations in fine nutritive roots of *Avicennia* and the total concentration in the sediment. Oxidizing activity of fine

**Table 6**

Translocation factors (TF = metal concentration in leaves/metal concentration in roots) of the various plants developing in the studied mangrove in Dumbea, New Caledonia.

	Translocation factors					
	Co	Cu	Fe	Mn	Ni	Zn
<i>Avicennia marina</i>						
	0.38	1.67	0.03	0.69	0.11	0.67
<i>Rhizophora stylosa</i>						
	0.03	0.56	0.06	4.08	0.13	0.34
<i>Salicornia</i>						
	0.19	1.38	0.15	0.29	0.22	0.37



**Fig. 5.** Principal components analysis plot of Varimax rotated factor loadings; Plotting of factor 1 against factor 2. (A) Fe, (B) Mn, (C) Ni, (D) Cu, (E) Zn, (F) Co. P1 is the organic phase; P4 is the residual phase, D is the dissolved concentrations, HI is the hydrogen index, OI is the oxygen index.

roots may concentrate a considerable amount of metals at their surface. However, Machado et al. (2002) suggested that iron plaques developing at root surface can contribute to moderate the uptake of potentially toxic metals by retaining them under insoluble forms outside root tissues. In the present study, metal concentrations in the fine roots and main roots were not significantly different. Finally, some trace metals (Cu, Zn, Pb) can be excreted by mangrove leaves, notably those of *Avicennia*, which are salt-excretor (MacFarlane and Burchett, 2000). Macfarlane et al. (2007) suggested that the functioning of root and glandular tissues to deal with the challenges of excess cations in saline environments may confer significant implications for metal accumulation, transport, partitioning and excretion in mangrove plants. Naidoo et al. (2014) also suggest that salt glands of *Avicennia* do contribute eliminating at least part of physiologically essential trace metals if taken up in excess. Excretion ability of mangrove trees, like *A. marina*, may also have an impact on the export of trace metals towards adjacent ecosystems and trophic chains and thus on trace metals budget in the mangrove.

### 3.2. Partitioning and transfer of trace metals characterized by high bioconcentration factors: Cu and Zn

Cu and Zn are known as essential elements necessary for mangrove growth. Cu has a direct impact on photosynthesis 1, being a constituent of plastocyanin, which is involved in the photosynthetic electron transport chain (Maksymiec, 1997). Regarding Zinc, it has been reported to be an integral component of hundreds of enzymes in higher plants, being the only metal present in the 6 enzymes classes (Auld, 2001; Broadley et al., 2007), its role in plant physiology is thus primordial. In the present study, both metals were characterized by BCF higher than those of others (Table 5). In the sediment, their mean concentrations were lower than  $1 \mu\text{mol}\cdot\text{g}^{-1}$  (Table 2), and in the porewater lower than  $10 \mu\text{mol}\cdot\text{l}^{-1}$  (Fig. 4). However, these 2 elements presented the highest ratios “dissolved concentration: solid concentration” (Fig. 6), meaning that they can be more easily bioavailable for plants, and partly explaining their high BCF, being of 2 for Cu for *Avicennia* leaves. Nath et al. (2013) also measured BCF higher than 2 for Cu in *Avicennia* leaves.

**Table 7**

Correlation half matrix of total metal concentrations in the sediment and co-variables (TOC, TS, pH, Eh) ( $n = 31$ ). Bold print indicate correlation higher than 0.5.

Variables	Co total	Cu total	Fe total	Mn total	Ni total	Zn total	TOC	TS	pH	Eh
Co total	<b>1</b>									
Cu total	0.42	<b>1</b>								
Fe total	0.47	-0.07	<b>1</b>							
Mn total	<b>0.56</b>	0.33	0.42	<b>1</b>						
Ni total	<b>0.62</b>	0.27	0.19	<b>0.60</b>	<b>1</b>					
Zn total	<b>0.71</b>	0.45	0.25	<b>0.75</b>	<b>0.81</b>	<b>1</b>				
TOC	0.33	<b>0.72</b>	-0.12	0.30	-0.01	0.25	<b>1</b>			
TS	<b>0.79</b>	0.66	0.37	<b>0.63</b>	0.42	<b>0.72</b>	<b>0.62</b>	<b>1</b>		
pH	- <b>0.60</b>	- <b>0.59</b>	-0.17	-0.37	-0.19	-0.33	- <b>0.70</b>	- <b>0.79</b>	<b>1</b>	
Eh	-0.24	-0.46	0.38	-0.06	-0.10	-0.31	-0.42	-0.47	0.37	<b>1</b>

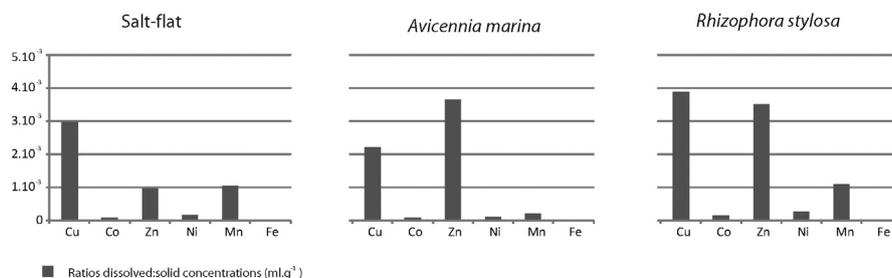
**Table 8**

Mean concentrations of trace metals in sediments and plants measured in this study compared with the literature in New Caledonia and worldwide.

		Co	Cu	Fe	Mn	Ni	Zn
		( $\mu\text{g}\cdot\text{g}^{-1}$ )					
Mangrove sediments							
This study	Min	122	9	100,000	370	2.145	38
	Max	230	17	120,000	609	2.834	56
New Caledonia ultrabasic watershed	Min			40,000		500	
	Max			140,000		5200	
New Caledonia non-ultrabasic watershed	Min	0.59	5.04	1300	62.15	1.77	44.2
	Max	22.42	32.13	54,400	770	209.45	153.4
Worldwide	Min	0.6	0.01			0.03	0.28
	Max	58	4050			208	2371
Mangrove plants							
		Co	Cu	Fe	Mn	Ni	Zn
This study (all plants, all tissues)	Min	1.18	8.82	313	46	36	9.1
	Max	46.61	16.38	12.901	75	669	32.5
Worldwide (all plants, all tissues)	Min		0.1		0.42	0.4	0.03
	Max		207		2.472	108	1.988

Cu accumulated in the roots at concentrations equal to or greater than those of sediments (BCF root: 0.86 to 1.51), and translocation to the leaves was important for *A. marina* and *Salicornia* (TF: 1.67 and 1.38 respectively) but lower for *R. stylosa* (TF: 0.56) (Tables 5, 6). Therefore, it appears that BCF and TF differ according to species that may have different requirements. The highest Cu concentrations in mangrove tissues measured in this study was not higher than  $17 \mu\text{g}\cdot\text{g}^{-1}$  (Table 8), while in the literature values up to  $200 \mu\text{g}\cdot\text{g}^{-1}$  were reported (Bayen, 2012). Some authors observed that Cu showed limited accumulation to leaf tissue, following a linear relationship at lower sediment concentrations, with saturation at higher sediment Cu concentrations (MacFarlane and Burchett, 2002). In mangrove sediments, Cu concentrations can each up to  $4000 \mu\text{g}\cdot\text{g}^{-1}$  (Bayen, 2012), which can be toxic, inhibiting plant growth and impairing important cellular processes and photosynthesis (Fernandes and Henriques, 1991; Baron et al., 1995; Yruela, 1995). In the present study, its concentrations in the sediment did not exceed  $17 \mu\text{g}\cdot\text{g}^{-1}$  with partitioning varying with depth and between stands (Fig. 2). In oxic to suboxic conditions, like in the salt-flat or in the upper layers of the *Avicennia* and the *Rhizophora* stands, it can be associated with the exchangeable phase, while in the anoxic conditions it was associated with the refractory phase and the carbonate-bound phase (Fig. 2). Iron geochemistry can strongly influence Cu cycling in the sediment, notably because copper can be adsorbed onto mangrove oxides. Teasdale et al. (2003) observed that maximum concentrations of Cu in porewater was correlated with the zone of maximum Fe(II) oxidation, and the formation of amorphous iron oxyhydroxide, which can be really important in mangrove sediments, notably in the highly reactive upper layer that is subject to continuous precipitation-dissolution of iron oxides because of tidal cycling (Noël et al., 2014). In the present study, Cu concentrations in the sediment are well correlated with the TOC concentrations (Table 7), and is the metal with the highest affinities for fresh organic matter. Organic

matter in mangrove sediments was suggested to be the main driver of Cu bioavailability, the latter having high affinities for OC (Chakraborty et al., 2015). In the present study, Cu associated with the exchangeable phase is strongly dependent on the Hydrogen Index (PCA, Fig. 5). We suggest that in the suboxic layers, where iron cycling is intense, Cu can be desorbed from iron oxides surface and it can then be associated with the freshly introduced organic matter. Nissenbaum and Swaine (1976) showed the high affinities of Cu for humic substances both in sediments and porewaters. Cu was the only metals associated with the carbonate-bound phase in this study. We ruled out the hypothesis of carbonate neoformation in the sediment, as suggested in French Guiana for anoxic deep layers (Marchand et al., 2008), taking into account that they were found at all depth and in all stands. We rather suggest a source of Cu-carbonate in the watershed. In the present study, Zn concentrations never exceeded 56 and  $32 \mu\text{g}\cdot\text{g}^{-1}$  for mangrove sediments and tissues, respectively, which is 2 orders of magnitude lower than the highest values reported in the literature (Table 8; Lewis et al., 2011; Bayen, 2012). Regarding *A. marina* and *Salicornia*, Zn accumulated in the roots at concentrations slightly lower than or equal to those of the sediment, with BCF of 0.75 to 1.04 (Table 5). Its translocation to the leaves of *Avicennia* was quite high (TF: 0.67), compared to the two other species (TF: 0.34 and 0.37 for *Rhizophora* and *Salicornia*, respectively) (Table 6). Some authors observed that zinc was the most mobile of all metals studied and was accumulated in leaf tissue in a dose dependant relationship (Macfarlane and Burchett, 1999). Additionally, they observed that Zn was also excreted from salt glands on the adaxial surface of *Avicennia* leaves. Regarding *Rhizophora*, BCF and TF were moderate, with a BCF ranging from 0.48 to 0.58, showing different plant requirements since Zn was not less bioavailable beneath *Rhizophora* (Table 5). The highest Zn concentrations in the porewaters were measured in this stand, and 90 to 100% of Zn was associated with the exchangeable fraction (Fig. 2), hence easily bioavailable for mangrove

**Fig. 6.** Ratios of trace metals concentrations in the porewater vs concentration in the sediment for the 3 different stands studied.

plants. In Sepetiba Bay near Rio de Janeiro, Silva et al. (1998) reported similar Zn concentrations in *Rhizophora* mangrove, both in the sediment and in the tissues. Conversely to Cu, Zn is associated with the organic phase in the anoxic conditions, while in the suboxic conditions prevailing beneath *Avicennia* and *Salicornia*, it is mainly associated with the refractory phase (Fig. 2). Total Zn concentrations in the sediment seems to be correlated with TS, Co, Mn, and Ni (Table 7). Surprisingly, Zn associated with the organic phase increased in the sulfidic layers (when TS increased), while when associated with the refractory phase, it decreased when the pH decreased (Fig. 5). pH is considered as the dominant factor determining Zn partitioning in soils (Broadley et al., 2007), its solubility increases with increasing acidity. There is a strong inverse relationship between pH and TOC (Table 7). In the present study pH decreased with depth as the result of the high amount of OM to be decomposed (Marchand et al., 2012). This lower pH may induce desorption of Zn and a transfer to the OM, organic Zn-ligand complexes increase at low pH (Broadley et al., 2007). Usually, Zinc toxicity is far less widespread than Zn deficiency (Broadley et al., 2007). In case of high Zn concentrations in the sediment like in urban or peri-urban mangroves receiving lots of sewage effluents, it was reported that Zn mobility may be reduced to prevent toxicity hence limiting metal translocation (MacFarlane et al., 2007). Cu and Zn, thus, presented relatively low concentrations both in leaves and roots, probably related to low concentrations of these metals in sediments. However, the fact that they were both strongly associated with the organic phase and that they presented a high ratio of concentrations in the porewater/concentrations in the sediment (Fig. 6) made them highly bioavailable for mangrove plants, resulting in bioconcentration factors superior to other metals (Table 5). Their translocation factors were also quite high indicating their greater mobility in the plant probably due to the importance of these metals in their metabolism (Table 6). As a result of the increased reactivity of the sediment from the landside to the seaside, and the increased association of these trace metals with the exchangeable phase, their stocks also decreased from the salt-flat to the *Rhizophora* stand, but in lower proportion than for the other metals (half against 2/3), from 0.18 to 0.09 and from 0.04 to 0.02 t·ha<sup>-1</sup> for Zn and Cu, respectively (Table 3). Bioconcentrations and leaf translocation are elevated for these elements, resulting in leaf concentrations as high as in the sediment. When the leaves fall, these elements are restituted to the sediment, which may limit their export towards coastal ecosystems through tidal action, and thus the loss of Cu and Zn compared to Fe and Ni. This process of metal conservation within the ecosystem can be limited for the stand the closest to the shore, which are subject to strong tidal flushing.

#### 4. Conclusions

Erosion of lateritic soils rich in Fe and Ni resulted in high concentrations of these metals both in mangrove sediments and plants. However, Fe and Ni bioconcentration factors and translocation factors as well as those of Mn and Co were low resulting from a combination of: i) low bioavailability due to their presence as oxides and sulfide forms, and ii) physiological parameters, notably the root system acting as a barrier to the transfer. Concerning, essential elements (Cu and Zn), their concentrations were relatively low both in leaves and roots, probably due to their low concentrations in the sediment. However, they were characterized by a greater mobility, with bioconcentration and translocation factors superiors to those of other metals probably related to their usefulness for trees metabolism. The increased reactivity of the mangrove sediment, resulting from OM enrichment towards the seaside and leading to continuous dissolution/precipitation of bearing phases, resulted in a strong decrease of trace metal stock in the sediment. Dissolved trace metals being easily exported through the tidal action towards adjacent ecosystems. Further studies on metal transfer to plants should be focused on the redox boundary, where oxides and/or sulphides are dissolved, and where they can be easily uptake by mangrove roots and/or

transferred to the trophic chain. Additionally, studies dealing with the export of trace metal with porewater seepage should be developed and may help to decipher between the role of mangrove as sink or source for trace metal along tropical coastlines.

#### Acknowledgements

Laure Landi is gratefully acknowledged for her help in the lab. We are grateful to anonymous reviewers who provided useful comments to improve this manuscript.

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