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ORIGINAL PAPER

Distribution and characteristics of dissolved organic matter in mangrove sediment pore waters along the coastline of French Guiana

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Abstract Mangroves represent a major environment of tropical coasts. They are highly productive, and act both as a source and a sink of organic carbon. Concentrations and characteristics (fluorescence and hydrophobic–hydrophilic fractions) of dissolved organic matter (DOM) were investigated in relation to the organic content of sediments and to the chemistry of pore waters along the coastline of French Guiana. The pore waters studied were extracted (centrifugation, soil moisture sampler) from sediments cored beneath *A. germinans* mangrove stands representative of development stages: pioneer, mature and senescent. In order to asses the effects of seasonal changes, two cores were performed in each location, just after dry and wet seasons, respectively. Dissolved organic carbon (DOC) concentrations in pore waters of the upper sediment were found to increase, from 0.7 mmol l^{-1} under the pioneers to 9 under senescent mangroves. The evolution of sedimentary organic carbon (SedOC) in the same sediment paralleled that of DOC, increasing from 0.7 to 28%. On the contrary, in the lower parts of sediment cores SedOC and DOC displayed contrasting vertical trends: SedOC decreased sharply with depth while DOC increased, reaching concentrations up to 30 mmol l^{-1} at 50 cm in the older, senescent mangroves. In addition, the Fluorescence/DOC ratios and the hydrophobic contents of DOC were higher at greater depths in most cores, expressing changes in the DOC composition. These results suggest that the DOC of the upper layers originated directly from the SedOC of the enclosing sediment, while the hydrophobic and fluorescent DOC accumulated in the anoxic bottom layer. The mechanisms responsible for this accumulation at depth requires additional research to be fully understood. However, the anoxic conditions and high pH values prevailing in the lower sediment, by lessening DOM sorption and enhancing SedOC dissolution, may be partly responsible for the high DOC concentrations and fluorescences at depth. In addition, seasonal variation may be involved. During the rainy season, water sources were mixed resulting in lower DOC concentrations in the upper sediment, whereas during the dry season, increased evapotranspiration concentrate salts and DOC, which are transported vertically with percolating water.

Keywords Mangrove · Pore water · Dissolved organic carbon · Fluorescence · French Guiana

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Introduction

Dissolved organic carbon (DOC) is a key constituent of soils and sediments, playing a major part in carbon cycling. Its concentration and composition are closely linked to the biogeochemistry of the substrate and strong interactions exist between sedimentary organic matter (SedOM), microorganisms, mineral phase and DOC. Many studies on dissolved organic matter (DOM) in soils have been recently performed; however many questions are still unanswered (McDowell, 2003). DOM dynamics in soils and sediments are a result of competing processes including production, decomposition, sorption and transportation, all of which are influenced by many factors (Marschner and Kalbitz 2003). Inorganic solutes (Al, Fe, heavy metals) (Buffle et al. 1982), and physicochemical properties of pore waters such as pH (You et al. 1999) are predominant among internal factors. In addition, external parameters such as vegetation and seasons (Kaiser et al. 2002) have to be considered.

Mangrove environments represent nearly 75% of the world's tropical and subtropical coastline. These forests, developing in the intertidal zone, are considered as a very productive area (Odum and Heald 1975) with high rates of organic carbon accumulation. 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). In mangrove swamps, many studies have dealt with SedOM and their decay processes (Hesse 1961; Pezeshki et al. 1997; Alongi et al. 1999). However, far fewer studies have been performed concerning pore water DOM (Boto et al. 1989; Mueller and Ayukai 1998), and mainly deal with the export of DOM from mangrove and the relationships with adjacent coastal waters.

The fringing mangroves of the Guiana coasts develop on fine-grained sediments, mainly composed of illite, chlorite, kaolinite and smectite (Para and Pujos 1998), coming from the huge mud discharge of the Amazon River. This discharge is partly deflected northwestward by the current of the Guianas, and migrates towards the Orinoco River delta in the form of a series of mudwaves. The extreme mobility of this oceanic coastline results in two main characteristics: (i) the seafloor and continental boundary act as a massive, suboxic, fluidised bed reactor (Aller 1998), (ii) the limited span of life of the mangrove forests (30–50 years) due to the rapid displacement of the mudwaves on which they develop, 1.4 km year^{-1} (Allison et al. 2000; Baltzer et al. 2004). Thus, the study of pore water DOM in such an environment may be of a great interest. First, the organic carbon derived from higher plant is introduced at high rates in an homogeneous clayey substrate characterized by intense microbial activities (Aller et al. 2004), which induce great variations in physicochemical parameters. Secondly, the short lifetime of mangrove forests in this environment, limited to a few decades, allows for an assessment of the efficiency of their chemical and sedimentological influences. The main goal of the present work is to characterize the spatial distribution and characteristics of DOM in relation to the development of the mangrove forests and the seasons. To achieve this, we conducted field sampling in various mangroves of French Guiana at the end of the rainy season and at the end of the dry season. The other objective is to determine, in this natural laboratory, the influence of seasonal variations of pore water parameters (pH ranging from 4 to 7, Eh from –100 mV to 500 mV and salinity from 2 to 70) on DOC distribution and properties.

Materials and methods

Study sites

The mangrove forests studied are located on the right bank of the Sinnamary River, 50 km northwest of Kourou (Fig. 1). These mangroves develop on huge mud banks, 30 km long (total length of one bank) and can be up to 5 km wide. This mangrove forest, not subject to anthropogenic exploitation, is dominated by *Avicennia germinans*; however abundant epiphytes, creepers and pteridophytes develop in the senescent forest.

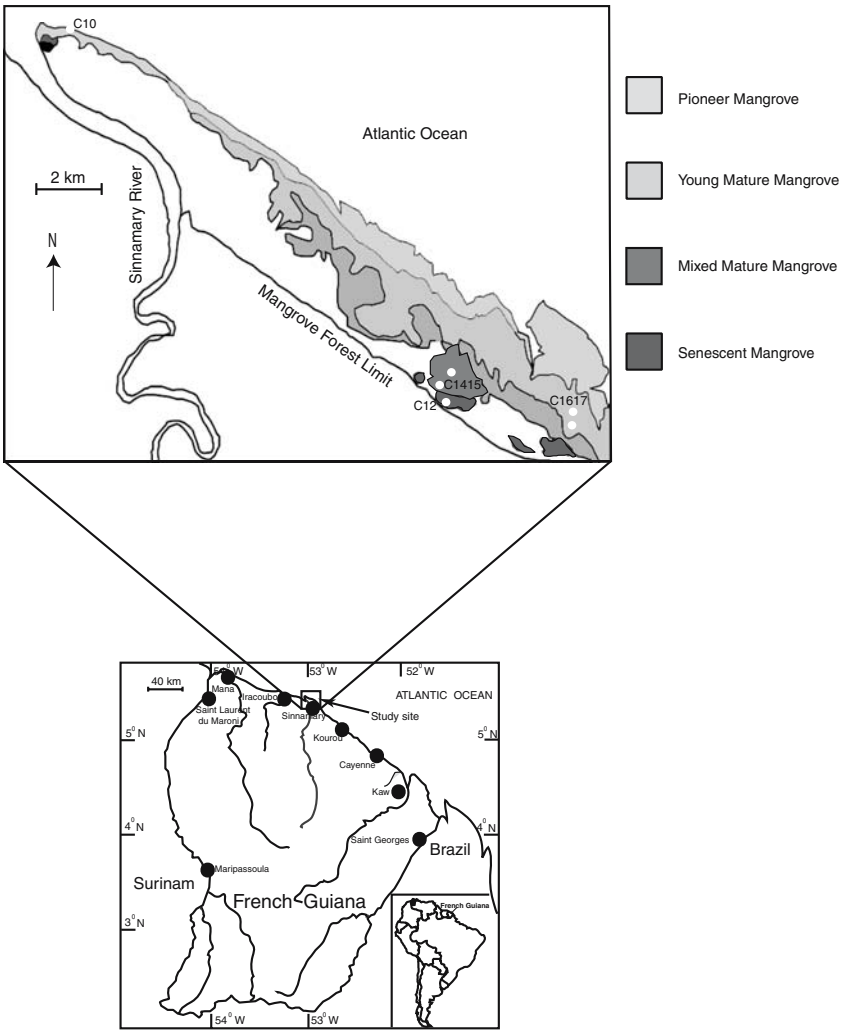

Fig. 1 Map of the study area showing the location of cores (adapted from Fromard et al. 1998)

Some *Rhizophora* spp. were also observed in the mixed mature forest and in the senescent part of this forest. In the early stages of mangrove (pioneer, young mature) and prior to mangrove settlement, different types of algae and microbial mats cover the sediment: diatoms, diatoms and cyanophyceae, micro-green algae (De Wit, oral communication). The frequency of biofilms decreases with forest age. Field observations reveal that pioneer and young mature mangrove forests are flooded at each tide, whereas the higher topography of the mature zone prevents all but spring tides to overflow them and so to reach the soil of the mixed mature and the senescent mangrove. For this reason, 10–40 cm of freshwater covers the older parts of the forest during rainy seasons. The various developmental stages of the *Avicennia*-dominated mangrove of Sinnamary were described relative to their structural and biological features (Fromard et al. 1998) (Table 1).

Climate

French Guiana (2°N–6°N) is characterized by a subequatorial climate with mean annual rainfalls ranging from 2500 to 3000 mm year^{-1}. Monthly averages display a bimodal pattern with two rainy seasons unequal in importance and duration. Average monthly air temperatures fluctuate between 26°C and 30°C. The mean annual total insolation attains 2200 h, with a peak in October

Table 1 Characteristics of mangrove forests at the 4 stations

Station	Stage of forest evolution	Period of sampling	Description of areas	Characteristics
C10	Pioneer forest	July 2001	*A. germinans* 1 m high	flooded at each tide Closest to the shore
C1617	Young mature forest	July 2001 December 2004	*A. germinans* 20 m high	flooded at each tide
C1415	Mixed mature forest	July 2001 December 2004	*A. germinans* 20 m high *Rhizophora mangle*	flooded at spring tide Covered by fresh water during rainy season
C12	Senescent forest	July 2001	*A. germinans* epiphytes, creepers and pteridophytes 30 m high	flooded at spring tide Covered by fresh water during rainy season

(Meteo France). However, very high interannual variations are common, and seasons can be shifted several weeks before or after the mode, or be skipped. Tides are semi-diurnal with mean tidal range of 1.8 m (SHOM 2001).

Sampling and measurements

Sample collection

Fieldwork was carried out at the end of the rainy season (July 2001) and at the end of the dry season (December 2004) in order to have a record as complete as possible of the geochemical effects of the season. Sediments were sampled using an Eijkelkamp gouge auger. In mangrove sediments, pore water extraction may be very laborious due to the fine-grained nature of the sediment and the roots density. In order to precisely define the depth intervals, pore waters were extracted using centrifuge rather than in situ peepers (Gribsholt and Khristensen 2002) during the first fieldtrip. Centrifugation was done on the very day of coring as recommended by Albéric and co-authors (1996) in order to avoid enrichment in colloidal material (Chin and Gschwend 1991). Root debris was carefully eliminated in the mud samples before centrifuging them in order to prevent the leakage of dissolved components from the roots. Centrifugation was done at 5000 rpm during 20 min. Pore water extraction was made on samples representing 5 or 10 cm intervals. We collected around 10 ml of pore water, which represent between 10% and 15% of the total water contained in a piece of core of 150 cm^3. However during the second fieldtrip, pore water was extracted with soil moisture sampler Rhizon® (Song et al. 2003), which were directly inserted into PVC box-cores or piece of core from the gouge auger during 2 h. The sampler is connected to a syringe using luer-lock fittings and PVC tubing. Evacuating the syringe by drawing the piston allows to collect pore water from sediments. The output was better than that obtained by centrifugation; we collected around 20 ml of pore water for a piece of core of 150 cm^3. All samples were filtered through 0.45 μm Sartorius® filters under air pressure and acidified to pH 2 with Suprapur® HNO_3. Samples were stored in cleaned 14 ml polypropylene tubes, in a cold room ($T = 4°C$) until analysis. These storage conditions were expected to reduce the loss of carbon to a minimum.

Samples studied herein come from 4 mangrove areas defined in terms of vegetation composition, stage of development and location in the swamp, i.e. pioneer, young mature, mixed mature and senescent mangroves. One area was sampled for the pioneer and the senescent swamps whereas for the young mature and the mixed mature swamps two areas were sampled. Results presented are mean values from the two areas. The young and the mature stages were sampled at both seasons. In each area, cores and their duplicates were collected at low tide. One core was used for the study of sedimentary organic matter at the bulk level (Marchand et al. 2003) and at the molecular level (Marchand et al. 2005); the other core for the study of dissolved organic matter. In both cores, pH, salinity, Eh, sulphide concentrations and SedOC were measured (Marchand et al. 2004). Surface waters were also

collected, in several creeks running into the mangrove and above the soils of every stages of mangrove development. After being collected, cores were wrapped in plastic film and aluminum foil in order to limit gas exchange. Measurements of the physicochemical properties measurements were performed at the following depth-spans: every 2 cm from 0 to 20 cm depth, every 5 cm from 20 to 60 cm depth and every 20 cm below. Samples for SedOM were collected following the same depth scale and preserved by refrigeration. Measurements of physicochemical parameters (pH and redox) were performed in an air-conditioned laboratory, on the day of coring as described in Marchand et al. (2004). The water content ($W\%$) was calculated as: $W\% = 100^{*}(W_{wet}–W_{dry})/W_{wet}$, where W_{wet} is the wet weight of the sediment and W_{dry} is the weight of the sediment after drying at 40°C.

Dissolved organic carbon measurements

DOC concentrations were determined using a Shimadzu® TOC 5000A total organic carbon analyzer, which is a high temperature catalytic oxidation type of device with infrared detection, equipped with a ASI 5000A auto-sampler. Pore water samples were diluted, using UV-treated milli-Q water, and acidified to pH 2 (HNO3) before automatic sparging with the single gaz type (oxygen) used by the system. Blanks for the filtration and storage procedure were run in order to check that our samples were not contaminated with DOC. Results were below 0.4 mmol l^{-1}. DOC concentrations were measured in triplicate with a coefficient of variations better than 3%.

Fluorescence measurements

Fluorescence measurements were made with a Shimadzu® fluorescence HPLC detector. Fluorescence intensity (F) was calibrated against a 1 mgl^{-1} quinine sulphate solution in 0.1 M $HClO_4$. F was set to 100 Fl.U., at excitation and emission wavelengths of 370 and 460 nm respectively (Donard et al. 1989). Fluorescence measurements of pore water were made at excitation and emission wavelengths of 345 and 415 nm respectively, wavelengths usually attributed to humic substances. Considering that pH can have a strong effect on fluorescence spectra (Laane 1982) and that high DOC concentrations have an influence on the wavelength at the maximum intensity of emission and excitation (Buffle et al. 1982), samples were diluted and acidified to pH 2 before measurements. Samples with DOC concentrations higher than 3 mmol l^{-1} were diluted by a factor of 5 or 10. Thus, fluorescence measurements were done on samples which have a concentration ranging from 0.5 to 3 mmol l^{-1}. Ratio F/DOC (relative fluorescence), with DOC expressed in g l^{-1}, was used to distinguish several groups of organic matter.

DOC Fractionation

Hydrophobic substances (acid and neutral) and hydrophilic substances were fractionated using a XAD-8 column (Thurman and Malcolm 1981; Leenher 1981). Because of the limited volume of samples available, an analytical fractionation method derived from Schwarzenbach et al. (1983) and Shneider et al. (1984) was used (Albéric et al. 2001). The hydrophilic fraction represents those organic compounds that are not adsorbed onto XAD-8 resin at acidic pH. In contrast, the hydrophobic fraction, commonly defined as the aquatic humic substances, represents the organic compounds that XAD-8 resin does adsorb at acidic pH. Before each sample run, the XAD-8 resin was cleaned with 0.01 M HNO_3 and 0.1 M NaOH. The resin was also periodically rinsed with water, 0.1 M HNO_3 and acetonitrile. The XAD-8 resin column was connected to a Shimadzu fluorometric detector (RF 530) in order to detect the arrival of both fractions, monitored at 345ex/415em. Effluents were collected during the fluorescence peak. A 5 ml sample of acidified and diluted pore water was injected in the column with pH 2 HNO_3 as eluant. After 5 min of percolation at a rate of 2 ml min^{-1}, the column was percolated 10 min with NAOH 0.1 M at the same rate, (Fig. 2). The hydrophobic neutral was not desorbed from resin. Volume and DOC of effluent fractions were subsequently measured. For duplicate analysis, the absolute difference for most samples was less

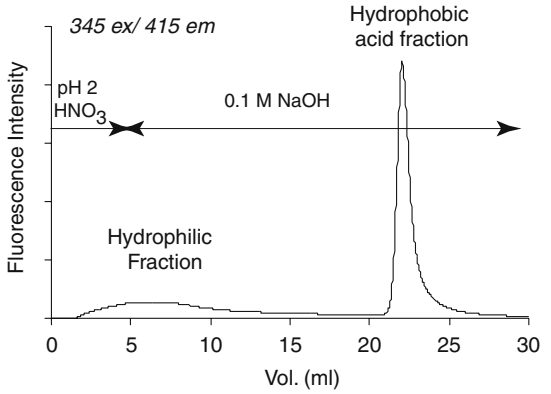

Fig. 2 Elution curve representing fractionation between hydrophilic compounds and hydrophobic acids compounds

than 10%, which is acceptable considering the great variations that occurred between pore water samples.

Data analysis

In order to assess the relationships between DOC, fluorescence, F/DOC and co-variables (Eh, pH, SedOC, salinity, and water content) a Principal Components Analysis (PCA) was done on 59 samples. 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.

Results

DOC distribution

Sediment pore water DOC concentrations varied greatly between the various stages of mangrove development, increasing with forest evolution, ranging from 0.7 mmol l^{-1} under the pioneer mangrove (Fig. 3) to 30 mmol l^{-1} under the senescent mangrove (Fig. 4). Moreover, all stages of mangrove development showed an increase of DOC concentration with depth whatever the season. DOC concentrations of deeper layers reached up to two or three times those of the upper sediment. For example, our data demonstrated a change from 0.7 mmol l^{-1} to more than 2 mmol l^{-1} for the young mature mangrove during the dry season (Fig. 5), and from 2 mol l^{-1} to 7 mmol l^{-1} for the mixed mature mangrove stands during the rainy season (Fig. 6). Surface waters in the back mangrove, i.e. not submitted to daily tidal flushing, displayed DOC concentrations that varied from 0.5 to 2 mmol l^{-1}.

DOM characteristics

Fluorescence

Fluorescence intensities and their vertical trend varied greatly depending on forest stage. In the early stages of mangrove development, i.e. pioneer and young mature mangrove, pore water fluorescence intensities varied between 10 and 50 Fl.U. (Fig. 3 and 7). The vertical trend of the pioneer mangrove showed a moderate increase with depth, stabilizing around 45 Fl.U. whereas the vertical distribution of the young mature mangrove was quite stable, centered on 40 Fl.U. Values were significantly higher in the mixed mature and in the senescent mangroves (Fig. 6 and 4); moreover intensities became higher with increasing depth. During the rainy season and in the upper part of the core, fluorescence intensities did not exceed 20 Fl.U. while they reached, for example, more than 900 Fl.U. at 40 cm deep in the senescent mangrove. During the dry season, fluorescence also increased with depth, from 10 to 35 Fl.U. and from 10 to 150 Fl.U. for the young mature and the mixed mature respectively (Fig. 5 and 8). Fluorescence intensities of surface water of the back mangrove varied between 10 and 40 Fl.U. Taking into account the relationship between DOC concentration and fluorescence intensities, the latter were normalized to DOC concentrations, in order to make an accurate comparison between the various sites in the discussion.

Fractionation of DOC

Fractionation was only made on samples collected during the first field trip, i.e. at the end of the rainy season. Pore water samples from the

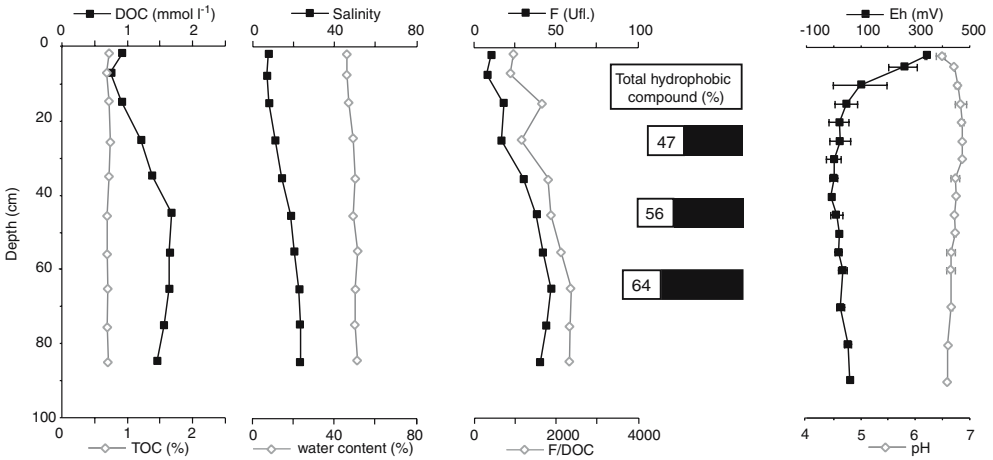

Fig. 3 Depth distribution of various parameters from sediment cores collected in pioneer mangrove (C10) at the end of the rainy season (TOC, salinity, Eh and pH data from Marchand et al. 2004)

various mangroves exhibited different carbon distribution among the XAD-8 fractions. In the young mature mangrove, the total hydrophobic fraction dominated in the whole profile with values ranging from 70 to 75% (Fig. 7), whereas in the other mangroves, fractionation showed a vertical stratification. The hydrophilic fraction dominated the upper parts of cores, i.e. the hydrophobic fraction represented only 15% in the upper 10 cm of senescent mangrove forest (Fig. 4). At depth, distributions stabilized with a total hydrophobic fraction close to 70%. Surface water of the back mangrove also showed a total hydrophobic fraction close to 70%.

All elution curves were normalized to total DOC of pore-water sample in order to compare them. In addition, the areas of individual fluorescence peaks were normalised to the quantity of carbon collected during the peak in order to compare the fluorescence of each fraction (Fig. 9). In young mangrove swamps, the fluorescence of the hydrophobic and the hydrophilic fractions were quite stable with depth, that of the hydrophobic fraction being higher. In the older mangroves, the fluorescence of both fractions increased with depth; moreover the fluorescence increase of the hydrophilic fraction was higher than that of the hydrophobic one.

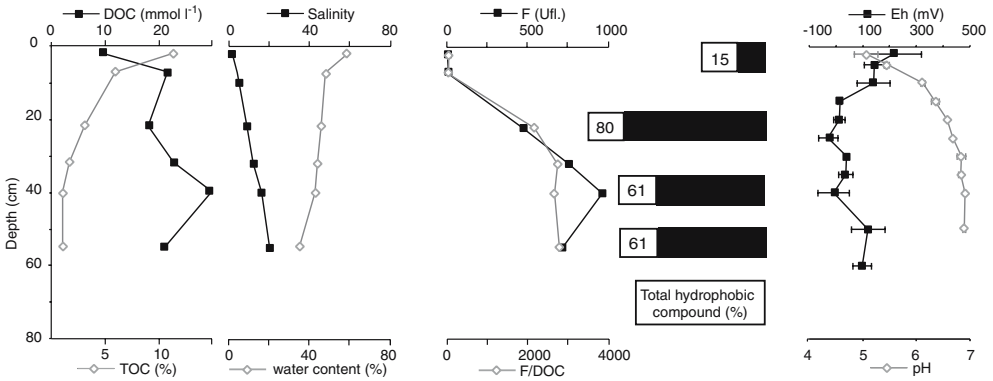

Fig. 4 Depth distribution of various parameters from sediment cores collected in senescent mangrove (C12) at the end of the rainy season (TOC, salinity, Eh and pH data from Marchand et al. 2004)

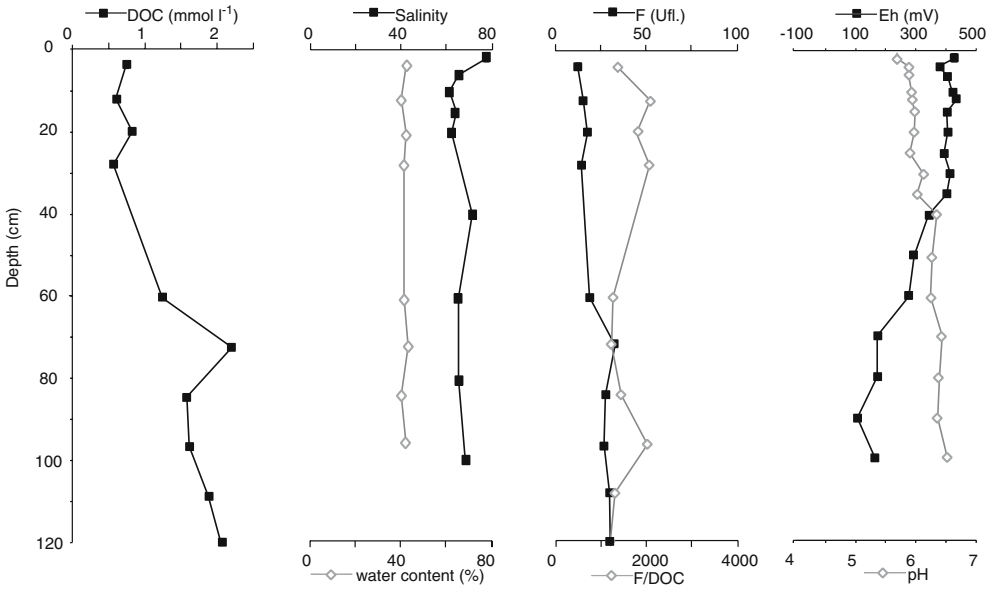

Fig. 5 Depth distribution of various parameters from sediment cores collected in young mature mangrove (C1617) at the end of the dry season

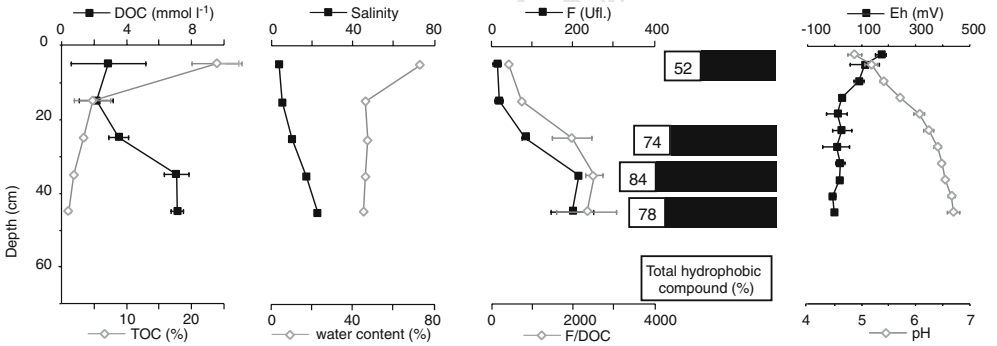

Fig. 6 Depth distribution of various parameters from sediment cores collected in mixed mature mangrove (C1415) at the end of the rainy season (TOC, salinity, Eh and pH data from Marchand et al. 2004)

Principal components analysis

Correlation half matrix (Table 2) highlighted major points:

- a strong positive correlation between DOC and fluorescence (0.87) and between water content and SedOC (0.81),
- a good positive correlation between pH and F/DOC (0.67),
- a negative correlation between pH and SedOC (–0.55) and between pH and Eh (–0.50).

In order to have a better understanding of relationships between co-variables (DOC, fluorescence, F/DOC, Eh, pH, SedOC, salinity, and water content) a PCA was performed on 59 samples. This analysis showed that there are three main factors accounting for more than 80% of the total variance (Table 3). Factors 1, 2 and 3 represented 36.6, 29.9 and 15.6% of the total variance, respectively. A Varimax rotation was applied to these principal components to improve the factor structure (Table 4) and factors were plotted together (Fig. 10). It appeared that:

- factor 1 was characterized by high positive loadings for F/DOC and pH and negative loading for Eh,

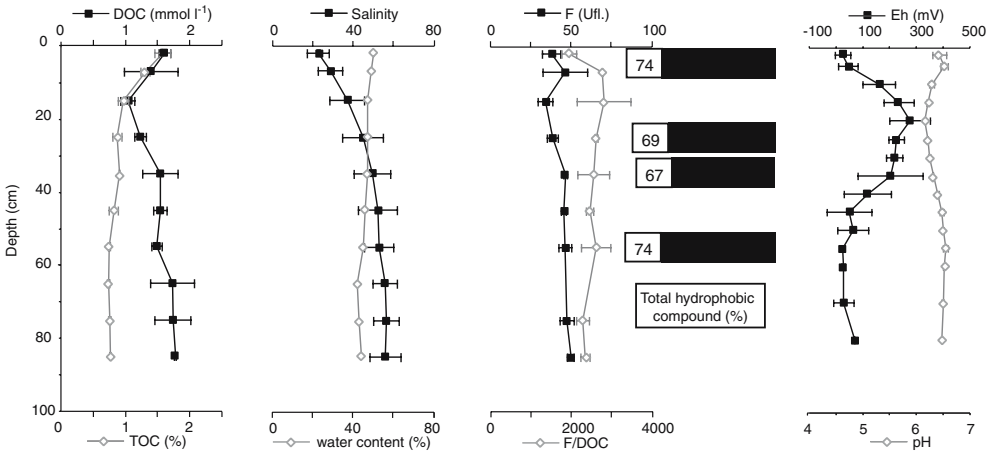

Fig. 7 Depth distribution of various parameters from sediment cores collected in young mature mangrove (C1617) at the end of the rainy season (TOC, Salinity, Eh and pH data from Marchand et al. 2004)

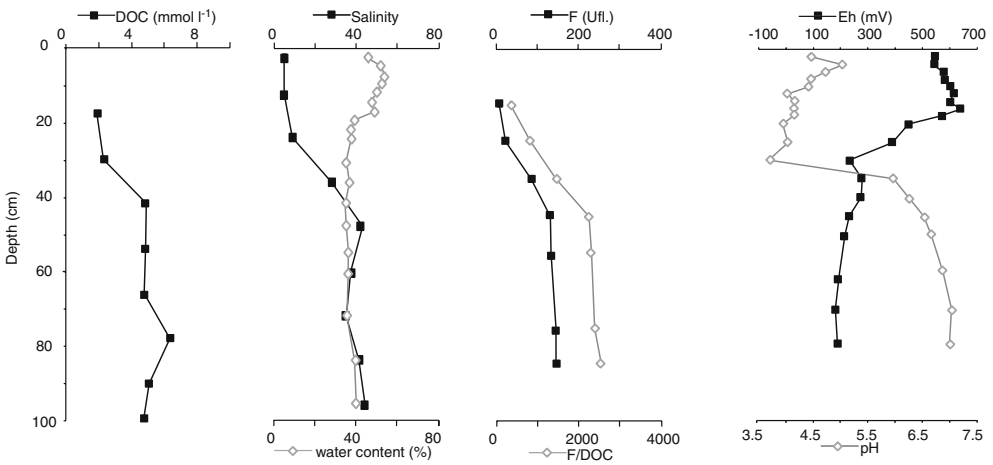

Fig. 8 Depth distribution of various parameters from sediment cores collected in mixed mature mangrove (C1415) at the end of the dry season

– factor 2 was characterized by high positive loadings for DOC and fluorescence,
– factor 3 was characterized by high positive loadings for SedOC and water content and negative loading for salinity.

Discussion

Results highlighted three major points: (i) a general increase of DOC concentrations with mangrove forest development, (ii) an increase of DOC concentrations with depth, (iii) a low fluorescence combined with a low hydrophobic content in the upper part of most cores. The PCA did not highlight any good direct relationship between DOC concentrations and co-variables but showed a correlation between F/DOC ratios and pH.

Specificities of DOM in the pore waters of mangrove soils

To our knowledge, few studies have been performed on DOM of mangrove pore waters and consequently few data are available for comparisons. DOC concentrations ranged from 0.7 to 30 mmol l^{-1}, in the ground pore waters of most of the Guiana mangroves examined. These figures

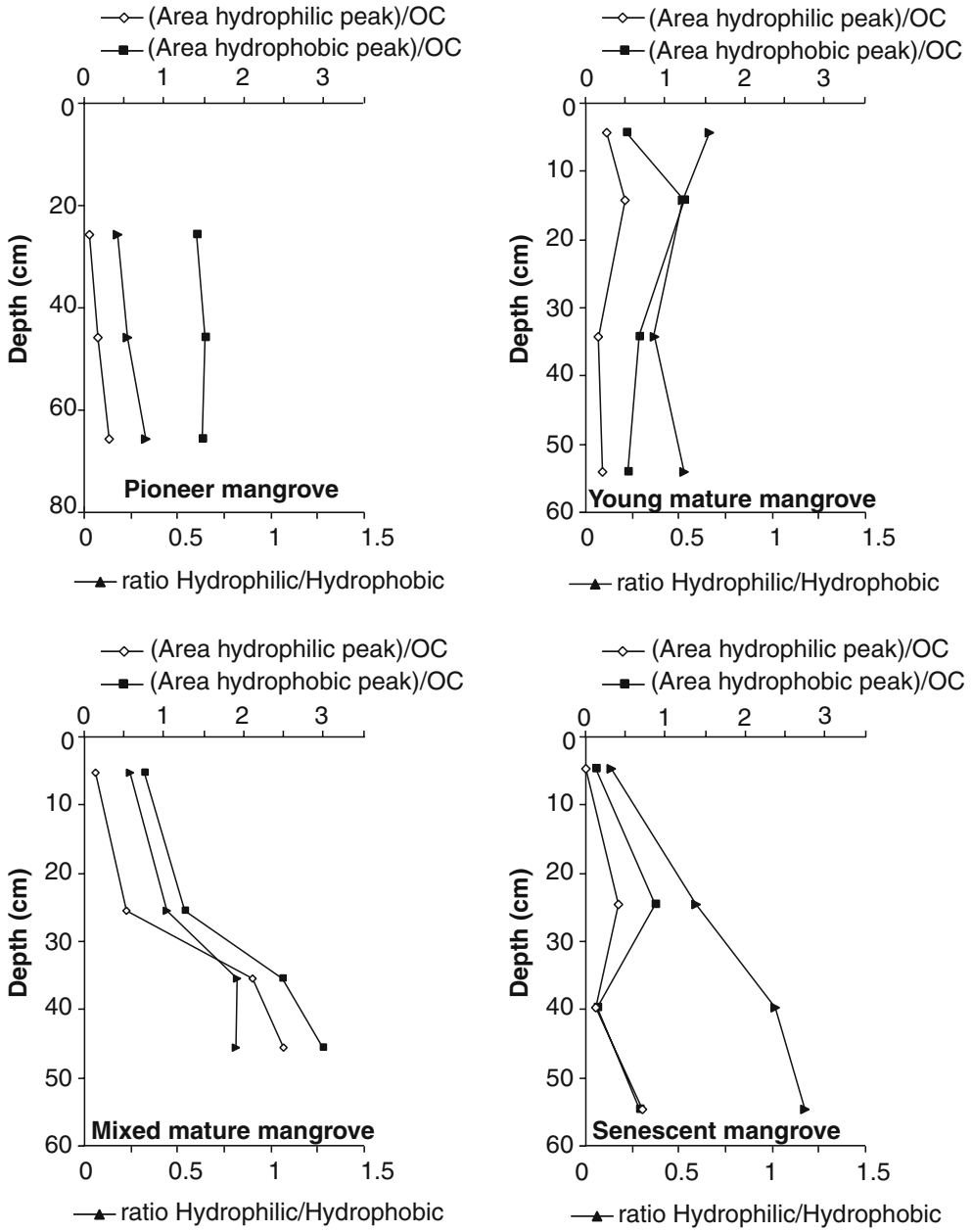

Fig. 9 Fluorescences of hydrophobic and hydrophilic fractions at various depths and at various stages of mangrove development at the end of the rainy season. Fluorescence of each fraction presented herein is the area of fluorescence peak normalized to the mass of carbon (mg) collected during the peak

are higher than those reported from Australian mangroves, ~0.3–4.2 mmol l^{-1} (Boto et al. 1989) and from the Everglades, ~0.9–7 mmol l^{-1} (Qualls and Richardson, 2003). This range is also higher than what is reported from soils of temperate forests; DOC in pore waters from soils of deciduous forest ranged from 0.1 to 5 mmol l^{-1} (Qualls et al. 2000). In addition, the vertical trend of concentrations in the soils of upland forest is opposite to that in our mangrove sediments. While DOC concentrations increase with depth in these French Guiana mangroves, they generally decrease rapidly with depth in the soils of upland forest; for example, from 3.4 to 0.7 mmol l^{-1} at

Table 2 Correlation half matrix (n = 59)

	DOC	Fluorescence	F/DOC	TOC	Salinity	Water Content	Eh	pH
DOC	1							
Fluorescence	***0.87***	1						
F/DOC	0.08	0.38	1					
TOC	0.05	–0.11	–0.49	1				
Salinity	–0.32	–0.20	0.23	–0.39	1			
Water Content	–0.12	–0.22	–0.23	***0.81***	–0.37	1		
Eh	–0.42	–0.42	–0.32	–0.06	0.38	–0.29	1	
pH	0.16	0.33	***0.67***	***–0.55***	0.11	–0.21	***–0.50***	1

Bold and italicized print indicate correlation higher than 0.5

5 cm and at 40 cm depth, respectively (Raastad and Mulder 1999). The mangroves of French Guiana show similar depth profiles of DOC concentrations than peat bogs (Glatzel et al. 2003), but have lower concentrations. In the pore waters of marine sediments, DOC concentrations generally increase with depth (Burdige and Gardner, 1998), but with lower concentrations.

Another specific finding was that the distributions of hydrophobic compounds and F/DOC ratios exhibited the same vertical profiles, both remaining stable in the young mature mangrove and increasing with depth in the more advanced stages of mangrove development. This trend is also opposite to the trend usually found in forest soils (Qualls and Haines 1991; Raastad and Mulder 1999) but similar to what has been described by Komada et al. (2004) in marine sediments. However, the fact that fluorescence intensities increase with depth is not only the result of an increase in hydrophobic compounds, although these compounds are considered to be the most fluorescent fraction. In fact, both the fluorescences of hydrophobic and hydrophilic fractions increased with depth; and the increase in fluorescence intensities of the hydrophilic compounds was even stronger than that of the hydrophobic compounds (Fig. 9). To our knowledge, few studies on soil pore water used fluorescence (Zsolnay et al. 1999). This tool was applied more frequently in studies dealing with seawater (Chen and Bada 1992) or with pore waters of marine sediments (Chen and Bada 1994; Sierra et al. 2001). Sierra and co-authors (2001) described fluorescence intensity close to 1 Fl.U. for seawater and close to 40 Fl.U. for marine sediments pore waters. Considering that fluorescence intensities undoubtedly depend on DOC concentrations (Buffle et al. 1982) as confirmed by our PCA analyses (Table 4 and Fig. 10), it would be difficult to compare the results obtained in our organic rich mangrove sediments with oceanic data. In addition, the wavelengths of excitation and emission were not precisely the same. Nevertheless, in the early stages of mangrove development, characterized by little organic accumulation, the intensities of fluorescence were in the same range as those found in marine sediments by Sierra and co-authors (2001). Concerning the increase of fluorescence with depth in marine sediments, Komada et al. (2004) observed that anoxic pore waters turned out to be enriched in fluorescent compounds when compared to the overlying

Table 3 Eigenvalues and variance explained for the main factors (Eigenvalue >1) in principal components analysis

Factor	Eigenvalue	% Total Variance	Cumulative % Variance
1	2.92	36.60	36.60
2	2.40	29.99	66.59
3	1.25	15.65	82.24

Table 4 Varimax rotated factor loadings from a principal components analysis

Variable	Factor 1	Factor 2	Factor 3
DOC	0.05	***0.96***	0.06
Fluorescence	0.27	***0.91***	–0.08
F/DOC	***0.83***	0.07	–0.26
TOC	–0.45	–0.00	***0.81***
Salinity	0.10	–0.41	***–0.63***
Water content	–0.03	–0.22	***0.92***
Eh	***–0.65***	–0.38	–0.50
pH	***0.89***	0.11	–0.17

Marked loadings (in italic) are higher than 0.60

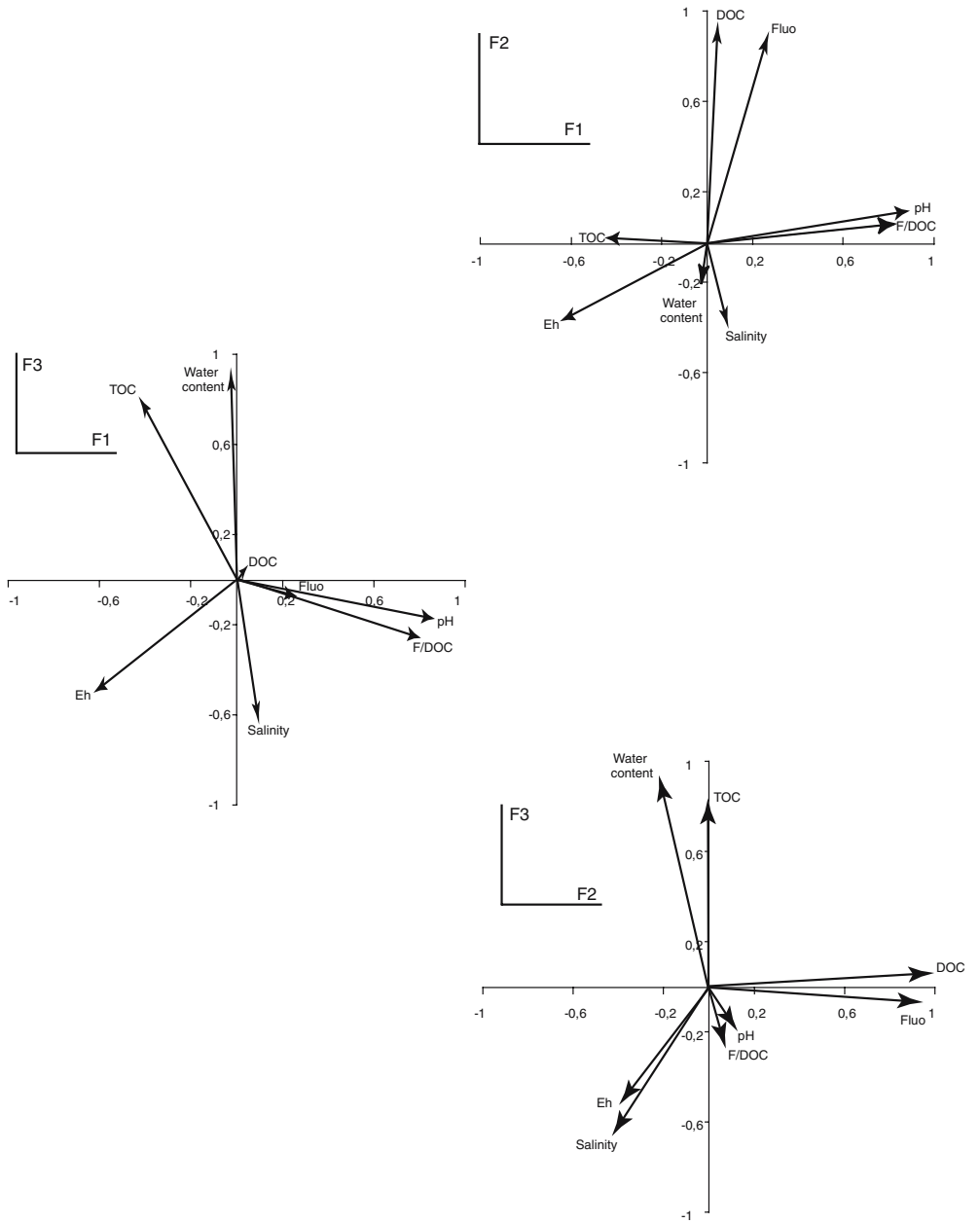

Fig. 10 Principal components analysis plot of Varimax rotated factor loadings. (A) Plotting of factor 1 against factor 2, (B) Plotting of factor 1 against factor 3, (C) Plotting of factor 2 against factor 3

mixed redox zone. Nevertheless, our results suggest that mangrove sediments should be considered neither as equivalent to the soils of continental forests nor as marine sediments. Thus, the mechanisms of DOM accumulation probably differed largely from what has been described in these two other environments.

Relationships between stages in mangrove forest development, and concentrations in SedOC and DOC

The following discussion is based on two previous studies concerning the sedimentary organic matter of the same mangrove swamps (Marchand

et al. 2003, 2005). We showed that in the mangrove sediment of French Guiana, two layers have to be differentiated. In the upper layer, ~30 cm thick, OC is abundant, up to 40%, and mostly autochthonous. In the basal layer, OC is much less abundant, stable around 0.7%, and predominantly represented by allochthonous highly humified debris, as indicated by Rock-Eval VI analyses and optical observations (Marchand et al. 2003), originated from the Amazon watershed. The SedOC concentrations of the sediment underlying the organic rich mangrove layer is the same as that of the unvegetated shoreface sediment. In the upper, 30 cm thick layer, concentration and origin of SedOM are strongly linked to the stages in the development of the forest. In the early stages of mangrove development, the autochthonous part is composed, on the one hand, of very labile, algal derived, organic matter and, on the other hand, of higher plant debris deriving from roots; litter is not incorporated in the sediment because it is flushed by tides. The development of mangrove trees induces an increase in biomass (Fromard et al. 1998) and a corresponding increase in SedOC. In mixed mature and in senescent mangrove swamps, SedOC concentrations exceed 20% in the upper layer. SedOM derive mostly from higher plant debris, i.e. from roots this time again and—in contrast with early stages of mangrove forest—from mangrove leaf litter, thanks to the sheltered conditions of senescent mangrove forests. Consequently, the increase in DOC concentrations observed in the upper soil layer from pioneer to senescent mangrove seems to reflect an increase in SedOC. The higher the biomass, the higher the SedOC and the higher the DOC concentrations in the upper sediments. This relationship was not shown by the PCA, probably because this analysis took the whole sedimentary column into account. At greater depth, relationships between SedOM and DOM are less obvious: we measured very high DOC concentrations even when SedOC concentrations were very low. In addition, the DOC release is usually inversely correlated with the humification degree of the material (Moore and Dalva 2001). Consequently, the presence of highly refractory and oxidized material at greater depths cannot be an explanation for these high DOC concentrations. Moreover, the quantities and compositions of SedOM were similar in the basal soil-layer of mangrove swamps at any stage of development from pioneer to senescent. In contrast to SedOC, the DOC concentrations at 50 cm depth, were ten times higher in senescent mangrove than in pioneer mangroves. Therefore the distribution of DOC concentrations at 50 cm depth parallels the distribution of SedOC in the upper layer.

Relationships between pore water properties and DOM characteristics

The following discussion aims at evaluating how seasonal variations of pore water parameters may influence the evolution of DOM concentrations and properties with depth. It is based on a previous study made in the same mangrove swamps (Marchand et al. 2004).

In mangrove pore waters, salinity values increase with depth and with forest development, exceeding sometimes twice that of seawater, up to 70. However and like SedOM, two different systems should be distinguished, (i) the upper sediment, for which the salinities of pore waters vary with tides, rains, or proximity to river or percolating freshwater, factors that tend to lower salinity, and wind, droughts and evapo-transpiration that tend to increase it; (ii) the basal layer, where high and stable salinity concentrations where measured year-round. Consequently, salinity and DOC concentrations seem to behave the same way in most mangrove sediments, displaying high concentrations at deeper layers. Many studies have investigated pore water salinity in mangrove swamps (Baltzer 1982; Baltzer et al. 1994; Sam and Ridd 1998; Hollins et al. 2000). However and to our knowledge, the depth distribution of salinity is poorly documented (Juster et al. 1997; Bava and Seralathan 1999). In a previous study (Marchand et al. 2004), we suggested that due to the extension of the cable roots, evapotranspiration mainly took place in the upper sediment and that the salinity increase with depth resulted from vertical physical processes leading to stratification between saline seawater penetrating mangrove sediments and continental fresh water as described in other mangroves

(Baltzer, 1982; Baltzer et al. 1994; Thibodeau et al. 1998). Our hypothesis is that during the rainy season, depth profiles can be explained by the mixing of two water sources, DOC-poor rain penetrating the surface and DOC-rich saline pore water. This process resulted in higher water contents and smaller DOC concentrations and salinity of pore water in the upper sediments. Conversely during the dry season, salts and DOC concentrates with increasing evaporation. In addition, we suggest that the percolation of gravitational water can induce a transport of salt and DOM to greater depths. This hypothesis is being tested in a present research effort using isotopes methods. Nevertheless, it may not be the only explanation for the specific DOC depth profile.

Redox and pH conditions may also be responsible for the increasing DOC concentrations with depth. In mangrove sediments of French Guiana, specific redox conditions occurred due to the activity of radial cable roots of *A. germinans*. High Eh values that highlight oxic to suboxic conditions prevailed in the upper sediments and overlay an anoxic zone (Marchand et al. 2004). Consequently, the greater oxygen exposure, by inducing enhanced oxidation, may also partly explain the lower DOC concentrations measured in the upper zone. In marine sediments, Burdige and Gardner (1998) and then Komada et al. (2004) suggested that selective preservation of refractory DOC with low molecular weight leads to accumulation in anoxic zone, whereas in mixed redox zone, suppressed production and enhanced oxidation of refractory components resulted in low DOC concentrations. However in mangrove sediments, boundary conditions strongly varied with the seasonal dynamics of the water table, in contrast to what is observed in subtidal marine sediments. Our PCA indicated only a weak negative correlation between Eh and DOC (Table 2 and Fig. 10). In addition, opposite to marine sediments, the input of OM derived from higher plant debris is continuous in this upper layer and thus, DOC production is probably enhanced and not suppressed in this zone. Consequently, we suggest that the model presented by Komada et al. (2004) cannot be simply applied to the pore waters of mangrove sediments, even when oxic conditions may decrease DOC concentrations in the upper layer. Redox conditions may also be indirectly play a part in the variations of DOC concentrations by controlling the alternation of dissolution and precipitations of oxy-hydroxydes which have a high capacity of adsorption of DOM (Kaiser and Zech 1998; Fiedler and Kalbitz 2003; Guggenberger and Kaiser 2003). We observed that in the transition zone between the oxic and the suboxic upper layer, Fe concentrations increased in the soluble phase, reflecting the reduction of oxy-hydroxides by bacteria. At the same time, at depth, in the anoxic zone, Fe increased in the solid phase reflecting its co-precipitation with S in the form of pyrite (Marchand et al. 2006). The lack of Fe oxides at greater depth as a result of the anoxic conditions may partly explain the increasing DOM concentrations with depths, which agrees with the results of Hagedorn et al. (2000) in forested gleysols. Finally, pH can have a strong influence on the net quantity of DOM released and on its composition. The solubility of DOM depends on its charge density, which in turn depends on pH. Consequently more DOM becomes soluble at higher pH (Tipping and Hurley 1988). Thus, the increase in pH with depth may also be responsible for the increase in DOC concentrations with depth. Concerning the F/DOC increase with depth, You and co-authors (1999) observed a decrease in the fulvic/humic acid ratio with increasing pH, humic acids being more fluorescent that the fulvic acids. In addition, the factor 1 of our PCA is characterized by high positive loadings for F/DOC and pH. Therefore, we suggest that the low F/DOC ratios and the low content of hydrophobic compounds in the upper layers are also linked to low pH and partly reflected either the precipitation of humic substances or a smaller dissolution of SedOM.

Conclusions

The behaviour of DOM in the pore waters of mangrove soils, seems to differ remarkably from what has been described in continental forests and marine sediments. Our conclusions can be summarized as follows:

(1) DOC concentrations increased from pioneer to senescent mangrove forests, reflecting a progressive increase in the SedOC introduced in the upper sediment through forest development.
(2) DOC concentrations increased with depth at every stage of mangrove development, opposite to the vertical trend of SedOC and to the trend usually observed in forest soils, resulting in some of the highest values ever found in natural environments.
(3) Hydrophobic compounds and Fluorescence/DOC ratios also increased with depth in most mangrove soil. The fluorescence of both the hydrophobic and the hydrophilic fractions increased, demonstrating that the increase in hydrophobic contents was not the only factor that caused fluorescence to increase with depth.
(4) The high DOM concentrations characterizing the pore waters of deep sediments can be explained in part by the anoxic conditions and the high pH values prevailing in the bottom layer: both tend to reduce the sorption of DOM and/or to increase the dissolution of SedOM.
(5) Since both DOC and salinity values were higher in the basal layers than in the upper sediment, we suggest that seasonal variations in rainfall significantly affected dynamics of DOC in the pore water of mangrove sediment. During rainy seasons, pore waters were diluted with rain and run-off waters, resulting in lower DOC concentrations, salinities and densities. The corresponding water table tends to float over dense waters. In contrast, during dry seasons, strongly enhanced evapotranspiration processes and minimized run-off increase the concentration of salts and, most importantly, of DOC. The increased DOC load associated with the high salinity, high density pore waters then percolate downward.

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