



Determining the Influence of Urbanization on Mangrove Zones of Northeastern Brazil: Characterization of Ceará State Coastal Zone Organic Matter Inputs

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Abstract

Mangrove zones in Brazil are extremely sensitive to impacts from global climate change and urbanization. To understand the effects of urbanization on organic matter inputs in the coastal zone of Ceará State (northeastern Brazil), seasonal campaigns were carried out in two of the most environmentally significant river/mangrove systems within the region: the Cocó river, in the metropolitan region of the huge city of Fortaleza, and the Pacoti River, an environmental protection area, without urban influence, on the east coast of the state. Additionally, a spatial study was conducted along the Jaguaribe River, the largest river in the state connected a mangrove area. Organic matter characterization by dissolved organic carbon, spectrofluorescence and fluorescence quenching, and metal complexation capacity shows clearly that under urban pressure, the produced organic matter in mangrove areas is different, proving that carbon budget and pollutant fate have to be revised to take in account this difference.

Keywords

Mangrove · Organic matter · Fluorescence · Metal complexation · Urban pressure

10.1 Introduction

The global dispersion of man-made pollutants in pristine systems and the high levels of metals raise serious questions about their effects on ecosystems. These contaminants

accumulate in organisms and undergo biomagnification in the food web, reaching harmful concentrations, including to human health by the consumption of animals of high trophic level species (Doney 2010; Bisi et al. 2012). The continent-ocean interface encompasses processes in the drainage basins of affluent rivers, ocean dynamics, both on the continental shelf and in the deep ocean and atmospheric processes. These define the magnitude and variability of flows and material dynamics through the land-sea gradient. These processes are affected by anthropogenic actions both locally and globally, and are also influenced by global climate change, which affects both continental and oceanic forcing (Jennerjahn et al. 2010). It is in the estuary, where all these processes interact, that environmental changes are more significant.

Estuaries are natural traps that “capture” continental materials transported by rivers. The gentle slope of the coastal strip creates extensive estuarine areas where the residence time of the waters is greater. During transport at the continent-ocean interface significant biogeochemical transformations of the transported materials occur and the intensity of these transformations is mostly related to the residence time of the water mass in the estuary, where the hydrochemical and hydrological dynamics is more complex. The residence time of the water body in estuaries is a function of the magnitude of the fluvial discharge and the intensity of the oceanic forcing on the continental shelf and on the estuarine region varying according to the interaction between these forces.

In mangroves, the residence time is greater than in estuaries and many pollutants are retained permanently. This accumulation leads to a specific biochemical environment that can induce changes in ecosystem’s functioning. The objectives of this work are to investigate at the organic matter level the impact of urbanization and the tidal effect on the organic matter from local mangroves in river/mangrove systems along the coast of Ceará State in North-eastern Brazil.

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10.2 Study Sites

The metropolitan region of Fortaleza is located in the north-eastern state of Ceará, Brazil. It is made up of nine cities (Aquiraz, Caucaia, Eusébio, Fortaleza, Guaiúba, Itaitinga, Maracanaú, Maranguape and Pacatuba) and witnessed a great expansion in the recent years (Brandão 1995). This region has several river mouths summing up 1,522 ha of mangrove (Godoy 2015). These areas host several species that sustain biodiversity and also the local economy (SDU 1994).

The three most important mangrove areas of the metropolitan region are fed by the Cocó, Pacoti and Ceara rivers (Fig. 10.1), these areas has remained relatively stable from 2000 to 2004, as well as the total mangrove area in the State, totalling about 14,000 ha. Annual precipitation is 1,000 mm and occurs principally in March and June. In 2004, however, at the east coast of Ceará state, from Fortaleza to the Jaguaribe basin area, rainfall was abnormally high. In January, for example, month rainfall reached 404 mm and 378 mm, respectively, against a historical average of 105 mm and 82 mm, respectively (Xavier 2004). The average temperature ranges from 24 to 26 °C with a variability of 6 °C at maximum.

The fourth study area is the Jaguaribe river, the largest basin area to the state and the largest mangrove area in the eastern coast. It is also the major freshwater supply to the metropolitan region through a series of diversion canals. Table 10.1 summarizes the geographical information for the four river basins studied.

10.3 Description of the Studied Basins

10.3.1 The Cocó River

This river initiated in the Serra da Aratanha (Pacatuba) and has a length of 50 km with a basin area of 485 km². The river crosses the cities of Aquiraz, Pacatuba and Fortaleza. At the estuary, it meets with the Coaçu river, basin area of 375 ha, most of them covered by mangroves that expands up to 11 km inland (Miranda et al. 1988; SDU 1994) and covers about 452 ha (Godoy 2015). Human impact on the river is important because of garbage, cattle ranching, industrial activity and water use (Mavignier 1992), particularly over the last 24 km. Sixty percent of the metropolitan region is covered by the Cocó River basin. Detailed information is available in (Stanford 1986) and for climatology, geology and hydrology in the report of the “Study of the life of the Cocó River” AUMEF/Government of Ceará 1988. Mainly four types of geological formation are found in the basin: sand dunes covered by vegetation or already urbanized,

clayey sediments rich in organic clay, sandy-clayey districts and in the interior with crystalline formation.

The mangrove vegetation at the estuary is composed by *Avecinia germinans* (black mangrove), *Laguncularia racemosa* (white mangrove) and *Rhizophora mangle* (red mangrove). The land-mangrove interface harbours many species of grasses and shrubs, coconut, hose, cashew. Mangrove vegetation harbours a great variety of fish, 23 out of 25 are marine. Upstream the river is hypereutrophic, with algae blooms and abundant aquatic macrophytes. In the rainy season, the materials transported are deposited on beaches and are responsible for black spots generally confused with pollution by the population.

The industrial district of Maracanaú is situated 15 km from the centre of Fortaleza. It counts 41 companies (chemical, fabric, metallurgy, food, mineral and non-metallic exploitation, ...) (Mavignier 1992). The wastewater treatment station (WWTS) built since the beginning of the area development is already oversized. Since (1992) retention basins have been implanted. The last one of them leaks in the Maranguapinho River. An anaerobic lagoon followed by ripening lagoons (792,000 m³) allows a residence time of 28 days with a flow rate of 840 L.s⁻¹. But it is not the totality of the urban effluents that are collected.

The contaminant content in the river seems low for fecal coliform, heavy metals and Biological Oxygen Demand (BOD). The general parameters observed in the Cocó River water are summarized in the Table 10.2.

There is an amplification of the concentrations of copper (Cu) and lead (Pb) in the animals across the food chain (Mavignier 1992). Leaching appears to be the main source of pollutants; however, metal concentrations in waters are lower than Brazilian legal standards (CONAMA standards). The leachate composition shows a very high organic matter concentration (Analyzed from 21/02/90 to 21/05/91).

10.3.2 The Pacoti River

The Pacoti river has its source in Baturite Mountain chain and has a length of 150 km. Its 1,800 km² basin includes the contributory rivers Agua Verde, Jua and Guaiuba. The Pacoti river flows through some small towns and possesses many small islands. The mangroves in its estuary cover 158 ha (Miranda et al. 1988; SDU 1994). The influence of the sea is measured up to 15 km from the mouth in the dry season (Freire et al. 1991a, b, c). In this river human impact is weak because the activities are dominated by cattle and forest exploitation. This mangrove is chemically reductive because of the presence of large amount of organic matter (Freire et al. 1991a, b, c; Freire and Maia 1991).



Fig. 10.1 Location of the studied river basins in Ceara state. The Ceara river (up right), the Cocó river (middle up right), Pacoti river (middle down right) and Jaguaribe river (down right) in the hydrological

network of the state of Ceará. This map was produced by the Labomar (UFC, Ceara) and Google Earth pictures

Table 10.1 Extension and basin areas of the studied rivers and their respective mangrove areas

River	Extention (km)	Basin area (km ²)	Mangrove area (km ²)
Cocó	50	485	4.52
Ceará	60	900	7.26
Pacoti	150	1,800	3.40
Jaguaribe	610	75,669	7.29

Table 10.2 Annual anthropogenic emissions (ton.year⁻¹) of N, P, Cu, Zn, Pb, Cd and Hg to the lower basins of the four estudied rivers (Lacerda et al. 2008; SEMACE 2005)

Fluxes	Cu	Zn	Pb	Cd	Hg	P	N
Ceará	7.09	102.2	7.37	0.77	0.072	393	815
Cocó	35.1	84.0	103.0	4.80	0.464	738	2,588
Pacoti	4.04	19.4	2.91	0.31	0.026	697	1,097
Jaguaribe	9.2	4.79	0.45	0.15	0.011	330	798

10.3.3 The Ceara River

The Ceara River is born in the Maranguape hill. Its length is 60 km with a basin of 900 km². The river crosses the cities of Maranguape, Caucaia and Fortaleza. The main tributary is the Maranguapinho with a confluence located about 7 km from the mouth. Total mangrove area reaches 726 ha (Godoy 2015) with an expanse up to 14 km inland (SDU 1994). The industrial district of Maracanaú is situated 15 km from the centre of Fortaleza. It harbours 41 companies (chemical, fabric, metallurgy, food, mineral and non-metallic exploitation) (Mavignier 1992). The waste water treatment station (WWTS) built since beginning of the area development is already oversized. Since 1992 retention basins have been implanted.

10.3.4 The Jaguaribe River

The basin of the Jaguaribe River is 75,669 km² for a length of 610 km. The river is much greater than the Pacoti, Ceara and Cocó rivers and does not allow a valid comparison among them. The population density was less than 30 hab.km⁻² with a total population of 2,064,535 (data of 1996) (Gatto 1999). Main land uses are traditional agriculture together with livestock. Sixty percent of the basin has a semi-arid climate with locally with spots under moist, sub-humid and arid climate. Approximately 50% of the basin is in the state of Ceara, the other part is shared with the states of Piauí, Pernambuco, Paraíba and Rio Grande do Norte. The dominant vegetation is the Caatinga (Savanna). The most abundant species are *Anadenathera colubrina*, *Tabebuia chrysotricha*, *Auxemma oncocalyx*, *Astronium urundeuva*, *Caesalpinia pyramidalis*, *Aspidosperma pyriformium*, *Bumelia sartorum*, *Erythrina velutina* *Croton* spp., *Mimosa tenuiflora*, *Combretum*

leprosum, and cacti *Pilosocereus piauhiensis*, *Cereus jamacaru*. Most rains (80%) occur between January and May (600–1,200 mm) and varies in temperature between 24 and 27 °C.

In the rivers's lower basin and inshore waters; fishing, shrimp farming, lobster and crab are the major extractive activities. The Jaguaribe River is a well-regulated river that has many dams, both in the river proper or in its tributaries, of notice are the largest Castanhão reservoir with 6.7 million m³, the Orós reservoir with 2.1 million m³ of capacity and the Banabuiu, with 1.7 million m³ capacity, these three reservoirs are responsible for over 95% of the total water storage capacity of the entire basin. Climatological monitoring is done by 17 rain stations, 4 on the main course and 13 on the tributaries. During low waters, the flow of the Jaguaribe (about 20 m³ s⁻¹) is controlled downstream by the large Castanhão dam. As a result of extensive damming of the river, semi-arid climate and meso-tides make that the Jaguaribe estuary is frequently an importer of seawater and marine materials (Lacerda et al. 2013). The waters of the Jaguaribe River are of the bicarbonate-mixed type (Instituto Brasileiro Geografia e Estatística, IBGE, 1996, <http://www.ibge.gov.br/home/estatistica/populacao/contagem/>). The Banabuiu River presents mixed waters with chloride and sodium. Eighty percent (80%) of the basin drains crystalline rock geology with weak hydraulic potentiality. The groundwater is chloro-mixed to chloro-sodium. The Jaguaribe River Basin receives untreated effluents from urban, agriculture, aquaculture and, to a certain degree, industries.

The general environmental characterized situation of the four rivers, relative to pathogenic micro-organisms; toxicology and sediment quality and contamination by nutrients and metals have been summarized by Nilin et al. (2013). A summary of anthropogenic emissions of nutrients and selected trace metals is presented in Table 10.2.

All the studied rivers show a varied state of human impact, particularly from urban areas and agriculture (Fig. 10.1). Major anthropogenic contaminants to the four rivers studied are trace metals of environmental significance and nutrients, mostly from urban sources, in the metropolitan area (Ceará and Cocó rivers) and agriculture and husbandry in the more rural basins (Pacoti and Jaguaribe rivers) (SEMACE 2005; Lacerda et al. 2008). Faecal coliforms and high biological oxygen demand (BOD) frequently occurs in the metropolitan area rivers. Annual loads of the most significant environmental contaminates to the four studied rivers are shown in Table 2.

10.3.5 Particularity of Mangroves

Mangroves are particularly sensitive ecosystems both ecologically (Blasco et al. 1996) and chemically (Otero and

Macías 2002). Most of the sediments carried by rivers reach the coastal zone with reduced speed, tides also contribute to choke the rivers, whereas mangrove trees trap the sediments as well as most pollutants associated with them, either metallic or organic (Da Silva et al. 1998). Mangrove vegetation is one of the most important driver of these process, also because of the large production of organic matter (Alberts et al. 1988; Lacerda et al. 1995). This sequestration is permanent due to the low remobilization of pollutants, as far as the natural mangrove biogeochemical conditions are preserved (Machado et al. 2002). This permanent sequestration has been reported even in highly polluted urban areas (Burke et al. 2000). However, changes in biogeochemical conditions of the sediments may result in remobilization of pollutants (Marins et al. 1997). The organic carbon concentration in mangroves ranges from 318 to 2,043 μM , depending on season and location and has no visible transition between the terrestrial and the marine end-members when observing the natural organic matter by fluorescence, for example (Jaffé et al. 2004). The modification of the uses in the basin can modify the flows of pollutants that enter the mangroves. Dam construction modifies physical-chemical conditions that alter river fluxes, producing an erosion of the coast and a migration or destruction of the mangroves (Lacerda et al. 2013; Lacerda and Marins 2002). For example the transformation of forest into agriculture causes the mercury trapped in the soils to be released (Lacerda et al. 2004). As mangroves only exert themselves in specific conditions, they are influenced by all modification of local and global environment conditions. A subtle change in the conditions can lead to an important response of the mangrove ecosystem that can die, move, and transform (Blasco et al. 1996).

It is therefore important to have geochemical indicators of the natural state. As organic material is an important mode of transmission of trace metals (Lu and Jaffe 2001; Mounier et al. 2001) and how little data exists on the fluorescence spectroscopy as a monitoring tool for mangroves (Alberts et al. 1988), this work proposed to use fluorescence spectroscopy on the Fortaleza city rivers to monitor the quality and quantity of the organic matter as an indicator of the impact of the soil use onto the mangroves geochemistry. Particular attention will be paid to the Pacoti, Cocó and Ceara rivers because their basins are of similar size but drastically different in soil uses.

10.4 Strategy and Comparison of the Cocó and Pacoti Rivers

Cocó and Pacoti rivers were sampled around the region of Fortaleza. Each river is divided into three zones: one near the source called “river zone”, one inside the mangrove zone

called “mangrove zone” and one at the mouth of the river to have the marine part called “marine zone”.

Every month between May 2004 and September 2004 a sample of each zone was made. Filtration was done in the field with a 13 mm diameter burnt glass filter using a syringe and a HDPE filter holder. Six vacuum tubes, two by zone, were filled with the sample, two of them stabilized with 50 μL of 1 M NaN_3 for carbon, fluorescence quenching and anion concentration, and two treated with hydrochloric acid for cation analysis. The tubes were kept in the cold and dark until measurement. The filters were dried and used to measure the particulate organic carbon (POC) with a SSM SHIMADZU TOC instrument.

The physico-chemical parameters were measured at the same time of the water sampling, using a field multi-parameter instrument for pH, dissolved oxygen, conductivity. The probes were calibrated before each measurement. The results are presented in Table 10.3.

10.4.1 Analyzes

Measurements of the major elements, cations and anions, were done on a Dionex DX 120 ion chromatography with a ISOCRAT AS9-HC column and CS12A ISOCRAT column. The eluents are respectively Na_2CO_3 9 Mm, 950 $\text{mg}\cdot\text{L}^{-1}$ and methane sulfonic acid (M.S.A) 20 mM, 1.3 $\text{mL}\cdot\text{L}^{-1}$. The flow rate was set at 1 $\text{mL}\cdot\text{min}^{-1}$ and the injection volume set at 100 μL .

Measurement of total organic carbon was done with a SHIMADZU TOC5000. The standard used was a solution of potassium phthalate. Each sample was acidified (100 μL of 5 N HCl in the 5 mL sample) and bubbled with nitrogen gas before measurement for eliminating the carbonates.

Fluorescence was measured with an HITACHI4500. Excitation Emission Matrix of Fluorescence (EEM) were made in a quartz cell at natural pH with the following parameters: 250–450 nm for excitation, 300–600 for emission, a scan speed of 30,000 $\text{nm}\cdot\text{min}^{-1}$ and excitation and emission slit fixed at 5 nm.

To study the properties of complexation the fluorescence quenching was used. By placing the sample in a glass vessel, the pH was fixed to 5 with a buffer solution of $\text{Na}_2\text{PO}_4\cdot\text{H}_2\text{O}$, and addition of copper $\text{Cu}(\text{NO}_3)_2$ with 0.1, 1 and 10 $\text{mg}\cdot\text{L}^{-1}$ of copper solution till a stabilization of the fluorescence signal extinction. The fluorescence measurement was done with an excitation spectrum from 200 to 400 nm and an emission wavelength fixed at 420 nm, all other parameters were identical to the EEM measurement.

Table 10.3 Values of the physico-chemical parameters of river water samples in the river, mangrove and marine zones of the Pacoti and Cocó rivers, Ceará State, north eastern Brazil

River	Field number	Date	Reference	T (°C)	Cond. ($\mu\text{S}\cdot\text{cm}^{-1}$)	pH	Sal.	O ₂ ($\text{mg}\cdot\text{L}^{-1}$)	Zone
Cocó	1	07/05/04	Co101	29.5	764	6.14	0.4	6.1	River
Cocó	1	07/05/04	Co102	28	949	6.38	0.5	0.5	Mangrove
Cocó	1	07/05/04	Co103	29.1	46,600	7.8	30.0	2.5	Marine
Pacoti	1	25/05/04	Pa101	28.7	2,008	6.38	0.9	3.8	River
Pacoti	1	25/05/04	Pa102	29.5	54,300	8.2	35.4	4.6	Mangrove
Pacoti	1	25/05/04	Pa103	29.1	54,500	8.2	35.1	5.2	Marine
Cocó	2	09/06/04	Co201	26.4	770	6.54	0.4	6.3	River
Cocó	2	09/06/04	Co202	26.9	982	6.65	0.5	1.8	Mangrove
Cocó	2	09/06/04	Co203	27.5	53,100	8.12	35.0	3.2	Marine
Pacoti	2	09/06/04	Pa201	27	3,332	6.75	1.7	4.5	River
Pacoti	2	09/06/04	Pa202	27.4	56,600	8.23	35.7	4.6	Mangrove
Pacoti	2	09/06/04	Pa203	27.2	56,400	8.23	35.7	4.5	Marine
Cocó	3	30/06/04	Co301	28.3	756	6.45	0.4	9.8	River
Cocó	3	30/06/04	Co302	27.4	378	7.1	0.2	5.8	Mangrove
Cocó	3	30/06/04	Co303	28.3	52,700	8.1	34.6	4.7	Marine
Pacoti	3	30/06/04	Pa301	27.0	916	5.68	0.4	3.8	River
Pacoti	3	30/06/04	Pa302	28.9	12,220	6.25	6.4	3.6	Mangrove
Pacoti	3	30/06/04	Pa303	28.3	29,770	6.93	17.2	3.9	Marine
Cocó	4	04/08/04	Co401	25.8	753	7.07	0.3	5.0	River
Cocó	4	04/08/04	Co402	25.8	2,566	7.67	1.3	3.6	Mangrove
Cocó	4	04/08/04	Co403	25.8	52,100	8.21	32.9	3.3	Marine
Pacoti	4	04/08/04	Pa401	25.7	3,772	8.04	1.9	4.9	River
Pacoti	4	04/08/04	Pa402	25.5	54,000	8.2	34.3	4.0	Mangrove
Pacoti	4	04/08/04	Pa403	25.5	54,100	8.29	34.4	4.9	Marine
Cocó	5	27/08/04	Co501	–	878	6.62	0.4	5.5	River
Cocó	5	27/08/04	Co502	–	839	6.9	0.5	5.0	Mangrove
Cocó	5	27/08/04	Co503	–	30,670	7.01	20.5	5.0	Marine
Pacoti	5	27/08/04	Pa501	–	8,190	8.33	4.5	6.0	River
Pacoti	5	27/08/04	Pa502	–	41,420	8.0	26.6	4.5	Mangrove
Pacoti	5	27/08/04	Pa503	–	49,250	7.31	32.3	4.4	Marine
Cocó	6	17/09/04	Co601	27.6	752	6.99	0.4	4.9	River
Cocó	6	17/09/04	Co602	26.0	7,310	7.01	4.0	3.3	Mangrove
Cocó	6	17/09/04	Co603	27.2	51,400	8.09	33.7	3.5	Marine
Pacoti	6	17/09/04	Co601	27.5	8,550	8.12	4.7	4.5	River
Pacoti	6	17/09/04	Co602	26.9	53,500	8.13	35.3	5.2	Mangrove
Pacoti	6	17/09/04	Co603	26.7	53,300	8.18	35.2	5.4	Marine

10.4.2 Results

10.4.2.1 Dissolved and Particulate Organic Carbon

The results presented in Fig. 10.2 show that for the Cocó River the concentration of dissolved carbon is always higher in the mangrove area. For Pacoti, on the contrary, there is a systematic increase from the river zone to the marine zone. The salinity suddenly increases at the marine zone in the Cocó river and in the mangrove zone in the Pacoti rivers, except for the month 3 (June 2004) where a low salinity was observed probably due to a low tide conjugated to a high discharge. The pH always increases from the Cocó river zone (~7) to the marine zone (~8), while it change more stochastically in the Pacoti River. Concerning the particulate organic carbon (POC), there is no trend along the period and among

the zones. The average POC concentration is about 0.2 mg of C L⁻¹ (± 0.1) except for the Cocó River at the river zone where a greater variability is observed leading to an average value of 0.5 ± 0.6 mg of C L⁻¹.

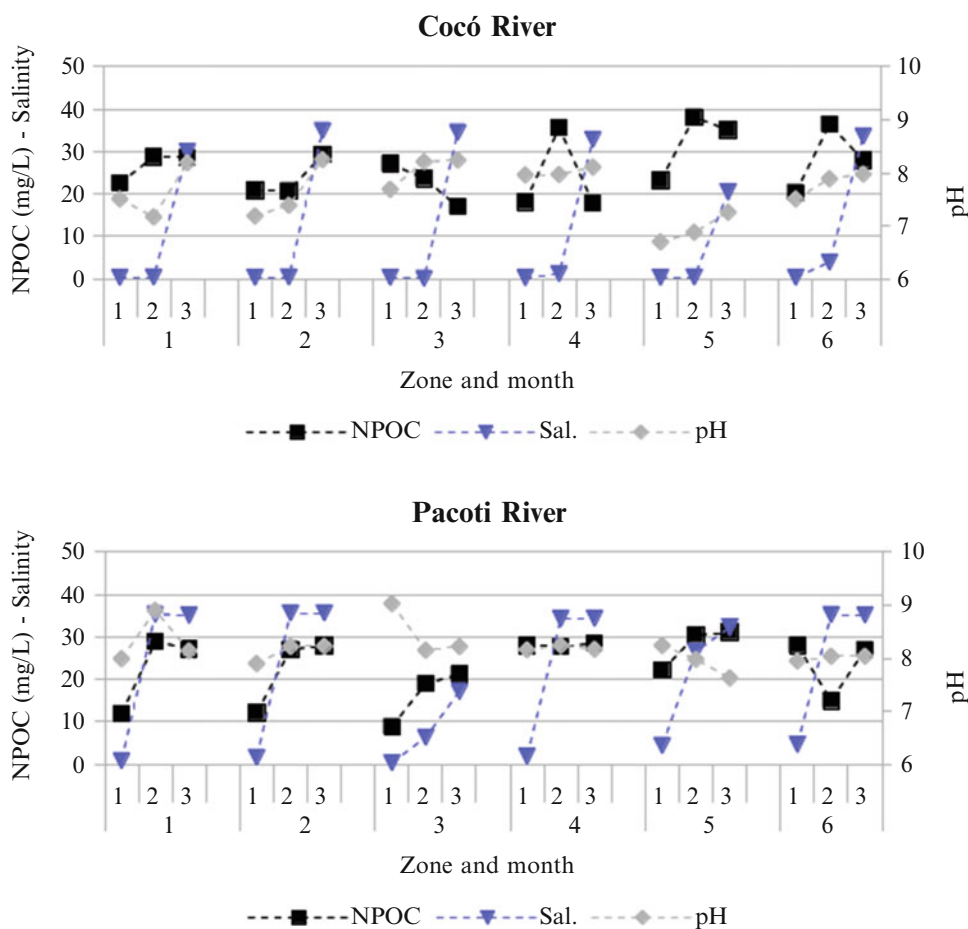
With these results it is already possible to say that these two ecosystem do not have the same dynamic. Apparently it seems to have a carbon production in the mangroves of the Cocó River not present in the Pacoti River.

10.4.2.2 Fluorescence Spectroscopy

The 2D Fluorescence

The measurement of the fluorescence intensity at peak A ($\lambda_{\text{ex}} = 250/\lambda_{\text{em}} = 450$) and peak C ($\lambda_{\text{ex}} = 350/\lambda_{\text{em}} = 450$) shows that for the Cocó River intensity is higher for the

Fig. 10.2 Results of dissolved organic carbon concentration in ppm (black square), salinity (blue triangle) and pH (grey losange) for the Cocó and Pacoti rivers. Points 1, 2, 3 representing the river, mangrove and marine zones respectively



mangrove area (Fig. 10.3, solid lines), as for its organic carbon concentration. In the Pacoti River the only fields that behave in the same way are field 3 and 5 where salinity and pH behave differently.

Observing the ratio between the two intensities allows one to see the quality of the organic material (Mounier et al. 1999). When $r_{a,c}$ decreases, maturity increases as intensity from the type C increases more than the type A (Fig. 10.4). This ratio does not depend on the carbon concentration (Patel-Sorrentino et al. 2002). All the values are similar and around value of 1, except for the Cocó river in field 4 where the ratio is about 1.5. In the Cocó River there is a decrease from the river zone until the marine zone. This could be due to a maturation of the organic material during the transport. In contrast in the Pacoti River, the variation is not recorded with maximum in mangrove area except in field 2. For the Pacoti River, the maximum often appears in the marine zone, indicating a recent organic material (fields 1, 3, 4, 5 and 6).

3D Fluorescence

3D fluorescence is a map of all the photons emitted by the organic matter that fluoresce (Fig. 10.5). This measurement

gives a quantification of the fluorescent organic material as well as qualitative information using the excitation and emission wavelength position. Generally the most popular peaks are the peak A ($\lambda_{ex} = 250/\lambda_{em} = 450$) and the peak C ($\lambda_{ex} = 350/\lambda_{em} = 450$). We can observe that the fluorescence is more intense in the Cocó River.

The peak T (tyrosin-like) corresponding to the signal of the proteins is not observed. The waters are mainly composed of humic type (peak C) as presented in Figs. 10.6 and 10.7.

From the 3D fluorescence of all the excitation emission matrices of fluorescence presented above, the CP/PARAFAC separation algorithm was used. Two components were extracted (CORCONDIA 96%) and are represented by the two components in Fig. 10.8.

The first component shows a maximum at 300 nm of excitation and 400 nm of emission. Its shape is circular, and related to the fluorescence domain. It represents the humic-like type components linked to fulvic acids. The component C2 exhibit two excitation maxima one secondary at 280 nm and one principal at 350 nm. The emission wavelength is around 480 nm. This later component represents the humic-like substances coming from terrestrial origin. No more than two components were found meaning that

Fig. 10.3 Fluorescence of Ic and Ia (dark and grey solid, respectively) of the Cocó river and fluorescence Ic and Ia of the Pacoti river samples (dark and grey dashed, respectively)

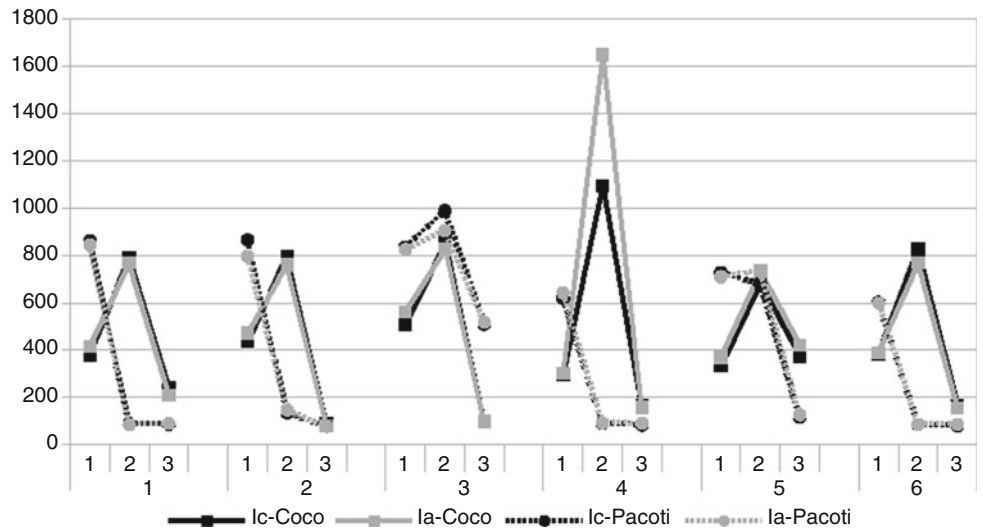


Fig. 10.4 Ratio for the fluorescence peaks of the Cocó and Pacoti rivers

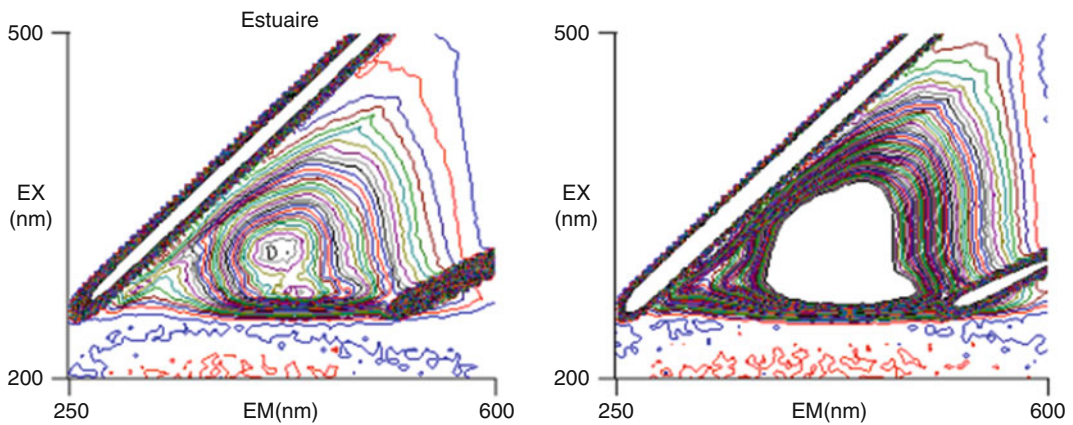
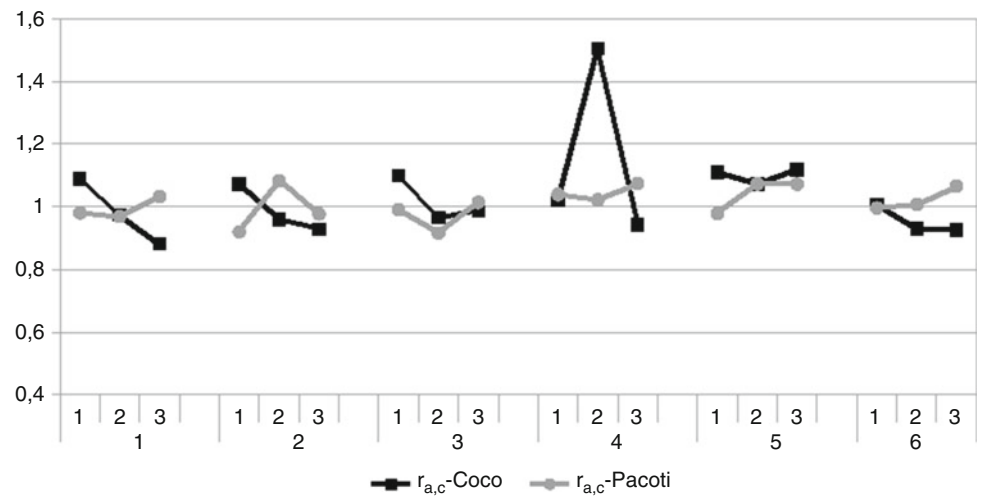
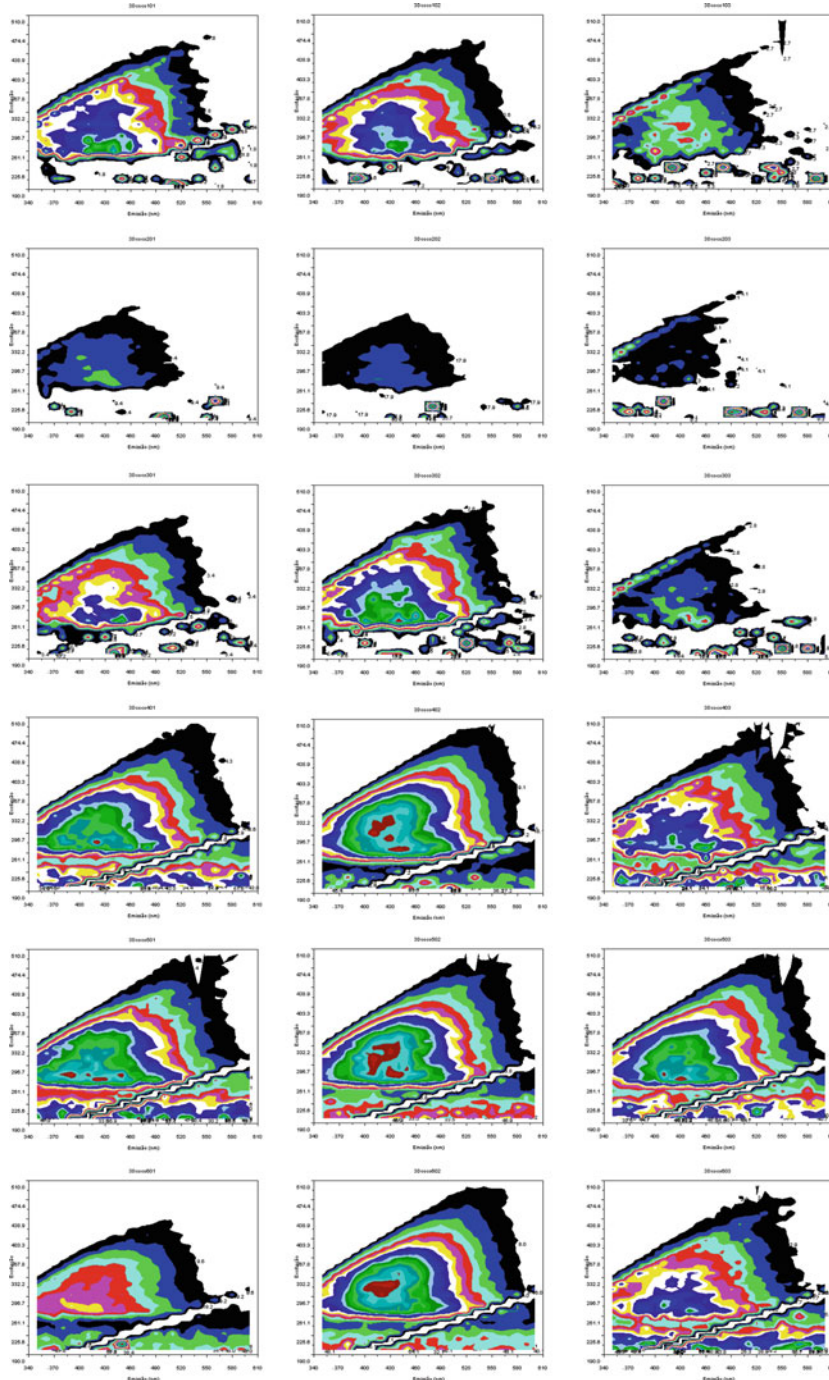


Fig. 10.5 Excitation emission fluorescence matrices example of the Cocó water river (left) and the Pacoti river (right)

Fig. 10.6 Excitation Emission Matrices of the Cocó River false colour representation. Column 1, 2 and 3 represent the river, mangrove and marine zones and line represent the line correspond to field campaign 1, 2, 3, 4, 5 and 6



possible fluorescence biological activity was not statistically extracted.

Their evolution along the rivers and through time is shown in Fig. 10.9. The Cocó River presents a higher C1 contribution in the mangrove zone. Each sampling has the variation of the C1 contribution in mangrove zone higher than the C1 in river and marine zone (Fig. 10.9). The C2 component on the contrary does not vary. The urban impacted mangrove zone

produced more fulvic components. This is confirmed by the $r_{a,c}$ ratio that is systematically higher in mangrove zone except for the campaign 1 and 2 (Fig. 10.9, grey line).

The Pacoti River shows a different trend from the Cocó River. Indeed, the fulvic contribution decreases regularly from river zone to the marine zone. Moreover the $r_{a,c}$ is also decreasing meaning that the organic matter become more and more terrestrial like during the transport to the mangrove

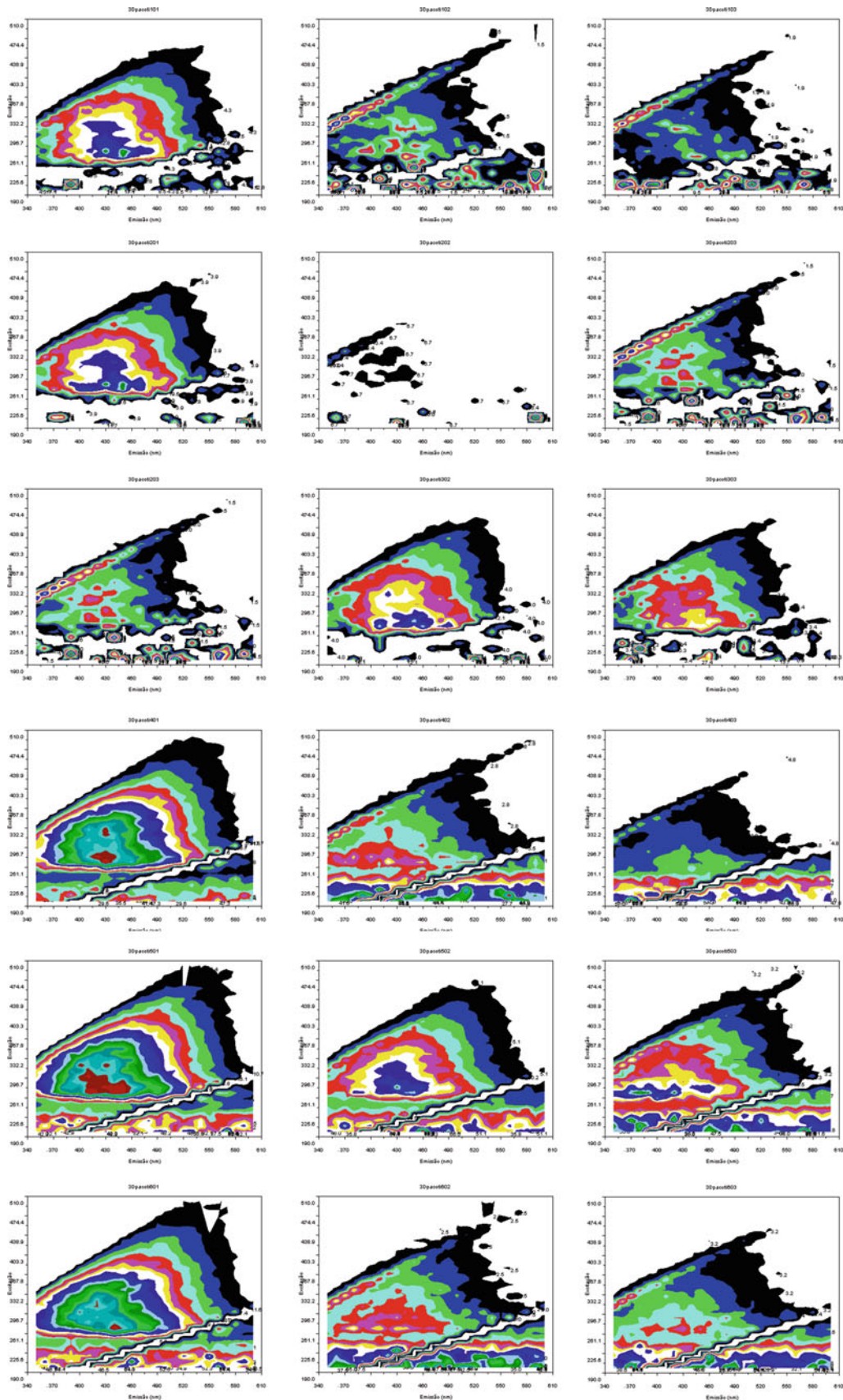


Fig. 10.7 Excitation Emission Matrices of the Pacoti River false colour representation. Column 1, 2 and 3 represent the river, mangrove and marine zones and line represent the line correspond to field campaign 1, 2, 3, 4, 5 and 6

zone. In field 1–3, the fulvic contribution was higher than the terrestrial one (C2), but in fields 4, 5 and 6 it is the contrary for mangrove and marine zones.

Hence by fluorescence measurement, it is observable that the organic matter produced by the mangrove differs a lot between urban impacted and non-impacted mangroves, except on month 3 when the fluorescence organic matter is similar to the Cocó River pattern. More fulvic like components are produced in the Cocó River, maybe as a defence mechanism, since herbivory tends to be more intense under more stressed conditions and fulvic components are frequently associated with plant defences against herbivores.

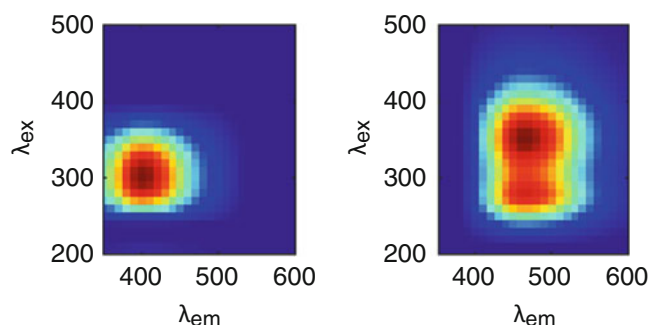
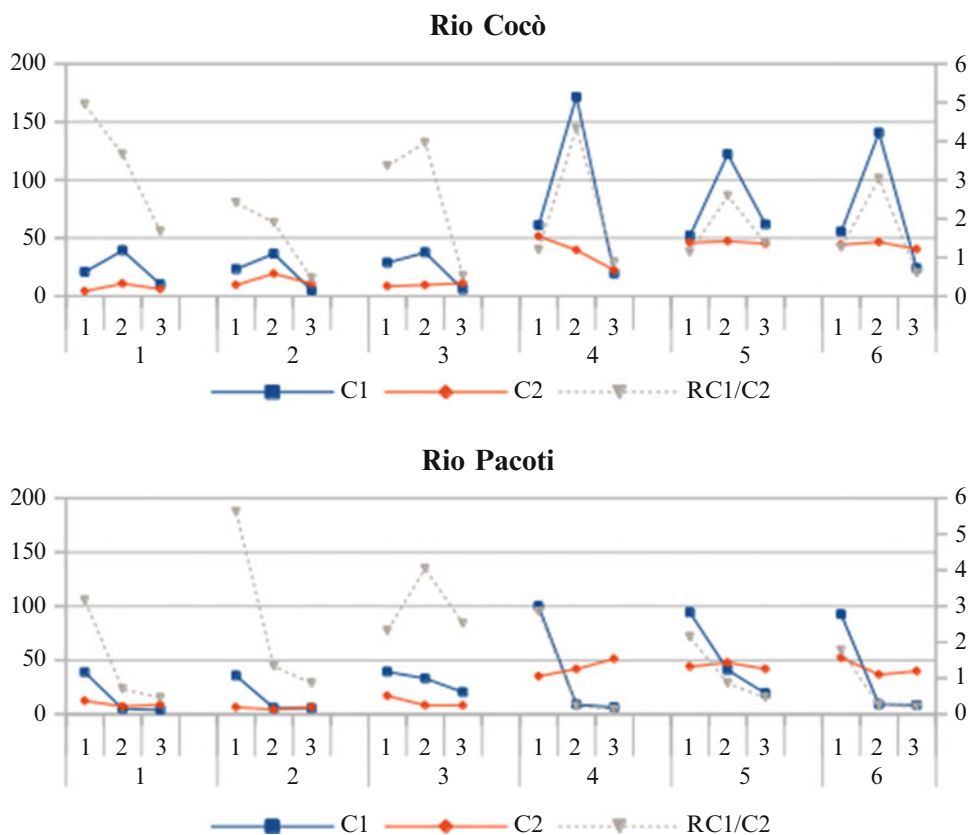


Fig. 10.8 PARAFAC component extracted from the Cocó and Pacoti rivers excitation emission matrices of fluorescence

Fig. 10.9 Evolution of the contribution of the CP/PARAFAC components along the rivers. The component C1 and C2 are represented by the blue and red solid line respectively. The ratio of their contribution C1/C2 is represented by the grey dashed line.



10.4.3 Major Elements

10.4.3.1 The Cations

The concentrations of the cations (Fig. 10.10) present high values for the Na in the marine zone, as expected due to stronger sea influence. Indeed it is connected with the proportion of sea water in the system. In the other zones the dominant cation is Na⁺ but also K⁺ and Mg²⁺. It only has anomaly during field campaign 4, where K⁺ and NH₄⁺ present a higher concentration than Ca²⁺.

The patterns for the Pacoti River are different but have the same relation and influence as related to the sea, with an increase of the Mg²⁺ and Na⁺ concentration. One can see that the Pacoti River is more invaded by the sea intrusion in the mangrove zone (Fig. 10.11) than the Cocó River.

10.4.3.2 The Anions

The anion concentrations in the Cocó River are shown in (Figs. 10.12 and 10.13). The increase of concentrations results from the influence of seawater. That is true except for nitrate and sulphate, which disappear when salinity increases.

The Pacoti River again does not presents the same variation as the Cocó River (Fig. 10.14). From these analyses it is difficult to interpret the results. But one can say that during the study, nitrate concentration is high at the river zone.

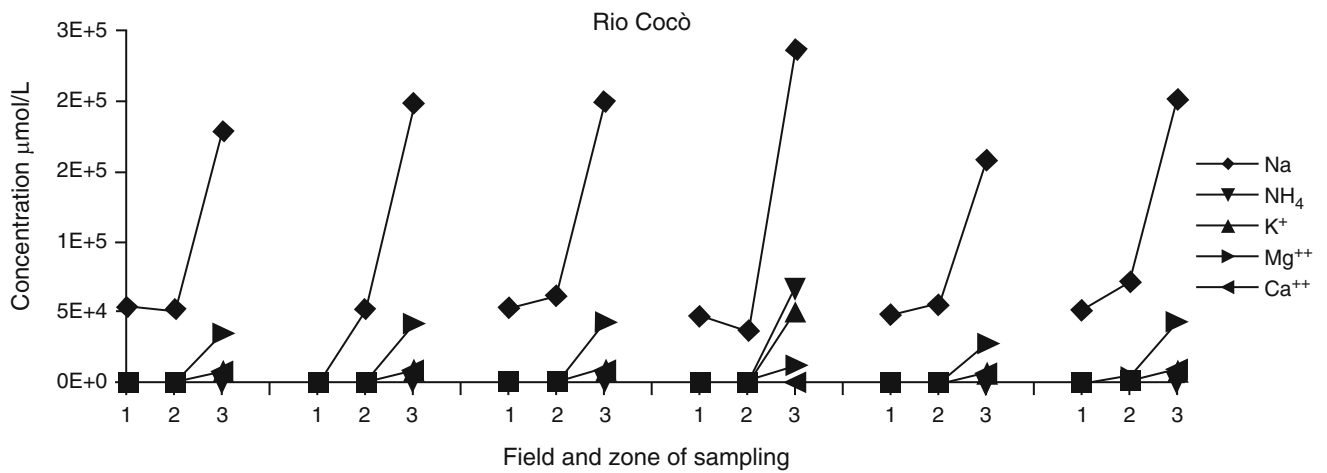


Fig. 10.10 Variation of cation concentration in the Cocó River

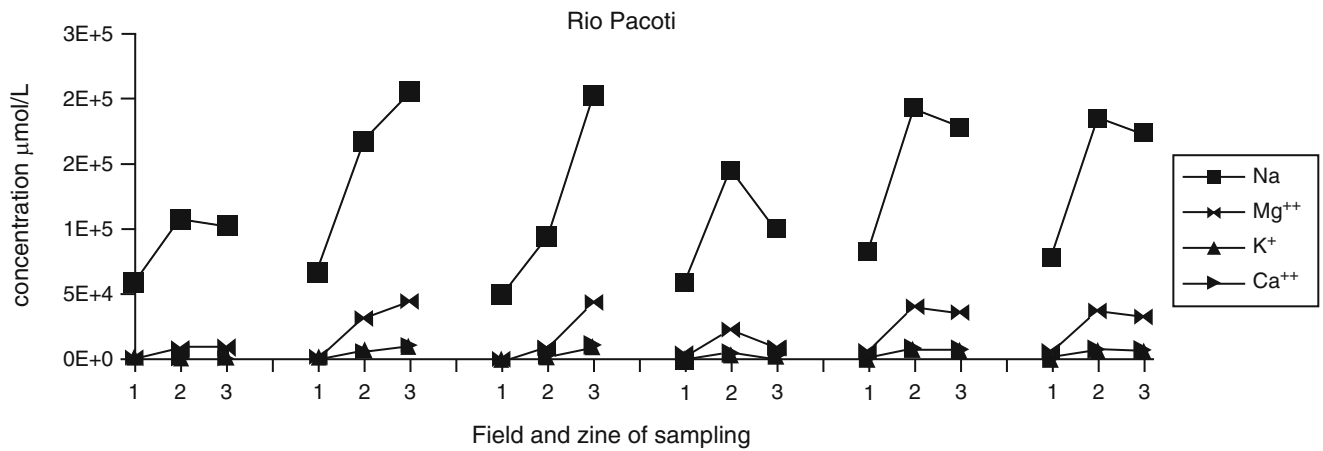


Fig. 10.11 Variations of cation concentrations in the Pacoti River

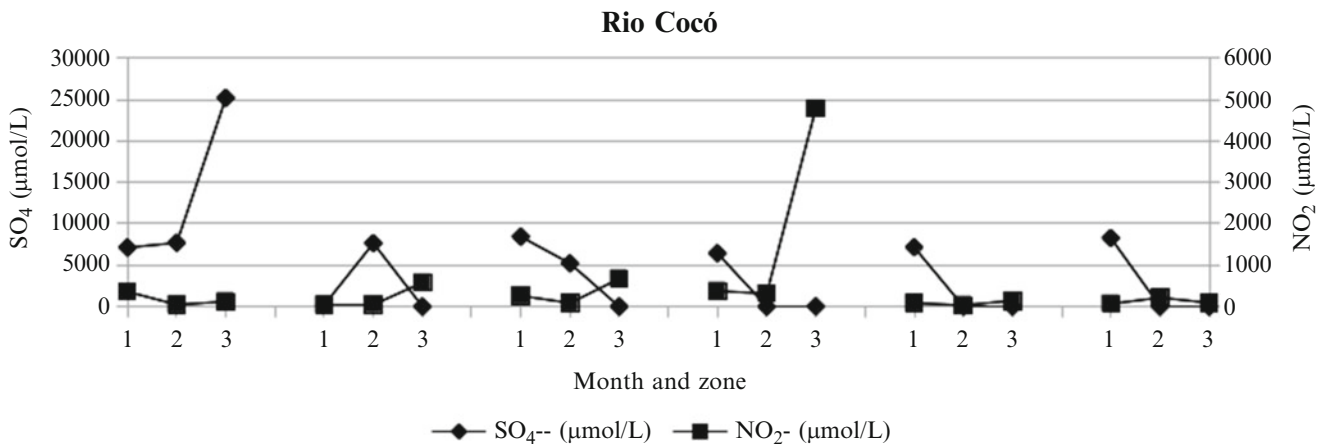


Fig. 10.12 Variation of sulphate and nitrate concentration in the Cocó River

10.4.3.3 Fluorescence Quenching

Complexing capacity is the ability of the natural organic matter (NOM) to complex the metals forming a metal-

NOM complex. For a sample, the site concentration of complexation is expressed in $\mu\text{mol/L}$ of metal, and the

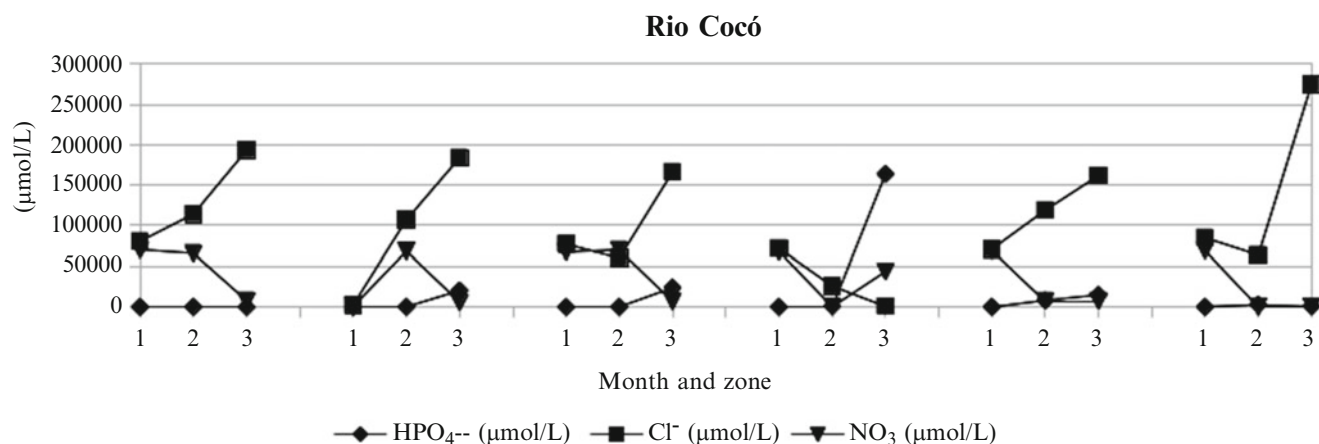


Fig. 10.13 Variation of phosphate, chloride and nitrate concentration in the Cocó River

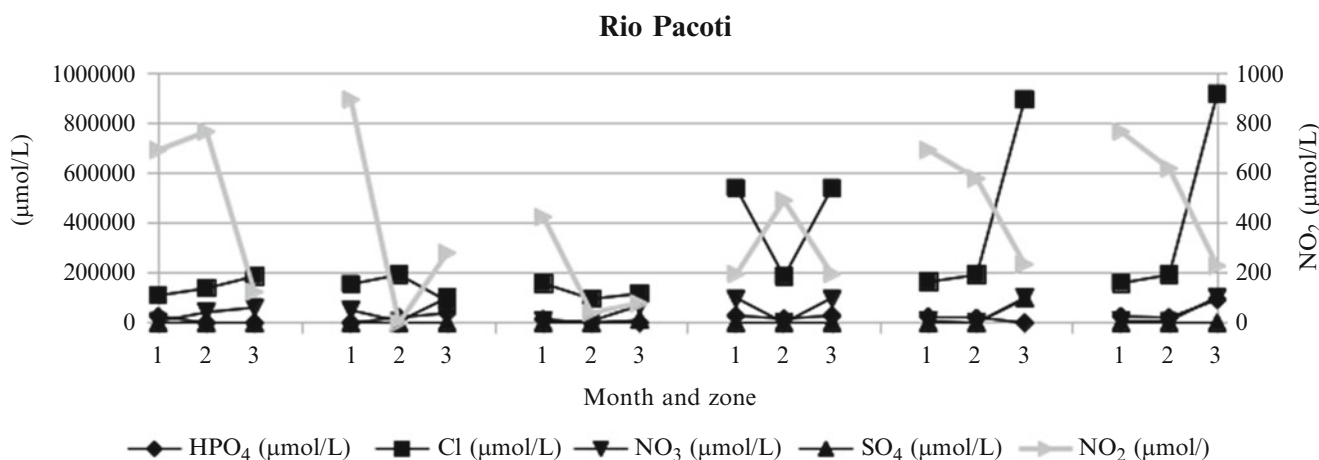


Fig. 10.14 Variation of anion concentrations in the Pacoti River

complexion capacity is the value in μmol of site/mg of carbon (μmol of Cu^{2+} /mg of C).

Using the Ryan and Weber (1982) model, it is possible to calculate the total site concentration L_T and the equilibrium complexation constant K_L , which represent the strength of the complex bound (Ryan and Weber 1982).

The obtained results are represented in Figs. 10.15 and 10.16. The Cocó River shows a greater capacity for the river zone and the marine zone. Systematically the complexation capacity is minor for the mangrove zone. This can be explained by a specific production of carbon with weak complexation properties. In the mangrove zone metals are less complexed than in the Cocó River mouth. At the contrary in the Pacoti River the complexation capacity always increases from the river zone until the marine zone. In Pacoti, organic matter site density increases continuously and metals have more and more probability to be complexed. There is no production of specific organic material in the mangrove zone

of the Pacoti River. Based on the results of quenching of fluorescence it appears that the dynamic of the two rivers is not similar in term of NOM production. The Cocó River, more affected by anthropogenic activities, produces non complexant organic matter in the mangrove zone, while in the Pacoti basin the NOM complexant capacity increases. The results do not show trend on complexant capacity during the 6 months sampling period in both rivers.

10.5 Sampling Strategy on the Jaguaribe River

10.5.1 Spatial Sampling

Two fields campaigns were carried out (Table 10.4) in April and September 2004 to have variation of physical-chemical parameters of the waters of the lower Jaguaribe basin. The

Fig. 10.15 Distribution of complexation capacity for copper in the Pacoti River and Cocó River along the river. 1 River; 2 mangrove; 3 marine zones

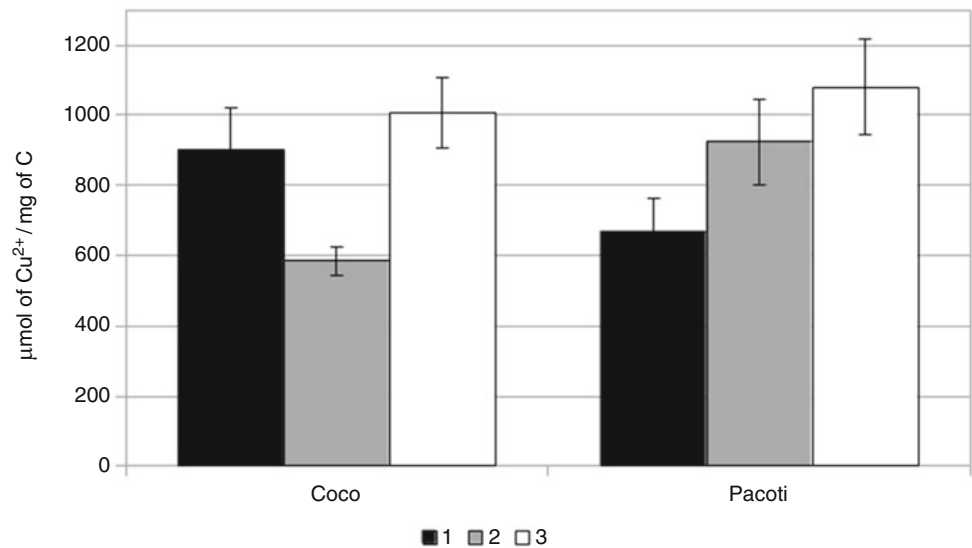
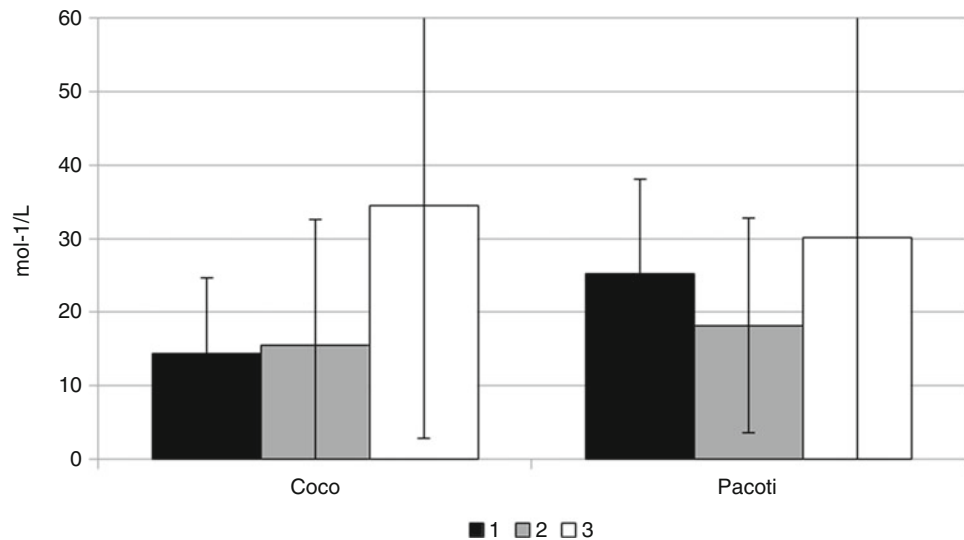


Fig. 10.16 Distribution of complexation constant for copper in the Pacoti River and Cocó River along the river. 1 River; 2 mangrove; 3 marine zones



mangrove zone of the Jaguaribe occurs between the point 2 (Barra) and 4 (Raimundinho) (Fig. 10.17).

10.5.2 Sampling During a Tide

The waters of the Jaguaribe River were sampled along time during a tide period. These 15 samples were sampled in front of the Ilha Grande Island (Fig. 10.17, Table 10.5).

10.5.3 Results of the Spacial Distribution Study

10.5.3.1 Dissolved Organic Carbon

It can be observed that the concentration of organic carbon in the Jaguaribe river basin increases in April and September. Figure 10.18 shows the concentrations observed from the site 1 (Marine) to Itaiçaba (River) throughout the continent-sea

gradient. There is a decrease in carbon concentration showing dilutive effect from land to sea both in April and September. In April the carbon concentration is very low, particularly downstream the dam of Itaiçaba and in Aracati (downstream the bridge) while the values upstream the bridge are very high. If the value after the dam can be a false response, we can consider a large dilution after the Aracati point (after the bridge). The value of carbon concentration is higher in September than in April. The dilution effect is confirmed by the linear correlation between DOC and Cl⁻ concentration ($r^2 = 0.89$) (Fig. 10.18).

10.5.3.2 Fluorescence Spectroscopy

The fluorescence results (Figs. 10.19 and 10.20) show a very different fluorescence response in April and September. Clearly fluorescence is highest in April, the period with lower concentrations of dissolved organic carbon. Once reaching the sea (site 2) in April the fluorescence decreases

Table 10.4 Location of sampling points on the Jaguaribe River, and values of copper (Cu^{2+}), dissolved organic carbon (DOC) and inorganic carbon (IC)

River	Campaign	Date	Reference	Cu^{2+} $\mu g L^{-1}$	DOC mg of C L^{-1}	IC mg of C L^{-1}	Comment
Jaguaribe	1	30/04/04	Ja101	nd	7.1	21.1	Mar
Jaguaribe	1	30/04/04	Ja102	nd	7.0	26.2	Barra
Jaguaribe	1	30/04/04	Ja103	2.1	10.4	25.2	Ilha Grande
Jaguaribe	1	30/04/04	Ja104	3.52	10.8	27.1	Raimundinho
Jaguaribe	1	30/04/04	Ja105	2.6	11.7	25.8	Aracati (quando ver ponte)
Jaguaribe	1	30/04/04	Ja106	3.26	7.5	25.9	Aracati (depois da ponte)
Jaguaribe	1	30/04/04	Ja107	1.92	19.0	24.4	Cabreiro
Jaguaribe	1	30/04/04	Ja108	1.64	0.26	23.2	Itaiçaba (antes da Barragem)
Jaguaribe	1	30/04/04	Ja109	1.63	20.6	22.4	Itaiçaba (depois da Barragem)
Jaguaribe	2	19/09/04	Ja201	nd	12.4	27.4	Mar
Jaguaribe	2	19/09/04	Ja202	nd	12.3	25.6	Barra
Jaguaribe	2	19/09/04	Ja203	nd	13.9	24.0	Ilha Grande
Jaguaribe	2	19/09/04	Ja204	nd	16.0	26.1	Raimundinho
Jaguaribe	2	19/09/04	Ja205	nd	17.0	24.4	Aracati (quando ver ponte)
Jaguaribe	2	19/09/04	Ja206	2.11	17.1	22.4	Aracati (depois da ponte)
Jaguaribe	2	19/09/04	Ja207	2.27	17.6	21.6	Cabreiro
Jaguaribe	2	19/09/04	Ja208	1.21	19.3	19.5	Itaiçaba (antes da Barragem)
Jaguaribe	2	19/09/04	Ja209	0.99	19.2	18.7	Itaiçaba (depois da Barragem)

**Fig. 10.17** The mangrove zone of the Jaguaribe River (Ilha Grande sampling stations)

drastically. From site 3–9 the fluorescence reaches the values of 500 u.a (arbitrary unit) and becomes quasi constant. In contrast, in September fluorescence values are weak (less than 400 u.a., Fig. 10.19) and one can observe from point 3 an increase in the fluorescence of peak A which represents the young organic matter. This is confirmed by graph (Fig. 10.20) where the ratio increases from point 3. One can also observe that the $r_{a,c}$ does not increase in April. This confirms a production of young organic matter at the end of the river path and at the end of the basin, where the influence of the sea is the greatest in the mangrove zone.

As the concentration of organic carbon increases in September, the $r_{a,c}$ increases only at three points in the basin near the sea. In other words, the carbon inputs are

variable up and down. The production of young organic material only takes place during the September sampling campaign in the basin of the Jaguaribe.

10.5.4 Results of the Temporal Study

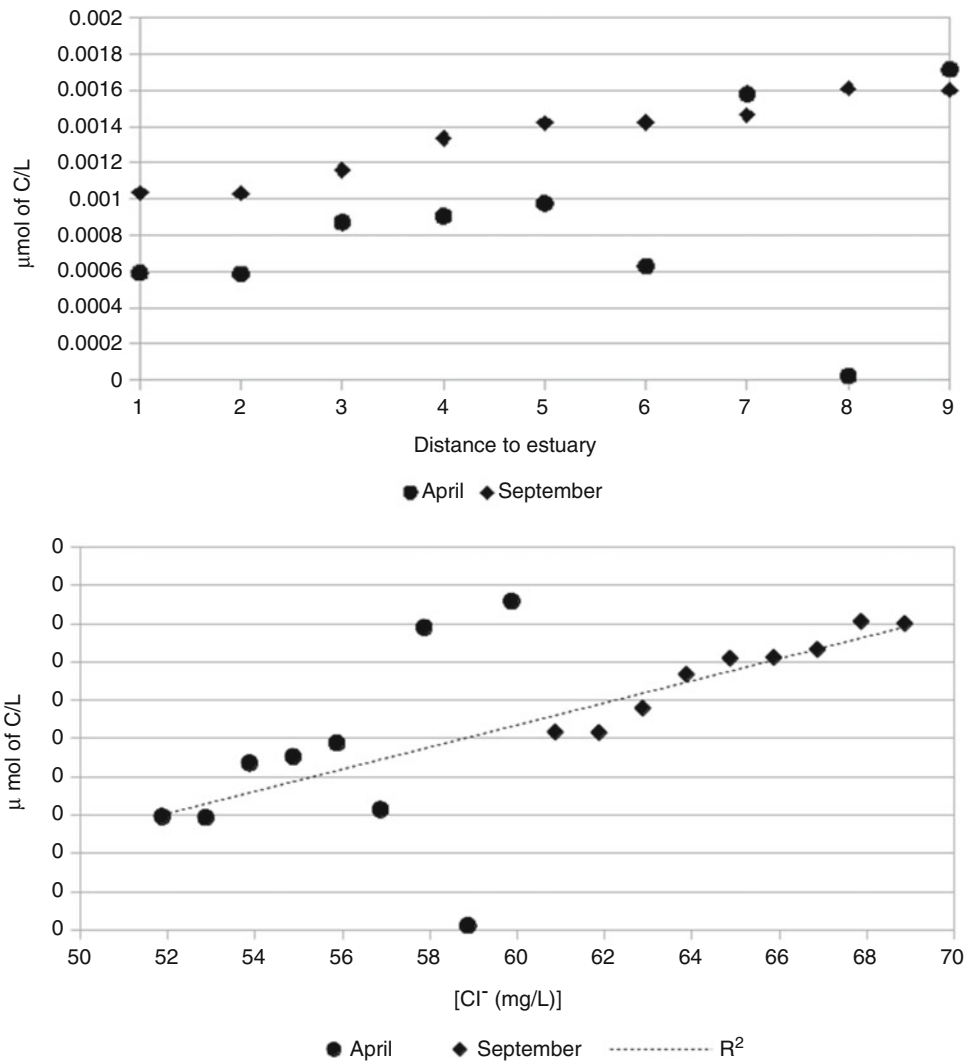
10.5.4.1 Organic Carbon, pH and Salinity

The salinity varies from 8 to 20 with a sinuous curve. The minimum salinity occurs at 11:35 p.m. and the maximums happen at 6:00 p.m. and 5:00 p.m. Maximum pH values were observed during highest salinity. The total organic carbon shows anomaly during the same moments (Fig. 10.21).

Table 10.5 Samples from the 20/06/04 field campaign for temporal studies during a tidal cycle

River	Number	Hour	Reference	Cu ²⁺ (µg L ⁻¹)	POC (mg of C L ⁻¹)	DOC (mg of C L ⁻¹)	IC (mg of C L ⁻¹)	T°C	Cond.mS cm ⁻¹	Sal.	pH
Jaguaribe	1	05h40	TJa01	2.87	1.00	17.9	37.0	26.0	30.65	18.2	7.91
Jaguaribe	2	06h35	TJa02	2.86	1.65	19.2	34.5	27.0	14.8	8.1	7.88
Jaguaribe	3	07h30	TJa03	2.84	3.15	19.9	29.1	28.0	1.19	0.6	8.01
Jaguaribe	4	08h35	TJa04	–	1.89	4.3	31.1	–	35.16	20.4	8.05
Jaguaribe	5	09h35	TJa05	2.48	2.09	0.2	30.2	–	33.39	19.1	8.03
Jaguaribe	6	10h40	TJa06	2.65	2.59	0.3	–	–	29.29	16.7	7.93
Jaguaribe	7	11h35	TJa07	2.50	2.33	20.6	31.5	–	24.33	13.8	7.95
Jaguaribe	8	12h50	TJa08	2.77	1.75	–	27.6	29.0	18.00	10.4	8.02
Jaguaribe	9	13h35	TJa09	3.18	2.27	20.7	26.1	29.2	15.68	8.4	8.17
Jaguaribe	10	14h30	TJa10	3.10	2.24	22.7	26.7	–	14.29	7.6	8.38
Jaguaribe	11	15h35	TJa11	3.13	2.61	–	30.3	28.1	7.76	4.0	8.22
Jaguaribe	12	16h35	TJa12	3.00	2.16	0.23	28.9	–	19.70	10.8	8.14
Jaguaribe	13	17h35	TJa13	7.38	2.02	18.9	26.1	–	25.17	14.2	–
Jaguaribe	14	18h35	TJa14	–	3.28	20.4	25.6	–	29.31	16.6	8.09
Jaguaribe	15	19h25	TJa15	2.34	1.75	21.8	23.7	–	30.89	17.8	8.13

Fig. 10.18 Variation of the dissolved organic carbon during the two sampling campaigns and the relation to salinity



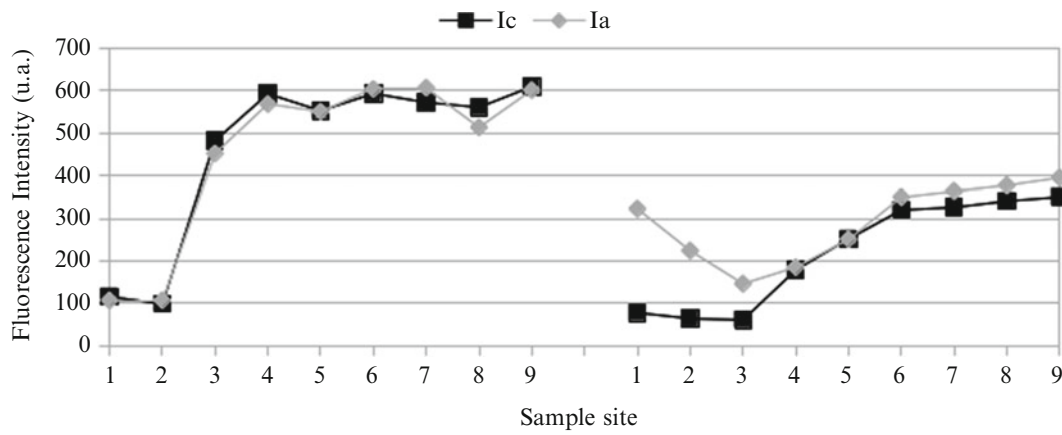


Fig. 10.19 Fluorescence of peaks A (dark square) and C (gray losange) (Coble 1996) in the Jaguaribe river basin, in April (left) and September (right)

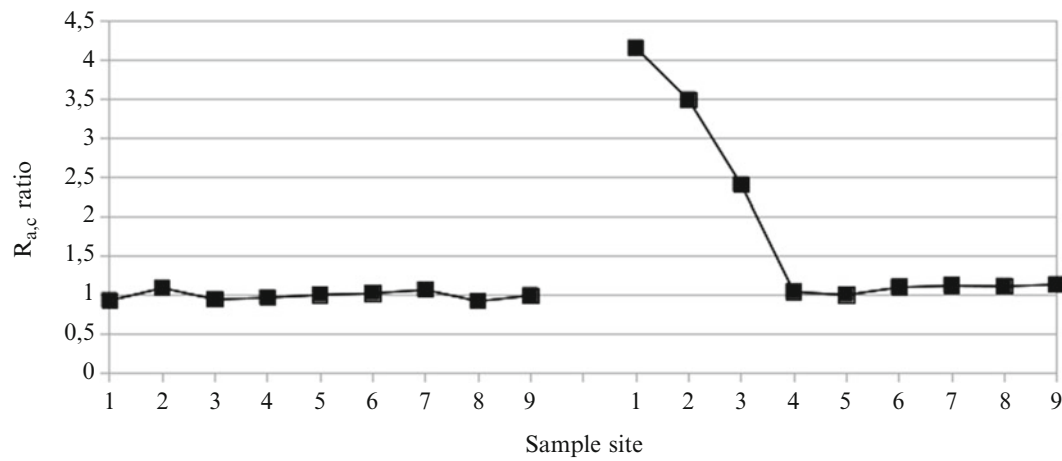


Fig. 10.20 Reason for fluorescence intensity of the Jaguaribe river basin in April (left) and September (right)

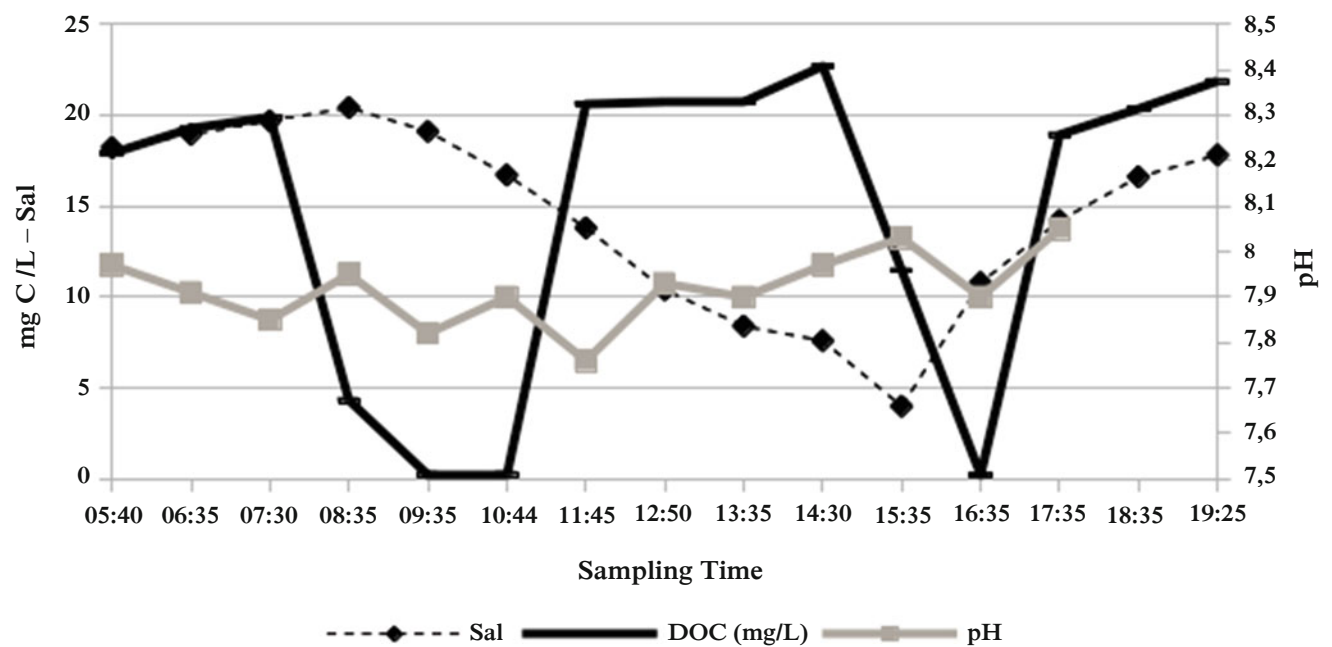


Fig. 10.21 Variation of carbon, pH and salinity during a tidal episode

10.5.4.2 Fluorescence Spectroscopy

The fluorescence of peaks A and C in the Jaguaribe River shows a maximum during low tide when the influence of the sea minor the salinity is lowest. The fluorescence increases to 500 versus 300 when the salinity is to the maximum (Fig. 10.22).

From the graph in Fig. 10.23, we can see that the ratio is quasi constant throughout the tidal period after 7H30 a.m. This means that there is no variation in the quality of the organic material, either in low or high tide. The variation of concentration comes solely from the dilution of river waters by sea waters and does not change the carbon quality. The rapid increase from 5H40 to 7H40 suggests a different

biogeodynamic, less juvenil fluorescent dissolved organic matter during the night that should be investigated.

At least we can note that this variation does not match the variations of dissolved organic carbon. One can consider that during the tide the quality of carbon is constant during the event, even if its quantity changes.

The 3D fluorescence of Jaguaribe samples during the tide shows that the quality of the fluorescent organic matter is constant. There is a peak excited at 380 nm with an emission around 430 nm (Fig. 10.24). Only the intensity seems to change during the sampled tidal cycle. These data were treated by CP/PARAFAC to extract subtle variations that occurred during the event.

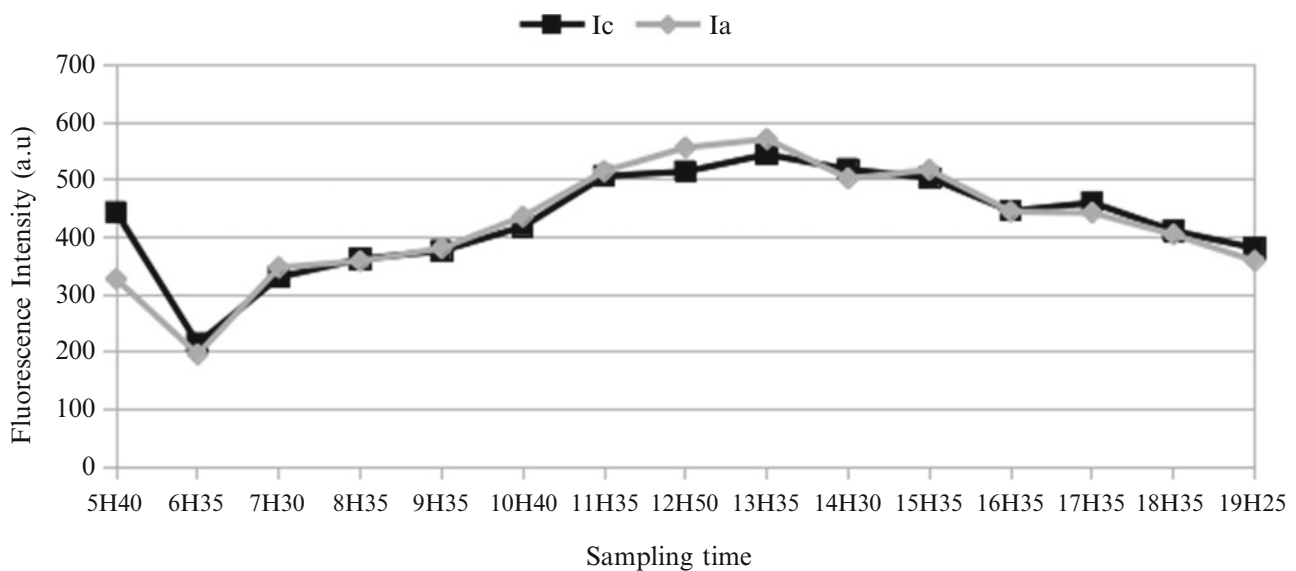


Fig. 10.22 Fluorescence of peaks A and C for the Jaguaribe River in April during the temporal sampling

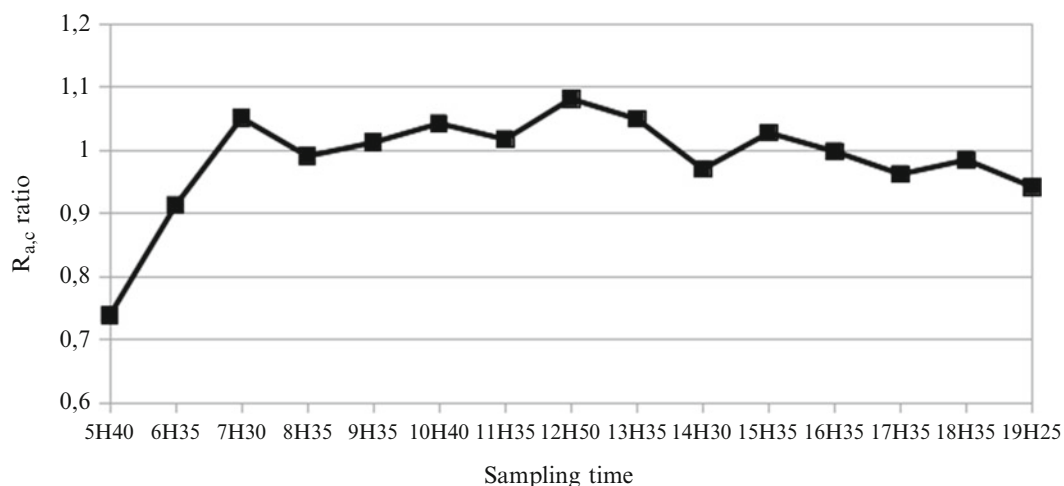


Fig. 10.23 Values the ratio $R_{a,c}$ for the Jaguaribe river in April during the temporal sampling

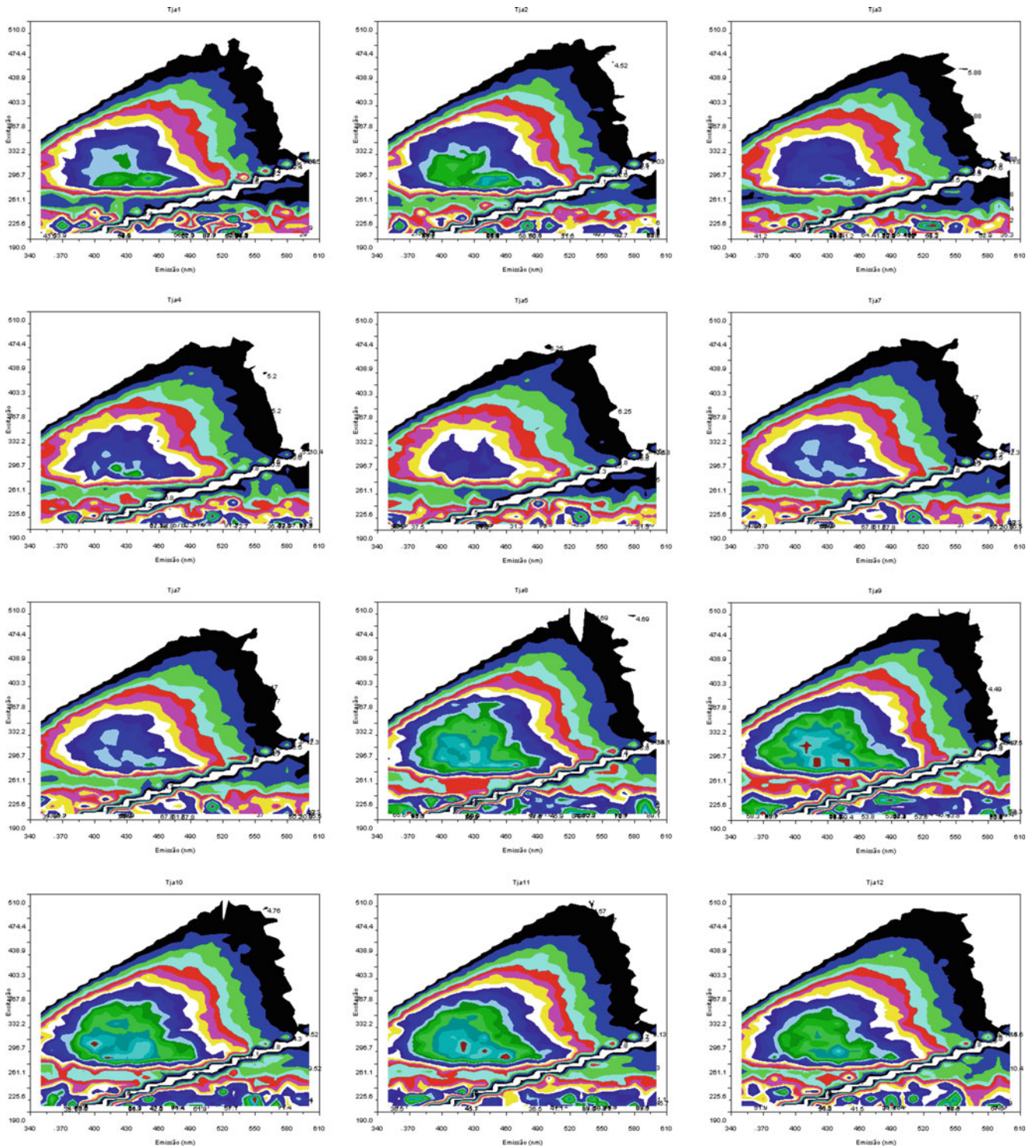


Fig. 10.24 Excitation Emission Matrices of fluorescence of the Jaguaribe representing fluorescent organic matter during tide event (in false colour).

10.5.5 Variation of the Major Elements

10.5.5.1 Space Strategy

Changes in cation and anion concentrations in the Jaguaribe River Basin in April and September 2004 are represented respectively in Figs. 10.25 and 10.26. We observed a higher mean concentration for all elements again in September. Particularly Na^+ with highest concentrations in point 6 (Aracati downstream the bridge). It also has an inland sea influence in September with a strong concentration of K^+ , Na^+ and Ca^{2+} up to point 6 in September versus point 3 in April.

Except for the anomaly of K^+ in point 4 in April (Raimundinho), the waters are therefore sodic.

Representing the K^+ , Mg^{2+} and the Ca^{2+} concentration versus the Na^+ one (Fig. 10.26), it is observed that except for the river before the dam, sample site 9, the cations concentration are highly correlated to the Na^+ , which represent the sea influence. The point 6 differs from its K^+ and Ca^{2+} concentration that confirms it out of sea influence behaviour.

The anions concentrations are also controlled by the sea influence for Cl^- and $(\text{HCO}_3^-, \text{CO}_3^{2-})$, except for site 2 in September (Fig. 10.27). For NO_3^- and SO_4^{2-} anions, it is

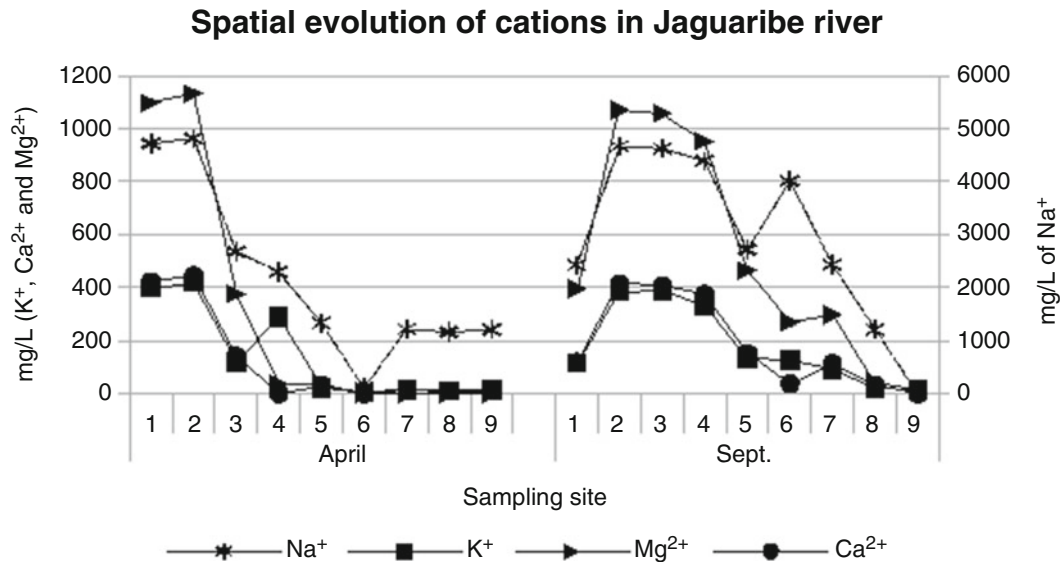


Fig. 10.25 Variation of cations in the Jaguaribe River basin in April (left) and in September (right)

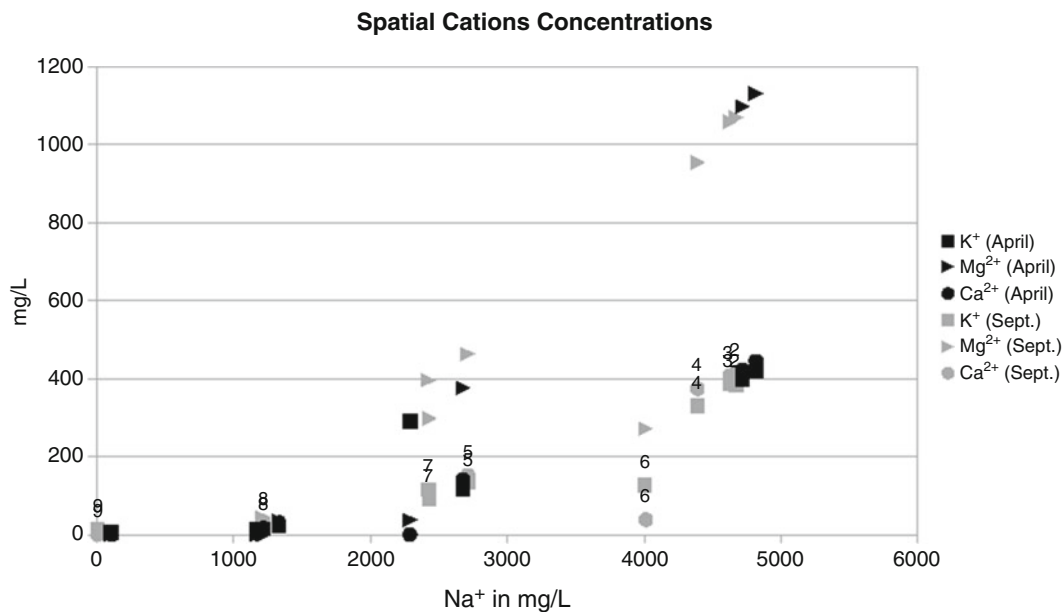


Fig. 10.26 Sodium to cations concentration relation for the Jaguaribe River along downstream

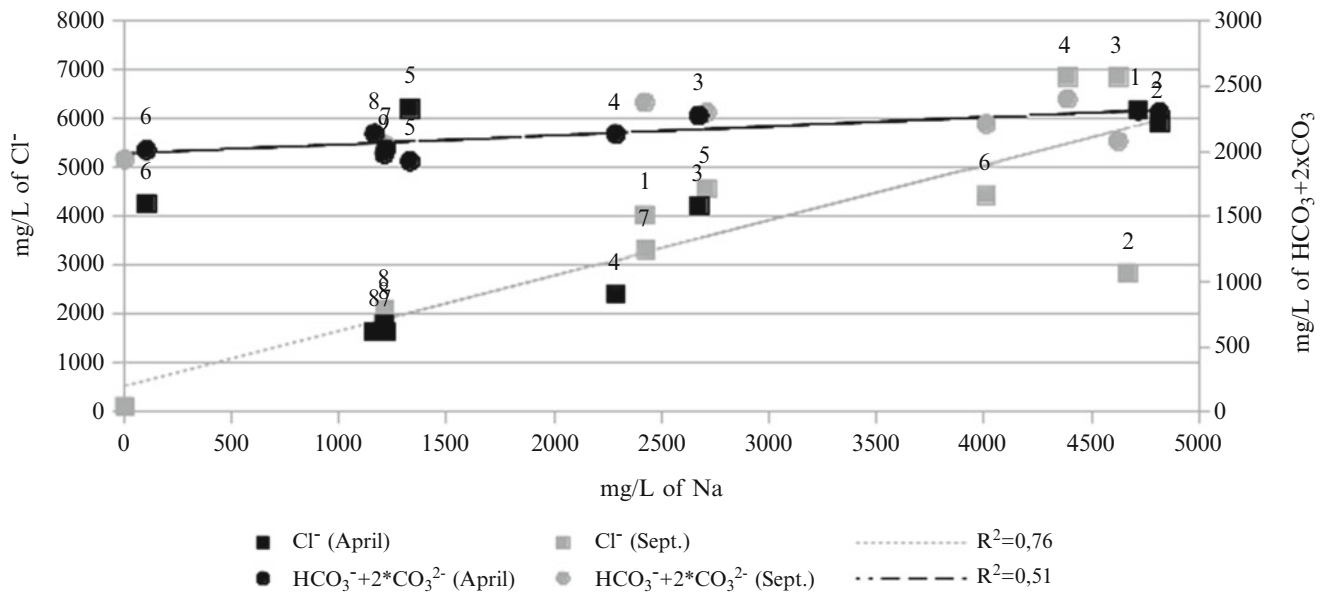


Fig. 10.27 Variation of the anions in the Jaguaribe basin in April (left) and in September (right)

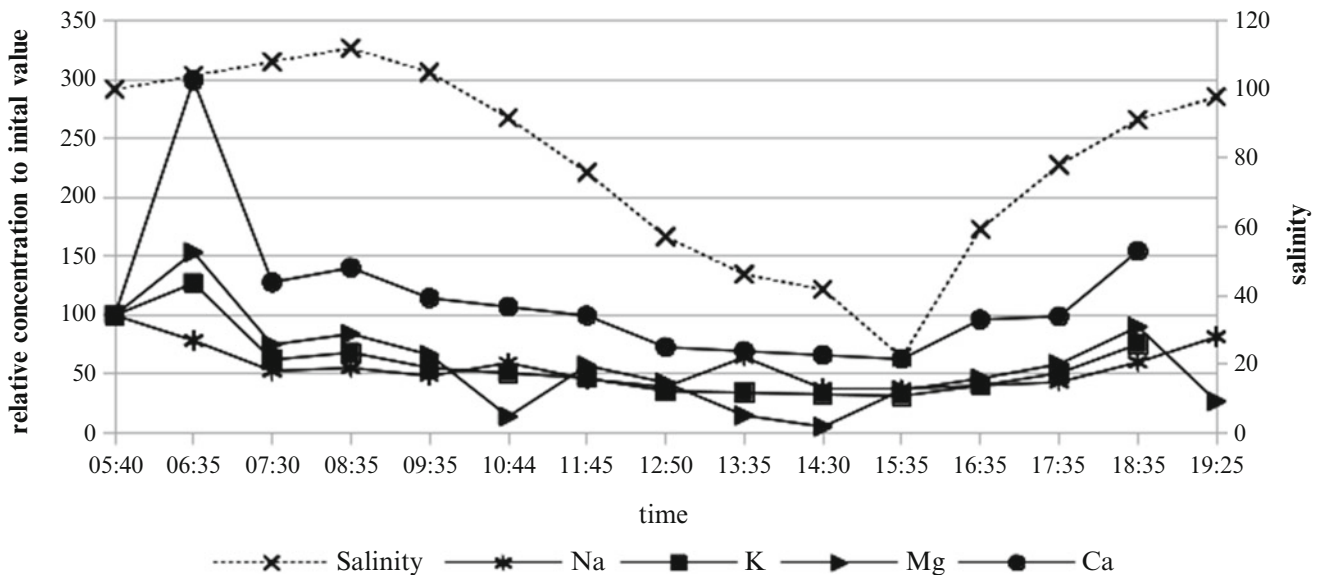


Fig. 10.28 Variation of the cations in the Jaguaribe basin during the temporal sampling

clear that the concentrations decrease after the sea influence. In the Jaguaribe, the carbonates are highly stable and represent with the Cl^- the major anions.

10.5.5.2 Time Strategy

The temporal sampling in April is presented in Fig. 10.28 for the cations and in Fig. 10.29 for the anions. The graph represents the percentage variation of the initial concentration to accentuate the relationship with the salinity. The salinity

starts at 18.2 with a maximum of 20.4–08:30. The minimum of salinity occurs in the afternoon around 3:30 p.m. and has a salinity of 4. The results in concentrations are summarized in Table 10.6. Clearly the concentrations in cations and anions are normally associated with salinity. The most concentrated element is Ca^{2+} (Fig. 10.28). For the other elements concentration, it decreases until the minimum salinity is reached.

These results do not show an influence of the activities above the sampling point. Except the first point in the early

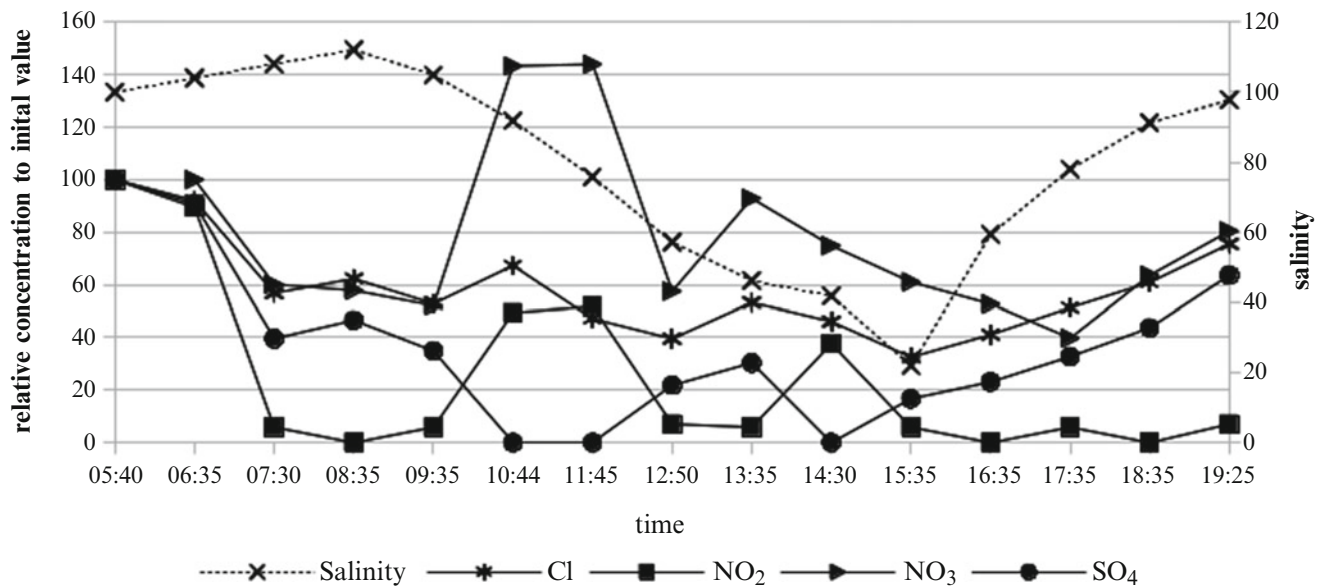


Fig. 10.29 Variation of the anions in the Jaguaribe basin during the temporal sampling

Table 10.6 Results on larger elements of temporal sampling

Ref	Hour	Sal.	Anion in mol L ⁻¹ (*1000)					Cation in mol L ⁻¹ (*1000)				
			HPO ₄ ²⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Tja01	05:40	18.2	ND	183	1	ND	18	193	ND	4	18	2
Tja02	06:35	—	ND	169	1	8	16	151	ND	5	28	6
Tja03	07:30	—	ND	104	ND	5	7	101	ND	3	14	3
Tja04	08:35	20.4	ND	114	ND	5	8	106	ND	3	16	3
Tja05	09:35	19.1	ND	97	ND	4	6	93	ND	2	12	2
Tja06	10:44	16.7	ND	123	ND	12	0	115	6	14	3	ND
Tja07	11:45	13.8	ND	86	ND	12	0	88	ND	2	11	2
Tja08	12:50	10.4	ND	72	ND	5	4	75	ND	1	8	2
Tja09	13:35	8.4	ND	98	ND	8	5	124	5	12	3	ND
Tja10	14:30	7.6	ND	84	ND	6	ND	74	ND	6	1	ND
Tja11	15:35	4.0	ND	60	ND	5	3	72	ND	1	7	1
Tja12	16:35	10.8	ND	75	ND	4	4	77	ND	2	9	2
Tja13	17:35	14.2	ND	94	ND	3	6	83	ND	2	11	2
Tja14	18:35	16.6	ND	112	ND	5	8	116	ND	3	17	3
Tja15	19,25	17.8	ND	138	ND	7	11	157	21	23	5	ND

morning that could be an outlier, there is a perfect correlation between the Na⁺ concentration and the Ca²⁺, Mg²⁺ concentration. Considering that Na⁺ is principally coming from sea, this means that during the Jaguaribe tide event, there is only mixing of water. The two nitrate concentrations (10:00–11:00) should be pointed out that there is a pulse during this period coming from the mangroves but this must be confirmed. The same trend is observed for the anions where correlation of Cl⁻ and SO₄²⁻ is about $r^2 = 0.88$ and $r^2 = 0.85$ respectively, while the carbonate is quite constant during the tide as it does not represent a good sea end member. In conclusion, there is no entry of major elements during the tidal episode sampled in this experiment.

10.6 Conclusion

This work allowed for the first characterization of natural organic matter within two zones of mangrove, one urban (Cocó River) and another less affected by urban activities (Pacoti River). A characterization of the Jaguaribe River basin was also made temporally and spatially. The results showed that the two mangrove zones in the Fortaleza metropolitan area are very similar from the point of view of larger elements and the 2D or 3D fluorescence. However, they showed slight differences in the quality of the organic matter in relation to the metals complexing and the intensity of

fluorescence. The Cocó River basin seems to have a production of specific organic matter. The properties of complexation then can appear weak for the Cocó river with a higher production of young (fulvic-like) less complexing organic matter. Also, the ability to fluoresce is greater for the organic matter of this zone. These differences appear throughout the sampling period showing that it is not in relation to time, but to human activities, which mainly influence the quality and behaviour of the two mangrove areas.

For the lower part of the Jaguaribe River, measurements of dissolved organic carbon and major elements were made. A comparison of the results showed a strong seasonal variability, with concentrations generally higher in September (dry season) than in April (rainy season). There is a steady decrease in concentrations from more inland stations to sea-influenced ones. No external or unusual inputs were detected. The influence of the sea is visible up to point 5 (Aracati) in September but only to point 3 (Ilha Grande) in April. During the tide, there is only variation of the elements with the salinity. The fluorescence failed to detect any specific processes during the tidal cycle.

During this study many measures were performed. It has shown a strong influence of the urbanization on the geochemistry of the organic material produced in the mangrove zones. This modification may play an important role in the transport of pollutants such as metals.

In the future it would be necessary to do a more complete study on the flows coming in and out of the mangrove zone. Also a study on metals at the same time could be important to really understand what happens in that zone and the consequences on coastal geochemistry.

Acknowledgement This work was supported by the Brazilian Research Center (CNPq, Processo n° 309342/3003-4), the Toulon University (CRCT Campaign 2004) and PQ 309718/2016-3 to RVM. The FUNCAP/CNPq PRONEX Project PR2-0101-00052.01.00/15, also supported part of this study.

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