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Chapter X

Characterization of the Ceara Costal Zone Organic Matter Inputs

Stéphane Jean Louis MOUNIER[†], Rozane Valente MARINS[‡], Luiz Drude LACERDA[‡]

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Abstract : Mangroves are extremely sensitive to the global climate change and urbanization impacts. To understand the effect of the urbanization on the organic matter of the coastal zone of Ceará State in north eastern Brazil, a seasonal field campaigns were carried on in two most environmentally significant river/mangrove systems in 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. A spatial study was also done along the Jaguaribe river, which is the largest river in the state also connected to the largest 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 area is different, meaning 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

[†] Laboratoire PROTEE, Université de Toulon, CS 60584, TOULON Cedex 09, France
e-mail: stephane.mounier@univ-tln.fr

[‡] Universidade Federal do Ceara, LABOMAR, Av. Abolição, 3207, Fortaleza, CE, 60165-081, FORTALEZA, Brazil

Introduction :

The global dispersion of man-made pollutants in pristine systems and the high levels of metals raises serious questions about their effects on the 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, oceanic 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 induced changes in ecosystem's functioning. The objectives of this work are to investigated 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 Northeastern Brazil.

Sites study.

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 hectares 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 (figure 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 1 summarizes the geographical information for the four river basins studied.

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

Tableau 1: Extention and basin areas of the studied rivers and their respective mangrove areas



Figure 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.

Description of the studied basins.

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 meeting with the Coaçu river, basin area of 375 hectares, most of them covered by mangroves that expands up to 11 km inland (Miranda et al., 1988; SDU, 1994). Human impact of men 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 (Beltrão and Manoel Filho, 1973) 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 harbors many species of grasses and shrubs, coconut, hose, cashew. Mangrove vegetation harbors 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 waste water treatment station (WWTS) built since 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 1.

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

Table 2: Annual anthropogenic emissions (ton.yr-1) of N, P, Cu, Zn, Pb, Cd and Hg to the lower basins of the four studied rivers (Lacerda et al., 2008; SEMACE, 2005).

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 - 21/05/91).

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, Guaiuba. The Pacoti river flows through some small towns and possesses many small islands. The mangroves in its estuary cover 158 hectares (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., 1991; George Satander Sá Freire et al., 1991). In this river human impact is weak because the activities are dominated by cattle raising and exploitation of the forest. This mangrove is chemically reductive because of the presence of large amount of organic matter (Freire et al., 1991; Freire and Maia, 1991).

The Ceara river

The source of the river Ceara is born in the Maranguape hill. The 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. Mangrove land is 675 ha (Miranda et al., 1988) 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. 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 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 to compare with them. The population density was less than 30 hab.km⁻² with a total population of 2,064,535 (data of 1996) (Gatto, 1999). The main uses of the space is 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 pyriformis*, *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 to 1,200 mm) and varies in temperature between 24 °C and 27 °C.

In the lower basin inshore fishing, shrimp farming, lobster and crab are the major extractive activities. The Jaguaribe River is a well-regulated river that has many dams (Table 2). The control is done by 17 rain stations, 4 on the main course and 13 on the tributaries. During the low waters the flow of the Jaguaribe is controlled by the large Castanhão dam and is about 20 m³.s⁻¹ downstream. 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). All the studied rivers show a varied state of human impact, particularly from Figure 1. The Jaguaribe river Basin compared to the metropolitan basin in Ceará State, north eastern Brazil. 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 microorganisms; toxicology and sediment quality and contamination by nutrients and metals (Nilin et al., 2013). A summary of anthropogenic emissions of nutrients and selected trace metals is presented in table 2.

<i>Dam</i>	<i>localisation</i>	<i>River</i>	<i>Capacity 1000 m³</i>	<i>Alt.</i>	<i>Made in ...</i>
Alto Jaguaribe					
Caiçaras	Tauá	Riacho Carrapateira	1,072	6	1988
Favelas	Tauá	Riacho Favela	30,100	18	1988
Forquilha I	Tauá	Riacho Carrapateira	3,000	12.6	1988
Orós	Orós	Jaguaribe	2,100,000	54	1961
P. da Pedra	C. sales	Conceição	52,000	31.4	1958
V. do Boi	Tauá	Riacho Carrapateira	51,900	17.4	1954
Médio Jaguaribe					
Ema	Iracema	Iracema	10,395	18.5	1932
Feiticeiro	Jaguaribe	Feiticeiro	24,105	20.5	1933
N. Floresta	Jaguaribe	M. Lopes	7,619	15.6	1926
P. do Barro	M. Nova	Livramento	54,704	23	1956
R. Sangue	Solonópole	R. Sangue	68,194	24	1918
Velame	Jaguaribara	R. Velame	2,566	8.5	1920
Castanhão	Jaguaribara	R. Jaguaribe	6,700,000	10	2004
Baixo Jaguaribe					
L. Pombas	Aracati	L. Pombas	2,231	4.6	1910
S.A. Russas	Russas	Palhano	24,000	14	1928
Bacia do rios Salgado					
Gomes	Mauriti	R. Gomes	2,394	29	1967
L. Campos	Icó	R.S. João	66,382	19	1932
Quixibinha	Mauriti	R. Bois	32,150	35	1967
R. Carneiros	Caririaçu	R. Carneiros	37,181	35,3	1985
Umari	Crato	Carás	28,788	28,7	1982
Bacia do rio Banabuiú					
Banabuiú	Banabuiú	Banabuiú	1,700,000	57,7	1966
Cedro	Quixadá	Sitiá	125,684	20	1906
M.J. Cândido	B. Viagem	R. Fernandes	3,863	19.5	1967
Patu	S. Pompeu	Patu	71,829	44.4	1987
P. Brancas	Quixadá	Sitiá	434,049	33.6	1978
Quixeramobim	Quixeramobim	Quixeramobim	54,000	13.8	1960

Table 3: Dams on the Jaguaribe River Basin (ANEL)

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 Banabuiú river presents mixed waters with chloride and sodium. Eighty percent (80%) of the basin drains a crystalline rock geology with weak hydraulic potentiality. The groundwater is chloro-mixed to chloro-sodium.

Particularity of mangroves.

Mangroves are particularly sensitive ecologically (Blasco et al., 1996) and chemically (Otero and Macías, 2002) sensitive ecosystems. 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 (Esteves 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 μM to 2,043 μM , depending on season and location and has no visible transition between the terrestrial and the marine end-membre 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 condition 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). Also the dam construction modifies physical-chemical condition that alter the flow and speed producing an erosion of the coast and a migration or a destruction of the mangroves. 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 lead to an important response of the mangrove ecosystem that can die, move, 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.

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 μ l 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 using a on field multi-parameter instrument for pH, dissolved oxygen, conductivity. The probes were calibrated before each measurement. The results are presented in table 5.

River	Field number	Date	Reference	T (°C)	Cond. ($\mu\text{S.cm}^{-1}$)	pH	Sal.	O ₂ (mg.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	28,1	949	6,38	0,5	0,48	Mangrove.
Cocó	1	07/05/04	Co103	29,1	46600	7,8	30	2,5	Marine
Pacoti	1	25/05/04	Pa101	28,7	2008	6,38	0,9	3,8	River
Pacoti	1	25/05/04	Pa102	29,5	54300	8,2	35,4	4,6	Mangrove
Pacoti	1	25/05/04	Pa103	29,1	54500	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	53100	8,12	35	3,2	Marine
Pacoti	2	09/06/04	Pa201	27	3332	6,75	1,7	4,5	River
Pacoti	2	09/06/04	Pa202	27,4	56600	8,23	35,7	4,6	Mangrove
Pacoti	2	09/06/04	Pa203	27,2	56400	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	7,09	0,2	5,8	Mangrove
Cocó	3	30/06/04	Co303	28,3	52700	8,1	34,6	4,7	Marine
Pacoti	3	30/06/04	Pa301	27	916	5,68	0,4	3,83	River
Pacoti	3	30/06/04	Pa302	28,9	12220	6,25	6,4	3,63	Mangrove.
Pacoti	3	30/06/04	Pa303	28,3	29770	6,93	17,2	3,95	Marine
Cocó	4	04/08/04	Co401	25,8	753	7,07	0,3	5	River
Cocó	4	04/08/04	Co402	25,8	2566	7,67	1,3	3,6	Mangrove
Cocó	4	04/08/04	Co403	25,8	52100	8,21	32,9	3,3	Marine
Pacoti	4	04/08/04	Pa401	25,7	3772	8,04	1,9	4,9	River
Pacoti	4	04/08/04	Pa402	25,5	54000	8,2	34,3	4	Mangrove
Pacoti	4	04/08/04	Pa403	25,5	54100	8,29	34,4	4,9	Marine
Cocó	5	27/08/04	Co501	-	878	6,62	0,4	5,49	River
Cocó	5	27/08/04	Co502	-	839	6,9	0,5	4,98	Mangrove
Cocó	5	27/08/04	Co503	-	30670	7,01	20,5	5	Marine
Pacoti	5	27/08/04	Pa501	-	8190	8,33	4,5	6,04	River
Pacoti	5	27/08/04	Pa502	-	41420	8	26,6	4,52	Mangrove
Pacoti	5	27/08/04	Pa503	-	49250	7,31	32,3	4,45	Marine
Cocó	6	17/09/04	Co601	27,6	752	6,99	0,4	4,9	River
Cocó	6	17/09/04	Co602	26	7310	7,01	4	3,3	Mangrove
Cocó	6	17/09/04	Co603	27,2	51400	8,09	33,7	3,5	Marine
Pacoti	6	17/09/04	Co601	27,5	8550	8,12	4,7	4,5	River
Pacoti	6	17/09/04	Co602	26,9	53500	8,13	35,3	5,2	Mangrove
Pacoti	6	17/09/04	Co603	26,7	53300	8,18	35,2	5,4	Marine

Table 4: 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.

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 Na₂CO₃ 9Mm, 950mg.L⁻¹ and methane sulfonic acid (M.S.A) 20mM, 1.3 mL.L⁻¹. The flow rate was set at 1 mL.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 5N 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 ppm 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.

Results

Dissolved and Particulate organic carbon

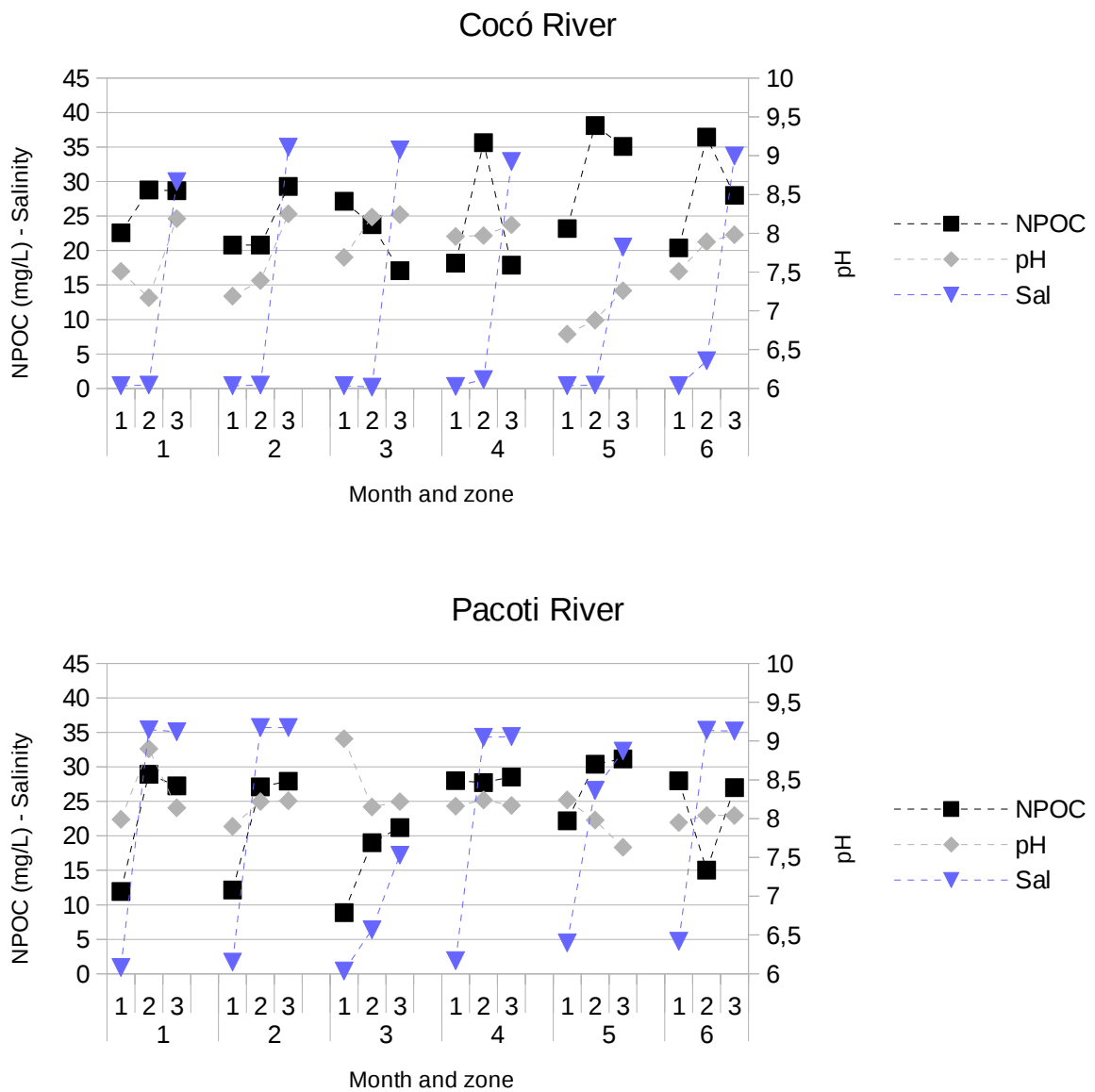


Figure 2: Results of dissolved organic carbon concentration in ppm (black square), salinity (blue triangle) and pH (grey losange) for the Cocó and Pacoti rivers. Points 1, 2, 3 representing the river, mangrove and marine zones respectively.

The results presented in Figure 3 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 $0.2 \text{ mg of C L}^{-1} (\pm 0.1)$ except for the Cocó river at the river zone where a greater variability is observed leading to an average value of $0.5 \pm 0.6 \text{ mg of C L}^{-1}$.

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.

Fluorescence spectroscopy

The 2D fluorescence

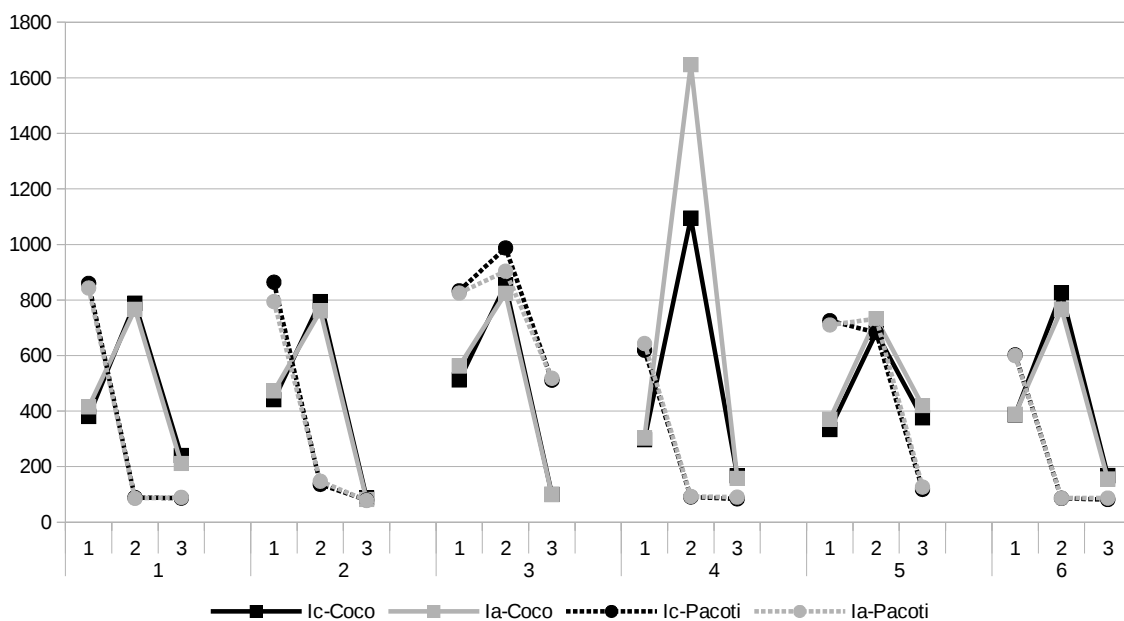


Figure 3: Fluorescence of Ic and Ia (dark and grey solid, respectively) of the Cocó river and fluorescence Ic and Ia of the Pacoti river samples (dark and grey dashed, respectively)

The measurement of the fluorescence intensity at peak A ($\lambda_{ex} = 250 / \lambda_{em} = 450$) and peak C ($\lambda_{ex} = 350 / \lambda_{em} = 450$) shows that for the Cocó River intensity is higher for the mangrove area (figure 4, 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.

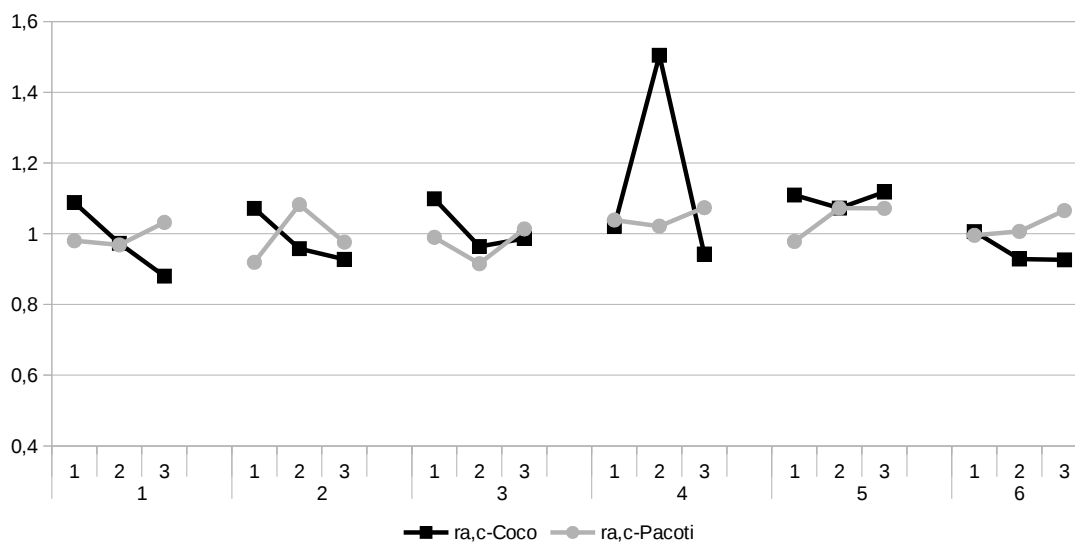


Figure 4: Ratio for the fluorescence peaks of the Cocó and Pacoti rivers

Observing the ratio of the two intensity 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 (figure 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 (Figures 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.

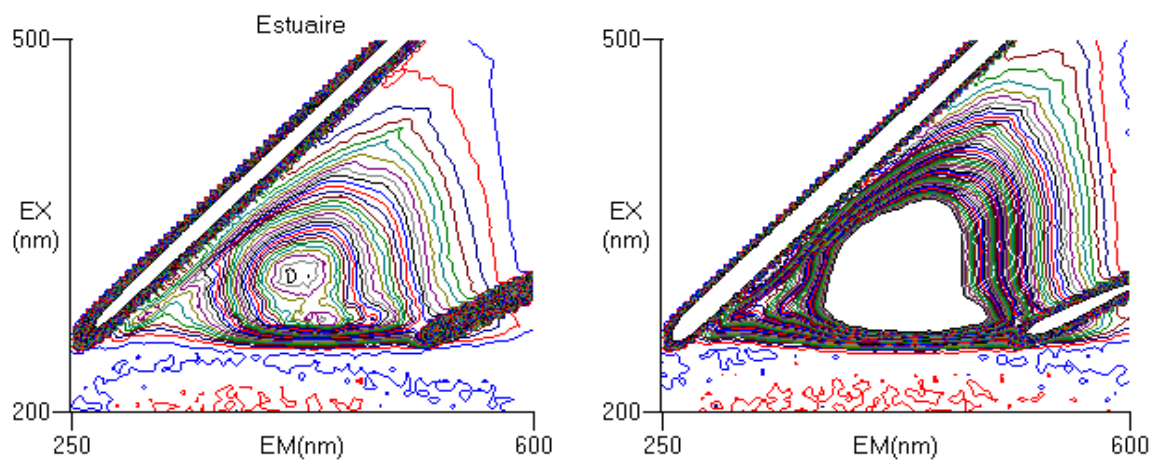


Figure 5: Excitation emission fluorescence matrices example of the Cocó water river (left) and the Pacoti river (right).

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 figures 6 and 7.

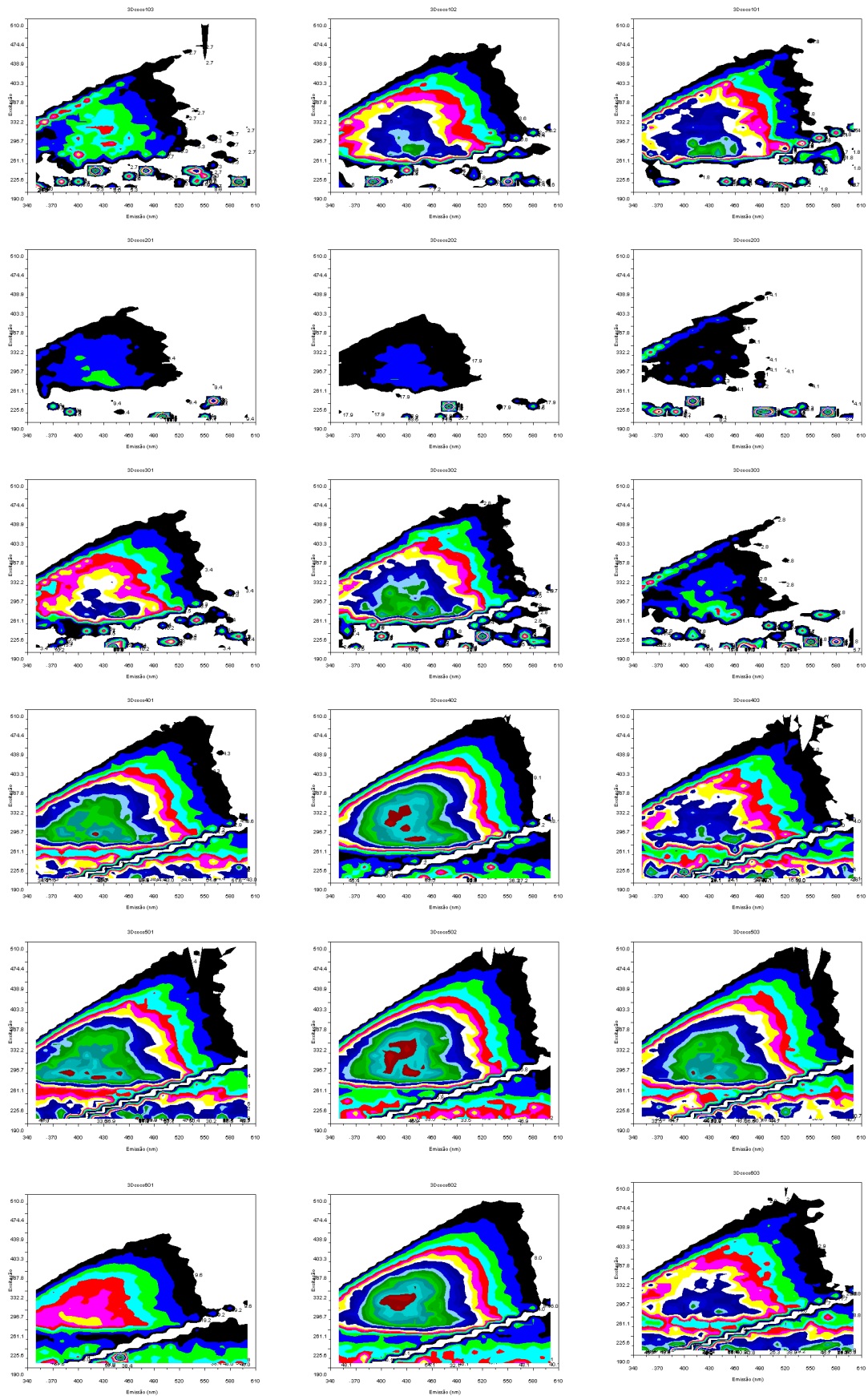


Figure 6: Excitation Emission Matrices of the Cocó river false colour representation. Column 1,2 and 3 represent the river, mangrove and marine zones and line represent the line correspond to field campaign 1,2,3,4,5 and 6.

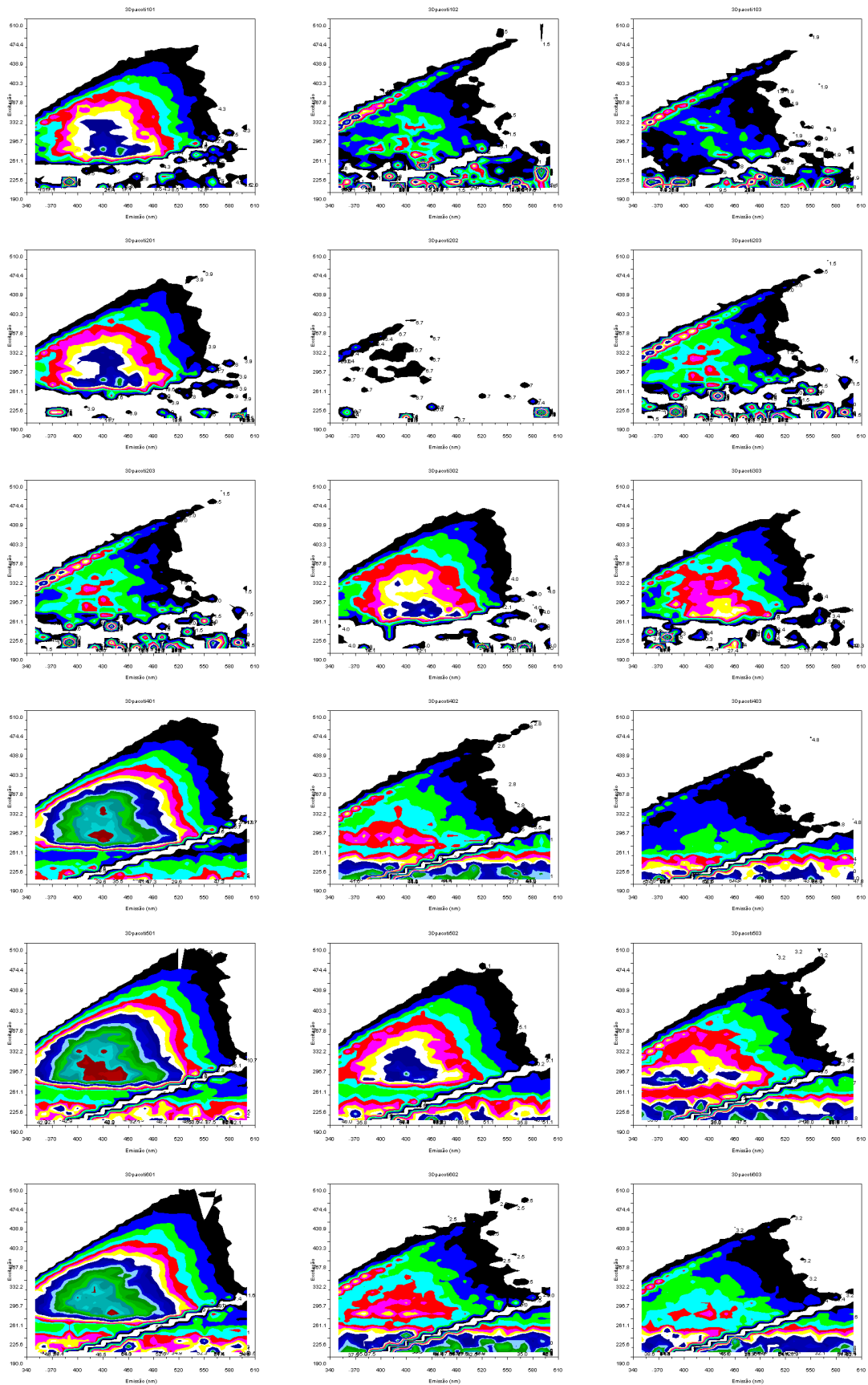


Figure 7: Excitation Emission Matrices of the Pacot river false colour representation. Column 1,2 and 3 represent the river, mangrove and marine zones and line represent the line correspond to field campaign 1,2,3,4,5 and 6.

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 figures 8.

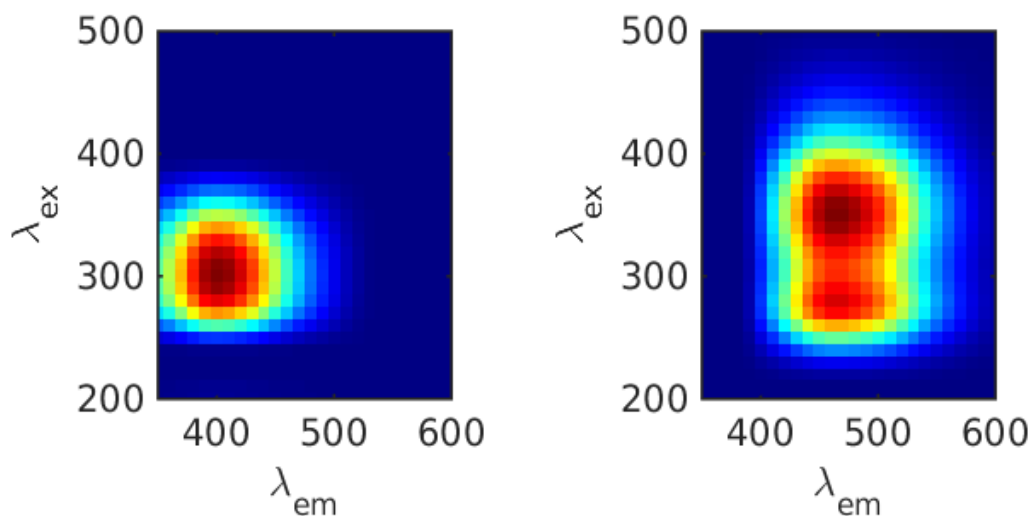


Figure 8: PARAFAC component extracted from the Cocó and Pacoti rivers excitation emission matrices of fluorescence.

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 possible fluorescence biological activity was not statistically extracted.

Their evolution along the rivers and during the time are shown in figure 9. The Cocó river presents an 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 (figure 9). Particularly during the campaign 4, 5 and 6 when the difference is bigger. The C2 component on the contrary does not vary. The urban impacted mangrove zone produce more fulvic components. This is confirmed by the $r_{a,c}$ ratio that is systematically higher zone the mangrove zone except for the campaign 1 and 2 (figure 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 zone. In field 1 to 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.

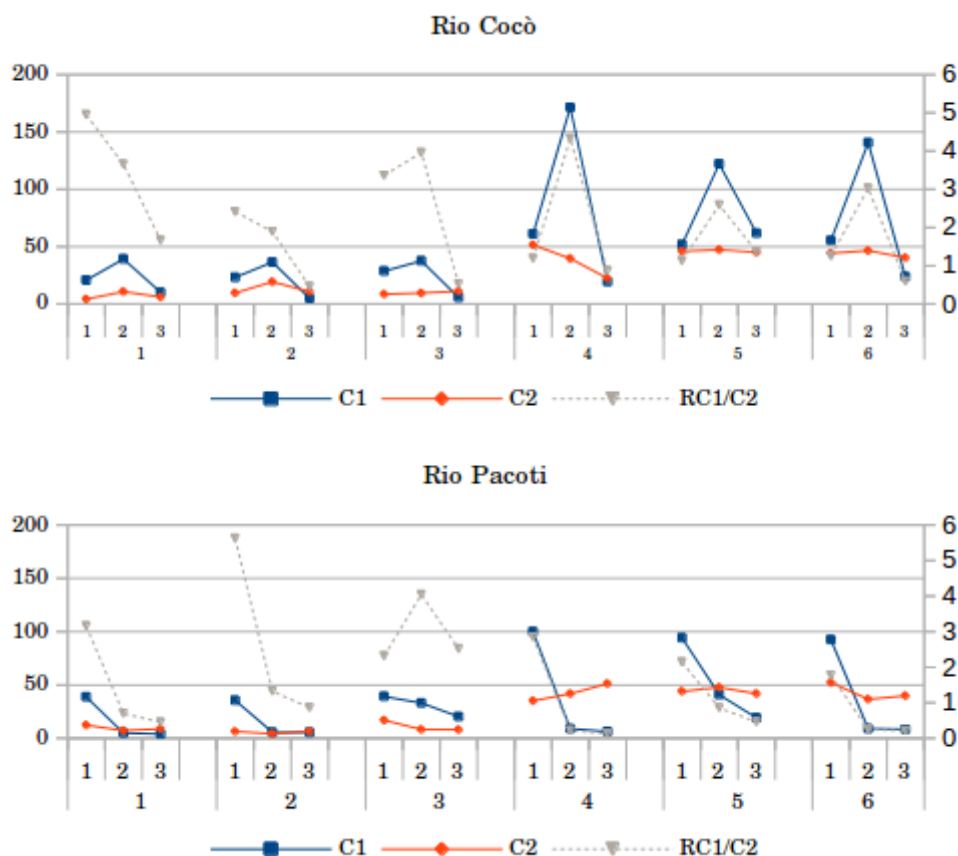


Figure 9: Evolution of the contribution of the CP/PARAFAC components along the rivers. The component C1 and C2 are represented by the blue and red solid line respectively. The ratio of their contribution C1/C2 is represented by the grey dashed line.

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 where 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.

Major elements:

The cations

The concentrations of the cations (figure 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⁺.

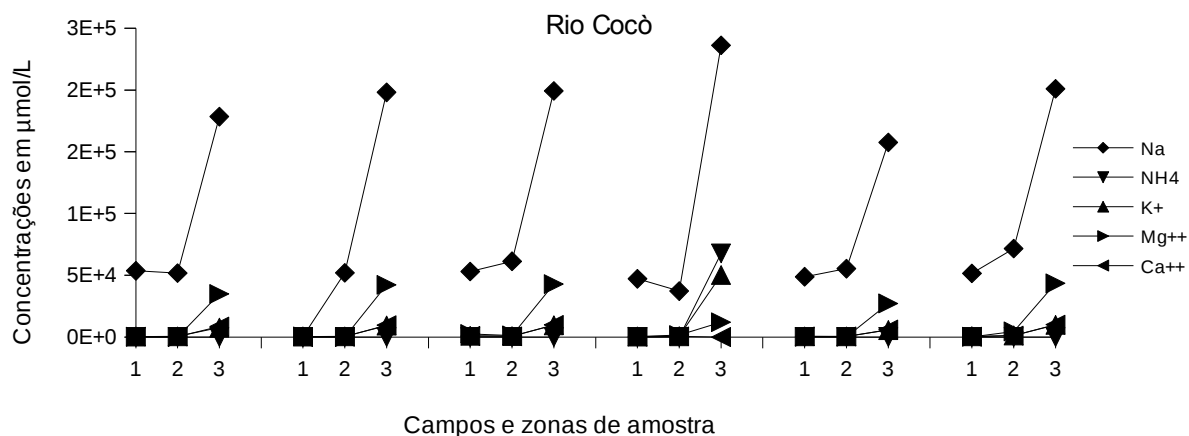


Figure 10: Variation of cation concentration in the Cocó River

The patterns for the Pacoti river are different but have the same relation as the same influence related to the sea, with an increase of the Mg^{2+} and Na^+ concentration. One can see that the Pacoti river is more invaded by the sea intrusion in the mangrove zone (figure 11) than the Cocó river.

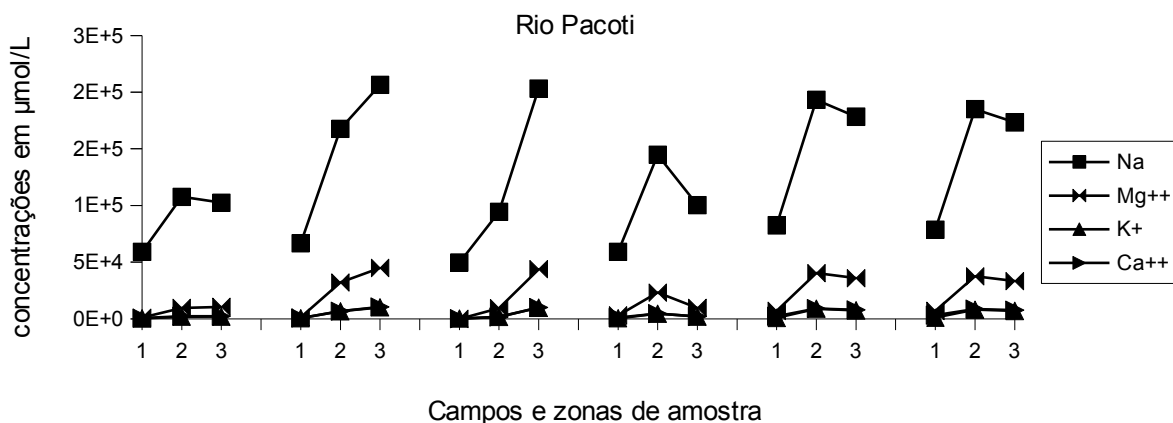


Figure 11: Variations of cation concentrations in the Pacoti River.

The anions

The anion concentrations in the Cocó river are shown in (figure 12 and 13). The increase of concentrations results from the influence of seawater. Except for nitrate and sulphate that disappear when salinity increases.

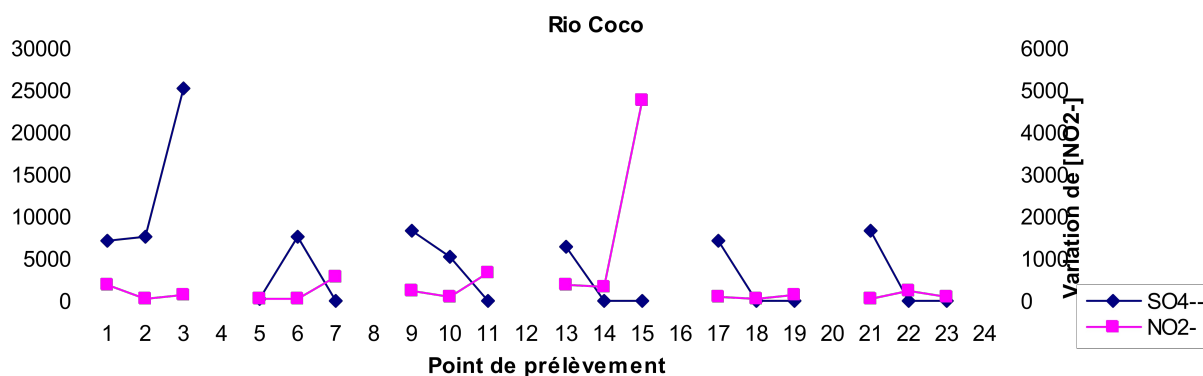


Figura 12: Variation of sulfate and nitrate concentration in the Cocó River

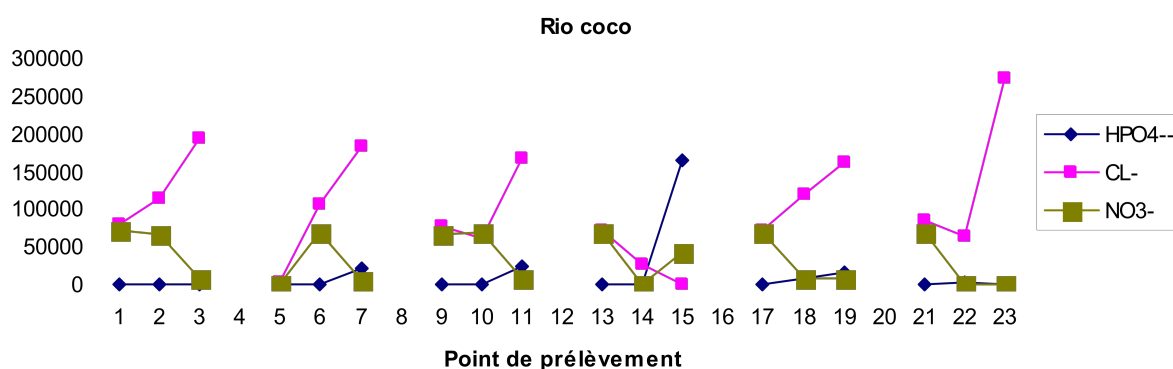


Figura 13: Variation of phosphate, chloride and nitrate concentration in the Cocó River

The Pacoti river again does not presents the same variation as the Cocó river (Figure 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.

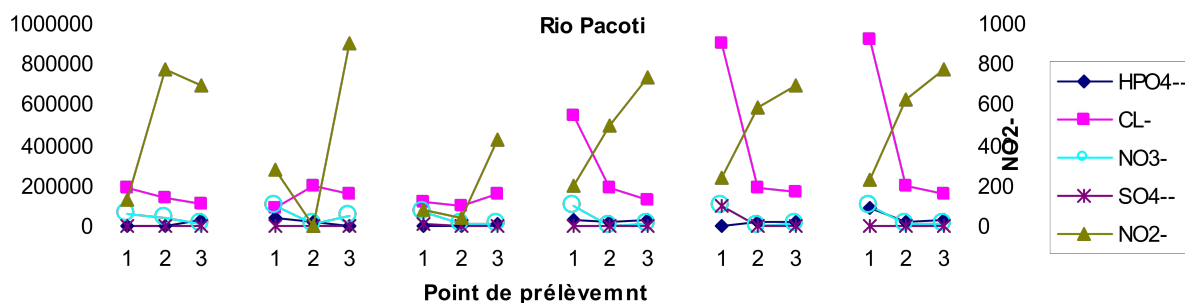


Figura 14: Variation of anion concentrations in the Pacoti river

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 $\mu\text{mol} / \text{L}$ of metal, and the complexation 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 figure 15 and 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.

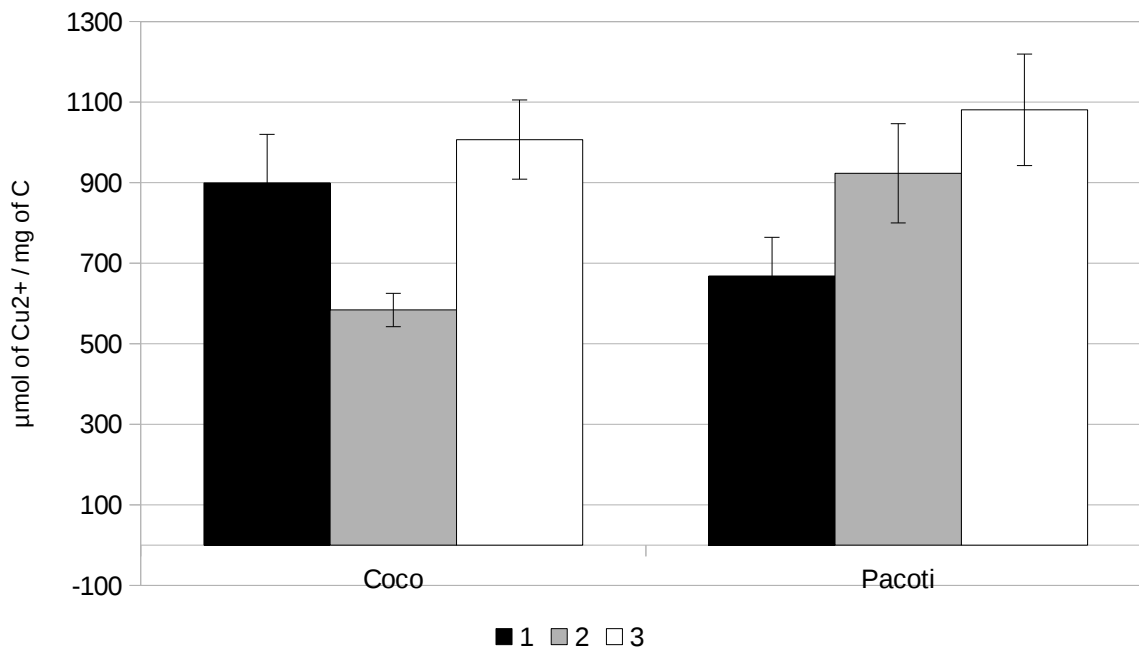


Figura 15: Distribution of complexation capacity for copper in the Pacoti river and Cocó river along the river. 1 – River; 2 – mangrove; 3 – marine zones.

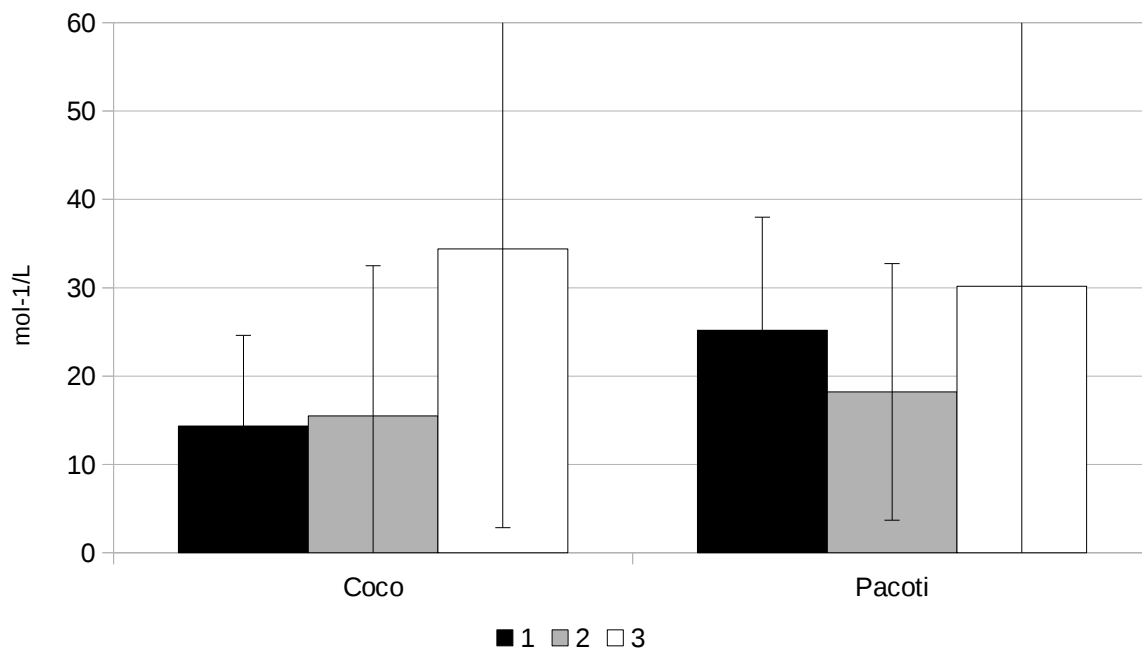


Figure 16: Distribution of complexation constant for copper in the Pacoti river and Cocó river along the river. 1 – River; 2 – mangrove; 3 – marine zones.

Sampling strategy on the Jaguaribe River

Spatial sampling



Figure 17: The mangrove zone of the Jaguaribe River (Ilha Grande sampling stations)

Two field campaigns were carried out (Table 5) in April and September 2004 to have variation of physical-chemical parameters of the waters of the lower Jaguaribe basin. The mangrove zone of the Jaguaribe occurs between the point 2 (Barra) and 4 (Raimundinho) (figure 17).

River	Campaign	Date	Reference	Cu ²⁺ µg/L	DOC ppm	IC	Comment
Jaguaribe	1	30/04/04	Ja101	nd	7,1	21,11	Mar
Jaguaribe	1	30/04/04	Ja102	nd	7,04	26,26	Barra
Jaguaribe	1	30/04/04	Ja103	2,1	10,46	25,21	Ilha Grande
Jaguaribe	1	30/04/04	Ja104	3,52	10,86	27,09	Raimundinho
Jaguaribe	1	30/04/04	Ja105	2,6	11,71	25,83	Aracati (quando ver ponte)
Jaguaribe	1	30/04/04	Ja106	3,26	7,54	25,89	Aracati (depois da ponte)
Jaguaribe	1	30/04/04	Ja107	1,92	18,96	24,47	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	22,39	Itaiçaba (depois da Barragem)
Jaguaribe	2	19/09/04	Ja201	nd	12,4	27,45	Mar
Jaguaribe	2	19/09/04	Ja202	nd	12,37	25,58	Barra
Jaguaribe	2	19/09/04	Ja203	nd	13,9	24,04	Ilha Grande
Jaguaribe	2	19/09/04	Ja204	nd	16,02	26,08	Raimundinho
Jaguaribe	2	19/09/04	Ja205	nd	17,03	24,4	Aracati (quando ver ponte)
Jaguaribe	2	19/09/04	Ja206	2,11	17,08	22,41	Aracati (depois da ponte)
Jaguaribe	2	19/09/04	Ja207	2,27	17,58	21,59	Cabreiro
Jaguaribe	2	19/09/04	Ja208	1,21	19,34	19,52	Itaiçaba (antes da Barragem)
Jaguaribe	2	19/09/04	Ja209	0,99	19,21	18,7	Itaiçaba (depois da Barragem)

Table 5: Location of sampling points on the Jaguaribe River, and values of copper (Cu²⁺), dissolved organic carbon (DOC) and inorganic carbon (IC).

Sampling during a tide

The 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 (Figure 17, Table 6).

River	Number	Hour	Reference	Cu ²⁺ (µg/L)	POC (mg/L)	DOC (mg/L)	IC (mg/L)	T°C	Cond.	Sal.	pH
Jaguaribe	1	05h40	TJa01	2,87	1	17,9	37,03	26	30,65	18,2	7,91
Jaguaribe	2	06h35	TJa02	2,86	1,65	19,27	34,48	27	14,8	8,1	7,88
Jaguaribe	3	07h30	TJa03	2,84	3,15	19,88	29,11	28	1,19	0,6	8,01
Jaguaribe	4	08h35	TJa04	-	1,89	4,33	31,11	-	35,16	20,4	8,05
Jaguaribe	5	09h35	TJa05	2,48	2,09	0,27	30,21	-	33,39	19,1	8,03
Jaguaribe	6	10h40	TJa06	2,65	2,59	0,28	-	-	29,29	16,7	7,93
Jaguaribe	7	11h35	TJa07	2,5	2,33	20,6	31,53	-	24,33	13,8	7,95
Jaguaribe	8	12h50	TJa08	2,77	1,75	-	27,63	29	18	10,4	8,02
Jaguaribe	9	13h35	TJa09	3,18	2,27	20,74	26,08	29,2	15,68	8,4	8,17
Jaguaribe	10	14h30	TJa10	3,1	2,24	22,68	26,68	-	14,29	7,6	8,38
Jaguaribe	11	15h35	TJa11	3,13	2,61	-	30,31	28,1	7,76	4	8,22
Jaguaribe	12	16h35	TJa12	3	2,16	0,23	28,9	-	19,7	10,8	8,14
Jaguaribe	13	17h35	TJa13	7,38	2,02	18,92	26,12	-	25,17	14,2	-
Jaguaribe	14	18h35	TJa14	-	3,28	20,34	25,61	-	29,31	16,6	8,09
Jaguaribe	15	19h25	TJa15	2,34	1,75	21,86	23,77	-	30,89	17,8	8,13

Table 6: Samples from the 20/06/04 field campaign for temporal studies during a tidal cycle.

Results of the spacial distribution study

Dissolved organic carbon.

It can be observed that the concentration of organic carbon in the Jaguaribe river basin increases in April and September. Figure 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 ($r^2=0,89$) (Figure 18).

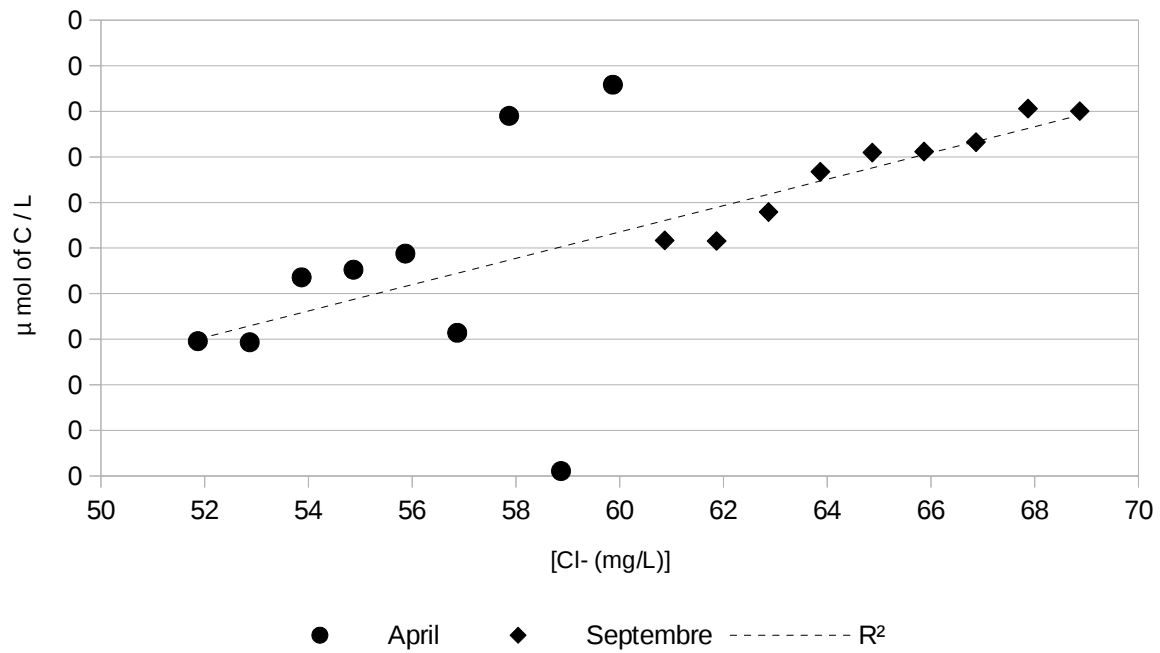
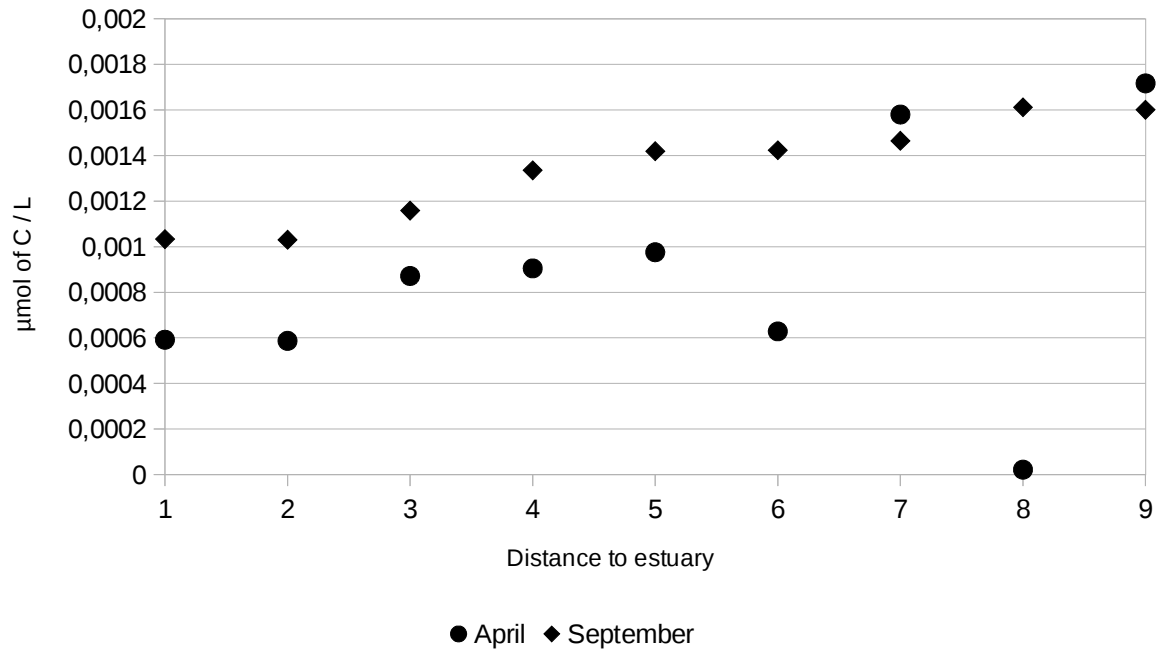


Figure 18: Variation of the dissolved organic carbon during the two sampling campaigns and the relation to salinity.

Fluorescence spectroscopy

The fluorescence results (figures 19 and 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 drastically. From site 3 to 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., figure 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 (Figure 19) where the ratio increases from point 3. One can also observe that the $r_{a,c}$ do not increase in April. This is in agreement with a production of young organic matter at the end of the river path at the end of the basin when the influence of the sea is great and in the mangrove zone.

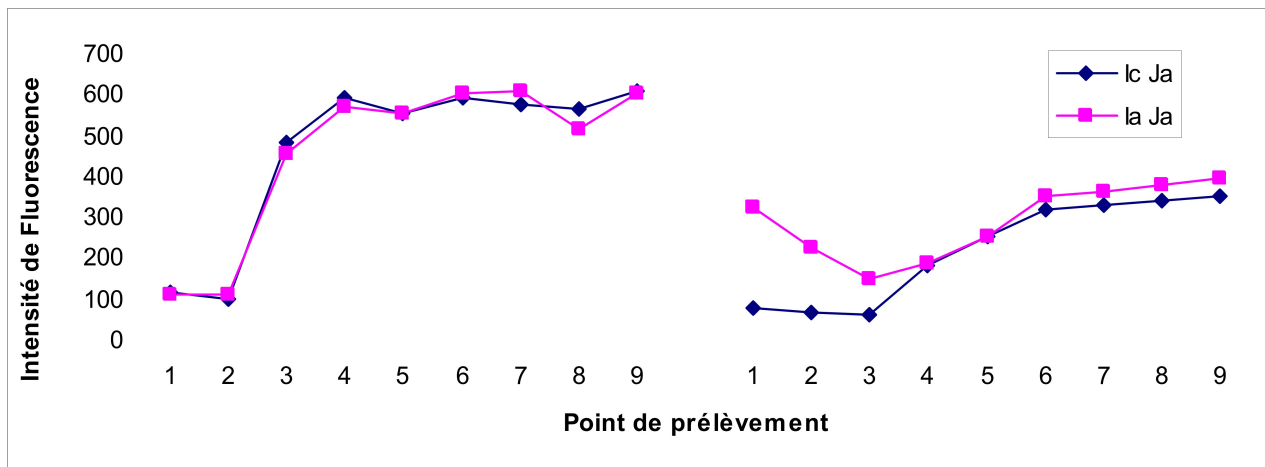


Figure 19: Fluorescence of peaks A (rose) and C (dark blue) (Coble 1996) in the Jaguaribe river basin, in April (left) and September (right)

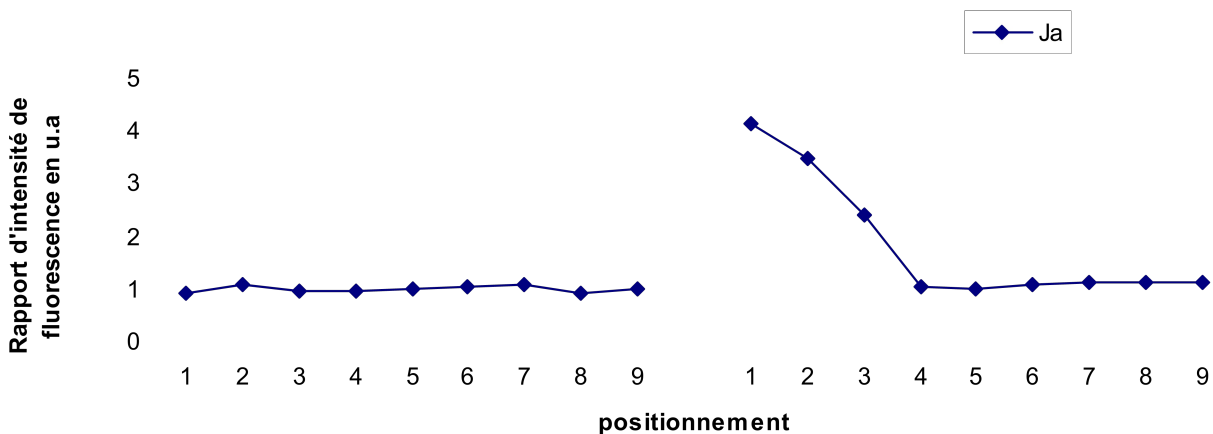


Figure 20: Reason for fluorescence intensity of the Jaguaribe river basin in April (left) and September (right)

As the concentration of organic carbon increases in September we can speak of a production of young organic matter in September, the a young dissolved organic carbon input. The $r_{a,c}$ increases only at three points in the basin near the sea, that is to say that the carbon inputs are different up and down. The production of young organic material only takes place in the cruise of September in the basin of the Jaguaribe.

Results of the temporal study

Organic carbon, pH and salinity

The salinity varies from 8 to 20 with a sinuous curve. The minimum salinity happens at 11:35 p.m. and the maximums happen by 6:00 p.m. and 5:00 p.m. The pH value shows maximum during growth and salinity decline. The total organic carbon shows anomaly during the same moments (figure 20).

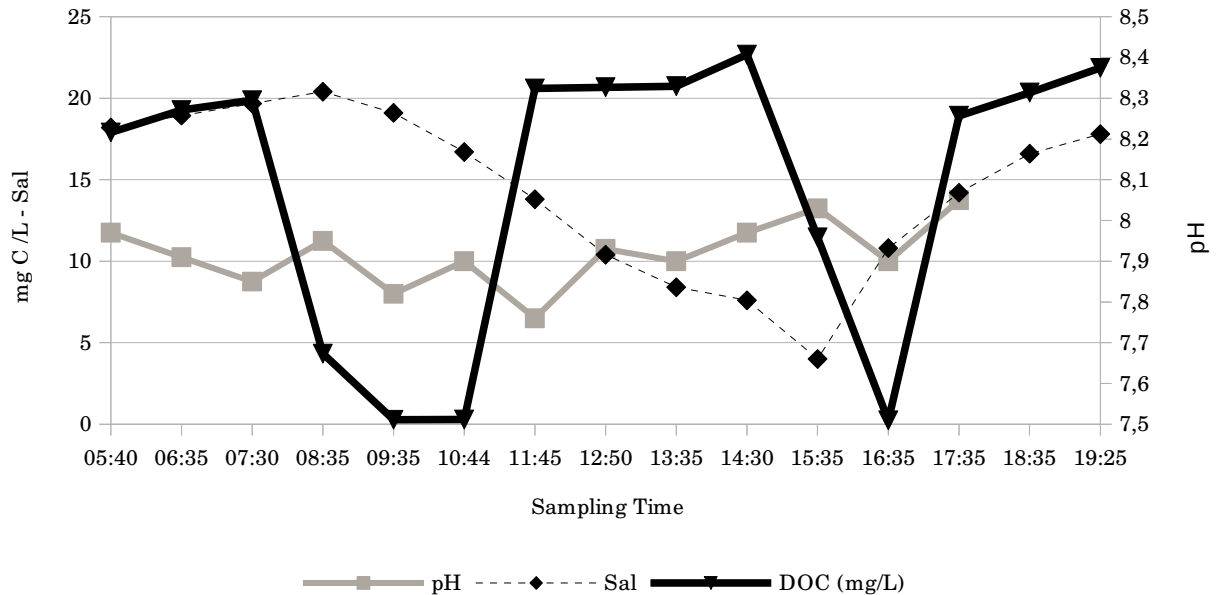


Figure 21: Variation of carbon, pH and salinity during a tidal episode.

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 is minor the salinity is lowest. The fluorescence increases to 500 versus 300 when the salinity is to the maximum.

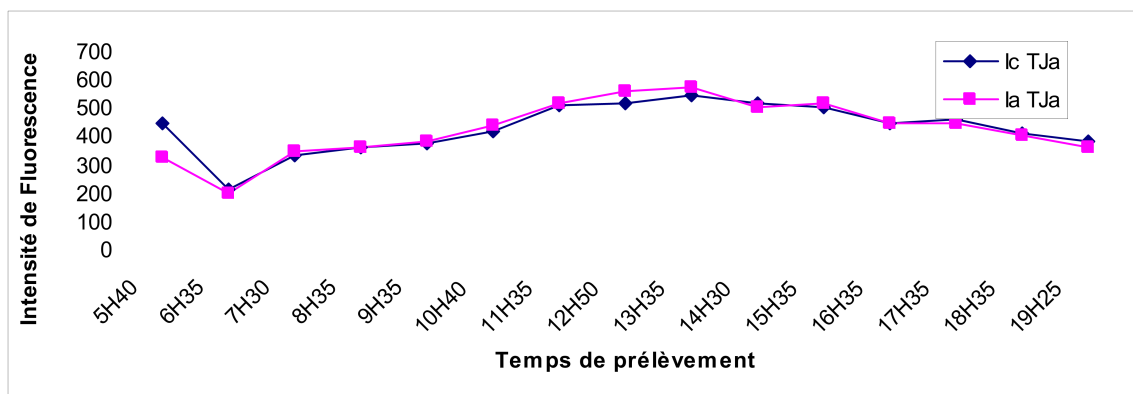


Figure 22: Fluorescence of peaks A and C for the Jaguaribe River in April during the temporal sampling.

From the graph in figure 23 we can see that the ratio is quasi constant throughout the tidal period. 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.

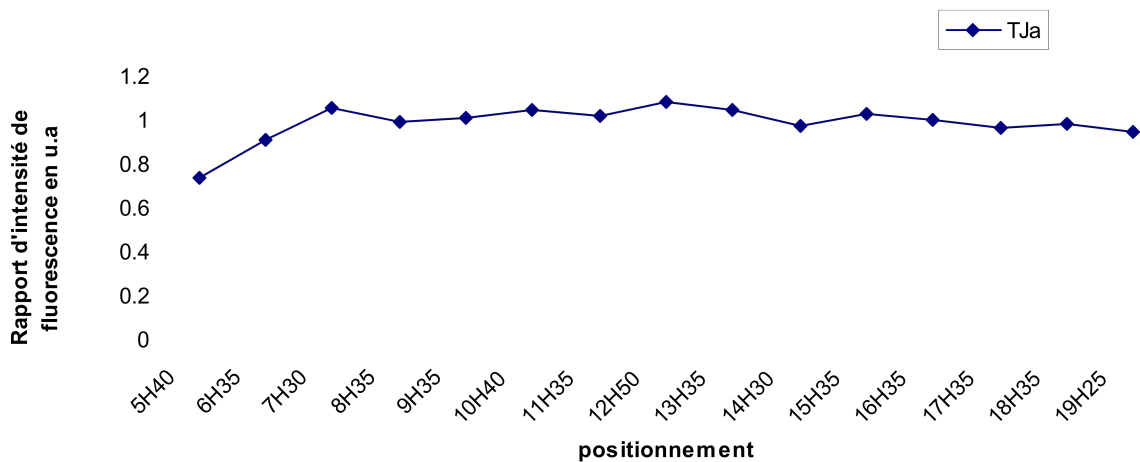


Figure 23: Values the ratio I_a / I_c for the Jaguaribe river in April during the temporal sampling.

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 change.

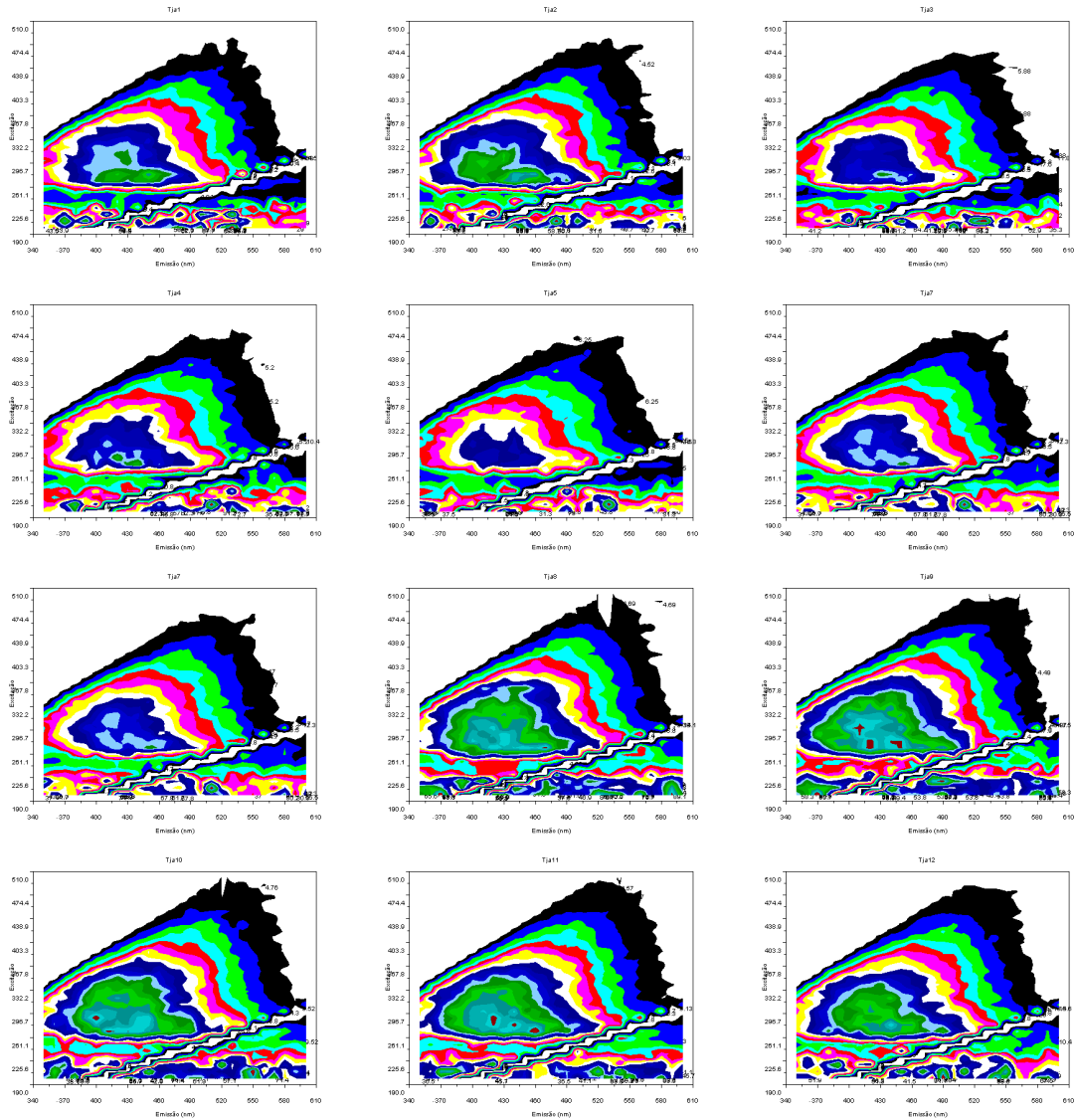


Figure 24: Excitation Emission Matrices of fluorescence of the Jaguaribe representing fluorescent organic matter during tide event (in false colour).

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 (figure 24). Only the intensity seems change during the sampled tidal cycle. These data were treated by CP/PARAFAC to extracted subtle variations that occurs during the event.

Variation of the major elements

Space strategy

Changes in cation and anion concentrations in the Jaguaribe River Basin in April and September 2004 are represented respectively respectively in figures 25 and 27. 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.

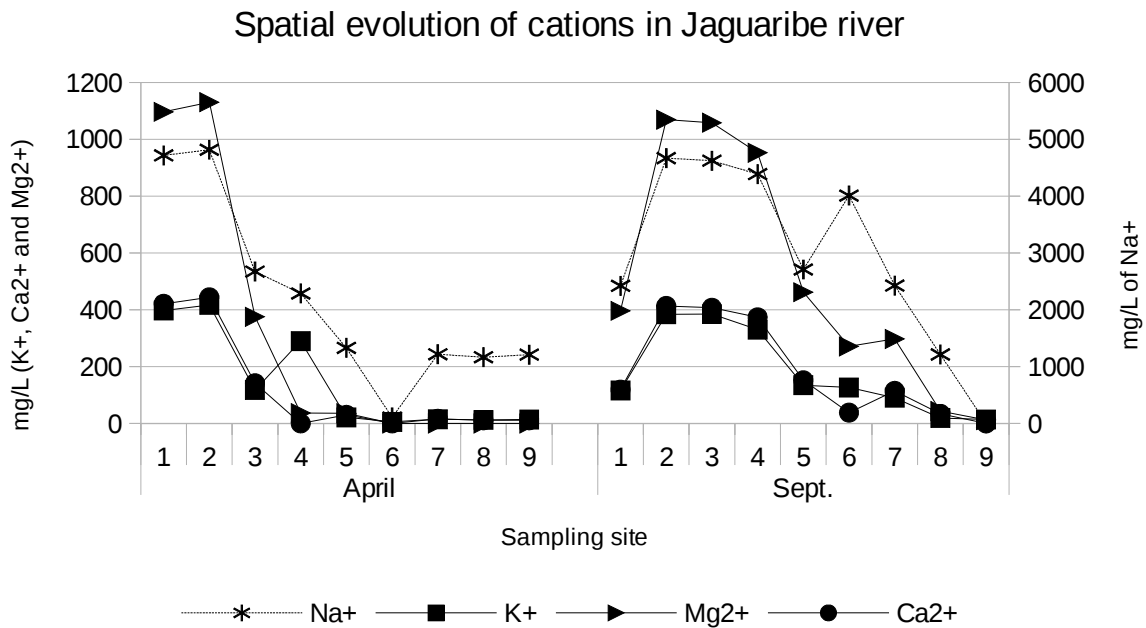


Figure 25: Variation of cations in the Jaguaribe river basin in April (left) and in September (right).

Representing the K^+ , Mg^{2+} and the Ca^{2+} concentration versus the Na^+ one (figure 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.

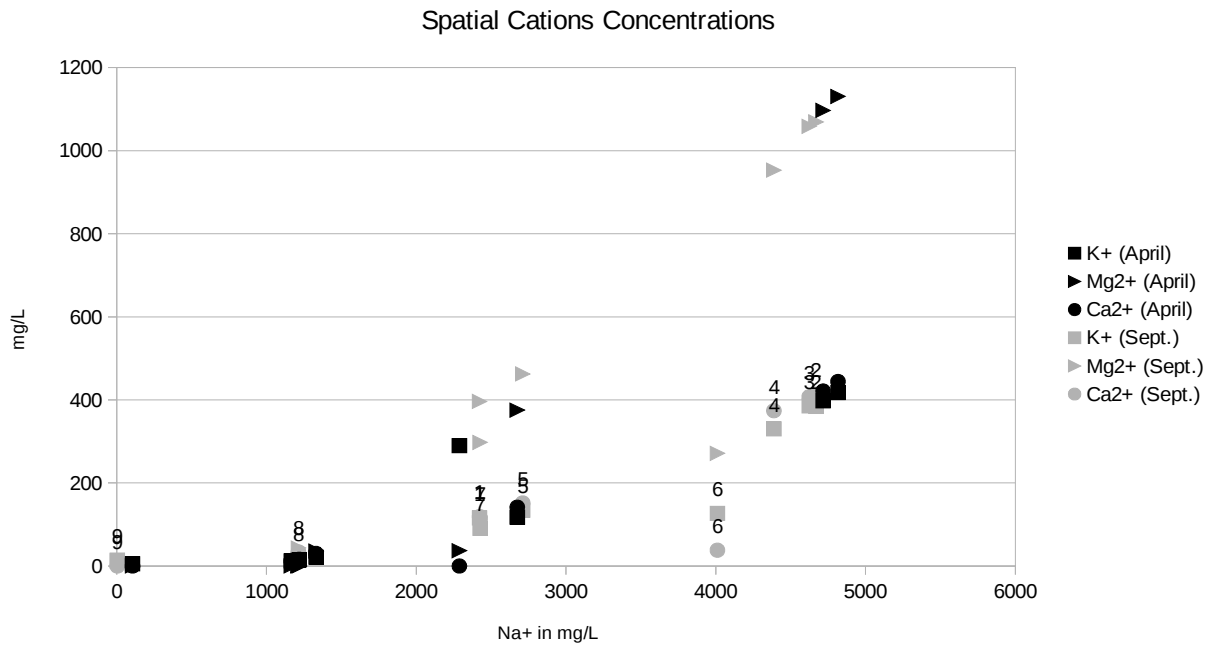


Figure 26: Sodium to cations concentration relation for the Jaguaribe river along downstream.

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 (figure 27). For NO_3^- and SO_4^{2-} anions, it is clear that the concentrations fall down after the sea influence, and after the point 5 in April and 7 in September. In the Jaguaribe, the carbonate are highly stable and represent with the Cl^- the major anions.

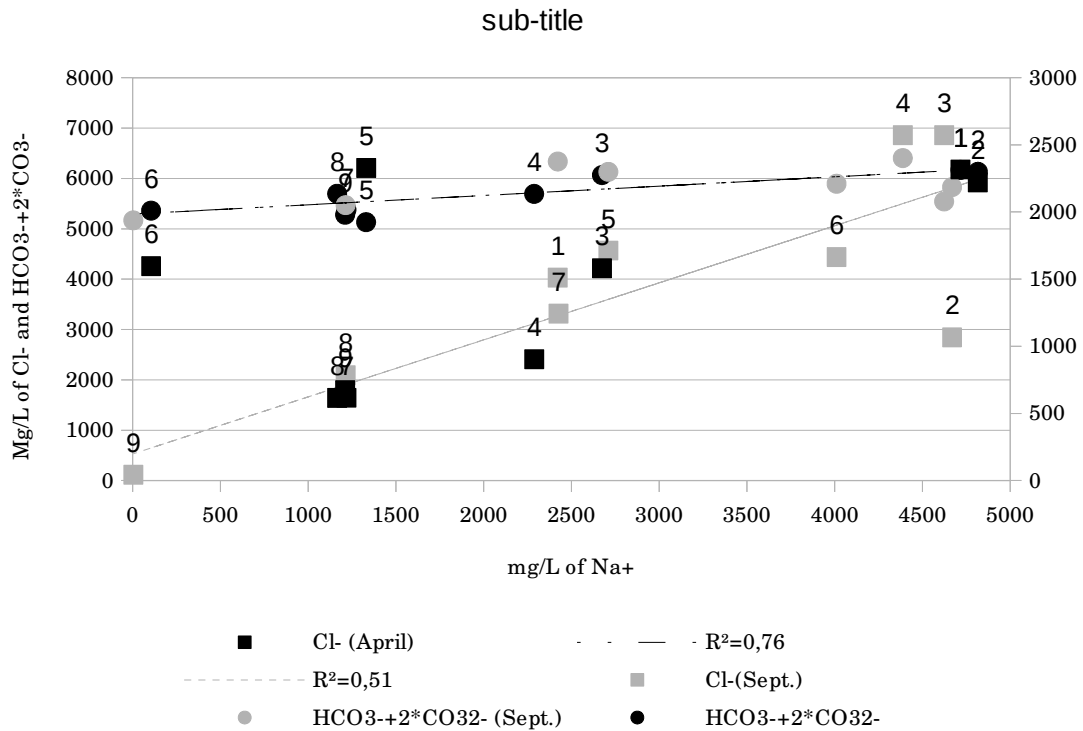


Figure 27: Variation of the anions in the Jaguaribe basin in April (left) and in September (right).

Time strategy

The temporal sampling in April is presented in figure 28 for the cations and in figure 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 to 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 8. Clearly the concentrations in cations and anions are normally associated with salinity. The most connected elements is Ca²⁺ (figure 28). For the other elements concentration, it decreases until the minimum salinity is reached.

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	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

Table 7: Results on larger elements of temporal sampling

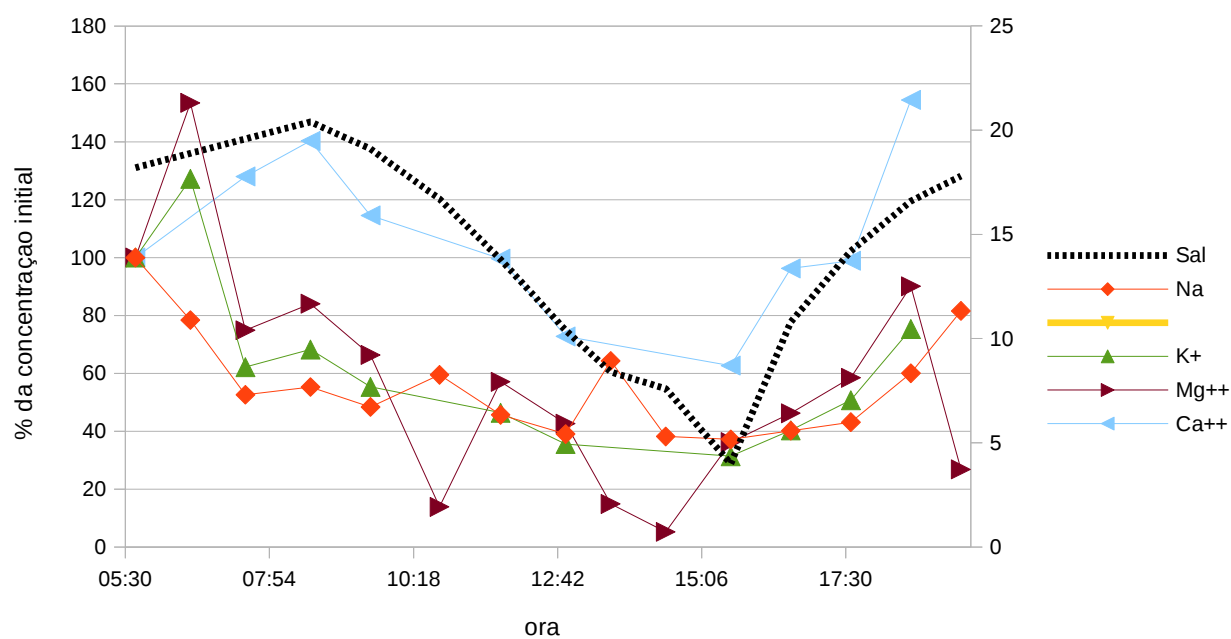


Figure 28: Variation of the cations in the Jaguaribe basin during the temporal sampling.

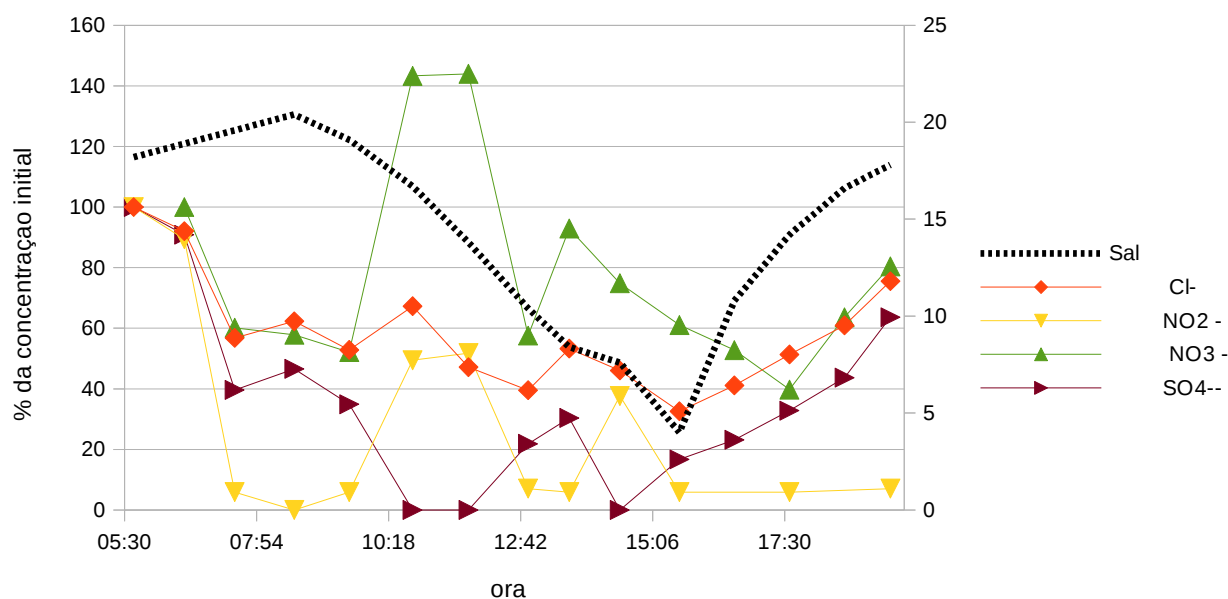


Figure 29: Variation of the anions in the Jaguaribe basin during the temporal sampling.

These results do not show an influence of the activities above the sampling point. Except the first point in the early morning that could be by an outlier, there is a perfect correlation between the Na^+ concentration and the Ca^{2+} , Mg^{2+} 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 SO_4^{2-} 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.

Conclusion

This work allowed to make a first characterization of the natural organic matter in 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 comparing the mangroves in the Fortaleza metropolitan area, in general, the two mangrove zones are very similar from the point of view of the larger elements and the 2D or 3D fluorescence. But 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 river Cocó with a higher production of young (fulvic like) less complexant 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 influences the quality and behaviour of the two mangrove areas.

Geochemistry of the Jaguaribe River

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.

General conclusion

During this study many measures were performed. It has been 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.

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