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Impact of Drainage Basin Changes on Suspended Matter and Particulate Copper and Zinc Discharges to the Ocean from the Jaguaribe River in the Semiarid NE Brazilian Coast

Francisco Jose da Silva Dias, Rozane Valente Marins, and Luis Parente Maia

Instituto de Ciências do Mar
Federal University of Ceará
Av. Abolição 3207, Meireles
Fortaleza, Ceará, 60165.081, Brazil
geofranzedias@gmail.com

ABSTRACT

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This study aims to understand the fluvial contribution to the estuary and thence to the ocean and the behavior of the suspended particulate matter (SPM) and particulate Cu and Zn during spring tide cycles and during the dry and rainy seasons in 2005, 2006, and 2008, at the Jaguaribe River Estuary, NE Brazil. The distribution of metals concentrations in SPM during dry and rainy seasons suggests a lithogenic origin of aluminum (Al), iron (Fe), and copper (Cu), as a result of erosion and leaching of soils in the drainage basin due to anthropogenic drivers, such as urbanization, shrimp farming, and agriculture. Anthropogenic drivers also affect Zn flows associated with SPM during the dry season. The highest discharges of SPM and particulate metals occurred during rainy periods due higher freshwater volumes observed in the estuarine channel. The results strongly suggest that the high variability of discharges typical of semiarid drainage basins can be underestimated with the use of secondary data, showing the necessity of obtaining data *in situ*.

ADDITIONAL INDEX WORDS: *Anthropogenic drivers, SPM discharge, particulate metal, river discharge.*

INTRODUCTION

Most estuaries located along the Brazilian semiarid coast are submitted to environmental impacts resulting from anthropogenic activities occurring in their watersheds, in particular, from waste disposal, urbanization, agriculture, aquaculture, and hydropower generation. These impacts result from a complex chain of events varying in space and time, but in this region, they can be attributable to an ultimate pressure: the decrease of the freshwater discharges from rivers to estuaries (ecological flows) due to the construction of dams designed to increase water availability for human uses. The reduction in river discharges also intensifies the effects of meteorological phenomena like El Niño, La Niña, and global climate changes (Gonçalves and Carvalho, 2008; Lacerda, 2006).

Recently, Dias, Marins, and Maia (2009) and Dias *et al*. (2011) showed that preliminary results on fluxes measured at the Jaguaribe estuary have to consider the sum of vectors with different directions: the fluvial influx to the estuary and tidal forcing.

Suspended particulate matter (SPM) is represented by a wide combination of inorganic material (*i.e*. clay minerals; Fe and Mn oxyhydroxides) and organic matter (detritic or alive). These particles, due to their high surface area and chemical properties, are the main carriers of substances in aquatic systems (Cave *et al.,* 2005; Turner and Millward, 2002), playing an important role of in the transport of metals from the continents to coastal areas (Hay, 1998; Knoppers, Ekau, and Figueiredo, 1999; Knoppers *et al.,* 2006; Salomons and Förstner, 1984).

In estuaries, metals concentrations in SPM are generally orders of magnitude higher than the dissolved concentrations (Balls, 1989; De Paula and Mozeto, 2001; Machado and Lacerda, 2004). Therefore, the fate of these elements is very closely related to the SPM dynamics. The composition and variability of SPM in estuaries are affected by complex geochemical processes such as precipitation and flocculation, desorption, and adsorption, as well as by physical processes such as freshwater flows, tidal energy, and currents (Machado and Lacerda, 2004; Marques *et al.,* 2004; Radakovitch *et al.,* 2008).

The exact knowledge of SPM behavior in hydrological cycles (seasonal cycles), considering the basin drainage characteristics, is necessary for estimating substances loads and mass balances of fluvial systems (Audry, Blanc, and Schäfer, 2004; Schäfer *et al.,* 2002).

The SPM carried out to the adjacent coastal zone by rivers represents an important control on the erosion and geochemistry processes of our planet (Horowitz, Elrick, and Smith, 2001; Lawson, Mason, and Laporte, 2001; Mayer *et al.,* 1998; Neal *et al.,* 1997). Also, estuaries can act as a "geochemical

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reactor," changing the chemical forms of continental-derived trace metals (Chiffoleau *et al.,* 1994; Lacerda *et al.,* 2001, 2002; Medeiros *et al.,* 2007; Smoak, Krest, and Swarzenski, 2005). The role of an estuarine system in the transformation and exportation of metals to coastal areas will depend upon several intrinsic characteristics of each estuary.

At the Jaguaribe River Estuary, environmental changes are currently taking place due to river damming, water withdrawal for agriculture and aquaculture purposes, and increasing human population demand. A major aspect of these changes is the reduction of freshwater discharge into the ocean, particularly during the dry season, leading to changes in the hydrochemistry and in the erosion-sedimentation equilibrium along river banks, at the river mouth, and along the shore just adjacent to the estuary (Lacerda and Marins, 2002; Marins *et al.,* 2002, 2003).

The aim of the present study is to understand the behavior of suspended particulate matter (SPM) and the metals in SPM and quantify materials discharges from the drainage basin into the estuary during dry and rainy seasons during three years.

STUDY SITE

The Jaguaribe basin covers about 72,000 km^2, representing almost half of the Ceará State's territory. Sandy coastal plains with large eolian dune fields, driven by the nearly year-round constant winds from the SE, characterize the coastline. The Jaguaribe River Estuary is located between 4°23′26″ S and 4°36′58″ S and 37°43′58″ W and 37°43′45″ W (Figure 1).

Regional climate, including rainfall seasonal variations, is regulated by the Intertropical Convergence Zone (ITCZ), where air masses from both hemispheres converge. During austral winter and spring, the ITCZ weakens and moves northwards, resulting in very dry months with strong eastern winds in the Southern Hemisphere. The magnitude of the ITCZ displacement is affected by El Niño teleconnections (FUNCEME, 2008), and can modify the migration of sand dunes, which dominate Ceará's coastline (Maia, Freire, and Lacerda, 2005). Local climate is semiarid, with average annual rainfall increasing from 400 mm inland to 983 mm at Aracati (17 km from the mouth of Jaguaribe River). Historical rainfall data show higher precipitation (200 to 400 mm per month) between March and April. During the peak of the dry period, between August and November, precipitation can be frequently zero (FUNCEME, 2008) (Figure 2).

The tidal co-oscillation at the estuary mouth is classified as mesotidal and semidiurnal according to its height and periodicity, respectively, ranging between 1.1 and 1.4 and 1.8 and 2.0 m in neap and spring tide periods, respectively (Dias, Marins, and Maia, 2009; Dias *et al.,* 2011). The generally low freshwater supply results in the intrusion of high-salinity water a few kilometers inland (Marins *et al.,* 2003). The brackish tidal floodplains are covered by about 13,000 ha of mangroves (Lacerda *et al.,* 2006; Maia *et al.,* 2006). The Jaguaribe River is responsible for about 70% of the total freshwater input to the adjacent Atlantic Ocean from the oriental NE Brazilian coast. Average freshwater discharge ranged from 60 to 130 m^3 s^{-1} prior to the building of major dams. With the construction of the new Castanhão Reservoir

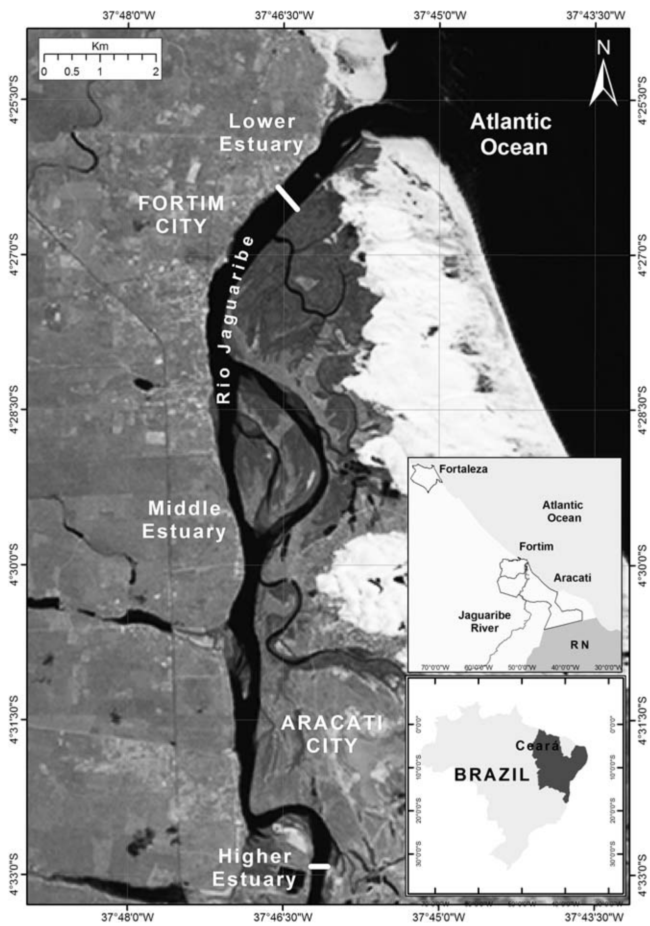

Figure 1. Location map of Jaguaribe River Estuary, NE Brazil, and the two river sections (white lines) used for ADP measurements, ZR/ZM (higher estuary), and ZM/ZC (lower estuary).

(4.5×10^9 m^3 of storage capacity), the freshwater input to the ocean decreased further to about 20 m^3 s^{-1}. However, the actual discharges to the ocean and associated sediment fluxes are highly dependent on the estuarine hydrological dynamics, and the determination of this discharge is a major scope of this work. Similarly, sediment fluxes are also affected (Marins and Lacerda, 2007).

MATERIALS AND METHODS

Measurements of Flows with ADP and Tidal Variation in the Estuarine Channel

The estuarine channel circulation was characterized by using an acoustic current meter (Acoustic Doppler Current Profiler [ADP], 1500 kHz, SONTEK/YSI) along two sections in the Jaguaribe River Estuary, at the interface between the higher to the middle estuary (fluvial zone [ZR]/mixing zone [ZM]) and the middle to the lower estuary (mixing zone [ZM]/coastal zone [ZC]) (Figure 1), the latter of which is responsible for integrating the incoming continental materials from the watershed to the estuarine channel and from there to the ocean

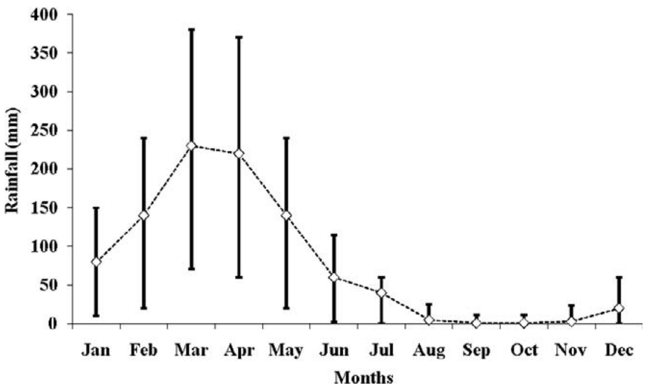

Figure 2. Average monthly rainfall for the years 1912 to 2008 for the lower Jaguaribe region.

(Miranda, Castro, and Kjerfve, 2002). Hourly profiles were registered through 13 hours in the four transects. Vertical and horizontal velocities were recorded at three depths every 5 seconds within a range of 0.1 to 1.000 cm s^{-1} and a precision of $\pm 1\%$ for horizontal velocity with a resolution of 0.1 cm s^{-1}. The boat speed (from bottom-track data) was subtracted from the measured water velocity to give the absolute current profile independent of boat motion. This also applies to the layer of fluid mud.

The tidal variation along the estuarine channel during the evaluated period was performed with the aid of tide pressure gauges (Diver/Schlumberger) installed on a metal base at the bottom of the river, with measurements performed every 5 minutes over a period of 14 hours.

Sampling and Analysis

Samples from the estuarine channel were collected in September 2005 (representing dry conditions), February and June 2006, and February 2008 (representing rainy conditions). Water samples were collected at 2 hour intervals with a Van Dorn sampler and stored in polyethylene flasks in duplicate, along the tidal cycle, at the fluvial zone/mixing zone interface (ZR/ZM) (Figure 1). Samples were kept at 4°C during the transport to the laboratory. In the laboratory, the samples were filtered in duplicate through Millipore AP 040 filters and decontaminated with a 10% HCl solution (Melo *et al.,* 2003), and SPM was determined by gravimetry (Strickland and Parsons, 1972).

Duplicate SPM subsamples were digested with 50% *aqua regia* solution in a block digester for 2 hours under controlled temperature (80°C) (Aguiar, Marins, and Almeida, 2007). The metals Zn, Cu, Fe, and Al were measured in an atomic absorption spectrophotometer (Shimadzu AA 6200). The analytical methodology was referenced with certified material (estuarine sediments from National Institute of Standard and Technology, NIST 1646a; APHA, 2007) (Table 1). The results obtained in the present study can be considered accurate for the proposed objectives where the interest is in the total fraction available to geochemical superficial reactions excluding the lithogenic matrix.

Table 1. *Certified and obtained concentrations in reference material 1646a Estuarine Sediments (NIST).*

Metals	Certified (μg/g)	Obtained (μg/g)	Recuperation (%)
Cu	10.01 (0.34)	7.3 (0.1)	72
Zn	48.9 (1.6)	36.4 (0.3)	74
Fe (%)	20.08 (2)	16.7 (1)	83
Al (%)	22.97 (1)	11.92 (0.9)	52

The detection limits of the method (mg L^{-1}; Miller and Miller, 1994) were 0.01 μg g^{-1} for Cu and Fe; 0.02 μg g^{-1} for Zn, and 0.03 μg g^{-1} for Al.

Calculation of Instantaneous Discharges of SPM and Metals Particulate Discharges

The suspended particulate matter discharges (D_{spm}), were obtained according to Miranda, Castro, and Kjerfve (2002):

$$D_{spm} = \iint_A \varphi \vec{v} \cdot \vec{n} dA = \iint_A \varphi u dA = \overline{\varphi} \overline{u} A \qquad (1)$$

where D_{spm} = SPM discharges (kg s^{-1}), $\bar{u}$ = mean velocity of the water column (m s^{-1}), $\bar{\phi}$ = mean SPM concentration (mg L^{-1}), and A is the section area (m^2), for each hour measured. The wet section of each profile varies in time; therefore, an ADP profile was obtained for each hourly wet section.

Metals discharges at SPM were obtained according to:

$$D_{mi} = \gamma_i \cdot D_{spm} \qquad (2)$$

where D_{mi} = metals discharges in SPM (kg s^{-1}), and γ_i = metals concentrations in SPM in each performed campaign (μg g^{-1}).

The values of the determined D_{spm} and D_{mi}, the resultant discharge from the drainage basin to the estuary, and discharge from there to the adjacent coastal zone were used to calculate annual discharges of SPM and particulate metals, according Equation (3):

$$D_t = D_n \cdot 3.2 \cdot 10^7 \qquad (3)$$

where D_t = the annual yield (annual discharge/lower basin area) expressed in ton $year^{-1}$. D_n = D_{spm} or D_{mi} (kg s^{-1}), and the constant value (3.2×10^7) is a value that provides the transformation of kg s^{-1} to kg y^{-1}. Average values of flood and ebb tide periods were used for this estimate.

RESULTS AND DISCUSSION

Tidal Variation and Outflows in the Estuarine Channel

In the dry season of September 2005, the tide ranged from 2.1 to 3.3 m, with level variation of 1.2 m, whereas for the rainy seasons (February 2006, June 2006, and February 2008), tides varied from 1.0 to 2.5 m, 1.3 to 2.9 m, and 0.3 to 3.5 m, with mean amplitudes of 1.5, 1.6, and 3.2 m, respectively (Figure 3).

Dias, Marins, and Maia (2009) observed that due to dam construction along the river course, the freshwater input from the drainage basin to the estuary is greatly minimized, modifying estuarine hydrodynamics, mainly during the dry season, due to higher tidal action. The authors also observed that tides can increase the water volume and probably intensify the materials transport in the estuarine channel, with SPM

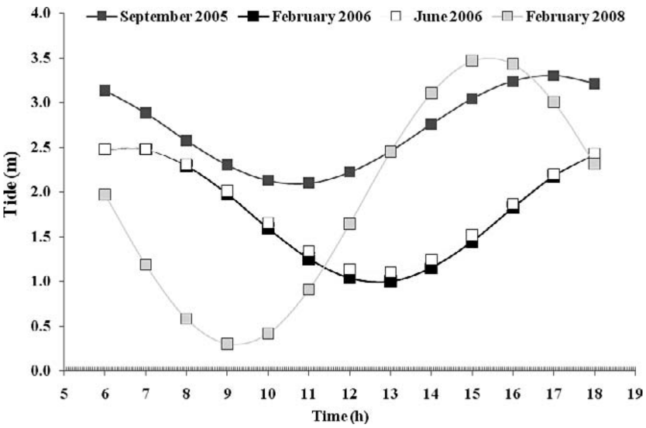

Figure 3. Variability of the spring tide in the estuarine channel, for the dry and rainy seasons.

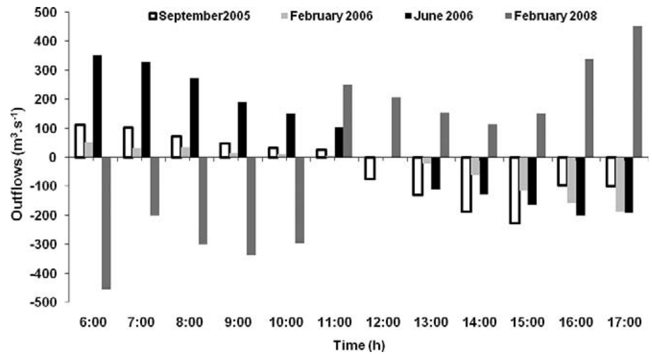

Figure 4. ADP outflows measured at the interface between the fluvial and mixing zones (ZR/ZM) in the Jaguaribe River Estuary.

flows upstream (flood tide) and downstream (low tide) in the estuary. This event is also observed in the rainy season, when the freshwater discharge is more significant.

The estuarine channel outflows measured at the interface between fluvial and mixing zones varied from 26.5 to 226.7 m^3 s^{-1}, 1 to 188.6 m^3 s^{-1}, 2 to 351 m^3 s^{-1}, and 114.4 to 454.4 m^3 s^{-1} in September 2005, February and June 2006, and February 2008, respectively (Figure 4).

By analyzing the flows during different tidal periods, it can be observed that in September 2005, the outflows during ebb and flood period varied from 26.5 to 111.8 m^3 s^{-1} and from 75.8 to 226.7 m^3 s^{-1}, respectively. In 2006, the flows varied from 1.0 to 52.7 m^3 s^{-1} and 21.0 to 188.6 m^3 s^{-1} during ebb tide and from 2.0 to 351 m^3 s^{-1} and 110.0 to 201.0 m^3 s^{-1} in flood tide, respectively, for February and June. Flows observed in February 2008 varied from 114.4 to 451.6 m^3 s^{-1} in ebb tide and from 201.0 to 454.4 m^3 s^{-1} for the flood tide.

The highest outflows in flood tide were observed for September 2005 and February 2006. Although February is historically considered the month of highest rainfall, for the year 2006 this behavior was not observed due to the low level of rainfall recorded, showing a similar behavior to the dry season months, as in September 2005. Months with negative hydrological balance probably reflect the dissipative effect of the tide wave in the inundation area of the Jaguaribe River.

In June 2006, ebb flows were stronger, probably indicating a period of positive hydrological balance, similar to the results by Medeiros and Kjerfve (1993) for the Itamaraca estuarine system on the NE Brazilian coast, and reflecting the domain of the freshwater input. However, in February 2008, the ebb and flood flows varied in the same order of magnitude and showed the tidal domain in the estuarine channel. This domain reflects the control of fluvial fluxes (freshwater) that are minimized due to the presence of successive dams along the Jaguaribe River. In the Brazilian NE, dams are constructed to increase water availability for multiple uses (*e.g*. human supply and agriculture), thus dramatically reducing the freshwater volume reaching the estuary system, particularly during the dry season.

Tidal Cycle Behavior of SPM and Particulate Metals

During the dry period (September 2005) and low fluvial flows, the estuarine system was strongly leached by seawater, and the SPM concentrations varied from 7.0 to 34.0 mg L^{-1}, with an average of 13 mg L^{-1}. However, during rainy periods (February and June 2006) and increased fluvial of flows, higher SPM concentrations were observed, varying from 48.0 to 89.7 mg L^{-1}, with an average of 62.6 mg L^{-1}, and 22.4 to 44.7 mg L^{-1}, with an average of 32.1 mg L^{-1}, respectively. The exception was the variability observed in SPM concentrations in February 2008 (rainy period), from 5.2 to 12.3 mg L^{-1}, with an average of 8.7 mg L^{-1}.

Analyzing the SPM concentration in relation to the ebb and flood tides, an increase in SPM concentrations in ebb tide can be observed, ranging from 10.2 to 14.4 mg L^{-1}, with an average of 12 mg L^{-1}, in September 2005. At the change of tide, a three times increase in SPM (34 mg L^{-1}) was observed, probably due to material retention caused by tidal forcing. At flood tide, the SPM concentrations remained constant, decreasing to values ranging from 7.0 to 11.5 mg L^{-1}, with an average of 9.6 mg L^{-1} (Figure 5).

In February 2006, SPM concentrations showed similar behavior to that of September 2005, increasing during the ebb tidal event, from 48.0 to 79.2 mg L^{-1}, with an average of 58.7 mg L^{-1}. At the changes of tide, SPM concentrations were also higher, imposed by the tidal forcing, ranging from 69.0 to 89.7 mg L^{-1}, with an average of 77.1 mg L^{-1}. After the ebb tide, the SPM concentrations presented a slight decreasing tendency during the flood tide, ranging from 51.7 to 53.7 mg L^{-1}, with an average of 52.7 mg L^{-1} (Figure 6).

In June 2006, higher SPM concentrations were observed during the ebb tide (22.4 to 44.8 mg L^{-1}, with a mean of 34.8 mg L^{-1}). During the flood tide, SPM concentrations showed a decrease, varying from 23.4 to 38 mg L^{-1}, with a mean of 30.3 mg L^{-1}. At the changing of the tide, high SPM concentrations were again observed (35.0 to 38.0 mg L^{-1}) (Figure 7).

In February 2008 (Figure 8), the observed variability of SPM concentrations (5.2 to 12.3 mg L^{-1}) can be compared to the

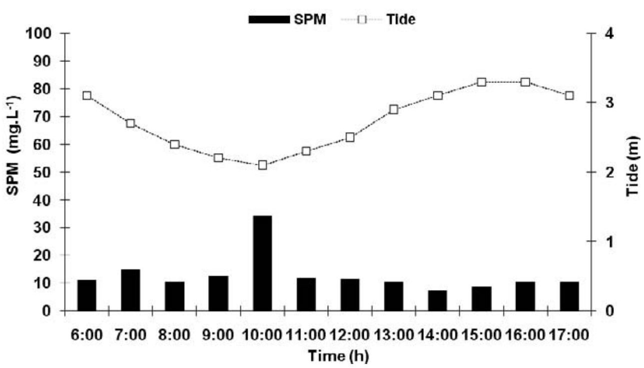

Figure 5. SPM concentrations in the ebb and flood tides for the Jaguaribe River Estuary in September 2005.

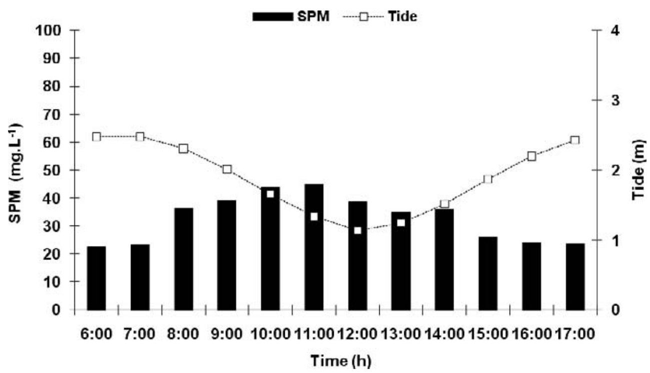

Figure 7. SPM concentrations in the ebb and flood tides for the Jaguaribe River Estuary in June 2006.

observed variability for the dry period in 2005, with concentrations similar to seawater (0.5 and 10 mg L^{-1}) (Chester, 1990), probably reflecting the influence of the high amplitude of that spring tide cycle. During the ebb tide event, the SPM concentrations showed a slight increase, varying from 5.2 to 10.8 mg L^{-1}, with an average of 7.6 mg L^{-1}. However, during flood tide, SPM concentrations decreased and varied from 6.4 to 12.3 mg L^{-1}, with a mean of 10.1 mg L^{-1}. Dias (2007) showed that a negative tide prism, associated with a larger residence time and a decrease in the freshwater input, results in very low SPM concentrations in the estuarine channel.

SPM concentrations found in the present study can be compared to other concentrations found in rivers of medium size located on the Brazilian coast and others, as can be observed in Table 2. Although there is a lack of results from the semiarid region, our data showed similar SPM concentrations in Jaguaribe River to those reported for the São Francisco River (Souza and Knoppers, 2003), both on the NE Brazilian coast and both impacted by numerous dams. In the Jaguaribe River, other important factors in determining the spatial-temporal patterns of SPM dispersion are the drainage basin soil properties. The drainage basin of the Jaguaribe River presents, in general, shallow, stony soils, which allow fast removal of the surface layer during rainfall events. Notwithstanding, SPM concentrations in estuaries of the NE Brazilian coast are lower than those observed in rivers and estuaries of tropical humid regions (Carvalho *et al.,* 2002; Salomão *et al.,* 2001; Schettini and Toldo Júnior, 2006).

Particulate metal concentrations obtained in this study are presented in the Table 3. The highest particulate Al and Fe concentrations were observed in June 2006 and February 2008, probably due to higher input of materials with intensification of the drainage basin soils erosion in the rainy period, markedly different from the dry season, when the rainfall was zero or very low. Consequently, the lowest particulate concentrations were observed in the dry period of 2005.

Particulate copper (Cu) concentrations had the same behavior as particulate Al and Fe. However, particulate Zn, during the dry period (September 2005) presented higher concentrations. Particulate metals concentrations observed in the present study are in the same order of magnitude as concentrations reported for Guanabara Bay in SE Brazil, which is a highly contaminated environment. However, they

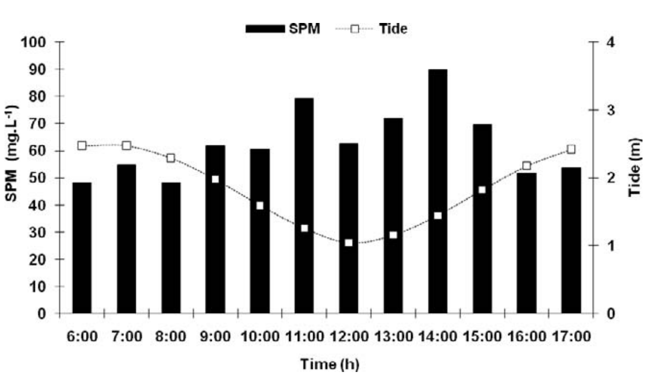

Figure 6. SPM concentrations in the ebb and flood tides for the Jaguaribe River Estuary in February 2006.

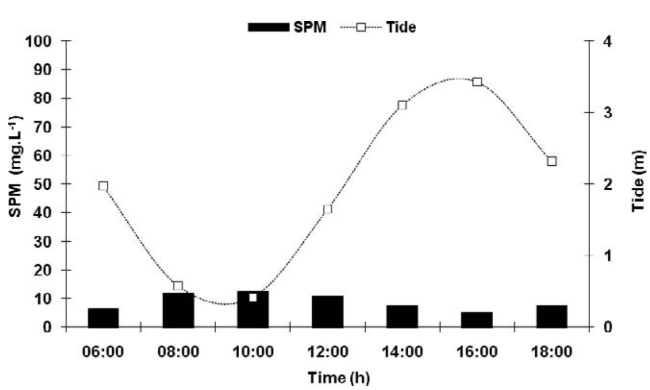

Figure 8. SPM concentrations in the ebb and flood tides for the Jaguaribe River Estuary in February 2008.

Table 2. *SPM concentrations on the Brazilian coast and other parts of the world.*

Study Area	Suspended Particulate Matter (mg L^{-1})
Itajaí-Açu Estuary[a]	55 to 1000
Itajaí-Açu off inner shelf[b]	7 to 12
De La Plata River[c]	100 to 200
Paraná River[d]	20 to 70
Paraiba do Sul River[e,f]	5 to 200
Amazon River Estuary[g]	2000
São Francisco River[h]	10 to 100
Jaguaribe River[i]	7 to 90

[a] Schettini and Toldo Júnior (2006).
[b] Schettini *et al*. (2005).
[c] Framinãn and Brown (1996).
[d] Depetris and Paolini (1991).
[e] Salomão *et al*. (2001).
[f] Carvalho *et al*. (2002).
[g] Biggs (1987).
[h] Souza and Knoppers (2003).
[i] Present study.

are lower than the concentrations reported for the Paraiba do Sul River, also in SE Brazil, and the global average, as observed in Table 4.

The correlation matrix presented in Table 5 corroborates this discussion. Two groups of metals can be easily characterized: (1) Fe, Al, and Cu, which showed a reduction in concentrations during the dry season, and (2) Zn, which showed increasing concentrations during the dry season. This suggests that the first group originates from soil erosion and transport by rains, whereas Zn may be directly released to the estuary by anthropogenic sources. Fe and Al are ubiquitous and abundant natural elements from the Jaguaribe basin soils (Oliveira and Marins, 2011), while Cu is largely used as fungicide in the large-scale irrigated fruit agriculture in the basin (ZEE, 2007). Therefore, either from natural or anthropogenic sources, mobilization of these three elements from soils will depend on rainfall. On the other hand, Zn is a ubiquitous component of urban effluents, mostly wastewaters, urban runoff, and inadequate solid wastes disposal, as well as from intensive shrimp farming in the Jaguaribe Basin (ZEE, 2007) and, therefore, may be released directly into the estuary, both in particulate and dissolved forms, thus also affecting estuarine water concentrations (Grassi, Tonietto, and Lombardi, 2005).

Table 4. *Particulate metals concentrations on the Brazilian coast and other parts of the world.*

	Al (mg g^{-1})	Fe (mg g^{-1})	Cu (mg g^{-1})	Zn (mg g^{-1})
Paraíba do Sul River[a]	117	71	–	143
Global average[b]	91	48	–	350
Mediterranean[c]	–	510	7	22
Danube River[d]	14	13	328	193
Guanabara Bay[e]	–	0.17	0.015	0.56
Jaguaribe River[f]	18	27	0.02	2

[a] Gonçalves and Carvalho (2008).
[b] Martin and Meybeck (1979).
[c] Abdallah (2008).
[d] Yigiterhan and Murray (2008).
[e] Rezende and Lacerda (1986).
[f] Present study.

The highest concentrations of Zn were observed in the dry season, when leaching of soils is minimum but direct discharges from anthropogenic activities not only continue, but are less diluted due to the absence of rainfall.

Discharges of SPM and Particulate Metals

The concentrations results suggest that anthropic sources of Zn dominated fluxes associated with the suspended matter to the estuarine channel of the Jaguaribe River for both the rainy and dry seasons. However, when the discharges were calculated, the Zn particulate behavior was similar to the other metals (Table 6). In general, the relation between SPM and particulate metals discharges showed, as expected, an increase of the SPM and particulate metals discharges during the rainy period, due to an increase of soil runoff.

During the dry period, in September of 2005, when the Jaguaribe River Estuary was strongly controlled by tidal forcing, the discharges of SPM and particulate metals yields were 3.8×10^{-5} tons km^{-2} y^{-1} of Cu; 1×10^{-2} tons km^{-2} y^{-1} of Zn; 4.4×10^{-2} tons km^{-2} y^{-1} of Fe; and 4.1×10^{-2} tons km^{-2} y^{-1} of Al. During February of 2006, the SPM yield was 6.8 tons km^{-2} y^{-1}, with corresponding metal yields of 5.1×10^{-5} tons km^{-2} y^{-1} of Cu; 2×10^{-2} tons km^{-2} y^{-1} of Zn; 1.5×10^{-1} tons km^{-2} y^{-1} of Fe; and 8.2×10^{-2} tons km^{-2} y^{-1} of Al.

During the rainy period, in June of 2006, when the estuarine system was strongly controlled by freshwater input, the SPM yield was of 37 tons km^{-2} y^{-1}, with corresponding metal yields

Table 3. *Variability of particulate metal concentrations along the Jaguaribe River Estuary for the dry and rainy seasons.*

	September 2005			February 2006			June 2006			February 2008		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Flood tide												
Cu (μg g^{-1})	8.7	20.0	13.2	1.7	10	5.8	14	17.7	15.3	7.5	9.5	8.5
Zn (mg g^{-1})	0.7	7.1	3.5	1	3.2	2.4	6.3	8.6	6.9	Nd [a]	Nd	Nd
Fe (mg g^{-1})	12.3	24.7	15.6	19	26	22	41.6	47.3	45.3	20	21.8	21.2
Al (mg g^{-1})	6.7	21.9	14	11	25.3	14	21.2	28.5	23.9	Nd	26.7	26.7
Ebb tide												
Cu (μg g^{-1})	12.6	20.8	15	3.8	17.5	7.4	15.5	21	18.4	Nd	6.42	**
Zn (mg g^{-1})	2.9	8.9	4.5	0.9	8.9	3.0	0.4	1.2	0.9	1.6	4.4	2.7
Fe (mg g^{-1})	4.6	17.3	22.3	14.4	30.3	21.3	44.3	51.4	47.6	23.3	29.2	25.7
Al (mg g^{-1})	11.6	22.3	16.7	8.3	24.5	12	17.4	32.4	27.2	43.5	47.3	45.4

[a] ND = not detectable.

Table 5. *Spearman correlation between SPM and particulate metals concentrations.*

	SPM	Cu	Zn	Fe	Al
SPM	1.00				
Cu	−0.25	1.00			
Zn	−0.04	−0.07	1.00		
Fe	0.15	**0.36** [a]	**−0.44** [a]	1.00	
Al	−0.11	0.25	0.09	**0.47** [a]	1.00

[a] Bold values = significant correlation at $p < 0.05$; $n = 42$ samples.

of 6.9×10^{-4} tons km^{-2} y^{-1} of Cu; 3.3×10^{-2} tons km^{-2} y^{-1} of Zn; 1.8 tons km^{-2} y^{-1} of Fe; and 1 ton km^{-2} y^{-1} of Al.

For the rainy period of 2008, the SPM yield was of 9.8 tons km^{-2} y^{-1}, with metal yields of 6×10^{-5} tons km^{-2} y^{-1} of Cu; 2.7×10^{-2} tons km^{-2} y^{-1} of Zn; 2.5 tons km^{-2} y^{-1} of Fe; and 4.4×10^{-1} tons km^{-2} y^{-1} of Al.

The behavior of particulate Zn flows was singular relative to the others metals. It showed a smaller flux in September 2005 and relatively similar flows during the three other campaigns. In the Jaguaribe River, biogeochemical controls of Zn are probably different compared from the other studied metals and are probably related to water residence time and the proportion of freshwater to the total estuarine volume. As observed by Dias *et al*. (2011), the water residence time in the estuarine mixing zone increases the residence time in suspension of particles associated with a low river flow. This behavior probably tends to increase the concentrations of metals from anthropogenic sources, such as Zn.

The decrease of SPM and particulate metals transport during the dry period due to low freshwater input to the estuarine system and numerous dams constructed along the Jaguaribe River shows that the water flows not are effective in transporting particulate metals to the coastal zone. Retention of particulate matter and particulate metals in the estuary is probably occurring. This behavior was also observed in the dry season in 2004, when the tidal effect seemed to be dominant in the estuarine canal, with the flood flows higher than the ebb flows, denoting a classification of importer estuary, in the dry season, for the estuary of the Jaguaribe River (Dias, Marins, and Maia, 2009).

CONCLUSION

The dilution capacity and materials transport through the Jaguaribe River Estuary is strongly related to the physical and hydrological characteristics, such as the total water volume and freshwater volume, tidal prism, and residence time (Dias, 2007; Dias, Marins, and Maia, 2009). Considering the historical values, there has been a gradual decrease of outflows in the Jaguaribe River, and this strongly affects estuarine dynamics by decreasing sediment transport to the coastal zone, and altering the geochemistry of estuarine sediments (Marins and Lacerda, 2007; Marins *et al.,* 2003). The lowest SPM discharges were observed in the dry period, and the highest SPM discharges were observed in rainy periods, showing that the major contributions of the SPM are from erosion and leaching of the drainage basin soils to the estuary, which is more intense in the rainy season; this is also true for Al, Fe, and Cu. The discharges of particulate Zn, however, showed strong influence from anthropogenic sources, irrespective of rainfall intensity.

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Table 6. *SPM and particulate metals discharges in the Jaguaribe River*.

	SPM (kg y^{-1})	Cu (kg y^{-1})	Zn (kg y^{-1})	Al (kg y^{-1})	Fe (kg y^{-1})
September 2005	1.9×10^{7}	2.6×10^{2}	7.1×10^{4}	2.8×10^{5}	3×10^{5}
February 2006	4.7×10^{7}	3.5×10^{2}	1.4×10^{5}	5.6×10^{5}	5.6×10^{5}
June 2006	2.6×10^{8}	4.7×10^{3}	2.3×10^{5}	6.9×10^{6}	6.9×10^{7}
February 2008	9×10^{7}	7×10^{2}	9.3×10^{5}	3×10^{6}	2.4×10^{7}

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