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Hydrochemistry in tropical hyper-saline and positive estuaries

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Abstract. Samples were collected from estuarine mixing, upstream and inshore zones and measured for salinity, temperature, DO, pH, total alkalinity (TA) and nutrients. The aim was to characterize hyper-saline and positive estuarine systems and identify changes in physicochemical properties as a result of anthropic activities in surrounding areas. Mean salinity values (38.42-46.06), DO saturation (76.86%-103.79%), pH (7.90-8.22),TA (2.55 mM -2.80 mM) and NH_3 (0.82 µM -112.02 µM) were higher in northern systems. Agricultural effluents, shrimp farms effluents and domestic sewage have a serious impact on eastern estuaries. These factors are responsible for the increased mean nutrient concentrations (TP, NO_3^-, NO_2^- and $Si(OH)_4$) and lower mean pH (7.65), TA (1.60 mM) and DO saturation values (37.32%). Rainfall may also have a negative impact on estuarine waters because of increased runoff flow. This is apparent in the eastern estuaries where rainfall rates were significantly higher than those in the north. Northern hyper-saline estuaries were also found to be more resistant to changes in pH, owing to higher values of TA when compared with positive estuaries.

Key words: water quality, hyper-saline estuary, CO_2 system, phosphate, nitrogen

Resumo. Hidroquímica em estuários tropicais positivos e hipersalinos. As amostras foram coletadas na zona de mistura estuarina, zona de maré do rio e zona costeira e foram medidas a salinidade, temperatura, OD, pH, alcalinidade total (AT). O objetivo foi de caracterizar os sistemas estuarinos hiper-salinos e positivos e identificar mudanças nas variáveis físico-químicas como resultado das atividades antrópicas desenvolvidas no entorno. A variação média da salinidade (38,42-46,06 g/kg), saturação do OD (76.86%-103.79%), pH (7,90-8,22), AT (2,55-2,80 mM) e NH_3 (0,82-112.02 µM) foram maiores nos sistemas do litoral norte. Os efluentes da agricultura, fazenda de camarão e esgoto domestico afetam seriamente os estuários do litoral leste. Estes fatores são responsáveis pelas maiores concentrações de nutrientes (TP, NO_3^-, NO_2^- and $Si(OH)_4$) e pelas menores concentrações médias de pH (7,65), AT (1,60 mM) e saturação do OD (37,32%). A precipitação pode também ter um impacto negativo netas propriedades pelo aumento do fluxo de escoamento. Isto esta aparente nos estuários do litoral leste onde ocorreram significativamente as maiores precipitações. Os estuários hiper-salinos do litoral norte mostraram ser também mais resistentes a mudanças no pH, devido ao elevada AT, quando comparados com os estuários positivos.

Palavras-chave: qualidade da água, estuários hipersalinos, sistema CO_2, fosfato, nitrogênio

Introduction

Rainfall and intense human activities have had a significant influence on both fragile habitats and aquatic communities within estuarine ecosystems (Lacerda et al., 2006). Seven shallow coastal estuaries in Rio Grande do Norte (RN), Northeastern Brazil, were studied. Four of these, Apodi, Cavalos, Conchas and Assu, are classified as hyper-saline estuaries and are located in a more arid region of Northern RN. The other three systems, Ceará-Mirim, Potengi and Guaraíra Lagoon Complex, are positive estuaries located in the eastern region of the state, where most domestic effluents, rich in nitrogen and phosphorus are not properly treated. Excess of both nutrients promotes a bloom of phytoplankton that undergoes decomposition along with the organic material from domestic effluents, thereby causing a decrease in oxygen concentration in the water (Kennish, 1991; Zhang, 1996; Braga et al., 2000). The most common anthropogenic activities affecting the estuarine ecosystems of Rio Grande do Norte are shrimp and agricultural farming, sewage dumping and salt ponds (Ramos e Silva et al., 2003).

Shrimp farming affects the environment primarily through the discharge of harmful effluents (fertilizers and other chemicals) and mangrove deforestation. This results in eutrophication (changes in the nutrient cycle and oxygen depletion) and degradation in the quality of estuarine water available for human, plant and animal use and aquaculture activities.

This study aims to investigate the chemical properties involved in water quality for the first time, namely temperature, salinity, pH, oxygen, alkalinity, nitrate (NO_3^-), nitrite (NO_2^-), ammonia ($NH_3 = NH_3 + NH_4^+$), silicate ($Si(OH)_3O^-$), phosphate ($PO_4 = H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$) and total dissolved phosphate (TP = PO + organic phosphate).

Materials and Methods

Study area

Northern coastal sites. The Apodi (APO), Conchas (CON), Cavalos (CAV) and Assu (ASS) estuaries are located approximately 200 km north of the city of Natal, Brazil (Table I). The climate in this region is semi-arid and the estuaries are surrounded by shrimp farms, salt ponds and, agricultural areas and also receive domestic sewage (Ramos and Silva et al., 2003; Lacerda et al., 2006). The population in areas surrounding these shallow systems is 330,000 inhabitants, with 86.9 km^2 (CAERN, 2003; IDEMA, 2005) - see Table II. Mean annual temperature in the region is 32ºC with a mean annual rainfall of less than 750 mm. Mean evaporation is approximately 2,600 mm yr^{-1}. The dry season extends from June to February and the rainy season March to May (RADAMBRASIL, 1981).

Eastern coastal sites. Eastern coastal sites include the Potengi (POT) river estuary, which crosses Natal (the capital of RN), the Ceará-Mirim (CEM) river estuary, located 40 km south of Natal and the Guaraíra Lagoon Complex (GUR) 80 km south of Natal (Table I). These shallow estuary systems are also influenced by shrimp farming, agriculture and domestic sewage (Lacerda et al., 2006; Ramos e Silva et al., 2006). Mangrove forests bordering these estuaries have been replaced by tanks used for the culture of marine shrimp. There are approximately 1,060,000 inhabitants in the surrounding areas and shrimp farms of about 20.3 km^2 (CAERN, 2003; IDEMA, 2005; Lacerda et al., 2006) - see Table II. The dry season in this region is from September to December and the rainy season from March to July. The mean temperature is 25ºC with a mean rainfall of 1,400 mm yr^{-1} (EMPARN, 2007). Higher precipitation levels have been recorded in this area since January 2001, reaching a record 383.9 mm in January 2004 (INMET, 2007). Annual mean evaporation is approximately 1,600 mm yr^{-1}.

Table I. Estuary locations.

ESTUARIES	MERIDIANS
North coast	
Apodi	between 37º07’30” W to 37º11’30” W and 4º56’15” S to 5º01’15” S
Conchas	between 36º45’00”W to 36º 47’ 30” W and 5º02’30”S to 5º07’30”S
Cavalos	36º42’30”W to 36º45’00” W and 5º05’00” S to 5º08’45” S
Assu	between 36º37’30” W to 36º42’30” W and 5º05’00” S to 5º10’30” S
East coast	
Potengi	between 35º12’00” W to 35º16’00 W and 5º45’00” S to 5º48’30 S
Ceará-Mirim	between 35º13’00” W to 35º15’00” W and 5º40’00” S to 5º41’00” S
Guaraíra Lagoon Complex	35º06’30” W to 35º10’00” W and 6º07’00” S to 6º12’30” S

Table II. General features of the seven shallow estuarine systems studied.

Coastal Sites	Estuary	Rainfall[1] (mm yr^{-1})	Area (km^2)	Mean Depth (m)	Tide Range (m)	Tidal Excursion (km)	Population[2]	Shrimp Pond Area[3] (km^2)	Salt Production[3] (ton)
North	APO	750	11.0	4.3	≈ 0.0–2.8	11.5–31.0	256,857	≈ 10.67	2,490,914
	CON	600	2.4	2.5	≈ 0.0–2.8	11.5–31.0	4,650	≈ 12.72	-
	CAV	600	4.1	3.5	≈ 0.0–2.8	-	8,527	≈ 29.68	-
	ASS	600	5.6	2.7	≈ 0.0–2.8	-	47,274	≈ 33.83	1,977,877
East	CEM	1,300	2.5	2.5	≈ -0.1–2.7	10.0	89,640	≈ 3.63	-
	POT	1,900	14.1	7.5	≈ -0.1–2.7	27.1	908,893	≈ 3.92	-
	GUR	1,400	21.6	2.0	≈ -0.1–2.7	-	53,118	≈ 12.75	-

[1] INMET – Instituto Nacional de Meteorologia (Normais Climatológicas de 1961-1990), 2008.
[2] IBGE- Instituto Brasileiro de Geografia e Estatística 2004.
[3] IDEMA- Instituto de Desenvolvimento Econômico de Meio Ambiente do Rio Grande do Norte 2004 and 2005.

Water sampling and water analysis

Eastern estuaries were sampled in 2002 (September and October) and 2004 (January and February) and, the northern estuaries in 2001 (April and May) and 2003 (November). Experiments were carried out during neap tide, three days before the last quarter moon and continued through the following three days to the lunar phase (7 days). Data were collected at low tide, during the transition between the waning and waxing half moon, before and after 2 and 3-hour intervals, respectively. The total sampling period was approximately 3 hours from the beginning to end.

Our aim was to study the estuaries under their worst anthropogenic conditions since these appear more unfavorable for pollutant dispersion. A strictly controlled tidal regime was therefore used to ensure a reliable comparison between the seasons, sites and estuaries. Sampling was carried out in each estuary at stations numbered from 1 (estuary mouth) to 5 (up-river) over time intervals during neap low slack water. The vertical salinity profile of the estuaries studied under these tidal conditions demonstrates weak stratification; while the vertical profile of u-velocity is almost zero (Da Silva et al., 2006). Estuarine circulation is low in these conditions. Consequently, there is no tidal variability. Stations were geo-referenced using GPS (Garmin, model 12 XL).

Surface sampling was carried out using a Go-Flow bottle (General Oceanics, model 1080). Oxygen samples were transferred to 300 mL BOD bottles (Kimble) fixed and determined according to Winkler's method, as described by Ramos and Silva (2004). Based on salinity and temperature data, each dissolved oxygen concentration was converted into saturation values using AQM software (Análises Químicas Marinhas). Transparency was measured with a Secchi disc.

For total alkalinity and pH, the samples were transferred to 300 mL BOD bottles (Kimble) and, treated with mercuric chloride (DOE, 1994). They were then determined using open cell titration in accordance with Van den Berg & Rogers (1987), and calculated with AQM software. The pH was determined according to methodology defined for estuarine waters (Millero, 1986; Millero et al., 1993; Nenzer et al., 2005) and total pH scale (m) was used in each estuary. The pH value of each water sample was measured at 25°C to avoid temperature- bias (Pérez & Fraga, 1987). These values were then corrected to the temperature at the moment of sampling, using the AQM software.

Samples for dissolved inorganic nitrate (NO_3^-), nitrite (NO_2^-), ammonia ($NH_3 = NH_3 + NH_4^+$), silicate ($Si(OH)_3O^-$), phosphate ($PO_4 = H_2PO_4^- + HPO_4^{2-} + PO_4^{3-}$) and total dissolved phosphate ($TP = PO_4$ + dissolved organic phosphate) were treated with 4.5 M H_2SO_4 and filtered (except for the ammonia samples) through 0.45 µm cellulose acetate membranes using a Nalgene filtration system, . They were then soaked with 0.5 M HCl and rinsed three times with distilled water. Analyses were carried out using a Varian Cary, 100 UV-VIS spectrophotometer (Grasshoff et al., 1983). NH_3 samples were treated with 4.5 M H_2SO_4, purged for 2 min with N_2 (analytical grade) and analyzed according to the methodology described by Ramos e Silva (2004). TP was collected and determined according to Grasshoff et al. (1983).

Standards for each analysis were established using deionized water and repeated analysis precision (n = 10) for nutrient determinations ranged from <1.0 to 6.3%.

Salinity data of samples collected in 2001 and 2002 were obtained through a new salinity-chlorinate relation (S = 1.80655 x Cl) used for the calibration of the IAPSO Standard Seawater (P 137). Results were calculated according to Millero (1997).

Vertical profiles of hydrographic properties for estuary classification at the moment of the sampling were measured in 2003 and 2004 using a Valeport CTD/current meter, model MkIII. There was no difference between the chemical and physical methods used in salinity measurements.

Freshwater river and inshore samplings

Water sampling was conducted in both the upriver zones (salinity 0) in the APO, ASS, CEM and POT estuaries, as described before. This was approximately 20 km from the mouth of the estuaries and inshore waters (salinity of about 35), 5 km from the mouth of these estuaries.

Results

The form-number, defined by A. Courtier in 1938 (Defant, 1960; Davies, 1964), to classify the tidal type, was computed for both regions as the ratio of the amplitude of the main diurnal to semidiurnal tidal harmonic constituents. The calculated form-numbers and maximum tide heights indicate that all the estuaries studied are influenced by semidiurnal and mesotidal conditions.

Salinity

Northern coastal sites

Salinity in the northern estuaries ranged from 38 to 51 during the dry season, with a mean of salinity of 38.84 ± 9.97. These levels are due to the high evaporation rate, which exceeds land drainage. Low rainfall, high evaporation index and probably the salt input from the large salt production (Table II).

Eastern coastal sites

Salinity observed in the eastern estuaries ranged from low (0.20) in the CEM estuary during the rainy season, to high during the dry season (35.70) in the GUR. Mean salinity in all eastern costal sites was 11.19 ± 11.62 (Table III).

Temperature

Northern coastal sites

Thermal properties in all the estuaries indicate a narrow temperature variation, with temperature ranging from 27.90 °C to 29.94 °C and a, mean of 28.71 ºC ± 0.59. The lowest temperature was observed in the CON, while the highest was recorded in the CAV (Table III).

Eastern coastal sites

Temperature variation in these estuaries was also small. Temperatures ranged from 27.55 °C to 30.42 °C, with a mean of 28.85 °C ± 0.87. The lowest temperature was recorded in the GUR and the highest in the CEM (Table III).

pH (total scale – $[H^+] + [HSO_4^-]$)

Northern coastal sites

On the whole, northern estuaries had higher pH values. These varied between 7.74 (CAV) and 8.34 (APO) with a mean of 8.05 ± 0.17. See Table II for details on each estuary.

Eastern coastal sites

The pH values in these estuaries were lower those on the north coast and ranged from 7.04 (CEM) to 8.22 (POT). A Mean value of 7.60 ± 0.37 (Table III) was recorded in the eastern coastal sites.

Dissolved oxygen (DO)

Northern coastal sites

The largest DO concentration was observed in the CAV (240.00 µM) and APO (251.00 µM) over the rainy season, with a mean of 181.68 ± 33.30. The lowest value was recorded in the CON (123.07 µM) during the dry season. These estuaries were well oxygenated with a mean dissolved oxygen saturation of 92.91 % ± 15.91.

Eastern coastal sites

In the eastern estuaries, the lowest concentrations were found during the rainy season (CEM = <1.00 µM and GUR = 90.19 µM) (Table III). Oxygen concentration ranged from <1.00 µM (CEM) to 227.20 µM (CEM) with a mean concentration of 131.04 µM ± 58.74µM. These estuaries were moderately oxygenated (<01.0 % - 97.31 %) through dissolved oxygen saturation in the CEM) (Table II). The mean dissolved oxygen saturation for the east coast sites was 58.64 % ± 27.35 %.

Total alkalinity (TA)

Northern coastal sites

Higher TA values were observed in the northern estuaries (Table III). Concentration varied between 1.88 mM (ASS) and 3.08 mM (CAV), with a mean concentration of 2.75 mM ± 0.20 mM.

Eastern coastal sites

The eastern estuaries registered the lowest TA values, ranging from 0.88 mM (GUR) to 2.57 mM (GUR) (Table III). A mean concentration of 1.75 mM ± 0.49 mM was recorded in these areas.

Nutrients

Northern coastal sites

Overall, APO, CON and CAV estuaries had the highest concentration values of PO_4, TP, NO_3^-, NO_2^-, NH_3 and $Si(OH)_4$ along the estuarine mixing zone (Table III). The mean concentration at these sites was 1.56 µM ± 2.45 µM (PO_4), 3.14 µM ± 4.17 µM (PT), 0.54 µM ± 0.61 µM (NO_3), 0.57 µM ± 0.99 µM (NO_2), 28.44 µM ± 57.44 µM (NH_3), 30.01 µM ± 34.57 µM ($Si(OH)_4$) and 8.83 ± 9.84 ($DIN:PO_4$), respectively.

Table III. Chemical and physical-chemical variables.

Environmental Variables	Northern Costal Sites	Concentration		Eastern Coastal Sites	Concentration	
		Range	Mean (SD)		Range	Mean (SD)
Salinity	APO	39.68-49.30	44.04 (3.02)	CEM	0.20-30.60	3.53 (9.78)
	CON	37.50-44.78	38.82 (5.94	POT	19.16-30.75	23.83 (4.69)
	CAV	41.44-44.12	42.82 (13.81)	GUR	0.30-35.70	10.72 (11.63)
	ASS	40.65-50.79	46.06 (3.73)	-	-	-
Temp °C	APO	28.33-29.02	28.64 (0.24)	CEM	28.80-30.42	29.88 (0.60)
	CON	27.90-28.64	28.20 (0.25)	POT	29.14-29.69	29.35 (0.20)
	CAV	28.09-29.94	29.52 (0.21)	GUR	27.55-29.75	28.34 (0.57)
	ASS	28.14-28.42	28.26 (0.11)	-	-	-
pH_T	APO	8.14-8.34	8.22 (0.07)	CEM	7.04-8.16	7.42 (0.39)
	CON	7.75-8.15	7.95 (0.13)	POT	7.57-7.74	7.66 (0.07)
	CAV	7.74-8.11	7.90 (0.13)	GUR	7.10-8.22	7.65 (0.38)
	ASS	8.16-8.19	8.17 (0.02)	-	-	-
TA (mM)	APO	2.49-2.90	2.76 (0.12)	CEM	1.17-2.31	1.60 (0.43)
	CON	2.63-2.88	2.79 (0.08)	POT	1.81-2.42	2.21 (0.26)
	CAV	2.40-3.08	2.80 (0.20)	GUR	0.88-2.57	1.71 (0.50)
	ASS	1.88-2.81	2.55 (0.39)	-	-	-
DO Saturation (%)	APO	83.02-130.97	103.79 (16.19)	CEM	<1.00-97.31	37.32 (40.87)
	CON	64.98-100.46	76.86 (10.73)	POT	58.70-85.13	69.36 (9.65)
	CAV	75.92-102.08	94.41 (9.19)	GUR	36.84-92,26	65.03 (17.81)
	ASS	83.47-107.15	100.25 (9.64)	-	-	-
PO_4 (µM)	APO	<0.10-0.40	0.18 (0.12)	CEM	<0.10-3.10	1.51 (1.39)
	CON	0.30-2.40	1.40 (0.76)	POT	2.10-3.70	3.18 (0.62)
	CAV	0.90-10.50	3.65 (3.70)	GUR	<0.10-4.00	1.62 (1.43)
	ASS	<0.10-0.80	0.42 (0.28)	-	-	-
TP (µM)	APO	0.40-3.30	1.44 (0.95)	CEM	0.30-7.60	4.46 (3.09)
	CON	1.00-3.20	2.08 (0.70)	POT	4.20-7.90	6.20 (1.34)
	CAV	2.30-19.40	6.68 (6.66)	GUR	0.40-46.60	9.13 (11.05)
	ASS	0.50-2.70	1.58 (0.81)	-	-	-
NO_3^- (µM)	APO	<0.10-0.70	0.28 (0.25)	CEM	<0.10-1.40	0.56 (0.50)
	CON	0.20-2.30	1.14 (0.79)	POT	6.60-12.70	10.10 (2.36)
	CAV	<0.10-1.60	0.56 (0.60)	GUR	9.30-20.65	15.59 (4.31)
	ASS	<0.10-0.20	0.18 (0.04)	-	-	-
NO_2^- (µM)	APO	<0.10	<0.10	CEM	<0.1-0.40	0.24 (0.11)
	CON	<0.10-1.00	0.52 (0.34)	POT	2.10-57.00	41.32 (22.19)
	CAV	0.20-3.90	1.54 (1.67)	GUR	<0.10-0.35	5.16 (24.80)
	ASS	<0.01-0.10	<0.10	-	-	-
NH_3 (µM)	APO	<0.10-2.00	0,82 (0.79	CEM	0.20-0.90	0.46 (0.22)
	CON	<0.10	-	POT	14.40-39.00	24.72 (9.62)
	CAV	32.90-166.80	112.02 (63.46)	GUR	<0.10-11.90	3.24 (4.65)
	ASS	<0.10-2.60	0.82 (1.10)	-	-	-
DIN:PO_4 (ratio)	APO	3.00-23.00	9.80 (7.73)	CEM	0.23-1.29	0.53 (0.43)
	CON	0.71-1.32	1.04 (0.27)	POT	11.00-29.79	22.94 (7.16)
	CAV	16.15-30.27	22.37 (5.93)	GUR	4.55-11.00	6.90 (1.89)
	ASS	0.50-3.50	2.12 (1.37)	-	-	-
$Si(OH)_4$ (µM)	APO	5.30-14.60	10.92 (3.49)	CEM	12.50-386.10	90.06 (165.51)
	CON	16.40-72.20	47.76 (22.49)	POT	24.90-100.50	65.00 (30.24)
	CAV	<0.10-130.00	52.14 (56.09)	GUR	<0.10-124.20	27.58 (29.15)
	ASS	6.50-13.80	9.22 (3.15)	-	-	-

Temp = Temperature; TA = Total Alkalinity; DO = Dissolved Oxygen; $PO_4 = H_2PO_4^+ + HPO_4^{2-} + PO_4^3$.
SD = Standard Deviation (±).

Eastern coastal sites

The highest mean concentrations of PO4 (3.18 µM) and nitrite (41.32 µM) were found in the POT Estuary. TP was also observed in higher mean concentrations in the POT (6.20 µM) and in the GUR Lagoon Complex (9.13 µM) (Table III).

Figure 1 summarizes nutrient concentrations in upriver, mixing zone and inshore samples. The same behavior was observed in positive (CEM and POT) and hyper-saline (APO and ASS) estuaries for TP. That is, where the mixing zone (MZ) was a source of TP or was influenced by adjacent agriculture, aquaculture and urban sewage areas, since none of these effluents are treated before being released into estuaries (Lacerda et al, 2006). Both PO_4 and NO_2^-concentrations followed the same trend described for TP in the POT estuary.

Freshwater river and inshore sampling

The largest concentrations for all the nutrients (PO_4, TP, NO_3^-, NO_2^-, NH_3 and $Si(OH)_3O^-$) were recorded upriver rather than, inshore (Table IV).

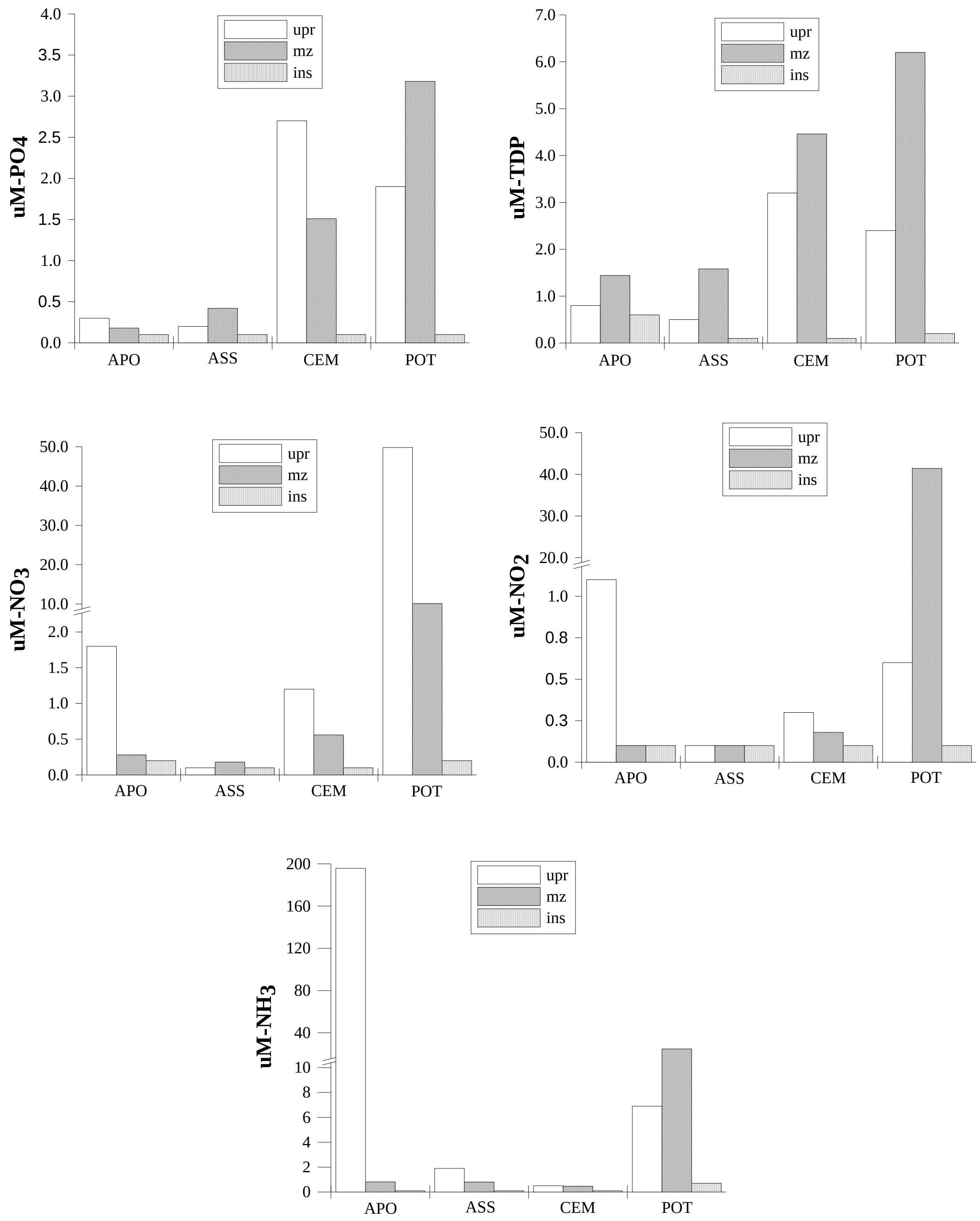

Figure 1. Mean nutrient concentration in upriver, mixing zone and inshore waters in the Apodi, Assu, Ceará-Mirim and Potengi estuaries. APO = Apodi estuary, ASS = Assu estuary, CEM = Ceará-Mirim estuary, POT = Potengi estuary, upr = upriver, mz = mixing zone, ins = inshore.

Table IV. Water sampling in upriver and inshore areas.

Shallow Systems	Season (Date)	Sampling	PO_4 (µM)	TP (µM)	NO^-_3 (µM)	NO^-_2 (µM)	NH_3 (µM)	Salinity
Apodi (North)	Dry 11.15.03	upriver	0.30	0.80	1.80	1.10	195.80	0.00
	Dry 11.15.03	inshore	<0.10	0.60	0.20	<0.10	<0.10	36.00
Assu (North)	Dry 11.18.03	upriver	0.20	0.50	<0.10	<0.10	1.90	0.00
Ceará-Mirim (East)	Rainy 02.12.04	upriver	2.70	3.20	1.20	0.30	0.50	0.00
Potengi (East)	Dry 11.18.03	upriver	1.90	2.40	49.80	0.60	6.90	0.00
	Dry 11.18.03	inshore	<0.10	0.20	0.20	<0.10	0.70	36.00

Discussion

Types of Estuaries. Salinity, u-velocity components and vertical profiles at the moment of the sampling were considered and, the systems studied were then classified in accordance with the calculation of Richardson's layer number (RiL), as defined by Miranda et al. (2002). The systems showed weak vertical salinity stratification and instability in u-velocity component profiles. Their respective RiL values therefore, indicated reasonable mixing processes during sampling. As a result, all estuaries were classified from weakly stratified to well-mixed, under a semidiurnal mesotidal regime.

Salinity. Estuaries can be classified according to their circulation pattern and salinity (Miranda et al., 2002). Positive estuaries are determined by freshwater input from the river to the sea surface and the seawater flow upriver underneath the freshwater. However, hyper-saline (or negative) estuaries generally have low discharge of riverine freshwater input and are located in high evaporation index regions where evaporation exceeds the freshwater supply (Table II). Although salinity at the surface remains unchanged from the ocean towards the inner estuary, water loss through evaporation, increases the salinity along the estuary interior. As density increases, the high-salinity water sinks. As a result, water in the estuary circulates inwards near the surface and near the bottom as it reaches the sea. Water in these estuaries consequently becomes more saline than in the open ocean (inshore).

Based on salinity stratification in the water, shallow systems located in the northern and eastern regions should be classified as hyper-saline (or inverse) and positive estuaries, respectively.

pH (total scale – $[H^+] + [HSO_4^-]$). There is a relationship between bicarbonate/carbonate concentration and pH when the system is at equilibrium with the atmosphere and CO_2 dissociation constants (k_1 and k_2) are higher, as is typically seen in salt water (Pankow, 1991; Gómez-Parra and Forja, 1994; Millero, 2001).

The low saline levels in the eastern positive estuaries (CEM, POT and GUR) due to heavy rainfall (283.0 mm, see Table II), had lower pH values than those recorded in the northern hypersaline estuaries. This may be caused not only by the dissociation constants of carbon dioxide mentioned above, but also by high organic matter input, leading to heterotrophic activity.

Natal, with a population of 750,000 inhabitants, is situated around the Potengi estuary and discharges more than 60% of its untreated sewage directly into the estuary (Ramos e Silva et al., 2006). Ceará Mirim and Guaraíra Lagoon Complex also, receive large amounts of organic waste although they have a low dilution capacity (area to volume ratio = 257 and 134 m^2/m^3, respectively) (Lacerda et al., 2006). Heavy rainfall prior to the sampling period may also have led to increased runoff from shrimp ponds and agriculture (Lacerda et al., 2006), resulting in the lowest pH values reported (7.04 and 7.10) (Table III). Rainwater is naturally acidic because of atmospheric carbon dioxide. As rain falls into the estuary, each drop becomes saturated with CO2 and pH decreases. Braga et al. (2000) found pH values below 8.00 in the Baixada Santista estuarine system. This system is highly polluted because of urban, industrial and, harbor activities.

Low freshwater discharges and rainfall in the northern region might be responsible for the high seawater admixtures, which buffered the pH to the higher values observed. pH values in the hyper-saline estuaries (8.11 - 8.34) are correlated to dissolved oxygen saturation (0.56, $p<0.05$), suggesting that such pH deviation may occur because of photosynthetic activity.

Dissolved oxygen (DO). Although oxygen solubility is related to salinity and temperature (Millero, 1997), biological production and respiration can also affect the DO concentration in aquatic systems (Chester, 1990; Millero, 1996). Domestic organic matter may also influence this parameter, since nearby cities discharge about 60 to 100% of untreated sewage directly into the systems studied (Ramos and Silva et al., 2001; Lacerda et al., 2006; Ramos e Silva et al., 2006). The number of inhabitants in the eastern region is significantly higher than in the north (Table II). Rainfall also contributes indirectly to DO depletion by transporting organic matter from agriculture and shrimps ponds through CEM estuary runoffs (Lacerda et al., 2006). This depletion was observed during sampling in January 2004, when rainfall was much higher than at the other sampling sites. Water transparency measured with a Secchi disc was lower than 3 cm and DO concentration was lower than 1.00 µM. Ovalle et al. (1990), Balls (1994), Müller et al. (1994) and Braga et al. (2000) also found that suspended organic matter affected the dissolved oxygen concentration in estuaries.

Oxygen saturation indicates that saturation depends on both salinity and temperature (Millero, 2006). Our values of oxygen saturation showed that hyper-saline estuaries are more oxygenated than positive estuaries. The difference in oxygen saturation between estuaries is not likely to be related to temperature, since both estuarine systems presented a similar variation. Organisms consume oxygen to decompose organic matter and may therefore be responsible for lowering dissolved oxygen saturation, particularly in positive estuaries (< 1.0%). The dissolved oxygen saturation in the hyper-saline systems showed a positive correlation with pH (0.56, $p<0.05$), which was weaker than the correlation observed for positive estuaries (0.81, $p<0.05$). However, correlation between salinity and pH (0.80, $p<0.05$) suggests this result may be associated with seawater mass and the influence of continental water mass along the tidal excursion.

Total alkalinity (TA). A number of physical parameters and biological processes such as salinity, photosynthesis and respiration (organic matter decomposition) can affect TA in estuarine systems. The TA and pH within the estuaries studied appeared to have both conservative and non-conservative behavior.

Higher TA values observed in the northern estuaries indicate that these values were compatible with the salinity (Friis et al., 2003), since HCO_3^- is the main seawater component (Millero, 1996) and is primarily responsible for the conservative behavior shown.

Although the physical and biological processes responsible for TA changes among the systems were not determined, it is clear that salinity is responsible for the highest concentrations of bicarbonate and carbonate in the northern sites (Zeebe & Wolf-Gladrow, 2005). Salinity affects the dissociation constants (k_1 and k_2) of the CO_2 system (Dickson and Millero, 1987; Lueker et al., 2000; Ramos and Silva et al., 2002) and, therefore, affects both bicarbonate and carbonate concentrations. Using the equations for carbonate system dissociation constants (Dickson, 1990; Roy et al., 1993; Millero, 1996), we found a higher contribution of bicarbonate and carbonate in the hyper-saline estuaries (0.00200 ± 0.00028 mol kg^{-1}-H_2O and 0.00036 ± 0.00011 mol kg^{-1}-H_2O, respectively).

The positive correlation between pH and dissolved oxygen saturation in hyper-saline and positive estuaries (0.56 and 0.85, respectively, $p<0.05$) demonstrates that microscopic plants may use CO_2 for photosynthesis, removing carbonic acid (H_2CO_3) and increasing pH (Millero, 1996).

Nutrients. In the hyper-saline estuaries, NH_3 concentrations were very low, except in the CAV where they were extremely high (32.90-166.80 µM) (Table III) compared with the other systems studied. Ammonification (NH_4^+ release from organic matter) in shallow estuarine systems is regulated by the quality and quantity of the organic matter supplied to the sediment (Herbert, 1999). The reason for the high concentration found in CAV waters is not clear. Autochthonous sources (decomposition of labile organic matter) cannot be responsible for these values, since dissolved oxygen saturation is high (mean 94.9%). A significant fraction of nitrogen emissions (≈ 1,200 t yr^{-1}; Lacerda et al., 2006) from anthropogenic sources may reach the CAV estuary in the form of NH_3.

Previous studies indicated a high level of organic pollution in the POT estuary (Ramos e Silva et al., 2001; Ramos e Silva et al., 2003), which might explain its high concentration of PO_4 and TP. The GUR estuary had the highest TP concentrations among the estuaries studied. It is surrounded by shrimp farms (≈1.91 km^2), agricultural areas and a population of 21,660 inhabitants that discharge their effluents and untreated sewage directly into the estuarine system. This estuary is a small water body (≈2.9 km^2) with a low turnover rate (Ramos e Silva et al., 2001), which may explain the high TP values. McDonald et al. (1994) also related population growth to increased phosphate concentrations within estuaries.

When developed under non-sustainable conditions, shrimp production has a negative effect (e.g., increased phosphate concentration) on shallow estuarine systems (Twilley et al., 1999, Burford et al., 2003). Lacerda et al. (2006) stated that phosphate emissions from shrimp farms are directly dumped into estuarine waters and the response of the estuary metabolism is therefore probably faster than that of other sources. Rainfall conditions may intensify these negative impacts because of increased runoff. For example, PO_4 and TP varied seasonally in some of the estuaries studied, with the highest concentrations observed during rainy seasons.

Table V. Chemical and physical-chemical variables under seasonal weather.

Weather	Environmental Variables	Shallow Systems North	Concentration		Shallow Systems East	Concentration	
			Mean	Standard Deviation		Mean	Standard Deviation
DRY	PO_4 µM	CON	1.64	0.86	CEM	0.28	0.11
		CAV	5.96	4.16	GUR	0.20	0.10
	TP µM	COM	2.38	0.85	CEM	1.60	0.97
		CAV	10.40	8.06	GUR	0.76	0.25
RAINY	PO_4 µM	COM	1.10	0.59	CEM	2.74	0.75
		CAV	1.45	0.29	GUR	3.20	0.39
	TP µM	COM	1.70	0.38	CEM	7.32	0.27
		CAV	3.05	0.39	GUR	6.95	1.25

The low rainfall in the hyper-saline estuaries implies lower nutrient inputs through runoff (Table V). On the other hand, the CON and CAV estuaries did not show increased nutrient concentrations over rainy seasons. The drainage system in these estuaries may be less effective, with minor superficial runoff during the rainy season. Rainfall would therefore play a significant role, leading to direct dilution of nutrient concentration in both estuaries.

This pattern would be inversely related to flow with substantial impact over low flow periods, when dilution might decrease to minimum values. McDonald et al. (1994) also observed an inverse relationship between phosphate concentration and water flow that may partially explain our results.

Silicate concentrations did not indicate clear distribution between hyper-saline and positive estuaries. Dissolved silica may be consumed by biota in low turbidity and stagnant aquatic systems. These different silicate concentrations might be related to natural processes (rock and soil weathering). High levels of dissolved silica in the CON and CAV hyper-saline estuaries suggest that terrigenous supply always exceeds biological consumption (Aston, 1983).

N:P Redfield ratio. The synthesis of organic matter through marine photosynthetic activity is a selective process resulting in specific composition products. Phytoplankton analysis indicates that N and P atoms are present in seawater at a mean constant molar ratio of 16:1, known as the Redfield ratio (Redfield et al., 1963). According to Liebig's minimum law, the seawater component present at the lowest concentration required for organism growth should be regarded as the limiting factor. The ratio in phytoplankton (N:P = 16:1) is close to the DIN (NO_3^- + NO_2^- + NH_3) and PO_4 ratio available in the seawater and required for the formation of organic matter by phytoplankton (DIN:PO_4 = 15:1). Therefore, both nitrogen and phosphorus ratios appear to be limiting components in the seawater (Burkhardt et al., 1999). In the hyper-saline estuaries, at the moment of the sampling, the mean DIN:PO_4 ratio for CON and ASS was lower than 16. Consequently, nitrogen appears to be limiting phosotynthesis. The DIN:PO_4 ratio (CEM, GUR) in the positive estuaries also had significant deviations at less than 16 (N:P Redfield ratio), indicating a putative nitrogen limitation as well (Table III). However, the positive Potengi estuary and the hypersaline APO and CAV estuaries had a DIN:PO_4 ratio higher than 16 (N:P Redfield ratio=22.9).

Available data strongly suggests that many marine systems show seasonal variation in nutrient limitation. In Hiroshima Bay, Japan, for example phosphorus limitation was detected in August and May and nitrogen limitation was found during the other periods (Lee et al., 1996). An instantaneous measurement, such as the one used in the present study, may therefore be an inaccurate indicator of nutrient limitation (e.g., Soetaert et al., 2006). However, both the low and high DIN:PO_4 ratios found in the sampled estuaries clearly indicate that N or P could play a major putative role in eutrophication in these regions. Thus it would be necessary to control both nitrogen and phosphorus sources into the estuaries.

Freshwater river and marine end members. The highest concentrations in the upriver end member of an estuary are recognized in the scientific literature (Ovalle et al., 1990; Shengquan et al., 1993; Zhang, 1996; Cabeçadas et al., 1999, Jennerjajn et al., 2004), and are related to large anthropogenic nutrient inputs at the head of the estuary. These very different upriver concentrations are caused by anthropogenic input from untreated sewage released directly into the POT. However, there are also several other sources of organic effluent along the POT (Ramos e Silva et al., 2001). In addition, mangrove forests have been removed on the CEM side of the estuary the mangrove to make room for shrimp farming ponds.

In our first observations, data on NO_3^- (Figure 1) indicate that upriver waters are diluted in the mixing zones in the APO, CEM and POT estuaries by oligotrophic waters from the Atlantic Ocean. Curiously, the same physical dilution process is not recorded for the TP ratio. The same scenario is observed for NH_3 and NO_2^- in the APO estuary and the biogeochemical barriers along the estuary might also explain these low concentrations in the MZ.

Conclusion

The results of the present study, based on collection conditions, show significant differences in chemical and physicochemical properties between the northern and eastern estuaries. The latter appear more susceptible to eutrophication caused by anthropic activities. This is intensified by the higher pluviometric rates recorded in the eastern regions when compared with the north.

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