

## Factors Affecting the Hydrochemistry of a Mangrove Tidal Creek, Sepetiba Bay, Brazil

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We studied the porewater chemistry, and spatial and temporal variation of mangrove creek hydrochemistry. Except for nitrate porewater, the concentrations of nutrients we analysed were higher than for creek water. Groundwater is a source of silica and phosphate, whereas total alkalinity and ammonium are related to mangrove porewater migration to the creek. Open bay waters contribute chlorine, dissolved oxygen and elevated pH. The results also suggest that nitrate is related to nitrification inside the creek. During flood tides, salinity, chlorine, dissolved oxygen and pH increase, whereas total alkalinity decreases. This pattern is reversed at ebb tides. Silica, phosphate, nitrate and ammonium show an erratic behaviour during the tidal cycle. Tidal dynamics, precipitation events and nitrification inside the creek were identified as major control factors and an estimate of tidal exchanges indicate that the system is in an equilibrium state.

### Introduction

Tidal exchange studies between salt marshes and coastal waters have been carried out since the classical report of Teal (1962) introduced the concept of 'outwelling' of nutrients and organic material. However, further research suggests that salt marshes are nitrogen transformer systems, rather than simple exporters of substances (Nixon, 1980).

Similarities between salt marsh and mangrove biogeochemical processes are related to high productivity and daily tidal inundation that favour organic matter decomposition mediated by sulphate reduction and associated fermentation reactions (Lord & Church, 1983; Boon & Cain, 1988). However, studies concerning chemical and biological interactions between mangroves and adjacent coastal areas are still scarce (Boto & Bunt, 1981; Boto & Wellington, 1988; Wolanski *et al.*, 1980; Woodroffe, 1985; Lacerda *et al.*, 1988; Rezende *et al.*, 1990).

The present study evaluates hydrochemical variations in a mangrove tidal creek, identifying major control factors and estimating exchanges with an adjoining bay.

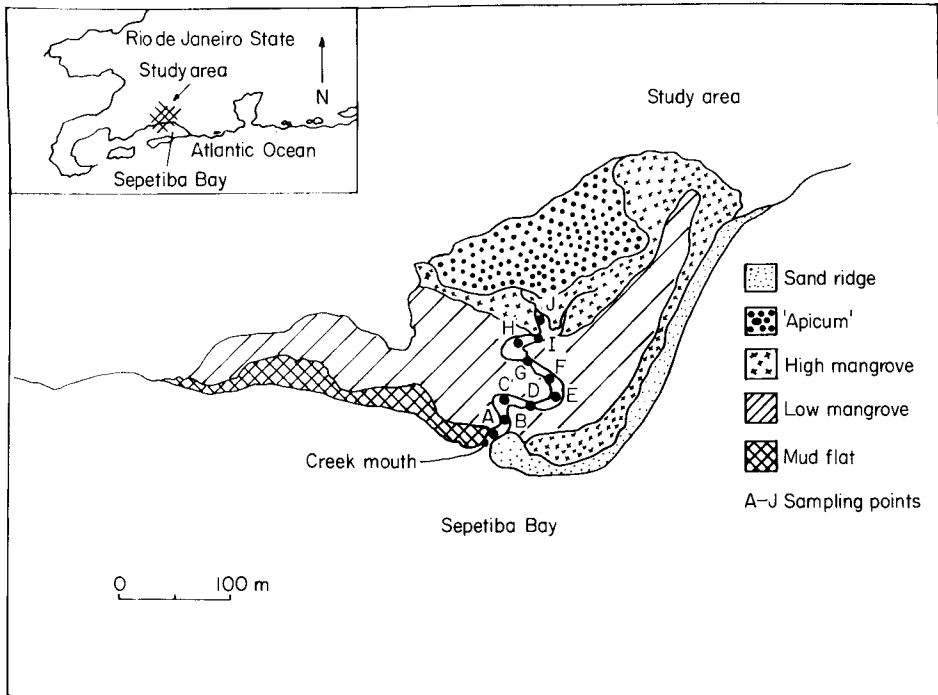


Figure 1. Map of the study area.

### Material and methods

The study site was located at the Itacuruçá Experimental Forest, Sepetiba Bay, Rio de Janeiro State, south-east Brazil (Figure 1). The forest is a 4-ha monospecific stand of the red mangrove *Rhizophora mangle* L., drained by a tidal creek 100 m long with a maximum width and depth at high tide of about 5 and 1.8 m, respectively, and minimum width and depth at low tide of about 2 and 0.6 m, respectively. A mud flat 30 m wide is located in front of the forest, while a non-vegetated salty zone locally called 'apicum' separates the mangrove forest from terrestrial vegetation. Two different topographic units can be identified in the forest: 'low mangrove' flooded daily by tides, with highest biomass and tree density growing over muddy sediments; and 'high mangrove' only flooded during spring tides, with lower biomass and tree density growing over sandy soils. There are no streams at the study site, with freshwater input originating only through groundwater flow and precipitation (Lacerda *et al.*, 1988). Details on forest structure, biomass and soil characteristics can be found in Silva *et al.* (1990a,b) and Lacerda and Rezende (1987).

The approach used here is based on an initial characterization of porewater chemistry and spatial variation of creek hydrochemistry in high and low tidal situations (Martinet *et al.*, 1982; Nedwell, 1975). Along the tidal creek, bay water, mangrove porewater and fresh groundwater have different levels of mixing, allowing a comparative identification of their hydrochemical properties (Ovalle *et al.*, 1987). Hydrochemical monitoring of tidal cycles during summer and winter allows analysis of the effects of seasonal and diel fluctuation patterns, as well as evaluation of the effects of meteorological variables and estimates of tidal exchanges.

TABLE 1. Porewater chemistry in high mangrove (H), low mangrove (L) and mud flat (M); Eh in mV, salinity (S) in ‰, chlorine (Cl) and total alkalinity ( $\text{HCO}_3^-$ ) in meq/l; others in  $\mu\text{M}$

P	pH	Eh	S	$\text{PO}_4$	$\text{NO}_3$	$\text{SiO}_2$	$\text{NH}_4$	Cl	$\text{HCO}_3^-$
L1	7.13	-362	31	32.9	1.5	160	235	589	21.3
L2	6.96	-355	31	35.0	1.0	198	113	640	22.3
H1	6.37	-265	25	25.2	2.3	93	50	290	3.9
H2	6.39	-110	26	9.7	3.2	67	209	488	5.2
M1	7.47	-186	28	17.3	2.8	45	111	605	4.0
M2	7.36	-240	28	51.4	2.1	143	119	577	8.2

Porewater was collected using a PVC extractor tube with a porcelain porous end tip. The tubes were installed in duplicate in the mud flat, low mangrove and high mangrove at a depth of 30 cm. Before sampling, the extractors were treated with distilled water for 4 days and with bay water for 2 days. The first sample, collected 2 h after installation was discarded.

The spatial variation of creek hydrochemistry was measured twice by sampling at 10 points distributed each 10 m along the channel, one with control variables (salinity, pH, Eh and dissolved oxygen) in a non-rainy period and another with a complete characterization during rainy period. The location of sampling points in relation to vegetation type is presented in Figure 1.

Three sampling periods of 30 h were conducted in summer (2) and winter (1) to study tidal fluctuations. Creek water was sampled at 30-min intervals at the creek mouth (point A in Figure 1) with a Van Dorn bottle at the central part of the channel, at a depth of about 30 cm in order to avoid floating detritus. A flowmeter was installed at the sampling point.

For each sample, we measured (on site) the pH, dissolved oxygen, Eh, temperature and salinity with portable equipment. Subsamples were filtered through a GF/C Whatman membrane and stored on ice for transport. Silica, phosphate, nitrate and ammonium were analysed following the method of Grasshoff *et al.* (1983). Total alkalinity and chlorine were determined by potentiometric titration using the Gran method (Gran, 1952).

An estimate of tidal exchange was performed by multiplying instantaneous discharge and concentration of measured compounds in each sample, and assuming a constant flow during the sampling period.

## Results and discussion

### Porewater chemistry

Table 1 summarizes hydrochemical characteristics of porewater in different portions of the mangrove forest. Those for mangrove creek water are listed in Table 2. A comparison of porewater and creek water shows that except for nitrate, chlorine and pH, porewater concentrations are much higher than those in creek water along tidal cycles, as would be expected for a sulphate-reduction-dominated environment (Giblin & Howarth, 1984; Malcolm *et al.*, 1986; Nixon, 1980; Nedwell, 1975). A spatial gradient between porewater characteristics in high mangrove, mud flat and low mangrove is identified. Salinity and, to a lesser extent, chlorine in the low mangrove were higher than in a mud flat and high

TABLE 2. Spatial variation of creek hydrochemistry at low tide stage (upper half) and high tide stage (lower half); from A (mouth of the mangrove creek) to J (upstream end); Eh in mV; salinity (S) in ‰; chlorine (Cl) and total alkalinity (HCO<sub>3</sub>) in meq/l; others in μM

P	pH	Eh	S	PO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>	NH <sub>4</sub>	Cl	HCO <sub>3</sub>	O <sub>2</sub>
A	7.17	133	14	0.74	2.7	16.7	2.3	285	2.0	4.8
B	7.15	136	14	0.84	3.2	12.0	2.7	357	1.2	4.7
C	7.13	136	13	0.84	2.1	30.0	2.4	167	1.8	4.9
D	7.18	161	14	1.16	1.6	13.3	7.0	253	2.5	4.9
E	7.17	136	14	1.05	2.5	16.0	7.4	277	2.5	4.9
F	7.20	185	13	1.79	1.3	33.3	2.7	111	2.8	4.8
G	7.23	141	16	1.05	4.9	23.3	3.1	239	2.1	3.6
H	7.29	140	15	1.05	3.4	33.3	5.5	162	2.2	5.3
I	7.26	206	13	1.58	2.1	20.0	1.4	155	1.4	6.0
J	7.25	132	16	1.16	2.6	19.2	1.5	314	1.2	5.9
A	7.46	136	29	0.53	1.2	19.3	0.9	585	1.2	4.9
B	7.43	121	27	0.53	1.7	27.8	2.5	306	1.2	5.8
C	7.36	122	27	0.53	1.2	22.3	1.5	569	2.2	4.7
D	7.40	144	27	0.53	1.5	23.3	2.0	439	1.5	5.8
E	7.31	133	27	0.53	1.2	21.7	1.9	414	1.5	4.6
F	7.34	134	26	0.74	1.0	26.7	3.1	435	0.6	4.8
G	7.24	191	27	0.53	1.3	13.0	1.1	476	0.9	4.8
H	7.36	169	26	0.74	1.0	28.3	0.6	342	0.9	5.1
I	7.39	282	26	0.84	0.8	30.0	3.4	250	0.7	5.2
J	7.55	152	25	0.53	1.0	26.0	1.4	311	1.4	6.5

mangrove, a consequence of evapotranspiration concentrating salts in rhizosphere of this dense stand (Wolanski & Gardiner, 1981). The low tree density and sandy soils facilitate washing of salts from the high mangrove area. The pH values are close to neutral in the low mangrove portion and slightly acidic in the high mangrove, whereas pH in the mud-flat porewater is higher due to proximity of bay water. Total alkalinity is increased by a factor of 20 in low mangrove porewater compared to creek water, whereas in the mud flat and high mangrove porewater it is only increased by a factor of two.

The porewater chemistry reflects an intense sulphate reduction that produces ammonium and total alkalinity, turning the environment strongly reducing as reflected by negative Eh values (Giblin & Howard, 1984).

#### *Spatial variation of creek hydrochemistry*

Variation in creek hydrochemistry (creek mouth–low mangrove–high mangrove) during low and high tide stages is evident from Table 2. The positive gradient for phosphate (increasing concentration from the mouth to high mangrove) in the two stages reveals that groundwater is probably an important source of this compound to creek water, with salinity and chlorine showing inverse patterns. Ammonium and total alkalinity generally show higher values upstream in the mangrove creek correspondent to low mangrove areas during low tide stage, reflecting sulphate reduction processes at the sediment level. Nitrate shows a consistent negative gradient at both tide stages (decreasing concentration values entering the mangrove) pointing to groundwater as a minor source when compared to bay water and mangrove porewater. Higher nitrate values during low tide suggest that nitrification of ammonium originating in mangrove porewater could be occurring in the mangrove creek (Wolaver *et al.*, 1984; Blackburn, 1986). Rainwater has nitrate in the same order of

magnitude as the lower values for creek water (Pedlovisky, unpubl. data), and thus could not be responsible for the nitrate concentration peaks in creek water, as reported by Whiting *et al.* (1989).

Variation in silica and Eh shows no consistent patterns, although the major silica values in low mangrove points of low tide may be related to porewater inflow in the creek. pH shows a positive gradient during low tide and a negative gradient during high tide, with inner points showing minor variation compared to the creek mouth.

A comparison of the spatial variation in a wet and dry period (data not shown), reveals that rainfall smooths and decreases dissolved oxygen and Eh values, suggesting that precipitation at low tide promotes the flow of mangrove porewater to the creek channel. Wolanski and Gardiner (1981) noted that rainfall occurring at low tide percolates directly into mangrove sediment. The salinity variations suggest that precipitation has an important role on fluxing to the creek of the salt accumulated not only in mangrove sediments by evapotranspiration (Wolanski & Gardiner, 1981), but also in the non-vegetated salty zone ('apicum') adjacent to the forest.

#### *Tidal variations*

During tidal cycles, a consistent pattern of hydrochemical variation was identified at the creek mouth. Bay water entering at the mangrove flood tide leads to an increase in salinity, chlorine, pH and dissolved oxygen in creek water, whereas total alkalinity decreases (Figure 2). These results correspond closely to those of Glocke *et al.* (1981), Valiela *et al.* (1978) and Harbinson (1986). Silica, phosphate, nitrate and ammonium behaviours are characterized by a sequence of low values punctuated by frequent peaks of high concentration generally associated with high discharge periods (Figure 3). Silica and phosphate also presented irregular peak values at low discharge, in two cycles at least. However, Whiting *et al.* (1987, 1989), Wolaver *et al.* (1984) and Boto and Wellington (1989) report tidal signatures for nitrate, ammonium and phosphate. Eh shows a well defined range of variation with no consistent pattern (data not shown).

The first sampling period in December 1986 presented a sequence of quarter diurnal cycles with creek depth varying from 70 to 182 cm (Figure 2). The ranges of parameter variation were: temperature, 24–28 °C; pH, 7.05–8.09; O<sub>2</sub>, 4.3–9.0 mg/l; salinity, 16–28‰; chlorine, 311–497 meq/l; total alkalinity, 1.57–2.63 meq/l; SiO<sub>2</sub>, 24.7–81.9 µM; PO<sub>4</sub>, 0.90–3.16 µM; NH<sub>4</sub>, 2.0–22.6 µM; NO<sub>3</sub>, 1.5–13.4 µM; Eh, 136–251 mV.

During the first half of this first sampling the study area was under the influence of a cold front system accompanied by intense precipitation. This event affected the general pattern described above, as the amplitude of variation in total alkalinity and salinity was reduced, but did not affect pH and dissolved oxygen (Figure 2). Ovalle *et al.* (1987) showed that nitrate, silica and phosphate were also influenced by precipitation events when several peaks of high concentration occurred. Whiting *et al.* (1987) found this same behaviour for nitrate in a salt marsh.

The second sampling period for June 1987 was also composed of quarter diurnal cycles, with creek depth varying from 80 to 185 cm (Figure 3). The ranges of parameter variation were: temperature, 19–22 °C; salinity, 22–30‰; pH, 7.01–8.23; O<sub>2</sub>, 4.5–8.0 mg/l; chlorine, 380–720 meq/l; total alkalinity, 1.01–2.10 meq/l; SiO<sub>2</sub>, 15.2–75.4 µM; PO<sub>4</sub>, 0.61–12.7 µM; NH<sub>4</sub>, 2.36–15.4 µM; NO<sub>3</sub>, 1.22–4.71 µM; Eh, 135–264 mV.

During the first 10 h of this sampling, the studied area was under the influence of a cold front passage that affected the general pattern described initially. Intense precipitation occurred at the lowest tide stage during this sampling, followed by a sharp elevation of

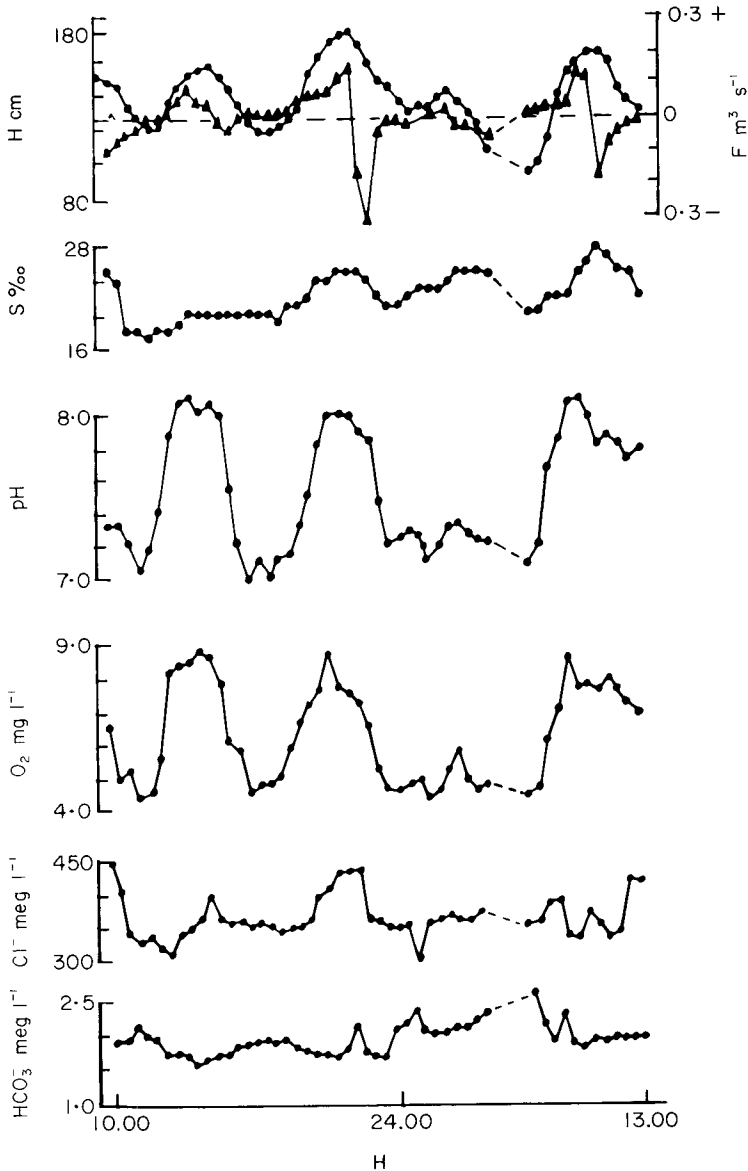


Figure 2. Representative temporal variations of creek depth (H), instantaneous discharge (F), salinity (S), pH, dissolved oxygen ( $O_2$ ), chlorine ( $Cl^-$ ) and total alkalinity ( $HCO_3^-$ ).

creek depth (from 80 to 185 cm) in a short period of time (maximum depth was achieved in 2 h). Freshwater input to the mangrove by groundwater and precipitation appear to be largely trapped inside the mangrove in a manner analogous to that described by Wolanski and Ridd (1986). At the following ebb and flood tides this water strongly influenced creek hydrochemistry, as total alkalinity decreased, silica and phosphate peaks increased, and the usual wide fluctuations in ammonium concentration were largely smoothed (Figure 3).

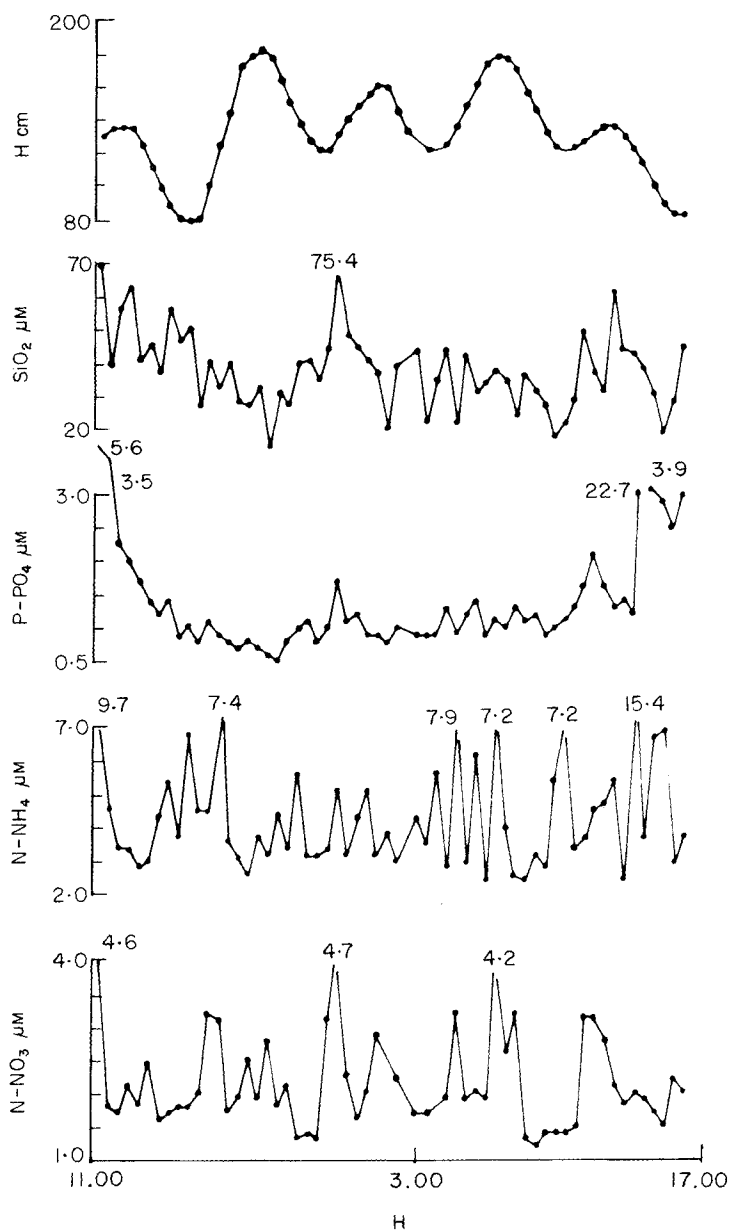


Figure 3. Representative temporal variation of creek depth (H), silica ( $\text{SiO}_2$ ), phosphate ( $\text{P-PO}_4$ ), ammonium ( $\text{N-NH}_4$ ) and nitrate ( $\text{N-NO}_3$ ).

The third sampling period in December 1987 was composed of two semi-diurnal tidal cycles with creek depth varying from 63 to 154 cm. The ranges of parameter variation were: temperature, 25–29 °C; salinity, 22–31‰; pH, 7.25–8.20;  $\text{O}_2$ , 4.1–9.5 mg/l; chlorine, 454–667 meq/l; total alkalinity, 1.37–2.39 meq/l;  $\text{SiO}_2$ , 4.8–53.1  $\mu\text{M}$ ;  $\text{PO}_4$ , 0.21–7.6  $\mu\text{M}$ ;  $\text{NH}_4$ , 0.71–11.8  $\mu\text{M}$ ;  $\text{NO}_3$ , 1.6–12.2  $\mu\text{M}$ ; Eh, 169–254 mV.

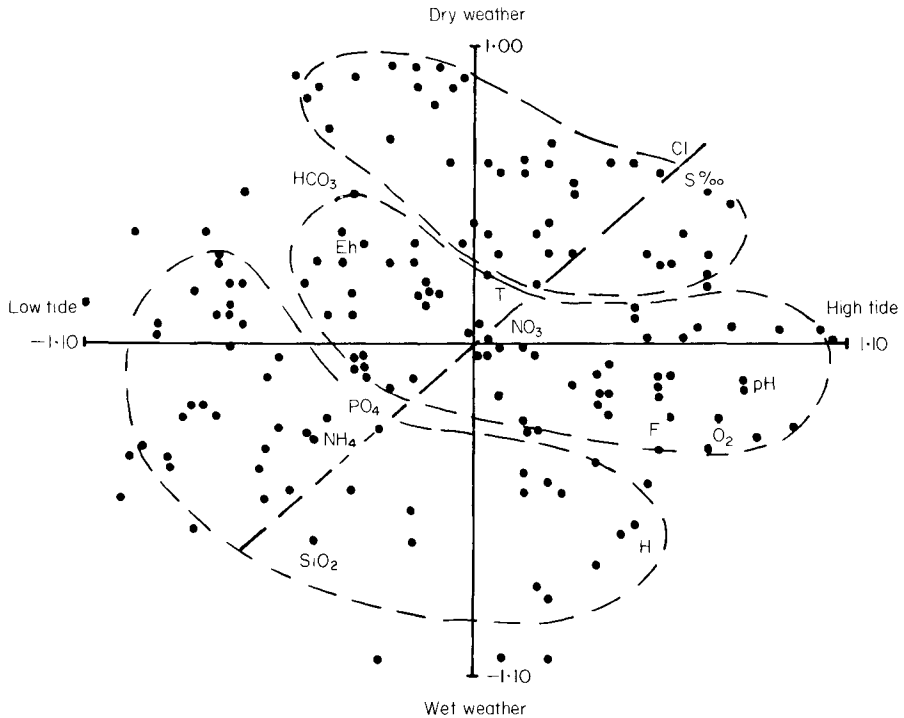


Figure 4. Graphic representation of principal component analysis; separated groups indicate the three sampling periods; from top to bottom, December 1987, June 1987 and December 1986; solid circles represent samples; F represents instantaneous discharge and H creek depth; see text for details.

This third sampling period was preceded by intense precipitation in the 2 days before, and during the second cycle. The precipitation event decreased salinity and chlorine, smoothing ammonium peaks, and increased silica and phosphate peaks. Nitrate levels had an irregular pattern.

Nutrient levels, other than ammonium, of the three sampling periods were higher than those of Valiela *et al.* (1978), Wolaver *et al.* (1984) and Boto and Wellington (1988). A strong groundwater input to creek water in the study area during all samplings, could be responsible for the higher values observed. Ranges of values between sampling periods were very similar, with no seasonal variation as was observed by Boto and Wellington (1989) and Whiting *et al.* (1987, 1989). As seasonal patterns may be related to variations in litter fall and decomposition processes, (Boto & Wellington, 1989) and since Silva (1988) showed that the mangrove forest studied does not show any seasonality in litter fall, this may explain the non-existence of a typical seasonal fluctuation in creek hydrochemistry.

#### *Principal component analysis*

The results of the three sampling periods were analysed with a principal component factorial analysis (Bouroche & Saporta, 1989) in order to identify the major controls of data variance.

Three principal factors, tidal variation, weather conditions and nitrification, were identified as major controls of creek hydrochemistry variation, explaining 24.4%, 17.8% and 15.2% of data variance respectively (see Figure 4). The parameters studied showed a



marked distribution in relation to the tidal variation axis. Salinity, chlorine, pH, dissolved oxygen, water flux and creek depth are positively associated with tidal amplitude, whereas silica, ammonium, phosphate, Eh and total alkalinity are negatively associated with tidal amplitude. This reflects an alternance between flood tide periods when bay water strongly influences creek hydrochemistry, and ebb tide periods when mangrove internal process influences prevail. The distribution of sampling points along this axis enhance this hypothesis.

The position of parameters is less clear in relation to weather conditions, but sampling point distributions reveal that values found during rainy periods are negatively associated with the weather axis, whereas values found during non-rainy periods are positively associated with the weather axis. The best example of the effect of precipitation can be visualized by opposite positions between silica and salinity and chlorine. Silica levels are higher during rainy periods at low tide as it is largely related to groundwater input, whereas chlorine and salinity levels are higher during non-rainy periods at high tide as they are largely related to bay water input.

Nitrification axis, not shown in Figure 4, is positively associated with nitrate and temperature, and to a lesser extent, with dissolved oxygen. This axis may be interpreted as being due to nitrification in creek waters during warmer days, independent of weather conditions. Although nitrate concentrations were similar, at these three sampling periods, lower nitrate values were observed in June, when creek water temperatures were lower. Boto and Wellington (1989) also found a similar positive relationship between nitrate and temperature in mangrove creek waters.

#### *Hydrochemical dynamics*

Compiling data from Harvey *et al.* (1987), Agosta (1985), Blackburn (1986) and from this study, a hydrochemical-hydrological model that can explain the principal creek chemistry variations is proposed. At low tide, creek water was dominated by an inflow of mangrove porewater ( $\text{NH}_4$ ,  $\text{HCO}_3$ ,  $\text{SiO}_2$ ,  $\text{PO}_4$  rich, Eh strongly negative). Nitrification of porewater derived ammonium in the creek occurs, as high temperature and dissolved oxygen concentration content are optimal for this reaction. At the start of the flood tide, bay water (dissolved oxygen, salinity and chlorine rich, elevated pH) interacts with mud-flat porewater before entering the tidal creek, resulting in high concentration peaks of ammonium, nitrate and silica in the creek water.

As water levels rise, mangrove porewater migration to the channel decreases until the sediment surface is inundated. As a consequence, pH, salinity, chlorine and dissolved oxygen increase in the creek water, whereas total alkalinity decreases. At this time a recharge of mangrove porewater occurs by infiltration. Bioturbation by crab activity could also play an important role enhancing hydraulic conductivity of the sediment (Warren & Underwood, 1986). A pilot measurement showed that more than 100 crab holes occur per square metre of sediment (up to 70% with a diameter of less than 1 cm). At ebb tide, the creek water level decreases and porewater migrates back to the creek until low tide, resulting in a decrease of pH, dissolved oxygen, salinity and chlorine, and an increase in total alkalinity. High concentration peaks of ammonium, silica, phosphate and nitrate also occur at this stage of the tide.

Precipitation affects this model at two levels. The first is direct precipitation over mangrove forest of low nutrient content rainwater, the second is an increase of groundwater input enriched with silica and phosphate. When precipitation occurs during low tide it enhances the outflow of mangrove porewater into the creek.

TABLE 3. Mass balance for nine complete tidal cycles, mean values and standard deviation (SD); negative values denote net export; water balance in m<sup>3</sup>; chlorine (Cl) in kg; others in g

Date	M <sup>3</sup>	Cl	HCO <sub>3</sub>	SiO <sub>2</sub>	NH <sub>4</sub>	NO <sub>3</sub>	PO <sub>4</sub>
12.86	232	2.9	22	381	37	13	13
12.86	-177	-1.5	-13	-112	-25	-1.8	-2.0
12.86	127	1.9	15	67	1	-0.7	2.5
06.87	-136	-7.1	6	280	19	-2.0	0.0
06.87	-148	0.4	-7	84	-3	3.1	1.6
06.87	64	-1.2	-5	-196	-34	-17	-1.6
06.87	-10	-0.1	-1	-8	-1	-0.1	-3.4
12.87	-186	-3.6	-26	4	-10	-11	-4.0
12.87	106	2.0	12	45	3	6.0	8.4
Mean	-14	-0.7	2	61	-1	-4.0	-0.4
SD	154	3.1	15	179	21	7.7	9.3

### *Tidal exchanges*

A mass balance for nine tidal cycles is shown in Table 3. As the concentration patterns along tidal cycles do not show consistent differences between ebb and flood tide, as observed elsewhere (Boto & Wellington, 1989; Whiting *et al.*, 1987, 1989; Valiela *et al.*, 1978), the discharge values are the dominant term controlling the average tidal exchange. A discharge asymmetry was observed in almost all tidal cycles (Figure 2). Higher discharge values were observed during the ebb tide, in response to the freshwater input (Reed, 1987), and non-linear friction effects in the mangrove swamp (Wolanski *et al.*, 1980).

The balances for most constituents follow the water balance, with an alternation between net import and net export. Mean net values are small when compared with peak tidal transport, with a great variability between tidal cycles, as reflected by a high standard deviation. Boto and Wellington (1988) also report low values for the net flux of nutrients compared to the peak tidal fluxes and concluded that their system is in a balanced state.

In our case the mud flat-mangrove interaction must be taken into account, as the sampling point for tidal variation monitoring was located at the interface between these two subsystems. This interaction may prevent export of all dissolved nutrients outwelled from the mangrove, as some nutrients are trapped in porewater in the mud flat during ebb tide, returning to the forest on the following flood tide.

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