

# Distribution of Carbon in a Tropical Hypersaline Estuary, The Casamance (Senegal, West Africa)

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**ABSTRACT:** The Casamance estuary, on the coast of Senegal, is an inverse hypersaline estuary: salinity increases landward, and dry season salinity values are up to 172 psu due to the evaporation of seawater. Dissolved inorganic carbon (DIC) concentrations decreased landward as a negative linear function of salinity. Thermodynamic modelling and the absence of CaCO<sub>3</sub> in the sediments indicate that this loss of DIC was not due to calcite precipitation in the main water body. The innermost, almost landlocked, waters contained high phytoplankton biomass (50–300 µg chl l<sup>-1</sup>) and high concentrations of allochthonous dissolved organic carbon. Photosynthetic uptake of DIC and subsequent particulate organic carbon sedimentation is proposed as hypothetical explanation of the relationship between DIC and salinity; localized overheating in shallow waters might also be involved.

## Introduction

Hypersaline waters offer many examples of the adaptability of living resources, and there have been numerous studies of the biology of these waters since the work of Dunal (1837). In parallel, there is an abundant literature on the chemistry and physics of hypersaline waters. Salinity is the most obvious feature for classifying these waters and Por (1979) showed that biological characteristics, including species diversity, closely parallel salinity along the gradient away from seawater in thalassic as well as athalassic environments.

Although numerous studies have been published on hyperhaline lagoons, the hypersaline Casamance estuary is unusual for two reasons. First, the estuary became an "inverse estuary" around 1975, after a small, natural alteration of its water budget. The hydraulic functioning of the estuary has been described elsewhere (Pagès and Debenay 1987; Savenije and Pagès 1992), and is not the main subject of the present paper. The distur-

bance of such a tropical estuarine ecosystem by a minimal shift in precipitation is significant of how these systems may respond to climate change.

Second, the Casamance has an abnormal distribution of dissolved inorganic carbon (DIC). Since Usiglio's observations (in Deffeyes et al. 1973), many authors have studied the chemical evolution of evaporating seawater. Experimental studies have been complemented by modelling to analyze the successive precipitation of major and minor compounds. Despite these studies, the behaviour of calcium and inorganic carbon during initial stages of seawater evaporation (before gypsum precipitation) is not clear. Javor (1989, p. 192) stresses the differences between laboratory experiments (and modelling) and the events in sabkhas, lagoons, and salterns; the role of natural conditions, and especially of dissolved organic matter, is important. Different studies, probably under slightly different conditions, lead to divergent results: calcite supersaturation is often mentioned (Berner 1965, 1976; Long and Gudramovis 1983; Hudec and Sonnenfeld 1989), and aragonite precipitation has also

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been observed (Deffeyes et al. 1973; Arakel 1981; Plummer and Sundquist 1982; Oomori et al. 1988). Magnesium also modifies these processes, either by contaminating calcite (Cooke and Kepkay 1984) or in Mg-calcite (Gunatilaka et al. 1984; Miyamoto and Pingitore 1992). Dolomite is also one of the numerous carbonates that precipitate in evaporated solutions (Hardie 1987; Oomori et al. 1988). These studies all agree that there is an increase of inorganic carbon in concentrating seawater. These studies also describe a constant or an increased alkalinity with increasing salinity (Lazar et al. 1983). In sharp contrast to these results, we found an inverse relationship between salinity and DIC, leading to lower DIC levels in the landward reaches of the Casamance. We also found high phytoplankton biomass in the saline, DIC-depleted, waters in contrast to other generalizations that proliferating, specialized organisms (planktonic or benthic) in saline waters occur with high DIC concentrations (Talling et al. 1973; Talling 1976; Javor and Castenholz 1981; Melack 1988; Wood and Talling 1988).

The purpose of this paper is to describe the hydroclimate of a tropical estuary impacted by decrease in freshwater input, with special reference to the carbon concentrations. Although several aspects of the Casamance estuary have been dealt with elsewhere (Pagès et al. 1987), some of its characteristics, which may influence the distribution of DIC, are described here.

#### Materials and Methods

Data were gathered during 10 field trips from 1985 to 1987. Our surveys were mostly limited to that portion of the estuary situated between station 11 (Fig. 1) and station 39. The location of a station or of a particular feature will be given by its distance in km from the mouth (KP). The waters downstream of station 11 appeared to be undiluted seawater. Upstream, the narrow channel was impassable above station 40. Most samples were taken with a 5-l plastic bucket, but we also used a Niskin 2.7-l bottle for sampling bottom layers. As a rule, our stations were located in the middle of the main channel.

Salinity was measured in the field with a handheld refractometer (Atago 20, an accuracy of  $\pm 2$  psu). Some samples were also measured in the laboratory with a Grundy A 230 induction salinometer as a check of field measurements. Temperature was measured with a mercury thermometer ( $\pm 0.1^\circ\text{C}$ ) and pH with a Cole-Parmer "Digi/sense" field pH meter recalibrated about every hour with pH 7 buffer. The pH data are given without correction for either temperature or the effects of salt (Krumgalz et al. 1980). Major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,

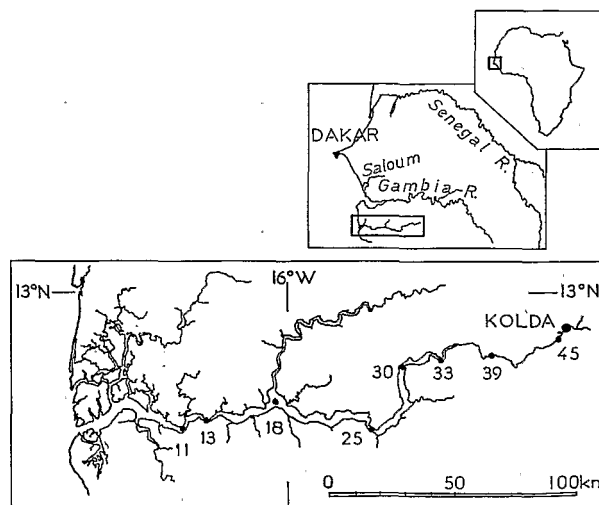


Fig. 1. Map of the Casamance estuary, showing the location of some stations.

$\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) were only assessed in June 1986 on samples poisoned with  $\text{HgCl}_2$ . After suitable dilution with deionized water, the cations were analyzed by atomic absorption spectrophotometry and anions by standard potentiometric methods (Golterman et al. 1978). Dissolved oxygen concentrations were measured with a YSI-57 oxygen probe and meter set at "Freshwater." The readings were corrected for salinity using extrapolated oxygen solubility equations (Benson and Krause 1984), which agree reasonably with the recent work by Sherwood et al. (1991).

Samples for the determination of stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) were taken in November 1985, after the rains, and in June 1986, at the end of the dry season. Standard mass spectrometry methods were used to determine the isotopic enrichment of  $^{18}\text{O}$  and  $^2\text{H}$  relative to the international SMOW standard; accuracy was 0.2‰ for  $^{18}\text{O}$  and 1‰ for  $^2\text{H}$  (Jusserand et al. 1989).

Dissolved inorganic carbon (DIC) was determined by two methods. During the first three surveys, we used the usual acidimetric method of alkalinity determination: 0.05 N HCl titration monitored by pH meter. For other surveys, we used gas chromatography (Oudot et al. 1987). Samples (8 ml) were poisoned with 1% (v/v) saturated  $\text{HgCl}_2$ . Determination was carried out on decanted 2-ml subsamples. After acidification with 0.2 ml pure  $\text{H}_3\text{PO}_4$ , the resulting gaseous  $\text{CO}_2$  was determined by gas chromatography with an Intersmat IGC 15, using helium as carrier gas through a Porapak Q column with thermal conductivity detection. Peak area was determined with a Hewlett Packard 3380A integrator. Standardization was achieved with sea-

water spiked with known amounts of  $\text{Na}_2\text{CO}_3$ ; overall accuracy was  $\pm 0.2\%$ .

Dissolved organic carbon (DOC) concentration was monitored indirectly from light absorbance of samples filtered with GF/C filters (Pagès and Gadel 1990). As a first approximation, carbon concentration (in  $\text{mg l}^{-1}$ ) was determined from absorbance at 254 nm ( $A_{254}$ , in  $\text{cm}^{-1}$ ) by the following equation:

$$\text{DOC} = -1.25 + 65.7 A_{254}$$

Chlorophyll was determined by fluorometry (Turner 110) of methanol extracts (Nusch 1980), with calibration against trichromatic spectrophotometry. Particulate organic matter (C and N) was measured during the May 1987 survey. Particulate matter collected on precombusted 25-mm GF/F filters was analyzed with a Hewlett-Packard HP 185B analyzer.

Photosynthesis was assessed by the  $^{14}\text{C}$  method in "simulated in situ" incubations (Head 1976) under natural light. Pyrex 250-ml screw-cap bottles were wrapped in one or several layers of black plastic mosquito netting (transmittance of 55% as determined with a LiCor quantum meter). We used a small (80 cm X 40 cm) plexiglass incubator filled with river water, which was changed frequently during incubation. Samples were spiked with about 2  $\mu\text{Ci}$  of  $\text{Na}_2^{14}\text{CO}_3$  in aqueous solution (CMM 53B from C.E.A., originally at 56  $\text{mCi mmol}^{-1}$ , diluted with  $\text{H}_2\text{O}$  at pH 9). After incubation, subsamples of 60–180 ml were filtered onto 25-mm GF/C filters, which were rinsed with 10 ml of prefiltered river water. The filters, sucked dry, were kept in plastic scintillation vials at  $0^\circ\text{C}$  (in the field) then at  $-20^\circ\text{C}$ . The dried filters were counted by liquid scintillation (with 10 ml of either ReadySolv or toluene-PPO-POPOP cocktail) on a Philips P4700 with external standard. Corrections (quenching) were sometimes complicated by heavy inorganic loads. Calculation of  $^{14}\text{C}$  uptake took into account the actual DIC concentration but disregarded possible effects of tracer uptake kinetics.

### Study Site

The Casamance estuary lies along the southern border of Sénégal (Fig. 1). This drowned river valley is under tidal influence along its whole length, about 260 km. The seaward 90 km are bordered by mangroves. The semidiurnal tides have an amplitude of about 1 m at the mouth and strong tidal currents scour a relatively narrow and deep central channel, while shallows and mud banks are extensive. Above station 30 (KP 180), the average depth decreases to 0.6–0.2 m and broad lateral marshes are occupied by *Phragmites australis*. This riparian vegetation was well developed above station 33 at

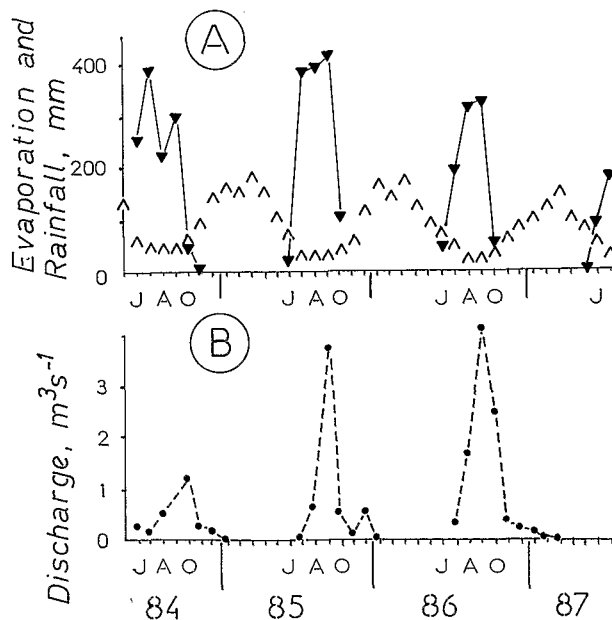


Fig. 2. Some elements of the water budget of the Casamance region during the study. A) Monthly rainfall ( $\blacktriangledown$ ) and Piche evaporation ( $\Delta$ ) at Ziguinchor. B) Monthly-averaged discharge at Kolda. The months of June, August, and October are shown by initials. Absence of symbol indicates no rainfall or discharge. Data from Dacosta (1989).

the beginning of our study in 1984 but increasing salinities led to a retreat of the *Phragmites* above station 43. Dead vegetation and litter were still found at station 33 in mid 1987.

### CLIMATE AND HYDROLOGY

The Casamance region lies about  $15^\circ\text{N}$ , in the sudanian zone and rains fall only between July and October (Fig. 2A). Rainfall has decreased, as it has across the whole Sahel (Palmer 1986; Fontaine 1990), since about 1965. Taking Ziguinchor (the regional capital, at our station 13) as a basis of comparison, yearly average rainfall decreased from 1,800 mm (mean for period 1920–1950) to 1,050 mm (mean for 1960–1980; figures from Dacosta 1989). Evaporation is highest in February (Fig. 2A); annual evaporative losses (measured with Piche-type evaporimeters) vary between 1,500 mm (at Ziguinchor) and 2,100 mm farther inland (at Kolda). Across the catchment, the annual average ratio of evaporation to precipitation has changed from 0.9 (1920–1950) to 1.5 (1960–1980).

The main significance of this climate change is that it corresponds to a relatively modest southward shift of rainfall isolines. Along the southern limit of the Sahara desert, vegetation has retreated several hundreds of kilometers between 1970 and 1982 (Tucker et al. 1991). Since the Casamance catchment lies in the sharp gradient between the

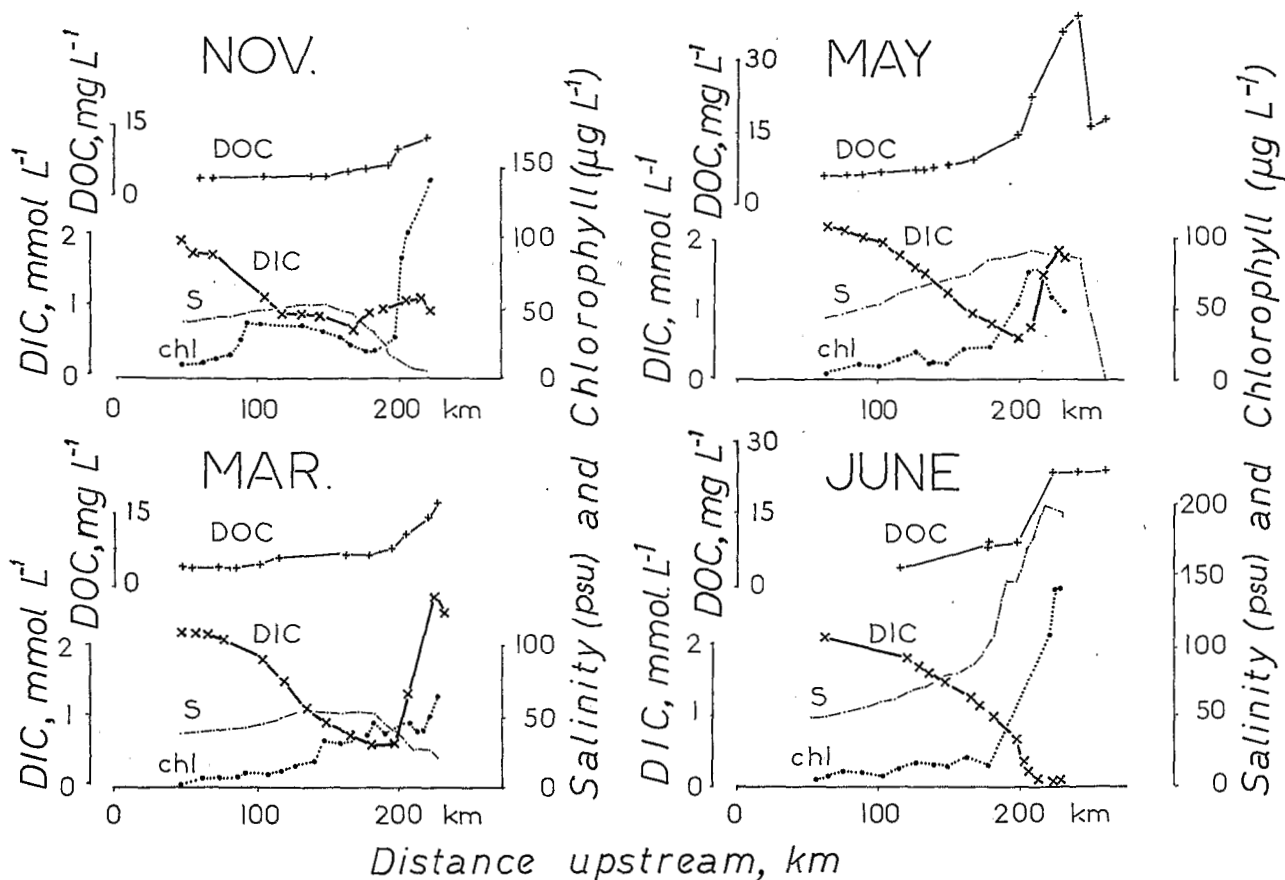


Fig. 3. Distribution of some water characteristics at four typical situations in 1985–1986: salinity (S), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and phytoplankton chlorophyll (chl).

sudanese-type and guinean-type climates, a shift of less than 100 km in the rainfall isolines (Dacosta 1989) has caused the Casamance catchment to cross a critical boundary. From our hydraulic models (Pagès and Debenay 1987; Savenije and Pagès 1992), we estimate that a rainfall of around 1,100 mm is necessary to maintain a “normal” (fresh water) estuary.

The effects of the decrease in freshwater input are amplified by the morphology of the basin. Run-off coefficients are low; the discharge at Kolda (the only freshwater source apart from direct rainfall) had an annual average of  $0.2\text{--}1.0\text{ m}^3\text{ s}^{-1}$  during our study (Fig. 2B), down from about  $5\text{ m}^3\text{ s}^{-1}$  before 1965 (Dacosta 1989). This amounts to some  $30 \times 10^6\text{ m}^3\text{ yr}^{-1}$ , compared to evaporative losses of about  $1300 \times 10^6\text{ m}^3\text{ yr}^{-1}$  for the portion above station 13.

#### SALINITY AND HYDRAULICS

Historical accounts dating back to about 1840 describe the Casamance as a freshwater stream. The hydrological study done in 1968–1969 (Bru-

net-Moret 1970) showed a normal estuary, with salinities decreasing landward to about 0.1 psu above station 30. This “humid phase” condition has been altered, since at least 1973, to an “inverse estuary” situation, with salinity increasing landward up to a peak (Fig. 3), which varies in its precise location. Further upstream the salinity of the estuary declines. This distribution is analogous to the “salinity plug” described by Wolanski (1986) under a similar climate. In the Casamance, at the end of the rains, we found salinity maxima of about 65 psu around station 25, some 140 km from the sea. During the dry season, overall salinities increased and the peak concentrations occurred further upriver. During the period under study (1984–1987), salinities during the dry season peaked at about 150 psu at station 38 (KP 223), with an absolute maximum of 175 psu in June 1986.

The hypersaline region of the estuary seaward of the peak salinities corresponds to evaporated seawater, as shown by its ionic composition (see below) and by the <sup>18</sup>O and <sup>2</sup>H data (Jusserand et al. 1989). We shall call this portion the “thalassic”

estuary. The region landward of peak salinities had steep salinity gradients, and contained concentrated brines mixed with rain or with continental fresh water derived from the catchment. We shall call this region the "athalassic" estuary. The "continental" portion of the river, above station 45, is protected from seawater by a topographic sill.

The isotopic distribution, water budget, and salinity evolution indicate two important aspects of the hydraulic functioning of the estuary; a kinetic one on a monthly scale, and a global one on an interannual scale. Kinetically, the estuary behaves like a series of separated boxes. During the dry season, all boxes shrink under evaporative losses. This results in a general landward drift with no mixing between the boxes. We estimated this drift to be about  $0.1 \text{ cm s}^{-1}$  (Pagès and Debenay 1987); as an example, the box around station 25 in October (at the end of the rainy season) will drift landward by about 15 km during the dry season. The rains will bring an overall swelling of the various boxes, resulting in a seaward drift of similar magnitude.

On an interannual scale, we observed that the salinity distributions in a given season were comparable from year to year during the 4 yr of our study. The small variations could be ascribed to the equally small variations in water budget (amount and timing of rains). We may then consider that, at least between 1984 and 1987, seasonal seaward and landward movements were such that a large part of the water remained trapped in the estuary. A water mass located at station 25 in June (before the rains) would not be flushed out to sea at the end of the rains. The upper part of the thalassic portion would then contain water that was several years old. As far as we know, this situation had not greatly changed up to June 1992 (Gac personal communication, 1993).

## Results

### WATER CHEMISTRY

Major ions were analyzed in the June 1986 samples, which showed record salinities. The ionic composition corresponded to evaporated seawater, with a slight depletion of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (Fig. 4) above salinities of about 100 psu. As a first approximation, the depletion of these two ions agrees with the observed presence of gypsum crystals in the superficial sediments (Guillou et al. 1991). No calcite could be detected, either by microscopic examination or by X-ray diffraction (Guillou personal communication).

Concentrations of  $\text{SO}_4^{2-}$  become more depleted than expected if gypsum precipitation had been

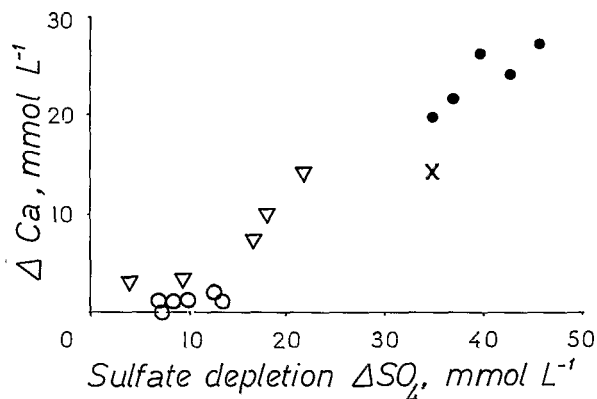


Fig. 4. Comparison of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  depletion (see text for computation) in June 1986. Several regions are shown: (o) = stations 18–27, with  $3 \text{ mg DOC l}^{-1}$ ; ( $\Delta$ ) = stations 28–35, with  $7\text{--}9 \text{ mg DOC l}^{-1}$ ; ( $\bullet$ ) = stations 36–39, with  $23 \text{ mg DOC l}^{-1}$ ; (x) is station 41, in the athalassic portion.

the only removal process. Taking  $\text{Mg}^{2+}$  as a conservative element in this salinity range (Arakel 1981; Lazar et al. 1983; Javor 1989), we calculated the depletion  $\Delta$  of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  as the difference between actual concentration and the concentration which would correspond to the increase in  $\text{Mg}^{2+}$  (Fig. 4). Sulphate depletion appears too high (compared with calcium depletion) above station 35, in waters with a high DOC content. This excess  $\text{SO}_4^{2-}$  depletion may be related to bacterial processes since sulphate-reducing and methanogenic bacteria were active even in the concentrated upstream brines sampled in June 1986 (Jacq personal communication, September 1986). These two processes have been shown to be mutually compatible in hypersaline waters (King 1988).

In the thalassic portion of the estuary, measured pH values were mostly around 7.5. Some high values (8.2–8.5) were observed in the (relatively) low-salinity athalassic waters that had a high phytoplankton biomass (see below). Low pH values (down to 6.3) were observed in June 1986 at high salinities (140–170 psu), which may be attributed to the effect of salt (Krumgalz et al. 1980; Lazar et al. 1983). Photosynthetic activity generally resulted in small pH variations (0.1–0.3 pH).

None of the primary inorganic nutrients ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$ ) showed any clear distribution pattern, either in absolute concentrations or in ratios (Pagès 1992). Nitrate was often very low in the upper reaches but occasionally increased to  $15 \mu\text{mol l}^{-1}$  in the downstream region. Ammonium was often high in the landward regions, with several peaks of up to  $30 \mu\text{mol l}^{-1}$ . Overall, inorganic nitrogen concentration increased with salinity in the thalassic portion, without any recognizable seasonal trend. Phosphate concentrations spanned a

wide range, between  $0.2 \mu\text{mol l}^{-1}$  and  $2.5 \mu\text{mol l}^{-1}$ , with no pattern either in time or in space.

#### ORGANIC MATTER

Dissolved organic carbon (DOC) concentrations increased landward (Fig. 3). In the lower and median portion of the estuary, DOC concentrations were around  $0.2\text{--}0.3 \text{ mmol C l}^{-1}$  while peak DOC values of about  $1.5\text{--}2.0 \text{ mmol C l}^{-1}$  were found in the uppermost reaches, above station 34, coincident with the dense zone of *Phragmites*. An extreme value of  $3.2 \text{ mmol C l}^{-1}$  was observed at station 39 in May 1987.

Data on sedimentary organic matter in the Casamance estuary are scarce. From our few cores, interstitial waters have DOC values of about  $5 \text{ mmol C l}^{-1}$  (Pagès unpublished data). Total sedimentary organic carbon represented between 2% and 6% (dry weight) with an irregular increase between station 13 and station 40 (Debenay et al. 1991).

#### PHYTOPLANKTON

Total chlorophyll concentration (chl) increased landward in all our surveys. The downstream and middle portions of the estuary showed values from  $5 \mu\text{g l}^{-1}$  to  $15 \mu\text{g l}^{-1}$ . Maximum biomass was nearly always found at the landward stations, where an average chlorophyll concentration was about  $100 \mu\text{g l}^{-1}$ , with a peak of  $320 \mu\text{g l}^{-1}$ . The healthy physiological condition of these abundant upstream phytoplankton is indicated by: a) low phaeopigment ratios, b) low particulate organic carbon: particulate organic nitrogen atomic ratios (6–8; see below), and c) high dissolved oxygen concentrations during the day. In June 1986, a reddish discoloration indicated an abundance of *Dunaliella salina* in the high-salinity portion ( $S > 120 \text{ psu}$ ) of the estuary. While the whole dataset indicated that chl increased with  $S$  in the thalassic portion of the estuary ( $r = 0.77$  for 87 data points), there was no seasonal pattern.

Particulate organic carbon (POC) and nitrogen (PON) were measured in May 1987 only. Their distribution closely paralleled that of chl, with values up to  $0.7 \text{ mmol POC l}^{-1}$  at stations 38–39 (data not shown). POC:chl ratios ranged between 90 and 400 (by weight), with a significant landward decrease (Spearman rank test). The high upstream biomass (stations 28–37) had a lower POC:chl ratio (range 90–160, mean 145 w:w) than observed at the seaward stations. The molar POC:PON ratio remained around 8 (ranging between 7.2 and 9.1).

Photosynthesis was mostly in the range of  $5 \mu\text{mol C l}^{-1} \text{ h}^{-1}$  to  $30 \mu\text{mol C l}^{-1} \text{ h}^{-1}$ . An absolute maximum of about  $100 \text{ mmol C l}^{-1} \text{ h}^{-1}$  was observed at station 38 in December 1984 and February 1985, with chl values of about  $200 \mu\text{g l}^{-1}$ . Biomass-spe-

cific photosynthesis ("assimilation number") mostly ranged between 2 and  $10 \mu\text{g C } (\mu\text{g chl})^{-1} \text{ h}^{-1}$ . Integrated gross production amounted to between 5 and  $20 \text{ mmol C}^{-1} \text{ m}^{-2} \text{ h}^{-1}$ . The nightly oxygen uptake (measured in situ) was correlated with the sum of chl and DOC, indicating high heterotrophic (bacterial) activity coexisting with the high autotrophic biomass. Respiration ranged between  $50 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  and  $150 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ .

#### DISSOLVED INORGANIC CARBON

##### *Spatial Distribution*

Single subsurface samples were used to characterize the water column as the water column was generally homogeneous in the thalassic region of the estuary. Only the uppermost reaches (stations 35–39) occasionally showed some vertical stratification, with slightly higher DIC concentrations in the bottom waters during the early morning. The greatest difference,  $2.6 \text{ mmol C l}^{-1}$  compared to 2.4, was observed at station 38 in April 1985.

All longitudinal DIC profiles were opposite images of the salinity profiles, with a steady decline of DIC throughout the thalassic portion of the estuary (Fig. 3). This landward decline of DIC was observed, with only small variations, in all surveys. The seaward waters exhibited marine DIC concentrations of about  $2.2 \text{ mmol C l}^{-1}$ . Minimum DIC values of about  $0.5\text{--}0.7 \text{ mmol C l}^{-1}$  were found some 180–200 km from the sea. The June 1986 survey had exceptionally low DIC concentrations, down to  $0.08 \text{ mmol C l}^{-1}$ . In the uppermost athalassic waters, DIC concentrations reached their highest measured values in March ( $2.8\text{--}3.9 \text{ mmol C l}^{-1}$ ), although freshwater discharge at Kolda had been negligible since about December (see Fig. 2B).

##### *DIC and Salinity*

For each survey in the thalassic section of the estuary, there is a linear decrease of DIC with increasing salinity (Fig. 5), with correlation coefficients ranging from 0.93 to 0.99. The slope for each survey differs, but there is a common peak DIC concentration nearly corresponding to seawater. Data for the rainy season surveys are restricted to the low-salinity range, resulting in steep slopes with DIC. The dry season data include higher salinities with lower slopes, with the June 1986 survey as an extreme example. The slopes of DIC versus  $S$  decrease between November (beginning of the dry season) and June (Spearman rank test:  $r_s = 0.76$ ).

The correlation between salinity and DIC is similar for a given month during the 3 yr of data. This consistency in correlation suggests that at least the upper half of the estuary was effectively isolated

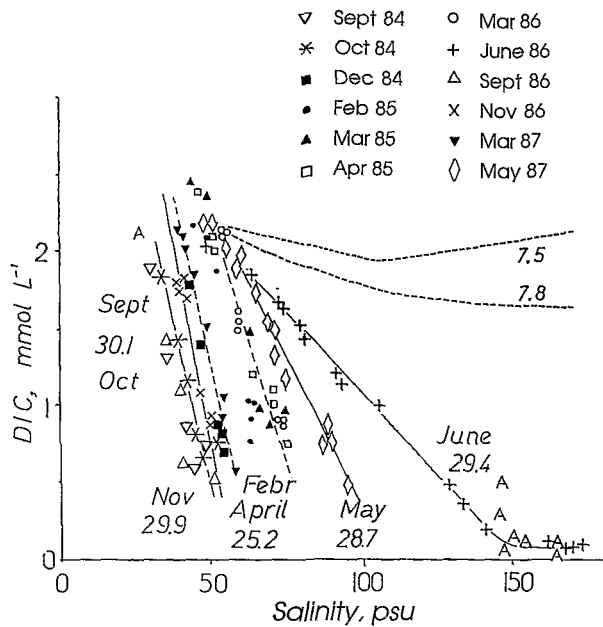


Fig. 5. Decreasing dissolved inorganic carbon concentration (DIC) under increasing salinity in the thalassic portion of the estuary, as observed during several surveys. Average water temperatures ( $^{\circ}\text{C}$ ) are indicated in italics. Symbols (A) replotted from Arakel (1981). The two dashed curves are simulations (EVAPOR model) run at pH 7.5 and 7.8 (see text).

from the sea. A possible exception to this consistent interannual pattern was seen in March 1987, with lower DIC for a given salinity, than in 1985 and early 1986. This could result from the strong decline in DIC observed in June 1986. Excluding this latter survey, the minimum DIC values range between  $0.52 \text{ mmol l}^{-1}$  and  $0.88 \text{ mmol l}^{-1}$  (mean of  $0.71 \text{ mmol C l}^{-1}$ ).

Sampling of the athalassic portion of the estuary was infrequent owing to practical difficulties in the field. However, we did find an increase of DIC in the landward, low-salinity athalassic waters. Plotting DIC versus salinity for this region does not yield a clear picture (Fig. 6). The March 1986 survey is the only one having a classical mixing diagram, with a high-DIC freshwater concentration opposed to a low-DIC seawater concentration. The overall picture suggests that nonpoint DIC sources occur, possibly originating from the *Phragmites* swamps (due to the relatively dense vegetation between stations 34 and 39) rather than from the "continental" waters above Kolda. This was especially obvious in October and December 1985, when station 34 yielded the highest measured DIC values. The end member is hence not river water (for instance brought by the flood) but diffuse marsh waters flushed by rain.

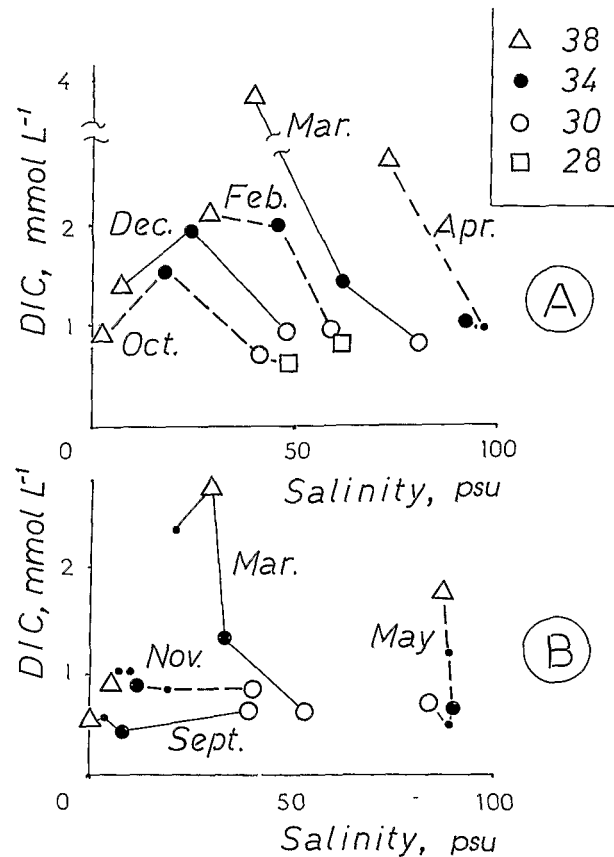


Fig. 6. Distribution of dissolved inorganic carbon (DIC) as a function of salinity in the athalassic portion, as observed during several surveys in 1985–1986 (A) and 1986–1987 (B). Four main stations are labelled, small dots mark intermediate ones. A mixing diagram is only obtained in March 1985.

#### DIC and Other Characteristics

In the athalassic portion of the estuary, DIC and DOC increased simultaneously (see the March and May situations in Fig. 3). This parallel trend suggests a common source for both forms of carbon in the stretch between stations 33 and 39. Mineralization of DOC into DIC, while possible, was not supported by existing information.

As previously described, high phytoplankton biomass was always observed at the landward stations, often located in the athalassic portion. A plot of chl against DIC yields no clear pattern if all data are used. However, when only data from the thalassic section are considered, there is an inverse relationship between chl and DIC (Fig. 7). This relationship was expected from the distribution of S, chl, and DIC, and cannot be interpreted as a cause and effect.

Phytoplankton biomass (expressed as POC) does not fully account for the "missing" DIC, since the sum (DIC + POC) also decreases upstream (land-

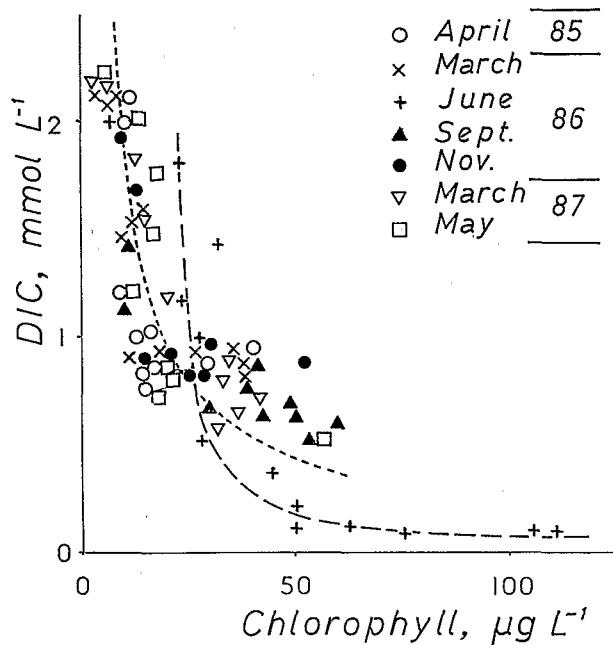


Fig. 7. The inverse relationship between phytoplankton chlorophyll and dissolved inorganic carbon (DIC) in the thalassic portion of the Casamance estuary. The June 1986 data (long dashes) give the regression:  $\text{Chl} = 22.1 + 5.62/\text{DIC}$  ( $r = 0.88$ ,  $n = 18$ ); all other data (short dashes) yield:  $\text{Chl} = 11.0 + 11.4/\text{DIC}$  ( $r = 0.88$ ,  $n = 57$ ).

ward) in the thalassic portion (Fig. 8). The decrease is relatively small, since phytoplankton carbon amounts to about  $1 \text{ mmol POC l}^{-1}$  in the upstream portion. For a given survey, at the station where DIC is lowest, the sum of DIC and POC varies between  $0.86 \text{ mmol l}^{-1}$  (station 28, September 1986) and  $1.67 \text{ mmol l}^{-1}$  (station 28, March 1985). The sum (DIC+POC) shows a bimodal distribution: one group of surveys (mean:  $1.37 \text{ mmol TC l}^{-1}$ ) occurred between March and June while another group of surveys (mean:  $0.86 \text{ mmol TC l}^{-1}$ ) occurred between September and February (end of the rainy season and early dry season).

With regard to photosynthetic production, DIC fluxes were higher upstream. Biomass-specific photosynthesis remained high even at the DIC minimum. During the day, intense photosynthesis depleted DIC, and increased in situ  $\text{O}_2$  concentrations, but high community respiration resulted in low net production values. The allochthonous DOC contribution probably allowed "new" production just above zero but our data are not sufficiently accurate to allow for calculation of a precise carbon budget.

#### Discussion

Natural hyperhaline water bodies are common (Butler 1969; Hermann et al. 1973) and the evap-

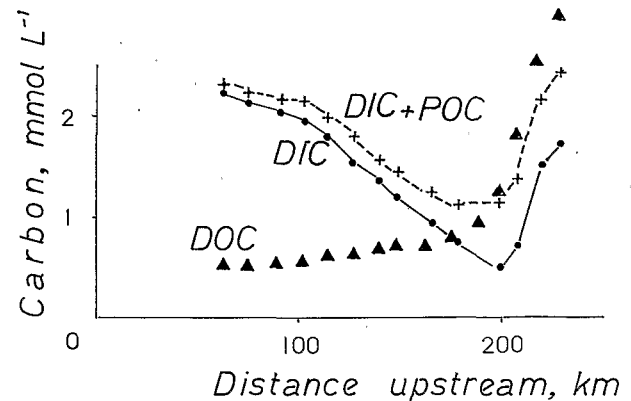


Fig. 8. Distribution of DIC and of "total carbon" (DIC + POC) in May 1987 along the whole estuary. DOC is mostly allochthonous and was not included in the sum.

orative processes are well known, from observation, experimentation, and theory (Deffeyes et al. 1973; Arakel 1981; review in Javor 1989; Pierre and Fritz 1992). The Casamance estuary is a unique hyperhaline system that does not follow the more general pattern of increasing DIC concentrations (or alkalinities) in increasingly concentrated waters (Krumgalz et al. 1980; Lazar et al. 1983). We have found only one dataset (Arakel 1981) with a DIC distribution comparable to ours (Fig. 5), having very low  $\text{HCO}_3^-$  concentrations in the salinity range of 120–180 psu. However, the general functioning of the coastal sabkhas studied by Arakel is completely different from that of the Casamance estuary. An obvious difference is the presence of evaporite crusts in Arakel's site, where the biological conditions prevailing are also unclear. There is thus a distinct pattern of "missing" DIC in the Casamance estuary, (which has not been discussed for other hypersaline systems); the most obvious explanation for which would be calcite precipitation. However, the loss of DIC may be explained by other abiotic factors or by some biological processes.

In the course of the dry season, the progressive shift toward higher salinities seems to lead also to increased DIC values. Accurately quantifying this evolution would require following a given water mass. If we accept that station numbers are reasonable markers, the evolution of DIC and S during a dry season roughly corresponds to concentration of the original water. This representation, albeit approximate, would fit with the hydraulic functioning inferred from other features. It would first mean that DIC behaves as a conservative element of marine origin, without any gain or loss. It would also mean that the observed DIC depletion either results from the summation of undetectable small deviations, or has been inherited from past pro-



cesses occurring during the transformation into an inverse estuary.

#### CALCITE PRECIPITATION AND ABIOTIC FACTORS

The standard view is that carbonates precipitate in the early stages of seawater evaporation (Friedman and Foner 1982; McCaffrey et al. 1987). There are, however, some diverging views in the literature, and Javor does make some cautionary remarks (Javor 1989, p. 192–193). To test whether calcite precipitation can explain the DIC depletion observed in the Casamance estuary, we modelled the evaporation of standard seawater at 25°C, using the EVAPOR model (Fritz 1975, 1979; Risacher and Fritz 1984). We did two simulations at constant  $p_{\text{CO}_2}$ , with initial pH of 7.5 ( $p_{\text{CO}_2} = 0.00242$ ) and 7.8 ( $p_{\text{CO}_2} = 0.00113$ ). In both cases (Fig. 5), alkalinity increased, DIC remained at around 2.0 mmol  $\text{l}^{-1}$ , and calcite precipitation occurred. Another simulation (not shown) was run at increasing  $p_{\text{CO}_2}$  and yielded unrealistically high DIC values. We did not succeed in simulating decreasing DIC concentrations at increasing salinities, despite a satisfactory supersaturation of calcite. In contrast, we did obtain a good fit for  $\text{CaSO}_4$ . The EVAPOR model was also used with the actual ionic composition measured in the Casamance estuary in June 1986. Even for this period when DIC was comparatively more abundant, for a given salinity, than during the other surveys, the results indicated that calcite was undersaturated across the whole estuary. This undersaturation of calcite is confirmed by our inability to detect calcite (either by inspection or by X-ray diffraction) in the surficial sediments.

The DIC distribution observed in the Casamance estuary (and not only in June 1986) cannot be explained by the above simulation, implying the following: continuous evaporation of seawater under, constant temperature, and constant  $p_{\text{CO}_2}$ . However, departure from these conditions may explain the reasons for the discrepancy between simulated and actual data.

#### *Continuous Evaporation of Seawater*

We estimated above that waters upstream of station 25 (at least) have probably been trapped inside the estuary for several years. We are therefore not dealing with “standard” seawater undergoing one evaporative run but with waters which have been through several cycles of concentration and dilution. The whole estuary becomes homogeneous, with respect to the stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) at the end of the rains (Jusserand et al. 1989). Toward the end of the dry season, in June, the landward waters carry the stable isotope signature of the longest lasting period of evaporation. The

Casamance and the Western Australian lagoons studied by Arakel (1981) share the common feature of successive evaporation sequences separated by dilution periods during the rainy season.

#### *Constant Temperature*

Our field observations showed that diurnal heating had a maximum range of about 5°C in the “deep” waters of the main channel. In the numerous shallow margins, however, water temperature around noon could reach values up to 45°C in 5-cm deep nearshore waters. The evaporation rate would increase, especially in close proximity to (overheated) land and a simultaneous rise in temperature and salinity would lower  $\text{CO}_2$  solubility. These factors are most active in very shallow waters, and would then influence a relatively small water volume, as compared to the whole transverse section. A simple calculation applied to oxygen solubility, which is much easier to handle (Sherwood et al. 1991), indicates that a water mass starting at 4 ml  $\text{O}_2 \text{l}^{-1}$  (saturation for 25°C, 60 psu) would lose 0.1 ml  $\text{O}_2 \text{l}^{-1}$  (averaged across the whole transverse section) in one daily cycle. These microscale variations in the water characteristics would escape detection by a normal sampling pattern, but their cumulated effects could be important.

We have described what happens (or might happen) in the water itself. The low-lying salt flats along the shores are functionally analogous to playas (“flat surfaces above the local water table;” Arakel 1981) and may further alter the situation. In the mud flats around Lagos (Nigeria), Webb (1958) measured superficial temperatures of up to 65°C. We measured interstitial water salinities of up to 300 psu. Such brines, when flushed back into the main stream during the next tide, could markedly alter the overall thermodynamics.

#### *Constant $p_{\text{CO}_2}$*

High phytoplankton biomass was present, especially in the DIC-depleted upstream waters. From a geochemical perspective, intense photosynthesis could create micro-environments with decreased  $p_{\text{CO}_2}$ . More or less intense DIC depletions have been described in various systems (Stoessel 1992; Morse and He 1993) and so-called “whitings” are well known in other waters, caused either by physical effects in brines (Javor 1989) or by biological processes in freshwaters. The fact that we did not observe such “whitings” in the Casamance does not preclude their existence. On the other hand,  $p_{\text{CO}_2}$  could be increased (again on a very local scale) by the oxidation of organic matter (Morse et al. 1985). We shall deal with these biological factors in more detail below.

We thus see that the assumptions of our simu-

lations, although fully plausible, may not always occur in the actual Casamance. There could have been some localized calcite supersaturation due to abiotic factors. While such small-scale substractions would not be obvious, their cumulative effects would be expressed after several months (or even years). Moreover, the three points we have just discussed are only physical or chemical. Dissolved organic matter has been shown to modify equilibria by its mere presence, even at low concentrations (Cody 1991; Suarez et al. 1992) and its contribution to alkalinity need not be measurable (de Haan and Voerman 1988). Sulfate reduction (in fact, a biological process) also seriously interferes with calcium carbonate chemistry (Stoessel 1992).

#### BIOLOGICAL PROCESSES

A number of biological processes may participate in DIC depletion such as phytoplankton sedimentation, biological calcification, or loss of carbon through fish exportation. We have seen that a high phytoplankton biomass was consistently found in the upper portion of the Casamance estuary (Fig. 3). Dominance by *Dunaliella salina* was obvious at least once, in June 1986. From our  $^{14}\text{C}$  measurements, these populations did not appear to suffer limitation by the relatively low DIC concentrations, although DIC has been proposed as a possible limiting factor even in estuaries (Fogel et al. 1992). Moreover, the inverse relationship found between chlorophyll and DIC (Fig. 7), would fit the observations that  $\text{CO}_2$  does not limit the final biomass density (Goldman et al. 1981; Burns and Beardall 1987).

We are concerned here with the possible role of biomass in the long-term sequestering of nutrients, following the Comtois model (in Morrison et al. 1987). Photosynthesis amounts to DIC conversion into POC. The upstream waters of the Casamance are (hydraulically) isolated from the sea and might be likened to a single large batch reactor. We have seen above that the sum (DIC + POC) ranges between  $0.8 \text{ mmol l}^{-1}$  and  $1.6 \text{ mmol l}^{-1}$  in the waters with the lowest DIC values. This leaves at least  $0.6\text{--}1.4 \text{ mmol l}^{-1}$  unaccounted for, if the original seawater had  $2.2 \text{ mmol DIC l}^{-1}$  and a negligible biomass. We admit that the abundant DOC found upstream is solely allochthonous; our  $^{14}\text{C}$  measurements indicated that less than 5% of DOC could have been exuded by phytoplankton.

We measured tidal currents of about  $0.15 \text{ m s}^{-1}$  above station 28, which is in the range of turbulence where cells may settle (Oswald 1988). Higher chlorophyll concentrations were often found in the bottom layers, and could represent settling particles. We did find organic, nearly gelatinous, sediments in some shallow back-waters at station 25.

We have only one isolated estimation of sedimentation rate in the Casamance ( $0.8 \text{ mm yr}^{-1}$  at station 30; Pourchet personal communication 1988), and the high organic content of the sediment does not distinguish between the autochthonous and allochthonous organic matter in the sediment. Since the "standing crop" represents  $100\text{--}300 \text{ mmol POC m}^{-2}$ , a loss of between 1% and 3% would not be measurable. Our "missing" DIC, equivalent to  $300\text{--}700 \text{ mmol DIC m}^{-2}$ , might then correspond to sedimentation cumulated over several months (if not years).

Losses of POC to predation by fishes (the customary "exportation" term) are less plausible in the Casamance, since high salinities limit the presence of even *Sarotherodon melanotheron* to a few months each year (Albaret 1987). In many water bodies, biological calcification may represent a further sink for DIC. Bosence (1989, p. 430) estimated that Florida Bay molluscs deposit  $100\text{--}500 \text{ g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ . In the Casamance estuary, however, salinity again severely limits the extension of macrobenthic molluscs. Mangrove oysters (*Crassostrea gasar*) were not found above station 12 and the bivalve *Anadara senilis* was not observed above station 18.

We thus see that the most plausible biological process would be a sequestration of DIC as settled phytoplankton POC. The ultimate fate of this organic carbon is unclear, but, as mentioned above, methanogenesis was active even in the concentrated brines. The origin of the nutrients may be associated with the decaying *Phragmites* stands bordering the DIC-depleted portion of the estuary.

#### Conclusions

As a hyperhaline water body, the Casamance has a highly peculiar distribution of DIC concentrations. Is this tropical estuary equally peculiar in other respects or does it otherwise exhibit more general features? In particular, are we justified in considering that its recent evolution may give us a glimpse of the near future for other water bodies in the context of trophic functioning during global change?

The transformation of the Casamance "river" into a natural saltern was probably complete in less than 5 yr, approximately between 1973 and 1979 (Savenije and Pagès 1992). The immediate cause was a shift in rainfall distribution, but two other estuaries situated north of the Casamance (i.e., within the more arid zone) reacted differently. The Saloum has been hyperhaline since 1910 at least (Pagès and Citeau 1990); salinities did increase around 1973, but the general situation was altered only quantitatively. The Gambia River was, and still is, a "normal" estuary; this is because its main

catchment stretches far to the southeast, into the still rainy zone. Thus, the Casamance is not really a general example, since catchment morphology plays a role in the fate of such estuaries. On the other hand, the Casamance does confirm that our environment can change very rapidly, not at a geological pace but at a human one, a point already stressed by Dansgaard et al. (1989) in another context.

The Casamance also underlines a rather obvious (but easily forgotten) point about average depth. In any water body of mean depth  $Z$ , salinity is modified by the water budget at a rate proportional to  $\exp(1/Z)$ . At least in estuaries with large shallow margins, the hypsometry is such that a rise in sea level leads to a decrease in average water depth, and hence to an increased sensitivity to the water budget.

Several studies of lagoons, estuaries, or bays have shown that the measured heterotrophic activity could not be supplied by autochthonous primary production, so that allochthonous matter was necessary to balance the energy budget (Hedgpeth 1967; Lind and Davalos-Lind 1991; Findlay et al. 1992). In this respect, the upper Casamance fits the general trend, but the observed DIC depletion is still puzzling. Several studies indicate that heterotrophic bacteria may be limited by energy sources (labile carbon) more than by nutrients (N or P) (Keil and Kirchman 1991; Cotner and Wetzel 1992). In the Casamance, the only series of sestonic C:N data does not indicate any serious nitrogen depletion and phosphate was often abundant. Against this, nocturnal oxygen consumption (in the entire water column) is highly correlated with DOC concentration, and poorly correlated with photosynthetic biomass. The daytime DIC consumption in the euphotic zone must deplete pre-existing DIC, while nutrients may be taken up anywhere and at any time. Bacterial  $\text{CO}_2$  production thus cannot replenish DIC needs, while nutrients may be recycled and utilized. However, all of these interactions can only occur because the *Phragmites* had colonized the area before 1970, during the former humid phase. Thus, the mechanisms leading to DIC depletion (however hypothetical) could appear elsewhere in the estuary only with an equivalent upstream source of organic matter or nutrients. In this respect, the Casamance example may not be of general value.

The Casamance estuary presents a highly abnormal DIC distribution. The hyperhaline waters, of undisputed marine origin, are DIC-depleted and this depletion increases at increasing salinities. The more concentrated brines have been subjected to more evaporation (on an annual scale) and to a longer residence time (on an interannual scale).

To our knowledge, this negative DIC versus S pattern has not been observed in other evaporative environments, except by Arakel (1981). All evaporated seawaters, be it in nature, in experiments, or in simulations, show a steady or increasing DIC (or alkalinity). The observed DIC depletion in the Casamance estuary may be explained by inorganic processes occurring in the shallow margins. Although these processes affect small volumes, their repetition through daily and tidal cycles may result in the observed depletion. Inspection of the literature shows that, despite numerous studies, evaporation in hypersaline (or hyperhaline) environments is still poorly documented. In particular, organic or biological effects have been neglected. As McCaffrey et al. (1987) noted, further studies on seawater evaporation would be useful.

Among the hypotheses we propose, sedimentation of newly formed POC is the one which needs the least speculation. Taking "Occam's razor," biological removal of DIC should be the preferred hypothesis. Such a process would be specific to the Casamance estuary. This peculiarity may be due both to its current hydraulics (not specific to this estuary) and to its past history. The relic *Phragmites* stands, now nearly extinct, have been a source of nutrients allowing a continuous production of phytoplankton. We are aware that we have merely described a rather peculiar system. Our proposed hypotheses are not supported by measurements and cannot lead to a quantitative budget. Despite this, the carbon sink we have found deserves to be reported, and might suggest some further insights concerning the biogeochemistry of seawater brines.

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