

Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon: The local impact of extensive mangrove forests

Steven Bouillon,¹ Michel Frankignoulle,² Frank Dehairs,¹ Branko Velimirov,³ Alexander Eiler,³ Gwenaël Abril,⁴ Henri Etcheber,⁴ and Alberto Vieira Borges²

Received 20 December 2002; revised 18 August 2003; accepted 22 September 2003; published 13 December 2003.

[1] The distribution and sources of organic and inorganic carbon were studied in the Gautami Godavari estuary (Andhra Pradesh, India) and in a mangrove ecosystem in its delta during pre-monsoon. In the oligohaline and mesohaline section (salinity 0–15) of the estuary, internal production of total alkalinity (TAlk) and dissolved inorganic carbon (DIC) was recorded, and the $\delta^{13}\text{C}_{\text{DIC}}$ profile suggests that carbonate dissolution may be an important process determining the DIC dynamics in this section of the Godavari. The partial pressure of CO_2 ($p\text{CO}_2$) was fairly low along the entire salinity gradient, (293–500 ppm), but much higher and more variable (1375–6437 ppm) in the network of tidal mangrove creeks in the delta. Here, variations in the concentration and $\delta^{13}\text{C}$ of the DIC pool were shown to result largely from the mineralization of organic matter. The present study clearly identifies the mangrove creeks as an active site of mineralization and CO_2 efflux to the atmosphere, but shows that these changes in the aquatic biogeochemistry are a localized feature, rapidly fading in the adjacent Kakinada Bay. Our data indicate that mineralization of dissolved organic carbon (DOC) of mangrove origin, and its subsequent efflux as CO_2 to the atmosphere may represent an important fate for mangrove carbon. Although further quantification of this process in a variety of systems is required, we suggest that some of the current ideas on the role of mangroves in the carbon budget of the coastal zone may need to be reconsidered. *INDEX TERMS:* 4235

Oceanography: General: Estuarine processes; 4504 Oceanography: Physical: Air/sea interactions (0312); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4815 Oceanography: Biological and Chemical: Ecosystems, structure and dynamics; *KEYWORDS:* mangroves, mineralization, stable isotopes

Citation: Bouillon, S., M. Frankignoulle, F. Dehairs, B. Velimirov, A. Eiler, G. Abril, H. Etcheber, and A. V. Borges, Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon: The local impact of extensive mangrove forests, *Global Biogeochem. Cycles*, 17(4), 1114, doi:10.1029/2002GB002026, 2003.

1. Introduction

[2] The majority of large rivers show a marked oversaturation of CO_2 [Cole and Caraco, 2001], indicating a net flux of CO_2 to the atmosphere and suggesting an important role for rivers and estuaries, not merely as a pathway for transport of organic carbon [Ittekkot and Laane, 1991] but also for active processing of organic matter [Frankignoulle et al., 1998; Richey et al. 2002]. Research on the biogeochemistry

of the major rivers and estuaries on the Indian subcontinent is scarce, and only a limited number of studies have addressed the organic and inorganic carbon biogeochemistry of these systems [Sarma et al., 2001; Mukhopadhyay et al., 2002], despite the fact that the amounts of particulate organic carbon exported by some of India's river systems [see Gupta et al., 1997] are reported to be among the highest in the world.

[3] Mangrove ecosystems are a prominent feature of many tropical and subtropical estuaries, and they can reach high aboveground primary production [Twilley et al., 1992], which is potentially significant in the carbon budget of the tropical coastal zone [Jennerjahn and Ittekkot, 2002]. However, mangroves are disappearing at an alarming rate, and a better understanding of their carbon dynamics should help us to consider the consequences of their destruction on regional or global carbon budgets. The fate of the mangrove-derived production has long been an issue of debate, and although it has become clear that these systems may

¹Department of Analytical and Environmental Chemistry, Vrije Universiteit Brussel, Brussels, Belgium.

²Unité d'Océanographie Chimique, MARE, Université de Liège, Sart Tilman, Belgium.

³Institut für Medizinische Biologie, Arbeitsgruppe Allgemeine Mikrobiologie, Universität Wien, Vienna, Austria.

⁴Département de Géologie et Océanographie, Université de Bordeaux 1, Talence, France.

export significant amounts of carbon to the adjacent aquatic environments under certain conditions, the spatial extent to which export occurs appears to be limited (*Lee* [1995], but see, e.g., *Dittmar and Lara* [2001a, 2001b]). Similarly, the role of mangrove carbon in sustaining faunal communities in the intertidal zone [e.g., *Bouillon et al.*, 2002a] and the adjacent aquatic environment is less important than was previously hypothesized [e.g., *Bouillon et al.*, 2002b]. However, mineralization of mangrove-derived organic carbon and its subsequent efflux as CO_2 toward the atmosphere might represent a major, yet poorly studied, pathway for mangrove-derived carbon. The only study in which mineralization is quantified in detail in an integrated mangrove ecosystem carbon budget is that by *Alongi et al.* [1998] for Hinchinbrook Channel (Australia), where the overall role of mineralization (benthic and pelagic) was estimated (indirectly) at 20.4% of the total organic carbon inputs. In this study, we wish to evaluate the effects of the presence of a large mangrove forest on the carbon biogeochemistry in the water column during the pre-monsoon season, in particular on the sources of organic and dissolved inorganic carbon and on the CO_2 flux across the water-atmosphere boundary. The pre-monsoon season was chosen for a first survey as it represents the most stable conditions, with relatively uniform salinity within the network of mangrove creeks, and terrestrial (i.e., upland) inputs are expected to be minimal in view of the low discharge of the Godavari during this season. We therefore collected data from three connected systems in the Gautami Godavari estuary (Andhra Pradesh, India): (1) along the salinity gradient of the estuary proper, (2) the mangrove creeks located in its delta, and (3) the adjacent semi-enclosed Kakinada Bay (Figure 1).

2. Materials and Methods

2.1. Study Area

[4] The Godavari is one of India's major rivers, draining an area of more than 300,000 km^2 before opening into the Bay of Bengal. The river has two main branches, the Gautami and Vasishta Godavari, of which the former was sampled during this study. Two surveys (May 27 and June 1, 2001) were conducted on the Gautami Godavari, from its mouth up to the oligohaline zone (Figure 1). Two additional sample points in the Godavari mouth were visited on May 29. The Godavari has several small branches into the semi-enclosed Kakinada Bay, including Coringa and Gaderu (Figure 1). The Godavari and Kakinada bay are connected by a network of tidal creeks, and the area is covered by extensive mangrove forests and mudflats. Kakinada Bay (depth ranging from 3 to 8 m at high tide, with a tidal range of 1–2 m) covers approximately 150 km^2 and opens into the Bay of Bengal on its northern side, bordered along most of its eastern length by a narrow sandbar. During the pre-monsoon of 2001, the mangrove creeks and bay were sampled during two surveys (May 28 and 29), and one station in the mangrove-covered region was occupied during a 24-hour period (Figure 1) and sampled at 1- or 2-hour intervals. Monsoon rainfall in the area usually occurs between July and September, during which near-freshwater conditions are found in the southern part of the study area.

Discharge of the Godavari is also concentrated (~96% of annual amount) during the monsoon months.

2.2. Sampling and Analytical Techniques

[5] A Niskin bottle was used to sample surface water. Oxygen saturation level (% O_2) was measured immediately after collection with a polarographic electrode (WTW Oxi-340) calibrated on saturated air, with an accuracy of $\pm 1\%$. Samples for determination of TALK were obtained by filtering 100 mL of water through 0.7- μm filters, and were stored in polyethylene bottles until analysis. TALK was analyzed by automated electro-titration on 50-mL samples with 0.1 M HCl as titrant. The reproducibility of TALK was estimated at $\pm 4 \mu\text{mol kg}^{-1}$. The pH was measured using a Ross type combination electrode (ORION) calibrated on the NBS (U.S. National Bureau of Standards) scale, as described by *Frankignoulle and Borges* [2001], with a reproducibility of ± 0.005 pH units. The pCO_2 and DIC were computed from pH and TALK measurements with the thermodynamic constants described by *Frankignoulle and Borges* [2001], and the accuracy of computed DIC and pCO_2 values are estimated at $\pm 5 \mu\text{mol kg}^{-1}$ and ± 5 ppm, respectively. Wind speed data were collected at each site using a hand-held anemometer, and were used to compute CO_2 exchange across the water-air interface (see section 4.4). Water samples for the analysis of $\delta^{13}\text{C}_{\text{DIC}}$ were obtained by gently overfilling a 50-mL glass bottle, poisoning with 100 μl of a saturated HgCl_2 solution, and gas-tight capping with a rubber plug and aluminium cap. For the Godavari transects, however, part of these samples were lost and $\delta^{13}\text{C}_{\text{DIC}}$ analyses were performed on subsamples of the TALK samples (as described above). It was verified separately that the two techniques resulted in $\delta^{13}\text{C}$ values within 0.17‰ of each other, i.e., within the analytical precision of $\delta^{13}\text{C}_{\text{DIC}}$ analysis. DIC was extracted by acidification with H_3PO_4 in an evacuated glass line, cryogenically purified, and transferred to a glass sample tube.

[6] Samples for Chlorophyll *a* (hereinafter Chl *a*) were obtained by filtering a known volume of surface water on glass fiber filters (0.7 μm , Whatman GF/F). These were stored in a liquid nitrogen transporter (-196°C) until arrival in Belgium, and were then stored at -20°C . Pigments were extracted for approximately 12 hours in 15 mL of 90% acetone at 4°C and analyzed with a Turner TD-700 Fluorimeter. The accuracy of Chl *a* analysis was estimated to be $\pm 4\%$. POC was sampled by filtering 100 mL of surface water on pre-combusted glass-fiber filters (Whatman GF/F) and air- or oven-drying (60°C). Total suspended matter (TSM) was measured on the same filter. Samples for DOC were obtained by filtering surface water on pre-combusted glass fiber filters (Whatman GF/F, 0.7 μm), and were preserved by the addition of 50 μl of H_3PO_4 per 15 mL of sample. DOC was measured with a high-temperature catalytic oxidation analyzer (Shimadzu TOC 5000); replicates showed an accuracy around $\pm 50 \mu\text{g L}^{-1}$. Samples for the estimation of bacterial abundance were preserved with formaldehyde (2% v/v). Cells were counted and sized by epifluorescence microscopy and the acridine orange direct counting technique [*Hobbie et al.*, 1977], whereby at least 20 fields per subsample were counted. The size of

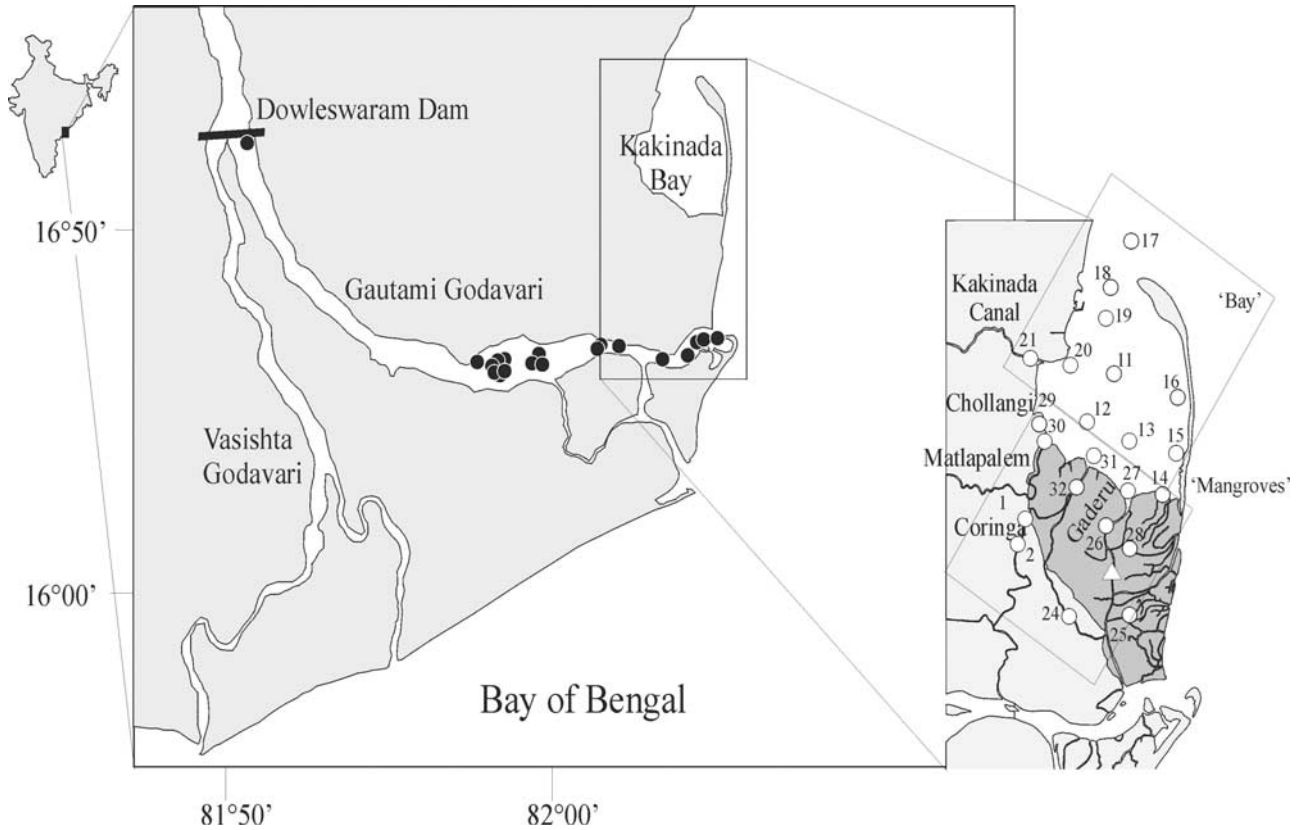


Figure 1. Location of the sampling sites along the Gautami Godavari estuary (solid circles), the mangrove creeks in its estuary, and Kakinada Bay (both as open circles) during the pre-monsoon period of 2001. The open triangle represents the location of the diel cycle sampling site.

the fields depended on the cell abundance to yield 20 to 40 cells per field. Volume estimations were based on the assumption that all cells are spheres or rods, i.e., cylinders with two hemispherical caps [Velimirov and Valenta-Simon, 1992]. At least 50 cells per morphotype and subsample (i.e., 600 cells per sample) were sized in length and width. Fluorescent latex beads with diameters of 0.1, 0.2, 0.6, and 0.88 μm (Polyscience Lim.) were used to calibrate this procedure [Velimirov and Valenta-Simon, 1992]. Cellular carbon content in fg C cell^{-1} was calculated from estimated cell volumes ($V, \mu\text{m}^3$) assuming the allometric relation $C = 120 V^{0.72}$ [Norland, 1993]. Elemental analysis (POC/PN, atom) of decarbonated (by HCl fumes) GF/F filters with suspended matter was done using a Carlo Erba NA-1500 elemental analyzer. Samples for $\delta^{13}\text{C}_{\text{POC}}$ were similarly decarbonated and combusted in the elemental analyzer, and the resulting CO_2 was cryogenically purified. The $\delta^{13}\text{C}$ (for both DIC and POC) was subsequently measured on a Finnigan Mat Delta E dual inlet isotope ratio mass spectrometer, and are reported in the δ notation relative to PDB (Pee Dee Belemnite) as

$$\delta^{13}\text{C} = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 10^3 \quad [\text{‰}], \quad (1)$$

where $R = {}^{13}\text{C}/{}^{12}\text{C}$. Reproducibility was better than $\pm 0.2\%$ for both $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$.

[7] Owing to technical problems during field sampling or lab analysis, not all data are available from all sampling locations. Missing data are mentioned in the figure captions.

3. Results

[8] The two surveys along the Godavari comprised almost the entire salinity range (0.5–34.3), whereas salinity in the mangrove creeks and Kakinada bay was overall high during the pre-monsoon (24.3–37.2). The pH in the Godavari was highest in the oligohaline/freshwater zone (up to 8.69) and decreased progressively toward values of 8.14 in the marine end of the estuary (Figure 2a). In the mangrove creeks and adjacent bay, pH was significantly lower than in the estuary proper (Table 1), with an average value of 7.66 ± 0.21 (Figure 2a). Oxygen saturation (Table 1, Figure 2b) was high along the entire Godavari salinity gradient ($105 \pm 8\%$) with no discernable pattern of variation. Oxygen saturation levels in the mangrove creeks were generally lower ($74 \pm 17\%$), but were high and notably variable in Kakinada bay ($106 \pm 25\%$). A general but relatively small decrease in TALK is observed along the salinity gradient of the Godavari, i.e., with lower values (approximately $2.26 \text{ mmol kg}^{-1}$) in the marine end of the estuary, yet with an apparent maximum in the 5–10 salinity zone. TALK was distinctly higher in the mangrove creeks and adjacent bay, with values reaching $3.20 \text{ mmol kg}^{-1}$ (albeit generally between 2.28 and 2.71

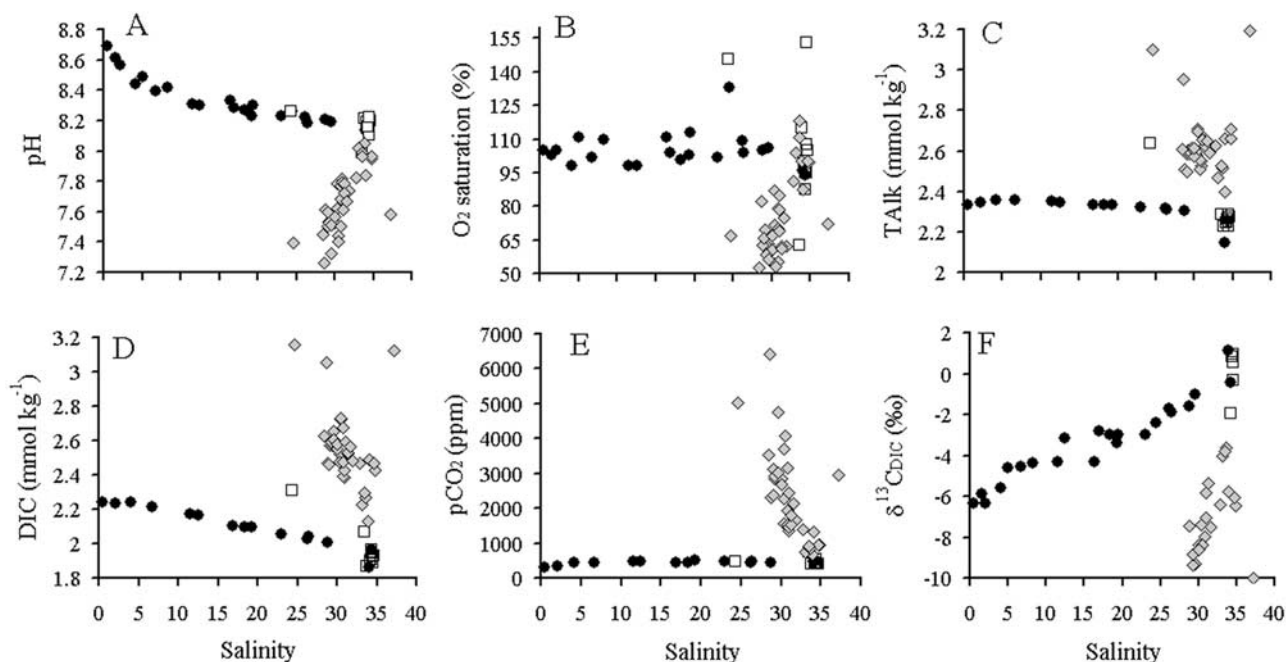


Figure 2. Variations of different physico-chemical variables as a function of salinity in the Gautami Godavari River (solid circles), at various locations in the tidal mangrove creeks (diamonds), and from the adjacent Kakinada Bay (squares) during the pre-monsoon period of 2001. (a) pH, (b) % O₂, (c) TALK, (d) DIC, (e) pCO₂, and (f) $\delta^{13}\text{C}_{\text{DIC}}$. Note that TALK and DIC data are missing from the majority of sites during the first Godavari transect, and that $\delta^{13}\text{C}_{\text{DIC}}$ data are missing for some of the Kakinada bay stations.

mmol kg⁻¹), and a similar trend was observed for DIC (Figures 2c and 2d).

[9] The pCO₂ values (Table 1) along the Godavari averaged 433 ± 77 ppm, with a marked undersaturation (minimum of 293 ppm; atmospheric pCO₂ during sampling period was 350 ppm) observed in the oligohaline zone, and values gradually increasing to 450–500 ppm toward the river mouth (Figure 2e). A sharp increase in pCO₂ is observed in the tidal mangrove creeks (2345 ± 1328 ppm), while in the adjacent Kakinada bay, pCO₂ again reaches values similar to those found in the euhaline zone of the estuary (471 ± 110 ppm). The resulting average fluxes showed a similar pattern (Table 1), i.e., a much higher flux in the tidal mangrove creeks compared to the Gautami Godavari and Kakinada bay.

[10] The $\delta^{13}\text{C}_{\text{DIC}}$ varied between -0.4 (at a salinity of 34.3) and -6.4‰ (salinity 0.5) over the studied length of the Godavari, with $\delta^{13}\text{C}_{\text{DIC}}$ values increasing gradually with salinity (Figure 2f). In the mangrove creeks, $\delta^{13}\text{C}$ values decreased sharply, with values in the creeks and bay ranging between -10.0‰ and +1.1‰ (Figure 2f). More negative $\delta^{13}\text{C}_{\text{DIC}}$ values coincided with higher DIC concentrations.

[11] The TSM concentration was low along the Godavari, and increased drastically in the tidal creeks (Figure 3a). Concentrations of POC decreased along the salinity gradient of the Godavari (Figure 3b) toward the marine end, with overall values between 0.493 and 1.808 mg L⁻¹, and again, values were markedly higher (0.692–2.824 mg L⁻¹) in the mangrove creeks. Consequently, the contribution of POC to

the TSM pool was generally high in the Godavari (mostly >10%), but much lower in the tidal creeks and bay (Figure 3c). DOC concentrations were similarly higher in the mangrove creeks (data from the diel cycle: 4.26 ± 2.12 mg L⁻¹, i.e., 72.9 ± 10.6% of the TOC pool) compared to the Godavari (2.03 ± 0.91 mg L⁻¹, i.e., 63.6 ± 6.3% of the TOC pool). DOC concentrations showed no marked profile along the Godavari salinity gradient (Figure 3d).

[12] Elemental (POC/PN) ratios of suspended matter were relatively low during both Godavari surveys and in the mangrove creeks, reflecting the dominance of phytoplankton in the POC pool during this season, and showed no clear trend along the salinity gradient (Figure 3e). However, the average POC/PN ratios during the second river transect

Table 1. Comparison of pCO₂ Values, Fluxes of CO₂ Across the Water-Air Interface, Oxygen Saturation Levels, and pH for the Gautami Godavari Estuary, the Tidal Mangrove Creeks, and the Adjacent Kakinada Bay^a

Area	pCO ₂ , ppm	Flux, mmol m ⁻² d ⁻¹	% O ₂	pH
Godavari	433 ± 77	21.9 ± 26.1	105 ± 8	8.33 ± 0.15
Mangroves	2345 ± 1328	70.2 ± 127.0	74 ± 17	7.66 ± 0.21
Kakinada Bay	471 ± 110	8.3 ± 13.6	106 ± 25	8.17 ± 0.07

^aSee Figure 1 for the grouping of sampling points. Numbers represent average ± 1 s.d. Atmospheric CO₂ data were taken from the NOAA air sampling network (Seychelles Islands). CO₂ fluxes were calculated according to Raymond and Cole [2001], and wind speed was measured in situ.

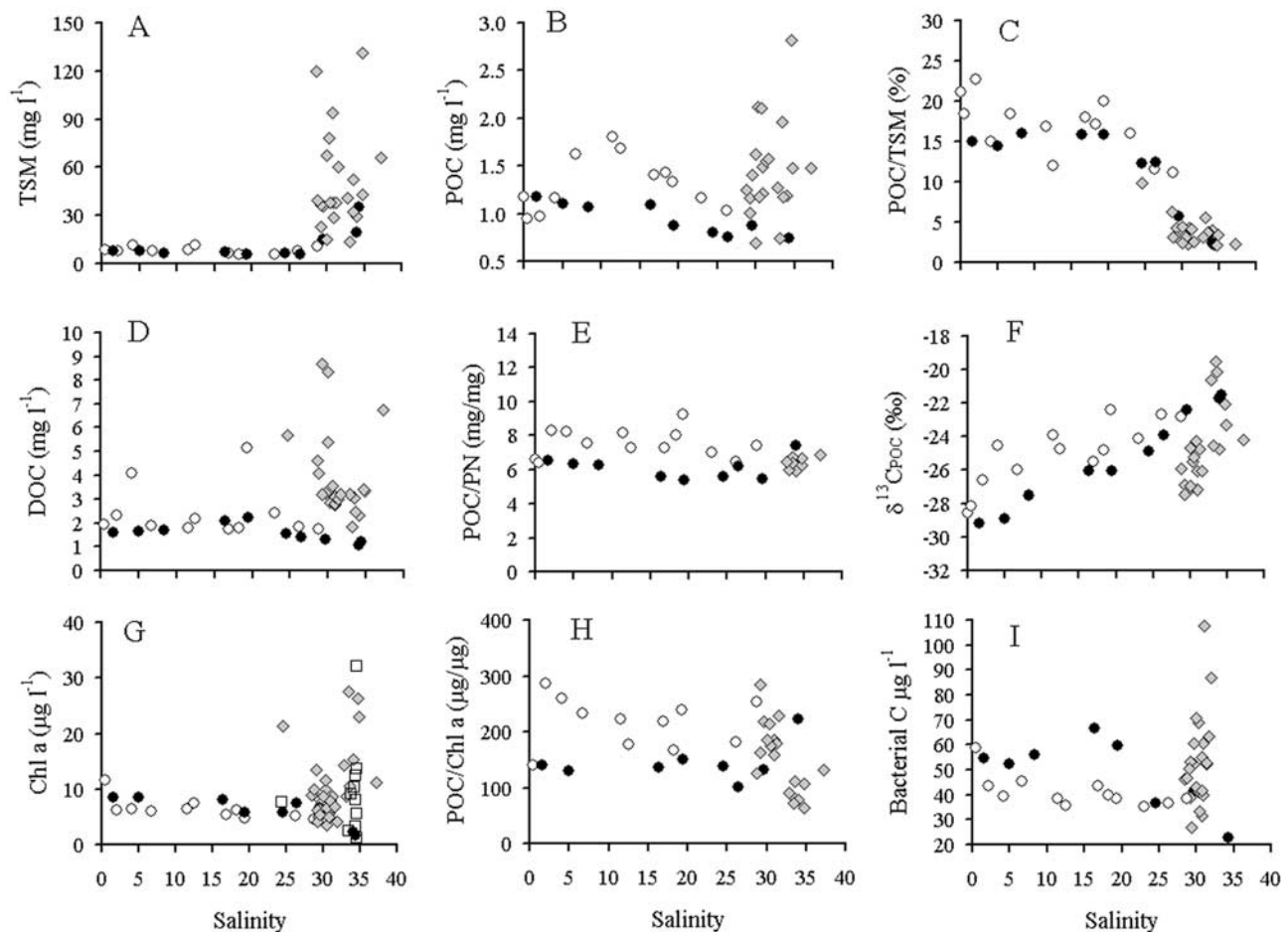


Figure 3. Variations of different variables characterizing the particulate and dissolved organic matter pool as a function of salinity in the Gautami Godavari River (solid circles and open circles represent the sampling on May 27 and June 2, respectively), at various locations in the tidal mangrove creeks (diamonds), and from the adjacent Kakinada Bay (squares) during pre-monsoon 2001. (a) TSM concentration, (b) POC concentration, (c) percentage contribution of POC to the TSM pool, (d) DOC concentration, (e) POC/PN ratios, (f) $\delta^{13}\text{C}_{\text{POC}}$, (g) Chl *a* concentration, (h) POC/Chl *a* ratio, and (i) bacterial carbon stocks. Note that for the majority of variables, no data from the bay are available, and that two high values from Coringa creek were not included in panel B and H as they were well out of the range of other data ($\text{POC} > 7000 \mu\text{g l}^{-1}$, $\text{POC/Chl } a > 1000$). Note that for many of the stations in Kakinada Bay, no data are available on $\delta^{13}\text{C}_{\text{POC}}$, TSM, DOC, POC, and POC/PN. Similarly, no POC/PN data are available for the diurnal cycle samples from a centrally located mangrove creek.

(7.5 ± 0.8) were significantly higher than during the first transect (5.9 ± 0.5). The almost linear pattern in $\delta^{13}\text{C}_{\text{POC}}$ values during the first Godavari survey ($R^2 = 0.97$) was much more distorted during the second transect ($R^2 = 0.64$), when $\delta^{13}\text{C}_{\text{POC}}$ was consistently higher at similar salinities (Figure 3f). The $\delta^{13}\text{C}_{\text{POC}}$ in mangrove creeks and Kakinada Bay were lower than those at similar salinities in the estuary proper (Figure 3f), but the decrease was less pronounced than observed for DIC (compare with Figure 2f).

[13] Chl *a* concentrations during the two Godavari transects averaged $6.4 \mu\text{g L}^{-1}$ and showed no marked variations along the salinity gradient nor between the two transects (Figure 3g). In Kakinada Bay and in the mangrove creeks, Chl *a* values were usually higher, with an overall range between 1.2 and $32.1 \mu\text{g L}^{-1}$, and with the highest values

observed in the tidal creeks (Figure 3g). POC/Chl *a* ratios were fairly constant along the Godavari salinity gradient, but with markedly higher values during the second survey (Figure 3h). POC/Chl *a* ratios in the tidal creeks were similar (diel cycle data), or even somewhat lower (spatial survey data, see Figure 3h). Estimates of bacterial carbon stocks averaged $53.1 \pm 17.8 \mu\text{g C L}^{-1}$ during the diel cycle in Gaderu creek (amounting to $1.0 \pm 0.3\%$ of the TOC pool), but were lower in the Gautami Godavari ($44.2 \pm 10.6 \mu\text{g C L}^{-1}$, i.e., $1.4 \pm 0.4\%$ of the TOC pool), with little variation along the salinity gradient, see Figure 3i).

[14] Large variations in most variables measured were observed during the diel sampling in a centrally located mangrove creek (figure not shown), but these data will mostly be discussed as an inherent part of the mangrove

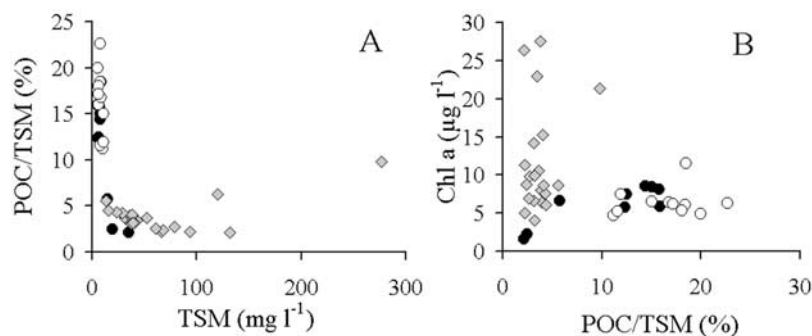


Figure 4. (a) Contribution of POC to the TSM pool as a function of total suspended matter concentrations, and (b) Chl *a* concentrations as a function of the contribution of POC to the TSM pool. Symbols are as in Figure 2. Note that POC and TSM data are unavailable for stations from Kakinada Bay.

creek data set, as the time frame considered makes it hard to unambiguously distinguish biological (day/night) and tidal effects in determining the observed variations [Borges *et al.*, 2003].

4. Discussion

4.1. General Remarks

[15] Before discussing the data in more detail, it is worth stressing the marked differences in most of the biogeochemical variables observed between the Godavari estuary proper and the mangrove creeks; that is, the latter were characterized by lower pH and oxygen saturation levels (Figures 2a and 2b), higher TAlk, DIC, and pCO₂ (Figures 2c, 2d, and 2e), higher TSM, POC, and DOC (Figures 3a, 3b, and 3d), and lower $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$ (Figures 2f and 3f). As will be outlined below, these differences reflect the local inputs of organic matter and the intense mineralization that takes place in the tidal mangrove creeks.

4.2. Sources and Distribution of Organic Carbon

[16] Only a limited number of studies have previously reported data on the organic carbon biogeochemistry of the Godavari River. Gupta *et al.* [1997] estimated the total annual POC flux of the Godavari at $2.8 \cdot 10^6 \text{ t POC yr}^{-1}$, ranking it among the highest in the world. The concentrations of DOC measured in this study for the Godavari ($2.02 \pm 0.91 \text{ mg L}^{-1}$) are clearly higher than those of Somayajulu *et al.* [1993] during the post-monsoon season ($0.3\text{--}1 \text{ mg L}^{-1}$), but remain in the lower range of values other major world rivers (between 2.4 and 16.1 mg L^{-1} [see Spitzzy and Leenheer, 1991]). No particular net change was detected in DOC concentrations along the salinity gradient of the Godavari (Figure 3d), whereas a decrease of POC (44%) occurred between the oligohaline zone and the river mouth (Figure 3b). In the Godavari, POC made a large contribution to the TSM pool, but a much lower contribution in the more turbid mangrove creeks and adjacent bay (Figure 4a). Such a relationship appears to be a general feature in rivers and estuaries, and has been suggested to be the result of a variable contribution of sedimentary material (low in organic carbon), and of lower primary production under high TSM concentrations [Ittekkot and Laane, 1991]. The latter would imply a different composition of the POC

pool, but in our study this was not the case as higher Chl *a* concentrations (and lower POC/Chl *a* ratios) coincided with higher TSM concentrations and lower POC/TSM ratios (e.g., Figure 4b). Similarly, POC/PN ratios were not markedly different in the Godavari (generally low TSM) when compared to the mangrove creeks and Kakinada Bay (generally higher TSM).

[17] It has been well described that the concentration of TSM is a major factor determining the relative importance of DOC and POC pools in rivers and estuaries [Ittekkot and Laane, 1991; Ludwig *et al.*, 1996; Abril *et al.*, 2002], with a generally higher DOC/POC ratio in low TSM systems. On the basis of the relationship established from compilations of data from various river systems [Ittekkot and Laane, 1991; Abril *et al.*, 2002], we would expect high DOC/POC ratios (~ 10) for the Gautami Godavari (Figure 5). The observed DOC/POC ratios in our study (1.9 ± 0.7) and those inferred from the data of Somayajulu *et al.* [1993] are, however, much lower. Thus the Godavari estuary proper appears to receive low inputs of DOC compared to other major river systems.

[18] POC/PN ratios of suspended matter were relatively low throughout the area, reflecting a dominance of phytoplankton during this season. The significantly higher POC/PN ratios during the second Godavari survey compared to the first (7.5 ± 0.8 versus 5.9 ± 0.5 ; see Figure 3e) suggest a larger terrestrial contribution in the POC pool, which is confirmed by the higher POC/Chl *a* ratios during the second survey (Figure 3h). Unexpectedly, $\delta^{13}\text{C}$ values of POC were significantly more enriched during the latter (by on average $\sim 1.5\text{‰}$; Figure 3f), which suggests that C₄-derived carbon (e.g., from sugarcane which is widely cultivated in the area) contributed to the Godavari POC pool during the second river survey (which was preceded by stormy weather). Concluding, the local effects of the presence of mangroves on the particulate organic matter dynamics were found to be less pronounced than expected, and were quantitative rather than qualitative during the pre-monsoon period. Even though concentrations of POC were higher in the mangrove creeks (Figure 3b), no marked difference in POC/PN ratios was observed (Figure 3e), and this increase coincided with a rise in Chl *a*, whereby POC/Chl *a* ratios were generally in the same range or even slightly lower in the mangrove creeks (Figure 3h).

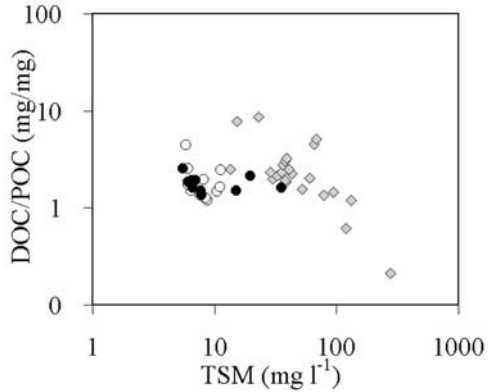


Figure 5. DOC/POC ratios as a function of the total suspended matter load (note: logarithmic X and Y axes). Symbols are as in Figure 2. Note that no POC or DOC data are available for stations in Kakinada Bay.

[19] The contrast in DOC concentrations between the Godavari and the mangrove creeks (an increase of $\sim 85\%$) was much more pronounced than the parallel increase in POC concentrations ($\sim 35\%$), and DOC therefore made a higher contribution to the total organic carbon pool in the mangrove creeks ($72.9 \pm 10.6\%$) than in the Godavari ($63.6 \pm 6.3\%$). From our data set, it is not possible to identify sources of the DOC pool in the studied area, although without significant terrestrial (river) inputs, it seems reasonable to assume that degraded mangrove litter makes up an important fraction of this material [see also *Kristensen and Suraswadi*, 2002]. The dominance of DOC as compared to POC in mangrove ecosystems has recently been stressed by a number of authors [e.g., *Dittmar et al.*, 2001; *Davis et al.*, 2001; *Kristensen and Suraswadi*, 2002]. Mangrove litter has been found to leach a significant fraction of its dry weight as dissolved organic matter during the initial stages of degradation (e.g., 30% after 9 days [see *Camilleri and Ribí*, 1986]), and the conversion of this DOC into microbial biomass has been shown to be fast and efficient [*Benner et al.*, 1986]. A local origin of this DOC would also be consistent with the abrupt local changes occurring in the intensity of mineralization (as inferred from, e.g., the % O_2 and pCO_2 patterns) of organic matter in the mangrove creeks compared to the marine/estuarine part of the Godavari and the adjacent bay. So far, only a handful of studies have tried to assess the origin of DOC in mangrove ecosystems. In general, mangrove carbon appears to be the dominant source of DOC, although the contribution of local phytoplankton production has been found to be significant in some cases. *Lara and Dittmar* [1999] and *Dittmar and Lara* [2001a] estimated the latter at $\sim 8\%$ of the total DOC pool, and *Kristensen and Suraswadi* [2002] suggested this contribution to be between 10 and 40%. *Moran et al.* [1991] estimated about 30% of the DOC pool in a mangrove swamp in the Bahamas to be algal-derived during low tide, and even higher during high tide. In contrast, *Boto and Wellington* [1988] found no apparent link between DOC and primary production (i.e., no day/night shifts in DOC concentrations) and concluded that the

bulk of the DOC was refractory. Perhaps the most thorough study of the sources of DOC is by *Dittmar et al.* [2001], who made estimates of the contributions of mangroves, terrestrial, and marine-derived organic matter to the DOC pool in a mangrove estuary in northern Brazil throughout 18 tidal cycles. Despite wide seasonal and spatial variations in the contributions of these three sources (which depended strongly on the parameters used in their calculations), DOC in a mangrove creek was shown to be mostly of mangrove origin ($\sim 60\%$), with marine-derived organic matter making up most of the remaining DOC ($\sim 35\%$). In view of the importance of DOC in the overall carbon pool, a more detailed characterization of its distribution, sources, and fate, currently lacking for mangrove ecosystems, should be more thoroughly investigated.

4.3. Nonconservative Mixing of DIC in the Estuary

[20] Before looking into the local differences in carbon dynamics between mangroves and the estuary proper, we first examine the behavior of DIC along the estuarine salinity gradient of the Godavari. TALK and DIC (and therefore, $\delta^{13}C_{DIC}$) are often considered to obey conservative behavior in estuaries [e.g., *Mook and Tan*, 1991; *Cai and Wang*, 1998; *Chanton and Lewis*, 1999], but this is certainly not universal as in situ processing of DIC, internal production or removal, may significantly alter this pattern [*Frankignoulle et al.*, 1996; *Coffin and Cifuentes*, 1999; *Hellings et al.*, 2001]. Whether or not conservative mixing applies can be examined by looking both at the DIC content and at the $\delta^{13}C$ signature of the DIC pool [*Hellings et al.*, 2001; *Fry*, 2002]. For DIC, conservative mixing implies that at any position along the transect,

$$DIC = \left(\frac{DIC_M - DIC_F}{Sal_M - Sal_F} \right) Sal + DIC_F, \quad (2)$$

where Sal is salinity, and subscripts refer to the marine end-member (M) and the freshwater end-member (F). Conservative mixing of TALK can be described by the same equation by substituting TALK for DIC. If conservative mixing applies, the $\delta^{13}C$ signature of the DIC pool obeys to the following equation (adapted from *Mook and Tan* [1991]):

$$\delta^{13}C = \frac{Sal(DIC_F \delta^{13}C_F - DIC_M \delta^{13}C_M) + Sal_F DIC_M \delta^{13}C_M - Sal_M DIC_F \delta^{13}C_F}{Sal(DIC_F - DIC_M) + Sal_F DIC_M - Sal_M DIC_F}, \quad (3)$$

where $\delta^{13}C$ represents the carbon isotope composition of DIC, and all other symbols are as in equation (2).

[21] For both DIC and TALK, there appears to be internal production in the oligohaline and mesohaline section (salinity 0–15). The $\delta^{13}C_{DIC}$ values are markedly higher than predicted based on conservative mixing in this zone, but comply downstream. These higher than predicted $\delta^{13}C_{DIC}$ values accompany an increase in DIC concentrations (Figure 6d), which excludes prolonged atmospheric efflux and biological CO_2 fixation as explanations, and which suggests that the dissolution of carbonates (with expected $\delta^{13}C$ values of $0 \pm 2\%$) may contribute significantly in

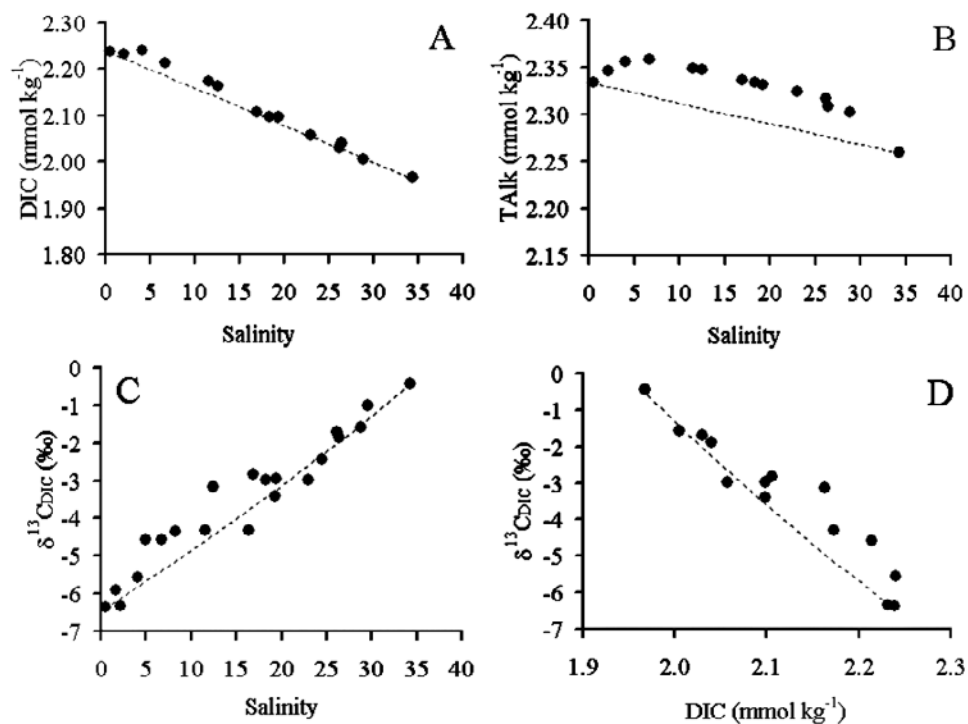


Figure 6. Examination of the conservative behavior of TALK and DIC along the Godavari salinity gradient: (a) DIC concentrations versus salinity, (b) TALK versus salinity, (c) $\delta^{13}\text{C}$ of the DIC pool versus salinity, and (d) $\delta^{13}\text{C}_{\text{DIC}}$ versus DIC concentrations.

determining the distribution of inorganic carbon species in the oligohaline and mesohaline zone of the Gautami Godavari during pre-monsoon. The $[\text{Ca}^{2+}]$ data for the pre-monsoon presented by *Padmavathi and Satyanarayana* [1999, Figure 4] also suggest internal production of Ca^{2+} in the oligohaline and mesohaline zone, although this possibility was not explicitly discussed by the latter authors.

4.4. Local Impact of Mangroves on the Sources and Distribution of DIC

[22] DIC in rivers and estuaries can generally be derived from various sources: the dissolution of carbonates or CO_2 from the atmosphere (both yielding $\delta^{13}\text{C}$ values of approximately 0‰), and the respiration of organic matter within the water column (yielding $\delta^{13}\text{C}$ values of $\sim -28\%$ if the dominant plant sources have a C_3 metabolism). The $\delta^{13}\text{C}$ values of DIC can thus be used to estimate the contribution of respiration of organic carbon to the DIC pool, according to

$$\delta^{13}\text{C}_{\text{DIC}} = X_{\text{atm+carb}} \times \delta^{13}\text{C}_{\text{atm+carb}} + X_{\text{resp}} \times \delta^{13}\text{C}_{\text{resp}}, \quad (4)$$

where $X_{\text{atm+carb}}$ and X_{resp} are the fractions of the DIC originating from the atmosphere or carbonate dissolution and from respiration, respectively, and $\delta^{13}\text{C}_{\text{atm+carb}}$ and $\delta^{13}\text{C}_{\text{resp}}$ are the isotope compositions of these two contributing sources (whereby in our calculations we use a value of 0‰ and -28% , respectively). Applying this method to our data set, we obtain estimates of the

contribution of respiration to the DIC pool ranging from -4.1% to 22.6% for the Gautami Godavari (for the marine and freshwater end-members, respectively), $24 \pm 8\%$ for mangrove creeks, and $0 \pm 4\%$ for Kakinada bay. It must be stressed that these are minimum estimates, as (1) intense photosynthesis and the presumably long residence time in the Godavari during the pre-monsoon season could have elevated the $\delta^{13}\text{C}_{\text{DIC}}$ significantly, and (2) C_4 -derived organic matter with more enriched $\delta^{13}\text{C}$ values is also a potential carbon source (see discussion above). If we assume that the source of the respired CO_2 in the mangrove creeks is mainly of mangrove origin (see below for argumentation), the dominant pool of mangrove-derived carbon in the water column is found to be in the DIC pool rather than in the TOC pool (either POC or DOC); the total stock of the latter two being much smaller than the calculated stock of mangrove-derived DIC. The pronounced impact of the presence of mangroves on the dissolved inorganic carbon biogeochemistry is most striking when plotting the $\delta^{13}\text{C}_{\text{DIC}}$ data versus salinity (i.e., Figure 2f): Along the Gautami Godavari estuary, they display a typical estuarine gradient, with more enriched values toward the marine environment, whereas DIC in the mangrove creeks (with similarly high salinities) showed a very strong depletion in ^{13}C , with $\delta^{13}\text{C}_{\text{DIC}}$ values decreasing to -10.0% , i.e., even lower than in the oligohaline part of the Godavari. This depletion in ^{13}C coincides with significantly higher DIC concentrations (Figure 2d) and pCO_2 (Figure 2e; Table 1), lower oxygen saturation (Figure 2b; Table 1), and lower pH (Figure 2a;

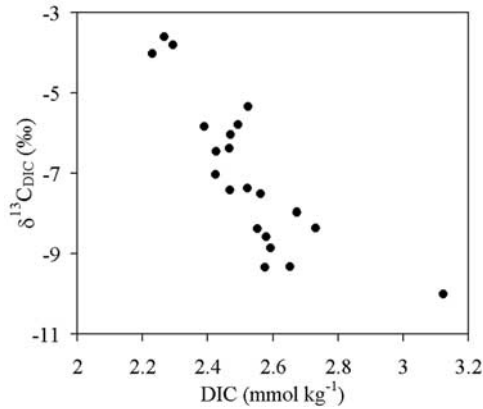


Figure 7. Relationship between DIC concentration and the carbon stable isotope composition of the DIC pool ($\delta^{13}\text{C}_{\text{DIC}}$) for the data from the mangrove tidal creeks.

Table 1). A negative correlation between DIC and $\delta^{13}\text{C}_{\text{DIC}}$ ($R^2 = 0.87$; Figure 7) suggests that the depletion in ^{13}C of the DIC pool observed in the mangrove creeks is to a large extent an effect of added (^{13}C -depleted) DIC. Therefore, besides the procedure described above, i.e., assuming a $\delta^{13}\text{C}$ value for the respired source and evaluating its contribution to the DIC pool, we can also use the combination of DIC concentration data and $\delta^{13}\text{C}_{\text{DIC}}$ values to estimate the $\delta^{13}\text{C}$ value of the respired carbon source. We then use the following equation:

$$\delta^{13}\text{C}_{\text{added}} = \frac{\text{DIC}_A \delta^{13}\text{C}_A - \text{DIC}_B \delta^{13}\text{C}_B}{\text{DIC}_A - \text{DIC}_B}, \quad (5)$$

where $\delta^{13}\text{C}_{\text{added}}$ represents the carbon isotope composition of added DIC; DIC_A and DIC_B represent the concentration of DIC at point A or B along the regression line; and $\delta^{13}\text{C}_A$, $\delta^{13}\text{C}_B$ denote the carbon stable isotope composition of the DIC pool corresponding to points A and B along the regression line.

[23] Applying this approach to the data from the mangrove creeks and Kakinada bay results in an estimate of $\delta^{13}\text{C}_{\text{added}}$ of -28.6‰ , which is characteristic for C_3 -vegetation (including mangroves), but also overlaps with the expected range found in local phytoplankton in the mangrove creeks (considering $\delta^{13}\text{C}_{\text{DIC}}$ values in these creeks were as low as -10‰). Although this calculation can therefore not unambiguously identify mangrove carbon as the dominant substrate for the observed mineralization, there are several additional arguments that lead us to hypothesize that mangrove carbon constitutes a major substrate for mineralization. First, although phytoplankton is clearly an important component of the POC pool, we have no direct indications as to the composition of the DOC pool, the latter being the dominant pool of organic carbon in the water column and the primary substrate pool for heterotrophic microbial communities. From other studies, however (see discussion above), it does appear that mangrove carbon is in most cases a major source of DOC. Second, it should be considered that the concentration of POC and its general composition (high proportion of phytoplankton, as seen

from C/N ratios and POC/Chl a ratios), is not drastically different in the mangrove creeks from the situation observed in Kakinada Bay or the estuarine end of the Godavari. In view of the absence of a significant freshwater inflow during the sampling period considered, a scenario whereby the additional C delivered by mangroves is a major substrate for this enhanced mineralization appears realistic. Another aspect which deserves clarification is the relative role of the intertidal sediments and the creek water column as sites for mineralization, as part of the variations observed in the tidal creek waters may have been the result of processes occurring in the intertidal pore waters (see, e.g., Sherr [1982] and Cai and Wang [1998] for salt and freshwater marshes, and Ovalle *et al.* [1990] and Dittmar *et al.* [2001] for mangrove systems). The high TALK values observed in the mangrove creeks and a positive relationship between TALK_{30} (i.e., normalized to a salinity of 30) and TOC for these data ($R^2 = 0.71$; figure not shown) would be consistent with such a hypothesis; that is, pore waters enriched in organic carbon and alkalinity [e.g., Ovalle *et al.*, 1990] drain into the creeks during ebb tides, and local variations may be related to these pore water inputs. Although two different mechanisms have been proposed to explain the high TALK of mangrove pore waters (sulphate reduction and carbonate dissolution, see Ovalle *et al.* [1990] and Middelburg *et al.* [1996], respectively), the slope of the DIC- $\delta^{13}\text{C}$ relationship (Figure 7; see discussion above) is consistent with sulphate reduction and/or aerobic mineralization, but not with a major role for carbonate dissolution.

[24] Thus a major difference exists in the factors determining the dissolved inorganic carbon dynamics between the mangrove creeks (and Kakinada Bay) and the Gautami Godavari estuary. In the former, much of the observed variations in DIC and $\delta^{13}\text{C}_{\text{DIC}}$ can be explained as the result of variable contributions of microbially respired CO_2 . In the Godavari, however, photosynthesis and mineralization are more balanced and carbonate dissolution is suggested to contribute significantly to the dissolved inorganic carbon distribution. Finally, the difference between Gautami Godavari estuary and the mangrove creeks in its delta is also apparent in other distinct patterns, such as (1) the negative trend between $\% \text{O}_2$ and $\delta^{13}\text{C}_{\text{DIC}}$ values in the data from the mangrove ecosystem ($R^2 = 0.59$), but the lack of such a relationship in the Gautami Godavari estuary data (figure not shown), and (2) the marked difference in the relationship between pH and $\delta^{13}\text{C}_{\text{DIC}}$; that is, lower $\delta^{13}\text{C}_{\text{DIC}}$ are accompanied by a decrease in pH in the mangrove ecosystem, but with an increase in pH in the Gautami Godavari estuary (figure not shown).

4.5. Flux of CO_2 Across the Water/Atmosphere Interface

[25] The pCO_2 values calculated from the pH-TALK couple can be used to estimate the flux of CO_2 across the water/atmosphere interface, as the magnitude of the latter is largely determined by the gradient in CO_2 between these two phases and the wind speed (which was measured in situ) according to the general equation,

$$\text{Flux} = k \alpha \Delta \text{pCO}_2, \quad (6)$$

where k is the gas transfer velocity, α is the solubility coefficient of CO_2 , and $\Delta p\text{CO}_2$ represents the difference in partial pressure of CO_2 between water and air. Here k was determined according to the algorithm presented by *Raymond and Cole* [2001], which we consider suitable under the environmental conditions encountered.

[26] The most striking pattern in the $p\text{CO}_2$ and resulting flux data is, first, the sharp contrast observed between the Godavari estuary proper and the mangrove tidal creeks (considering the local scale) and, second, the absence of a marked impact of the mangroves in the adjacent Kakinada Bay. In the latter, $p\text{CO}_2$ values (Table 1) are of the same magnitude as in the Gautami Godavari, and the resulting fluxes are even lower than in the latter, mostly due to differences in wind speed (e.g., wind speed averaged 6.1 m s^{-1} along the Godavari, but 1.5 m s^{-1} in the more sheltered mangrove creeks). These data, therefore, clearly indicate the very local processing of mangrove-derived organic matter during the season considered.

[27] When comparing our CO_2 flux estimates (for a discussion of the $p\text{CO}_2$ data collected during the diel cycle, see *Borges et al.* [2003]) with data on other riverine and estuarine systems (e.g., *Cole and Caraco* [2001]; for the Indian subcontinent, e.g., *Sarma et al.* [2001] and *Mukhopadhyay et al.* [2002]), it appears that the Godavari shows a relatively low degree of oversaturation, at least during the pre-monsoon season, whereas $p\text{CO}_2$ and the resulting fluxes in the mangrove creeks are high, and comparable to, for example, efflux estimates for highly polluted temperate estuaries such as the Scheldt [e.g., *Frankignoulle et al.*, 1996, 1998].

4.6. Implications for Mangrove Ecosystem Carbon Budgets

[28] In earlier studies in the same area, we found surprisingly little evidence for the incorporation of mangrove-derived carbon in subtidal and intertidal sediment pools, and little or no evidence was found for its role as a carbon source for zooplankton and subtidal benthic invertebrates [*Dehairs et al.*, 2000; *Bouillon et al.*, 2000, 2002b]. Nevertheless, export of organic carbon from mangrove forests is usually considered to comprise a significant fate of mangrove carbon (with global estimates ranging between 40 and 50% of aboveground production [see *Twilley et al.*, 1992; *Jennerjahn and Ittekkot*, 2002]). Therefore our study suggests that mineralization and subsequent efflux as CO_2 (even considering that part of the observed efflux results from mineralization of other sources, see discussion above) could represent a major pathway for mangrove carbon, but a spatially and seasonally integrated quantification is lacking for any mangrove system. Although our data set only represents the pre-monsoon season, monthly $\delta^{13}\text{C}_{\text{DIC}}$ data are available for a number of locations in the mangrove creeks and Kakinada bay (S. Bouillon, unpublished data, 2002), and these data indicate (1) that the large spatial trend in $\delta^{13}\text{C}_{\text{DIC}}$ values between mangroves and bay, reflective of the gradient in mineralization, is consistent throughout the year, but (2) that more negative $\delta^{13}\text{C}_{\text{DIC}}$ values are found throughout the area during the monsoon period (July–September),

when the area receives large quantities of freshwater from the Godavari. Although this does not give us an indication of the magnitude of the CO_2 fluxes across the water-air interface nor on the primary substrates for mineralization during the monsoon season, the latter data are consistent with a scenario whereby mangrove carbon is exported farther into the Bay along with upland sources of terrestrial carbon during the period of peak discharge.

[29] *Bano et al.* [1997] measured high bacterial production and turnover rates in mangrove creeks of the Indus Delta. Our observations are consistent with such a pattern, in that the large contrast in mineralization between the Godavari and the mangroves creeks (as evidenced by, e.g., the % O_2 , $p\text{CO}_2$ or flux differences; see Table 1) is accompanied by a comparatively low increase in bacterial C stocks (Figure 3i). A recent inter-ecosystem comparison study [*Borges et al.*, 2003] suggests that from the few mangrove systems in which CO_2 fluxes have been estimated, an average value of $50 \text{ mmol m}^{-2} \text{ d}^{-1}$ appears to be a reasonable first-order estimate. Although the absence of more comprehensive data sets precludes us from evaluating the overall quantitative role of mineralization and CO_2 efflux, comparing these data with a worldwide estimate for average mangrove litterfall ($\sim 108 \text{ mmol C m}^{-2} \text{ d}^{-1}$ [e.g., *Jennerjahn and Ittekkot*, 2002]), shows the very large potential for mineralization and efflux as a major and previously ignored pathway of mangrove production. *Jennerjahn and Ittekkot* [2002], for example, recently estimated that mangroves could account for 11% of the total annual organic carbon inputs into the ocean, and 15% of the total organic carbon accumulating in modern marine sediments. However, these estimates are based on the assumption that on average, 50% of mangrove aboveground production is exported to the coastal ocean, an estimate based on a variety of studies using different approaches, but in essence these export estimates often reflect the exchange of material between the intertidal mangrove forests and adjacent aquatic ecosystems. Although our results support a strong linkage between intertidal mangrove forests and the aquatic system via drainage of mangrove pore waters, this does not necessarily imply that major amounts of mangrove-derived carbon are exported to adjacent aquatic habitats. If local mineralization within the mangrove creeks and subsequent efflux as CO_2 accounts for a major proportion of the “exported” material across a range of mangrove ecosystems, which may differ strongly in the extent to which mangrove carbon is retained within the system [see *Bouillon et al.*, 2003], it remains to be determined whether a significant fraction of mangrove-derived carbon actually reaches the coastal ocean.

[30] **Acknowledgments.** Logistical support and assistance during fieldwork was provided in particular by A. V. Raman, A. V. V. S. Rao, and B. Satyanarayana. Financial support was provided by EC-INCO project contract ERB IC18-CT98-0295 (Assessment of mangrove degradation and resilience in the Indian sub-continent: The cases of Godavari estuary and South-west Sri Lanka), the Fonds voor Wetenschappelijk Onderzoek Vlaanderen (FWO, contract G.0118.02), and by the Fonds National de la Recherche Scientifique (FNRS, Belgium; contracts 2.4596.01, V3/5/134 - ILF.9990) with which M. F. and A. V. B. are a senior research associate and a postdoctoral researcher, respectively. The first author is a postdoctoral researcher at the Fonds voor Wetenschappelijk Onderzoek (FWO-Vlaanderen). We would like to thank two anonymous reviewers for their very

helpful suggestions and constructive comments on an earlier version of this manuscript.

References

- Abril, G., M. Nogueira, H. Etcheber, G. Cabeçadas, E. Lemaire, and M. J. Brogueira, Behaviour of organic carbon in nine contrasting European estuaries, *Estuarine Coastal Shelf Sci.*, *54*, 241–262, 2002.
- Alongi, D. M., T. Ayukai, G. J. Brunskill, B. F. Clough, and E. Wolanski, Sources, sinks, and export of organic carbon through a tropical, semi-enclosed delta (Hinchinbrook Channel, Australia), *Mangroves Salt Marshes*, *2*, 237–242, 1998.
- Bano, N., M. U. Nisa, N. Khan, M. Saleem, P. J. Harrison, S. I. Ahmed, and F. Azam, Significance of bacteria in the flux of organic matter in the tidal creeks of the mangrove ecosystem of the Indus River delta, Pakistan, *Mar. Ecol. Prog. Ser.*, *157*, 1–12, 1997.
- Benner, R., E. R. Peele, and R. E. Hodson, Microbial utilization of dissolved organic matter from leaves of the red mangrove, *Rhizophora mangle*, in the Fresh Creek estuary, Bahamas, *Estuarine Coastal Shelf Sci.*, *23*, 607–619, 1986.
- Borges, A. V., S. Djenidi, G. Lacroix, J. Théate, B. Delille, and M. Frankignoulle, Atmospheric CO₂ flux from mangrove surrounding waters, *Geophys. Res. Lett.*, *30*, 11–14, 2003.
- Boto, K. G., and J. T. Wellington, Seasonal variations in concentrations and fluxes of dissolved organic and inorganic materials in a tropical, tidally dominated waterway, *Mar. Ecol. Prog. Ser.*, *50*, 151–160, 1988.
- Bouillon, S., P. Chandra Mohan, N. Sreenivas, and F. Dehairs, Sources of suspended matter and selective feeding by zooplankton in an estuarine mangrove ecosystem, as traced by stable isotopes, *Mar. Ecol. Prog. Ser.*, *208*, 79–92, 2000.
- Bouillon, S., N. Koedam, A. V. Raman, and F. Dehairs, Primary producers sustaining macro-invertebrate communities in intertidal mangrove forests, *Oecologia*, *130*, 441–448, 2002a.
- Bouillon, S., A. V. Raman, P. Dauby, and F. Dehairs, Carbon and nitrogen stable isotope ratios of subtidal benthic invertebrates in an estuarine mangrove ecosystem (Andhra Pradesh, India), *Estuarine Coastal Shelf Sci.*, *54*, 901–913, 2002b.
- Bouillon, S., F. Dahdouh-Guebas, A. V. S. Rao, N. Koedam, and F. Dehairs, Sources of organic carbon in mangrove sediments: Variability and possible implications for ecosystem functioning, *Hydrobiologia*, *495*, 33–39, 2003.
- Cai, W. J., and Y. Wang, The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha rivers, Georgia, *Limnol. Oceanogr.*, *43*, 657–668, 1998.
- Camilleri, J. C., and G. Ribí, Leaching of dissolved organic carbon (DOC) from dead leaves, formation of flakes from DOC, and feeding on flakes by crustaceans in mangroves, *Mar. Biol.*, *91*, 337–344, 1986.
- Chanton, J. P., and F. G. Lewis, Plankton and dissolved inorganic carbon isotopic composition in a river-dominated estuary: Apalachicola Bay, Florida, *Estuaries*, *22*, 575–583, 1999.
- Coffin, R. B., and L. A. Cifuentes, Stable isotope analysis of carbon cycling in the Perdido estuary, Florida, *Estuaries*, *22*, 917–926, 1999.
- Cole, J. J., and N. F. Caraco, Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, *52*, 101–110, 2001.
- Davis, S. E., D. L. Childers, J. W. Day, D. T. Rudnick, and F. H. Sklar, Nutrient dynamics in vegetated and unvegetated areas of a southern Everglades mangrove creek, *Estuarine Coastal Shelf Sci.*, *52*, 753–768, 2001.
- Dehairs, F., R. G. Rao, P. Chandra Mohan, A. V. Raman, S. Marguillier, and L. Hellings, Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami-Godavari Delta, Bay of Bengal (India), *Hydrobiologia*, *431*, 225–241, 2000.
- Dittmar, T., and R. J. Lara, Driving forces behind nutrient and organic matter dynamics in a mangrove tidal creek in North Brazil, *Estuarine Coastal Shelf Sci.*, *52*, 249–259, 2001a.
- Dittmar, T., and R. J. Lara, Do mangroves rather than rivers provide nutrients to coastal environments south of the Amazon River? Evidence from long-term flux measurements, *Mar. Ecol. Prog. Ser.*, *213*, 67–77, 2001b.
- Dittmar, T., R. J. Lara, and G. Kattner, River or mangrove? Tracing major organic matter sources in tropical Brazilian coastal waters, *Mar. Chem.*, *73*, 253–271, 2001.
- Frankignoulle, M., and A. V. Borges, Direct and indirect pCO₂ measurements in a wide range of pCO₂ and salinity values (the Scheldt estuary), *Aquat. Geochem.*, *7*, 273–627, 2001.
- Frankignoulle, M., I. Bourge, and R. Wollast, Atmospheric CO₂ fluxes in a highly polluted estuary (the Scheldt), *Limnol. Oceanogr.*, *41*, 365–369, 1996.
- Frankignoulle, M., G. Abril, A. Borges, I. Bourge, C. Canon, B. Delille, E. Libert, and J.-M. Théate, Carbon dioxide emissions from European estuaries, *Science*, *282*, 434–436, 1998.
- Fry, B., Conservative mixing of stable isotopes across estuarine salinity gradients: A conceptual framework for monitoring watershed influences on downstream fisheries production, *Estuaries*, *25*, 264–271, 2002.
- Gupta, L. P., V. Subramanian, and V. Ittekkot, Biogeochemistry of particulate organic matter transported by the Godavari River, India, *Biogeochemistry*, *38*, 103–128, 1997.
- Hellings, L., F. Dehairs, S. Van Damme, and W. Baeyens, Dissolved inorganic carbon in a highly polluted estuary (the Scheldt), *Limnol. Oceanogr.*, *46*, 1406–1414, 2001.
- Hobbie, J. E., R. J. Dayley, and S. Jasper, Use of Nucleopore filters for counting bacteria by epifluorescence microscopy, *Appl. Environ. Microbiol.*, *33*, 1225–1228, 1977.
- Ittekkot, V., and R. W. P. M. Laane, Fate of riverine particulate organic matter, in *Biogeochemistry of Major World Rivers*, edited by E. T. Degens, S. Kempe, and J. E. Richey, pp. 233–234, John Wiley, New York, 1991.
- Jennerjahn, T. C., and V. Ittekkot, Relevance of mangroves for the production and deposition of organic matter along tropical continental margins, *Naturwissenschaften*, *89*, 23–30, 2002.
- Kristensen, E., and P. Suraswadi, Carbon, nitrogen and phosphorus dynamics in creek water of a Southeast Asian mangrove forest, *Hydrobiologia*, *474*, 197–211, 2002.
- Lara, R. J., and T. Dittmar, Nutrient dynamics in a mangrove creek (North Brazil) during the dry season, *Mangroves Salt Marshes*, *3*, 185–195, 1999.
- Lee, S. Y., Mangrove outwelling: A review, *Hydrobiologia*, *295*, 203–212, 1995.
- Ludwig, W., J. L. Probst, and S. Kempe, Predicting the oceanic input of organic carbon by continental erosion, *Global Biogeochem. Cycles*, *10*, 23–41, 1996.
- Middelburg, J. J., J. Nieuwenhuize, F. J. Slim, and B. Ohowa, Sediment biogeochemistry in an East African mangrove forest (Gazi Bay, Kenya), *Biogeochemistry*, *34*, 133–155, 1996.
- Mook, W. G., and F. C. Tan, Stable carbon isotopes in rivers and estuaries, in *Biogeochemistry of Major World Rivers*, edited by E. T. Degens, S. Kempe, and J. E. Richey, pp. 245–264, John Wiley, New York, 1991.
- Moran, M. A., R. J. Wicks, and R. E. Hodson, Export of dissolved organic matter from a mangrove swamp ecosystem: Evidence from natural fluorescence, dissolved lignin phenols, and bacterial secondary production, *Mar. Ecol. Prog. Ser.*, *76*, 175–184, 1991.
- Mukhopadhyay, S. K., H. Biswas, T. K. De, S. Sen, and T. K. Jana, Seasonal effects on the air-water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India, *J. Environ. Monit.*, *4*, 549–552, 2002.
- Norland, S., The relationship between biomass and volume of bacteria, in *Current Methods in Aquatic Microbial Ecology*, edited by P. F. Kemp, E. B. Sherr, and J. J. Cole, pp. 303–307, Lewis, Boca Raton, Fla., 1993.
- Ovalle, A. R. C., C. E. Rezende, L. D. Lacerda, and C. A. R. Silva, Factors affecting the hydrochemistry of a mangrove tidal creek, Sepetiba Bay, Brazil, *Estuarine Coastal Shelf Sci.*, *31*, 639–650, 1990.
- Padmavathi, D., and D. Satyanarayana, Distribution of nutrients and major elements in riverine, estuarine and adjoining coastal waters of Godavari, Bay of Bengal, *Indian J. Mar. Sci.*, *28*, 345–354, 1999.
- Raymond, P. A., and J. J. Cole, Gas exchange in rivers and estuaries: Choosing a gas transfer coefficient, *Estuaries*, *24*, 312–317, 2001.
- Richey, J. E., J. M. Melack, A. K. Aufdenkampe, V. M. Ballester, and L. L. Hess, Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO₂, *Nature*, *416*, 617–620, 2002.
- Sarma, V. V. S. S., M. D. Kumar, and M. Marerikar, Emission of carbon dioxide from a tropical estuarine system, Goa, India, *Geophys. Res. Lett.*, *28*, 1239–1242, 2001.
- Sherr, E. B., Carbon isotope composition of organic seston and sediments in a Georgia salt marsh estuary, *Geochim. Cosmochim. Acta*, *46*, 1227–1232, 1982.
- Somayajulu, B. L. K., J. M. Martin, D. Eisma, A. J. Thomas, D. V. Borole, and K. S. Rao, Geochemical studies in the Godavari estuary, India, *Mar. Chem.*, *43*, 83–93, 1993.
- Spitz, A., and J. Leenheer, Dissolved organic carbon in rivers, in *Biogeochemistry of Major World Rivers*, edited by E. T. Degens, S. Kempe, and J. E. Richey, 213–232, John Wiley, New York, 1991.
- Twilliey, R. R., R. H. Chen, and T. Hargis, Carbon sinks in mangrove forests and their implications to the carbon budget of tropical coastal ecosystems, *Water Air Soil Pollut.*, *64*, 265–288, 1992.

Velimirov, B., and M. Valenta-Simon, Seasonal changes in specific growth rates, production and biomass of a bacterial community in the water column above a Mediterranean seagrass system, *Mar. Ecol. Prog. Ser.*, 80, 237–248, 1992.

G. Abril and H. Etcheber, Département de Géologie et Océanographie, CNRS-UMR EPOC 5805, Université de Bordeaux I, Avenue des Facultés, F-33405 Talence, France. (abril@epoc.u-bordeaux.fr; etcheber@geocan.u-bordeaux.fr)

A. V. Borges and M. Frankignoulle, Unité d'Océanographie Chimique, MARE, Université de Liège, Sart Tilman, Belgium. (alberto.borges@ulg.ac.be; michel.frankignoulle@ulg.ac.be)

S. Bouillon and F. Dehairs, Department of Analytical and Environmental Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium. (steven.bouillon@vub.ac.be; fdehairs@vub.ac.be)

A. Eiler and B. Velimirov, Institut für Medizinische Biologie, Arbeitsgruppe Allgemeine Mikrobiologie, Universität Wien, Währingerstr. 10, A-1090 Wien, Austria. (branko.velimirov@univie.ac.at)