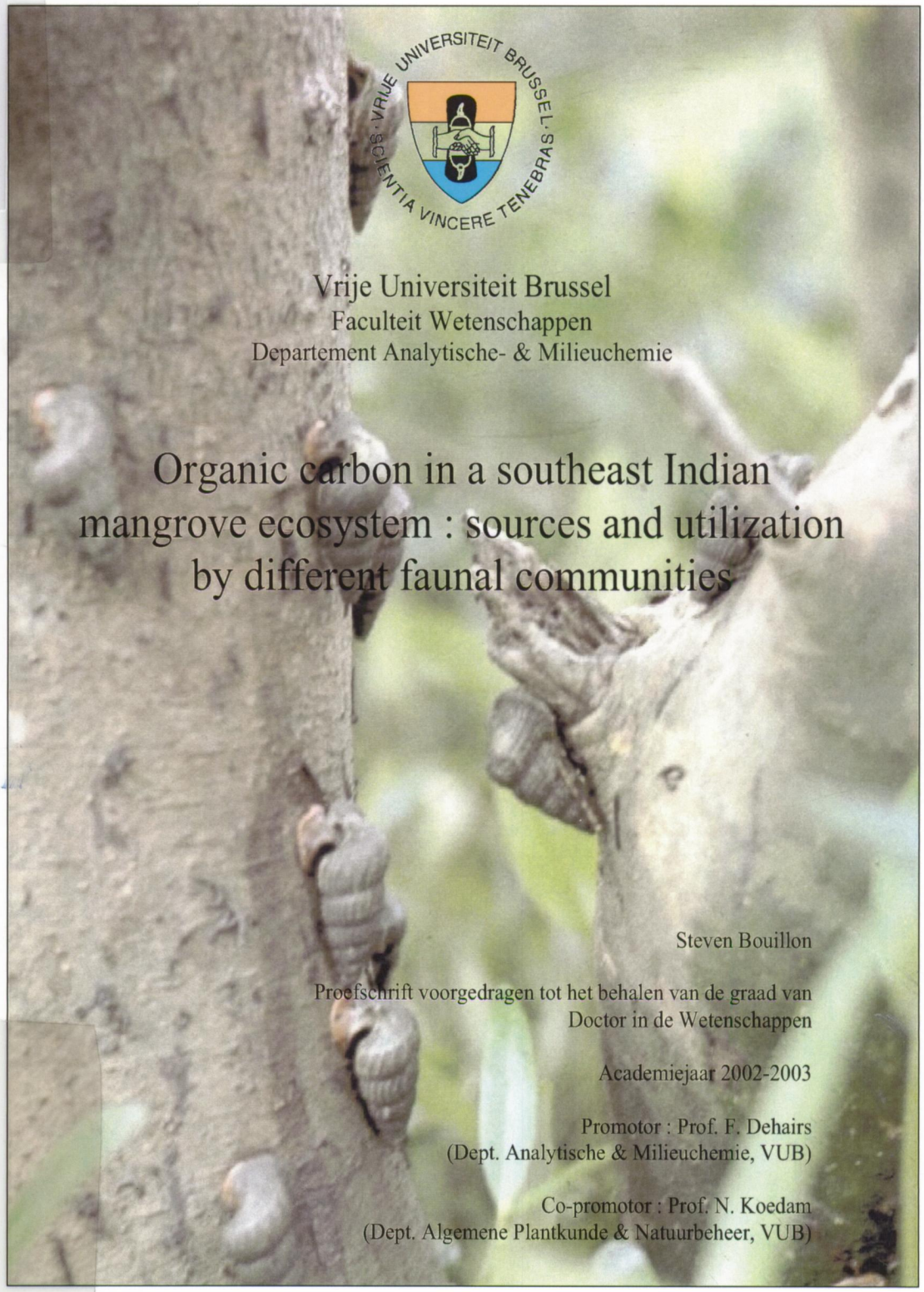


Vrije Universiteit Brussel
Faculteit Wetenschappen
Departement Analytische- & Milieuchemie

Organic carbon in a southeast Indian mangrove ecosystem : sources and utilization by different faunal communities

Steven Bouillon

Proefschrift voorgedragen tot het behalen van de graad van
Doctor in de Wetenschappen

Academiejaar 2002-2003

Promotor : Prof. F. Dehairs
(Dept. Analytische & Milieuchemie, VUB)

Co-promotor : Prof. N. Koedam
(Dept. Algemene Plantkunde & Natuurbeheer, VUB)

Vrije Universiteit Brussel
Faculteit Wetenschappen
Departement Analytische- & Milieuchemie

Organic carbon in a southeast Indian mangrove ecosystem : sources and utilization by different faunal communities

Steven Bouillon

Proefschrift voorgedragen tot het behalen van de graad van
Doctor in de Wetenschappen

Academiejaar 2002-2003

Promotor : Prof. F. Dehairs
(Dept. Analytische & Milieuchemie, VUB)

Co-promotor : Prof. N. Koedam
(Dept. Algemene Plantkunde & Natuurbeheer, VUB)

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

In the list of people who have in one way or another contributed to this thesis, the first in line are no doubt my promotor and co-promotor, Frank Dehairs and Nico Koedam. Not only for having given me the opportunity to work on this fascinating subject, for their expert advice when needed, for convincing me from time to time that I was doing something worth pursuing, but also for allowing me the freedom to direct my research work according to my interests.

Secondly, it has been a pleasure to co-operate with all partners in the EC-INCO project which provided the funding for this work ('Assessment of mangrove degradation and resilience in the Indian sub-continent : the cases of the Godavari estuary and South-west Sri Lanka', contract ERB IC18-CT98-0295) : Max Troell, Pat Rönnback, and Nils Kautsky (Dept. of Systems Ecology, Stockholm University, Sweden), Gerard van der Velde and Sanjeevi Rajugopal (Dept. of Animal Ecology and Ecophysiology, Katholieke Universiteit Nijmegen, the Netherlands), Marie-Claire Guerro, Benoit Thierry and Danny lo Seen (French Institure of Pondicherry, India), Loku P. Jayatissa and Sanath Hettiarachi (Botany dept., Ruhuna University, Sri Lanka), the team of the Marine Biology Laboratory, Andhra University, India : professors A.V. Raman, C. Kalavati and P. Chandra Mohan, and all PhD students, in particular A.V.V.S. Rao (Mani) and B. Satyanarayana (Satyam); and finally all the people involved here at the VUB (Anouk, David, and Farid, among others). Particular thanks go to Raju for all his help in organizing fieltrips and logistics, and to his delightful family who have been very hospitable during my several short stays in Chennai. The team of Andhra University have similarly been invaluable, both during my stays in India but most importantly in providing the necessary all-round sampling efforts without which this work would have been impossible. None of the fieldwork would have been successful or as pleasurable without the help of Krupa and Annavaram.

Similarly, it has been a pleasure to work with Alberto Borges, Michel Frankignoulle and Daniel Bay during the final sampling campaign in the Godavari delta. Several people have been indispensible in providing their expertise to identify a variety of invertebrate species from India and Sri Lanka. Particular thanks go to Peter Davie (Queensland Museum, Australia), Kees Swennen (Netherlands Institute for Sea Research, The Netherlands), and Guido Poppe. I am also grateful to Ana Colaco, Liesbet Hellings, and Koen van den Driessche for introducing me to various aspects of stable isotope techniques, and to Antoine van der Maele and Eddy Keppens for the use of their IRMS facilities and for their expertise in elucidating the mysterious cycles of functioning and malfunctioning of the mass spec. Patrick Dauby (Lab. for Oceanography, Univerity of Liège) has been most helpful in analyzing some samples when our own system was down for a while. From the whole team of the Dept. of Analytical and Environmental Chemistry, special thanks are due to the head of the Dept., Willy Baeyens, to Jean-Pierry Clement for his excellent technical assistance on innumerable occasions, and to Ramses, Arfan and Thierry who have alternated in spending their valuable time fixing my computer when it wasn't doing was it was supposed to.

Finally, but perhaps most importantly, I would like to express my gratitude towards my parents for the long years of endurance and encouragement, and to Ilse, Arne and Janne for their support, for the immense joy they provide, and for just being the wonderful threesome they are.

ABSTRACT

The role of mangrove primary production in the carbon cycle of mangrove ecosystems and in the coastal zone has long been an issue of debate. The present study investigates the organic matter dynamics in the mangrove ecosystem of the Coringa Wildlife Sanctuary located in the estuary of the Gautami Godavari, Andhra Pradesh, India (between 82°15' and 82°22' E, 16°43' and 17°00' N), and makes extensive use of carbon and nitrogen stable isotopes as natural tracers of organic matter sources and their utilisation by different faunal communities.
The mangrove creeks are clearly identified as an active site of mineralization of organic matter and CO_2 efflux, but our data also indicate that this processing of organic carbon is a rather localised feature. In contrast to the Godavari river where carbonate dissolution was found to be the main process influencing the inorganic carbon dynamics, variations in concentrations and stable isotope composition ($\delta^{13}C$) of the dissolved inorganic carbon pool (DIC) in the mangrove creeks were a result of the mineralization of organic matter, at least during the pre-monsoon season. The mangrove creeks and adjacent Kakinada bay showed distinct spatial and seasonal variations in $\delta^{13}C_{DIC}$ values, which are significantly more negative during and after the monsoon season. This pattern is hypothesized to be caused by the mineralization of the large amounts of terrestrial organic matter transported by the Godavari during monsoon, whereas mangrove litter is the main external source of organic carbon inputs during other seasons.
Particulate organic carbon (POC) was found to have a highly variable carbon stable isotope and elemental (POC/PN) composition, and our data show that the phytoplankton component has a seasonally and spatially variable $\delta^{13}C$ signature which is masked by the terrestrial signal, but may at times fall in the same range as the $\delta^{13}C$ of the allochtonous matter. Such variations are stressed to be important when using stable isotope data in evaluating the relative importance of different primary producers to aquatic faunal communities in such a dynamic ecosystem. Comparison of spatial and seasonal trends in $\delta^{13}C$ signatures of zooplankton and suspended matter revealed a marked selectivity of the former for local aquatic primary production. Similarly, the markedly larger spatial variations in $\delta^{13}C$ values of subtidal benthic invertebrates compared to the available carbon pools can be explained by the high selectivity of the benthic invertebrate community for pelagic and benthic microalgal food sources. Overall, mangrove-derived and other terrestrial carbon was found not to be a significant food source for zooplankton and benthic invertebrate communities in the aquatic environment.
Invertebrates in the mangrove-covered intertidal areas were found to display a wide range of stable isotope signatures, and our data overall show a fairly limited use of mangrove litter and a limited degree of (trophic) resource overlap. At least for the particular area studied, local and imported algae are a major source of carbon for intertidal benthic invertebrate communities. A compilation of stable isotope and elemental ratios from widely differing mangrove ecosystems showed that although organic carbon stocks in intertidal mangrove forests can be very high and almost entirely of mangrove origin, there are also systems in which deposited estuarine or marine suspended matter is the dominant source of organic carbon and nitrogen in these sediments. Such variations are expected to have a major impact on the carbon dynamics in mangrove ecosystems.

General Introduction

Mangrove forests are a prominent feature of large stretches of tropical and subtropical coastlines, and have intrigued researchers from various disciplines for a long time. They form a peculiar habitat in the intertidal zone, and with them, a diverse array of organisms have adapted themselves to live in this harsh environment. Despite their often uninviting settings for humans (anyone who has spent some time in mangroves will recall knee-deep mud and millions of mosquitos), they are also increasingly being exploited by humans, not only for fisheries, but also e.g. for the extraction of building materials and charcoal, and for conversion to aquaculture ponds following clearcutting – with the inevitable result that large degraded areas are becoming a more and more familiar sight. This rapid destruction might have consequences far beyond the simple loss of habitat and biodiverisity, as mangroves can play a vital role in the sedimentation of terrestrial inputs (thereby often enabling the establishment and survival of coral reefs nearby) and in protecting the coastline from erosion and during cyclonic events. The protection, management, and restoration of mangroves is therefore important not only from an ecological point of view, but also from socio-economic considerations.

A thorough understanding of the ecological functioning of mangroves and their interactions with adjacent ecosystems is important in providing a scientific basis accompanying the management and/or restoration of mangroves, and to enable us to predict the changes that may be expected after a certain (anthropogenic) modification or disturbance (or at least, to make an attempt do so so). For a number of decades now, the idea that mangroves play an important role in the carbon balance of the coastal environment has been an issue of continuing debate. Although in view of the high production rates of mangroves, they undoubtedly have an important quantitative role, the exact fate of their production is much less clear. Initially, it was hypothesized that mangrove litter provides an important energy source for the diverse faunal communities thriving in these habitats, thereby even sustaining nearshore fisheries. However appealing this hypothesis may be, very little evidence to sustain such a function has been presented, and most of the (few) recent studies indicate that other primary carbon sources are more important in sustaining consumers. If so, the question where the large amounts of biomass produced by mangroves ends up arises :

is it stored in the intertidal sediments, exported elsewhere and stored, or is it simply mineralized somewhere and thereby returned to the atmosphere ? The latter thought provides the general incentive for this study.

This work forms part of the project 'Assessment of mangrove degradation and resilience in the Indian sub-continent : the cases of the Godavari estuary and southwest Sri Lanka' (funded by the EC, and with partners from India, Sri Lanka, Sweden, the Netherlands, and Belgium), in which some fundamental aspects of the functioning of several mangrove sites on the Indian subcontinent are studied, with several specific attempts to describe or predict the natural dynamics of mangroves, and their response to various (human) disturbances.

In particular, the aim of our contribution in defining the functioning of the particular mangrove ecosystems studied and their interaction with adjacent systems was to address the following general questions :

1. What are the major sources of organic carbon (e.g. terrestrial, marine or local phytoplankton, mangrove litter, ...) present in the different organic matter pools, i.e. the intertidal and subtidal sediments, and the suspended organic matter pool in creeks and in the adjacent bay ?
2. Is there a quantitatively important trophic role for mangrove primary production in sustaining intertidal faunal communities (consisting mostly of brachyuran crabs and mollusks) and for subtidal communities in the tidal creeks and adjacent Kakinada Bay (the latter includes both benthic and pelagic consumers) ?
3. As it became clear that our initial results pointed towards a limited trophic role of mangrove litter, and that mangrove-derived organic carbon made a relatively small contribution in various organic matter pools, a survey was organized to explore the potential role of mineralization as a fate of mangrove production, by comparing the organic and inorganic carbon biogeochemistry in the Godavari estuary proper and in the mangrove creeks and adjacent bay.
4. Although the logistics and sampling requirements for such a study made it impossible to conduct an entirely parallel study in the Sri Lankan sites studied in the abovementioned project, efforts were made to compare selected aspects in the latter as results from one site are unlikely to be generally valid. Here, an emphasis was laid of the degree to which mangrove carbon is retained locally in the sedimentary records.

In order to study the dynamics of organic matter in these ecosystems, we made extensive use of the natural abundance of carbon and nitrogen stable isotopes. Small variations in the relative abundance of the 'heavier' and 'lighter' isotope of these elements occur in nature, and these can provide us insights on their origin and on the transformations which they have undergone. A brief discussion of the theory underlying the application of stable isotopes in this field will therefore be given (Chapter 1), as well as a general introduction on the ecology of mangrove ecosystems, with an emphasis of the existing literature on their carbon dynamics (Chapter 2). After a short introduction to the main study site and the methodologies used (Chapter 3), the results on different aspects of the organic matter dynamics are discussed (Chapters 4-9) whereby we have tried to present each chapter as an independent entity wich can be read without prior reading of other chapters. Finally, an effort is made to integrate the data presented in the different chapters and to view these conclusions in a broader context (Chapter 10).

CHAPTER 1 : A General Introduction to Stable Isotopes and their Major Applications in Ecological Studies

TABLE OF CONTENTS

CHAPTER 1 : A General Introduction to Stable Isotopes and their Major Applications in Ecological Studies

Introduction

The use of stable isotopes has recently evolved to an extremely powerful tool to study element cycles and various biological, physical, and chemical processes in research areas as diverse as archaeology, geology, medicine, ecology, paleoclimatology, and hydrology. This chapter is intended to provide an introduction to stable isotopes and some of their applications in ecological studies, with a strong emphasis on the stable isotopes of carbon and nitrogen, as these will be used extensively throughout further chapters. This has become an increasingly popular method to study the origin of organic matter in soils, sediments, and suspended matter, and to study the trophic dependancy of faunal communities on different sources of organic matter, to mention just a few possible applications. Interpreting stable isotope data should always be done cautiously, and can only be done if the underlying mechanisms of fractionation are understood and when the inherent shortcomings of the technique are kept in mind. In this chapter, we therefore discuss the basic principles of stable isotopes and the processes which may influence their distribution in biological material in some detail. It will also become evident that some fundamental aspects of stable isotope fractionation during biological processes are still far from fully understood, which is obviously a drawback in the interpretation of stable isotope data. Thus, further fundamental research should accompany the growing number of applied studies based on the natural abundance of stable isotopes.

1.1 Definitions

Many biologically important elements can occur as different isotopes. **Isotopes** are atoms of the same element (i.e. they have the same number of protons) having a different number of neutrons; thus, isotopes of a certain element have a different mass (mass number = number of protons + number of neutrons). As the chemical nature of an atom is mainly governed by the electron structure and the number of protons, isotopes of an element have -by and large-

identical chemical properties. Two types of isotopes are distinguished : **radioactive isotopes** such as the well-known ^{14}C, and **stable isotopes** such as ^{13}C in the case of carbon.

For carbon and nitrogen, the naturally occuring stable isotopes are ^{13}C and ^{12}C, and ^{15}N and ^{14}N, respectively. The average abundance of these isotopes in natural materials is given in Table 1, but small variations in these abundances occur and these can be accurately determined with stable isotope mass spectrometers (IRMS : Isotope Ratio Mass Spectrometer, see Chapter 3).

Table 1 : Average natural abundance of the main stable isotopes of carbon and nitrogen, according to Hoefs (1987).

Element/Isotope	Abundance (atom %)
CARBON	
^{12}C	98.890
^{13}C	1.110
NITROGEN	
^{14}N	99.640
^{15}N	0.360

As the natural variations in the relative abundance of 'light' and 'heavy' isotopes of an element are usually very small (e.g. the $^{13}C/^{12}C$ ratio may vary between 0.010225 and 0.011574), it is not very practical to express these variations as differences in (ratios of) the absolute abundance of the isotopes. Instead, the 'delta'-notation has become the standard notation to express natural variations in the stable isotope ratios of most elements.

The **stable isotope ratio (δ-value)** of an element is defined as :

$$\delta X = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] \times 10^3 \qquad [‰] \qquad (1)$$

where $R = {}^{13}C/{}^{12}C$ in the case of carbon and $R={}^{15}N/{}^{14}N$ in the case of nitrogen, i.e. the absolute ratio of the atom occurrence of the 'heavy' and 'light' isotope, and where $X = {}^{13}C$ or ^{15}N.

The primary standard for expressing $\delta^{13}C$ values is PDB, a fossil *Belemnitella americana* from the Pee Dee Formation in South Carolina, USA (Coplen 1996), and atmospheric

nitrogen is used as the standard for $\delta^{15}N$ (Mariotti 1983, 1984). The PDB standard is currently exhausted; measurements now need to be made relative to secondary standards -either carbonates or organic materials- the isotopic composition of which relative to PDB is well known, and the resulting values then need to be corrected and expressed relative to PDB. The absolute ratios of 'heavy' to 'light' isotopes ($R_{standard}$) are 0.0112372 for the PDB standard (Craig 1957) and 0.0036765 for atmospheric nitrogen (Mariotti 1983).

The usefulness of stable isotopes in studying element cycles and processes lies in the fact that the small but significant variations observed in nature do not occur at random, but are governed by **fractionation processes**, i.e. during an equilibrium reaction (either chemical, physical or biological) the different isotopes react with a different speed and this causes the end product to have an altered isotope composition compared to the source product.

The **fractionation factor**, α, expresses the degree of fractionation as :

$$\alpha = \frac{R_A}{R_B} \qquad (2)$$

for the reaction A $\Longleftrightarrow$ B

where R_A and R_B is the absolute ratio of the heavy to the light isotope in phase A (the source product) and phase B (the end product), respectively.
By substituting equation (2) in equation (1), it can easily be shown that the fractionation factor relates to the δ-values of source and end product as :

$$\alpha = \frac{\delta X_A + 10^3}{\delta X_B + 10^3} \qquad (3)$$

As during enzymatic reactions the light isotope usually reacts faster than the heavier isotope, fractionation factors for such reactions are usually > 1.
Another, more convenient way to express the changes in isotopic composition during any reaction is the degree of **discrimination**.
By definition, the discrimination ε for the reaction A $\Longleftrightarrow$ B is written as :

$$\varepsilon = \left[\frac{(R_A - R_B)}{R_B} \right] \times 10^3 \qquad (4)$$

or, in δ-notation :

$$\varepsilon = \left[\frac{\delta X_A - \delta X_B}{1 + (\frac{\delta X_B}{10^3})} \right] \qquad (5)$$

as $\delta X_B/10^3$ is usually negligible, this equation can be simplified as :

$$\varepsilon \approx \delta X_A - \delta X_B \qquad (6)$$

Values of ε are usually > 0.

A distinction is classically made between **thermodynamic fractionation** and **kinetic fractionation** :

- Thermodynamic fractionation occurs during equilibrium reactions, and in general, the heavier of the two isotopes are concentrated in the product where bonds strengths are greatest.
- Kinetic fractionation, on the other hand, occurs because the reaction rates for the different masses are different and thus applies for e.g. diffusion processes and enzymatic reactions.

Thus, during the reaction

$$A \longrightarrow B$$

The fractionation factor α can be formulated as :

$$\alpha = \frac{k_{12}}{k_{13}} \qquad (7)$$

where k_{12} and k_{13} are the reaction rate constants of the molecules with the light and heavy isotope, respectively. This formula applies in all 'open systems' where the substrate pool is

sufficiently large and is thus not depleted by the reaction itself. If all the substrate is converted into product, thereby completely consuming the substrate pool, then evidently no fractionation will occur. Diffusion processes show only a slight degree of fractionation, and the lighter of the two isotopes is more mobile than the heavy isotope. As will become apparent in the following sections, kinetic isotope effects during enzymatic reactions are responsible for much of the natural variations in $\delta^{13}C$ and $\delta^{15}N$.

1.2. Fractionation during biological reactions : the key to applications of stable isotopes

1.2.1. FRACTIONATION OF ^{13}C DURING PHOTOSYNTHESIS

Variations in the carbon stable isotope composition of terrestrial plants were first noted in the 1950's, and two decades later it was generally recognized that carbon stable isotope ratios could be used to distinguish among photosynthetic pathway types (e.g. O'Leary 1981). Whereas C_3 and C_4 plants have been found to show non-overlapping $\delta^{13}C$ distributions, plants using the CAM (Crassulacean Acid Metabolism) pathway show intermediate $\delta^{13}C$ signatures which may overlap with those of C_3 or C_4 plants. Once the underlying theory became more refined, the applications of stable isotopes in studying plant physiology became more complex. Relationships were discovered which allowed researchers to correlate carbon stable isotope ratios to some aspects of stomatal control, water stress, or water-use efficiency. Trees record variations in these parameters over longer time scales in their growth rings, and measurements of stable isotopes (carbon, oxygen, hydrogen) in these rings have shown to have multiple applications for reconstructing climatic data (e.g. Feng 1999) or historical trends in water use efficiency.

In aquatic plants and algae, $\delta^{13}C$ values show a much wider range of values, and are not a reliable indicator of the photosynthetic pathway used (Keeley 1990). A multitude of factors such as the concentration and isotopic composition of the substrate, the type of substrate used (CO_2 or HCO_3^-), growth rate, cell shape and volume, water flow rate, and temperature have been found to influence the carbon isotope composition of aquatic primary producers.

In this section, a brief overview will be given on the theory of stable isotope fractionation in terrestrial and aquatic primary producers. A number of recent reviews on different aspects of this subject are available (O'Leary et al. 1992, Lajtha & Marshall 1994).

Carbon Isotope Fractionation in Terrestrial Plants

The largest differences in $\delta^{13}C$ of terrestrial plants occur between plants using the C_3 and the C_4 photosynthetic pathways, where an average difference of about 14 ‰ is found. In **C_3 plants**, the major components of the overall fractionation are the differential diffusion rates of CO_2 through the stomata and the fractionation by ribulose biphosphate carboxylase/oxygenase (Rubisco), the initial enzyme of C_3-photosynthesis. According to Farquhar et al. (1989), overall discrimination in C_3 plants can be expressed as :

$$\Delta = a + (b - a) * \left(\frac{c_i}{c_a} \right) \qquad (8)$$

Where :

Δ : the overall carbon isotope discrimination by the leaf [‰]

a : the fractionation due to diffusion across the stomata (~ 4.4 ‰, constant)

b : the net fractionation caused by carboxylation (~27 ‰, constant)

c_i : the internal (intercellular) partial pressure of CO_2

c_a : the external (ambient) partial pressure of CO_2

If the leaf stomata are relatively closed, then c_i tends towards zero and Δ thus tends towards 4.4 ‰ (= a). If, on the other extreme, stomatal limitations are minimal, $c_i = c_a$ and Δ approaches 27 ‰ (= b). O'Leary et al. (1992) adapted this formula by adding a new term 'd', which involved contributions from various sources including respiration, liquid-phase diffusion, and some CO_2 fixation in C_3 plants by PEP carboxylase (see below), but these authors stressed that this factor is usually negligible. Stomatal opening is determined by the general physiological status of the plant : under hot and dry conditions, opening of stomata will be limited in order to conserve water loss during photosynthesis, whereas stomata will be maximally open under humid conditions. The carbon stable isotopic composition of leaves thus reflect the long-term physiological activity of the leaf.

As c_i/c_a values are typically between 0.4 and 0.8, the Δ range is about 13-22 ‰, and assuming a $\delta^{13}C$ of atmospheric CO_2 of -7.8 ‰ (Hoefs 1987), this leads to typical $\delta^{13}C$ values for C_3 plants ranging between -24 and -30 ‰ (rarely lower, e.g. Flanagan et al. 1997). Due to the combustion of fossil fuels (with $\delta^{13}C$ values of around -30 ‰), the $\delta^{13}C$ of atmospheric CO_2 has decreased by approximately 0.6 ‰ between 1956 and 1978 (or with 1.6 ‰ between 1744 and 1993 according to Ehleringer et al. 2000), a phenomenon known as the 'Suess effect' which can be traced in tree rings from arid climates (but is suppressed in many other tree ring chronologies by the effects of rising CO_2 concentrations and a trend of increasing water-use efficiency, see Feng 1999). Additionally, CO_2 under dense forest canopies may have significantly more negative $\delta^{13}C$ values compared to the overlying air layers due to the contribution of respired CO_2 from the soil (e.g. Flanagan et al. 1996). In climates where a distinct growth season can be distinguished, atmospheric CO_2 shows small but consistent seasonal changes in its carbon isotopic composition, with slightly more enriched values during the growth season when photosynthesis is responsible for the selective fixation of 'light' CO_2. In some studies, the relative importance of photosynthesis and respiration has been found to cause significant diurnal variations in the concentrations and $\delta^{13}C$ of CO_2 (e.g. Flanagan et al. 1996).

Thus, large variations in leaf or tissue $\delta^{13}C$ values may occur in C_3 plants, and these can be related either to the isotopic composition of the source $\delta^{13}C$ (see previous paragraph - although in most cases this is negligible) or to the physiological conditions of the plant or leaf. Not surprisingly, carbon stable isotope techniques have found wide applications in plant physiology studies (e.g. Handley et al. 1994, Moore et al. 1999, Korol et al. 1999). An overview of the literature on the variability in $\delta^{13}C$ for mangroves –which is of particular interest for this study- is given in the following box.

It should be noted that several recent studies have drawn attention to the fact that our understanding of carbon isotope fractionation is far from complete, as it has been found that other processes (i.e. besides fixation of CO_2 by Rubisco) such as photorespiration (in which dominant process is the conversion of 2 molecules of glycine to serine, CO_2, and NH_3) can also provide substantial isotope effects which may be crucial for a correct interpretation of plant $\delta^{13}C$ values (e.g. Ivlev et al. 1996, Igamberdiev et al. 2001). It is clear that more research will be needed to clarify such issues and to integrate them into existing models of carbon isotope fractionation (i.e. equation 8).

$\delta^{13}C$ variability in mangroves

As outlined above, the $\delta^{13}C$ of plant biomass can be influenced directly and indirectly by a number of factors. Even for C_3 plants such as mangrove trees, this results in a relatively wide range of $\delta^{13}C$ values reported in the literature and in this study (range : -35.1 to -21.9 ‰; average : -28.1 ± 2.0 ‰, n = 213, see Figure 1). In view of the importance of this parameter in this study, it is of interest to compile the current evidence on the factors responsible for this variability. Several studies have examined the effect of environmental conditions such as salinity, nutrient status, growth form, and humidity on mangrove $\delta^{13}C$ values, both in the natural environment (e.g. Medina & Francisco 1997, Kao & Chang 1998, McKee et al. 2002) and under culture conditions (e.g. Farquhar et al. 1982, Ish-Shalom-Gordon et al. 1992, Kao et al. 2001). So far, no studies have examined a possible role of variations in source (i.e. CO_2) $\delta^{13}C$ values, although it is not implausible that such variations occur to a significant extent in certain dense mangrove stands.

Several studies have reported that an increase in salinity decreases stomatal conductance (i.e. the stomata remain more closed, c_i/c_a decreases, and thus, $\delta^{13}C$ increases), as was experimentally demonstrated for *Avicennia marina* and *Aegiceras corniculatum*. Medina & Fransisco (1997) found generally lower $\delta^{13}C$ values in riverine mangroves (growing at salinities between 0 and 25 ppt) than in coastal plants (growing at interstitial salinity of ~ 40 ppt). This also agrees well with the conclusion of Lin & Sternberg (1992b) and Kao et al. (2001) that increased salinity decreases the degree of ^{13}C discrimination in *Rhizophora mangle* and *Kandelia candel*, respectively. Dwarf ('scrub') mangroves of *K. candel* and *R. mangle* have been found to have higher $\delta^{13}C$ values than their tree-sized counterparts, indicating their higher long-term water use efficiency. Ish-Shalom-Gordon et al. (1992) note, however, that the relationship salinity-$\delta^{13}C$ is not linear (and, in addition, that this relationship is species-specific), with plants grown at intermediate salinities having the lowest $\delta^{13}C$ values. Higher nutrient concentrations decreased $\delta^{13}C$ values in the study of Lin & Sternberg (1992a), but Kao et al. (2001) and McKee et al. (2002) found no evidence for such an effect in *K. candel* and *R. mangle*, respectively. In conclusion, it appears that the relationship between the $\delta^{13}C$ of mangroves and environmental factors may be more complex than sometimes assumed, making their interpretation somewhat speculative. More experimental and field studies are required to shed more light on this. Few data are available on the distribution of

$\delta^{13}C$ values between different components or tissues of mangrove trees. Ellison et al. (1996) compared the $\delta^{13}C$ of different components of *Rhizophora mangle* (Table 1), and found no significant differences between leaves, branches, and twigs, but cable roots and small rootlets were all significantly enriched in ^{13}C relative to leaf material. Rao (1998) compared the stable carbon isotope composition of leaves, flowers, and propagules of *Avicennia officinalis* and *Excoecaria agallocha*, but the data are too limited to conclude whether there were any significant differences between these components. In our study (see further chapters), wood tissue of an *Avicennia* log was also found to be relatively enriched relative to leaf material, but Ish-Shalom-Gordon et al. (1992) found little or no consistent difference in $\delta^{13}C$ of leaves and stems in their experimental study for *A. germinans*.

Table 1 : $\delta^{13}C$ values for different components of *Rhizophora mangle*. Data from Ellison et al. (1996). Average ± 1 s.d. are given, numbers between brackets indicate the number of samples.

Component	$\delta^{13}C$
leaves	-28.7 ± 0.7 (n=7)
twigs	-28.7 ± 0.5 (n=7)
branches	-28.7 ± 0.4 (n=7)
cable roots above water	-26.6 ± 0.7 (n=7)
cable roots below water	-25.8 ± 0.3 (n=7)
rootlets	-25.0 ± 0.4 (n=3)

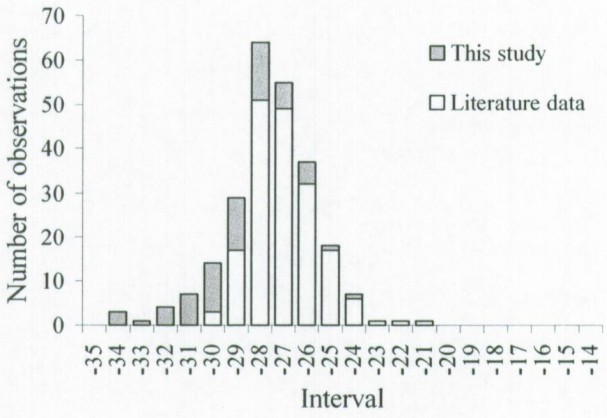


Figure 1 : Distribution of $\delta^{13}C$ data of mangrove leaf tissue (literature data and this study).The $\delta^{13}C$ value indicates the upper (i.e. least negative) value of the interval. Note that data from studies explicitely investigating the effect of environmental conditions or nutrient availability are not included.

C_4-plants use a different strategy for photosynthesis, which is specifically adapted to allow photosynthesis to occur with smaller water losses compared to C_3-photosynthesis. In contrast to C_3 plants, the initial step is the fixation of HCO_3^- (not CO_2 !) by phosphoenolpyruvate carboxylase (PEPc). This step occurs in the mesophyll cells, but the product of the initial reaction (malate) is then transported to the bundle sheet cells. Here, decarboxylation occurs and the released CO_2 is fixed by Rubisco (i.e. the same enzyme responsible for CO_2 fixation in C_3-plants).

Discrimination in C_4-plants is thus more complicated, and can be described as (Farquhar 1983) :

$$\Delta = a + (b_4 + b_3 * \Phi - a) * \left(\frac{c_i}{c_a} \right) \qquad (9)$$

Where :

Δ : The overall carbon isotope discrimination by the leaf [‰]

a : the fractionation due to diffusion across the stomata (~ 4.4 ‰, constant)

b_4 : the discrimination caused by RuBP carboxylase (~ 27 ‰, constant)

b_3 : the discrimination by PEP carboxylase against gaseous CO_2 (~ -5.7 ‰, constant)

Φ : the leakage rate of CO_2 out of the bundle sheath cells (range 0.1-0.6)

c_i : the internal (intercellular) partial pressure of CO_2

c_a : the external (ambient) partial pressure of CO_2

Although the general layout of equation (9) is similar to that for C_3 plants (equation 8), $\delta^{13}C$ values of C_4 plants show a much more restricted range of values and are not as useful for physiological studies as is the case for C_3 plants. This is due to the different morphology of the two plant types, and the resulting smaller variability in c_i/c_a ratios in C_4 plants.

A third strategy for photosynthesis used by some succulent plants is the **Crassulacean Acid Metabolism** (CAM) pathway and allows plants to survive under extremely dry conditions. **CAM plants** may either fix atmospheric carbon in the manner of C_3 plant (in which case they are *facultative CAM-plants* and display $\delta^{13}C$ values in the range of those expected for C_3 plants) or in a time-separated C_4-like sequence in which fixation of HCO_3^- by PEP-carboxylase is the initial step, carried out in the dark when temperatures are usually lower and

humidity higher than during the daytime. Malate is transformed into malic acid and stored in vacuoles. During the following light period, the malic acid is decarboxylated and the resulting CO_2 is fixed by Rubisco (a reaction which requires energy from light). CAM plants thus exhibit widely varying carbon isotope ratios, and cannot always be unambiguously distinguished from C_4 or C_3 plants by $\delta^{13}C$ analysis alone.

Carbon Isotope Fractionation in The Aquatic Environment

AQUATIC MACROPHYTES

Aquatic plants have been found to show widely varying stable isotope signatures (e.g. McMillan et al. 1980, Boon & Bunn 1994, Hemminga & Mateo 1996, Boyce et al. 2001). Although the relatively enriched $\delta^{13}C$ values in many aquatic plants have been initially interpreted as an indication for the utilization of the C_4 pathway, it has since been established that in many cases the C_3 pathway is operating. C_4 photosynthesis is, however, present in many aquatic species but it is not associated with the specialized anatomy found in terrestrial C_4 plants (and, evidently, does not offer them the same advantage). Some plants have also been shown to exhibit CAM photosynthesis (see Keeley 1990), mainly in oligotrophic waters where it enhances competitive ability in carbon acquisition. In aquatic plants, however, the $\delta^{13}C$ value is not directly indicative of the photosynthetic pathway, and there are several causes for this : (1) the possible ability to take up HCO_3^-, which is isotopically enriched (i.e. has a higher $\delta^{13}C$ value) compared to dissolved CO_2, (2) boundary layer effects, and (3) isotopic composition of the DIC source can vary spatially and seasonally in aquatic ecosystems.

Two major differences with terrestrial plants are that the substrate for photosynthesis is carbon dioxide (or bicarbonate) in the dissolved form, and that gases diffuse about 10^4 times slower in water than in air. The latter can cause photosynthesis to deplete the boundary layer of carbon dioxide during the daytime, and such a depletion should result in reduced overall fractionation.

The major factors influencing the carbon isotopic composition of aquatic plants can be divided into (1) the isotopic composition of the substrate, (2) the substrate type (i.e. bicarbonate or carbon dioxide), and (3) water velocity; although factors such as temperature and irradiance may also have significant (albeit mostly indirect) effects (e.g. Hemminga & Mateo 1996). Effects of growth rate will be dealt with specifically when discussing aquatic

microalgae (see below), as most studies on the effect of this parameter on fractionation have been done on this group.

(1) Isotopic composition of the substrate

The isotopic composition of the substrate for photosynthesis (either dissolved CO_2 or HCO_3^-) is an important variable affecting the isotopic composition of aquatic primary producers. Due to the thermodynamic isotope fractionation associated with the equilibrium reaction between CO_2 and HCO_3^- :

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

these two possible substrates for photosynthesis have a different isotopic composition, CO_2 (aq.) being depleted in ^{13}C by ~ 9 ‰ relative to bicarbonate at 25 °C (Mook et al. 1974).
If there is an equilibrium with CO_2 from the atmosphere, $\delta^{13}C$ values for DIC (DIC = CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}) approach 0 ‰. Several processes may alter the isotope composition of the DIC pool, which may be summarised as follows (Chanton & Lewis 1999). **Autotrophic production** in the water column causes the residual DIC pool to become enriched in ^{13}C, due to the preferential fixation of ^{12}C during photosynthesis. Similarly, the **diffusive efflux of CO_2 to the atmosphere** (which occurs e.g. in many estuarine ecosystems, see Frankignoulle et al. 1998) causes the residual DIC pool to be enriched in ^{13}C, as 'lighter' CO_2 diffuses at a faster rate. The **dissolution or precipitation of $CaCO_3$** will evidently influence the overall $\delta^{13}C_{DIC}$, a carbonates usually have high $\delta^{13}C$ values. Finally, **respiration** processes (e.g. microbial respiration of local or terrestrial organic matter, respiration by fauna) result in the addition of relatively ^{13}C-depleted CO_2 as the $\delta^{13}C$ of this respired CO_2 will be similar to that of the organic substrate.
Thus, in seawater with limited influence from continental organic carbon inputs, the $\delta^{13}C_{DIC}$ shows an overall fairly limited range of values (roughly between -2 and +2 ‰, e.g. Mook & Tan 1991) although there remains some regional, local, seasonal, and depth-dependent variability. Surface water tends to have slightly higher $\delta^{13}C_{DIC}$ values due to the preferential fixation of ^{12}C during photosynthesis in this zone, leaving the residual DIC pool enriched in ^{13}C (Mook & Tan 1991). During the night, $\delta^{13}C_{DIC}$ values may be expected to become more

negative due to the absence of photosynthesis and the increased relative importance of respiration processes.

In estuarine and freshwater ecosystems, the effects of respiration are often much more pronounced, as these systems may receive large quantities of organic matter. The respiration of this material, either in the water column or in the sediments, may result in a significant ^{13}C-depletion of the DIC pool (values as low as -28 ‰ have been recorded in the Amazon basin, see Longinelli & Edmond (1983, cited in Mook & Tan 1991), and in certain headwater streams similarly low values may be encountered – e.g. Palmer et al. 2001), and spatial or seasonal changes in the inputs of organic matter or in the importance of respiratory processes *versus* autotrophic production result in seasonal dynamics in the $\delta^{13}C_{DIC}$ (e.g. Hellings et al. 1999). Combined with the fact that groundwater inputs are often depleted in ^{13}C, this often – but not always- results in typical $\delta^{13}C_{DIC}$ trends along salinity gradients in estuaries, with lower values in the freshwater stretches (where respiration of organic matter can be a major source of DIC) and values approaching 0 ‰ in the marine part of the estuary (Mook & Tan 1991, Chanton & Lewis 1999, Hellings et al. 1999). An extremely wide range of $\delta^{13}C$ values may be encountered in freshwater lakes (e.g. from -26.3 ‰ to + 12.5 ‰, see Striegl et al. 2001 and Gu et al. 1996a, respectively) and rivers depending on the relative importance of CO_2 from carbonates, respiration of terrestrial organic matter, and methanogenesis.

(2) Substrate type

Unlike terrestrial plants, some submerged plants and algae may also use HCO_3^- in addition to CO_2, but the proportion of each depends on the plant species concerned, the pH, and other factors. The proportion of the total DIC available as CO_2 varies dramatically from about 80 % at pH=5.5 to less than 1 % at pH=8.4, and DIC concentrations may also vary over 2 orders of magnitude. Although bicarbonate is enriched in ^{13}C relative to $CO_{2\,(aq)}$, Maberly et al. (1992) found that 24 species of marine macrophytes known to be capable of using bicarbonate as a substrate for photosynthesis had $\delta^{13}C$ values between -8.8 and -22.6 ‰, whereas 6 species for which it is known that they are only capable of using CO_2 had values in the range -9.9 to -34.5 ‰. Thus, overall fractionation between substrate and biomass appears to be less pronounced with bicarbonate as a substrate than with CO_2 as a substrate.

(3) Effect of water velocity

The viscosity of water creates a stagnant boundary layer around aquatic plants. This boundary layer has been reported to be up to 150 µm for macrophytes and more than 1 mm in thickness for benthic microalgae (see France 1995c for references). This boundary layer restricts the diffusion of inorganic carbon and nutrients, and may be a major rate-limiting step in photosynthesis. In case of a thicker stagnant boundary layer, diffusion of CO_2 will occur at slower rates, and this will result in decreased overall carbon isotope fractionation. As the thickness of the boundary layer is to a major extent determined by the water velocity, it may be expected that similar species growing in fast-flowing conditions will exhibit more pronounced isotope fractionation (lower $\delta^{13}C$ values) than those in low turbulence sites. In agreement with this hypothesis, algae growing in environments where water current velocity is high have been found to be more depleted than the same species growing in nearby low-current sites (France & Holmquist 1997, Finlay et al. 1999), but only in cases where CO_2 availability is relatively low and when other factors, such as differences in the isotopic signature of the DIC pool (France & Holmquist 1997) are eliminated. Only one study has paid attention to this phenomenon under laboratory conditions (MacLeod & Barton 1998), but failed to find any effect between current velocity and periphyton $\delta^{13}C$ values. However, CO_2 was present in supersaturated concentrations in this study, so that diffusion limitation may not have been present even under low velocity conditions.

Osmond et al. (1981) compared the $\delta^{13}C$ signatures of a wide range of aquatic macrophytes from fast-flowing rivers and from stagnant waters, and found the lowest values associated with fast-flowing rivers, which could only partially be explained by lower $\delta^{13}C_{DIC}$ values in this environment, consistent with the notion that boundary layer diffusion and/or HCO_3^- uptake may determine the $\delta^{13}C$ value of submerged aquatic plants in these circumstances.

PHYTOPLANKTON AND BENTHIC MICROALGAE : A SPECIAL CASE

Although the principles of carbon isotope fractionation outlined above are valid for aquatic macrophytes as well as for benthic, epiphytic and pelagic microalgae, a few additional factors influencing isotope fractionation are particularly important for microalgae and these have received considerable attention in the literature. These factors, which include the growth rate and the size and shape of the cells, will be discussed here. One of the main reasons for the

renewed interest for the (often small) variations in plankton $\delta^{13}C$ is the idea that the $\delta^{13}C$ of sedimentary organic matter (or specific organic compounds preserved in the sediment) may record past variations of $[CO_2]_{aq}$ in the surface ocean (see Goericke & Fry 1994) or of historical trends in primary productivity in lacustrine environments (Leggett et al. 1999). Goericke & Fry (1994), however, caution that a robust relationship between $[CO_2(aq)]$ and the $\delta^{13}C$ of oceanic POC (particulate organic carbon) does not appear to exist, and that biological effects may have larger effects on the $\delta^{13}C_{POC}$ than $[CO_2(aq)]$. In addition, there may be a bias due to the 'Suess effect', as the penetration of anthropogenic carbon in the ocean has led to an increase in $[CO_2]_{aq}$ and a decrease in $\delta^{13}C$. Although the direct efect of the latter may be fairly small (~ 0.01-0.02 ‰ per year according to Sonnerup et al. 1999, see also Bauch et al. 2000 and references therein), the increase in $[CO_2]$ may have more significant effects on the carbon isotope discrimination in phytoplankton (see Schell 2000, 2001, and Cullen et al. 2001).

As for other aquatic plants and macroalgae, the substrate for photosynthesis by phytoplankton and subtidal and intertidal benthic microalgae is dissolved inorganic carbon (DIC) from the water column (i.e. either dissolved CO_2 or HCO_3^-), and the fixation of DIC by algae is associated with considerable fractionation. Typical ocean plankton $\delta^{13}C$ values range between -18 and -28 ‰, but lower values of -25 to -35 ‰ are observed in the Antarctic regions. For slow-growing algae that fix CO_2 via the Calvin cycle, one would expect plankton $\delta^{13}C$ values to be much more negative (around –40 ‰) than those commonly observed. Several possible explanations for this have been proposed, including limitation of photosynthesis by the low concentrations of free aqueous CO_2 (e.g. Rau et al. 1992 – now considered unlikely to occur under natural conditions, e.g. Tortell et al. 2000), the fixation of bicarbonate rather than CO_2 by β-carboxylases as an additional fixation pathway (Descolas-Gros & Fontugne 1990), and the active uptake of inorganic carbon from the aqueous medium (see Tortell et al. 2000). Current evidence favours the latter explanation as the most likely cause of ^{13}C-enrichment in phytoplankton (Goericke et al. 1994) but in addition, the existence use of the C_4-pathway for photosynthesis has been demonstrated for some diatom species, and the latter finding might call for a re-interpretation of some earlier studies (see Reinfelder et al. 2000 and Riebesell 2000). It has been well established that several factors may influence the degree of carbon isotope fractionation in phytoplankton, including the availability of DIC (e.g. Rau et al. 1992, Burkhardt et al. 1999a), growth rate limiting factors such as nutrients or light (Fry & Wainright 1991, Burkhardt et al. 1999a and 1999b, Riebesell et al. 2000), temperature

(Fontugne & Duplessy 1978 and 1981, Fry 1996), species (e.g. Falkowski 1991, Hinga et al. 1994), and the size and dimensions of the cells (Popp et al. 1998, Burkhardt et al. 1999b). A particularly enlightening recent study is the one by Tortell et al. (2000), who showed that the diffusion-based model of C isotope fractionation -i.e. CO_2 supplied by diffusion is the substrate for photosynthesis, and therefore, the overall discrimination between CO_2 and biomass (ε_p) should vary linearly with the ratio between growth rate and CO_2 concentration (i.e. $\mu/[CO_2]_{aq}$, see Laws et al. 1995, Bidigare et al. 1997) does not adequately describe observed patterns (see Figure 2). At $\mu/[CO_2]_{aq} > 0.2$, active C uptake presumably contributes significantly to cellular C requirements, and ε_p no longer varies as strongly with changes in μ or $[CO_2]_{aq}$ (Tortell et al. 2000). Gervais & Riebesell (2001) recently showed experimentally that under P limitation, ε_p of a diatom culture increases, irrespective of the initial $[CO_2]_{aq}$, by 2-3 ‰ despite the decreasing $[CO_2]_{aq}$ during the experiment. This implies the dominance of the decreasing growth rate (in this case by P limitation) rather than declining CO_2 availability on overall carbon isotope discrimination. Thus, attempts to provide models to describe carbon isotope fractionation in phytoplankton taking growth rate and extracellular carbon concentrations into account (even though these models so far do not explain all field and laboratory observations, see Baird et al. 2001) may provide a way to relate sedimentary $\delta^{13}C$ values to reconstruct paleo-oceanographic environmental conditions.

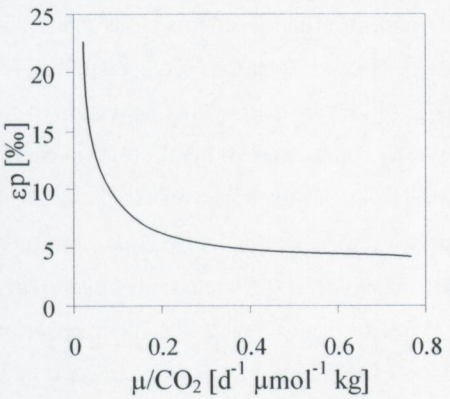


Figure 2 : Fitted curve through a compilation of field and laboratory data of stable isotope fractionation (ε_p), phytoplankton growth rates (μ) and CO_2 concentrations. Redrawn from Tortell et al (2000).

Benthic microalgae have been found to be consistently enriched in ^{13}C relative to their pelagic counterparts by an average of ~ 7 ‰ (France 1995c). The mechanism which is most commonly invoked to explain this, is that the overall fractionation decreases due to boundary-

layer effects. The presence of a much larger stagnant boundary layer in benthic or epiphytic algae (more than 1 mm, Riber & Wetzel 1987 cit. in France 1995; up to 7 mm according to MacLeod & Barton 1998) when compared to pelagic algae from the same environment causes diffusion-limitation of CO_2 to occur, and consequently a decrease in the overall fractionation (see France 1995c). This boundary layer will be reduced under conditions of higher water currents, and consequently $\delta^{13}C$ values will decrease.

Typical values for intertidal benthic microalgae reported in the literature range between -12 and -20 ‰ (e.g. Couch 1989, Currin et al. 1995, Newell et al. 1995, Créach et al. 1997, Lee 2000, Dittel et al. 2000).

This difference in $\delta^{13}C$ values between benthic and pelagic microalgae is consistent enough to be reflected in consumer $\delta^{13}C$ values and has been proposed as a valuable tool to distinguish between benthic and pelagic food sources for coastal animals (France 1995).

One of the drawbacks in studying the $\delta^{13}C$ of microalgae under natural conditions is the fact that they are often difficult to separate from their substrate (in the case of benthic and epiphytic algae) or from the mixture of organic matter in suspension (in the case of phytoplantkon). Several authors have succesfully extracted benthic microalgae from sediments by allowing the algae to migrate through different layers of precombusted sand (or other media) and nitex screens (e.g. Couch 1989, Currin et al. 1995, Riera et al. 1999), but the applicability of this technique in the field is dependent on the local conditions (pers. obs.). Only one study describes a methodology to separate phytoplankton from mixed samples (Hamilton & Lewis 1992), although Fry (1996) mentions the successful application of flow cytometry for this purpose. New possibilities are being offered by the introduction of GC/C/IRMS (Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry) which allows the measurement of $\delta^{13}C$ values of specific biomarker molecules (e.g. fatty acids, sterols, amino acids - see Fry 1996, Boschker & Middelburg 2002) wich can be used to derive a stable isotope signature for specific (groups of) micro-organisms if the relation between the isotope composition of the whole cell and the biomarker is robust and well characterized, but their widespread application requires more thorough experimental calibration.

1.2.2. FRACTIONATION DURING N-ASSIMILATION

In contrast to the relatively large number of studies on the fractionation of ^{13}C during primary production, the current knowledge on fractionation processes during N-assimilation remains fairly limited. However, $\delta^{15}N$ signatures of primary producers in both aquatic and terrestrial ecosystems may be useful indicators of N sources and transformations. Both within- as between-ecosystem differences in plant $\delta^{15}N$ have been shown to exist and may provide useful information on N-processes (e.g. Handley & Raven 1992, Handley et al. 1999, Martinelli et al. 1999).

$\delta^{15}N$ in aquatic primary producers and bacteria

Kinetic isotope fractionation is associated with most biological reactions involving inorganic nitrogen. These processes include the assimilation of DIN (either NO_3^-, NO_2^-, or NH_4^+) by phytoplankton or microheterotrophs (bacteria, fungi), nitrification and denitrification, and N_2 fixation. As expected from theoretical considerations, in the majority of cases the end product becomes depleted in ^{15}N relative to the substrate, leaving a ^{15}N-enriched residual substrate pool. The largest isotope fractionation effects are those associated with denitrification, presumably due to the cleavage of the particularly strong N-O bond. In any case, no single value applies for the degree of isotope fractionation associated with a particular process, as a multitude of factors may have an influence, notably temperature, the reaction rate, and the substrate concentrations.

A number of controlled laboratory studies have been conducted to study fractionation processes (see Waser et al. 1998 and Waser et al. 1999 for recent overviews), and have revealed wide variations with light intensity, species, N substrate, and culture conditions, resulting in fractionation values for algae between 0.7 and 23 ‰ (for NO_3^-), 0.7 ‰ (for NO_2^-), and between -9.7 and 14 ‰ (for NH_4^+). A strong relationship exists between the growth rate of diatoms and the degree of fractionation during N-uptake (Wada & Hattori 1978). Similarly, a decrease in the degree of fractionation occurs with decreasing concentrations of nitrate or ammonium (e.g. Wada & Hattori 1978).

Although most $\delta^{15}N$ values found in biological materials range between -5 and + 20 ‰, some notable extreme values have been recorded : Wada et al. (1981) recorded a $\delta^{15}N$ value of -49 ‰ in epibenthic algae in an Antarctic environment, and this was hypothesized to be

associated with extremely slow growth rates and high nitrate concentrations, both factors known to allow isotope fractionation to be maximal. In the same study, very high $\delta^{15}N$ values were recorded in algae close to a penguin rookery, which suggests that ammonia excreted by penguins and its subsequent volatilization resulted in a ^{15}N-enriched residual DIN pool, a hypothesis confirmed by Erskine et al. (1998) who found elevated $\delta^{15}N$ ratios in primary producers near bird rookeries. Another example of elevated $\delta^{15}N$ values are estuarine ecosystems where nitrification or denitrification are important processes (e.g. Mariotti et al. 1984, Montoya et al. 1990, Riera et al. 2000, De Brabandere et al. in press).

Nitrogen fixation by autotrophs or miroheterotrophs is perhaps one of the most important N-transforming processes in the global N budget (Handley & Raven 1992). It was noted in several studies that little or no isotope fractionation is associated with this process (e.g. see Owens 1987, Handley & Raven 1992, and Goericke et al. 1994 for an overview), implying that organisms deriving most of their N from N_2-fixation should have $\delta^{15}N$ values close to 0 ‰, the isotope composition of dissolved and atmospheric N_2 (the latter being the standard for $\delta^{15}N$, Mariotti 1983,1984). Not surprisingly, this has been exploited as a tool to investigate the importance of N_2-fixation for different terrestrial plants and in marine ecosystems.

The transport mechanism used for the uptake of DIN obviously also influences the overall fractionation. Hoch et al. (1992) showed that uptake of NH_4^+ by the bacterium *Vibrio harveyi* was mainly by diffusion of NH_3 and subsequent assimilation by glutamate dehydrogenase when concentrations were > 1 mM NH_4^+, but in lower concentrations, active ammonium transport and assimilation catalysed by glutamine synthetase. In this context, it is the combination of direct effects of DIN concentrations and the transport mechanism used (i.e. diffusive *vs.* active) which will determine the isotope fractionation associated with DIN assimilation.

$\delta^{15}N$ in terrestrial plants

Although a thorough understanding of the fractionation of ^{15}N during N-uptake by plants and its subsequent transformations within the plant is still largely lacking, some general patterns in plant $\delta^{15}N$ between ecosystems are frequently observed, and these patterns may hold clues to better understand N-cycling and the associated isotopic transformations in terrestrial ecosystems (Handley et al. 1999, see recent reviews by Robinson 2001 and Evans 2001).

Plant $\delta^{15}N$ values will reflect not only the isotope composition of the source N (which can be NH_4^+ or NO_3^-), but also the (possible) fractionation during uptake (note that two uptake mechanisms exist for both ammonium and nitrate, depending on their concentration), fractionation during enzymatic assimilation, and the efflux of nitrogen from the plant. In addition, plants associated with mycorrhizal fungi -the latter acting as an intermediate for some of the plants' N supply- may have different $\delta^{15}N$ values than non-mycorrhizal plants grown under the same conditions. Several studies have reported a negative correlation between the $\delta^{15}N$ of plants (or soils) and water availability or rainfall, and a large compilation of global literature data by Handley et al. (1999) confirmed this trend. On a smaller scale, however, the relationship is inversed, with wet sites being ^{15}N-enriched relative to drier nearby sites, and this is usually attributed to the higher denitrification rates in wetter ecosystems, leaving the residual N-pool available for plant uptake enriched in ^{15}N. Overall, Handley et al. (1999) conclude, $\delta^{15}N$ of plant tissues and soils appears to be related to the residence time of the ecosystems N-pool.

1.3. Stable isotopes as tracers of organic matter and foodweb interactions

The application of stable isotopes at the natural abundance level as indicators of the origin of organic matter and of trophic interactions is based upon three important hypotheses :

(1) differences (may) exist in the $\delta^{13}C$ and/or $\delta^{15}N$ signatures of different primary producers
(2) these differences are maintained or altered in a sufficiently predictable way during degradation processes
(3) consistent and predictable changes in the isotopic signatures occur during transfer to higher trophic levels

The first postulate was discussed in section 1.2., whereby the principle of fractionation of carbon and nitrogen stable isotopes during primary production was addressed. This section is intended to provide a literature overview of the processes of isotopic fractionation of C and N stable isotopes during organic matter degradation and between different trophic levels, and the possibilities of deriving quantitative and/or qualitative information on the contribution of different sources to a mixture or to a consumers' diet using stable isotope ratios of one or more elements. Finally, a few major gaps in our current knowledge on these processes will be highlighted.

A number of reviews on this subject have been produced during the last two decades (e.g. Fry & Sherr 1984, Peterson & Fry 1987, Wada et al. 1991), but a number of recent studies add some significant new information to our understanding of the isotopic changes during organic matter processing (or rather, they adequately demonstrated our lack thereof).

As a final remark, it should be mentioned that stable isotopes of other biologically important elements, such as hydrogen, oxygen, or sulphur, have also been shown to be extremely useful in ecological studies, but are outside the scope of this discussion.

1.3.1. FRACTIONATION DURING DEGRADATION OF ORGANIC MATTER

Carbon

A crucial factor allowing stable isotopes to be useful as tracers of organic matter is the fact that little or no alteration of the carbon isotopic composition of bulk organic matter takes place during decomposition, and thus that the sedimentary $\delta^{13}C$ record largely reflects the source carbon of this pool. Although in most short-term degradation experiments, little changes in $\delta^{13}C$ values of litter have been observed (e.g. Fenton & Ritz 1988, Zieman et al. 1984, Wedin et al. 1995, Schweizer et al. 1999, Fogel & Tuross 1999), the soil organic matter pool (SOM) has been found to be slightly, but consistently, enriched in ^{13}C when compared to the litter of the dominant vegetation, and this enrichment often increases with depth (see Ehleringer et al. 2000 for references). In addition, the offset between $\delta^{13}C$ values of litter and of SOM appears to be dependant on the soil carbon content (Balesdent et al. 1993, cit in Ehleringer et al. 2000). There have been a number of studies on the isotopic changes during decomposition, and several hypotheses have been proposed to explain the observed patterns, although the subject remains an issue of controversy :

(1) **The influence of atmospheric change.** As mentioned earlier (section 1.2.1), the carbon isotope composition of atmospheric carbon dioxide has changed by approximately -1.3 ‰ between 1744 and 1993 (see Friedli et al. 1987 and Trolier et al. 1996, both cit. in Ehleringer et al. 2000) due to the combustion of fossil fuels. Since SOM in deeper soil layers is of older age, these soil layers should have originated when the carbon isotope ratio of the litter was higher than it is currently. The change in the $\delta^{13}C$ of atmospheric CO_2 is, however, smaller than that usually found in soil profiles, and it is therefore debatable how much of the $\delta^{13}C$ variations in soil profiles can be attributed to temporal changes in atmospheric CO_2 $\delta^{13}C$ (Ehleringer et al. 2000).

(2) **Differential rates of decomposition for plant components.** Individual plant components can vary substantially in their $\delta^{13}C$ values, according to the specific synthesis pathways. Lignin, for example, is usually depleted by 2-7 ‰ relative to the bulk plant material (Wedin et al. 1995; Schweizer et al. 1999 and references therein), whereas the cellulose fraction is usually enriched. Thus, the relative non-degradability of lignin (e.g. Dittmar et al. 2001c estimated a half-life of ~150 yr for mangrove-derived lignin) has been suggested to result in a

depletion in ^{13}C of plant litter during decomposition (e.g. Benner et al. 1991 for salt marsh ecosystems). Although an appealing hypothesis and although lignin:C ratios obviously do increase during decomposition, the SOM pool is usually enriched rather than depleted in ^{13}C, with the exception of salt marsh ecosystems (i.e. where Benner and colleagues worked on when they formulated their hypothesis), but the enrichment in the latter case is more likely to be caused by the import of allochtonous material (Middelburg et al. 1997, see also Chapter 7). Wedin et al. (1995) studied changes in bulk $\delta^{13}C$ and lignin $\delta^{13}C$ during two years of decomposition for 4 grass species (2 C_3-plants, 2 C_4-plants). Their initial hypothesis that $\delta^{13}C$ values would decrease during decomposition due to the selective preservation of lignin did not appear to hold true : $\delta^{13}C$ values for C_3 and C_4 plants changed little, but in opposite direction : C_3 : + 0.4 to 0.7 ‰; C_4 : -1.0 to 1.5 ‰, and Bouchard et al. (1998) found a decrease in $\delta^{13}C$ values (~ 1.5 ‰) of the (C_3) salt marsh grass *Spartina*. According to Ehleringer et al. (2000), it is therefore unlikely that such selective preservation of certain compounds has any significant effects on total SOM $\delta^{13}C$ values.

(3) **Fractionation during microbial degradation**. If microbial reactions preferentially use ^{13}C-depleted carbon sources in *metabolic* reactions associated with litter decomposition, then the residual SOM should become progressively more enriched in ^{13}C. Ehleringer et al. (2000) point out that there is currently no direct, compelling evidence of microbial fractionation during SOM breakdown, and this was confirmed recently by the *in situ* experiments of Ekblad et al. (2002). According to the Ehleringer et al. (2000), the absence of significant fractionation during mineralization should not be confused with the frequent observation that microbial and fungal carbon is enriched in ^{13}C compared to litter, as not all of the microbial and fungal carbon is likely to be derived from decomposing soil organic matter.

(4) **Soil carbon mixing**.

Ehleringer et al. (2000) proposed that an increase in microbial and fungal residues accounts for the observed ^{13}C enrichment in residual SOM. The rationale behind their hypothesis is that bacteria and fungi can be expected to be enriched relative to their substrate as a result of carboxylation reactions. Whenever a carboxylation reaction is involved in catabolism, the required CO_2 molecule is likely to be derived from the soil atmosphere, and as this CO_2 is enriched relative to the SOM pool, this will result in an enrichment of the microbial biomass, even if only a small percentage of the total microbial biomass is derived this way. If there is a

general trend for the remaining SOM to become progressively enriched with fungal/microbial derived components, we would expect the SOM pool to become enriched in ^{13}C over time.

Relationship between the $\delta^{13}C$ values of bacteria and fungi and their substrate

When **bacteria** are grown on single substrates, a large degree of fractionation has been found to occur in several studies (e.g. Macko & Estep 1984, Barghoorn et al. 1977 and Ivlev et al. 1982, cit. in Fry & Sherr 1984), but such large effects do not appear to occur under natural conditions, presumably because of the diverse composition of litter and of the microbial community (Macko & Estep 1984). Recent studies on **fungi** have demonstrated that significant isotopic effects can be apparent when fungal tissues are compared to their presumed plant substrate. Consistent differences have been observed between mycorrhizal (EM) and saprophytic (SAP) fungi in several studies (the 'EM-SAP divide', Hobbie et al. 1999, Kohzu et al. 1999, Högberg et al. 1999, Wallander et al. 2001), with saprophytic fungi being much more enriched (by ~ 3.5 to 5 ‰) relative to the plant substrate compared to mycorrhizal fungi (which are enriched by about 1.4 to 2 ‰). Henn & Chapela (2001), however, note that this distinction holds only for studies within a restricted ecosystem and becomes less distinct over larger geographical regions. For **mycorrhizal fungi** (see Hobbie et al. 1999), the observed enrichment has been explained by (1) their reliance on primarily sugars, i.e. compounds which are relatively enriched in ^{13}C, (2) differences in the isotopic composition of sugars fixed during photosynthesis and those actually delivered to the fungi in the root zone, and (3) the respiration of isotopically light CO_2. For **saprophytic fungi**, the isotopic enrichment is attributed primarily to a 2 ‰ enrichment during chitin formation (Gleixner et al. 1993, cited in Hobbie et al. 1999), and secondarily to the acquisition of isotopically enriched cellulose during wood and litter degradation. An interesting observation in this context is that there is little or no evidence for significant incorporation of lignin-derived carbon (always found to be isotopically depleted relative to bulk material or cellulose) into fungal biomass, despite the fact that most wood-inhabiting fungi are able to degrade lignin (see Gleixner et al. 1993). Henn & Chapela (2000) have shown convincing evidence that fractionation of ^{13}C by fungi grown on sucrose derived from C_3 plants and C_4 plants was significantly different, and these patterns were explained by the differences in the intramolecular distribution of ^{13}C between sucrose derived from C_3 plants and sucrose derived

from C_4 plants. In addition, the study by Henn & Chapela (2000) was unable to find a correlation between ecological role (*sensu* saprophytic or mycorrhizal) and intrinsic isotopic discrimination effects in the three species they studied. The latter suggests that the segregation of $\delta^{13}C$ values of mycorrhizal and saprophytic fungi observed under natural conditions (e.g. Hobbie et al. 1999, Kohzu et al. 1999) may be caused by ecological determinants (such as substrate effects) rather than from differences in intrinsic isotopic discrimination. Henn & Chapela (2001) have indeed shown that when substrate effects are removed, the clear separation between EM and SAP $\delta^{13}C$ values disappears, confirming that the EM-SAP divide is determined more by the nature of the substrate being utilized (i.e. recently synthesised simple carbohydrates for EM fungi and more complex, plant/microbial/animal substrates that have undergone repeated re-processing for SAP fungi) rather than by strong physiological differences between EM and SAP fungi.

One of the problems in using stable isotope techniques to study microbial processing of organic matter sources under field conditions is that bacteria cannot be separated from their substrate for stable isotope analysis. With the recent advances in GC-C-IRMS (gas chromatography-combustion-isotope ratio mass spectrometry), the measurement of stable isotope ratios in specific compounds has been made feasible (Meier-Augustein 1999, Boschker & Middelburg 2002). This has the particular advantage of enabling the stable isotope analysis of 'biomarker' molecules, such as specific fatty acids that are known to occur only in bacteria. If and when the relation between the isotopic composition of the substrate and the isotopic composition of the biomarker molecule is known and does not show too much variability (Abraham et al. 1998), this opens new perspectives to study microbial substrate utilization patterns under natural and experimental conditions (e.g. Boschker et al. 1999, 2000).

Nitrogen

In contrast to the situation for $\delta^{13}C$, where only very small changes have been found to occur in short-term degradation experiments, and where $\delta^{13}C$ shifts over long time scales are consistent in direction, the limited number of studies on $\delta^{15}N$ dynamics during decomposition have resulted in apparently contradictory conclusions. Some authors have reported (large) depletions in ^{15}N during decomposition (e.g. Zieman et al. 1984 for mangrove litter), whereas others have found significant increases in $\delta^{15}N$ (e.g. Turner et al. 1983 and DeNiro & Hastorf

1985, cit. in Owens 1987, Caraco et al. 1998), an increase or decrease depending on the oxic or anoxic conditions (Fogel & Tuross 1999), or no significant changes at all (e.g. Dehairs et al. 2000 and S. Marguillier, unpublished data, for mangrove litter, and Zieman et al. 1984 for seagrass litter). This apparent contradiction is, however, easily explained : the changes in $\delta^{15}N$ (if any) are not necessarily changes in the isotopic composition of the substrate N pool, but are rather the result of nitrogen added by microbial immobilization. Such immobilization ('MAD' : microbially added nitrogen, Caraco et al. 1998) has been shown to be significant in the N balance of the decomposing litter (e.g. Caraco et al. 1998), and thus, the magnitude and direction of $\delta^{15}N$ changes will depend on a multitude of factors including the inorganic N-substrate used by bacteria or fungi (in most cases NH_4^+), its concentration and isotopic composition, and the degree of fractionation exerted by the heterotrophic community.
Fungi have been found to exhibit a wide range of $\delta^{15}N$ values under natural conditions (between -7.1 and +21.8 ‰, see Henn & Chapela 2001 for a recent review), with consistent differences between ectomycorrhizal fungi (average $\delta^{15}N$: +6.4 ± 0.4 ‰) and saprophytic fungi ($\delta^{15}N$: + 0.8 ± 0.4 ‰, Henn & Chapela 2001), albeit with a considerable overlap when data from different regions are pooled. To date, however, a mechanistic understanding of this pattern does not exist (Henn & Chapela 2001), partly because of the uncertainty associated with the N-substrate used and its isotopic composition.

In conclusion, it appears that the $\delta^{13}C$ signature of organic matter is relatively conservative and can be used to infer sources of organic matter in the sedimentary record, bearing in mind that, over long periods of time, a small but significant isotopic shift can take place. The mechanisms underlying this isotopic enrichment are currently not yet fully understood. For $\delta^{15}N$, however, degradation appears to be able to alter the isotopic signature due to the microbial immobilization of dissolved inorganic nitrogen, but the direction and magnitude of the isotopic shift (i.e. no effect, depletion, or enrichment) is difficult if not impossible to predict.

1.3.2. FRACTIONATION OF ^{13}C AND ^{15}N BETWEEN TROPHIC LEVELS

One of the key hypotheses underlying the application of stable isotope data to study carbon sources and foodweb relationships in faunal communities is that there exists a relatively constant (and known) degree of isotopic fractionation between an animal and its diet. In this section, we will present an overview of the literature on this subject, and summarize the methods frequently used to use stable isotope data quantitatively in mixing models to estimate the contribution of different food sources to an organisms' diet. Despite some of the shortcomings and uncertainties which will be mentioned, stable isotope analysis offers an excellent tool to study the primary producers used by faunal communities and to assess an organisms dietary history, provided that results are interpreted cautiously and with sufficient ecological background knowledge.

For $\delta^{13}C$, it is generally recognized that a small degree of enrichment occurs (0-1 ‰, DeNiro & Epstein 1978, but actually more variable e.g. between -2.1 and + 2.8 ‰ for aquatic systems, see Vander Zanden & Rasmussen 2001), whereas for $\delta^{15}N$, it is usually stated that the enrichment is around 2.7 to 3.4 ‰ (Minagawa & Wada 1984, Owens 1987). The latter values should be considered as average values, however, as the range of enrichment values found for e.g. $\delta^{15}N$ is actually quite wide (in aquatic systems : between -0.7 and + 9.2 ‰, see Vander Zanden & Rasmussen (2001) for a recent review; see also Pinnegar et al. 2001 for an extension of this range down to -2.4 ‰), and the use of such average values to calculate the trophic level or position of consumers (e.g. Vander Zanden et al. 1999a,b, Branstrator et al. 2000) might therefore not be appropriate. Since the pioneering work of e.g. DeNiro & Epstein (1978) and Minagawa & Wada (1984), there have been surprisingly few laboratory experiments (e.g. Fry & Arnold 1982, Macko et al. 1982, Tieszen et al. 1983, Checkley & Entzeroth 1985, Hobson et al. 1996, Ostrom et al. 1997, Focken & Becker 1998, Webb et al. 1998, Gorokhova & Hansson 1999, Oelbermann & Scheu 2001) or field estimates (*sensu* Vander Zanden & Rasmussen 2001) to confirm these enrichment factors and to study the mechanisms causing them. Overall, it appears that, in aquatic ecosystems, the trophic fractionation for both C and N is more variable for invertebrates than for fish, that laboratory results are more variable than field estimates, and that trophic fractionation in herbivores is more variable than in carnivores (Vander Zanden & Rasmussen 2001). The enrichment in ^{13}C is most frequently explained by the preferential respiration of light (i.e. ^{13}C-depleted) CO_2, whereas ^{15}N enrichment is often attributed to the preferential excretion of ^{15}N-depleted N-

compounds in urine (NH_3, urea, ... e.g. Peterson & Fry 1987). Ponsard & Averbuch (1999), however, recently challenged the latter hypothesis, and provided a simple model to show that that this preferential excretion of 'light' N is neither sufficient nor necessary to explain ^{15}N-enrichment along food chains. As an adult organism for which the nitrogen mass balance is achieved (i.e. the amount of excreted nitrogen is identical to the amount it consumes) appears to have a constant $\delta^{15}N$ over time (i.e. $\delta^{15}N$ does not increase with age without a change in diet), the total excreted nitrogen (via faeces and urine) should have the same isotopic composition as the food.

The growing interest in stable isotope studies should thus coincide with more laboratory studies on the mechanisms and variability of the fractionation phenomena associated with metabolism (Gannes et al. 1997). A few recent examples of deviations on this general pattern of enrichment clearly stress the need for more fundamental studies on these underlying principles :

- Scrimgeour et al. (1995) reported unusually high $\delta^{15}N$ values (~ 13 ‰) for overwintered larval and adult raspberry beetles (*Byturus tomentosus*) relative to their food sources ($\delta^{15}N$ ~ 3 ‰), whereas other life stages showed $\delta^{15}N$ values within the expected range. This was attributed to the fact that these stages had not been feeding for prolonged periods, thus requiring the breakdown and re-synthesis of endogenous protein stores. Nitrogenous by-products from amino-acid recycling are known to be depleted in ^{15}N because of fractionation effects during transamination reactions, and thus the remaining body N pool becomes enriched in ^{15}N. Such an enrichment in ^{15}N has also been observed in other faunal groups during periods of fasting (e.g. Hobson et al. 1993, Adams & Sterner 2000, Oelbermann & Scheu 2001).
- Adams & Sterner (2000) studied the effect of dietary nitrogen content on the degree of trophic level ^{15}N enrichment by raising daphnids under laboratory conditions and feeding them green algae with a highly variable N content. It was shown that, as the C/N ratio of the algae (between 7.3 and 24.8) increased, the trophic enrichment factor increased correspondingly from nearly 0 ‰ to almost 6 ‰, and although there is currently no direct evidence concerning the mechanism responsible for this trend, these examples clearly indicate the caution required in interpreting consumer $\delta^{15}N$ values. In contrast with the results of Adams & Sterner (2000), Hobson & Clark (1992) had found higher diet-tissue fractionation values for American crows (*Corvus brachyrhynchos*) when grown on an N-

rich food source (fish) than those raised on a plant-based diet. Similarly, Oelbermann & Sheu (2001) recently found a spider species to show $\delta^{15}N$ enrichment of ~ 3 ‰ when fed on a N-rich diet, but its $\delta^{15}N$ were similar to the diet when the latter was N-poor.

- Webb et al. (1998), in an experiment whereby locusts were fed a constant diet throughout their life cycle, also found evidence for an effect of dietary quality on fractionation of ^{15}N, as animals raised on a C_4 diet showed larger fractionation of ^{15}N than did animals raised on a C_3 diet. Body recycling of proteins was hypothesized to be responsible for the enrichment in ^{15}N over time. In addition, these authors found chitin to be consistently and strongly depleted in ^{15}N (by ~ 4 ‰ relative to the diet) due to the fact that all N used in chitin formation is derived from excretory ammonia.
- Pinnegar et al. (2001) found a consistent depletion in ^{15}N in 4 different fish endoparasites in comparison with the fish (host) tissues, in constrast to the expected pattern.

Vanderzanden & Rasmussen (2001) hypothesized that one of the possible causes for the high variability in trophic fractionation of ^{15}N (which they noted in particular in herbivores) may be that assimilative fractionation (i.e. isotopic differences between assimilated and unassimilated N pools in the diet) and urea recycling (urea-derived N being used for the synthesis of nonessential amino acids) may be important factors to consider.

Another potentially confounding factor is the fact that, for both $\delta^{13}C$ and $\delta^{15}N$, different animal tissues are known to have different isotopic signatures, as well as different turnover times (i.e. the time required to adapt isotopically to a change in diet). The liver, for example is well know to be relatively depleted in ^{13}C in comparison with other tissues (e.g. Tieszen et al. 1983, Hobson & Clark 1992, Hobson et al. 1996, Pinnegar & Polunin 1999), and most studies therefore select muscle tissue -where possible- for stable isotope analysis. Differences in turnover time can also be an important factor. Whereas blood plasma of certain bird species was shown to have a half-life of about 3 days after a change in diet (Hobson & Clark 1993), the cellular blood fraction had a half-life about 10 times longer. Large differences in the half-life of fish tissues was also observed by Tieszen et al. (1983), with a much shorter half-life for liver (6.4 days) than fat tissue (15.6 days), muscle tissue (27.6 days), brain tissue (28.2 days), or hair (47.5 days). The growth rate of an animal is of course an important parameter influencing the time required for an organism to equilibrate isotopically with a new diet (Fry & Arnold 1982).

A simplified graphical representation of the combined use of C and N stable isotopes to estimate the contribution of two food sources to an organisms diet is presented in Figure 3.

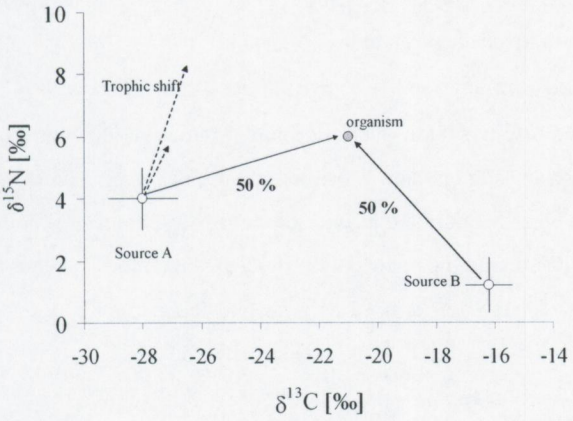


Figure 3 : Simplified graphical representation of the combined use of C and N stable isotopes to estimate the contribution of two food sources to an organisms diet : any organism deriving equal proportions of its diet from source A and B is expected to have an isotopic composition close to that shown in the figure.

Several authors have used two-source mixing models in the form :

$$\delta^{13}C_{consumer} = (X_A.\delta^{13}C_A + X_B.\delta^{13}C_B) + \Delta$$
$$= X_A.(\delta^{13}C_A + \Delta) + X_B.(\delta^{13}C_B + \Delta)$$

where :

$\delta^{13}C_A$: carbon isotope composition of dietary source A

$\delta^{13}C_B$: carbon isotope composition of dietary source B

X_A : proportion of source A to the consumers diet ($0 < X_A < 1$)

X_B : proportion of source B to the consumers diet ($X_B = 1-X_A$)

Δ : the fractionation associated with one trophic step

to quantitatively assess the contribution of different sources to an organisms' diet, but there are serious limitations related to the substantial errors which can arise when the isotopic difference between the two sources becomes smaller (e.g. Sagers et al. 2000) or when the variability in $\delta^{13}C$ values of a single source becomes larger. Whereas such two-source mixing models are of course often an oversimplification of natural systems, they may be useful in

many cases – even if only to put some constraints on the contribution of 2 potential sources (or even 3 potential sources, see e.g. Dauby 1989). Other stable isotope based methods to analyse food web interactions and estimate the relative magnitude of different pathways of carbon flow such as the 'trophic position isotope spectrum' (TPIS, proposed by Monteiro et al. 1991) have not found their way into subsequent studies.

When multiple stable isotope ratios are analysed (e.g. as is most often the case, $\delta^{13}C$ and $\delta^{15}N$), it would become tempting to use this additional information to derive the contribution of three different food sources to a consumers diet. Most commonly, the Euclidean distance between the corrected (i.e. for the enrichment in the heavy isotope) isotope values of food and each individual consumer is calculated, and the contribution of each source to the diet is then inversely related to this distance. When $\delta^{15}N$ is used as a second indicator, however, two major restrictions arise :

(1) As discussed above, the degree of fractionation of ^{15}N during one trophic transfer has been found to be quite variable, and the errors resulting from this uncertainty may be large, and

(2) In contrast to the 'large' differences in $\delta^{13}C$ which may be found between different food sources (e.g. C_3-vegetation, phytoplankton, microalgae, ...), different primary producers often show markedly little differences in their $\delta^{15}N$ signatures, making them unreliable as source indicators.

In addition, the procedures used to solve the 3-source mixing model are subject to some discussion, and different analytical equations proposed may result in different outcomes (see Phillips 2001 and Ben-David & Schell 2001 for a recent discussion). One particular problem with most of the proposed 3-source models is that is that they assume that proportion of C derived from any source is the same as the proportion of N derived from that source, an assumption reasonable when the food sources have similar C and N concentrations, but no longer valid when animals consume e.g. both plant and animal material – which differ markedly in their N content. Therefore, Phillips & Koch (2001) have outlined procedures for a three-source mixing model, taking into account (a) trophic fractionation, and (b) differences in the concentrations of C and N in the three potential sources. An example of the discrepancy between the linear 3-source mixing models and the concentration-dependant model is illustrated in Figure 4. In this example, we have used 3 different food sources, with $\delta^{13}C$, $\delta^{15}N$, [C], and [N] as outlined in Table 3.

Table 3 : $\delta^{13}C$, $\delta^{15}N$ (both corrected for trophic enrichment), [C], [N], and C/N for the three different sources and the consumer used in Figure 4.

Source/consumer	$\delta^{13}C$	$\delta^{15}N$	[C] (%)	[N] (%)	C/N (atom)
A	-28.6	+ 4.6	42	1.7	24.7
B	-23.0	+ 4.0	40	6.1	6.1
C	-17.3	+ 1.7	11	1.11	9.9
Consumer	-22.0	+ 2.9			

The results of both models are presented in Table 4. Using the linear model, the contributions of C and N of each source are assumed to be similar, whereas the concentration-dependent model clearly shows the differential contribution of C and N by the different sources. In addition, the linear model appeared to have overestimated the contribution of source A (and, to a lesser extent, source C) in providing C and N to the consumer and thereby neglected the contribution of source B to the carbon and nitrogen requirements of the consumer. Note that sources and consumer used in this example show some resemblance to potential sources and consumers in intertidal mangrove habitats (see chapter 8).

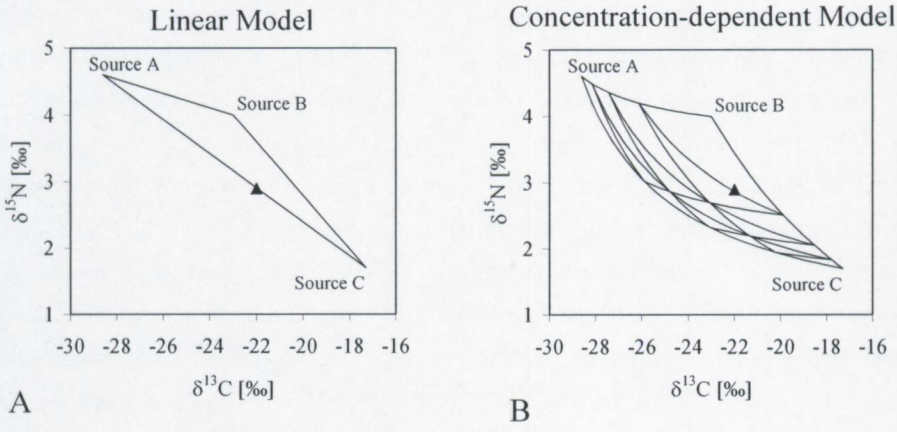


Figure 4. Contribution of 3 different sources (A, B, and C) to the diet of an organism (represented by the triangle) according to (A) a linear 3-source mixing model (Phillips & Gregg 2001), and (B) a concentration-dependent 3-source mixing model (Phillips & Koch 2001). Note that the $\delta^{13}C$ and $\delta^{15}N$ values of the food sources have been corrected for trophic enrichment.

Table 4 : estimated contributions of the different sources to the consumer's diet (using the data in Table 3) using the linear 3-source mixing model (Phillips & Gregg 2001) and the concentration-dependant mixing model (Phillips & Koch 2001).

	LINEAR MODEL		CONCENTRATION-DEPENDENT MODEL	
Source	**Contribution (C)**	**Contribution (N)**	**Contribution (C)**	**Contribution (N)**
A	42.0	42.0	18.0	6.7
B	-0.7	-0.7	35.2	49.6
C	58.8	58.8	46.9	43.7

One of the advantages of **stable isotope analyses** compared to other, more traditional, methods to study the diet of animals (e.g. **stomach content analyses**) is that it is a measure of what is actually *assimilated* rather than what is *ingested*. There may be cases where large amounts of relatively refractory material (such as detritus or vascular plant material) are ingested, but where this is not assimilated to the same extent as other food sources (e.g. Rodelli et al. 1984). Differences in the residence time of food sources in the stomach also lead to an overestimation of food sources that are difficult to assimilate. In addition, gut content analyses has the disadvantage of being impractical when very small species are concerned, and the material retrieved is often difficult to identify. On the other hand, stable isotope analyses cannot offer the same degree of taxonomic resolution that may sometimes be offered by gut content analyses. Although this may be regarded as a disadvantage, when the issue is to resolve the base of the food web (i.e. the major ultimate source(s) of primary production sustaining the faunal community or specific species) a detailed taxonomic list of prey items of a predator will not be very informative. Here, stable isotope analysis may also prove to offer a better solution. Another technique frequently used to infer dietary sources is the analyses of **fatty acid profiles** (e.g. Meziane & Tsuchiya 2000, Goedkoop et al. 2000; combined with stable isotope analysis : Canuel et al. 1995, Kharlamenko et al. 2001). As different sources of primary or secondary producers (vascular plants, diatoms, bacteria, ...) are often found to contain highly specific fatty acids, and as these appear to be partially conserved in consumers, the occurrence and relative abundances of such 'biomarker' fatty acids may provide dietary information, often very specific. A particular disadvantage of this technique, however, is the complexity in the interpretation of the results and the absence of reliable methods to make quantitative conclusions concerning the relative importance of different sources.

STATISTICAL TREATMENT OF STABLE ISOTOPE DATA

Very few studies have been concerned with the statistical treatment of stable isotope data. However, as Rosing et al. (1998) point out, sample sizes in many studies are fairly small (associated with the relatively high cost of the analyses) and the data seldom have a normal distribution. Parametric techniques are thus in theory inappropriate to analyse stable isotope data (Rosing et al. 1998). Rosing et al. (1998) therefore proposed a randomization test based on the K-nearest neighbour approach, which treats stable isotope data of 2 elements (e.g. $\delta^{13}C$ and $\delta^{15}N$) as spatial data. This procedure has not found widespread application, however, and most studies still use more common statistics to treat stable isotope data – even though there might be a need to be cautious when applying certain procedures. A discussion of the uncertainty associated with using two- or three-source mixing models is presented by Phillips & Gregg (2001) and Phillips & Koch (2001).

Another commonly observed error is that the variability of stable isotope signatures within a population are expressed as CV's (coefficient of variation) (e.g. Lancaster & Waldron 2001), which is a meaningless parameter for stable isotope data, as the latter is a *relative* expression (i.e. relative to a commonly agreed standard) of the isotopic composition rather than an absolute one. Thus a CV of 10 % obtained for a population of individuals with a mean $\delta^{13}C$ = -20 ‰ is rather large, whereas a similar CV for population with a mean $\delta^{13}C$ = -1 ‰ is not. Similarly, comparing $\delta^{13}C$ values of different organisms and expressing the differences as percentages (e.g. Ellison et al. (1996) : '[individual] sponges growing on mangrove roots with fine rootlets [...] have a 1-3 % lower $\delta^{13}C$ than [those] growing on roots without rootlets') is equally meaningless.

1.3.3. STABLE ISOTOPE COMPOSITION OF INDIVIDUAL COMPOUNDS

During the last 15 years, one of the most promising analytical advances in stable isotope techniques has no doubt been the combination of traditional GC techniques, followed by combustion of individual compounds as they elute, and automated coupling of the resulting gases to IRMS for the determination of stable isotope ratios (currently mostly $\delta^{13}C$, but δD and $\delta^{15}N$ have also been succesfully applied) of single compounds – on the condition that they are amenable to GC analysis, such as various hydrocarbon compounds, fatty acids and sterols, amino acids, and although not yet in common use, pigments such as chlorophylls. Often,

derivatization is a prerequisite, and obtained stable isotope ratios thus need to be corrected for any atoms added during this step of the element analyzed, and corrections need to be made for fractionation processes –if any- during the whole procedure. Although these techniques are still very recent, they have proven to be useful in a wide range of applications. As some of the compounds which can thus be analysed are known to be specific biomarkers (i.e. only synthesized in significant amounts by a limited number of species or functional groups), the potential of this technique is evident (e.g. see p. 24-25).

CHAPTER 2 : Mangrove Ecosystems : a Brief Introduction

TABLE OF CONTENTS

CHAPTER 2 : Mangrove Ecosystems : a Brief Introduction

Introduction

Mangrove forests are a dominant feature of many tropical and subtropical coastlines, but are disappearing at an alarming rate. The main causes for the rapid destruction and clearing of mangrove forests include urbanization, population growth, water diversion, aquaculture and salt-pond construction (e.g. Farnsworth & Ellison 1997).

This chapter is intended to serve as a brief introduction to some aspects of mangrove ecosystem structure and functioning. An overview is provided on the environmental settings in which mangrove forests occur, a description of the most important floral and faunal components, and a short literature overview on some basic aspects of organic matter dynamics in mangrove ecosystems. As the latter forms the main subject of this thesis, only some general features will be dealt with in detail in this chapter in order to provide a general framework, but for a more detailed discussion and the significance of recent findings we refer to Chapters 4-10.

2.1. Distribution And Classification Of Mangrove Forests

On a global scale, mangrove plants are found throughout the tropical and subtropical regions of the world (Chapman 1984, Duke 1992), and two species of *Avicennia* have penetrated into the warm temperate areas of both hemispheres. Mangroves generally match the winter 20°C isotherm -suggesting the importance of water temperature rather than air temperature to this habitat- with three notable exceptions, i.e. eastern South America, around Australia and the North Island of New Zealand. According to Duke (1992), this is most likely a result of relict populations reflecting a more poleward distribution in the past. The species richness varies substantially with longitude : whereas about 30 species occur in most 15° zones of Southeast Asia, the Caribbean regions have less than 5 species (Tomlinson 1986, Ellison & Farnsworth 2001). Although it was previously hypothesized that all mangrove taxa originated in the Indo-West Pacific, more recent studies have provided evidence that continental drift and vicariant events could offer a better explanation for the observed current diversity patterns (see Ellison et al. 1999). Substantial variations in diversity also occur on a regional scale, but the

mechanisms for the establishment of these patterns are still little understood. The environmental settings in which mangrove forests occur can be extremely diverse, and Lugo & Snedaker (1974) have proposed a classification scheme for mangrove forest types, which has been fairly widely adopted : (1) **riverine mangrove forests** are those occuring along river drainages and are inundated by most high tides and flooded during the wet season, (2) **basin forests** are partially impounded depressions which are inundated by very few high tides during the dry season, but by most high tides during the wet season, (3) **fringe forests** occur along shorelines with steep elevation gradients which are inundated by all high tides, (4) **overwash forests** consist of low islands or small peninsulas which are completely overwashed during all high tides, and (5) **dwarf forests** are those occuring on higher elevations (i.e. above mean high water) and which are subsequently only inundated during the wet season. Finally, a sixth category, the **hammock forest** has been proposed which comprises a special type of basin forests mainly encountered in the Everglades, due to its particular geological settings.

2.2. Biological Components

2.2.1. Mangroves and mangrove associates

The definition of mangroves is a continuing issue of debate. A mangrove is a tree, shrub, palm or ground fern which normally grows above mean sea level in the intertidal zone of marine, coastal, or estuarine environments. It is, however, not always clear which species can be considered 'mangrove' and which cannot. Therefore, species have often been classified as either 'true mangrove' species or 'mangrove associates'. There is as yet no universal agreement on these terms, often causing confusion between different authors regarding the number of mangrove species occuring at sites or in certain regions (e.g. Jayatissa et al. 2002). Duke (1992) mentions mangroves to occur in 20 families, of which only 2 are exclusively mangrove. Thus, mangrove plants do not form a phylogenetically related group of species but are rather species form very diverse plant groups sharing common morphological and physiological adaptations to life in the intertidal zone, which have evolved independantly through convergence rather than common descent. Different taxa, however, can have different mechanisms for coping with e.g. the high salt concentrations and anoxic conditions. Some species have salt-excreting glands on their leaves (*Avicennia* spp.), or exclude salt at the roots

(e.g. *Avicennia* and *Aegiceras*), and still others transfer salt into senescent leaves (*Excoecaria, Xylocarpus*) or by storing it in bark or wood (*Avicennia, Rhizophora, Sonneratia, Xylocarpus*). Mangroves have also adapted different strategies to endure growing in water-saturated and therefore often anoxic substrates. Some species such as those of the genus *Rhizophora* have aerial prop roots bending down from the stem or branches, whereas others (such as *Avicennia* spp.) have shallow, subsurface cable roots with series of vertical, stem-like breathing roots called pneumatophores popping up from the soil.

Within one site, mangrove species often appear to occupy distinct and discrete zones of tree species along the tidal gradient, or in some cases may appear in relatively homogeneous patches. Certain species are noted to occur on the seaward fringes, whereas others are found in the upland reaches, with different degrees of overlap. These 'zonation patterns' have been attributed to factors such as interspecific differences in tolerance to salinity, factors related to tidal elevation, sorting of dispersed propagules during stranding, interspecific competition, and frequency-dependent preferences of seed predators. However, there have been few studies which provided experimental tests of the hypotheses attempting to explain apparent mangrove species zonation, and the whole concept of zonation has even been questioned (e.g. Ellison et al. 2000) as the overlap between species is often blurring discrete vegetation zones.

2.2.2. OTHER PRIMARY PRODUCERS IN THE INTERTIDAL HABITATS

Microphytobenthos and microepiphytes

Benthic microalgae remain a relatively poorly studied group in mangrove ecosystems, and microepiphytes on mangrove stems, roots, and leaves have even less well been studied. The vertical distribution of cyanobacteria on pneumatophores has been studied by e.g. Dor (1984), and only two studies (Sheridan 1991, 1992) describe the existence of epiphytic cyanobacterial crusts on mangrove stems, and showed that these were N_2-fixing species. Few studies also exist on the species composition and dynamics of benthic microalgae in mangrove environments (e.g. see references in Alongi & Sasekumar 1992, Siqueiros Beltrones & Castrejón 1999), despite their potentially important role in the carbon cycle. Standing stocks of benthic microalgae (as expressed by Chl-a concentrations) in mangrove sediments are usually low (generally < 10 µg Chl-a per g DW, see Table 1), and the few studies available show little seasonal or spatial variation in these standing stocks (but see Holmer et al. 2001).

Several factors have been invoked to explain these low Chl-a levels, such as the low light intensity under the mangrove canopy (Alongi 1988), the inhibitory effect of soluble phenolic compounds and tannins (Cooksey et al. 1975), the frequency of tidal wetting, nutrient limitation, and grazing by herbivores (Alongi & Sasekumar 1992). Kristensen et al. (1988) and Alongi (1994) pointed out that light (and to a lesser extent DIN) availability were probably the major limiting factors, in agreement with Underwood & Kromkamp (1999) who, in their review on benthic and pelagic primary production in estuarine ecosystems, stated that irradiance explains 30-60 % of the observed variation in primary productivity of benthic microalgae. It should be stressed, however, that these generally low standing stocks do not exclude microphytobenthos from potentially playing an important role in intertidal C and N cycling as (1) productivity is a more important parameter to consider, and (2) due to the low C/N ratios in these producers compared to mangroves, a relatively small contribution in terms of biomass or organic C may coincides with a very substantial contribution in terms of nitrogen.

Rates of primary production for benthic microalgae have been reported from different mangrove ecosystems, and range between 0 and 0.88 g C m^{-2} d^{-1} (see Gattuso et al. 1998). Krishnamurthy et al. (1987, cit in Kathiresan 2000) measured benthic microalgal primary productivity in the Pichavaram mangroves (Tamil Nadu, India) and found higher photosynthesis rates (0.41 g C m^{-2} d^{-1}) in the interior parts of the forest than in the lower reaches of the mangroves (0.29 g C m^{-2} d^{-1}). When comparing the latter data with imputs from mangrove litter fall (e.g. *Excoecaria agallocha* : 1.67 g C m^{-2} d^{-1} and *Avicennia officinalis* : 0.81 g C m^{-2} d^{-1} in the Coringa Wildlife Sanctuary, see Dehairs et al. 2000), this indicates that under certain conditions, benthic microalgal production can make a very significant contribution (30 – 40 % of mangrove litterfall in terms of C, but presumably > 100 % in terms of N) to primary productivity in the intertidal areas, especially considering the labile nature and nutritional value of this source compared to vascular plant litter. It also appears that benthic microalgae in mangrove sediments have relatively high photosynthetic efficiencies (Kristensen et al. 1988), as indicated by their high assimilation numbers (i.e. the rate of carbon fixation per unit of Chlorophyll a) – a phenomenon which appears to be characteristic of microalgae from tropical waters (Parsons et al. 1984, cited in Kristensen et al. 1988).

To our knowledge, no quantification has been attempted of the standing stocks or productivity of epiphytic microalgae, cyanobacteria, or lichen in mangrove forests.

Table 1 : Non-exhaustive overview of literature data on microphytobenthic primary production and standing stocks in intertidal mangrove ecosystems.

Site / Region	gross primary production (mg C m^{-2} d^{-1})	Standing stocks ([a] : µg Chl a cm^{-2} sediment) ([b] : µg Chl a g^{-1} sediment)	Remarks	Data source
Bangrong, Thailand		4.59 ± 0.14 [a]	Site A, dry season	Holmer et al. (2001)
Bangrong, Thailand		2.97 ± 0.71 [a]	Site A, wet season	Holmer et al. (2001)
Bangrong, Thailand		5.26 ± 1.75 [a]	Site B, dry season	Holmer et al. (2001)
Bangrong, Thailand		6.44 ± 1.73 [a]	Site B, wet season	Holmer et al. (2001)
India		2.6 – 6.1 [b]		Krishnamurhty et al. (1984)
Taiwan		0.17 – 0.45 [b]	Different seasons	Cheng & Chang (1999)
Australia		0.0 – 4.4 [b]	Different sites & seasons	Alongi (1988)
Phuket, Thailand	202 ± 22 *	1.92 ± 0.22 [a]	Sunlit site	Kristensen et al. (1988)
Phuket, Thailand	139 ± 14 *	1.55 ± 0.23 [a]	Shaded site	Kristensen et al. (1988)
Papua New Guinea		0.2 ± 0.3 [b]	*Sonneratia -Avicennia*	Alongi et al. (1993)
Papua New Guinea		< 0.1 [b]	*Sonneratia -Avicennia*	Alongi et al. (1993)
Papua New Guinea		0.5 ± 0.1 [b]	*Rhizophora - Bruguiera*	Alongi et al. (1993)
Papua New Guinea		1.5 ± 0.7 [b]	*Sonneratia -Avicennia*	Alongi et al. (1993)
Papua New Guinea		0.5 – 0.6 [b]	*Rhizophora*	Alongi (1991)
Inhaca Island, Mozambique		3.3 – 7.3 [a]	along transect **	Guerreiro et al. (1996)
Inhaca Island, Mozambique		4.0 – 17.0 [a]	along transect **	Guerreiro et al. (1996)
Pichavaram, TN, India	410***		Interior of forest	cit. in Kathiresan (2000)
Pichavaram, TN, India	290***		Lower reaches of forest	cit. in Kathiresan (2000)
Queensland, Australia		0.2 – 7.0 [b]	Different elevations and tidal stage	Alongi (1994)
	0 – 880		Literature compilation	Gattuso et al. (1998)

*: assuming 12 hours of light per day, and based on ^{14}C-uptake.
**: data from non-vegetated areas are not included.
***: not specified whether gross or net primary production.

In other, temperate, estuarine ecosystems the contribution of benthic microalgae to the total estuarine primary production ranges between 17 and 64 % (reviewed by Underwood & Kromkamp 1999). The potential importance of benthic microalgae in mangrove ecosystem functioning and overall carbon flow has been very little studied. Kristensen et al. (1988) proposed that benthic microalgae may represent an important input of labile organic matter (i.e. easily degradable) to the microbial detritus food chain, due to the rapid decomposition of algal cells compared to the decomposition of mangrove litter. There is also evidence from stable isotope studies that benthic microalgae can be an important food source for some invertebrates such as *Uca* spp. (Rodelli et al. 1984, France 1995, this study – see Chapter 8) and some gastropod species (Rodelli et al. 1984, this study - see Chapter 8). Overall, the relative importance of benthic microalgal production in the total mangrove ecosystem has been estimated to be trivial by some (e.g. Alongi 1994), but significant by others (e.g. Kristensen et al. 1988). As microalgal production is influenced by a variety of factors such as tidal wetting, light and nutrient status, it can be expected that generalizations of the importance of microalgal production cannot be made, and it can be concluded that microalgal production in intertidal mangrove forests is highly variable, but may be very significant under certain conditions, especially in terms of nitrogen.

It is worth mentioning here that primary production rates, or biomass estimates, do not necessarily correlate with the importance of a certain source as a carbon source for consumers. Lee (2000), for example, points out that the results of his study in Deep Bay (China) demonstrates a more important trophic role for microphytobenthos than that predicted based on mass-balance considerations (Li & Lee 1998).

For the Coringa Wildlife Sanctuary, the species composition of benthic microalgae has been studied by C. Kalavati and co-workers (see Raman 2000). The shallow areas of the mangrove creeks were found to support a rich population of cyanobacteria, whereas the intertidal mangrove sediments contained more diatoms (24 species overall, *Navicula* spp. and *Nitzschia* spp. as the dominant genera) with little seasonal variation in abundance (generally ~ 20,000 cells per cm^2). Similarly, 51 species of benthic diatoms have been recorded in the Pichavaram mangrove area (Tamil Nadu, India) by Jayachandran (1990, cit. in Kathiresan 2000).

Benthic and epiphytic macroalgae

Pneumatophores, stilt roots, the base of mangrove trees, and to a lesser extent the sediment surface can harbour a rich macroalgal flora, dominated by red algae (e.g. *Bostrychia* spp.,

Caloglossa spp., *Catenella* spp. and *Gracilaria* spp.), and a distinct vertical zonation in the species assemblages is often noted (e.g. Alongi & Sasekumar 1992 and references therein). The assemblages of macroalgae and microalgae on pneumatophores and aerial roots are often referred to as the 'bostrychietum', after its often principal component, *Bostrychia* spp. Little is known on the productivity of these algae and on their trophic significance in mangrove ecosystems, but their standing stocks can be high under certain conditions (Rodriguez & Stoner 1990) and there is evidence of feeding on macroalgae by crabs such as *Macrophthalmus* spp. (Wada & Wowor 1989), *Metopograpsus* spp. (e.g. Dahdouh-Guebas et al. 1999, M. Skov unpublished data), and *Selatium elongatum* (Cannici et al. 1999).

Rao (1995) studied the growth and biomass of red algae on *Rhizophora* prop roots and pneumatophores of *Avicennia* and *Sonneratia* in the Coringa river (Andhra Pradesh, India) and found an overall biomass in the range of 20-45 g DW m^{-2} of root/pneumatophore surface, with an annual peak in biomass during January-March. Although to our knowledge there are no data on primary production on an areal basis for epiphytic macroalgae, some studies have suggested that their production may be significant, at least under certain conditions (e.g. for lagoonal systems see Koch & Madden 2001). The latter authors, however, did measure high primary production rates in mangroves sediments (between 4 and 6 g C m^{-2} d^{-1}) and noted that the benthic algal community in these sediments was dominated by filamentous macroalgae such as *Chaetomorpha* spp.

2.2.3. AQUATIC PRIMARY PRODUCTION

A relatively recent overview of studies on phytoplankton species composition, densities, and primary production rates in mangrove ecosystems is given by Robertson & Blaber (1992). It appears that phytoplankton density and primary production in mangrove ecosystems can be highly variable (Table 2, compare with data from temperate systems presented in Underwood & Kromkamp 1999) and it has been suggested that productivity may be significantly lower in estuarine mangrove areas (e.g. the Fly River delta of Papua New Guinea : 22-693 mg C m^{-2} d^{-1}, Robertson et al. 1992) than in mangrove-lined lagoons (e.g. Ivory Coast : up to 5 g C m^{-2} d^{-1}, see references in Robertson & Blaber 1992), although there appear to be exceptions to this general rule, as e.g. net primary productivity of phytoplankton in the (estuarine) Pichavaram mangroves has been reported to attain values as high as 6.3 g C m^{-3} d^{-1} (Krishnamurthy & Sundararaj 1973, cit. in Kathiresan 2000). In two mangrove creeks in the Indus delta

(Pakistan), Harrison et al. (1997) found no apparent seasonal cycle in Chl-a or primary productivity, and suggested that nutrients were rarely limiting (except P during bloom periods) but that light limitation was probable during most of the year.

The relative importance of phytoplankton to the total mangrove ecosystem primary productivity is expected to vary with the geomorphology of the site, the flow rates, turbidity and nutrient levels. Estimates of the relative importance of phytoplankton to mangrove primary production thus range considerably (e.g. around 20 % for the Fly River delta, Papua New Guinea (Robertson et al. 1992), 50 % in the Terminos Lagoon system, Mexico (Day et al. 1982), but far exceeding mangrove inputs in other ecosystems (e.g. Wafar et al. 1997, Li & Lee 2000).

Table 2 : Non-exhaustive overview of literature data on aquatic primary production in mangrove ecosystems. Adapted from Robertson & Blaber (1992) and updated with more recent literature data. Note that primary production rates were obtained by different techniques, and that they are expressed either per surface area or per volume. Data from the Indian study site are presented in detail.

Site / Region	Primary production (units as specified)	Chl a ($\mu g\ l^{-1}$)	Remarks	Source
Hong Kong	55 mg C m^{-2} d^{-1}	3-5	Mangrove estuary	Lee (1990)
Mauretania	215 mg C m^{-3} d^{-1}	0.20 - 1.07	Mangrove creek	See Roberston & Blaber (1992)
Gambia	1 - 445 mg C m^{-3} d^{-1}	0.3 - 8.2	Estuarine mangroves	See Roberston & Blaber (1992)
Kenya	377 / 540 mg C m^{-3} d^{-1}	(**)	Mangrove creek, average for dry/wet season	Kitheka et al. (1996)
Mauretania	580 mg C m^{-3} d^{-1}	0.46 - 3.60	Mangrove bay	See Roberston & Blaber (1992)
India	60 - 662 mg C m^{-3} d^{-1}	4.4 - 39.8	Coastal lagoon	See Roberston & Blaber (1992)
New Guinea	22 - 693 mg C m^{-3} d^{-1}	0.3 - 5.1	Estuarine mangroves	Robertson et al. (1992)
Brazil	100 - 800 mg C m^{-2} d^{-1}	1.1 - 19.3	Estuarine mangroves	See Roberston & Blaber (1992)
Malaysia	274 - 959 mg C m^{-2} d^{-1}		Estuarine mangroves	See Roberston & Blaber (1992)
Indus Delta, Pakistan	200 - >1000 mg C m^{-2} d^{-1}	1-40	Estuarine mangrove creeks	Harrison et al. (1997)
Malaysia	10 - 1068 mg C m^{-3} d^{-1}	0.5 - 21.2	Estuarine mangroves	See Roberston & Blaber (1992)
Mexico	1200 mg C m^{-2} d^{-1}	0.3 - 8.2	Coastal lagoons	See Roberston & Blaber (1992)
India	120- 1200 mg C m^{-3} d^{-1} (*)		Estuarine mangroves	Cit. in Wafar et al. (1997)
India	232 - 1211 mg C m^{-2} d^{-1}	2.5 - 14.0	Estuary	See Roberston & Blaber (1992)
Ghana	385 - 1420 mg C m^{-3} d^{-1}		Coastal lagoon	See Roberston & Blaber (1992)
India	190 - 1540 mg C m^{-2} d^{-1}	2.1	Estuarine mangroves	See Roberston & Blaber (1992)

(*) converted from mg C m^{-3} h^{-1} for reasons of conformity by assuming a 12-h daylight period. (**) : contrasting data in tables and text, therefore not shown.

Table 2 (continued).

Site / Region	Primary production (units as specified)	Chl a ($\mu g\ l^{-1}$)	Remarks	Source
Guadeloupe	8 - 1700 mg C m^{-3} d^{-1}	10 - 60	Mangrove channel	See Roberston & Blaber (1992)
Ghana	626 - 1992 mg C m^{-3} d^{-1}		Coastal lagoon	See Roberston & Blaber (1992)
Mexico	2450 mg C m^{-2} d^{-1}		Coastal lagoon	See Roberston & Blaber (1992)
Ivory Coast	200 - 5000 mg C m^{-2} d^{-1}		Coastal lagoons	See Roberston & Blaber (1992)
India (west coast)		0.1 – 21.6	Mangrove estuary	Dham et al. (2002)
Brazil		2.5 (average)	Mangrove creeks	Schories et al. (2001) **
Australia		1.3	Mangrove creek	Boto & Bunt (1981)
Kakinada, AP, India	989 mg C m^{-3} d^{-1} (gross) (*) 374 mg C m^{-3} d^{-1} (net) (*)		Marine station (Kakinada Bay)	Selvam et al. 1992
Kakinada, AP, India	3148 mg C m^{-3} d^{-1} (gross) (*) 1368 mg C m^{-3} d^{-1} (net) (*)		Mangrove station	Selvam et al. 1992
Kakinada, AP, India	1200 ± 972 mg C m^{-3} d^{-1} (*)		Gaderu (mangrove creek)	A.V. Raman (unpublished data) and Raman (2000)
Kakinada, AP, India	864 ± 804 mg C m^{-3} d^{-1} (*)		Coringa (mangrove creek)	
Kakinada, AP, India	1932 ± 2340 mg C m^{-3} d^{-1} (*)		Southern Kakinada Bay	
Kakinada, AP, India	2664 ± 1596 mg C m^{-3} d^{-1} (*)		Northern Kakinada Bay	
Kakinada, AP, India		3.5 - 32.1	Mangrove creeks and bay	A. Borges & M. Frankignoulle, unpublished data (see Chapter 4)
Kakinada, AP, India		5.3 – 581.9	Mangrove creeks	Raman (2000)
Kakinada, AP, India		3.0-390.1	Adjacent bay	Raman (2000)

(*) converted from mg C m^{-3} h^{-1} for reasons of conformity by assuming a 12-h daylight period, which approximates the annual average daylength time in that area. (**) : cited in Dittmar & Lara (2001a)

2.2.4. BENTHIC FAUNAL COMMUNITIES OF THE INTERTIDAL HABITATS

Benthic faunal communities in intertidal mangrove forests are usually dominated by brachyuran crabs and mollusks (gastropods and bivalves). A detailed description of the diversity, zonation, ecology and function of these invertebrate groups is beyond the scope of this section, but a general overview of some important aspects will be given. Major restrictions hampering the study of these communities in mangrove habitats include the taxonomical uncertainties in many regions of the world, and the difficulties in obtaining quantitative estimates of their abundance (e.g. Nobbs & McGuinness 1999). Other faunal groups which have received less attention include the meiofaunal component which is usually dominated by nematodes, harpacticoid copepods, and foraminiferans (see Alongi & Sasekumar 1992 and Schrijvers et al. 1995, 1996 for details on this group). For a short overview of the dominant species found in the main study area (Coringa Wildlife Sanctuary, Andhra Pradesh, India), we refer to Chapter 3.

Mollusca

Molluscs are a prominent component of the invertebrate community, and occupy a wide range of ecological niches. The distribution of **bivalves** is usually restricted to a narrow zone along the creek banks, as they require frequent inundation to enable feeding. Bivalves of the family *Lucinidae* have also been found in mangrove sediments (e.g. Frenkiel et al. 1996), and as all members of this family harbour endosymbiotic autotrophic bacteria (located mostly in the gills), this restriction may not hold for them. Another special group of bivalves in mangrove ecosystems are the wood-boring *Teredinidae* ('shipworms'). These bivalves not only bore dead trees but can also colonise living *Avicennia* and *Rhizophora* wood, and their biomass can be substantial. The soft parts of these animals can reach a length of several tens of centimeters, whereas the shell of the largest species known (*Dicyathifer caroli*) reaches only up to 2 cm. These woodboring bivalves are ecologically significant as they stimulate the decomposition of wood and live in symbiosis with nitrogen-fixing bacteria (Waterbury et al. 1983), and it has been suggested that the latter process may represent a very significant yet overlooked source of nitrogen fixation in mangrove ecosystems in view of the abundance of dead wood and *Teredinidae* (Boto & Robertson 1990).

Gastropods include many sediment-dwelling species (e.g. *Assiminea* sp., *Telescopium telescopium*, ...), other species are found on roots, pneumatophores, stems, branches or

leaves. Members of the genus *Littoraria*, in particular, are commonly found on leaves and branches, often high up in the trees. The distribution of gastropod species within a mangrove forest is influenced by a variety of factors such as light (as a major factor determining algal growth and as a factor influencing humidity), tidal exposure, salinity, and substrate type. The trophic position of gastropods is equally varied : sediment dwellers feed -selectively or not- on sediment organic matter and/or microphytobenthos, *Littoraria* spp. feed on epibenthic crusts on stems and roots, and some species have been reported to feed on mangrove litter and/or propagules (such as *Melampus coffeus* and adult *Terebralia palustris*). Predatory and scavenging species such as *Thais* spp. and *Nassarius* spp. are much less abundant. Another particularly interesting groups of gastropods are sacoglossans, of which at least some species are known to occur in mangrove habitats (Swennen 1997, see also Chapter 8 and 9). Many members of this group obtain plastids from algae, which they retain intercellularly and which can remain functional for prolonged periods of time ('kleptoplasty', see Chapter 9 for details). Although the majority of ecological studies on mangrove invertebrates focus on crabs, molluscs can attain a very high species diversity in some mangrove ecosystems : Camilleri (1992) mentions 39 species of gastropods in an Australian mangrove, Jiang & Li (1995) found 52 species of molluscs (24 bivalves, 28 gastropods) in a Chinese mangrove habitat, and Wells (1990) reports 23 mollusc species from a mangrove forest in Hong-Kong. On the other hand, species diversity differs strongly in different parts of the world, e.g. *Melampus coffeus* is the only gastropod present in the mangroves of Guadeloupe. The numerical abundance and biomass of molluscs can be equally impressive (e.g. Sasekumar 1974), and they can even reach higher densities and biomass than brachyuran crabs in some cases (e.g. Wells 1984), although the number of comparative studies is limited.

Brachyura

Together with molluscs, brachyuran crabs are the dominant macrofauna in most intertidal mangrove ecosystems. Early reports on the species diversity of mangrove-associated crabs in the Indo-Pacific (Sasekumar 1974, Jones 1984) now appear to be outdated (see Lee 1998), and as taxonomical difficulties are still a major restriction, the diversity and distribution of mangrove-associated crabs is likely to be far from understood. Ocypodid crabs (*Uca* spp., *Macrophthalmus* spp.) and grapsids (*Sesarminae*, *Metopograpsus* spp., *Metaplax* spp.) usually dominate the crab fauna and species often exhibit marked horizontal and vertical zonation patterns (e.g. Frith et al. 1979, Jones 1984, Frusher et al. 1994, Sivasothi 2000).

Whether these distribution patterns are related to physico-chemical characteristics of the environment (e.g. Frusher et al. 1994), or to the presence of specific tree species or tree diversity, remains to be determined (see Lee 1997, Dahdouh-Guebas et al. 2002).

Similar to the situation observed for molluscs, crabs may show highly diverse feeding patterns. The role of sesarmid crabs in the removal of leaf litter has been well acknowledged in the literature (e.g. Roberston et al. 1986, Lee 1998, Skov & Hartnoll 2002), although recent research indicates that, even though they remove and consume large amounts of mangrove litter as a community, the importance of mangrove litter may not be as important as previously thought (see Chapter 8), and most species of sesarmids spend a considerable amount of time feeding off the sediment surface (Skov & Hartnoll 2002) and will consume a variety of other food sources when available. In addition, it appears that a diet consisting solely of mangrove leaves is insufficient for the long-term survival and for the reproduction of sesarmids (see Skov & Hartnoll 2002 for a discussion). Many other species such as *Uca* spp., *Macrophthalmus* spp. and *Metaplax* spp. are deposit feeders, with differing selectivities for benthic diatoms or cyanobacteria (e.g. Rodelli et al. 1984, France 1998, M. Skov & E. Olaffson unpublished data, see Chapter 8), although there remains considerable contrasting evidence regarding the food sources for *Uca* spp. (e.g. see Dye & Lasiak 1986, 1987, France 1998, Meziane & Tsuchiya 2000). Where present, macroalgae may also be exploited by *Metopgrapsus* spp. (e.g. Dahdouh-Guebas et al. 1999, Fratini et al. 2000b). Predatory or scavenging species include *Scylla* spp., *Thalamita crenata*, *Epixanthus dentatus* (Cannici et al. 1998), and some species of *Metopograpsus* (e.g. Reid 1986a). For more details on the diversity of feeding patterns and the relative importance of mangrove-derived carbon for the brachyuran communities, we refer to Chapter 8.

Due to their large numbers and biomass, crabs play a crucial role in the cycling of organic matter in mangrove ecosystems, and in particular, sesarmid crabs have been documented to be able to retain (i.e. bury and/or consume) significant amounts of leaf litter (e.g. Robertson 1986, McIvor & Smith 1995, Lee 1998). As the diversity and abundance of the intertidal crab fauna -in particular grapsids- in the Indo-Pacific is greater than that in the Caribbean, McIvor & Smith (1995) tested the hypothesis first proposed by Robertson (1987) that leaf litter dynamics may differ strongly in these two biogeographical regions. In their study in the Caribbean, they found no tethered leaves to be consumed by crabs during two days of experimental exposure in the field. In other mangrove forests in the Caribbean region, however, leaf removal by crabs does occur and may be significant (Wiebe & Saucerman, cit. in McIvor & Smith 1995) and even as high as found in Old World mangrove ecosystems

(Twilley et al. 1997). According to Twilley et al. (1997), the relative effects of ecological (mainly retention by crabs) and geophysical processes on litter dynamics can be evaluated by comparing global patterns of leaf fall relative to leaf litter standing crops : higher levels of processing by fauna result in much lower litter standing crops for similar rates of litter fall, and thus, a much higher turnover rate.

Brachyurans are not only an important group of consumers, they also constitute important prey items. Predation on sesarmids by fish has been documented by Sheaves & Molony (2000), and other groups such as *Uca* spp. may also be heavily predated on (e.g. Wilson 1989, Sasekumar et al. 1984).

2.2.5. PELAGIC FAUNA

The abundance and diversity of fish in mangrove creeks and estuaries (e.g. Sasekumar et al. 1992, Robertson & Blaber 1992, Kimani 1996, Ley et al. 1999, Kuo et al. 1999, Vidy 2000), and the large proportion of juveniles that is often found has fueled the idea for decades that mangroves are an important 'nursery area' for fish and certain crustaceans (e.g. penaeid prawns), many of which are of commercial value (e.g. Rönnbäck 1999). The mangrove – fisheries connection has been an issue of a multitude of studies, and an effort is made here to summarise some of the results.

According to Chong (1995, cited in Hogarth 1999), the world-wide distribution of penaeid prawns closely matches that of mangroves. Although the distribution of the two indeed match fairly well, penaeids have a broader distribution, extending to the 15 °C winter isotherm (for mangroves, this is ~ 20 °C) to areas such as California and the Mediterranean (Hogarth 1999). Several authors have found a significant correlation between the annual catch of prawns or fish and the surface area covered by mangroves in a particular region, or the length of the coastline fringed by mangroves (e.g. see Baran & Hambrey 1998 for a recent review). The value of finding such a correlation, however, can be put to question as there is no unambiguous evidence for a direct causal relationship. As Hogarth (1999) correctly states, both extensive areas of mangroves and sizeable populations of penaeids may correlate with the existence of large river estuaries, and thus, mangroves and penaeids may simply both be related to the availability of estuarine conditions. Vidy (2000) also notes that mangroves are often associated with estuarine conditions, making it difficult to distinguish the relative role of mangroves and the presence of estuarine conditions as determinants for the abundance of fish.

His study in an 'inversed estuary' in Senegal (i.e. no freshwater inflow, higher salinities upstream) suggested that good estuarine conditions alone are probably sufficient for a good nursery function, but mangroves alone are not : mangroves in environments without sufficient freshwater inflow were found to harbour significantly less abundant and diverse fish populations.

If there is a true mangrove – fisheries connection, the question arises which factors determine the causes of such a relationship, and several hypotheses have evolved in the literature (note that these hypotheses are mutually non-exclusive) : (1) the *structural heterogeneity hypothesis*, i.e. juveniles are attracted to the structural heterogeneity of mangroves, (2) the *predation risk hypothesis*, i.e. risk of predation in mangrove habitats is lower than in other nearby habitats (which, in turn, may be due to the structural complexity of this habitat), (3) the *food availability hypothesis*, i.e. food is more abundant or more easily accessible in mangrove habitats compared to nearby environments, and (4) the *lateral trapping hypothesis*, i.e. the different hydrodynamics inside the mangroves enable the retention of larvae and juveniles (e.g. see Chong et al. 1996). Note that the food availability hypothesis does not necessarily imply a direct or indirect trophic link between mangroves and fish, but that mangroves may simply harbour a more abundant stock of potential prey items. Recently, Laegdsgaard & Johnson (2001) tested the first three hypotheses in both field and laboratory experiments, and found that juvenile fish were not attracted to structure *per se* but will move into shelter in the presence of predators or when food is associated with shelter. That an increase in structural complexity decreases the risk of predation on penaeids was shown experimentally by Primavera (1997). Laegdsgaard & Johnson (2001) suggested that the interplay between reduced risk of predation and reduced foraging succes (both as a result of increased structural complexity) favoured mangrove habitats to seagrass beds for juvenile fish. It should be mentioned that some of these results can probably not be extrapolated to all fish species, as coral reefs, seagrass beds and mangroves (co-occurring in many areas of the world) may all function as nursery sites, with different species preferring different habitats (e.g. Nagelkerken et al. 2000b).

2.3. Carbon Flow in Mangrove Ecosystems

The fate of mangrove litter has been a longstanding issue of debate in the literature. In the 1970's, Odum & Heald proposed their 'outwelling' hypothesis, stating that aquatic foodwebs in estuarine mangrove ecosystems are largely driven by the inputs of leaf litter. Although many aspects of the fate of mangrove carbon and other primary producers will be dealt with more thoroughly in Chapters 4-10 as the results of this study will be discussed, a general overview will be presented of the production of mangrove biomass and its potential fate in the environment (e.g. degradation, burial, export, and utilization by fauna). A simplified representation of the major pathways through which mangrove biomass may be processed is shown in Figure 1.

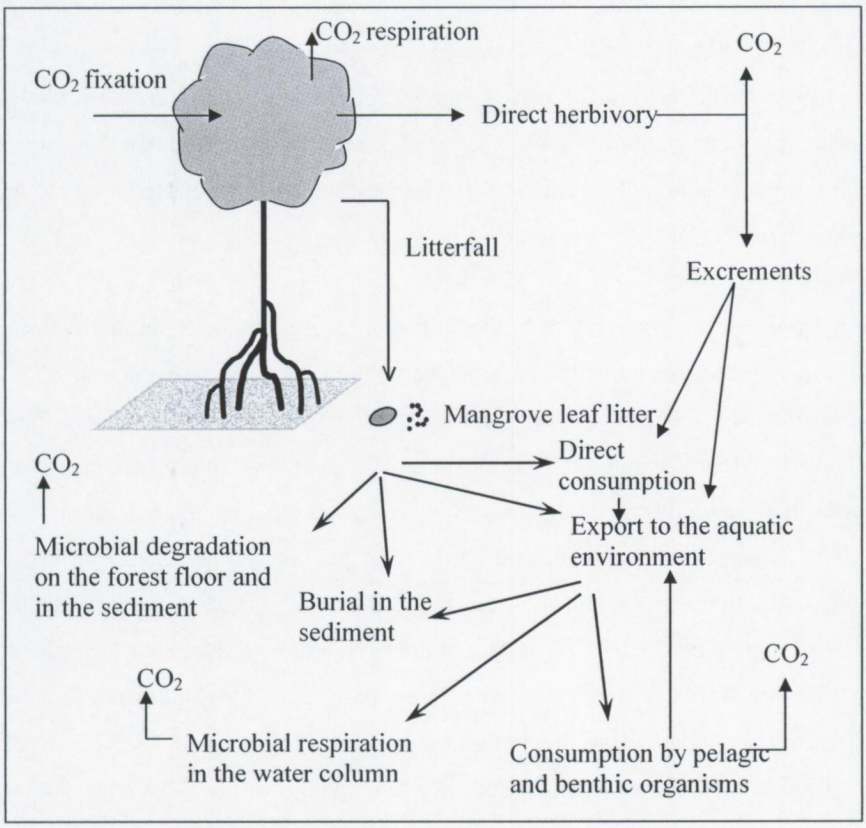


Figure 1 : Schematic representation of the potential fate of mangrove primary production.

2.3.1. PRODUCTION OF MANGROVE BIOMASS

The measurement of mangrove **biomass** (belowground and aboveground) is not a simple operation, and is usually estimated based on empirical relationships between practical measures of tree size and total biomass, established by cutting down a sample of trees over a range of sizes, weighing them and correlating this with either DBH or GBH (diameter at breast hight and girth at breast hight, respectively). This method, although not always being very accurate (see Hogarth 1999), remains the most convenient way to estimate biomass standing stocks.

Total aboveground biomass estimates vary widely, being higher at low latitudes and declining to the north and south (as with primary productivity, see below), albeit with considerable local variability (Twilley et al. 1992). Biomass estimates thus range from near 0 to over 400 tons per hectare (see Twilley et al. 1992). The main trunk of the tree dominates the biomass, with aerial roots (if present), branches and leaves being much less important. Few reliable estimates exist for belowground biomass, but the few estimates that have been made indicate a very substantial contribution : 29.7 % for an Australian mangrove forest (Matsui 1998) and a overall estimate between 36.5 and 54.8 % (Twilley et al. 1992, but see Gong & Ong 1990 : < 20 %).

Whereas biomass of mangrove forests in equilibrium is a static measure, the rate of **primary production** may be ecologically more relevant, as it indicates the amount of energy or organic matter which becomes available for export, burial, respiration or as a food source. One widely used (e.g. Clough 1998, Alongi et al. 2000a) method to estimate *potential* primary production is to measure the attenuation of light as it passes through the canopy, and apply some basic assumptions on the relative amounts of chlorophyll per leaf at different heights and the assimilation efficiency of the trees to calculate the (**gross**) primary production (Bunt et al. 1979, English et al. 1997, cit in Hogarth 1999), although this method tends to provide only a 'snapshot' view. As some of the carbon initially fixed by photosynthesis will be used for respiratory processes, these should be deducted in order to obtain an estimate of the **net** primary productivity. A more simple and time-integrated method to estimate the rate of net primary production is therefore simply to directly measure the increase in standing biomass and the amount of shedded biomass (**litter fall**, i.e. leaves, flowers, twigs) by collecting it at periodic intervals in litter traps of an appropriate mesh size. Although the method obviously

also has its restrictions (the most important one being that the increase in root and wood tissue is difficult to measure and is thus usually not taken into consideration), most studies have reverted to it to measure net primary production. Litter fall rates (absolute) appear to decrease with distance from the equator (see Twilley et al. 1992 and Alongi 1998), and are -evidently- lower in 'dwarf' or stunted mangroves (Twilley et al. 1992). Litter fall may also differ between species (e.g. Rao 1998) or between different zones within a forest (e.g. higher near the water front, Amarasinghe & Balasubramaniam 1992). Table 3 gives a non-exhaustive overview of some literature data (see also Twilley et al. 1992). Litter fall may be seasonal in some locations (e.g. Duke et al. 1984, Saenger & Snedaker 1993, Twilley et al. 1997, for *Excoecaria agallocha* in Dehairs et al. 2000), but not in others (e.g. for *Avicennia marina* in Dehairs et al. 2000).

Table 3 : Examples of rates of litterfall (LF) -as a proxy for net primary production- for various mangrove forests. Rates are expressed in g dry weight (DW) m^{-2} y^{-1}. More data can be found in Twilley et al. (1992) and Saenger & Snedaker (1993). Available data from the study area are grey-shaded.

Location	Species	LF	Data Source and Remarks
New Zealand	*Avicennia marina*	180 - 620	May (1999)
Kenya	*Ceriops tagal*	374	Slim et al. (1996)
Sri Lanka	Mixed, fringing	407*	Amarasinghe & Balusubramaniam (1992)
Ecuador	Mixed *Rhizophora* spp.	518	Twilley et al. (1997)
Sri Lanka	Mixed, estuarine	588*	Amarasinghe & Balusubramaniam (1992)
Florida	*Rhizophora mangle*	620	McKee & Faulkner (2000), site WS
Ecuador	Mixed *Rhizophora* spp.	639	Twilley et al. (1997)
Australia	mixed	640	Clough (1998)
India	*Avicennia marina*	653	Rao (1998)
Tanzania	*Ceriops tagal*	700	Shunula & Whittick (1999)
New Zealand	*Avicennia marina*	760	Woodroffe (1985)
Florida	*Rhizophora mangle*	767	McKee & Faulkner (2000), site HC
Tuvalu	*Rhizophora stylosa*	777	Woodroffe & Moss (1984)
Australia	*Sonneratia alba*	790	Duke et al. (1981)
Australia	*Avicennia sp.*	805	Duke et al. (1981)
Kenya	*Rhizophora mucronata*	984	Slim et al. (1996)
Australia	*Rhizophora stylosa*	930	Duke et al. (1981)
Australia	*Bruguiera parviflora*	1000	Duke et al. (1981)
Malaysia	*Mixed species*	1018	Ashton et al. (1999)
India	*Avicennia officinalis*	1020	Wafar et al. (1997)
Ecuador	Mixed *Rhizophora* spp.	1055	Twilley et al. (1997)
China	*Aegiceras & Kandelia*	1069	Tam et al. (1998)
Mexico	*Laguncularia racemosa*	1100	Flores-Verdugo et al. (1987)
India	*Rhizophora apiculata*	1170	Wafar et al. (1997)
Kenya	*Rhizophora mucronata*	1175	Woitchik et al. (1997) - wet season
India	*Rhizophora mucronata*	1180	Wafar et al. (1997)
Tanzania	*Avicennia marina*	1200	Shunula & Whittick (1999)
India	*Excoecaria agallocha*	1360	Rao (1998)
Tanzania	*Rhizophora mucronata*	1400	Shunula & Whittick (1999)
Tanzania	*Bruguiera gymnorrhiza*	1600	Shunula & Whittick (1999)
India	*Avicennia marina*	1603	Ghosh et al. (1990)
India	*Sonneratia alba*	1700	Wafar et al. (1997)
Kenya	*Rhizophora mucronata*	1701	Woitchik et al. (1997) - dry season
Vietnam	*Rhizophora. apiculata*	941-1879[a]	Clough et al. (2000)
Hawaii	*Rhizophora. mangle*	2520	Cox & Allen (1999)

* : The same authors also report an annual rate of aboveground woody growth of 615 and 287 g m^{-2} for the estuarine and fringing mangroves, respectively.

[a] : range of values obtained for forest stands of different ages.

2.3.2. Degradation of Mangrove Litter

When leaves fall on the sediment, decay will be initiated, and rapid weight loss will occur. During the first 10-14 days this is mainly due to physical leaching of dissolved organic matter (see Wafar et al. 1997), causing up to 50 % of the initial dry weight to be lost (e.g. Rao 1998, see Figure 2). Subsequent weight loss is mainly due to the degradation by bacteria and fungi, which are initially inhibited by the concentrations of soluble tannins in the leaf. The decrease in dry weight (an example is shown in Figure 2) can be described by an exponential equation :

$$DW_t = DW_{t=0}\ e^{-k_d t} \qquad \text{(eq. 2.1)}$$

Where :

DW_t : dry weight remaining at time t [g], can also be expressed as a percentage of the initial weight.

$DW_{t=0}$: initial dry weight [g]

k_d : decay constant [day^{-1}]

t : time [day]

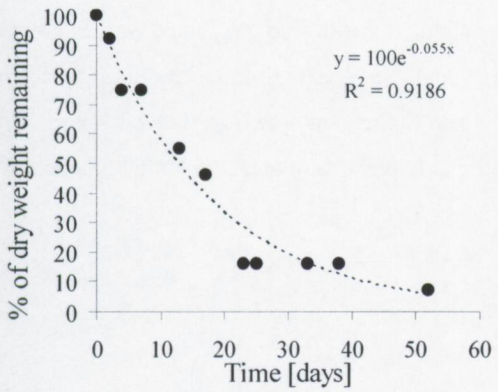


Figure 2 : Loss of dry weight (in %) for *Avicennia marina* litter during the wet season in the Coringa Wildlife Sanctuary, Andhra Pradesh, India (recalculated from data in Rao 1998). The dotted line represents an exponential fit.

The decay constant, k_d (see Table 4 for some examples) is a useful parameter to compare the relative degradability of litter of various mangrove species (Ashton et al. 1999) or different parts of mangrove trees (e.g. Mackey & Smail 1996, McKee & Faulkner 2000, Middleton & McKee 2001), the rate of microbial decay between seasons (e.g. Mackey & Smail 1996, Twilley et al. 1997), or sites on different elevations (Mackey and Smail 1996, Dick &

Osunkoya 2000, Mfilinge et al. 2002). Decomposition rates of litter thus appear to be significantly higher in lower elevation sites which are more frequently inundated -in agreement with the observation that degradation of litter is markedly faster under submerged conditions (e.g. Flores-Verdugo et al. 1987), and higher during the rainy season compared to the dry season (Twilley et al. 1997, Rao 1998). However, some authors have used a slightly different procedure to calculate k_d, e.g. Rao (1998) and Ashton et al. (1999) used an exponential fit to equation (2.1) but without fixing the intercept of the curve at the initial weight or at 100 %, and this may induce a large difference in the estimated k_d. Tam et al. (1990) even used a linear equation to describe the weight loss during decomposition of mangrove litter. Thus, some caution is required when comparing k_d values from different studies.

Although Mackey & Smail (1996) suggested that there might be a relationship between the decomposition rate of *A. marina* leaves and geographical latitude, a larger compilation of literature data for this species (see Table 4) does not appear to support this idea and suggests that local environmental factors (temperature, frequency of inundation) and nutrient status (Twilley et al. 1997) may be more important in determining k_d factors, which show a remarkably wide range of values (2 orders of magnitude) when results from various studies are compared (Table 4). Another important observation (which will be discussed further in later chapters) is that the decay coefficients measured in the Coringa Wildlife Sanctuary (i.e. the main study site) are in the upper range of recorded values, whereas the average litterfall for *Avicennia* and *Excoecaria* in this area is within the range of expected values for this latitude (Twilley et al. 1992) - suggesting that the relative importance of microbial decomposition is high in this site. This is shown in Figure 3 where litter fall rates and decay coefficients from different studies in which both parameters were measured, are compared.

Table 4 : Non-exhaustive overview of decay constant values (k_d) for mangrove leaf litter reported in the literature, arranged from low to high rates of decomposition. Data from the study sites are grey-shaded. Only data from experiments conducted in intertidal areas (i.e. not under continuously submerged conditions) are included.

Litter type	**Remarks**	**k_d [day^{-1}]**	**Source**
Avicennia marina	Landward zone	0.0014	Dick & Osukoya (2000)
Sonneratia alba		0.0019	Wafar et al. (1997)
Rhizophora mucronata		0.002	Wafar et al. (1997)
Avicennia marina	On iron-smelting slag	0.00234	Dick & Streever (2001)
Rhizophora apiculata		0.0024	Wafar et al. (1997)
Avicennia marina	On sand	0.00299	Dick & Streever (2001)
Rhizozphora mangle		0.003 – 0.005	Twilley et al. (1986)
Different species	Restored site	0.0040	McKee & Faulkner (2000)
Aegiceras corniculatum	Winter	0.0065	Tam et al. (1990)
Avicennia marina	Winter, high elevation	0.0071	Mackey & Smail (1996)
Bruguiera gymnorrhiza		0.008-0.012	Steinke & Ward (1987)[a]
Different species	Natural site	0.0080	McKee & Faulkner (2000)
Avicennia marina		0.0086	Dick & Osunkoya (2000)
Avicennia marina	Winter, low elevation	0.0089	Mackey & Smail (1996)
Bruguiera parviflora		0.010	Ashton et al. (1999)
Not specified		0.01	de Boer (2000)
Avicennia officinalis		0.0104	Wafar et al. (1997)
Rhizophora mucronata	Dry season	0.0112	Woitchik et al. (1997)[b]
Kandelia candel	Winter	0.0114	Lee (1989)
Different species	Restored site	0.0115	McKee & Faulkner (2000)
Avicennia marina	Summer, high elevation	0.0118	Mackey & Smail (1996)
Avicennia marina		0.012 - 0.021	Steinke & Ward (1987)[a]
Kandelia candel	Winter	0.0124	Lu & Lin (1990)[a]
Avicennia marina	Winter	0.0126	Tam et al. (1990)[a]
Avicennia marina	Dry season	0.013	Rao (1998)
Different species	Natural site	0.0132	McKee & Faulkner (2000)
Aegiceras corniculatum	summer	0.0146	Tam et al. (1998)
Avicennia marina	Summer, low elevation	0.0158	Mackey & Smail (1996)
Rhizophora apiculata		0.016	Ashton et al. (1999)*
Mixed *Rhizophora*	Different sites & seasons	0.003 – 0.016	Twilley et al. (1997)
Kandelia candel	winter	0.0164	Tam et al. (1990)

Table 4 (continued)

Litter type	Remarks	k_d [day^{-1}]	Source
Rhizophora stylosa		0.0178	Robertson (1988)[a]
Rhizophora mucronata		0.020	Ashton et al. (1999)*
Mixed species litter		0.020	Ashton et al. (1999)*
Bruguiera gymnorrhiza		0.022	Mfilinge et al. (2002)
Ceriops tagal		0.0257	Robertson (1988)[a]
Avicennia marina	Winter	0.0277	Lu & Lin (1990)[a]
Excoecaria agallocha	Dry season	0.034	Rao (1998)
Kandelia candel	Summer	0.0385	Lu & Lin (1990)[a]
Sonneratia alba		0.047	Ashton et al. (1999)*
Kandelia candel	Summer	0.0516	Tam et al. (1998)
Laguncularia racemosa		0.052	Flores-Verdugo et al. (1987)
Excoecaria agallocha	Wet season	0.053	Rao (1998)
Avicennia marina	Wet season	0.055	Rao (1998)
Kandelia candel		0.062	Mfilinge et al. (2002)
Avicennia marina		0.063	Robertson (1988)[a]
Rhizophora mucronata	Wet season	0.1004	Woitchik et al. (1997)[b]
Avicennia marina	Summer	0.1155	Lu & Lin (1990)[a]

* Note that these authors used a slightly different method of calculation k_d (see text for details).
[a] : cited in Tam et al. (1998).
[b] : calculated from the data given in the relevant publication.

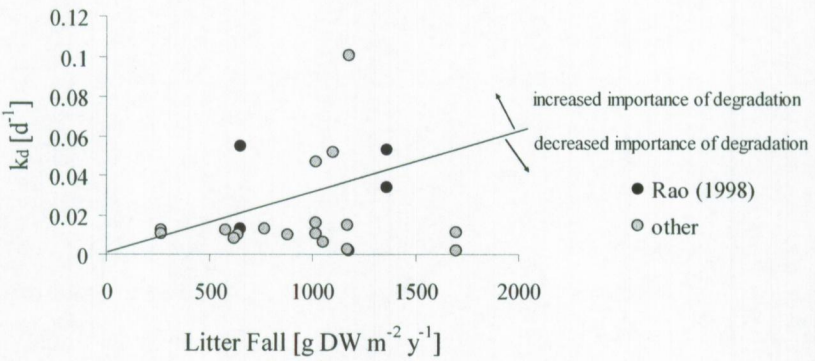


Figure 3 : Decay constant (k_d) versus litter fall for the Coringa Wildlife Sanctuary (*Avicennia officinalis* and *Excoecaria agallocha*) and other studies (Woodroffe 1985, Flores-Verdugo et al. 1987, Twilley et al. 1997, Wafar et al. 1997, Woitchik et al. 1997, Tam et al. 1998, Ashton et al. 1999, McKee & Faulkner 2000). Note that the data by Rao (1998) represent total annual litter fall rates, but decay constants for 2 different seasons per species.

Throughout the decomposition process, major **changes in leaf chemistry** occur (e.g. Neilson & Richards 1989), the most notable from an ecological perspective being the leaching of dissolved tannins (which have a negative effect on e.g. microbial activity and meiofaunal abundance, see e.g. Alongi 1987c, González-Farias & Mee 1988), and the changes in the carbon and nitrogen content of the litter. Re-absorption of N (e.g. Woitchik et al. 1997, McKee & Faulkner 2000) and other elements (e.g. P and K, see Lin & Wang 2001) before the leaves are shed appears to be an efficient way to preserve these elements, whereas other elements such as Na, Cl, Ca, and Mg accumulate in the senescent leaves and are thus discarded with leaf shedding. Although fresh (i.e. green) mangrove leaves are reported to have C:N ratios ranging between 20 and 78 (average around 50, e.g. Rao et al. 1994, Twilley et al. 1997, Sherman et al. 1998), this ratio increases two- to threefold during senescence due to re-absorption of 50 to 80 % of the nitrogen by the plants (Rao et al. 1994, Jennerjahn & Ittekkot 1997, Lin & Wang 2001). During subsequent decomposition and bacterial colonization, however, nitrogen enrichment occurs due to nitrogen fixation (Woitchik et al. 1997) and due to immobilization, both on the forest floor (Twilley et al. 1986) and in the water column (Cifuentes et al. 1996, see also Caraco et al. 1998). This results in much lower C:N ratios for mangrove detritus (e.g. Wafar et al. 1997). According to Cifuentes et al. (1996), suspended mangrove detritus (defined as suspended matter in the mangrove estuary they studied and having a carbon-to-chlorophyll a ratio higher than 1000) has an average C:N ratio of 12.1, whereas others (see Skov & Hartnoll 2002 for a more comprehensive overview) report C:N ratios of 24 to 51 after 45 days of decomposition for *Excoecaria agallocha* and *Avicennia marina,* respectively (Dehairs et al. 2000), C:N ratios approaching 24 after about 100 days of decomposition for *A. marina, A. corniculatum* and *Kandelia candel* (Tam et al. 1990), values between ~25 and 60 after 124 days of decomposition for *K. candel* and *Bruguiera gymnorrhiza* (Mgfilinge et al. 2002), and values as low as 5 to 20 for different mangrove species after 3 months of decomposition (Wafar et al. 1997). This decrease in C/N ratios is an important ecological process, as it is associated with an increase of the nutritional value of the organic matter (the 'Russel-Hunter Ratio' of 17.1 is often quoted as the maximum C/N ratio in order for a substrate to be of nutritional value for invertebrates).

Once litter becomes part of the sediment organic matter pool, microbial respiration continues but based on the available estimates, rates of **total sediment respiration** (see Table 5) appears at first to be fairly small compared to the net primary productivity of the mangrove trees:

- between 3 and 7 % for Western Australian sites (see Alongi et al. 2000a)
- estimated at 27 – 40 % in several *Rhizophora* forests in Thailand (Alongi et al. 2001)
- 18 and 28 % for two *Rhizophora* stands of different age in Malaysia (Alongi et al. 2000b)
- 18 % in Rookery Bay, Florida (see Alongi et al. 2000a)
- 9 % in north Queensland mangroves (see Alongi et al. 2000a)
- estimated at 98 to > 450 % (see text below for explanation) for *Rhizophora* and *Ceriops* in Gazi Bay, Kenya (from data in Slim et al. 1996 and Middelburg et al. 1996).

Table 5 : Overview of rates of total sediment respiration reported in the literature from (intertidal) mangrove sediments. All rates were converted to the same units.

Respiration rate (mmol CO_2 m^{-2} d^{-1})	**Source**	**Remarks**
8.9-20.9	Alongi et al. (1998b)	
46.5 - 52.9	Alongi et al. (2000a)	*Rhizophora*
28.5 - 48.3	Alongi et al. (2000a)	*Avicennia*
17.1	Alongi et al. (2000b)	8 yr old forest
48.1	Alongi et al. (2000b)	6 yr old forest
53.7	Alongi et al. (2000b)	35 yr old forest
92.6	Middelburg et al. (1996)	*Rhizophora*
192.6	Middelburg et al. (1996)	*Ceriops*
16.7	Lugo et al. (1974)*	
30.8	Golly et al. (1962)*	
-104 to 50	Kristensen et al. (1992)	
69.9 - 86.1	Kristensen et al. (1991)	
43.1 - 49.4	Kristensen et al. (2000)	
5.0 – 80.6	Alongi et al. (2001)	*Rhizophora***

* cit. in Lugo & Snedaker (1974).
** : range of values found in different sites and during different seasons.

Alongi et al. (2000a) compared these T_{COX}/NPP ratios (i.e. ratios of total sediment respiration to forest net primary production) with a limited number of data from 4 North American salt marsh ecosystems (T_{COX}/NPP between 40 and 89 %), and concluded that mangroves are more efficient at immobilizing and conserving organic carbon. However, the salt marshes along the North American coastline differ strongly from their European and SE United States counterparts in the proportion of local vascular plant production that is retained in the sediments (see Middelburg et al. 1997), and mangroves may show an equal variability in the contribution of mangrove carbon in the sediment organic matter pool (see Chapter 7).

Therefore, the suggestion of Alongi et al. (2000a) may not be universally valid. Indeed, Middelburg et al. (1996) measured total CO_2 fluxes in the sediments of Gazi Bay (Kenya), and found average fluxes of 192.6 and 92.6 mmol C m^{-2} d^{-1} for *Ceriops* and *Rhizophora* sediments, respectively. If we compare these with the litterfall estimates provided by Slim et al. (1996) for the same area (average of results for rainy season and dry season : 1.05 and 2.51 g m^{-2} day^{-1}, which amounts to 39.4 and 94.1 mmol C m^{-2} d^{-1} for *Ceriops* and *Rhizophora*, respectively), it becomes apparent that for the *Ceriops* sediments, the total CO_2 flux from the sediments appears to exceed substantially (> 450 %) the litter inputs, whereas for *Rhizophora* the total sediment respiration is as large as 98 % of the total litterfall. Although it should be noted that the different results may in part have been caused by the different methods used to measure CO_2 fluxes (see Kristensen et al. 1991) and that the flux data represent only a limited time frame, the latter estimates clearly suggest that the choice of study sites may have biased the suggestion of Alongi et al. (2000a).

Another aspect which has received little attention is the origin of the organic matter that is mineralized. CO_2 flux measurements do not discriminate between different sources, and comparing them solely with mangrove primary production may not always give a complete picture when microphytobenthic production is significant or when external inputs of organic matter (e.g. seagrass litter, phytoplankton) are important (see chapter 7). Some evidence for selective degradation is provided by the study of Holmer et al. (2001), who noted that changes in sediment organic matter composition along a mangrove-seagrass transect (as reflected by C/N ratios) were not accompanied by similar variations in porewater DIC/NH_4^+ ratios, and the generally low DIC/NH_4^+ ratios observed were interpreted as suggesting preferential decomposition of a more labile fraction of the SOM pool. Furthermore, Alongi et al. (2001) recently found that rates of total carbon mineralization in mangrove sediments did not correlate with mangrove primary productivity, but rather with rates of sediment accumulation, which may suggest that selective respiration of external carbon inputs takes place. Lee (1997, 1998) proposed an important role for sesarmid crabs in the decomposition process of mangrove litter by 'pre-processing' mangrove litter and making it available as faecal pellets – the latter being more readily available for bacterial decomposition and invertebrate consumers. Kristensen & Pilgaard (2001) recently confirmed experimentally that faecal pellets of sesarmids are decomposed more rapidly than fresh or water-leached *Rhizophora* leaves, although the importance of this effect on an ecosystem level is not yet known.

In many cases, oxic respiration and sulphate reduction appear to be the dominant metabolic pathway of sediment organic matter degradation (Kristensen et al. 1991, 1992, Nedwell et al.

1994, Alongi et al. 2000a,b, Kristensen & Pilgaard 2001), but precise interpretation of the relative importance of these two processes is difficult, as a discrepancy between rates of sulphate reduction and total CO_2 fluxes are often observed (i.e. the former being larger than the latter). In some areas, Fe(III) has also been reported to be an important electron acceptor for suboxic respiration in mangrove sediments (Kristensen et al. 2000). Clearly, there is a need for more comparative studies to understand the relative importance of different degradation pathways in different environmental settings.

2.3.3. MANGROVES : SOURCE OR SINK OF ORGANIC CARBON AND NUTRIENTS ?

The export of mangrove litter -as leaves, particulate or dissolved organic matter, or even as faunal biomass- has long been quoted as one of the important characteristics of mangrove ecosystems. As this exported material has even been considered to support offshore faunal communities, including commercially important prawn and fish stocks, it remains an often quoted argument for their conservation. The 'outwelling hypothesis', formulated by Odum & Heald (e.g. Odum & Heald 1972, 1975) was later challenged in a number of studies, and an excellent review on the subject can be found in Lee (1995), although a considerable amount of studies has appeared more recently. Lee concluded that export appears to be a feature of most tidally inundated mangroves, although there are also reports of mangroves being net importers of organic carbon and nitrogen (e.g. Morell & Corredor 1993 for the latter). An overview of most studies dealing with export of organic matter from mangrove forests is given in Table 6. It should be stressed, however, that not all studies used the same methodology to measure or estimate the degree of export, and that in some cases, only the amount of mangrove export is considered, but not the possible import of organic matter from the marine or estuarine environment. Therefore, export of mangrove carbon does not necessarily imply that *net* export of organic matter occurs between the mangrove forests and the adjacent environment, as the amount of organic matter imported during high tide may exceed that of outwelled mangrove carbon. Sedimentation is prevalent in many mangrove ecosystems (e.g. Twilley et al. 1992 for an overview, and Ellison 1998), and although a major fraction of the material that settles during inundation is usually inorganic (Twilley et al. 1992, Wolanski et al. 1998, Tanaka et al. 1998), the amount of organic matter from non-mangrove origin which is thus imported in mangrove ecosystems may represent a significant yet often ignored flux of organic matter.

Several recent long-term flux measurements offer particularly enlightening views on the export of organic matter and nutrients from mangrove forest, notably those by Dittmar & Lara (2001a, b), Dittmar et al. (2001) and Davis et al. (2001a, b). Dittmar & Lara (2001a, b) found strong evidence for outwelling of DOC and POC (as well as nutrients) from one of the world's largest mangrove forests in northern Brazil. According to these authors, a supply of inorganic nutrients in excess of the demand of the benthic community and the mangrove trees is an evident prerequisite for outwelling, and may partly explain the comparatively high export rates observed in their study. According to the same authors, such an excess of nutrients is closely related to nitrogen fixation rates and a positive sedimentation balance (i.e. net sedimentation, not erosion), the latter enabling high mineralization rates. The dominant pathway for nutrient and DOM outwelling according to Dittmar & Lara (2001a) is tidally induced porewater flow from the upper sediment horizon into the creek and subsequently into the estuary. Therefore, although phytoplankton activity can strongly influence the nutrient and organic matter concentrations in creeks and can lead to diel asymmetries in their fluxes, the flux *direction* itself is physically determined by the hydraulic gradient between pore- and creekwater. In addition, advective flow of nutrient-rich sediment water towards tidal creeks would lead to considerable potential outwelling, whereas diffusive solute exchange would be much less effective. The effect of the tidal regime is evident, as macrotidal settings are more likely to allow a significant flow of porewater to the tidal creeks.

Another striking finding is that DOC may be a more important form under which mangrove-derived carbon is being exported (e.g. Twilley 1985, Wafar et al. 1997, Dittmar et al. 2001), but few studies have incorportated DOC in their mass-balance equations or flux measurements. This implies that many of the quantitative data presented in Table 6 should be interpreted with caution as they only included the particulate organic fraction. In the few studies where concentrations of DOC and POC (or TOC) have simultaneously been measured, the former has invariably been found to be dominant (see Table 7, see also Mueller & Ayukai 1998). On the other hand, the magnitude and direction of DOC and POC fluxes are not necessarily proporional : Davis et al. (2001a, b) for example, found consistent and significant import of DOC, whereas POC flux direction and magnitude was highly variable.

Table 6. A non-exhaustive overview of reports of import/export rates of organic carbon in mangrove ecosystems. Adapted from Lee (1995), Ewel et al. (1998), and Jennerjahn & Ittekkot (2002).Whenever possible, export rates have been expressed in or converted to [g C m^{-2} y^{-1}] using related data on fluxes, areas, in the literature source.

LOCATION	MATERIAL	EXPORT/IMPORT	RATE	SOURCE
Florida, USA	OC	Export	186 g C m^{-2} y^{-1}	Heald (1969)[a]
Florida, USA	OC	Export	292 g C m^{-2} y^{-1}	Odum & Heald (1972)
Florida, USA	OC	Export	91 g C m^{-2} y^{-1}	Lugo & Snedaker (1974)
Australia	Detritus	Export	No quantitative data	Wolanski et al. (1980)
Australia	POC	Export	420 g C m^{-2} y^{-1}	Boto & Bunt (1981)
Florida, USA	POC and DOC	Export	63.7 g C m^{-2} y^{-1}, of which 75 % as DOC	Twilley (1985)
Australia	POC	Export	40 % of all litter produced	Van der Valk & Attiwill (1984)[b]
India	-	Export	261 t C y^{-1} to estuarine waters	Subramaniam et al. (1984)
Thailand	POC	Export	No quantitative data	Chansang & Poovachiranon (1985)[b]
Australia	OC	Export	No quantitative data	Clark (1985)[b]
Malaysia	Not specified	Export	176 g C m^{-2} y^{-1}	Gong & Ong (1990)
New Zealand	POC	Weak export	< 2 % of produced detritus < 110 g C m^{-2} y^{-1}	Woodroffe (1985a, b)
Australia	-	Export		Woodroffe et al. (1988)[c]
Australia	POC	Export	340 g C m^{-2} y^{-1}	Robertson (1986)
Australia	OC	Variable	No significant net flux	Boto & Wellington (1988)
Australia	OC	Export	No quantitative data	Robertson (1988)
Australia	POC	Export	No quantitative data	Robertson & Daniel (1989)
Hong Kong	POC	Limited export	2 g C m^{-2} yr^{-1} of mangrove origin exported	Lee (1989)

[a] : cited in Ewel et al. (1998)
[b] : cited in Lee (1995)
[c] : cited in Jennerjahn & Ittekkot (2002)

Table 6 (continued).

LOCATION	MATERIAL	EXPORT/IMPORT	RATE	SOURCE
Hong Kong	POC	Import	< 1 % exported, high accumulation	Lee (1990)
Bahamas	OM	Export	No quantitative data	Moran et al. (1991)
Australia	POC and DOC	Variable	Net import or export, depending on site and season. DOC : 20.5 g C m^{-2} y^{-1}	Ayukai et al. (1998)
Australia	POC	Export	Not expressed per unit area	Wolanski et al. (1998)
Australia	POC and DOC	Export	994 g C m^{-2} y^{-1}	Alongi et al. (1998)
Papua New Guinea		Export	343 g C m^{-2} y^{-1}	Robertson & Alongi (1995)
Florida	TOC and DOC	Variable	TOC : little net flux, variable DOC : consistent import, 6.4 -74.4 g C m^{-2} y^{-1}	Davis et al. (2001a,b)
Zanzibar	POC and DOC	Export	295 g C m^{-2} y^{-1}, of which 78 % as DOC	Machiwa (1999)
Brazil	DOC	Export	~ 43.8 g DOC m^{-2} y^{-1}	Dittmar & Lara (2001b)
India	POC and DOC	Export	183 g POC m^{-2} y^{-1} 320 g DOC m^{-2} y^{-1}	Wafar et al. (1997)

Table 7 : Comparison of concentrations of total, particulate, and dissolved organic carbon from different mangrove ecosystems.

LOCATION	TOC	POC	DOC	REMARKS	DATA SOURCE
Caeté estuary, Brazil	600 µM	240 µM	360 µM	Annual average	Dittmar & Lara (2001a, b)
Taylor River, Florida	727-1821 µM	On average 5 % of TOC	657-1691 µM	Annual range	Davis et al. (2001a)
Rookery Bay, Florida	783 - 1750 µM		583-1667 µM		Twilley (1985)
Coral Creek, Australia			92-125 µM		Boto & Wellington (1988)
Kakinada, AP, India		0.692 - 2.824 mg l^{-1}	1.3 -8.7 mg l^{-1} (average 73 % of TOC)	Only pre-monsoon data	see Chapter 4

The use of DOC by bacterial communities is an important step in the carbon flow in aquatic ecosystems, thereby either channeling DOC into a 'recycling loop' wherein it is ultimately respired or made available to higher trophic levels. Insights into the sources of DOC can be derived from either stable isotope analyses, the identification and quantification of specific compounds (e.g. Dittmar et al. 2001), or natural fluorescence (e.g. Moran et al. 1991), yet few studies exist on the sources of DOC in mangrove ecosystems.

Lara & Dittmar (1999) and Dittmar & Lara (2001a) concluded from the day/night shifts in DOC concentrations that photosynthetic activity (i.e. by phytoplankton) produced a measurable increase in DOC concentrations (by 25 ± 14 µM, i.e. ~ 8 % of the DOC pool). Holmer et al. (2001) found that efflux of DOC from mangrove sediments was higher during the day than during the night, suggesting that benthic microphytes contributed to the aquatic DOC pool releasing organic compounds. 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 higher during high tide. Offshore (~1 km), however, mangrove-derived carbon was estimated to comprise only about 10 % of the DOC pool. In contrast, Boto & Wellington (1988) found no apparent link between DOC and primary production (i.e. no day/night shifts in DOC concentrations) and concluded that the majority 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 DOM pool in a mangrove estuary in northern Brazil throughout 18 tidal cycles in the course of one year. The results of their study naturally show wide seasonal and spatial variations in the contributions of these 3 sources (which also depended strongly on the parameters used for the calculations), but notwithstanding these variations, DOM in a mangrove creek was shown to be mostly of mangrove origin (~ 60 %), with marine-derived organic matter making up most of the remaining DOM (~ 35 %). Surprisingly, mangrove DOM was found to behave conservatively in the estuary (in contrast to mangrove POM), suggesting outwelling of mangrove-derived DOM in their study area without much local processsing.

In any case, in those ecosystems where export of mangrove carbon has been established, the geographical extent to which this occurs appears to be much more limited than initially thought, often restricted to 1-2 km from the forest edge (see Lee 1995) . This is confirmed by stable isotope studies in which spatial gradients in $\delta^{13}C$ signatures (whether being the result of a decreasing importance of mangrove litter or the result of a spatial gradient in inorganic

carbon $\delta^{13}C$ is not relevant here, see Chapters 4-6) have been found to be very sharp. One of the causes underlying this limited spatial extent of outwelling may be the existence of stable coastal boundary layers (Wolanski 1995, Kitheka 1997).

One last aspect which deserves some consideration is the fact that both export and import of (different sources of) organic matter may occur simultaneously. E.g. it is quite conceivable that mangrove-derived carbon is exported by tidal action as macrolitter or e.g. as DOC via porewater entering tidal creeks (e.g. see Dittmar & Lara 2001a), whereas external C sources such as seagrass litter and phytoplankton are deposited during each tidal cycle. Machiwa (1999), for example, observed a net import of suspended particulate matter (SPM) in a mangrove forest in Zanzibar, and noted that ebb flow mobilized relatively low levels of SPM with a high organic carbon content, whereas during high tide, high concentrations of SPM were brought in, but these had a relatively low organic carbon content.

Most studies where the exchange of **inorganic nutrients** across the sediment-water interface have been studied (e.g. Boto & Wellington 1988, Kristensen et al. 1988, Alongi et al. 1993, Rivera-Monroy et al. 1995, Alongi 1996, Kristensen et al. 1998 Holmer et al. 2001) show a net uptake of inorganic nutrients (such as N, P, Si) by intertidal sediments, suggesting that mangrove forests are a net sink of these nutrients rather than a source. Other studies have directly estimated the exchange of nutrients between mangroves and adjacent systems, and from these studies, it appears that the import/export balance for nutrients is highly variable between different particular mangrove ecosystems. Import of dissolved nitrogen was observed in Terminos Lagoon (Mexico) by Rivera-Monroy et al. (1995). Simpson et al. (1997) found an almost balanced net exchange for nitrate between Malaysian mangroves and adjacent coastal waters, but other nutrients showed a large variability in their fluxes. Similarly, Davis et al. (2001a) found variable fluxes of nutrients with the major fluxes occuring in the vegetated zone. In the latter study, nitrate and nitrite dynamics were characterized by large imports, whereas NH_4^+ exhange was balanced (i.e. export $\approx$ import); in terms of total nitrogen (i.e. organic and inorganic, dissolved and particulate) there was significant net import, whereas for total P these authors found a net export. On the other hand, Wattayakorn et al. (1990) report outwelling of inorganic nutrients from mangroves in Klong Ngao (Thailand), and Dittmar & Lara (2001a, b) found a net export of both NH_4^+, Si, and P (NO_3^- fluxes were low). As the concentrations of nutrients in creek waters appear to be to a large extent determined by the inputs of interstitial waters from the intertidal areas, Dittmar & Lara (2001a) proposed that sustained export of inorganic nutrients from mangrove forests is only

possible when there is an excess of inorganic nutrients in the porewaters (e.g. provided by high rates of N_2 fixation, and a positive sedimentation balance and subsequent mineralization which results in inorganic nutrient inputs) and only in macrotidal regions where porewater can flow in considerable amounts to the tidal creeks and the ocean. The latter hypothesis is indeed appealing, and further long-term studies on nutrient dynamics will no doubt refine our understanding of these processes.

2.3.4. MANGROVE ECOSYSTEMS : HETEROTROPHIC OR AUTOTROPHIC ?

An ecosystem is defined as net autotrophic when production (of organic carbon) exceeds the consumption. When, on the other hand, consumption of organic carbon exceeds production, the ecosystem is considered net heterotrophic. Note, however, that net autotrophy does not necessarily imply a flux of CO_2 from the atmosphere to the aquatic system. The direction of the CO_2 flux is solely determined by the sign of the CO_2 pressure gradient, and if there is an external source of CO_2 (e.g. in upwelling areas, or where CO_2-rich groundwater enters the aquatic system) even an ecosystem which is net autotrophic can act as a source of CO_2 to the atmosphere. Additionally, calcification reactions result in the production of CO_2 which in turn can be an extra source of CO_2, thus potentially rendering an autotrophic system a source of CO_2. In a recent review, Gattuso et al. (1998) concluded that water column metabolism as well as (intertidal) sediments in mangrove ecosystems are largely heterotrophic, but that mangroves, on an ecosystem level, are generally –but not always- net autotrophic ecosystems (see Table 8). Recently, however, Holmer et al. (2001) showed from flux measurements (O_2 and CO_2) that sediments along a mangrove-seagrass transect in Thailand were mostly net autotrophic on a diurnal basis (although mangrove sediments were net heterotrophic during the wet season). Similarly, Kristensen et al. (1992) showed that mangrove sediments were net autotrophic under light conditions, but heterotrophic under dark conditions. It should also be noted that a net heterotophic sediment may be the result of high sediment respiration rates and high primary productivity rates coinciding (e.g. Koch & Madden 2001), and thus, that 'heterotrophy' should not necessarily be associated with low levels of primary production.
Lastly, it should be stressed that the number of studies which have tried to assess the net autotrophic or heterotrophic status of mangrove ecosystems or compartments thereof (i.e. sediments, water column) is currently rather limited, and that significant variability can be expected.

Table 8. Ecosystem production – respiration balance for several mangrove ecosystems, modified from Gattuso et al. (1998). P_g : Gross primary production, R : respiration, NEP : net ecosystem production. See Gattuso et al. (1998) for references.

Site	P_g (g C m^{-2} y^{-1})	R (g C m^{-2} y^{-1})	P_g (mol C m^{-2} y^{-1})	R (mol C m^{-2} y^{-1})	P/R	NEP (mol C m^{-2} y^{-1})	Reference
Puerto Rico, Red mangrove stand	3004	3343	250	279	0.90	-28	Golley et al. (1962)
Scrub Forest (Florida)	511	730	43	61	0.70	-18	Burns (unpubl., in Lugo & Snedaker, 1974)
Hammock Forest (Florida)	694	219	58	18	3.17	40	Burns (unpubl., in Lugo & Snedaker, 1974)
Upper Fahka Union River (Florida)	3760	1351	313	113	2.78	201	Carter et al. (1973, in Lugo & Snedaker, 1974)
Lower Fahka Union River basin (Florida)	4307	1570	359	131	2.74	228	Carter et al. (1973, in Lugo & Snedaker, 1974)
Fahkahatchee (Florida)	5074	3322	423	277	1.53	146	Carter et al. (1973, in Lugo & Snedaker, 1974)
Rookery Bay, Black mangrove stand	3292	2292	274	191	1.44	83	Lugo et al. (1975)
Rookery Bay, Red mangrove stand	2446	694	204	58	3.52	146	Lugo et al. (1975)
Key Largo (Florida), Red mangrove stand	1949	2208	162	184		-22	Miller (in Lugo et al., 1975)
Bahamas (lagoon, fringing mangroves)					1.6		Koch & Madden (2001)
Waitema Harbour (New Zealand)						39	Knox (1983, in Lee, 1990)
Hong Kong						36	Lee (1990)
Jamaica						221	Nedwell et al. (1994)
Average	**2562**	**1731**	**214**	**144**		**89**	-

2.3.5. TROPHIC SIGNIFICANCE OF MANGROVE LITTER *VERSUS* OTHER PRIMARY PRODUCERS

> *'The importance of mangrove leaf litter in the maintenance of detrital-based foodwebs in the coastal environment and their significance for coastal fisheries have been indicated for some time.' (Ashton et al. 1999)*

The main focus of this thesis lies in describing the sources of organic carbon in an estuarine mangrove ecosystem and their relative importance in sustaining benthic and pelagic faunal communities in the intertidal and adjacent system.

Historically, interest in carbon dynamics and foodweb structure in mangrove ecosystems has grown since the proposed 'outwelling hypothesis' by Odum & Heald (1974, 1975) was published. It was suggested that mangrove litter -a seemingly endless source of energy- formed the basis of an extensive foodweb, not only beneath the forest canopy but also -through export- of nearshore aquatic ecosystems. Not surprisingly, this hypothesis became (and still is) an often-quoted argument for the conservation of mangrove ecosystems.

The increasing interest in studying these aspects of mangrove ecosystem functioning, and the availability of new techniques (such as stable isotope analysis) to address these issues has changed our view on the role mangroves play in sustaining aquatic faunal communities. Although the number of studies remains fairly limited, most agree that the role of phytoplankton and microphytobenthos is presumably larger than that of mangroves (e.g. Primavera 1997, Lee 2000, Dehairs et al. 2000, see Chapter 6 for a thorough discussion) and that any influence of the latter is spatially quite restricted. Nevertheless, studies concluding the opposite still emerge from time to time (e.g. Chong et al. 2001). In view of the tremendous variability in settings in which mangrove forests are known to occur, it is not inconceivable that the importance of mangrove carbon in sustaining higher trophic level invertebrates may be equally variable among estuaries or among different types of mangrove forests (as suggested by e.g. Ewell et al. 1998). Thus, in order to be able to evaluate this proposed or assumed function of mangroves critically, it is imperative to have comparable studies from a wide range of mangrove ecosystems.

In contrast to the attention that has been given to the trophic role of mangroves to aquatic invertebrate communities, much less effort has been made to refine our understanding of foodwebs in the intertidal zone of mangrove forests. Although there is plenty of literature on the role of sesarmid crabs in leaf litter dynamics (see Skov & Hartnoll 2002 for an excellent

recent overview), an overall evaluation of the importance of different sources to the invertebrate community as a whole is entirely lacking - despite a handful of studies focussing on particular species or groups, e.g. Slim et al. 1997, France 1998, Christensen et al. 2001. Although there may be fewer incentives from a conservation or management point-of-view to conduct research into intertidal mangrove foodwebs (as most of the species of economic importance are harvested in the adjacent aquatic environment), the absence of a community-level understanding of intertidal foodwebs in mangroves is surprising. Again, a comparison of a range of different mangrove ecosystems will no doubt prove to be insightful in fill this gap in our current knowledge.

CHAPTER 3 : Materials and Methods

TABLE OF CONTENTS

CHAPTER 3 : Materials and Methods

Foreword

A first section of this chapter introduces the site in which most of the sampling for this study was carried out. This includes a description of the geographical, climatic, hydrological and environmental settings of this mangrove ecosystem, as well as a brief, non-exhaustive overview of the dominant flora and fauna occurring there. The most commonly used sampling procedures will be described, as well as the analytical techniques most frequently applied (elemental analysis of organic matter, and stable isotope analysis of bulk organic matter and dissolved inorganic carbon). Details of some particular techniques, such as the analysis of bulk lipid $\delta^{13}C$ will be described in the relevant chapters. Prof A.V. Raman (Marine Biology Laboratory, Zoology department, Andhra Univerisity) kindly provided nutrient data.

3.1. Description of the Godavari Estuary, Andhra Pradesh, India

Geographical location

The principal study site (Figure 1 and 2) is located near the mouth of the Gautami Godavari, Andhra Pradesh, on the east coast of India (between 82°15' and 82°22' E, 16°43' and 17°00' N). The Godavari is India's second largest river and has an average annual discharge of 1.1×10^{11} m³, of which 93-96 % occurs during the wet monsoon. It is listed as one of the major POC (particulate organic carbon) transporting rivers in the world, even though its catchment area and discharge rates are in the lower end of the major world rivers (see Table 3.1, adapted from Gupta et al. 1997). The Godavari has two main branches, the northern Gautami Godavari, while the more southern branch is known as the Vasishtha Godavari. Prior to its branching point, the river flow is regulated at Dowleswaram Dam (located near Rajahmundry and constructed in 1852) in order to provide water for the extensive irrigation networks for rice culture. The Gautami Godavari opens into the Bay of Bengal, but has several branches into Kakinada Bay, the largest and most important being Coringa which branches off near Yanam (total length of 26 km) and Gaderu which is connected to the river in

Bhairavapalem (total length of 11 km). Other waterways entering the Kakinada Bay include the small Chollangi creek and Matlapalem Canal (Figure 2). The shallow Kakinada Bay (depth ranging from 3 to 8 meters at high tide) covers approximately 150 km² and opens into the Bay of Bengal on its northern side. On the eastern end, it is bordered by a narrow sand bar (Hope Island), which experienced a breakthrough at the edge of the mangrove forest after the 1996 cyclone. Hope Island has several small settlements, which are occupied only during part of the year when the weather conditions allow and it is then used primarily as a setout point for the collection of prawn seed. Although most of the island is only sparsely vegetated or holds plantations of *Casuarina*, mangroves have settled at various places along its western shoreline, especially at the northern end of the island.

Tides are semidiurnal, and tidal amplitude in the Bay is around 0.5 to 2 meters, but is reported to be less substantial in the mangrove-covered areas.

Table 1 : Comparison of some important characteristics of the Godavari river with other major world rivers (see Gupta et al. 1997 for data sources). - : no data. For the Ganges, Indus, and Brahmaputra rivers, the given POC flux is the total flux for the three rivers combined. TSS : total suspended solids.

River	Basin area [10^3 km²]	Discharge [km³ y^{-1}]	TSS flux [10^6 t y^{-1}]	POC flux [10^3 t y^{-1}]
Amazon	6300	5520	900	13000
Ganges	970	412	573	
Indus	1170	224	100	18000
Brahmaputra	700	560	597	
Huanghe	752	44	681	6100
Zaire	3750	1267	48	2800
Orinoco	1000	1135	121	1990
Mackenzie	1810	249	-	1822
Godavari	**313**	**95**[a]	**170**	**2805**
Parana	2800	473	80	1270
Mississippi	3220	410	296	850
Niger	1162	154	25	660
Yukon	840	210	-	320
St Lawrence	1150	413	5	310
Nile	3000	38	2	190

[a] : note that Gupta et al. (1997) give a discharge of 92 km³ y^{-1} in their Table 4, but mention a dischare rate of 110 km³ y^{-1} in the text. The value used here (95 km³ y^{-1}) is based on the data in the UNH/GRDC database, see further.

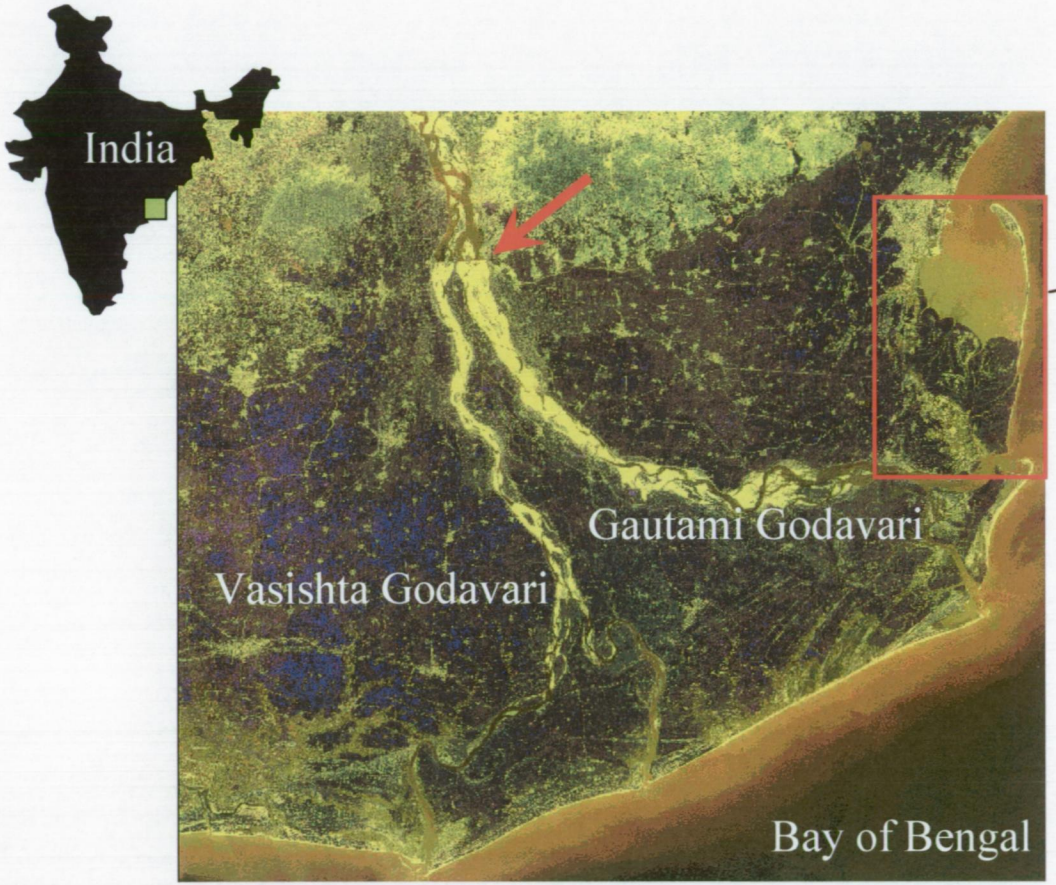


Figure 1: Satellite image (March 1993, Landsat) showing the location of the main study area. Taken during pre-monsoon period – the location of Dowleswaram Dam is clearly visible (indicated by the red arrow).

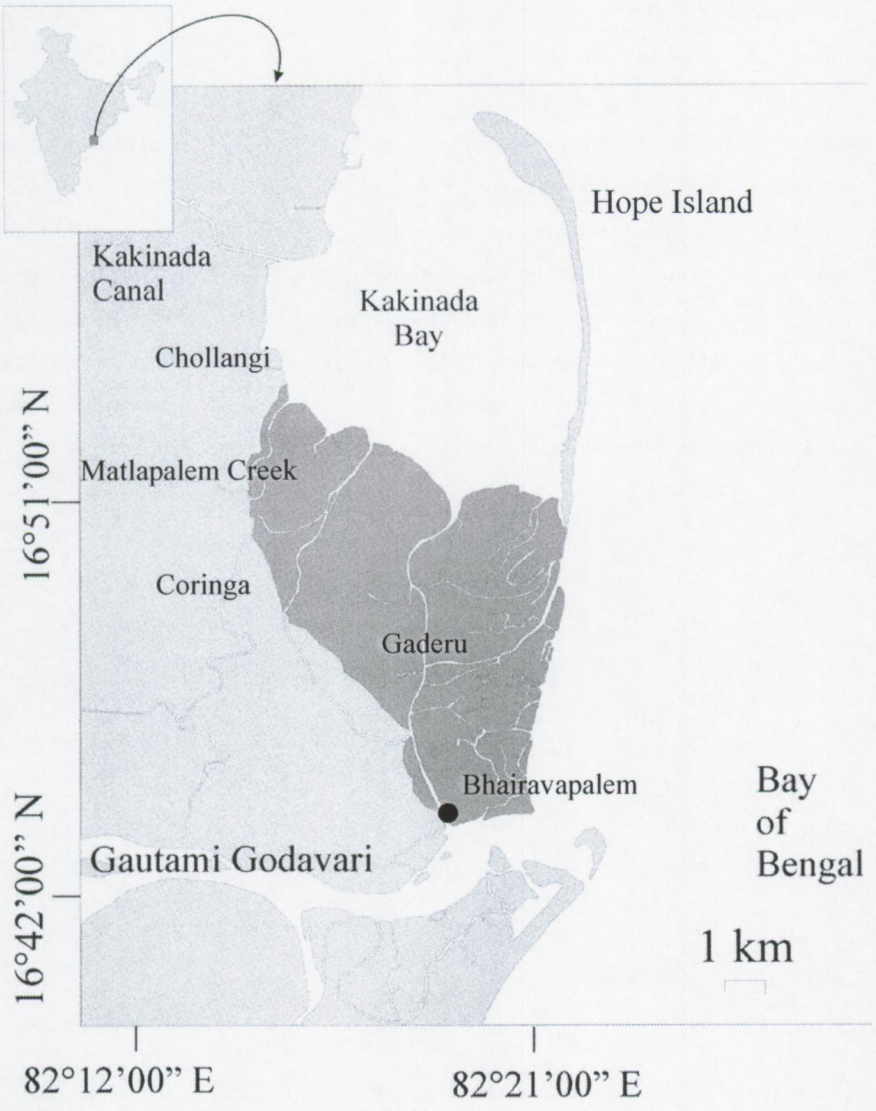


Figure 2 : Location of the Coringa Wildlife Sanctuary and adjacent Kakinada Bay (Andhra Pradesh, India), and the main rivers and creeks.

Mahadevan & Rao (1958) give an account of the evolution of the Gautami Godavari estuary based on charts published by the British Admiralty (dating from 1851, 1864, 1878, 1889, 1893, 1914, and 1929). On the earliest chart (1851), the present Hope Island is not indicated yet, and most of the area which is now Kakinada Bay appears to have consisted of intertidal mudflats. The main discharge of the Gautami Godavari was directed in a more northern direction than the current situation, and the river bed coincided approximately with the current Gaderu creek (Figure 3). From 1864 (but mainly from 1878) onwards, Hope Island slowly emerged on its current southern end, and reached almost its present shape by the early 20th century. As late as 1929, the main discharge of the Gautami Godavari river appeared to have taken place into Kakinada Bay rather than straight into the Bay of Bengal.

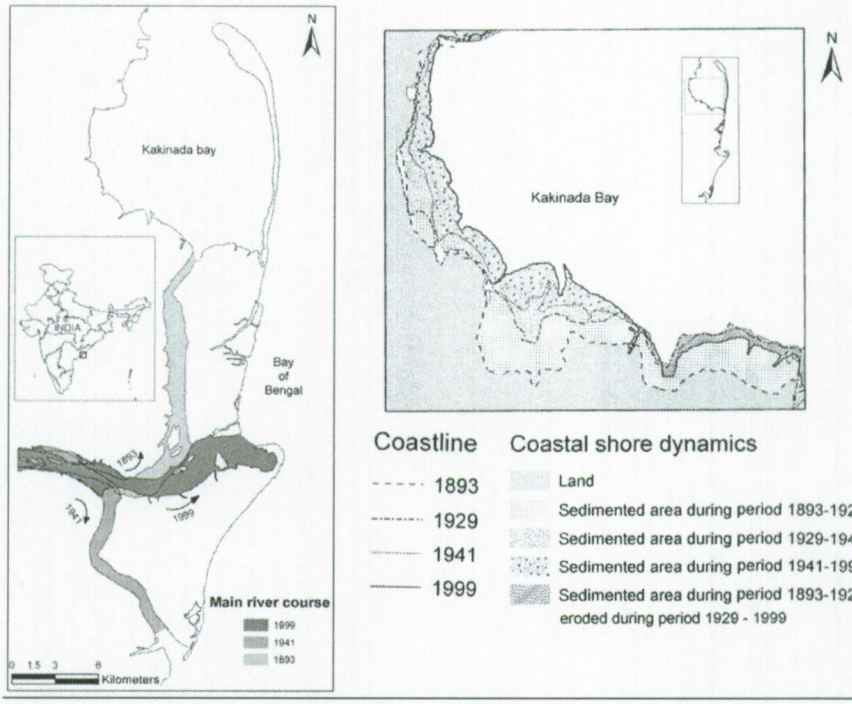


Figure 3 : Location of the main course of the Gautami Godavari in 1893, 1941, and 1999 (panel A), and evolution of the shoreline over the same time period. Figure provided by the French Institute of Pondicherry.

Discharge data of the Godavari river, which are available from Polavaram (81°78' E, 16° 92' N, i.e. before it is divided into the Gautami and Vasishtha branches, and located at ~ 133 km before opening into the Bay of Bengal), show very high average discharge rates during July, August, and September, medium discharge rates during October, and very little discharge during the rest of the year (Figure 4). This seasonal contrast in discharge is clearly visible on satellite images taken during the dry season, when most of the river bed is dry (see e.g. Figure 1). Integration of the data in the UNH/GRDC database (http://www.compositerunoff.sr.unh.edu/index.html) over time (i.e. converting the monthly average discharge rates, expressed in m^3/s, to total monthly discharge, and summing these for all months of the year) gives an average discharge of $9.5\ 10^{13} \pm 3.2\ 10^{13}$ l/year, which corresponds well to the values cited by Gupta et al. (1997) and Padmavathi & Satyanarayana (1999). When comparing the monthly average discharge rates of the Godavari and the precipitation data in Kakinada (Figure 4), it is clear that although heavy rainfall is common during approximately 6 months of the year, the period of maximum discharge is about 2 months shorter.

Climate

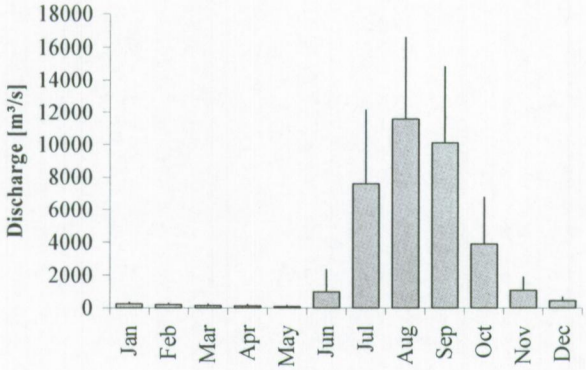
The study site experiences strong seasonal climatic variations. Four seasons can generally be recognized, although significant year-to-year variations occur :

- a cool and dry season from December to February
- a hot and relatively dry period from March to June
- abundant rains during the hot Southwest monsoon (July to September) when almost freshwater conditions prevail in the whole area
- a cooler transitional period during which estuarine and marine conditions are re-established in the Bay and mangrove creeks (October to November)

Average annual **precipitation** (based on data from 1860 to 1992) is 1032 ± 282 mm, but often shows a strongly bimodal distribution over the year (Figure 5). Cyclones are fairly frequent, mostly between July and November. Between 1995 and 1997, 5 cyclones have severely damaged the area, and have caused the breakthrough of the southern part of Hope Island. Air **temperatures** at Kakinada show a very distinct and consistent seasonal pattern, with a general increase between September and

February/March and a subsequent decrease towards September, but during the decrease a marked temperature rise occurs in June and July (Figure 6). Average monthly temperature for the period 1981-1990 was 28.6 ± 2.5 °C (source : IRI/LDEO Climate Data Library, http://ingrid.ldgo.columbia.edu/).

A



B

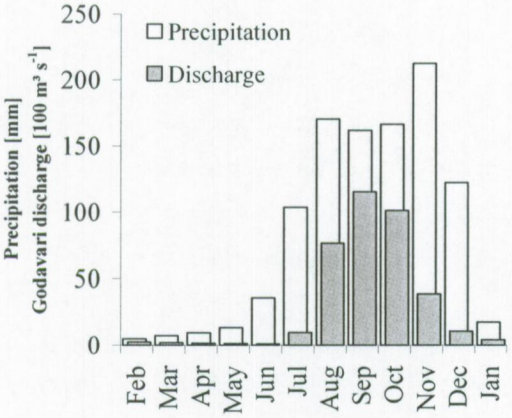


Figure 4 : (A) Average monthly discharge of Godavari (Polavaram), based on 1901-1960 and 1965-1979 data, and (B) a comparison of monthly discharge data of the Godavari with montly precipitation data in Kakinada. Error bars : 1 s.d. (Data sources : IRI/LDEO Climate Data Library and the University of New Hampshire Global Runoff Data Centre). See text for details.

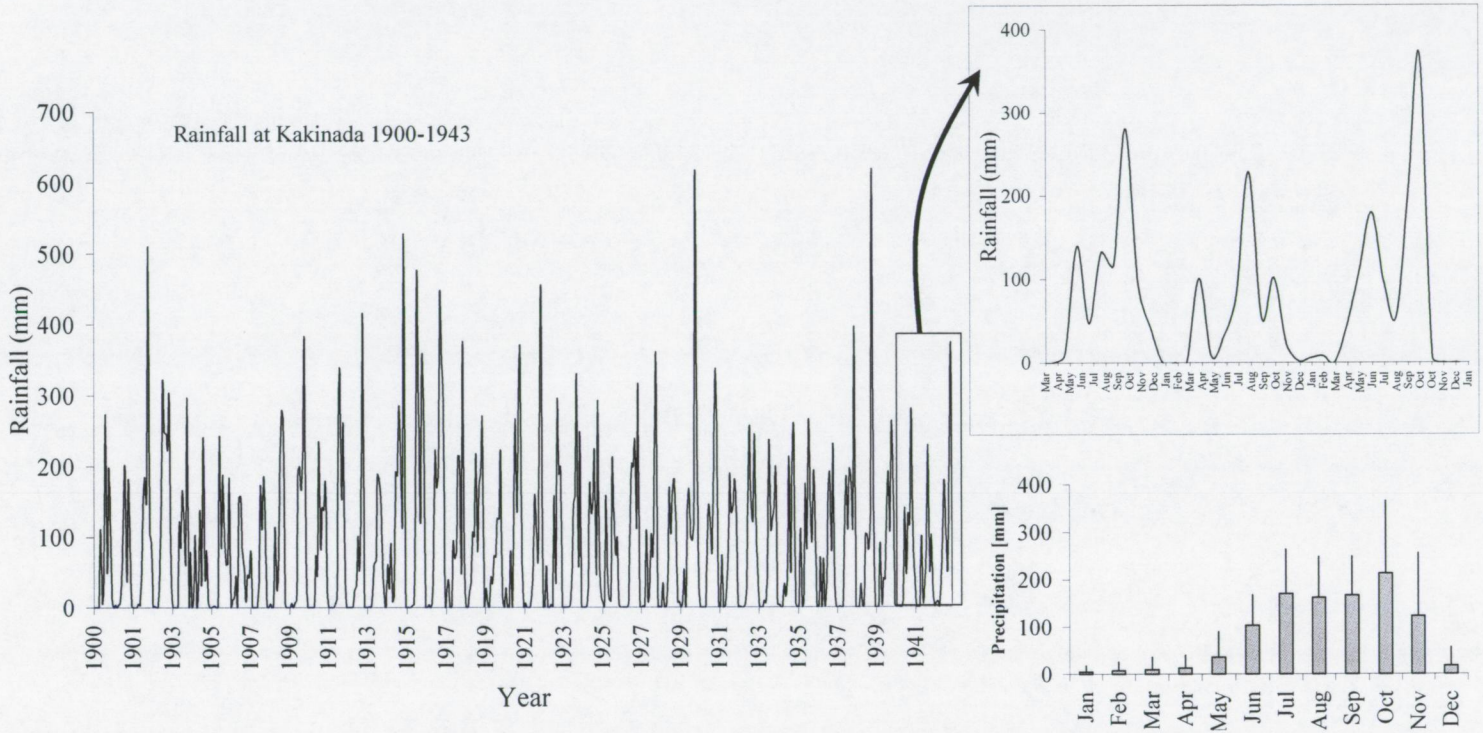


Figure 5 : Monthly precipitation data (in mm) for Kakinada, period 1900-1943 and (higher right panel) 1940 to 1943. Data from the IRI/LDEO Climate Data Library, http://ingrid.ldgo.columbia.edu/). Data in lower right panel are from Jan 1863 to Dec 1993, and error bars : 1 s.d.

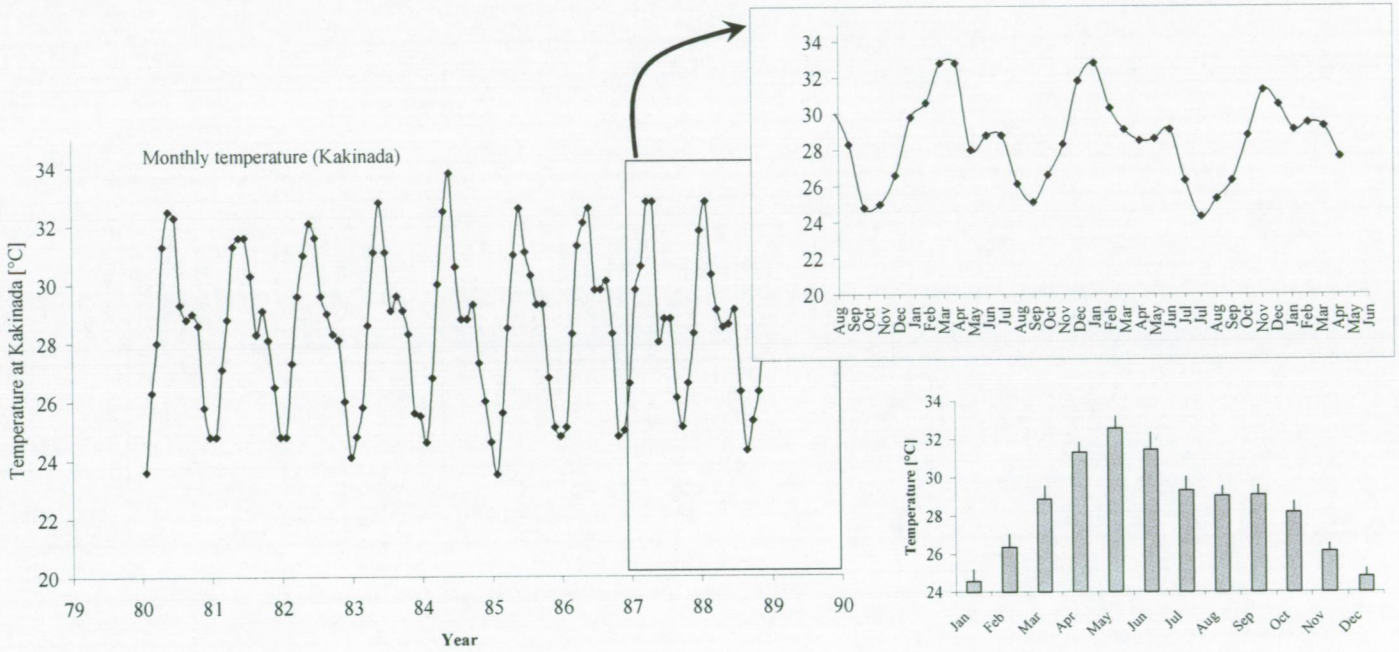


Figure 6 : Annual and seasonal variations in air temperature recorded in Kakinada between 1980 and 1990 (Source : IRI/LDEO Climate Data Library, http://ingrid.ldgo.columbia.edu/). Error bars in lower right panel indicate 1 s.d.

Human Impact

Estimates of the surface area covered by mangroves in India range between 3150 and 6700 km² (Aizpuru et al. 2000). Approximately 80 % of these areas are located along the Northeast coast (Orissa and West Bengal), and the bulk is found in large deltaic plains such as the Ganges delta (Sunderbans). Estimates of the Andhra Pradesh Forest Department give a surface area of 316 km² for the Godavari delta, of which 235 km² are legally protected as the Coringa Wildlife Sanctuary. Large areas of mangroves along the western and southwestern stretches of Kakinada bay have virtually disappeared.

The first measures for the protection of the mangroves in the Coringa area were taken as early as 1888, when the 'Coringa Forest Block' became a reserve. Extensions of the protected area came in 1921 (Coringa Extension Reserve Forest) and 1957 (Bhairavapalem Reserve Forest). During this period, however, the government allowed periodic clearings, and this practice -combined with the illegal clearing of the forest- resulted in a strong degradation of the ecosystem. In 1978, the 'Coringa Wildlife Sanctuary' (hereafter sometimes referred to as CWS) was declared protected in the framework of a rehabilitation project for saltwater crocodiles in the Godavari Estuary. The re-introduction of several specimens did not, however, result in the establishment of a new population of this species. Hope Island is a well known breeding ground for the threatened sea turtle *Lepidochelis olivacea* (Ridley sea turtle).

Human exploitation of the mangroves in the area did not cease when the CWS was declared. The intensity of rice culture has increased markedly over the last few decades (from 1.5 to 2.3 rotations per year between 1974 and 1997) which may have led to increasing amounts of herbicides in the aquatic environment and –perhaps more importantly- a decrease in the amount of freshwater from the drainage channels. Collection for fuelwood and fodder, clearing of forest patches for aquaculture ponds and saltpans, and possible over-exploitation of natural resources in the forest (crab, fish, mollusc, and prawn fisheries), continue to threaten this ecosystem. It was estimated that –besides areas that were already converted to rice paddies or bare land- some 600 ha of mangroves had been converted into aquaculture ponds by 1999. The collection of wild *Penaeus* seed for use in the aquaculture ponds is particularly destructive as the bycatch (fish larvae etc.) far exceeds the number of prawn seeds harvested and is usually discarded on the beach.

Besides these direct effects on the mangrove forest, the rapidly growing population and industrialisation have coincided with an increasing pollution, as evidenced by the significant rise in nutrient concentrations (e.g. nitrate, phosphate, A.V. Raman, Andhra University, pers. comm.) during the last decades. Benthic fauna in the Bay and creeks has witnessed a significant decrease in species diversity over the last 50 years (Deepti 1997).

A brief description of the dominant flora and fauna in the Coringa Wildlife Sanctuary

A number of studies have described -in various levels of detail and accuracy- some aspects of the flora and fauna of the Coringa Wildlife Sanctuary. Although there are insufficient reliable data available to present an exhaustive overview of the dominant flora and fauna relevant to this thesis, the available information and the data gathered during our own fieldwork is compiled here. A thorough study of the mangrove vegetation structure and dynamics in the area has recently been carried out by B. Satyanarayana and co-workers (Satyanarayana et al. 2002). The 'true' mangrove species (as defined by Duke 1992) found in the study area (the Coringa Wildlife Sanctuary, Andhra Pradesh, India) have been listed in Table 2. One additional species occuring abundantly throughout the area, but which has not been considered a true mangrove species by most authors (Duke 1992) is *Acanthus ilicifolius*. A noteworthy non-mangrove species is the grass *Myriostachya wightiana*, known only from the Godavari Delta and from Maharashtra (west coast of India).

Table 2: Occurrence of 'true' mangrove species and a (subjective) interpretation of their relative occurence in the main study site, the Coringa Wildlife Sanctuary, Andhra Pradesh, India. Sources : Azariah et al. (1992) and Satyanarayana et al. (2002), relative occurrence by B. Satyanarayana (Andhra University, pers. comm.).

SPECIES	OCCURRENCE
Aegiceras corniculatum (L.) BLASCO	Common
Avicennia alba BLUME	Local
Avicennia marina (FORSK.) VIERH.	Abundant
Avicennia officinalis L.	Abundant
Bruguiera cylindrica (L.) BLUME	Common
Bruguiera gymnorrhiza (L.) LAMK.	Common
Ceriops decandra (GRIFF.) DING HOU	Common
Excoecaria agallocha L.	Abundant
Lumnitzera racemosa WILLD.	Common
Rhizophora apiculata BL.	Local
Rhizophora mucronata LAMK.	Local
Sonneratia apetala BUCH.-HAM	Local
Sonneratia caseolaris (L.) ENGLER	Rare
Xylocarpus mekongensis PIERRE	Local

In contrast to the flora which has been fairly well studied, much less is known about the occurrence of invertebrates in the intertidal zone. There are some records cited in Murty & Rao (1977), but some of the species mentioned are likely to be the result of misidentifications, e.g. *Terebralia palustris* is mentioned as being very abundant, while *Cerithidea obtusa* is not mentioned, whereas our own observations and those of others (A.V. Raman, Andhra University, pers. comm.) show that *T. palustris* is absent and that *C. obtusa* is one of the most abundant gastropod species present. In additon, the fact that an undescribed species has been found (*Elysia coringaensis* sp. nov., see Chapter 8 and 9) and that the number of species found during a few short fieldwork campaigns was much higher than the number previously recorded could be indicative of a diversity of molluscs that is much higher than is currently evidenced. An overview of the species recorded in the area, along with an –estimated- indication of their relative abundance, is presented in Table 3 (whereby only species recorded in the intertidal mangrove flats have been included).

Table 3 : Occurrence of mollusc species in the study area, mainly based on personal observations, and an estimated indication of their frequency of occurence. Note that species recorded in creeks or in the adjacent Kakinada Bay but not in the intertidal areas are not included in this list.

SPECIES	OCCURRENCE
Anadara granosa LINNAEUS, 1758	Local; common in subtidal areas
Assiminea sp.	Abundant
Cassidula mustelina (DESHAYES, 1830)	Rare
Cerithidea cingulata (GMELIN, 1791)	Common
Cerithidea obtusa (LAMARCK, 1822)	Abundant
Ellobium sp.	Rare
Elysia coringaensis sp. nov.	Abundant but local
Littoraria (Littorinopis) delicatula (NEVILL, 1885)	Rare
Littoraria (Palustorina) melanostoma (GRAY, 1839)	abundant
Littoraria (Littorinopsis) scabra (LINNEAUS, 1758)	+[a]
Littoraria (Palustorina) articulata (PHILIPPI, 1846)	Common
Melampus fasciatus DESHHAYES, 1830	Common
Neritina violacea (GMELIN, 1791)	Common
Onchidium sp. 1	Common
Onchidium sp. 2	Rare
Polymesoda bengalensis LAMARCK, 1818	Abundant but local
Pythia plicata (DE FÉRUSSAC, 1821)	Common
Telescopium telescopium LINNAEUS, 1758	Abundant
Terebralia palustris (LINNAEUS, 1767)	+[b]
Teredinidae (unid.)	Abundant in dead wood

[a] : A.V. Raman, Andhra University, pers. comm.
[b]: reported by Murty & Rao (1977), but presumably a misidentification and referring to *Cerithidea obtusa.*

Similarly, very little information exists on the mangrove-associated crab fauna of the Indian east coast, and misidentifications and references to scientific names no longer in use (e.g. Kathiresan 2000) make the few available records unreliable and of restricted use. The available information (mostly from personal observations) on the occurrence of brachyuran crabs in the three main study areas has been summarized in Table 4. Again, this list is likely to be very incomplete but gives an indication that the species richness of intertdidal crabs is likely to be large. When comparing the diversity of known species of brachyuran crabs from the Coringa area with that of molluscs from the same site (Table 3), it becomes evident that –even though both species lists are likely to be far from complete- the species richness of both groups of invertebrates is quite comparable.

Table 4 : Occurrence of brachyuran crab species in the three main study sites. Mainly based on personal observations, and likely to be incomplete. Species recorded only in creeks, but not in the intertidal zone, are not included in this list.

SPECIES	CWS
Cardisoma carnifex (HERBST, 1794)	Common (local)
Episesarma lafondi (JACQUINOT, 1846)	Rare ?
Episesarma tetragonum (FABRICIUS, 1798)	Abundant
Episesarma versicolor (TWEEDIE, 1940)	Common
Metaplax distinctus H. MILNE EDWARDS, 1852	Abundant
Metaplax elegans DE MAN, 1888	Abundant
Metopograpsus messor (FORSKÅL, 1775)	Abundant, local
Metapograpsus maculatus H. MILNE EDWARDS, 1852	+[a]
Nanosesarma minuta (DE MAN, 1887)	+[a]
Parasesarma asperum (HELLER, 1865)	Abundant
Parasesarma plicatum (LATREILLE, 1806)	Abundant (local)
Perisesarma sp. nov.	Abundant (local)
Scylla paramamosain ESTAMPADOR, 1949	+[a]
Scylla tranquibarica (FABRICIUS, 1798)	+[a]
Scylla oceanica (DANA, 1852)	+[a]
Scylla serrata (FORSKÅLL, 1775)	Common
Thalamita crenata (LATREILLE, 1829)	+[a]
Uca annulipes	+[a]
Uca (Celuca) triangularis bengali CRANE, 1975	Very abundant
Uca (Deltuca) rosea (TWEEDIE, 1937)	Abundant
Uca urvillei (H. MILNE EDWARDS, 1852)	Local
Varuna litterata FABRICIUS, 1798	Common ?

[a] : D.E. Babu, Andhra University, pers. comm. The three additional species of *Scylla* mentioned by D.E. Babu are reported to enter the intertidal areas only during high tide.

Several of the species mentioned in Table 4 had not been previously recorded from the Indian east coast. *Uca urvillei*, for instance, had only been recorded from East Africa, Madagascar, Pakistan, and western India, and our record thus represents a major range extension for this species. Similarly, *Episesarma versicolor* had not been recorded from the east coast. In addition, an undescribed species of *Perisesarma* (Davie, in preparation) was found to be very abundant at several sites in June 2001, and was previously only known (only recently) from Sri Lanka (P. Davie, personal communication).

Physico-chemical characteristics of the mangrove creeks and Kakinada Bay

Physico-chemical water properties of Kakinada Bay and the mangrove creeks have been measured on a fairly regular basis for a number of years by the Marine Biology Laboratory (Andhra University, Visakhapatnam) in the framework of several local and international research programs (Dehairs 1999, Raman 2000). In addition, some historical data from the mid-20th century are available, and some sporadic data have also been published over the last two decades (e.g. Kondolarao & Ramanamurty 1988, Vijayakumar et al. 1991, Selvam et al. 1992, Rao 1995). As can be expected for an estuarine ecosystem under monsoonal influence, most physicochemical parameters show a tremendous variability – both seasonally and spatially. Some general trends will be discussed below based on the results provided by A.V. Raman for the ten sampling stations used for periodical monitoring of total alkalinity and $\delta^{13}C$ of the dissolved inorganic carbon pool (see Chapter 4) between April 2000 and August 2001. For a more thorough presentation of physico-chemical data, we refer to the abovementioned reports and publications, and details on various aspects of the biogeochemistry of the mangrove creeks and Bay can also be found in Chapters 4-6.

Salinity variations (Figure 7 A, i.e. top panels) show a relatively straightforward seasonal pattern, with a general decrease after the onset of the monsoon (the timing of which varies annually), and a gradual increase of salinity throughout the area towards the end of the pre-monsoon period. Coringa creek is somewhat of an exception in view of a relatively low salinity persistent throughout much of the year (which is related to the discharge of water from irrigation channels), although salinity may at times reach marine values, particularly at the end of the pre-monsoon period (Fig 7, top right). Although salinity is on average clearly lower in the mangrove creeks than in Kakinada Bay, it should be noted that even in the latter, periods of relatively low salinity (~ 15 ppt) are regularly observed. Levels of **dissolved oxygen** show a much less pronounced seasonal and spatial pattern (Fig 7 B), although in most stations, a general decrease could be observed during the monsoon period of 2000, indicating lower O_2 concentrations in the turbid Godavari discharge water, and a net increase towards the end of the pre-monsoon period (although there also appears to be a consistent decrease between Feb and May in the mangrove creeks). Again, O_2 concentrations are generally lower in the mangrove creeks than in the Kakinada Bay

area. Seasonal variations of dissolved inorganic nitrogen (Fig 7 C, D, E) show some notable patterns. First, concentrations of **ammonium** were low at the end of the pre-monsoon period of 2000, and gradually increased with the advent of the monsoon discharge. This import of NH_4^+ with freshwater is considered a recurrent pattern (A.V. Raman, pers. comm.). After the monsoon, however, NH_4^+ concentrations continue to increase towards the pre-monsoon period for 2001 (whereas in 2000 a decrease at the end of the pre-monsoon is visible, as wel as for Coringa and Chollangi for 2001). Such an increase in $[NH_4^+]$ could be explained by the local regeneration of ammonium (in excess of its consumption) by mineralization of organic matter or, locally, from anthropogenic inputs (e.g. fertilizers used in aquaculture or agriculture). It is worth noting that Dham et al. (2002) recently noted a similar pattern in a west Indian mangrove estuary, with high NH_4^+ concentrations towards the end of the pre-monsoon. In their extensive study of DIN dynamics, this was found to be caused by intense regeneration. Some of the very high NH_4^+ concentrations in Coringa and Chollangi creek which are most affected by human impact (Fig 7C, note difference in Y-axis) might favour the anthropogenic pollution hypothesis for these particular sites. Concentrations of **nitrate** show an altogether different seasonal pattern, with a decrease accompanying the dilution with freshwater during the monsoon discharge, and an (erratic) increase afterwards, which appears to decline again just at the end of the pre-monsoon period. For **nitrite**, seasonal variations are too erratic to draw any conclusions. The latter also holds for **phosphate** concentrations (Fig 7F), for which little consistent seasonality can be observed and for which a remarkable peak was observed in the entire area in May 2000, with concentrations 5 to 10-fold higher than usual. Such events might be related to the resuspension of bottom sediments (A.V. Raman, pers. comm.) Finally, for **silicate**, the data from the mangrove creeks and Kakinada Bay (Fig 7G) show increased concentrations during the monsoon as freshwater inputs increase (which is consistent with the $[Si(OH)_4]$ gradients observed along the Gautami Godavari salinity gradient, see e.g. Somayajulu et al. 1993 and Padmavathi & Satyanarayana 1999) but a maximum is also observed in March and April 2001 which does not coincide with a lower salinity. Towards the end of the pre-monsoon period, Si concentrations again decrease, presumably associated with removal by aquatic primary production. In Coringa, Si concentrations are markedly higher throughout the year compared to most other locations.

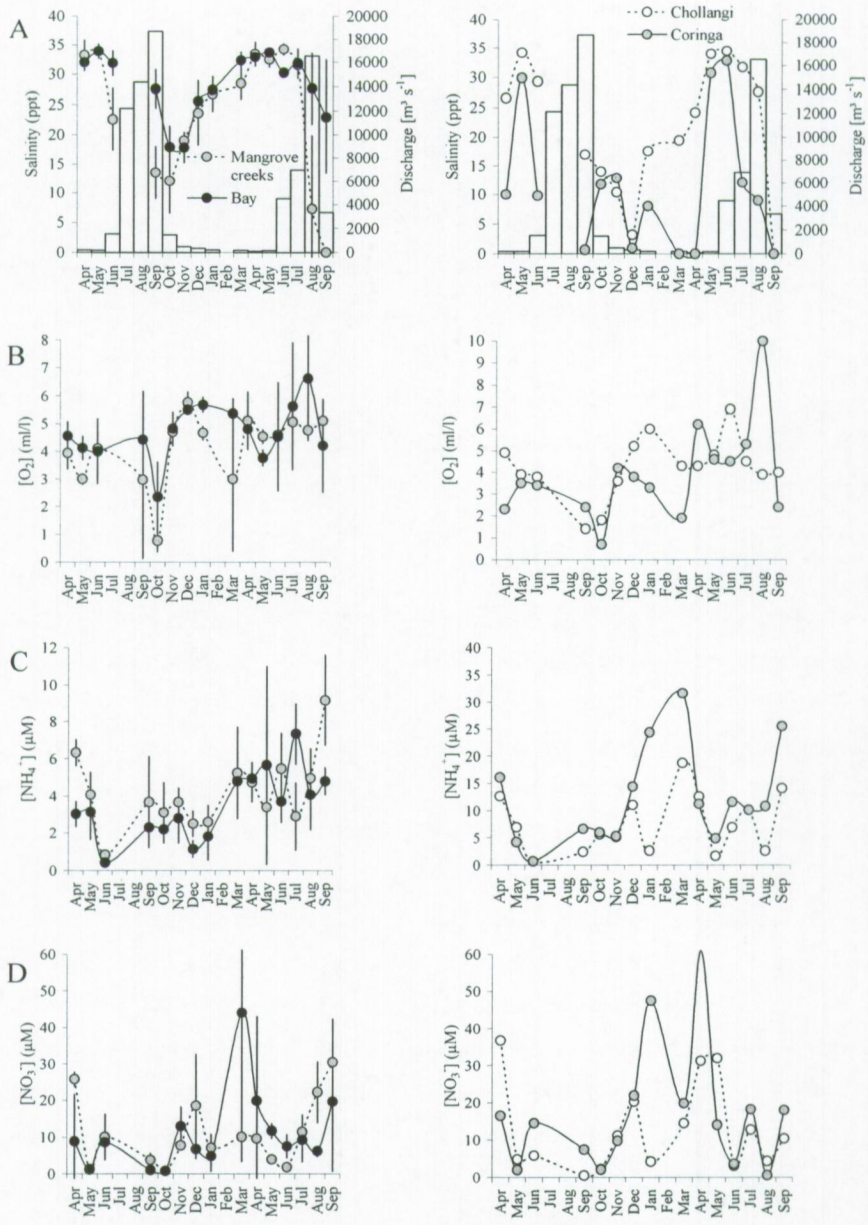


Figure 7 : Some physico-chemical parameters from mangrove creek locations (GA, Gc III, and LH), Bay locations (MD, GU, KB, KBN, and BB), and for two other creeks, Chollangi and Coringa between april 2000 and September 2001. See Chapter 4 for location of sampling stations. White bars on panel A (right-hand Y-axis) represent discharge rate of the Godavari at Dowleswaram Dam. Note the difference in Y-axis for panel B and C.

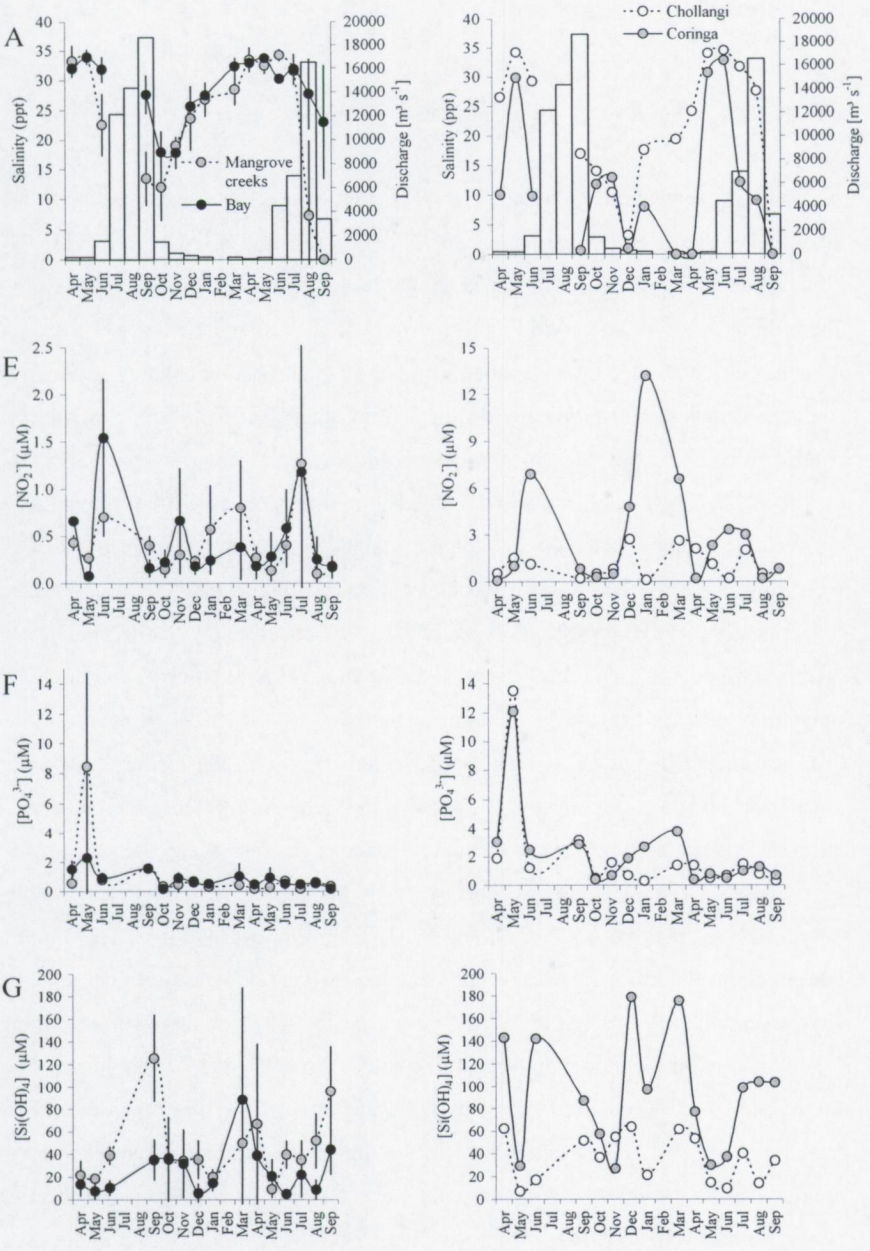


Figure 7 (continued) : Some physico-chemical parameters from mangrove creek locations (GA, Gc III, and LH), Bay locations (MD, GU, KB, KBN, and BB), and for two other creeks, Chollangi and Coringa between april 2000 and September 2001. See Chapter 4 for location of sampling stations. White bars on panel A (right-hand Y-axis) represent discharge rate of the Godavari at Dowleswaram Dam. Note the difference in Y-axis for panel B.

3.2. Sampling Procedures

3.2.1. VEGETATION, SEDIMENTS, AND FAUNA

All samples of **vegetation** (mangrove leaves, macroalgae, ...) were taken by hand, after which they were rinsed under tap water before being dried at 60 °C for 24-48 hours. For mangroves, in most cases green leaves were taken at a height of approximately 1.5 meters, avoiding the 'dwarf' or stunted mangrove trees wich occur on some elevated sites (as no faunal samples were taken at such sites and as dwarf trees are known to be isotopically different from others, see Chapter 1). Sampling of benthic microalgae was done by gently scraping the sediment surface in places where they formed a conspicuous layer. Although some of these samples may be expected to be slightly contaminated with sediments (and the associated organic matter), they were considered to be representative for benthic microalgae as the concentrations of organic carbon and nitrogen in bulk sediments were usually very low (see Chapter 7), thereby introducing only small errors. Experimentation with other techniques for the separation of benthic microalgae (modified technique of Couch 1989) proved to be of little use in the mangrove sediments under consideration, due to the abundance of aerial roots and the pronounced microrelief of the sediments. After several hours, little or no microalgae could be detected on the surface of the nylon screens. This may also have been due to the fact that, in contrast to salt marsh ecosystems, species capable of migrating are less dominant (see Alongi 1994).

Sediments in the intertidal areas were collected by hand, whereas subtidal sediments were taken with a Van Veen grab. These were carried to the field laboratory in plastic bags in an ice box, where they were immediately dried at 60 °C for at least 24 h. In some cases (mainly in the Sri Lankan sites, see Chapter 7), root material and shell remains were particularly abundant in the intertidal sediments, and these were removed from the dried sediments with pincers before further sample processing. Subtidal **macro-invertebrates** were sampled by both a Van Veen grab and a dredge which was pulled by a small motorized boat for several minutes. After hauling up the samples, they were sieved and sorted, fauna was transported in containers with local surface water to the field laboratory, where they were washed and dried, either whole or selected body parts. Several infaunal taxa, however, were collected by taking

sediment cores and sieving the contents on 250 µm stainless steel sieves. Most intertidal macro-invertebrates were collected by hand, either by simply collecting them from their substrate (sediment, roots, stems, leaves, dead wood) or by digging them out of their burrows in the case of several brachyurans. **Zooplankton** collections were made by towing 120 µm and/or 300 µm plankton nets from a motorized boat. After transport to the field lab in an ice box, these samples were filtered on pre-combusted glass fibre filters (Whatman GF/F) or on nitex screens of the corresponding mesh size. They were then immediately dried at 60 °C for a minimum of 24 h.

3.2.2. SUSPENDED MATTER

Samples of **total suspended matter** were taken by collecting a known volume of surface water (usually 250 or 500 ml), transporting it on ice to the field laboratory where it was filtered on pre-combusted (12 hours at 450 °C) glass-fibre filters (Whatman GF/F). These filters were dried at 60 °C for 24 hours prior to packing in aluminium foil or polystyrene holders (Millipore PetriSlides).

Different **size fractions** of suspended matter were sampled as follows :

- for the < **10 µm** fraction, a known volume of surface water (usually 250 ml) was passed through a sheet of nitex with a 10 µm mesh size. The water passing through was collected and, after transport to the field lab, filtered on pre-combusted glass fibre filters (Whatman GF/F).
- for the fractions **10 << 50 µm** and **50 << 118 µm**, custom-designed plankton nets (see Figure 6) were towed by a motorized boat for several minutes, after which the container (500 ml) containing the size fraction to be sampled was collected and stored on ice. All particles larger than the mesh size of the first nitex screen are retained on the net or in the first bottle, particles smaller will pass through but will be collected on the second nitex screen. As all particles smaller than the mesh size of this second screen will pass through, the second collection bottle will concentrate the particles which have a diameter larger than the smallest mesh size, but smaller than the largest. Upon arrival in the

field lab, the size fractions were collected on a nitex screen of the smaller mesh size, and dried as such at 60 °C for a minimum of 24 h.

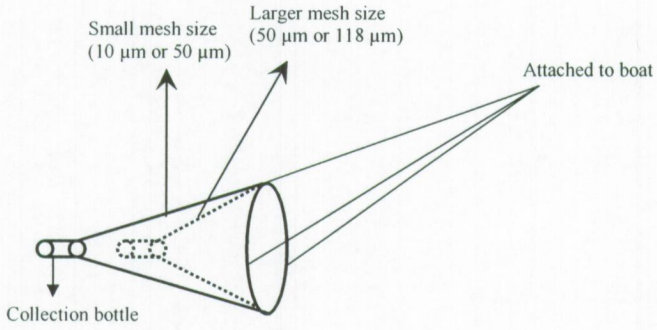


Figure 6 : Custom-made nets for the collection of different size-fractions of suspended matter.

EFFECTS OF SAMPLE PRESERVATION AND TREATMENT ON STABLE ISOTOPE RATIOS OF ORGANIC MATERIALS

Several studies have assessed the differences in $\delta^{13}C$ and $\delta^{15}N$ that result from the method of preservation, and from sample treatment (with or without acidification), and these studies often yielded contradictory results.

Bunn et al. (1995) found that **acid washing** did not affect the mean $\delta^{13}C$ ratios for seagrasses and penaeid shrimps, but there was an effect on the $\delta^{15}N$ signatures, albeit in opposite direction (decrease by -1.8 ‰ for seagrasses, + 3 ‰ for penaeid prawns). In addition, acid washing increased the variation among individuals, leading to a loss of statistical power. Goering et al. (1990) and Pinnegar & Polunin (1999) also reported effects of acid washing on $\delta^{15}N$ results, but both Bosley & Wainright (1999) and Fantle et al. (1999) found no effect on $\delta^{13}C$ or $\delta^{15}N$ of different animal tissues. No differences in stable isotope ratios were found between **freeze-dried** and **oven-dried** samples (Bosley & Wainright 1999, Kaehler & Pakhomov 2001), but different preservation techniques (**ethanol**, **formalin**, or a saturated $\mathbf{HgCl_2}$ solution) all appear to produce significant increases in $\delta^{15}N$ values (Bosley & Wainright 1999 : 0.5-1.4 ‰, Marguillier 1998 : 0-1 ‰, but see Kaehler & Pakhomov (2001) who found an increase, but not significant), as well as an increase in variability. Preservation

methods have also been found to produce significant effects on $\delta^{13}C$ values, either causing increased $\delta^{13}C$ signatures (e.g. **ethanol** : Leggett et al. 1999), or a strong depletion (**ethanol** : Hobson et al. 1997 cited in Kaehler & Pakhomov 2001, **formalin** : Marguillier 1998, Kaehler & Pakhomov 2001). Although it has therefore been suggested to avoid the use of preservatives for natural abundance stable isotope work, some authors continue to use e.g. ethanol prior to drying the samples for stable isotope analysis (e.g. Leggett et al. 1999) when other options are not available. Only one study has examined the effects of **short-term live storage** (up to 96 hours) of animals on their stable isotope signatures (as is e.g. often done to allow animals to clear their guts), but the study yielded surprising results : Kaehler & Pakhomov (2001) found a rapid significant increase in $\delta^{13}C$ values of littorinid snails (up to 2.3 ‰ after 96 h) and decrease in $\delta^{15}N$ values (1.2 ‰ after 96 h). Clearly, these results – although as yet not fully explained- show that the procedure of confining live animals for gut evacuation requires caution.

3.2.3. Dissolved Inorganic Carbon

Surface water samples for $\delta^{13}C$ analysis of DIC were collected by gently overfilling a glass bottle (20- 50 ml) which was previously rinsed several times with surface water, poisoning with 100 µl of a saturated $HgCl_2$ solution, and gas tight capping with a rubber plug and aluminium cap. These samples were sometimes stored for several months in the dark before being analysed, but this was found to have no effect on the $\delta^{13}C$ values (L. Hellings, Vrije Universiteit Brussel, pers. comm.). On one occasion (see Chapter 4), this method was compared with samples for TAlk obtained by filtering surface water through 0.2 µm filters.

3.3. Analytical techniques

3.3.1. ELEMENTAL ANALYSIS (POC, PN)

Prior to the analysis, all samples need to be decalcified as the presence of carbonates will interfere. For suspended matter collected on glass fibre filters, this was performed by keeping the samples in acid fumes (HNO_3) for several hours under partial vacuum. Afterwards, filters were re-dried at 60 °C. For sediments and other organic matter samples (animal or plant tissues), this method is not suited (see Schubert & Nielsen 2000) and decalcification was performed following a modified version of the technique described by Nieuwenhuize et al. (1994). Briefly, a weighed amount of sample is tranferred into a silver cup (5 x 12 mm) to which diluted HCl is added *in situ*. The sample is then dried at 60 °C for 24 hours, and if necesssary, the procedure is repeated untill no more carbonates are present (as evidenced from the absence of bubbling). The silver cup is then pinched closed and ready for analysis.

The method chosen for the determination of OC (particulate organic carbon content), TN (total nitrogen content) and C:N ratios (atom) was combustion in an Elemental Analyzer (Carlo Erba NA1500, see Verardo et al. 1990). Briefly, dried and homogenized organic material is packed in tin or silver capsules, and is 'flash combusted' at 1700 °C under excess oxygen in a column filled with chromium trioxide and silver-coated cobaltic oxide as catalysts. The combustion converts the organic matter into CO_2, H_2O, and NO_x gases, which are swept into the reduction column (at 650 °C) by the carrier gas (He) along with the excess O_2. This reduction column is packed with elemental copper and quartz granules, and this assures the conversion of the NO_x into N_2, while the excess O_2 oxidises the Cu and forms CuO. A $Mg(ClO_4)_2$ column traps the water, after which the gases (CO_2 and N_2) are separated on a gas chromatographic column, and detected by thermal conductivity. As the detection is non-destructive, the gases can either simply be discarded, or they can be swept into vacuum lines for the separation of CO_2 and N_2 (see section 3.3.2.). Quantification of C and N is achieved by comparing sample results with thoses of a standard (acetanilide, 71.03 % C, 10.31 % N) which is analysed in triplicate with each batch of samples, and after correction for blanks (i.e. empty tin or silver cups).

3.3.2. STABLE ISOTOPE ANALYSIS ($\delta^{13}C$, $\delta^{15}N$)

The measurement of stable isotope ratios of carbon and nitrogen requires first of all the quantitative conversion of the carbon (organic or inorganic) and/or nitrogen present in the sample to CO_2 and/or N_2. Only under this form can the isotope ratios be adequately measured on the IRMS, and when the conversion is not quantitative, fractionation may occur. For the stable isotope data collected in this work, the purification and separation of CO_2 and N_2 was performed in off-line cryogenic extraction lines; an on-line system became available for the automated analysis of $\delta^{13}C$ and $\delta^{15}N$ of organic samples only in a later stage.

3.3.2.1. Cryopurification of Organic Carbon and Nitrogen

For both carbon and nitrogen stable isotope analysis, the off-line procedure used consisted of :

(1) combustion of samples in an Elemental Analyzer (Carlo Erba NA 1500, as described in section 3.2.1.)
(2) cryogenic separation and purification of the resulting gases (either CO_2 or N_2) in a vacuum extraction line (see below), and
(3) measurement of the stable isotope composition of CO_2 or N_2 on a Finnigan Mat Delta E isotope ratio mass spectrometer (IRMS) in dual inlet mode (see section 3.3.2.3.)

Although several other methods were used for the extraction and purification of C and N from organic samples during the early years of stable isotope analysis (e.g. the Kjeldahl-Rittenberg method and Dumas combustion, see Owens 1987 for an overview), the use of elemental analysers has now become a common procedure, especially in view of the possibilities for coupling these devices to the IRMS via a continuous-flow system which directs the combustion gasses directly into the IRMS. Esssentially, the principle of an elemental analyser as described above is similar to the Dumas combustion technique. The most serious source of imprecision is when incomplete combustion takes place (this may happen e.g. when temperatures are not

sufficiently high, when oxygen is present in insufficient amounts, or with certain hard-to-combust materials such as graphite or large quantities of inorganic salts). Incomplete combustion may cause isotope fractionation (lower δ-values) as the 'light' compounds will usually react at slightly faster rates. Secondly, some by-products produced during incomplete combustion, e.g. CO, C_2H_4, and C_2H_5, may interfere during measurements as they will also be detected as m/z = 28 or 29. Another source of error may be the incomplete removal of CO_2 during the purification steps for N_2, as CO_2 will form CO^+ in the IRMS, which will be detected at m/z 29 (Owens 1987).

- **PURIFICATION OF CO_2**

Carbon dioxide resulting from sample combustion in the elemental analyser is collected in glass tubes by cryogenic separation in a vacuum extraction line. This extraction line consists of two cold traps and a removable sample tube, with valves enabling to close off certain sections of the line. Water and other impurities are retained in the first cold trap (immersed in isopropanol cooled down to -80 °C with liquid N_2), while CO_2 is retained in the second –coiled- cold trap. When all CO_2 resulting from the combustion has entered the extraction line, the connection with the Elemental Analyzer is closed off, and the carrier gas (He) is evacuated. CO_2 in the cold trap is then transferred to the sample tube (released with isopropanol at -80 °C, trapped in sample tube by immersion in liquid N_2), which is sealed by a torch and replaced. The overall process takes approximately 20-25 minutes per sample.
Internal standards used include IAEA-C6 (sucrose, reference $\delta^{13}C = -10.4 \pm 0.1$ ‰) and IAEA-CH-7 (polyethylene foil, reference $\delta^{13}C = -31.8 \pm 0.1$ ‰).

- **PURIFICATION OF N_2**

A second vacuum line was used for the purification of N_2 from organic samples. This extraction line was designed by S. Marguillier, who tested three different methods (quartz tube preparation method, combustion in the EA and a pyrex tube vacuum extraction line, and combustion in the EA and a stainless steel extraction line) and found the latter to show the best precision and accuracy. For a detailed description and comparison with other methods, we refer to Marguillier (1998). Briefly, the line

consists of two cold traps and a removable sample tube. The first cold trap is immersed in liquid N_2 and retains all CO_2 and impurities resulting from the combustion of the sample. The second cool trap is filled with a molecular sieve, which in combination with immersion in liquid nitrogen, holds all N_2 from the gas stream coming from the Elemental Analyzer. After the carrier gas and CO_2 are evacuated (the latter via a bypass), the trapped N_2 is transferred to the sample tube wich consists of a stainless steel tube filled with a molecular sieve and which can be closed off with a valve. One advantage of this design (compared to other methods tested by Marguillier 1998) is that for samples with low N content (such as certain sediments, or plant material) that would yield insufficient N for isotope analysis (15-50 µmoles is the minimum), multiple combustions can be performed whereby the resulting N_2 is collected in the same sample tube. The overall procedure takes approximately 45 minutes per sample.

Internal standards used were IAEA-N1 (ammonium sulphate, reference value $\delta^{15}N$ = + 0.43 ± 0.07 ‰), IAEA-N2 (ammonium sulphate, reference value $\delta^{15}N$ = + 20.41 ± 0.12 ‰), and IAEA-NO3 (ammonium nitrate, reference value $\delta^{15}N$ = + 4.72 ± 0.13 ‰).

3.3.2.2. Extraction and cryopurification of Dissolved Inorganic Carbon

The extraction of total inorganic carbon from water samples was performed using the principles outlined by Kroopnick (1974), using a vacuum extraction line designed and described in detail by L. Hellings (Hellings 2000). Briefly, a small volume of water (3-8 ml) is inserted in a flask on a vacuum line by a syringe through a rubber septum. The flask contains a stirrer and approximately 10 drops of pure *ortho*-phosphoric acid (99 % cryst.) and is immersed in a water bath at approximately 50 °C. Acidification will result in the quantitative release of all inorganic carbon as CO_2, which is subsequently swept through two cool traps (isopropanol at -80 °C) which retain the water vapour. The CO_2 is trapped in a third cool trap immersed in liquid nitrogen. The CO_2 is subsequently redried by releasing it (immersion in isopropanol at -80 °C) and trapping in the next coil with liquid N_2. The CO_2 is again released and is transferred to a glass sample tube immersed in liquid N_2, which is then sealed with a torch.

3.3.2.3. Measurement of $\delta^{13}C$ and $\delta^{15}N$

Measurements of $\delta^{13}C$ and $\delta^{15}N$ values of CO_2 and N_2 as extracted from organic matter or water samples (for DIC) as described above were made on a Finnigan Mat Delta E dual inlet mass spectrometer (IRMS : isotope ratio mass spectrometry). Very briefly, the sample gas is introduced into the ion source, where a heated filament ensures the ionization of part of the sample molecules. These ions are subsequently deflected in a strong magnetic field, whereby the radius of their course is determined by their mass (actually by the ratio of the mass to the charge but the latter is similar in all ions). The ions of different mass (28 and 29 for N_2, 44, 45, and 46 for CO_2) are collected on Faraday cups and the electric signal is amplified and transmitted to the PC. The same is done for a working standard gas (CO_2 produced from Carrara marble or pure N_2 from a tank), whereby during each sample measurement the instrument switches between sample and standard gas a predefined number of times.

For $\delta^{13}C$, the isotope composition of the working standard is verified daily by measuring a secondary standard (MAR 1, produced from carbonates with known $\delta^{13}C$ and $\delta^{18}O$ values which are checked against a certified carbonate standard, NBS-19). For $\delta^{15}N$, corrections for variations in the isotope composition of the standard gas are principally made based on the results of the internal standards (IAEA-N1, IAEA-N2, and IAEA-NO3, one each during each batch of samples), and in addition the working standard was regularly measured against a certified bottle of N_2 gas.

CHAPTER 4 : Impact of the presence of mangroves on the inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India).

Foreword

In this chapter, we present the results of a sampling campaign (organized jointly with the Chemical Oceanography Unit, University of Liège (Ulg), Belgium, and with the Marine Biology dept., Andhra Univerity, India) focussed on examining the distribution and sources of organic and inorganic carbon in the Gautami Godavari estuary (from freshwater conditions to the opening into the Bay of Bengal), and in the mangrove ecosystem comprising the network of tidal creeks and the adjacent Kakinada Bay located in the Gautami Godavari estuary. The presence of an extensive mangrove ecosystem was found to have a major impact on the organic and inorganic carbon biogeochemistry, and these results -although chronologically collected later than most other data presented in this thesis- therefore provide an ideal framework for the following chapters. The abovementioned sampling campaign only addresses the pre-monsoon situation, but partial results of a longer-term sampling effort (jointly with Andhra University) are presented to highlight the seasonality of –in particular- the dissolved inorganic carbon dynamics in this ecosystem.

It must be stressed that a large amount of data presented in this chapter were collected by the Chemical Oceanography Unit (ULg) (O_2, pH, TAlk and deduced parameters, Chl-a) or their collegues (H. Etcheber and G. Abril, Université de Bordaux for POC and DOC; B. Velimirov, Institut für Medizinische Biologie, Universitaet Wien for bacterial C) during the joint fieldwork, and were kindly provided in order to make the discussion of our own data ($\delta^{13}C_{POC}$, POC/PN, $\delta^{13}C_{DIC}$, and -during monthly sampling- TAlk) more comprehensive.

One publication related to this chapter is currently in preparation :

Bouillon S, Dehairs F, Abril G, Etcheber H, Velimirov B, Frankignoulle M, & Borges A (2002) Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon : the local impact of extensive mangrove forests.

Abstract

The present study investigates the distribution and sources of organic and inorganic carbon as well as the water/air exchange of CO_2 in the Gautami Godavari river (Andhra Pradesh, India) and in a mangrove ecosystem in its estuary during the pre-monsoon season. The presence of mangroves on the aquatic biogeochemistry was evidenced by markedly higher concentrations of dissolved inorganic carbon ([DIC]) and total alkalinity (TAlk), higher POC and DOC concentrations (particulate and dissolved organic carbon, respectively), more negative $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$, lower pH and dissolved oxygen concentrations, and a higher partial pressure of CO_2 (pCO_2) when compared to the marine part of the Godavari estuary. The present study clearly identifies the mangrove creeks as an active site of mineralization of organic matter (of which on average 72 % was present as dissolved organic carbon) and CO_2 efflux to the atmosphere, but also indicates that -at least during the period under study- this processing of organic carbon is a rather localised feature, with a limited impact on adjacent ecosystems. The Godavari river, on the other hand, was only a minor source of CO_2 to the atmosphere during the pre-monsoon season, and there was a net flux from atmosphere to the water column in the oligo- and mesohaline zone. In the Gautami Godavari, non-conservative behaviour was observed for DIC (internal production, mainly in the oligo-and mesohaline section), TAlk (internal production along most of the salinity gradient), and $\delta^{13}C_{DIC}$, the latter being higher than predicted for the oligo- and mesohaline section (0-20 ppt). This pattern can be explained by the dominance of carbonate dissolution as the main process influencing the inorganic carbon dynamics in the Gautami Godavari during pre-monsoon, especially in the oligo- and mesohaline zone. In the mangrove ecosystem located in its estuary, however, variations in concentrations and $\delta^{13}C$ of the DIC pool were a result of the degradation of organic matter, which is hypothesized to be of local origin (i.e. mangrove production) during pre-monsoon. Although the seasonality in the inorganic carbon geochemistry of the estuary remains unresolved, the mangrove creeks and adjacent bay showed little distinct seasonality in TAlk, but $\delta^{13}C_{DIC}$ was significantly more negative during and after the monsoon season. These variations are hypothesized to be caused by the mineralization of the large amounts of terrestrial organic matter transported by the Godavari during monsoon, whereas mangrove litter is the main external source of organic carbon inputs during other seasons.

Introduction

The majority of large rivers show a marked oversaturation of CO_2 (Cole & Caraco 2001), indicating a net flux of CO_2 from the river to the atmosphere. This suggests an important role for rivers and estuaries not only as a pathway of transport for organic carbon (e.g. see Ittekkot & Laane 1991), but also for active degassing of CO_2 to the atmosphere. For example, Hellings et al. (2001) estimated that the atmospheric CO_2 flux for the mesohaline, oligohaline, and freshwater zone of the Scheldt river (Belgium) constituted 13 % of the reported organic matter inputs in the Scheldt, and Frankignoulle et al. (1998) estimated that European estuaries as a whole are responsible for 5 to 10 % of current anthropogenic CO_2 emissions in Western Europe (but see Raymond & Cole 2001). The major primary sources of inorganic carbon in natural waters are CO_2 from the atmosphere, from the decay of organic matter, and from the dissolution of carbonates. Studies on the biogeochemistry of the major rivers and estuaries on the Indian subcontinent (in particular for the Godavari, e.g. see Spitzy & Leenheer 1991, Gupta et al. 1997, Padmavathi & Satyanarayana 1999) are scarce and the inorganic carbon chemistry of these systems is virtually uninvestigated (Sarma et al. 2001). The amounts of particulate organic carbon exported by some of India's river systems (e.g. Ganges, Indus, and Brahmaputra combined : 18.10^6 t POC y^{-1}, Godavari : 2.8 10^6 t POC y^{-1}, see Gupta et al. 1997 for details) are estimated to be among the highest in the world, yet few data are available on the potential of these systems to act as a source of CO_2 to the atmosphere. Sarma et al. (2001) found the Mandovi-Zuari estuary (Goa, India - a system with a basin area an order of magnitude smaller than that of the system studied here) to show oversaturation of CO_2 during both SW-monsoon and non-monsoon season, with surprisingly little difference between these two contrasting seasons, although the calculated fluxes of CO_2 were sixfold higher during the monsoon season, mainly due to differences in wind speed.

Data on the inorganic carbon chemistry in mangrove ecosystems –a common component of many tropical and subtropical estuaries- are also virtually non-existent (Ghosh et al. 1987, Ovalle et al. 1990, 1999, Millero et al. 2001), as most studies on the carbon dynamics in these ecosystems have dealt with organic carbon species (e.g. Lee 1995, Dittmar et al. 2001a, b, Davis et al. 2001a,b). Mangroves can obtain high primary production rates (see Twilley et al. 1992), and although it has become clear that these systems may export significant amounts of carbon to the aquatic

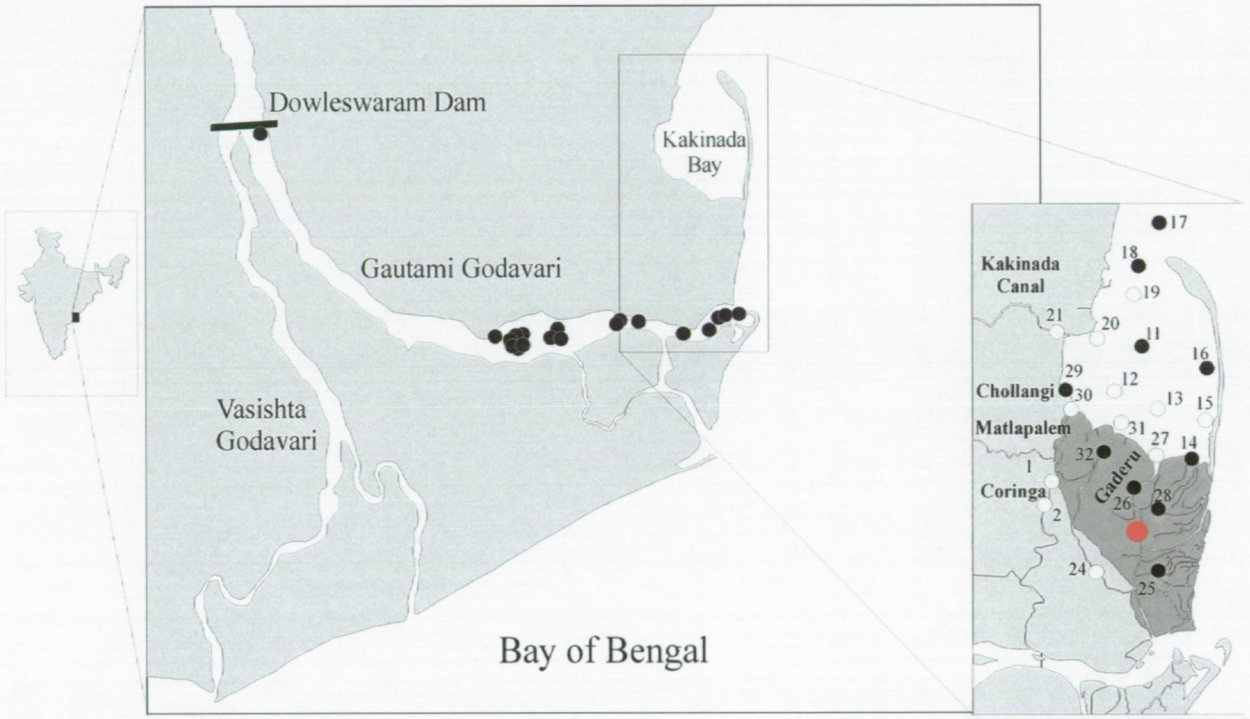
environment under certain conditions, the geographical extent to which this occurs and the fate of this material have been an issue of much debate in the literature. Recent studies show that in the majority of cases, mangrove-derived carbon can only be traced in a relatively narrow zone adjacent to the forest (Lee 1995, but see Dittmar et al. 2001), and that its role in sustaining secondary production is less important than previously hypothesised (e.g. Lee 2000, see Chapters 5, 6, 8, and 10). The role of dissolved organic carbon (DOC) has recently gained more attention and has been found to be the dominant form of organic carbon in the water column in several studies (e.g. Twilley 1985, Davis et al. 2001a, Dittmar & Lara 2001a, b), but little is known about the origin and fate of the DOC in these ecosystems. The importance of bacterial respiration in the water column as a potential fate of mangrove carbon has been very poorly studied. Bano et al. (1997), however, measured high bacterial carbon production rates (generally between 50 and 300 µg C per litre per day) in mangrove creeks in the Indus delta, coinciding with a relatively low bacterial abundance (20-80 µg C l^{-1}), thus indicating high specific growth rates (1-7 day^{-1}, but as high as 24 d^{-1} during a phytoplankton bloom). If such a tight coupling of bacterial production and removal is a common feature in these ecosystems, bacterial respiration might represent a major yet poorly studied pathway for mangrove-derived carbon.

Here, we present data collected during two surveys along the salinity gradient of the Gautami Godavari, the northern branch of the Godavari river, and during several surveys in the mangrove creeks located in its estuary and the adjacent semi-enclosed Kakinada Bay (Andhra Pradesh, India). In addition, a monthly sampling campaign was held in some of the tidal mangrove creeks and Kakinada Bay. The aim of our study was (a) to gain insight into the sources and fate of inorganic carbon along the salinity gradient in the Godavari river, (b) to assess to which extent the presence of an extensive mangrove forest could alter the organic and inorganic carbon chemistry and whether a potential impact was also discernable in the adjacent Kakinada Bay, and (c) to assess the seasonal variability in the stocks and sources of DIC in the mangrove creeks and adjacent bay. The systems studied exhibit a strong monsoonal influence (e.g. > 96 % of discharge for the Godavari occurs during the monsoon months, but note that the discharge is regulated artificially at Dowleswaram Dam, see 'Study area'), and the data from the Gautami Godavari presented here (all from June 2001, prior to the onset of the monsoon in 2001) thus provide only a very partial view of the river's organic and inorganic carbon dynamics.

Materials and methods

Study area

All sampling sites are located within the Godavari estuary, Andhra Pradesh, India. The Godavari is one of India's largest rivers, draining an area of more than 300,000 km² before opening into the Bay of Bengal. The river has two main branches, the Gautami and Vasishta Godavari, of which only the former was sampled for this study. Two surveys (May 27th, June 1st, 2001) were conducted on the Gautami Godavari proper, from its mouth in the Bay of Bengal up to the oligohaline zone (Figure 1). Furthermore, one sampling location was located just below the Dowleswaram Dam (constructed in 1852 and located before the Godavari branches into the Gautami and Vasishta) on June 2nd, 2001, and two additional sample points in the Godavari mouth were visited on May 29th. The Gautami Godavari has several small branches into the semi-enclosed Kakinada bay, including Coringa and Gaderu (Fig 1). The area between the Godavari and Kakinada bay is covered by extensive mangrove forests and tidal mudflats and a multitude of interconnected tidal creeks. Kakinada bay (depth ranging from 3 to 8 meters at high tide) covers approximately 150 km² and opens into the Bay of Bengal on its northern side, bordered along most of its eastern length by a narrow sand bar (Hope Island). The mangrove creeks and bay were sampled during two surveys (May 28 and 29, 2001), and one station in the mangrove-covered region was selected for sampling during a 24-h period (see Figure 1). Tides are semidiurnal, and tidal amplitude in the Bay varies between approximately 0.5 and 2 meters. 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. During the sampling period of this study, estuarine to marine conditions had re-established in the mangrove creeks and bay.



Monthly sampling locations

17 : BB (Bay of Bengal)

18 : KBN (Kakinada Bay, North)

11 : KB (Kakinada Bay)

16 : GU (Guticada)

29 : CHO (Chollangi)

14 : MD (Mukanali Dibba)

32 : CO (Coringa)

26 : GA (Gaderu)

28 : LH (Gaderu side creek, near old lighthouse)

25 : GcIII (Gaderu side creek)

Figure 1 : Location of the sampling sites along the salinity gradient of the Gautami Godavari estuary and of sampling sites in the mangrove creeks of the Coringa Wildlife Sanctuary and Kakinada Bay during the pre-monsoon period of 2001 (all locations) and during monthly sampling campaigns in the period 2000-2001 (black circles). Red circle shows location of diurnal cycle sampling. Abbreviations of monthly sampling stations as in Legend.

Sampling and analytical techniques

Salinity and temperature were measured *in situ* with a portable conductivity meter and temperature probe. A Niskin bottle was used to sample surface water for all other parameters. Dissolved oxygen was measured immediately after collection with a polarographic electrode (WTW Oxi-340) calibrated on saturated air. Accuracy of the level of saturation of O_2 is estimated to ± 1% of level of saturation. Samples for determination of total alkalinity (TAlk) were obtained by filtering 100 ml of water from the Niskin bottle through 0.2 µm filters, and were stored in polyethylene bottles until analysis. For the monthly sampling, samples for TAlk were obtained as for DIC (see below), and these samples were filtered (0.4 µm) just prior to TAlk determination. TAlk was analysed by automated electro-titration on 50 ml samples with 0.1 M HCl (for the pre-monsoon 2001 samples, taking into account the corrections for sulphate and fluoride interaction according to Hansson & Jagner 1973), or on 20-25 ml samples with 0.01 M HCl as titrant (for the seasonal samples). pH was measured using a Ross type combination electrode (ORION®) calibrated on the NBS scale, using home-made phthalate and phosphate buffers (A. Borges, pers. comm.), the calibration temperature correction was made according to Fuhrmann & Zirino (1988) and the correction to *in situ* temperature according to Pérez & Fraga (1987). The reproducibility of TAlk was estimated at ± 4 µeq kg^{-1} (for the May-June 2001 campaign) or ± 20 µeq kg^{-1} (see Hellings 2000) for the seasonal data; reproducibility of pH measurements during the pre-monsoon 2001 survey was estimated at ± 0.005.

The partial pressure of CO_2 (pCO_2) and the dissolved inorganic carbon concentrations ([DIC]) were computed from pH and TAlk measurements using the carbonic acid constants sets proposed by Mehrbach et al. (1973), the borate acidity constant from Lyman (1957) (the latter two are refitted by Millero 1979) and the CO_2 solubility coefficient of Weiss (1974). The accuracy of DIC and pCO_2 computed from the pH-TAlk couple are estimated to ± 5 µmol kg^{-1} and ± 5 µatm, respectively (A. Borges, pers. comm.).

Samples for Chlorophyll-a were obtained by filtering a known volume of surface water from the Niskin bottle on pre-combusted glass fibre filters (0.7 µm, Whatman GF/F). These filters were stored in a liquid nitrogen transporter until arrival in Belgium, and were later transferred to -20 °C. Pigments were extracted for

approximately 12 hours in 15 ml of 90% acetone at 4°C and analysed with a Turner TD-700 Fluorimeter, and the accuracy of Chl-a analysis was estimated to be ± 4 %.

Samples for dissolved organic carbon (DOC) were obtained by filtering a known volume of surface water (0.2 µm) and were preserved by the addition of 50 µl of Phosphoric Acid (H3PO4) per 15 ml of sample. DOC was measured with a high-temperature catalytic oxidation analyser (Shimadzu TOC 5000), replicates showed an accuracy around 0.05 mg l^{-1}. Samples for the determination of bacterial abundance were preserved with formaldehyde (2% v/v final conc.). Cells were counted and sized by epifluorescence microscopy and the acridine orange direct counting technique (Hobbie et al. 1977). At least 20 microscopic fields per sub-sample were counted. The size of 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 & Valenta-Simon 1992). At least 50 cells per morphotype and sub-sample (i.e. 600 cells per sample) were sized in length and width. In order to obtain reliable size estimations during direct observation in the epifluorescence microscope, fluorescent latex beads with diameters of 0.1, 0.2, 0.6 and 0.88 µm (Polyscience Lim.) were used to calibrate the sizing procedure (Velimirov & Valenta-Simon 1992). Cellular carbon content in fg C $cell^{-1}$ was calculated from estimated cell volumes (V, μm^3) assuming the allometric relation $C=120\ V^{0.72}$ (Norland 1993).

Water samples for the analysis of $\delta^{13}C_{DIC}$ (stable isotope composition of dissolved inorganic carbon) were obtained by gently overfilling a glass bottle with surface water from the Niskin 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, $\delta^{13}C_{DIC}$ analysis was done on samples for TAlk (as described above) and these were compared with the above-described method, to verify whether the two preservation methods affected $\delta^{13}C_{DIC}$ results. The two sampling methods resulted in $\delta^{13}C$ values within 0.17 ‰ of each other (n=4), i.e. within the analytical precision of $\delta^{13}C_{DIC}$ analysis. DIC was extracted by acidification with H_3PO_4 in an evacuated glass line, cryogenically purified and transferred to a glass sample tube.

POC was sampled by filtering 100 ml of surface water on pre-combusted (12 hours at 450 °C) glass-fibre filters (Whatman GF/F), and air-drying or oven-drying (60 °C).

Elemental analysis (POC/PN, atom) of decarbonated (dilute HCl) suspended matter was done using a Carlo Erba NA-1500 elemental analyser, with acetanilide as a standard. Samples for $\delta^{13}C_{POC}$ were decarbonated (acid fumes), combusted in an elemental analyser, and the resulting CO_2 was cryogenically separated and purified. $\delta^{13}C$ ratios (for both DIC and POC) were subsequently measured on a Finnigan Mat Delta E isotope ratio mass spectrometer, and are reported in the δ notation relative to PDB as :

$$\delta X = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] * 10^3 \qquad [‰] \qquad [1]$$

where X = ^{13}C, and R = $^{13}C/^{12}C$. Reproducibility was better than 0.2 ‰ for both $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$.

Results

Physico-chemical parameters

The two transects along the Gautami Godavari comprised the salinity range 0.5 – 34.3 ppt, and an additional sample at zero salinity was obtained from Dowleswaram Dam. In the mangrove creeks and Kakinada Bay, salinity was overall high during the pre-monsoon sampling, with a minimum of 24.3 ppt (at Coringa creek) and a maximum of 37.2 ppt (at one of Gaderu's side creeks). Surface water temperature was generally high throughout, ranging overall between 27.9 and 33.5 °C. pH values in the Godavari were highest in the oligohaline/freshwater[1] zone (up to ~8.8) and decreased continuously towards values of ~8.2 in the marine section (Figure 2, Table 1 and 2). In the mangrove creeks and Bay, however, pH values were markedly lower than under similar salinity conditions in the river (Figure 2), with values decreasing to a minimum of ~7.3. Oxygen saturation was high along the entire salinity gradient of the Godavari (94-133 %) with no observable variation along the transect (Figure 3, Table 1 and 2). Oxygen saturation in the mangrove creeks was generally lower (with a minimum of 52 % observed during the diurnal cycle), but also high in Kakinada Bay and some mangrove stations (Figure 3, Table 3 and 4).

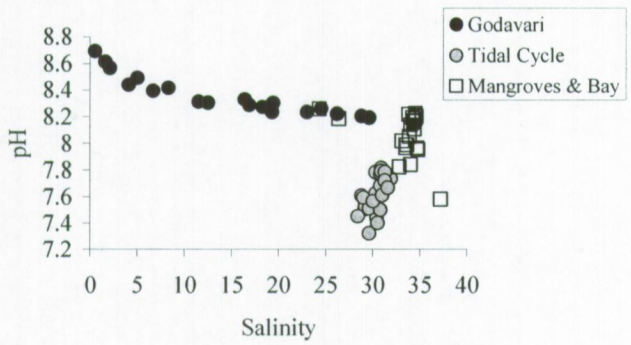


Figure 2 : pH variations along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.

[1] Definitions : oligohaline zone : salinity ranging between 0.05 and 5 ppt
mesohaline zone : salinity ranging between 5 and 18 ppt

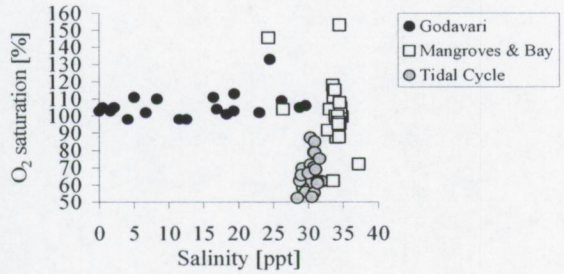


Figure 3 : Variations in the oxygen saturation state along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.

For total alkalinity (TAlk), a general albeit relatively minor decrease is observed along the salinity gradient of the Gautami Godavari, i.e. with lower values (approximately 2.26 meq l^{-1}) in the marine end of the estuary, but with an apparent maximum in the 5-10 ppt salinity zone (reaching approximately 2.36 meq l^{-1}, see Figure 4 and also Figure 20B). Variations along the river salinity gradient are thus rather small, but TAlk increased markedly in the mangrove creeks and Kakinada Bay, with values reaching a maximum of 3.197 meq l^{-1}, albeit generally between 2.28 and 2.71 meq l^{-1}). A similar trend was observed for [DIC] (Figure 5, see also Figure 20A).

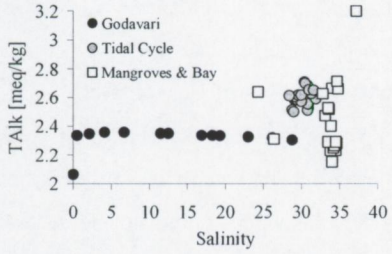


Figure 4: Variations in Total Alkalinity along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.

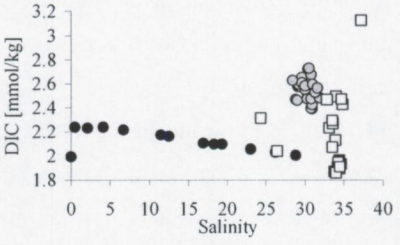


Figure 5: Variations in dissolved inorganic carbon concentration along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.

These spatial trends in TAlk and pH result in a marked gradient for pCO_2 (Figure 6, Table 1 to 4), with a low degree of supersaturation (~ 450 ppm, atmospheric concentration is currently ~360 ppm) along most of the Godavari (and even slightly undersaturated in the oligo- and mesohaline zone), but with a wide range of values in the mangrove creeks (ranging between 396 and 6437 ppm, usually > 2000 ppm) and intermediate values in Kakinada Bay (392-758 ppm).

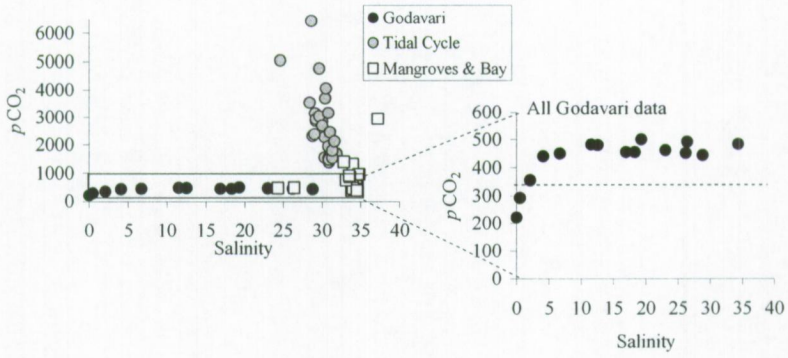


Figure 6 : Variations in the partial pressure of CO_2 (expressed in ppm) along the Gautami Godavari salinity gradient (enlarged section) and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001. Dotted line in insert represents equilibrium with the atmosphere.

In the mangrove creeks and Bay, TAlk was found to show little pronounced seasonality (Figure 7) but showed an overall consistent spatial gradient of lower alkalinity in the Bay region (stations GU, KB, KBN, and BB), higher TAlk in most of the mangrove creek locations (LH, CO, GA) and intermediate TAlk values in two locations apparently influenced by the vicinity of the Bay of Bengal (GcIII and MD, the latter being located near the recent breakthrough in Hope Island) and in Chollangi creek. Due to the uncertainty associated with pH measurements during the seasonal sampling campaigns, DIC concentrations and pCO_2 values could not be accurately calculated from our dataset.

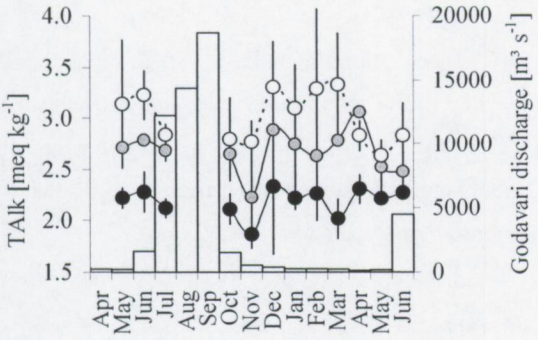


Figure 7 : Seasonality of Total Alkalinity at 10 sampling stations (see Figure 1B) in the mangrove creeks of the Coringa Wildlife Sanctuary and the adjacent Kakinada Bay. [Note : the choice of stations for which data were grouped in Fig 8 is the result of a paired t-test for data on $\delta^{13}C_{DIC}$, a similar approach for TAlk resulted in some additional significant differences -e.g. between GA on the one hand and LH and CO on the other hand- but for reasons of clarity these are not presented separately]. White bars indicate average monthly discharge for the Godavari at Dowleswaram Dam.

Carbon stable isotope composition of the DIC pool ($\delta^{13}C_{DIC}$)

$\delta^{13}C_{DIC}$ during the two Godavari transects varied between -0.4 (at a salinity of 34.3 ppt) and -6.4 ‰ (salinity 0.5 ppt) over the length of the estuary, and $\delta^{13}C_{DIC}$ values increased gradually with salinity (Figure 8, but see Discussion). No significant differences in $\delta^{13}C_{DIC}$ values were found between the two surveys. Upstream at Dowleswaram Dam (sal 0 ppt), the DIC pool was markedly enriched (-4.5 ‰) relative to the values found in freshwater conditions during the two transects. The relationship between $\delta^{13}C_{DIC}$ and salinity found along the Godavari transects, did not hold for the mangrove creeks and Kakinada Bay, where $\delta^{13}C$ values were found to be generally much lower than in the marine part of the river (Figure 8).

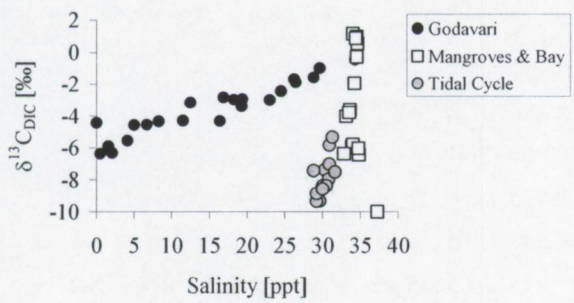


Figure 8 : Variations in the carbon isotope composition of the DIC pool along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.

In some of the bay stations, $\delta^{13}C_{DIC}$ values were as high as +1.1 ‰, whereas the lowest value recorded in the creeks was -10.0 ‰. $\delta^{13}C$ values of the DIC pool were overall well correlated to the DIC concentration (R^2=0.82, $p<0.01$ for all data pooled, but see Discussion for details). Significant variations in the carbon stable isotope composition of DIC (-9.3 to -5.3 ‰) and POC (-27.4 to -24.3 ‰) were also noted during the diurnal cycle in Gaderu, and both parameters were partially related to the (small) salinity variations (see Figure 16, compare panels A, C, and D).

A consistent spatial trend in $\delta^{13}C$ values of the DIC pool can be observed, with lower values in the mangrove creeks compared to the Kakinada Bay stations (Figure 9). Superimposed on this spatial gradient, $\delta^{13}C_{DIC}$ values show significant seasonality, with generally lower values during and shortly after the monsoon discharge, and gradually increasing towards maximum $\delta^{13}C$ values during the pre-monsoon period (Figure 9). At each sampling time, $\delta^{13}C_{DIC}$ values are well correlated with TAlk data (see Discussion, R^2 varies between 0.45 and 0.96), but this relationship usually no longer holds when seasonal data are pooled stationwise.

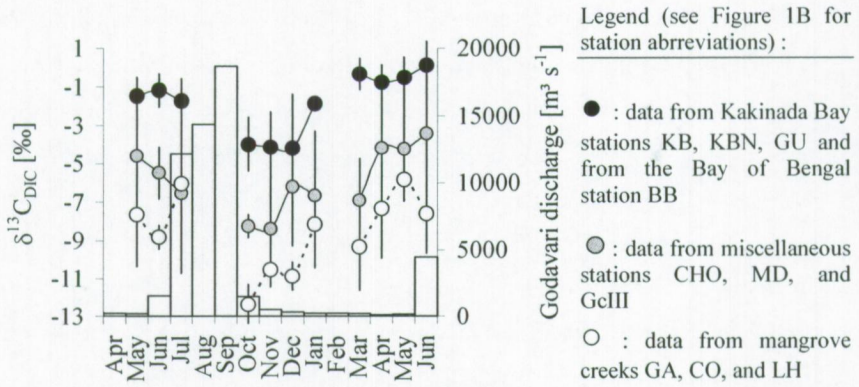


Figure 9 : Seasonality of $\delta^{13}C_{DIC}$ at 10 sampling stations (see Figure 1B) in the mangrove creeks of the Coringa Wildlife Sanctuary and the adjacent Kakinada Bay. White bars indicate average monthly discharge for the Godavari at Dowleswaram Dam. [Note : the choice of stations for which data were grouped in Fig 11 is the result of a paired t-test for $\delta^{13}C_{DIC}$ data].

Characterization of organic matter

Concentrations of particulate organic carbon decreased along the salinity gradient of the Gautami Godavari (Figure 10 A) towards the marine end, with overall values between 493 and 1808 µg l^{-1}, and values were markedly higher (692 - 2824 µg l^{-1}) in

the mangrove creeks. The contribution of POC to the total suspended matter pool was relatively high in most of the Gautami Godavari data (mostly > 10 %, Figure 10 B). Concentrations of DOC (dissolved organic carbon, see Figure 11 and Table 1-4) were markedly higher in the mangrove creeks (data from the diurnal cycle : on average 4.26 ± 2.12 mg l^{-1}, corresponding to 72.9 ± 10.6 % of the total organic matter pool in the water column) compared to the Godavari (on average 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 (see Figure 11). Estimates of bacterial carbon stocks averaged 53.1 ± 17.8 µg C l^{-1} during the diurnal cycle in Gaderu (amounting to 1.0 ± 0.3 % of the total organic carbon pool), but lower in the Gautami Godavari (44.2 ± 10.6 µg C l^{-1}, i.e. 1.4 ± 0.4 % of the TOC pool, with little variation along the salinity gradient, see Figure 12).

POC/PN ratios of suspended matter were relatively low during both Godavari transects and in the mangrove creeks, reflecting the dominance of phytoplankton during this season, with little or no trend along the salinity gradient (Figure 13). However, POC/PN ratios during the second river transect (7.5 ± 0.8) were significantly (check) higher than during the first transect (5.9 ± 0.5).

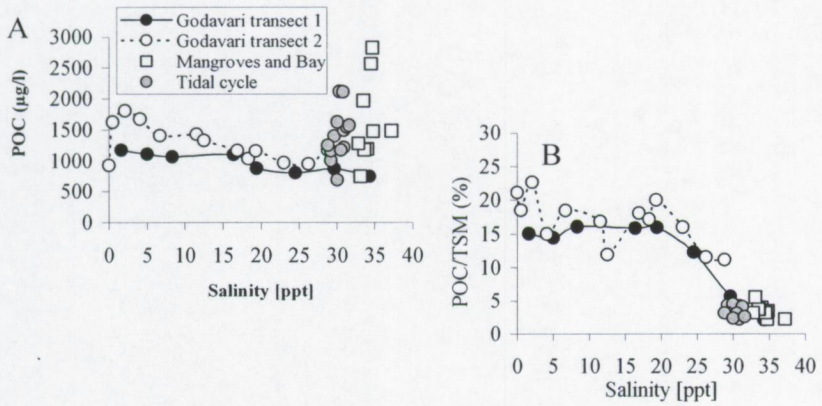


Figure 10 : (A) Concentrations of particulate organic carbon along the salinity gradient of the Gautami Godavari and in the mangrove creeks and Kakinada Bay (note that some data from Kakinada Bay are missing, see Table 3), and (B) contribution of organic carbon to the total suspended matter (TSM) pool. Legend as in panel A. Note that two high values from Coringa were not included as they were well out of the range of other data (POC > 7000 µg l^{-1} , see Table 3 for details).

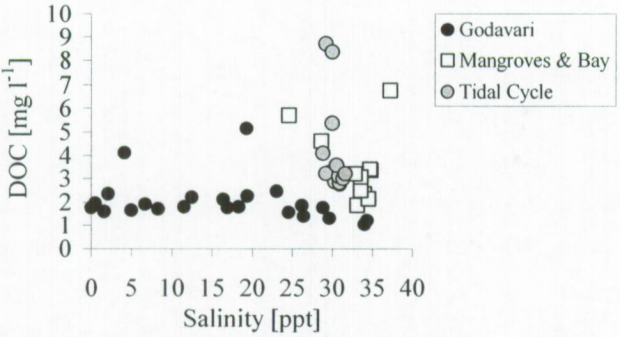


Figure 11 : Variations in the concentration of dissolved organic carbon (DOC) along the salinity gradient of the Gautami Godavari (black symbols), in the mangrove creeks and Kakinada Bay (open symbols + grey symbols taken during the diurnal cycle).

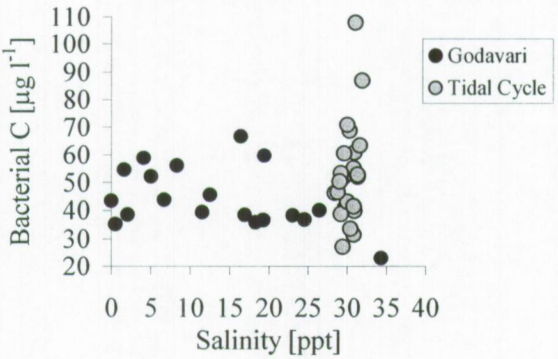


Figure 12 : Variations in the estimated stock of bacterial carbon in the water column along the salinity gradient of the Gautami Godavari (black symbols), and in a mangrove creek (Gaderu) during a diurnal cycle (grey symbols).

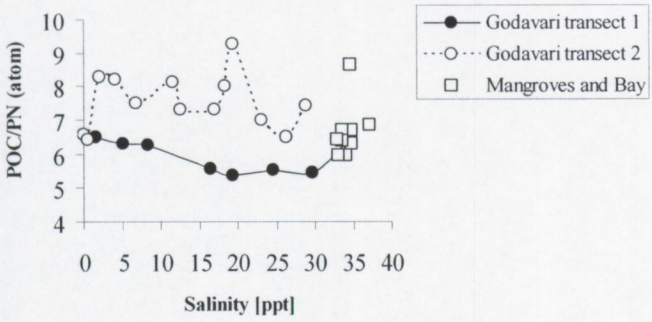
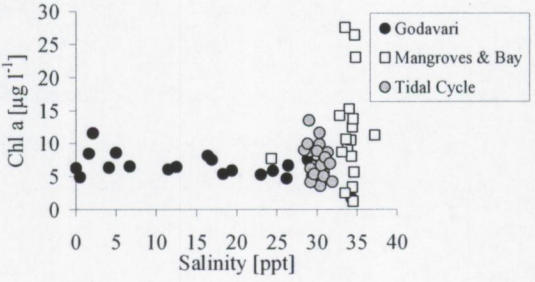


Figure 13 : Elemental composition (POC/PN) of suspended organic matter along the Gautami Godavari salinity gradient and in the mangrove creeks and Kakinada Bay (note that not data are available for most of the Bay stations nor for the diurnal cycle, see Table 3 and 4).

Chlorophyll a concentrations during the two Godavari transects averaged 6.43 $\mu g\ l^{-1}$ and showed no marked variations along the salinity gradient or between the two transects (Figure 14, Table 1 and 2). In Kakinada Bay and in the mangrove creeks, Chl a values were usually higher, with an overall range between 1.2 and 32.1 $\mu g\ l^{-1}$, and with the highest values being recorded in the creeks (Figure 14, Table 3 and 4). $\delta^{13}C_{POC}$ values during the first Godavari survey decreased linearly along the salinity gradient ($R^2 = 0.97$), but this pattern was much more distorted during the second transect ($R^2 = 0.64$), and $\delta^{13}C_{POC}$ values were generally higher for similar salinities than during the first transect (see Figure 15). $\delta^{13}C_{POC}$ in mangrove creeks and bay were lower than those at similar salinities in the estuary proper (Figure 15), but to a lesser extent than observed for DIC (compare Figures 9 and 15).

Figure 14 : Chlorophyll a concentrations ($\mu g\ l^{-1}$) along the salinity gradient of the Gautami Godavari and in the mangrove creeks and Kakinada Bay during the pre-monsoon period of 2001.



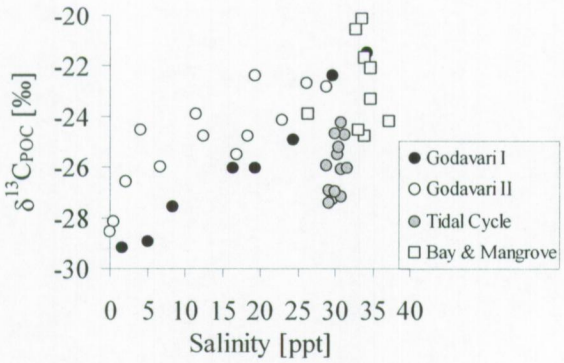


Figure 15 : Carbon isotope composition of suspended organic matter along the Gautami Godavari salinity gradient (both transects considered separately) and in the mangrove creeks and Kakinada Bay (note that no data are available for most of the Bay stations, see Table 3).

Diurnal variations of selected parameters in a mangrove creek

During the diurnal cycle at Gaderu creek, significant variations were observed in most physico-chemical and biogeochemical parameters (Figure 14, see also Figures 2 - 7, 9, 11, and 15), despite relatively minor overall salinity variations (28.4 - 31.9 ppt). Oxygen saturation ranged from 52.5 to 87.2 %, with generally lower values during the night, and gradually increasing during the day - although some relationship with salinity variations can also be discerned (Figure 16, top panel) with higher O_2 saturation at higher salinity. Similarly, Chl-a concentrations appeared to be lower during the night, and increased during daytime, but it can be noted that the early morning increase in Chl-a concentration preceded daylight, and is thus unlikely to be the result of the onset of photosynthesis but may also have been a tidal effect (note, however, that in general Chl-a concentrations were lower at higher salinities). Bacterial carbon stocks showed a somewhat erratic pattern, with apparently lower values during the night, and with no significant relationship with salinity (Figure not shown). DOC concentrations showed no discernable pattern, but a marked peak was observed during the night (Figure 16, second panel) -coinciding with a sharp decrease in pH, $\delta^{13}C_{DIC}$, and $[O_2]$- and a second peak during the day, also coinciding with low pH, $\delta^{13}C_{DIC}$. $\delta^{13}C_{DIC}$ variations showed to be strikingly similar to pH variations, with lower pH values coinciding with more negative $\delta^{13}C_{DIC}$ values (Figure 16, third panel). Furthermore, $\delta^{13}C_{DIC}$ variations were negatively correlated with DIC concentrations (Figure not shown but see Figure 19) and with O_2 saturation levels (Figure not shown). $\delta^{13}C_{POC}$ variations, on the other hand, coincided with variations in POC concentrations (Figure 16, lower panel).

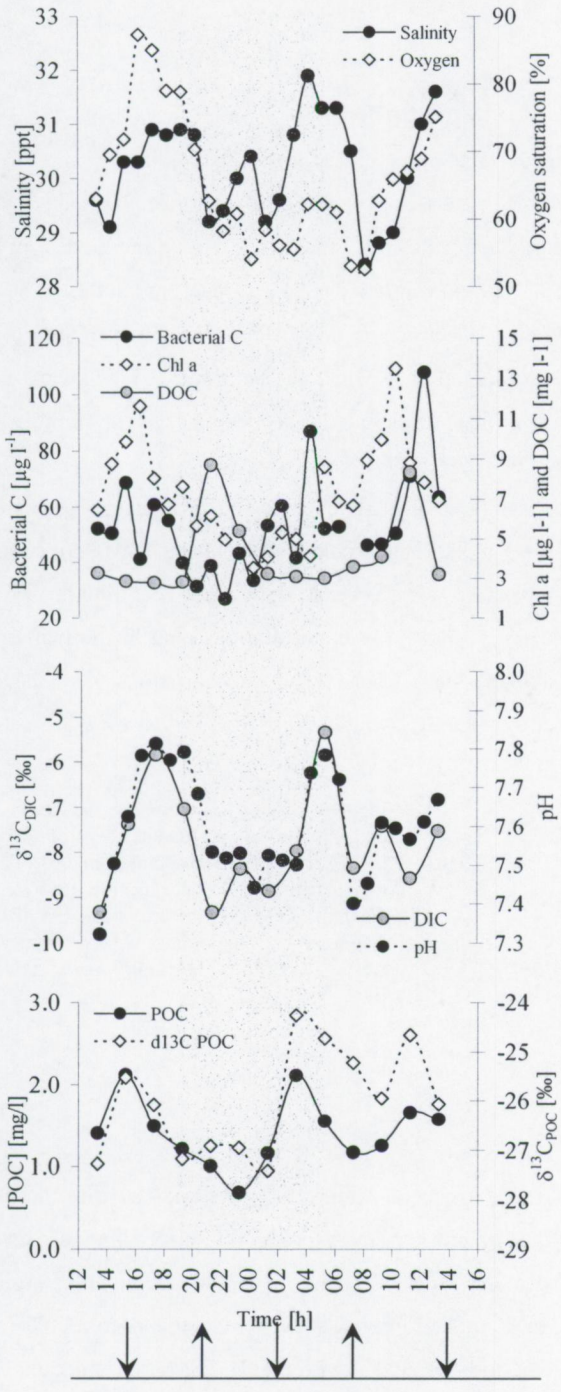


Figure 16 : Diurnal variations (at hourly or two-hourly resolution) of the stable carbon isotope composition of the DIC pool, pH, salinity, oxygen saturation state, bacterial C stock, Chlorophyll a concentration, DOC concentration, POC concentration, and stable carbon isotope composition of the POC pool at Gaderu creek (see Figure 1B for location). Grey-shaded area represents night time. Arrows pointing upward represent approximate high tide, arrows pointing downward represent approximate low tide.

Discussion

Sources and distribution of organic carbon

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 10^6 t POC y^{-1}, ranking it among the highest in the world (see Chapter 3, Table 1). The concentrations of DOC measured in this study for the Godavari (2.02 ± 0.91 mgl^{-1}) are clearly higher than those of Somayajulu et al. (1993) during the post-monsoon season (0.3 – 1 mg l^{-1}), but remain in the lower range of values other major world rivers (averages ranging between 2.4 for the Gambia and 16.1 for the Indus, see Spitzy & Leenheer 1991 for an overview).

Concentrations of POC were also relatively low in the Gautami Godavari during our study period, and POC generally made a large contribution to the TSM pool (Figure 10). Both parameters were inversely related, i.e. a higher POC contribution to the TSM pool coincided with lower overall TSM concentrations, and in the mangrove creeks and the adjacent Kakinada Bay, where TSM concentrations were usually higher than in the Godavari, lower POC/TSM ratios were found (Figure 17).

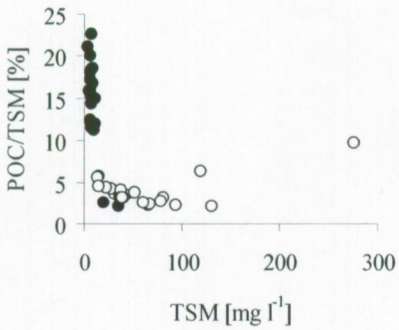


Figure 17 : Relationship between the contribution of particulate organic carbon (POC) to the total suspended matter (TSM) pool and the TSM concentration itself for the Gautami Godavari salinity gradient (black symbols) and the mangrove creeks of the Coringa Wildlife Sanctuary and Kakinada Bay.

Such a relationship appears to be a general feature in rivers and estuaries, and has been suggested to be the result of lower primary production under high suspended matter concentrations (Ittekkot & Laane 1991), which would additionally imply a different composition of the POC pool. However, as higher Chl a concentrations (and lower POC/Chl a ratios) in our study coincided with higher TSM concentrations and

lower POC/TSM ratios (e.g. Figure 18), the latter hypothesis does not appear to hold true.

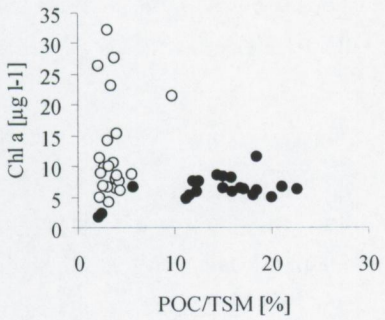


Figure 18 : Relationship between the contribution of POC to the TSM pool and Chlorophyll a concentrations during the pre-monsoon of 2001. Black symbols : data for the Gautami Godavari. Open symbols : data for the mangrove creeks and Kakinada Bay.

POC/PN ratios were also not markedly different in the Godavari (generally low TSM) when compared to the mangrove creeks and Kakinada Bay (generally higher TSM). It has been well established that the concentration of TSM is a major determinant for the relative importance of DOC and POC pools in rivers and estuaries (see Ittekkot & Laane 1991, Abril et al. 2002), with a higher DOC/POC ratio in low TSM systems. Based on the relationship described in Ittekkot & Laane (1991) and Abril et al. (2002), we would expect high DOC/POC ratios (~ 10) for the Gautami Godavari. Remarkably, however, the latter is not supported by the low DOC concentrations found in the Godavari in this study and by Somalayulu et al. (1993) and the data of point towards much lower DOC/POC ratios (1.9 ± 0.7 for the data gathered in this study). We hypothesize that the relationship between TSM and POC/TSM observed in our study (Figure 17) is essentially not related to the nature of the organic matter (terrestrial vs. local production) but may rather be the result of the more pronounced resuspension of lithogenic (sediment) matter in the relatively shallow and more tidally influenced creeks and Bay.

Overall, POC/PN ratios of suspended organic matter were relatively low, reflecting the dominance of phytoplankton during this season, with little or no trend along the salinity gradient, and with no marked differences between samples from the Gautami and the mangrove creeks and Bay. The significantly higher POC/PN ratios during the second transect compared to the first (7.5 ± 0.8 and 5.9 ± 0.5, respectively) suggest a larger contribution of terrestrial C in the POC pool during the second transect, but $\delta^{13}C$ values of POC were significantly more enriched during the latter (by ~ 1.5 ‰).

This might indicate that C_4-derived carbon (e.g. sugarcane which is widely cultivated in the area) contributed to the Godavari POC pool during the second transect (which was preceded by stormy weather).

Overall, the local effects of the presence of mangroves on the *particulate* organic matter chemistry was found to be relatively small, at least during the pre-monsoon period :

(1) even though concentrations of POC were higher (Figure 10A), no marked difference in POC/PN ratios was observed

(2) POC/Chl a ratios were also in the same range (except for one sample from Coringa, see Tables 1-4), even though Chl a concentrations were on average higher in the mangroves

(3) $\delta^{13}C_{POC}$ values in the mangrove creeks were lower than those in the same salinity zone in the Godavari (Figure 15), but these should not necessarily be ascribed to a larger contribution by terrestrial sources in view of the parallel gradient in $\delta^{13}C_{DIC}$ (Figure 9) which is expected to cause a parallel trend in the $\delta^{13}C$ signature of local aquatic primary production.

DOC made up an average of 72.9 ± 10.6 % (range : 57.3 – 89.7 %) of the total organic matter pool in the water column during the tidal cycle in Gaderu (Table 4), clearly demonstrating the dominance of dissolved organic carbon in these ecosystems. The importance of DOC in mangrove ecosystems has recently been stressed by a number of authors (e.g. Lee 1995, Dittmar et al. 2001, Davis et al. 2001a, b) and our results confirm that this neglected component deserves further characterisation. At this point, we have no indications for the relative contribution of different potential sources to this DOC pool, although with the absence of significant terrestrial (river) inputs it seems reasonable to assume that degraded mangrove litter makes up an important fraction of this material. Some evidence for the local origin of the DOC comes from the markedly higher DOC concentrations in the creeks compared to the estuary proper (see Figure 11), and from the pattern in [DIC] and $\delta^{13}C_{DIC}$ (see discussion below) which demonstrates the abrupt local changes in the amount of respired CO_2 in the mangrove creeks compared to the marine/estuarine part of the Godavari and compared to Kakinada Bay, which would be consistent with a large input of locally produced (i.e. mangrove) DOC in the creeks. So far, few studies have tried to assess the origin of DOC in mangrove ecosystems. Lara & Dittmar (1999) &

Dittmar & Lara (2001a) concluded from the day/night shifts in DOC concentrations that photosynthetic activity (i.e. by phytoplankton) produced a measurable amount of DOC (by ~ 8 %), and suggested the existence of a labile DOC pool of algal origin, and similarly, Holmer et al. (2001) found that efflux of DOC from mangrove sediments was higher during the day than during the night and suggested that benthic microphytes contributed to the aquatic DOC pool by releasing organic compounds. 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. Boto & 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 DOM pool in a mangrove estuary in northern Brazil throughout 18 tidal cycles in the course of one year. The results of their study naturally show wide seasonal and spatial variations in the contributions of these 3 sources (which also depended strongly on the parameters used in their calculations), but notwithstanding these variations DOM in a mangrove creek was shown to be mostly of mangrove origin (~ 60 %), with marine-derived organic matter making up most of the remaining DOM (~ 35 %). Surprisingly, mangrove DOM was found to behave conservatively in the estuary (in contrast to mangrove POM), suggesting outwelling of mangrove-derived DOM in their study area without much local processing. As the use of DOC by bacterial communities is an important step in the carbon flow in aquatic ecosystems (especially considering the dominance of DOC in the total organic matter pool), thereby either channelling DOC into a 'recycling loop' wherein it is ultimately respired or making it available to higher trophic levels, a closer examination of its distribution, sources and dynamics is definitively needed.

As would be expected from marked changes in the stocks and sources of inorganic carbon (see below), DOC concentrations in the creeks (i.e. the substrate for bacterial mineraliation) were more than 2-fold higher than in the Godavari, which is consistent with an hypothesis whereby a major pathway for mangrove carbon is its mineralization in the water column.

Sources and distribution of dissolved inorganic carbon : the local impact of mangroves

DIC in rivers and estuaries can generally be derived from various sources : the dissolution of carbonates or CO_2 from the atmosphere (both yielding $\delta^{13}C$ values of approximately 0 ‰), and the respiration of organic matter within the water column (yielding $\delta^{13}C$ values of ~ -28 ‰ if the dominant plant sources have a C_3 metabolism). $\delta^{13}C$ values of DIC can thus be used to estimate the contribution of respiration of organic carbon to the DIC pool, but as the other main processes affecting $\delta^{13}C_{DIC}$ -i.e. efflux to the atmosphere and photosynthesis- both result in an enrichment of the DIC pool in ^{13}C, these estimates should be regarded as *minimum* estimates. Applying this method to our dataset (and using a value of -28 ‰), we obtain estimates of the contribution of respiration to the DIC pool ranging between -4.1 % to 22.6 % for the Gautami Godavari (for the marine and freshwater end-members, respectively), 28 ± 4 % for the tidal cycle data, and between -3.5 and 35.7 % for the samples from the mangrove creeks and Bay. It must be stressed that these are *minimum* estimates, and that intense photosynthesis and the –presumably- long residence time in the Godavari during the pre-monsoon season could have elevated the $\delta^{13}C_{DIC}$ significantly (e.g. see Yang et al. 1996). If we assume that the source of the respired CO_2 in the mangrove creeks is of mangrove origin (see below for discussion), it becomes clear that the dominant pool of mangrove-derived carbon in the water column is DIC rather than organic pools (POC or DOC), as the stocks of the latter two are much smaller than the calculated stock of mangrove-derived DIC.

The pronounced impact of the presence of mangroves on the inorganic carbon biogeochemistry is most striking when plotting the $\delta^{13}C_{DIC}$ data versus salinity (Figure 8) : along the Gautami Godavari estuary, they display a typical estuarine gradient (although in some estuaries the reversed pattern is observed, e.g. Buhl et al. 1991), with more enriched values towards the marine environment, but DIC in the mangrove creeks (with similarly high salinities), showed a very strong depletion in ^{13}C, with $\delta^{13}C_{DIC}$ values between -9.3 and -5.3 ‰, i.e. even lower than in the freshwater part of the Gautami. This depletion in ^{13}C coincides with significantly higher DIC concentrations (Figure 5), lower oxygen saturation (Figure 3), and lower pH (Figure 2). An clear correlation between [DIC] and $\delta^{13}C_{DIC}$ is observed (Figure

19) and 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.

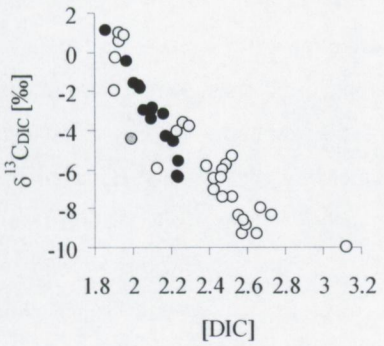


Figure 19 : Relationship between dissolved inorganic carbon concentration and its carbon isotope composition for data collected during the pre-monsoon period of 2001 along the Gautami Godavari (black symbols), and in the mangrove creeks and Kakinada Bay (open symbols). Grey symbol represents the sample from Dowleswaram Dam (see text for details).

Therefore, besides the procedure described above, i.e. assuming a $\delta^{13}C$ value for the respired source and evaluating its contribution to the DIC pool, we can also use the combination of DIC concentration data and $\delta^{13}C_{DIC}$ values to estimate the $\delta^{13}C$ value of the respired carbon source.

We then use the following equation (see Hellings et al. 2000) :

$$\delta^{13}C_{added} = \frac{[DIC]_A * \delta^{13}C_A - [DIC]_B * \delta^{13}C_B}{[DIC]_A - [DIC]_B} \qquad [2]$$

whereby :

$\delta^{13}C_{added}$: the carbon isotope composition of added DIC

$[DIC]_A$, $[DIC]_B$: concentration of DIC at point A or B, respectively, along the regression line

$\delta^{13}C_A$, $\delta^{13}C_B$: carbon stable isotope composition of the DIC pool corresponding to points A and B, respectively, along the regression line

We thus calculated the $\delta^{13}C_{added}$ (1) using only the data from the mangrove creeks and Kakinada Bay, and (2) using only the Godavari data except the sample collected below Dowleswaram Dam (grey symbol in Figure 19). This resulted in an estimate of

$\delta^{13}C_{added}$ of -28.6, and -45.4 ‰, respectively. These former value are typical values for C_3-vegetation (including mangroves, e.g. see Chapters 1 and 8) and this calculation thus strongly suggests that intense respiration of terrestrial (for the Godavari) or mangrove-derived organic matter is the principal source of the 'excess' DIC and low $\delta^{13}C_{DIC}$ values encountered in the mangrove creeks. As the generally high salinities in the creeks preclude large inputs of non-mangrove terrestrial organic matter, we hypothesize that the source of the respired CO_2 is local mangrove production rather than terrestrial organic matter brought in by the Godavari (note : even when this would result from 'accumulated' organic matter dating from the previous monsoon period, similarly low $\delta^{13}C_{DIC}$ values should be expected in the Kakinada Bay area as well, which is not the case – see Figure 8 and Table 3). For the Gautami Godavari data, however, the thus estimated $\delta^{13}C$ value of the respired CO_2 (-45.4 ‰) appears highly unrealistic and does not correspond to any known carbon source present, and other factors will need to be invoked to explain the DIC and $\delta^{13}C_{DIC}$ gradients. Therefore, in the following section we will examine whether TAlk and DIC behave conservatively along the salinity gradient.

One final important remark when discussing the major difference in [DIC] between Godavari and mangroves is that the above discussion does not imply that *all* the 'excess' DIC observed in the mangroves is derived from respiration, but rather that the local variations in [DIC] can be ascribed to respiratory processes. The major difference in TAlk between mangroves and Godavari (see Figure 5) could have been the result of (1) the dissolution of carbonates, e.g. one obvious possible source is the $CaCO_3$ in the intertidal sediments where the CO_2 generated by microbial respiration could dissolve carbonates according to $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2\ HCO_3^-$), or (2) anaerobic decomposition, e.g. sulphate reduction (known in some mangrove ecosystems to constitute an important pathway of degradation, e.g. see Chapter 2) which can generate alkality according to $2\ CH_2O + SO_4^{2-} \leftrightarrow H_2S + 2\ HCO_3^{2-}$.

Conservative mixing ?

In estuaries, alkalinity and DIC are often considered to obey conservative behaviour and therefore, $\delta^{13}C_{DIC}$ values are largely determined by the mixing of freshwater and seawater (e.g. Mook & Tan 1991, Cai & Wang 1998, Chanton & Lewis 1999), however this is not universal as *in situ* processing of dissolved inorganic carbon -

internal production or removal- may significantly alter this pattern (e.g. Coffin & Cifuentes 1999, Buhl et al. 1991, Hellings et al. 2001). Whether or not conservative mixing applies to a particular system can be examined by looking both at the DIC content and at the $\delta^{13}C$ signature of the DIC pool (e.g. Hellings et al. 2001).

For DIC, conservative mixing implies that, at any position along the transect :

$$DIC = (\frac{DIC_M - DIC_F}{Sal_M - Sal_F})Sal + DIC_F \quad [3]$$

where :

DIC : concentration of dissolved inorganic carbon, subscripts refer to the marine end-member (M) and the freshwater end-member (F)

Sal : Salinity

Conservative mixing of TAlk can be described by the same equation by substituting DIC for TAlk. If conservative mixing applies, the $\delta^{13}C$ signature of the DIC pool obeys to the following equation (adapted from Mook & Tan 1991) :

$$\delta^{13}C = \frac{Sal(DIC_F\delta^{13}C_F - DIC_M\delta^{13}C_M) + Sal_F DIC_M\delta^{13}C_M - Sal_M DIC_F\delta^{13}C_F}{Sal(DIC_F - DIC_M) + Sal_F DIC_M - Sal_M DIC_F} \quad [4]$$

where :

$\delta^{13}C$: carbon isotopic composition of DIC, subscripts refer to the freshwater end-member (F) or the marine end-member (M)

DIC : concentration of DIC in marine or freshwater end-member

Sal : Salinity

As the results of DIC, TAlk and $\delta^{13}C$ for the freshwater station (Dowleswaram dam) were markedly different from those obtained in the oligohaline zone of the river surveys (see Figure 8 and Tables 1 and 2), and considering the rather unnatural setting of this sampling location (in concrete flow-through pool below the barrage), we considered the Dowlewaram data not representative and used only the river survey data and data from the two Godavari stations sampled during the mangrove creek survey. Figure 20 (A, B, C) shows that non-conservative behaviour is evident for DIC, TAlk, and $\delta^{13}C$ in the Gautami Godavari. Although for DIC, there appears to be

some internal production mainly in the freshwater section (sal 0-15), TAlk seems to be generated along the whole salinity gradient (compare Figure 20 A and B). $\delta^{13}C_{DIC}$ values are higher than predicted based on conservative mixing for the freshwater section (0-20 ppt), but comply downstream (Figure 20 C).

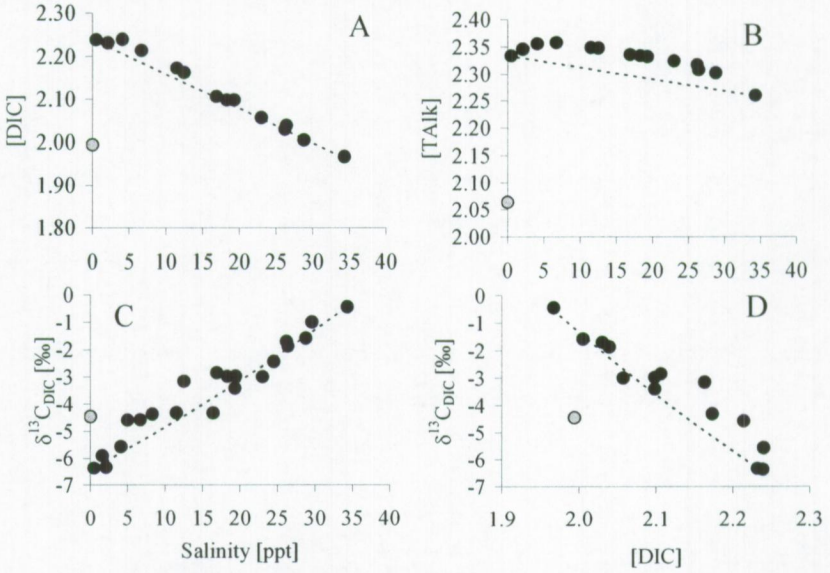


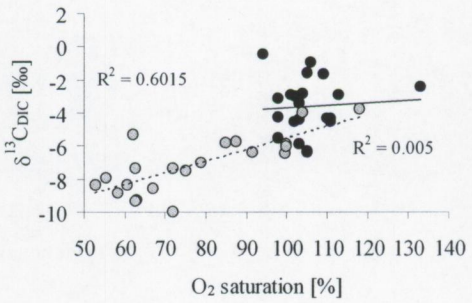
Figure 20 : Plot of (A) DIC concentrations *versus* salinity, (B) TAlk *versus* salinity, (C) $\delta^{13}C$ of the DIC pool *versus* salinity, and (D) $\delta^{13}C_{DIC}$ *versus* DIC concentrations for the Godavari samples (black symbols) and the sample from zero salinity at Dowleswaram Dam (grey symbol). Dotted curve represents conservative mixing.

The higher $\delta^{13}C_{DIC}$ values than predicted for the freshwater end of the river (see Figure 20 B) could in theory be interpreted as the result of either an efflux to the atmosphere, or photosynthesis, both processes result in an enrichment of the remaining DIC pool in ^{13}C. Although both hypotheses (which are non-exclusive) at first appear appealing, considering the relatively long expected residence of the Godavari during pre-monsoon (as the discharge rate, i.e. the volume of water let through at Dowleswaram Dam, was very low), Figure 20 D shows that this increase in $\delta^{13}C$ values in the freshwater zone compared to the conservative mixing situation is accompanied by an *increase*, not a decrease, in [DIC] – which excludes prolonged atmospheric efflux and biological CO_2 fixation as explanations. Therefore, dissolution of carbonates (with $\delta^{13}C$ values expected to be around ~ 0 ‰) is hypothesized for the freshwater to mesohaline zone of the Gautami Godavari during pre-monsoon. The

latter hypothesis is also consistent with the internal production of alkalinity observed in the Godavari (especially in the oligo- and mesohaline zone, see Figure 20 D).

It thus appears that a major difference in the factors determining the inorganic carbon chemistry dynamics exist between the mangrove creeks (and Kakinada Bay) and the Gautami Godavari. In the former -as discussed higher- we can explain much of the observed variations in [DIC] and $\delta^{13}C_{DIC}$ as the result of variable contribution of microbially respired CO_2 (see also Keough et al. 1998). In the Godavari, however, photosynthesis (mainly in the polyhaline and euhaline zone) and carbonate dissolution (the latter in the oligo- and mesohaline zone) appear to govern the inorganic carbon dynamics. The $[Ca^{2+}]$ data for the pre-monsoon presented by Padmavathi & Satyanarayana (1999 – Figure 4 in their study) also suggest internal production of Ca^{2+} in the oligo- and mesohaline zone, although these authors did not discuss this possibility. Finally, this marked difference between Godavari and mangroves is also evident from three other distinct patterns : (1) the negative trend between $[O_2]$ and $\delta^{13}C_{DIC}$ values in the data from the mangrove ecosystem, but the lack of such a relationship in the Godavari data (Figure 21), (2) the marked difference in the relationship between pCO_2 and $\delta^{13}C_{DIC}$, i.e. lower $\delta^{13}C_{DIC}$ values coincide with higher pCO_2 in the mangroves but not in the Godavari (Figure 22), and (3) the marked difference in the relationship between pH and $\delta^{13}C_{DIC}$ (Figure 23), i.e. lower $\delta^{13}C_{DIC}$ are accompanied by a decrease in pH in the mangrove ecosystem, but with an increase in pH in the Gautami.

Figure 21 : Relationship between oxygen saturation levels and the carbon stable isotope composition of the DIC pool ($\delta^{13}C_{DIC}$) for the Godavari data (black symbols) and the data from mangrove creeks but excluding Kakinada Bay data (grey symbols).



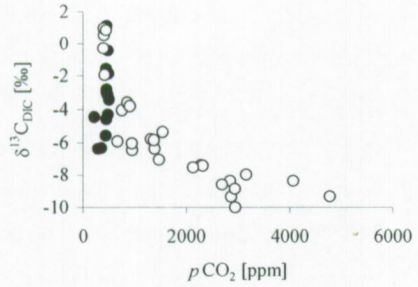
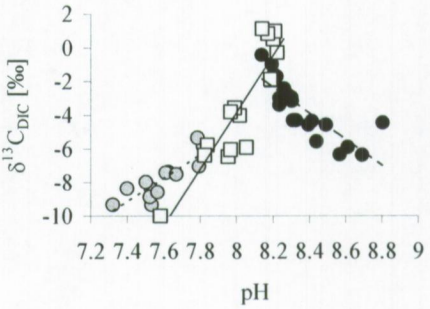


Figure 22 : Relationship between the partial pressure of CO_2 and the carbon stable isotope composition of the DIC pool for the Gautami Godavari (black symbols) and for the mangrove creeks and Kakinada Bay during the pre-monsoon of 2001.

Figure 23 : Relationship between pH and the carbon stable isotope composition of the DIC pool for the Gautami Godavari (black symbols) and for the mangrove creeks and Kakinada Bay (open squares, grey circles are for the diurnal cycle) during the pre-monsoon of 2001.



Flux of CO_2 across the water/atmosphere interface

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 this 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 :

$$\text{Flux} = K.K_{CO_2}[\Delta pCO_2] \qquad [5]$$

where :

K : gas transfer velocity for CO_2

K_{CO_2} : the CO_2 solubility coefficient

ΔpCO_2 : difference in the partial pressure of CO_2 between water and air, whereby pCO_2 (air) is taken as 360 μatm.

The gas exchange coefficient (i.e. K) is mainly dependent on environmental factors, such as wind speed, temperature, precipitation, the magnitude of waves, and the

turbulence of water and air. Raymond & Cole (2001) recently reviewed the algortihms used to describe the relationship between wind speed and the gas exchange coefficient for estuarine systems, and stressed that estimates of the CO_2 flux can vary substantially depending on the equations used, and therefore, that calculated CO_2 fluxes should be considered as mere estimates until the mechanisms determining the relationship between K and environmental condition are better understood. Furthermore, the use of lower frequency wind speed data (e.g. daily *versus* hourly, etc.) can have very large effects on the calculated CO_2 fluxes due to the non-linear relationship between K and wind speed (see Bates & Merlivat 2001).

The flux of CO_2 was calculated using three different algorithms (Marino & Howarth 1993, Carini et al. 1996, and Raymond et al. 2000) for the data collected during the pre-monsoon of 2001 (A. Borges & M. Frankignoulle, unpublished) and ranged between -10.3 and 41.3 mmol CO_2 m^{-2} d^{-1} for the Godavari salinity gradient and between 0 (when wind speed was nil) and an exceptionally high 555.7 mmol CO_2 m^{-2} d^{-1} for the mangrove creeks and Kakinada Bay (with generally higher values in the mangrove creeks). Due to the large temporal variability in wind speed and its effect on calculated CO_2 fluxes, it would be unreasonable to extrapolate these values to longer time scales, but in any case, the generally high pCO_2 values observed in the mangrove creeks –in sharp contrast with Kakinada Bay and the Gautami Godavari- clearly identify this zone as an active site for CO_2 outgassing (e.g. the values obtained for the mangrove creeks are similar in magnitude to the CO_2 gas efflux estimated by Hellings et al. (2001) for the highly polluted Scheldt estuary, Belgium). When comparing the calculated pCO_2 values for the Godavari with those presented in Cole & Caraco (2001) for a variety of rivers (49 out of 51 systems have pCO_2 values between 1000 and 10,000 ppm), it is immediately evident that the pre-monsoon data for the Gautami Godavari ranks the latter as the lowest in this series. At this stage, one can only speculate about the pCO_2 values during the monsoon season, when high loads of terrestrial OC are expected.

Even though the seasonal data do not allow us to make reliable estimates of pCO_2 (due to the large uncertainty associated with pH measurements), we expect that pCO_2 values in the mangrove creeks will be relatively high throughout the year (which does not imply that no large seasonal variations in pCO_2 might occur), as (i) TAlk data do not suggest major variations in overall DIC stocks, and more importantly (ii) as the pre-monsoon season is the period of highest aquatic primary production and probably

lowest overall organic matter mineralization (as suggested by the seasonal $\delta^{13}C_{DIC}$ data). Until more accurate seasonal surveys are conducted, an annual or even seasonal budget estimate remains an unrealistic goal.

Seasonal variations in the inorganic carbon dynamics of the mangrove creeks and Kakinada Bay

The seasonal TAlk and $\delta^{13}C_{DIC}$ data allow us to consider some aspects of the seasonality of the ecosystems biogeochemistry. $\delta^{13}C_{DIC}$ values showed strong seasonality (Figure 9), with significantly lower values after the monsoon discharge, and with values regaining a maximum during the pre-monsoon period. Such a pattern appears to be recurrent and had been predicted for the study area based on the seasonality of zooplankton $\delta^{13}C$ values and the evidence for the selective feeding of the latter on aquatic primary production (see Bouillon et al. 2000, i.e. Chapter 5). This seasonality is hypothesised to be the result of the large terrestrial inputs from the Godavari river during the monsoon discharge (see Gupta et al. 1997), i.e. a timing when we expect more negative $\delta^{13}C_{DIC}$ values. When estuarine/marine conditions re-establish, conditions which would lead to higher $\delta^{13}C_{DIC}$ values set in : the import of organic matter from the land diminishes and therefore only local mangrove litter inputs and aquatic production are available for degradation, turbidity decreases and aquatic primary production is on the increase. Under this hypothesis, the rate of mineralization of organic matter remains (i.e. as during the pre-monsoon period, see prior discussion) the dominant factor determining the inorganic carbon biogeochemistry, and this assumption requires validation, but it should be clear that other factors may also play an important, albeit yet unresolved, role as is evident from the slope of the TAlk-$\delta^{13}C_{DIC}$ relationship which varies seasonally (two extreme examples are shown in Figure 24). Data on DIC concentrations (and its speciation) would need to be collected concurrently in order to adeaquately assess the seasonal dynamics of the inorganic carbon chemistry.

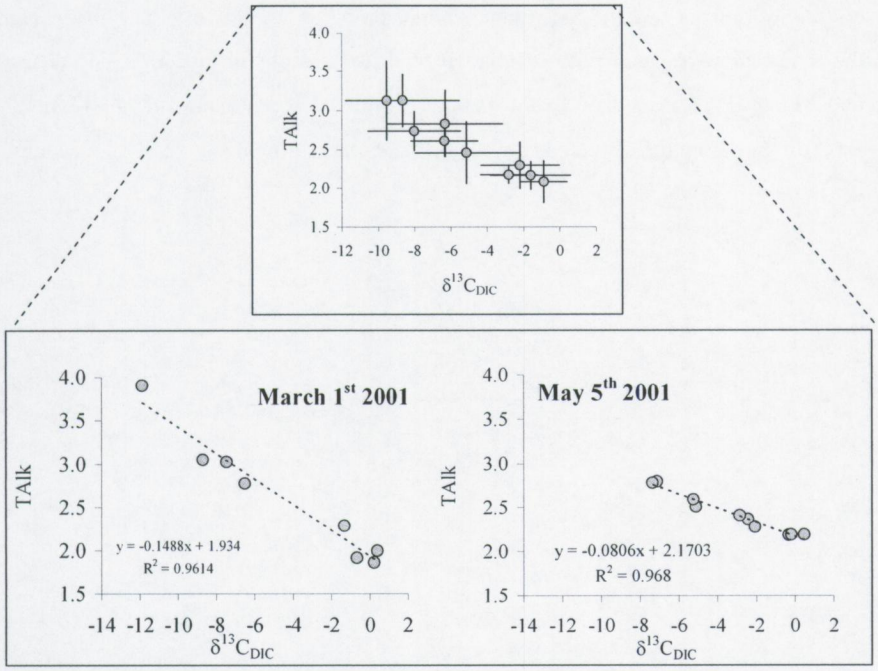


Figure 24 : TAlk-$\delta^{13}C_{DIC}$ relationship for the 10 sampling stations (see Figure 1) averaged over the entire sampling period (top panel, error bars indicate 1 s.d.) and for March 2001 (steep gradient) and early May 2001 (gradient less steep).

In any case, non-conservative behaviour of TAlk was observed on all sampling dates (e.g. see Figure 5 and Figure 25), with TAlk data being fairly scattered and unrelated to salinity (note : this is also seen in the pre-monsoon 2001 data).

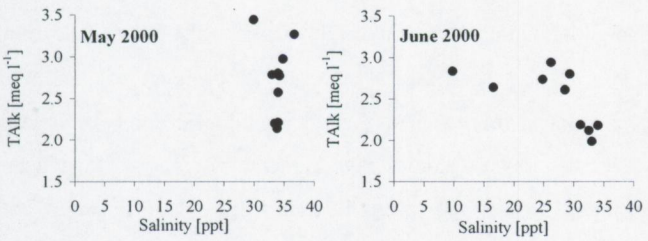


Figure 25 : Examples of the non-conservative behaviour of TAlk in the mangrove creeks and Kakinada Bay area. Data for May and June 2000 are shown.

If we plot average salinity *versus* the average $\delta^{13}C_{DIC}$ data for each location (Figure 26), the local effect of the presence of mangroves can be easily identified : if we take the most marine station (Bay of Bengal) and the Coringa station as the marine and oligohaline end-members, conservative mixing would imply all data to be on a curve such as the one shown in Figure 26 (note, however, that as we do not have DIC

concentration data, the proposed curve is not based on quantitative data). However, the true mangrove creek stations (Gaderu, the two stations in Gaderu's side creeks) and Mukanali Dibba (close to the mangroves in the southeast corner of Kakinada Bay) diverge from the expected pattern, with distinctly more negative $\delta^{13}C_{DIC}$ values.

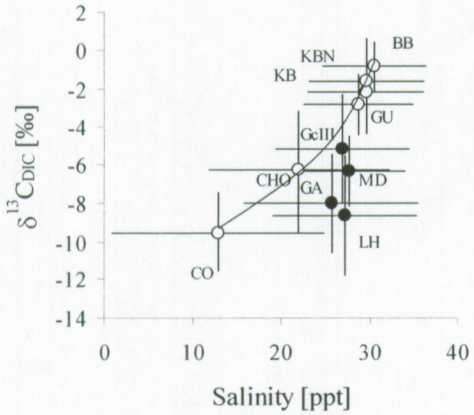


Figure 26 : Average $\delta^{13}C_{DIC}$ values for each of the seasonal sampling locations *versus* the average salinity at these locations. Error bars indicate 1 s.d. Abbreviations of sampling locations as in legend of Figure 1.

Concluding remarks

Our study clearly identifies the mangrove creeks of the Coringa Wildlife Sanctuary as a distinct entity in the Gautami Godavari estuary where mineralization of organic matter is significantly more prominent than in the river mouth or the adjacent Kakinada Bay. As the influx of non-mangrove terrestrial matter is expected to be minimal during this period of the year, it is reasonable to assume that a dominant source of this respired organic matter is of local origin, i.e. mangrove-derived carbon. Seasonal $\delta^{13}C_{DIC}$ data confirm the marked local effect of the presence of mangroves on the aquatic biogeochemistry, in particular the higher mineralization of organic matter in the mangrove creeks. Several studies have found surprisingly little evidence of the incorporation of mangrove-derived carbon in sediment pools in the study area (see Chapters 6 and 7), and its role as a carbon source for zooplankton, subtidal and intertidal benthic invertebrates was also found to be overall fairly limited (see Chapters 5, 6, and 8). The role of bacterial degradation in the water column was previously unexplored for our study area, but the data presented here suggest that this may be an important pathway for mangrove carbon. Bano et al. (1997) measured high bacterial carbon production rates (generally between 50 and 300 µg C per litre per

day) in mangrove creeks in the Indus Delta, and these coincided with relatively low bacterial abundance (20-80 μg C l^{-1}, i.e. the same range as that found in this study), indicating high specific growth rates and therefore, a tight coupling between bacterial production and removal. The bacterial degradation of DOC of mangrove origin and its efflux to the atmosphere thus represents a potentially important fate of mangrove primary production which deserves further study and quantification. Due to the high seasonality which may be expected, detailed studies during different seasons, including a better characterization of the DOC pool, would be required to shed more light on this.

One aspect which also deserves further work is the relative role of the intertidal zone and the network of tidal creeks as sites for mineralization. The importance of several intertidal habitats (both salt and freshwater marshes) as a source of (^{13}C-depleted) DIC has been suggested by Sherr (1982) and Cai & Wang (1998) who found lower $\delta^{13}C_{DIC}$ and higher [DIC] during low water. In our study, the sample with the lowest $\delta^{13}C_{DIC}$ and the markedly highest [DIC] is hypothesized to be representative of porewater draining the intertidal mangrove flats, as the salinity recorded is markedly high (37.2 ppt) which could be indicative of interstitial water (e.g. see Lara & Dittmar 1999 who showed that evaporation of water in the intertidal zone during the dry season may lead to higher salinities at low tide). The latter might indicate both respiration of organic matter in the intertidal sediments and in the creek waters were responsible for the marked local effect of the presence of mangroves on the creek water carbonate chemistry.

Finally, although the study of diurnal variations of biological, physico-chemical and biogeochemical parameters could offer valuable insights in the functioning of the aquatic system, a larger set of diurnal data collections is a prerequisite to be able to unambiguously distinguish day/night effects (i.e. effects of biological activity) from tidal effects.

Table 1 : Overview of results for selected parameters collected during the first transect (May 27th 2001) along the Gautami Godavari salinity gradient. - : not determined.

Salinity (ppt)	O_2 saturation (%)	pH	Chl a (µg/l)	Talk (meq/kg)	[DIC] (mmol/kg)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{13}C_{POC}$ (‰)	POC/PN (atom)	POC (µg/l)	DOC (mg/l)	TSM (mg/l)	POC/TSM (%)
1.6	103	8.61	8.41	-	-	-	-5.9	-29.2	6.5	1172	1.60	7.8	15.1
5.0	111	8.49	8.55	-	-	-	-4.6	-28.9	6.3	1105	1.65	7.7	14.4
8.3	110	8.42	-	-	-	-	-4.4	-27.6	6.3	1063	1.70	6.6	16.1
16.4	111	8.33	8.09	-	-	-	-4.3	-26.1	5.6	1098	2.10	6.9	15.8
19.4	113	8.30	5.84	-	-	-	-3.0	-26.1	5.4	879	2.25	5.5	15.9
24.5	133	8.26	5.80	-	-	-	-2.4	-24.9	5.5	807	1.55	6.6	12.3
29.6	106	8.19	6.63	-	-	-	-1.0	-22.4	5.4	872	1.30	15.2	5.8
34.3	94	8.14	1.65	2.260	1.967	483	-0.4	-21.5	6.3	742	1.20	35.3	2.1

Table 2 : Overview of results for selected parameters collected during the second transect (June 1st 2001) along the Gautami Godavari salinity gradient and Dowleswaram Dam (June 2nd 2001). - : not determined.

Salinity (ppt)	O_2 saturation (%)	pH	Chl a (µg/l)	Talk (meq/kg)	[DIC] (mmol/kg)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{13}C_{POC}$ (‰)	POC/PN (atom)	POC (µg/l)	DOC (mg/l)	TSM (mg/l)	POC/TSM (%)
0	103	8.80	6.60	2.064	1.994	221	-4.5	-28.5	6.6	927	-	4.39	21.10
0.5	105	8.69	11.55	2.334	2.239	293	-6.4	-28.1	6.4	1625	1.95	8.78	18.50
2.1	105	8.57	6.30	2.346	2.232	355	-6.3	-26.6	8.3	1808	2.35	7.98	22.65
4.1	98	8.44	6.48	2.356	2.24	440	-5.6	-24.5	8.2	1678	4.10	11.18	15.00
6.7	102	8.39	6.03	2.358	2.214	450	-4.6	-26.0	7.5	1410	1.90	7.64	18.45
11.5	98	8.31	6.41	2.349	2.173	482	-4.3	-23.9	8.1	1431	1.80	8.52	16.80
12.5	98	8.30	7.49	2.348	2.163	479	-3.2	-24.8	7.3	1331	2.20	11.13	11.95
16.9	104	8.29	5.34	2.336	2.106	455	-2.8	-25.5	7.3	1166	1.75	6.46	18.05
18.3	101	8.27	6.22	2.334	2.098	455	-3.0	-24.8	8.0	1036	1.80	6.04	17.15
19.3	103	8.23	4.87	2.332	2.098	500	-3.4	-22.4	9.3	1161	5.15	5.81	20.00
23	102	8.23	n.d.	2.324	2.057	461	-3.0	-24.2	7.0	971	2.45	6.07	16.00
26.2	109	8.22	5.22	2.317	2.03	451	-1.7	-22.7	6.5	948	1.85	8.17	11.60
28.8	105	8.20	4.65	2.302	2.005	444	-1.6	-22.8	7.4	1175	1.75	10.49	11.20

Table 3 : Overview of results for selected parameters collected during 2 cruises in the tidal mangrove creeks and the adjacent Kakinada Bay (May 28th-30th 2001). - : not determined. See Figure 1 for location of sampling sites. PR 22 and 23 are located in the mouth of the Gautami Godavari.

Location (PR ..)	Salinity (ppt)	O_2 saturation (%)	pH	Chl a (µg/l)	Talk (meq/kg)	[DIC] (mmol/kg)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{13}C_{POC}$ (‰)	POC/PN (atom)	POC (µg/l)	DOC (mg/l)	TSM (mg/l)	POC/TSM (%)
1	24.6	67.0	7.40	21.39	3.099	3.162	5046	-	-	-	27087	-	276.4	9.8
2	28.6	82.0	7.26	-	2.952	3.058	6437	-	-	-	7490	-	119.8	6.3
11	34.6	104.9	8.20	5.59	2.278	1.930	406	+0.5	-	-	-	-	-	-
12	34.4	87.7	8.11	12.45	2.253	1.963	534	-	-	-	-	-	-	-
13	34.5	95.2	8.19	13.72	2.230	1.891	424	-	-	-	-	-	-	-
14	33.9	100.0	8.05	-	2.399	2.128	674	-5.9	-	-	-	-	-	-
15	33.8	115.2	8.22	9.22	2.230	1.871	392	-	-	-	-	-	-	-
16	34.2	100.0	8.19	10.45	2.248	1.905	421	-2.0	-	-	-	-	-	-
17	34.5	107.8	8.21	1.19	2.273	1.926	397	+1.0	-	-	-	-	-	-
18	34.4	96.4	8.17	3.32	2.273	1.953	444	+0.9	-	-	-	-	-	-
19	34.3	95.2	8.16	7.98	2.262	1.943	457	-	-	-	-	-	-	-
20	33.5	62.5	7.99	2.43	2.288	2.071	758	-	-	-	-	-	-	-
21	24.3	145.6	8.26	7.63	2.638	2.312	481	-	-	-	-	-	-	-
22	26.4	107.0	8.19	7.53	2.308	2.039	492	-1.9	-23.9	6.2	757	1.40	6.1	12.5
23	34.0	96.0	8.14	2.22	2.149	1.860	461	+1.1	-21.7	7.4	493	1.05	19.7	2.5
24	34.0	87.5	7.84	15.29	2.663	2.493	1314	-5.8	-24.8	5.9	1190	-	29.8	4.0
25	33.1	104.0	8.12	8.64	2.471	2.230	758	-4.0	-24.5	6.0	744	-	13.4	5.6
26	34.8	99.5	7.95	23.01	2.659	2.427	956	-6.5	-23.3	6.3	1479	-	42.9	3.5
27	34.7	100.0	7.97	26.39	2.711	2.470	947	-6.1	-22.1	6.7	2824	-	131.4	2.2
28	37.2	72.0	7.58	11.28	3.197	3.123	2944	-10.0	-24.2	6.9	1482	-	65.8	2.3
29	34.5	153.0	8.22	32.07	2.288	1.908	396	-0.3	-18.7	8.6	2562	-	81.3	3.2
30	33.6	111.0	7.99	10.62	2.515	2.267	860	-3.6	-20.1	6.7	1179	-	32.3	3.7
31	33.5	118.0	7.97	27.56	2.525	2.294	911	-3.8	-19.5	6.4	1965	-	52.4	3.8
32	32.8	91.5	7.82	14.23	2.625	2.467	1390	-6.4	-20.6	6.4	1279	-	40.6	3.2

Table 4 : Overview of results for selected parameters collected during a 24-hour diurnal cycle in Gaderu creek (see Figure 1) on June 4th-5th 2001. - : not determined.

Time (h)	Salinity (ppt)	O_2 saturation (%)	pH	Chl a (µg/l)	Talk (meq/kg)	[DIC] (mmol/kg)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{13}C_{POC}$ (‰)	POC (µg/l)	DOC (mg/l)	TSM (mg/l)	POC/TSM (%)
14	29.6	63.0	7.32	6.45	2.589	2.652	4771	-9.3	-27.3	1405	3.27	35.6	4.0
15	29.1	69.5	7.50	8.76	2.583	2.575	3143	-	-	-	-	-	-
16	30.3	71.8	7.63	9.86	2.579	2.522	2277	-7.4	-25.5	2120	2.85	78.5	2.7
17	30.3	87.2	7.78	11.61	2.598	2.475	1552	-	-	-	-	-	-
18	30.9	84.9	7.81	8.04	2.525	2.389	1375	-5.9	-26.1	1492	2.77	38.3	3.9
19	30.8	79.0	7.77	6.73	2.511	2.395	1528	-	-	-	-	-	-
20	30.9	78.8	7.79	7.62	2.552	2.425	1472	-7.0	-27.2	1214	2.82	28.6	4.3
21	30.8	70.2	7.68	5.63	2.554	2.473	1933	-	-	-	-	-	-
22	29.2	62.7	7.53	6.14	2.592	2.576	2867	-9.3	-26.9	1004	8.70	23.1	4.4
23	29.4	58.2	7.52	4.96	2.584	2.573	2972	-	-	-	-	-	-
24	30.0	60.7	7.53	-	2.571	2.552	2843	-8.4	-27.0	692	5.37	15.4	4.5
01	30.4	54.0	7.44	3.54	2.707	2.723	3700	-	-	-	-	-	-
02	29.2	58.4	7.53	1.09	2.605	2.593	2935	-8.9	-27.4	1162	3.23	36.3	3.2
03	29.6	56.1	7.51	5.31	2.615	2.606	3038	-	-	-	-	-	-
04	30.8	55.5	7.50	5.00	2.683	2.674	3155	-8.0	-24.3	2111	3.09	93.8	2.3
05	31.9	62.2	7.74	4.15	2.590	2.483	1682	-	-	-	-	-	-
06	31.3	62.1	7.78	8.61	2.651	2.525	1539	-5.4	-24.7	1551	3.00	37.8	4.1
07	31.3	61.0	7.72	6.88	2.626	2.528	1789	-	-	-	-	-	-
08	30.5	53.0	7.40	6.67	2.699	2.731	4062	-8.4	-25.2	1170	3.57	37.8	3.1
09	28.4	52.5	7.45	8.95	2.610	2.628	3534	-	-	-	-	-	-
10	28.8	62.6	7.61	9.94	2.512	2.469	2316	-7.4	-26.0	1252	4.08	39.1	3.2
11	29.0	65.8	7.60	13.50	2.499	2.461	2373	-	-	-	-	-	-
12	30.0	66.9	7.57	8.80	2.615	2.580	2693	-8.6	-24.7	1627	8.35	67.8	2.4
13	31.0	68.9	7.61	7.83	2.653	2.594	2447	-	-	-	-	-	-
14	31.6	75.1	7.70	6.90	2.651	2.563	2128	-7.5	-26.1	1573	3.20	60.5	2.6

Table 5 : Salinity (ppt), Total alkalinity (mM), and carbon stable isotope composition of the dissolved inorganic carbon pool ($\delta^{13}C_{DIC}$, in ‰) sampled at regular intervals at 10 locations in the study area (see Figure 1 for abrreviations of locations). - : not determined.

	Apr 13-15, 2000			May 16-18, 2000			Jun 20-22, 2000		
Location	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$
LH	36.2	3.825	-9.2	36.7	3.267	-9.5	24.8	2.733	-1.0
GcIII	32.4	2.833	-2.1	33.0	2.781	-6.7	16.6	2.638	-9.3
CO	10.0	2.991	-9.3	29.9	3.442	-8.5	9.8	2.834	-10.3
GA	35.1	2.600	-4.6	34.8	2.971	-8.4	26.2	2.940	-6.8
MD	31.3	2.574	-6.3	34.0	2.799	-5.8	28.5	2.607	-6.0
GU	33.0	2.267	-2.9	33.4	2.198	-2.4	31.1	2.187	-3.4
CHO	26.6	2.718	-5.3	34.2	2.768	-4.0	29.3	2.799	-4.3
KB	36.1	2.335	-0.8	34.0	2.568	-1.1	32.5	2.117	-1.5
KBN	33.7	2.132	-1.1	33.8	2.136	-0.5	33.0	1.987	-0.8
BB	38.1	2.142	-1.1	34.0	2.207	-0.7	34.0	2.181	-1.3

	Sep 24-26, 2000			Oct 28-30, 2000			Nov 28-30, 2000		
Location	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$
LH	17.6	3.240	-13.5	13.0	2.773	-11.4	17.8	3.380	-11.0
GcIII	14.2	-	-8.5	17.0	1.661	-5.6	20.6	2.059	-2.9
CO	0.7	2.675	-12.3	11.8	2.968	-9.6	12.9	-	-10.1
GA	8.7	2.455	-11.4	6.1	2.559	-10.7	18.6	3.228	-11.5
MD	26.6	2.588	-7.6	13.0	2.605	-10.9	19.4	2.818	-6.8
GU	24.2	1.968	-4.6	15.4	2.005	-6.9	19.6	2.232	-2.1
CHO	17.0	2.713	-8.7	14.0	2.403	-8.7	10.4	3.780	-8.9
KB	31.0	2.212	-4.0	20.6	1.828	-3.2	14.2	3.013	-7.3
KBN	25.2	2.259	-5.3	20.4	1.868	-3.2	15.8	2.600	-5.7
BB	30.9	1.991	-2.0	20.2	1.734	-3.3	20.0	1.165	-1.6

	Dec 19-21, 2000			Feb 28 -Mar 2, 2001			Apr 2-4, 2001		
Location	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$
LH	20.6	2.963	-7.0	25.6	3.029	-7.5	34.6	2.862	-6.8
GcIII	29.8	2.275	-3.4	35.0	2.778	-6.5	32.3	-	-1.2
CO	1.0	3.574	-10.8	0.0	3.902	-11.9	0.0	2.948	-10.2
GA	20.4	2.748	-6.7	29.1	3.056	-8.7	34.6	2.668	-5.1
MD	22.8	2.787	-6.5	31.1	-	-4.9	31.1	-	-4.3
GU	25.4	2.112	-2.4	33.0	2.285	-1.3	34.0	-	-1.3
CHO	3.2	3.162	-10.1	19.4	-	-9.3	24.2	3.058	-7.0
KB	25.4	2.338	-1.9	34.0	1.915	-0.7	32.3	2.464	-1.7
KBN	27.2	2.128	-1.6	35.4	1.993	+0.4	33.4	2.216	-0.4
BB	27.2	2.288	-1.6	31.1	1.862	+0.2	35.6	2.229	+0.3

Table 5 (continued)

	May 4-6, 2001			May 28-30, 2001		
Location	Salinity	TAlk	$\delta^{13}C_{DIC}$	Salinity	TAlk	$\delta^{13}C_{DIC}$
LH	32.8	2.798	-7.1	37.2	3.197	-10.0
GcIII	34.0	2.366	-2.4	33.1	2.471	-4.0
CO	30.7	2.510	-5.1	32.8	2.625	-6.4
GA	33.6	2.592	-5.3	34.8	2.659	-6.5
MD	34.0	2.782	-7.4	33.9	2.399	-5.9
GU	34.4	2.278	-2.1	34.2	2.248	-2.0
CHO	34.0	2.412	-2.9	34.5	2.288	-0.3
KB	35.7	2.189	-0.3	34.4	2.278	+ 0.5
KBN	35.3	2.190	-0.2	34.6	2.273	+ 0.9
BB	34.0	2.191	+0.5	34.5	2.273	+ 1.0

CHAPTER 5 : Sources of suspended organic matter and selective feeding by zooplankton in an estuarine mangrove ecosystem, as traced by stable isotopes.

Foreword

In the preceding chapter, we have shown that the presence of extensive mangrove forests has a pronounced influence on the biogeochemistry of the aquatic ecosystem, in particular on the organic and inorganic carbon dynamics. A related question which has been a longstanding issue of debate in the literature is whether mangrove-derived carbon contributes to adjacent and offshore aquatic foodwebs. Although a number of studies have addressed the latter subject, most have neglected an important group of pelagic consumers, i.e. the zooplankton community. This chapter therefore examines the relative role of mangrove carbon and aquatic primary production in sustaining the zooplankton community in an estuarine mangrove ecosystem.

To a large extent, this chapter is based on the following publications :

Bouillon S, Chandra Mohan P, Sreenivas N, & Dehairs F (2000) 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

Bouillon S, & Dehairs F (2000) Estimating spatial and seasonal phytoplankton $\delta^{13}C$ variations in an estuarine mangrove ecosystem. Isot Environ Health Stud 36 : 273-284

On the other hand, a major amount of useful background data (see Chapter 4) and zooplankton data (A.V.V.S. Rao, unpublished) became available after their publication, so significant additions were made and some of the formerly tentative conclusions can now be supported by these additional data.

The sampling for this part of the study was carried out in the framework of a former DC-INCO project (An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India - project CI1*CT930320) and some of the samples had previously been processed and are discussed in Dehairs et al. (2000).

Abstract

Between January 1995 and August 1996, suspended matter and zooplankton were sampled at different locations in a mangrove ecosystem located in the Gautami Godavari estuary and adjacent Kakinada Bay (Andhra Pradesh, India). Particulate organic carbon (POC) was sampled at 13 different stations, and was found to have a highly variable carbon stable isotopic composition, with $\delta^{13}C$ values ranging overall between –31.0 and –19.2 ‰, and a highly variable elemental (POC/PN) composition. Our data show indirectly that the phytoplankton component has a seasonally and spatially variable $\delta^{13}C$ signature which is masked by the terrestrial signal, but may at times fall in the same range as the $\delta^{13}C$ of the allochtonous matter (i.e. mangrove litter or other terrestrial organic matter). It is argued that the phytoplankton $\delta^{13}C$ decreases after the onset of the monsoon rains, most likely due to the enrichment of the DIC pool in ^{12}C caused by the microbial respiration of terrestrial organic matter. At each of the four sites selected for concurrent zooplankton sampling, the zooplankton showed a much wider range of $\delta^{13}C$ than did the suspended matter, with overall $\delta^{13}C$ values between –30.1 and –16.5 ‰. In addition, spatial differences in average $\delta^{13}C$ were much more pronounced for zooplankton than for total suspended matter. These data indicate that zooplankton feed on a component of the POC pool which has more pronounced seasonal and spatial $\delta^{13}C$ variations than the total suspended matter. Spatio-temporal variations in phytoplankton $\delta^{13}C$ values were also estimated by a simple two-source mixing model based on POC/PN and $\delta^{13}C_{POC}$ data, and the general trends were in agreement with those observed in zooplankton and in the dissolved inorganic carbon pool. Thus, despite the influence of mangrove-derived carbon on the inorganic and organic carbon biogeochemistry in the aquatic environment, the zooplankton community appears to be sustained mostly by local aquatic primary production.

Introduction

Mangrove forests are often considered to be highly productive tropical ecosystems (Clough 1992). There remains, however, some uncertainty on the fate of the large amounts of leaf litter produced by these systems. The "outwelling hypothesis", stating that large amounts of mangrove detritus are exported to the aquatic nearshore environment (reviewed by Lee 1995), where they enhance or sustain secondary productivity, has been the subject of much debate. Based on gut content analysis of mangrove-inhabiting fauna, Odum & Heald (1975) stated that the major energy flow in these ecosystems occurs via the incorporation of microbially enriched mangrove detritus into secondary producers, which in turn support higher trophic levels. Although an appealing hypothesis, considering the potentially high productivity of these trees compared to other primary producers such as phytoplankton and microphytobenthos (Robertson et al. 1992, Alongi 1994, Gattuso et al. 1998), a number of recent studies have led to the conclusion that the importance of these other primary producers which have a higher nutritional value due to their higher nitrogen content, may have been underestimated (Newell et al. 1995, Primavera 1996, Marguillier et al. 1997, Loneragan et al. 1997, France 1998, see also Chapters 6 and 8). Similar conclusions have been obtained in a variety of other estuarine systems (e.g. Sullivan & Moncreiff 1990, Deegan & Garrit 1997). Others have concluded that mangrove detrital material constitutes an important food source for many aquatic organisms, yet only on a limited spatial scale, with phytoplankton becoming the primary carbon source in nearby coastal waters (Rodelli et al. 1984, Chong et al. 2001).

Suspension-feeding copepods often form the bulk of the zooplankton in estuarine ecosystems. Although results are contradictory, several experiments have shown convincing evidence that, besides being size-selective feeders, these organisms are capable of discriminating between live and dead algae (DeMott 1988, 1995, overview presented in Price 1988). Most of these results were obtained in laboratory experiments where copepods were offered only pairs of different particles, and DeMott (1995) correctly stresses that these may be misleading or irrelevant to understanding copepod feeding selectivity under natural conditions.

It has been well established that selectivity in zooplankton feeding may occur at different levels (see Price 1988), among which (1) selectivity during the *encounter* of the prey item, e.g. calanoid copepods have been shown to detect algal cells at several hundreds microns distance - therefore encounter of a prey item is not necessarily random, and (2) selectivity during the ingestion of the prey, when particles can be rejected just prior to ingestion or even

after ingestion. Thus, as Price (1988) states, the traditional view of zooplankton as relatively mechanical suspension feeders has been replaced by the recognition that a wide variety of mechanisms exist to detect, persue, capture and reject prey. Estuarine zooplankton, however, are still often considered to be indiscriminate, non-selective feeders (e.g. Hummel et al. 1988, Turner & Tester 1989). Wylie & Currie (1991) found that in zooplankton communities dominated by copepods, bacteria and picoplankton contributed insignificant amounts of C (and thus, that phytoplankton was the dominant source), but when cladocerans dominated, the significance of the former two groups increased. Considering the potentially important role of zooplankton as a trophic link between primary producers and higher trophic levels, which include many commercially important species, it is surprising that most stable isotope studies in mangrove ecosystems (e.g. Rodelli et al. 1984, Fleming et al. 1990, Newell et al. 1990) have not incorporated the zooplankton community –usually dominated by copepods- in their analysis or have made only a small number of measurements (Stoner & Zimmerman 1988, Ambler et al. 1994, Marguillier et al. 1997, Dittel et al. 1997) and did not include a thorough discussion of the possible carbon sources for zooplankton. The only detailed study so far is that by Schwamborn et al. (1999, 2002) who examined the possible role of mangrove carbon to zooplankton in Brazilian offshore waters and in the inner estuary of the same area. The latter authors found no evidence of incorporation of mangrove carbon by offshore zooplankton communities (nor of the presence of mangrove carbon in the POC pool offshore), and similarly a minimal contribution of mangrove carbon to larval stages of several crustaceans. For estuarine copepods, the latter authors suggested a contribution of 13-40 % mangrove detritus, but as the phytoplankton end-member used to calculate this contribution is unlikely to be valid (the $\delta^{13}C$ value of offshore plankton was used, without taking into account the possibility of a ^{13}C-depleted DIC pool in the estuary - see also discussion in Chapter 6), this estimate should *a priori* be considered to be an overestimate. As Robertson et al. (1992) pointed out, the relative importance of mangrove carbon and other sources to zooplankton nutrition in these ecosystems thus remains largely unknown and is a major gap in our understanding of mangrove food webs.

Analysis of the natural abundance of carbon and nitrogen stable isotopes provides a powerful method to trace sources and transfer of organic matter through foodwebs (Peterson & Fry 1987), provided that different primary producers have a distinct isotopic signature, and based on the assumptions that fractionation of ^{13}C between an organism and its diet is small or negligible (0-1 ‰; DeNiro & Epstein 1978), and that organisms are enriched in ^{15}N relative to their diet by an average of 2.6 (Owens 1987) to 3.4 ‰ (Minagawa & Wada 1984). These

fractionation values should be treated with some caution, as there is some recent evidence for differences in ^{15}N enrichment depending on the nitrogen content of an organisms diet (Webb et al. 1998, Fantle et al. 1999, Adams & Sterner 2000, Oelbermann & Sheu 2001 - note that is is presumably not the nitrogen content itself which influences ^{15}N fractionation, but rather the biochemical composition of the food source as reflected by differences in N content). Elemental and stable isotopic analysis has been used in a large number of studies to determine the spatial and/or temporal distribution of different sources of organic matter (allochthonous detritus and local phytoplankton) in suspended matter and sediments of estuarine systems (e.g. Cifuentes et al. 1996, Ogawa & Ogura 1997, Middelburg & Nieuwenhuize 1998; Hellings et al. 1999). The majority of these studies focus on temperate ecosystems, but several authors have used this approach to characterise suspended organic matter sources in tropical mangrove ecosystems (Rezende et al. 1990, Hemminga et al. 1994, Cifuentes et al. 1996, Dehairs et al. 2000). These studies have shown that suspended organic matter in these systems is comprised of a highly variable proportion of terrestrial detritus and algae (and seagrasses when present), and that substantial spatial, seasonal, and tidal variations in the $\delta^{13}C$ signal of suspended matter may occur. Such variations should be taken into account when suspended matter $\delta^{13}C$ data are used in foodweb analysis (Goering et al. 1990, Cifuentes et al. 1996), but this aspect is still neglected in many studies. Large seasonal and spatial variations have also been observed in zooplankton $\delta^{13}C$ and $\delta^{15}N$, both in marine and coastal environments (Fry & Wainright 1991, Malej et al. 1993, Wainright & Fry 1994, Zohary et al. 1994 and references therein) and freshwater ecosystems (Yoshioka et al. 1990, Toda & Wada 1990, Grey et al. 2001), with variability generally being larger in freshwater ecosystems (Zohary et al. 1994, but see Grey et al. 2000).

In this study, we wanted to gain insight into the sources of organic matter present in the suspended material in an estuarine mangrove ecosystem located near the mouth of the Gautami Godavari, Andhra Pradesh, India, by measuring elemental (POC/PN) and stable carbon isotope ratios in suspended particulate organic matter, collected at monthly intervals between January 1995 and August 1996 at 13 different locations, representing different environmental conditions. In addition, we wanted to assess whether the use of carbon and nitrogen stable isotope ratios could provide evidence for selective or non-selective feeding of zooplankton on different components of suspended matter. These data would also provide some baseline information on the spatio-temporal variability of suspended matter and

zooplankton isotopic ratios, which can be useful for further studies on the trophic dynamics in this ecosystem.

Materials & Methods

Study area

The study site (Figure 1) comprises the area between Kakinada Bay and the Gautami Godavari branch of the Godavari, the second largest river in India, and is located in the Southeastern state of Andhra Pradesh (between 16°43' and 17°00' N, 82°15' and 82°22' E). The Godavari has a mean annual discharge of 1.1×10^{11} m^3, of which 93-96 % occurs during the wet monsoon and it is recognized as one of the largest POC (particulate organic carbon) transporting rivers in the world (Gupta et al. 1997). The Gautami Godavari opens into the Bay of Bengal, but has several branches into Kakinada Bay, the largest and most important being Coringa (total length of 26 km) and Gaderu (total length of 11 km). The area is dominated by mangrove forests and tidal mudflats, the most abundant species being *Avicennia marina, A. officinalis, Excoecaria agallocha, Sonneratia apetala, Rhizophora mucronata* and *R. apiculata* (Azariah et al. 1992, Satyanarayana 1997). The shallow Kakinada Bay (depth at high tide ranging from 3 to 8 meters), which covers approximately 150 km^2, opens into the sea on its northern side, and is bordered along most of its eastern length by a narrow sand bar, which has experienced a breakthrough along its southern end after the November 1996 cyclone. Tides are semidiurnal, and tidal amplitude in the area varies between 0.5 and 2 meters, being less pronounded in the mangrove-covered areas.

The town of Kakinada (population ± 500,000), which hosts a large fishing harbour and several fertiliser factories, is located on the west side of Kakinada Bay. The whole area serves as an important fishing area for the local community, as well as for the collection of crabs, prawn 'seed' (mainly *Penaeus monodon* and *P. indicus*), and firewood (Rao 1998). Due to increased human pressure (e.g. aquaculture ponds) and pollution (e.g. fertilizer production, sewage disposal), the area has witnessed a significant decline in species diversity during the last 40 years (Deepti 1997).

In general, four seasons can be distinguished in the area, although substantial year-to-year variations in this pattern can be observed : (1) a cool and dry season from December to February; (2) a hot and relatively dry period from March to June; (3) abundant rains during

the hot Southwest monsoon (July to September) when almost freshwater conditions prevail in the whole area; and (4) a cooler transitional period during which estuarine and marine conditions are re-established in the Bay and mangrove creeks (October to November). During the period of this study, however, a bimodal rainfall distribution was noticed, with highest rainfall occurring in May 1996 and November 1996.

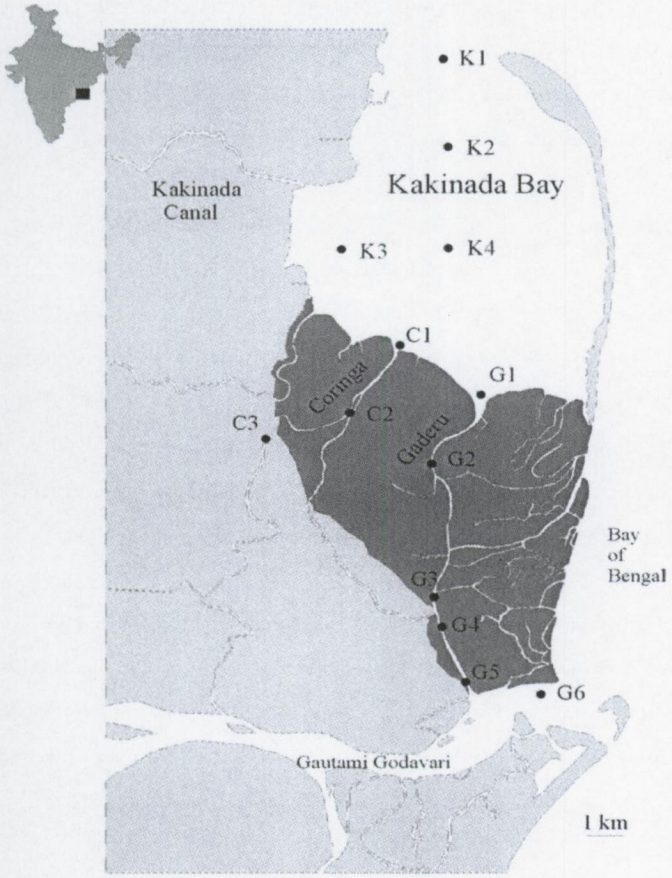


Figure 1 : Location of the study site and sampling locations. Darkest areas represent the major mangrove-covered regions north of the Gautami Godavari.

Sample collection and preparation

During the period from January 1995 to August 1996, zooplankton samples were collected at four different locations, representing different environmental and hydrological settings (Figure 1) : Kakinada North Bay (K_2), at the mouth of Coringa (C_1), central Gaderu (G_3), and at the mouth of Gautami Godavari (G_6). Particulate suspended matter was collected at approximately monthly intervals at these and nine additional locations. As it was impossible to collect all samples at the same tidal elevation, we examined the tidal variability of $\delta^{13}C_{SPOM}$ at one station (G_3) during a 24 hour period in November 1995.

Zooplankton samples were collected by towing a 120 µm plankton net equipped with a calibrated TSK flow meter at its opening. Material for stable isotopic analysis was kept in a cool box on board, and transported to the field laboratory were it was rinsed and dried at 60 °C for 24 hours. Subsamples were fixed on board in 5 % formaldehyde for quantitative studies and identification as discussed in Chandra Mohan et al. (1997) and Sreenivas (1998). Samples were ground to a fine powder, and subsamples for $\delta^{13}C$ analysis were rinsed with diluted HCl to remove carbonates, and redried. Subsamples for $\delta^{15}N$ analysis did not receive this acid treatment, as this has been reported to affect $\delta^{15}N$ values (Goering et al. 1990, Bunn et al. 1995). Suspended matter samples were obtained by collecting approximately 250 ml of subsurface water, which was kept in a cool box during transport, and was later filtered on pre-combusted glass-fibre filters (Whatmann GF/F). Filters were then dried at 60 °C for 24 hours and decalcified under acid vapour. Due to their low nitrogen content, no particulate nitrogen (PN) $\delta^{15}N$ measurements could be made. Salinity data are found in Murthy (1997) and Sreenivas (1998).

Measurement of elemental and stable isotope ratios

Most data on elemental ratios (POC/PN) of suspended matter were taken from Dehairs et al. (2000). Additional elemental analysis was performed using a Carlo Erba NA-1500 Elemental Analyser. Samples for stable isotope analysis were combusted in the same instrument, and the resulting gases (CO_2 and N_2) were separated by cryopurification using a Finnigan Mat CT-NT Trapping box (for CO_2), or with a manual extraction line (for CO_2, and N_2). Stable isotope ratios were then measured on a Delta E Finnigan Mat isotope ratio mass spectrometer, and are

expressed relative to the conventional standards, i.e. PDB limestone for carbon (Coplen 1996) and atmospheric N_2 for nitrogen (Mariotti 1983, 1984) as δ values, defined as :

$$\delta R = \left[\frac{X_{sample} - X_{standard}}{X_{standard}} \right] * 10^3 \qquad [‰]$$

where R = ^{13}C or ^{15}N, and X = $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The working standard for carbon was CO_2 produced from carrara marble, and high-purity tank N_2 was used as the working standard for nitrogen. Standard deviation on ten aliquots of the same sample is lower than 0.17 and 0.2 ‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively.

Results

ELEMENTAL AND STABLE CARBON ISOTOPE COMPOSITION OF SUSPENDED MATTER

$\delta^{13}C$ values for POC varied overall between –31.0 and –19.2 ‰, but average values per location ranged from a minimum of –25.5 (at C_1 and C_2) to –22.7 ‰ (at K_3) (Table 1, Figure 2). Suspended matter was, on average, more enriched in ^{13}C in the Bay stations, although significant overlap occurred (Table 1). Contrary to the expectation that this enrichment would increase along a linear gradient towards the bay opening, i.e. from station K_4 via K_2 to K_1, the reverse pattern was observed (average $\delta^{13}C$ values K_1 : -23.6 ‰; K_2 : -23.3 ‰; K_4 : -22.8 ‰), and most ^{13}C-enriched values (-22.7 ‰) were observed at K_3. Using a paired t-test, this enrichment of K_4 relative to K_1 was significant ($p = 0.041$; $\alpha = 0.05$), although the average difference was relatively small (0.72 ‰). A paired t-test revealed that K_2, K_3, and K_4 differed significantly from all Coringa, Gaderu and Gautami Godavari stations ($p < 0.043$; $\alpha = 0.05$), but POC from the northernmost station (K_1) was found to differ only from the three Coringa stations and the Gaderu stations G_2 ($p = 0.018$, $\alpha = 0.05$), G_3 ($p = 0.004$; $\alpha = 0.05$) and G_4 ($p = 0.006$; $\alpha = 0.05$). Most depleted average $\delta^{13}C_{SPOM}$ values were observed in the three Coringa stations, which all had an average value of –25.5 ‰ (Table 1). In Gaderu, suspended matter was found to be most depleted in ^{13}C in the central station (G_3 : -25.2 ‰), and became more enriched both towards Kakinada Bay (G_2 : -24.9 ‰; G_1 : -24.0 ‰) and towards the Gautami Godavari mouth (G_4 : -25.1 ‰; G_5 : -24.3 ‰) (Table 1). This enrichment compared to G_3 is significant (paired t-test) in G_1 ($p= 0.0077$; $\alpha = 0.05$) and G_5 ($p = 0.012$; $\alpha = 0.05$). At the Gautami Godavari station (G_6), suspended matter has an average $\delta^{13}C$ of –24.7 ‰.

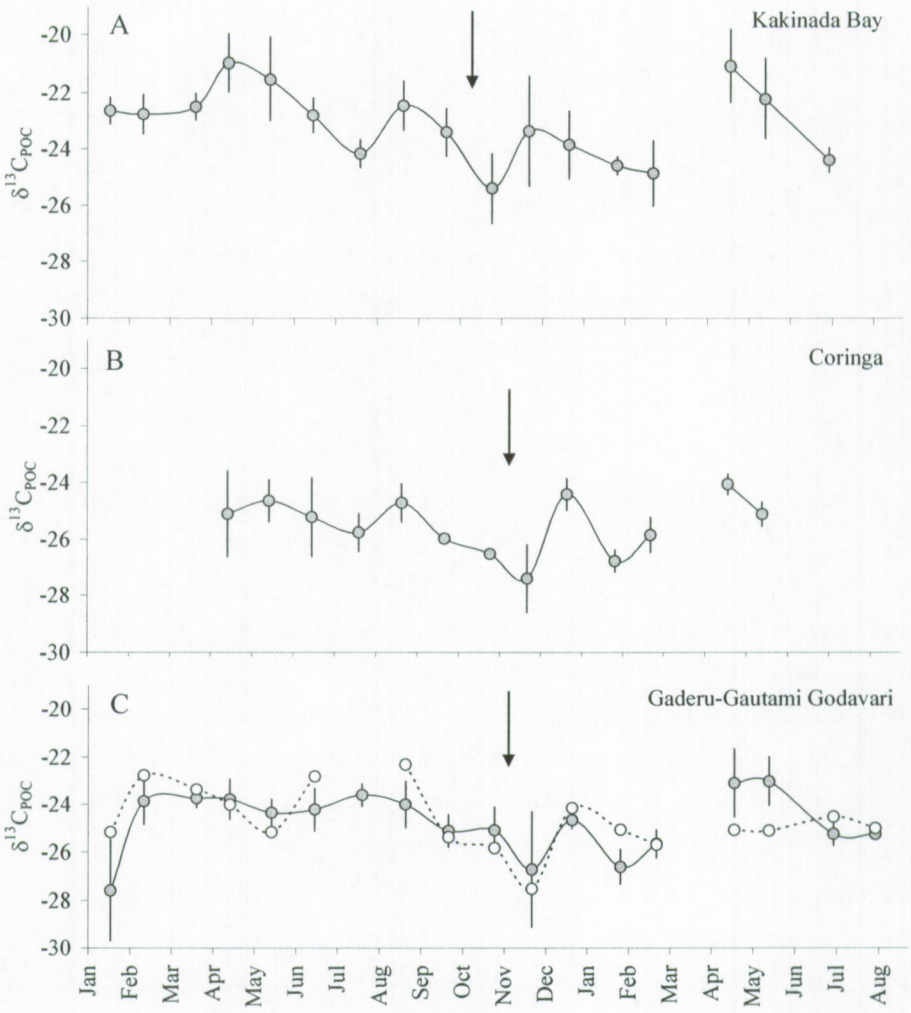


Figure 2 : Seasonal variations of $\delta^{13}C$ of POC, averaged over different stations in (A) Kakinada Bay, (B) Coringa, and (C) Gaderu (grey circles) and the mouth of Gautami Godavari (open circles). Error bars indicate ± 1 s.d. Arrow indicates a period in which a general depletion is noted, see text for details.

Table 1. Average (± 1 s.d.), minimum and maximum stable carbon isotope ratios ($\delta^{13}C$, expressed in ‰) and elemental (C :N) ratios of particulate organic carbon (POC), and average salinity (in ppt) at different sampling locations in the Gautami Godavari estuarine region. Abbreviations of sampling locations as in Figure 1. Numbers between brackets indicate the number of samples analysed.

	$\delta^{13}C \pm 1$ s.d.	min $\delta^{13}C_{POC}$	max $\delta^{13}C_{POC}$	POC/PN ± 1 s.d. *	Min POC/PN	Max POC/PN	Salinity**
KAKINADA BAY							
K_1	-23.6 ± 1.3 (n=16)	-26.0	-20.8	10.0 ± 4.9 (n= 15)	5.4	23.6	28.5
K_2	-23.3 ± 1.3 (n=17)	-25.8	-21.7	8.5 ± 2.4 (n=17)	5.8	14.0	27.3
K_3	-22.7 ± 2.2 (n=16)	-26.3	-19.2	8.3 ± 2.4 (n=15)	5.0	13.5	23.5
K_4	-22.8 ± 1.5 (n=17)	-26.4	-20.7	8.5 ± 3.2 (n=15)	4.8	17.3	25.8
CORINGA							
C_1	-25.5 ± 1.5 (n=13)	-28.8	-23.7	11.9 ± 8.8 (n=13)	5.6	32.7	10.6
C_2	-25.5 ± 0.9 (n=13)	-26.6	-23.7	12.7 ± 11.2 (n=12)	5.1	38.0	6.5
C_3	-25.5 ± 1.1 (n=13)	-26.8	-23.4	13.4 ± 12.2 (n=11)	6.2	42.4	4.2
GADERU							
G_1	-24.0 ± 1.2 (n=16)	-26.4	-22.0	9.3 ± 3.5 (n=15)	6.0	20.5	18.8
G_2	-24.9 ± 1.9 (n=16)	-30.9	-23.2	8.7 ± 2.9 (n= 15)	5.0	15.2	17.5
G_3	-25.2 ± 1.6 (n=18)	-29.5	-23.2	8.3 ± 2.5 (n=15)	5.7	13.2	17.6
G_4	-25.1 ± 1.6 (n=16)	-29.1	-23.2	8.7 ± 3.9 (n=15)	6.3	20.5	15.3
G_5	-24.3 ± 1.7 (n=16)	-27.1	-21.0	10.1 ± 5.6 (n= 15)	3.9	27.8	16.3
GAUTAMI GODAVARI							
G_6	-24.7 ± 1.3 (n=17)	-27.5	-22.3	9.2 ± 3.4 (n=15)	5.4	17.2	15.6

*: most POC/PN data from Dehairs et al. (2000)
**: salinity data from Murthy (1997)

Table 2. Seasonal variations in suspended matter $\delta^{13}C$ (in ‰) at the different sampling locations. Values marked with an asterisk were taken from Dehairs et al. (2000). Abbreviations of sampling locations as in Figure 1. - : not determined.

	Kakinada Bay				Coringa			Gaderu					Gautami Godavari
	K_1	K_2	K_3	K_4	C_1	C_2	C_3	G_1	G_2	G_3	G_4	G_5	G_6
Jan-95	-23.0	-22.5	-23.0	-22.0	-	-	-	-25.4	-30.9	-26.9	-28.0	-26.7	-25.2
Feb-95	-23.7	-22.9	-22.5	-22.0	-	-	-	-23.4	-25.2	-24.3	-23.8	-22.7	-22.8
Mar-95	-	-23.0*	-22.0*	-22.6*	-	-	-	-23.6*	-24.1*	-24.2*	-23.6*	-23.2*	-23.4*
Apr-95	-20.8	-22.4	-20.0	-20.7	-26.3	-25.6	-23.4	-22.2	-23.9	-24.1	-24.8	-24.0	-24.0
May-95	-23.4	-21.7	-19.8	-21.3	-24.2	-24.2	-25.5	-23.6	-24.7	-24.1	-25.0	-24.4	-25.2
Jun-95	-23.7*	-22.3*	-22.4	-22.9*	-23.7*	-25.6*	-26.4*	-22.9*	-24.5*	-25.0*	-24.4*	-24.3*	-22.8*
Jul-95	-24.1	-24.9	-23.8	-23.9	-26.4	-25.8	-25.0	-24.4	-23.6	-23.5	-23.6	-23.0	-
Aug-95	-23.7*	-22.4*	-21.9*	-21.8*	-24.1*	-25.5*	-24.6*	-24.1*	-23.2*	-23.2*	-24.6*	-25.0*	-22.3*
Sep-95	-23.1	-22.6	-24.6	-23.4	-26.1	-26.0	-25.9	-25.7	-24.5	-26.1	-25.0	-24.3	-25.4
Oct-95	-23.8	-25.1	-26.3	-26.4	-26.5	-26.4	-26.7	-24.5	-24.4	-26.8	-25.4	-24.4	-25.8
Nov-95	-22.4	-22.8	-26.3	-22.0	-28.8	-26.6	-26.8	-23.5	-24.5	-29.5	-29.1	-27.1	-27.5
Dec-95	-25.1*	-24.1*	-22.2*	-24.1*	-24.3*	-25.0*	-24.0*	-24.7*	-25.0*	-25.0*	-24.5*	-24.2*	-24.2*
Jan-96	-24.3	-24.9	-24.8	-24.4	-27.2	-26.4	-26.7	-26.4	-26.8	-26.6	-27.1	-26.1	-25.1
Feb-96	-26.0	-25.8	-24.1	-23.7	-25.3	-25.8	-26.5	-24.7	-25.5	-26.2	-25.6	-26.4	-25.7
Mar-96	-	-	-	-	-	-	-	-	-	-	-	-	-
Apr-96	-21.8	-21.8	-19.2	-21.6	-24.0	-23.7	-24.5	-22.7	-23.4	-24.2	-24.2	-21.0	-25.1
May-96	-23.2	-23.7	-21.0	-21.0	-24.9	-24.9	-25.6	-22.0	-23.6	-23.5	-23.2	-22.7	-25.1
Jun-96	-24.8	-24.0*	-	-24.4	-	-	-	-	-	-25.3*	-	-	-24.5*
Jul-96	-	-	-	-	-	-	-	-	-	-25.3*	-	-	-25.0*

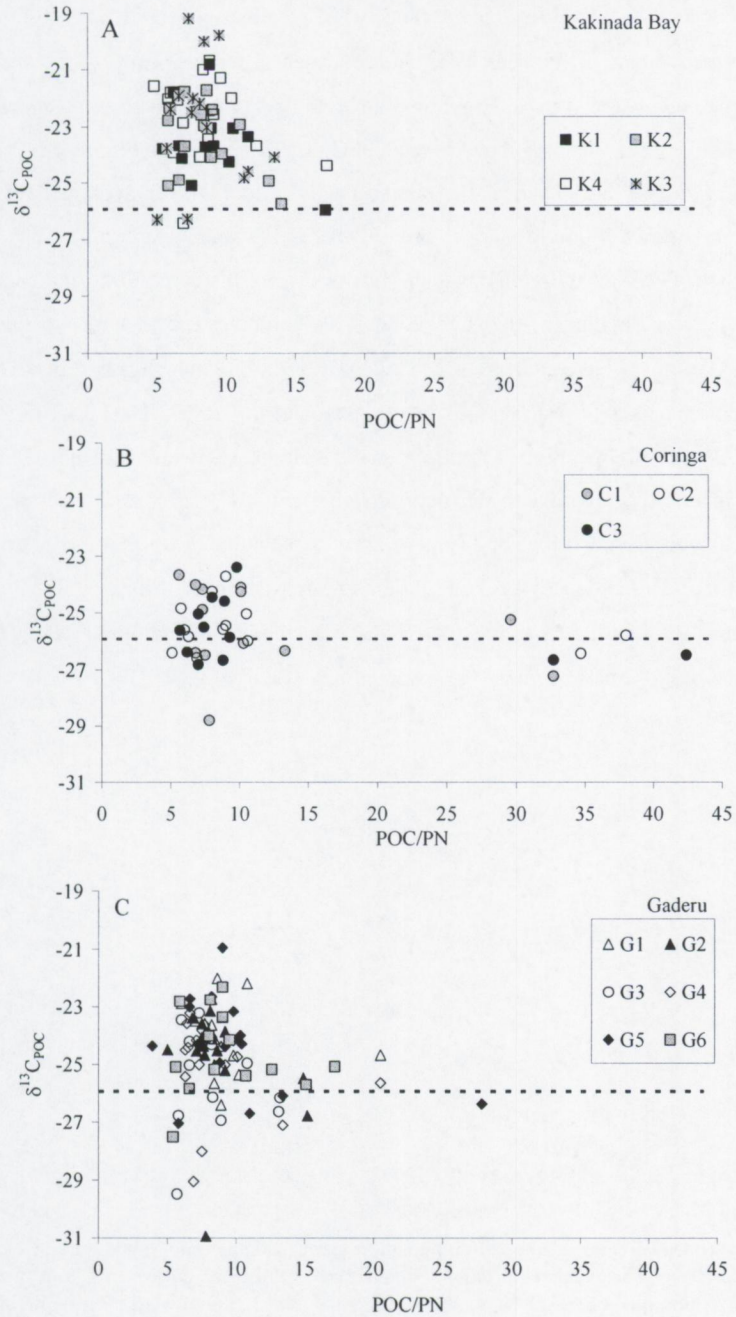


Figure 3 : Elemental (POC/PN) versus stable carbon isotope composition ($\delta^{13}C$, in ‰) of suspended organic matter from the different sampling stations in (a) Kakinada Bay, (b) Coringa, and (c) Gaderu and Gautami Godavari. The horizontal dotted line represents average $\delta^{13}C_{POC}$ (-25.9 ‰) for all samples with POC/PN > 12.

Seasonal variations in $\delta^{13}C_{POC}$ values (i.e. the range of $\delta^{13}C$ values observed) at each location were larger than the average differences in $\delta^{13}C_{POC}$ between different locations. An apparent depletion in ^{13}C can be observed during the transitional and dry season (between October and February), and is most pronounced in the Coringa and Gaderu stations (see Figure 2).

Overall, POC/PN ratios of suspended matter ranged from 3.9 to 42.4; but average values for all stations were between 8.3 (at G_3 and K_3) and 13.4 (at C_3) (Table 1, Figure 3). Suspended matter samples with POC/PN ratios higher than 12 are often considered to be indicative of containing mainly terrestrial detritus (Faganeli et al. 1988, Cifuentes et al. 1996). As shown in Figure 3 (dotted line), these have an average $\delta^{13}C$ value of –25.9 ‰, which is within the range of values reported for typical terrestrial C3-plants (Peterson & Fry 1987). The bulk of samples with lower POC/PN ratios (including all but four of the Kakinada Bay and Gautami Godavari samples) are enriched in ^{13}C relative to this detrital signal, but about 23 % of all samples, the majority of which come from Coringa and Gaderu, were depleted in ^{13}C (Figure 3).

During the tidal cycle recorded at Gaderu station G_3 in November 1995, $\delta^{13}C_{POC}$ varied between –26.5 and –28.3 ‰, and was well correlated with salinity fluctuations (R^2=0.62; p = 0.012), with low $\delta^{13}C_{POC}$ values occurring at lower salinity (Figure 4).

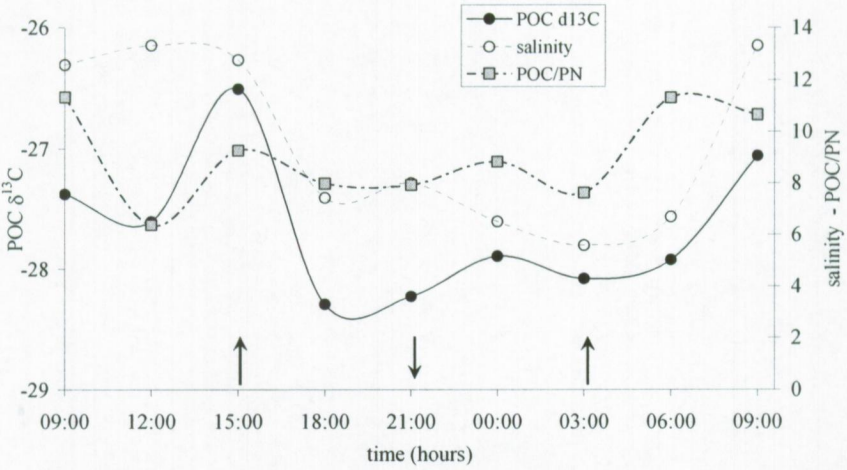


Figure 4 : Salinity (open circles), elemental composition (grey squares) and stable carbon isotopic composition (full circles) of suspended particulate organic matter collected during a 24 hour period at the central Gaderu station (G_3) on 16-17 November 1995. Arrows pointing upward indicate high tides, the arrow pointing downward indicated the time of low tide.

STABLE CARBON AND NITROGEN ISOTOPE COMPOSITION OF ZOOPLANKTON

The overall range of $\delta^{13}C$ values for zooplankton (-30.1 to –16.5 ‰) was larger than the range of $\delta^{13}C_{SPOM}$ values from the same locations (-29.5 to –21.7 ‰; Table 1 and 3). Zooplankton was most enriched in ^{13}C in Kakinada Bay (station K_2, average $\delta^{13}C_{ZP}$ = -21.0 ‰), but also exhibited the largest range at this station (-28.2 to –16.5 ‰). The average zooplankton $\delta^{13}C$ at the four sampling locations followed the same trend in ^{13}C-depletion as did the suspended matter from these stations (i.e. $K_2>G_6>G_3>C_1$), but the $\delta^{13}C$ gradient was more pronounced in the zooplankton, causing zooplankton to be –on average- enriched in ^{13}C relative to the suspended matter at K_2 (by 1.8 ‰ when using only data from months when both parameters were measured), G_6 (by 2.9 ‰) and in G_3 (by 0.1 ‰), but depleted at C_1 (by 0.1 ‰) (Figure 5). It should be noted, however, that there was a large variation in the $\delta^{13}C$ difference of concurrently collected zooplankton and suspended matter (Figure 6). As observed for POC, most depleted values were usually observed between the middle of the monsoon period (i.e. September) and the middle of the dry season (i.e. February) (Figure 6), and the range of $\delta^{13}C$ values observed at each station was larger than the average spatial differences (Table 3).

Zooplankton $\delta^{15}N$ values exhibited much less seasonal variation than the $\delta^{13}C_{ZP}$ variations (Table 3). Due to the small sample sizes, it was impossible to analyse the $\delta^{15}N$ of all samples, which makes it difficult to detect any clear seasonal trend in zooplankton $\delta^{15}N$. Based on these data, however, it seems that Coringa zooplankton was lower in $\delta^{15}N$ (+ 4.8 and + 5.2 ‰, n=2) than that at the three other stations, which were relatively similar in their average $\delta^{15}N$ values (average $\delta^{15}N$ = + 7.5 ‰ at G_3; + 7.9 ‰ at K_2; and + 8.4 ‰ at G_6). Due to the small amount of concurrent data from different stations, we were unable to detect any statistically significant spatial differences in $\delta^{15}N$.

Table 3. Average (± 1 s.d.), minimum and maximum $\delta^{13}C$ and $\delta^{15}N$ (in ‰) of zooplankton (ZP), collected at different locations in the Gautami Godavari estuarine region. Some of the zooplankton $\delta^{13}C$ data were taken from Dehairs et al. (2000). Abbreviations of sampling locations as in Figure 1.

	Kakinada Bay (K_2)	**Coringa (C_1)**	**Gaderu (G_3)**	**Gautami Godavari (G_6)**
$\delta^{13}C_{ZP}$	-21.0 ± 3.2 (n=19)	-25.9 ± 3.0 (n=9)	-24.3 ± 2.3 (n=14)	-22.0 ± 2.4 (n=13)
min	-28.2	-30.1	-26.9	-27.6
max	-16.5	-20.6	-19.1	-18.9
$\delta^{15}N_{ZP}$	+ 7.9 ± 1.4 (n=12)	+ 5.0 ± 0.3 (n=2)	+ 7.5 ± 0.9 (n=4)	+ 8.4 ± 1.2 (n=4)
min	+ 5.8	+ 4.8	+ 6.5	+ 7.5
max	+ 10.5	+ 5.2	+ 8.3	+ 10.0

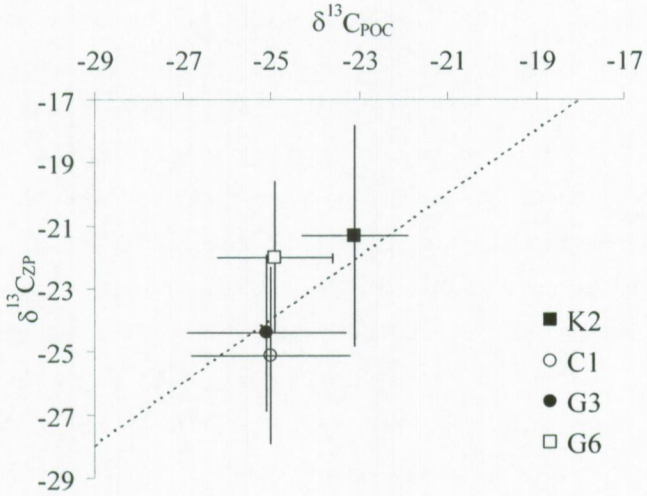


Figure 5 : Average zooplankton $\delta^{13}C$ (in ‰) versus average POC $\delta^{13}C$ (in ‰) for different locations. Note that only concurrently collected samples were used to construct this figure. Error bars indicate the standard deviation. The dotted line represents the $\delta^{13}C$ for the zooplankton food source assuming a trophic fractionation factor of 1 ‰.

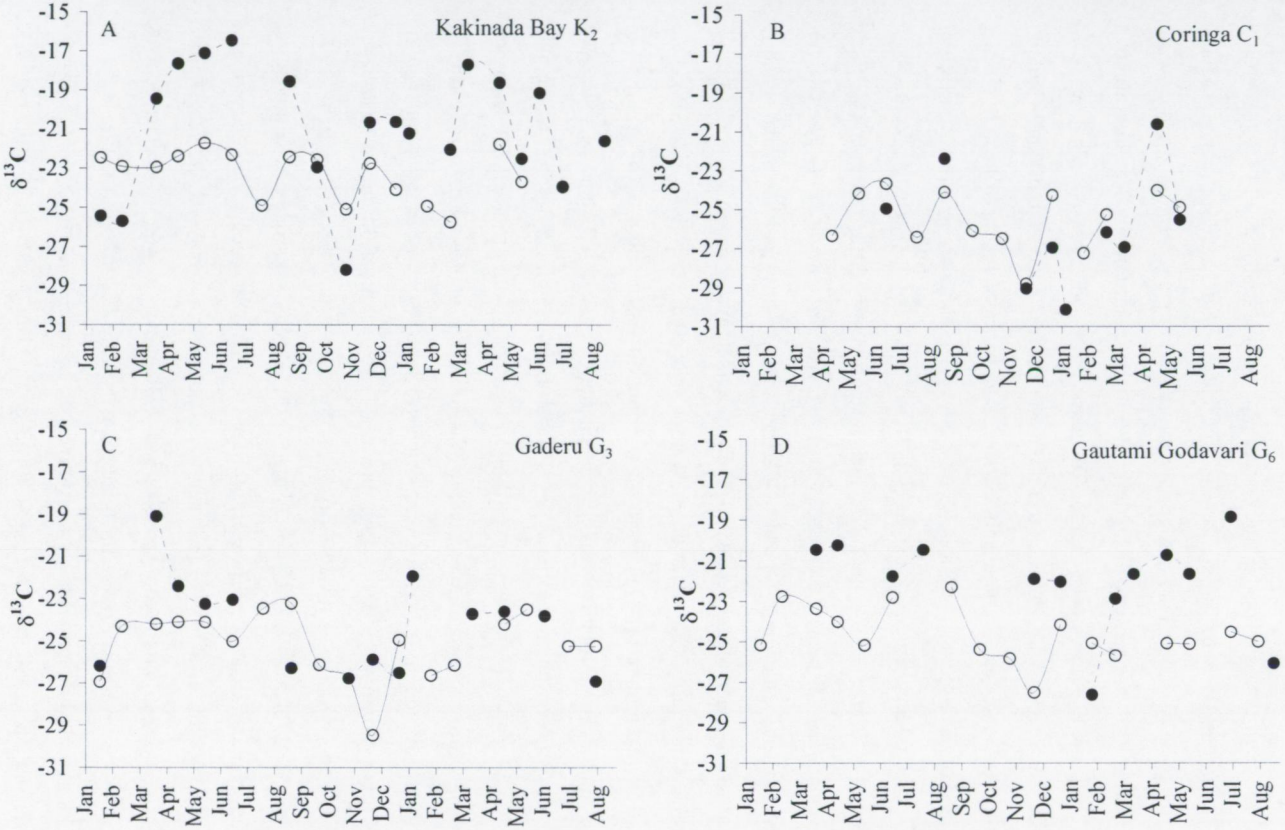


Figure 6 : Seasonal variation of zooplankton $\delta^{13}C$ (full circles) and POC $\delta^{13}C$ (open circles) at (a) Kakinada Bay K_2, (b) Coringa mouth C_1, (c) central Gaderu G_3, and (d) mouth of the Gautami Godavari G_6.

Discussion

SOURCES OF ORGANIC MATTER IN SUPENDED MATTER

Due to the high turbidity in the study area, aquatic macrophytes and seagrasses are virtually absent (Dehairs et al. 2000). The three main local primary producer categories to be considered are mangroves, phytoplankton, and benthic microalgae, of which the latter two are generally considered to be quantitatively less important in turbid estuarine mangrove ecosystems (Roberston et al. 1992, see also Chapter 2). In addition, some terrestrial detritus from outside the area, carried by the Gautami Godavari and entering Coringa and Gaderu, can be expected to contribute to the suspended organic matter load. Leaves of 7 out of 19 mangrove species occurring in the area showed an average $\delta^{13}C$ signal of -28.5 ± 1.5 ‰ ($n = 27$, Dehairs et al. 2000, Bouillon et al. 2002b, i.e. Chapter 8), which is consistent with literature data on these and other mangrove species (e.g. Rao et al. 1994, Hemminga et al. 1994, see Chapter 1 pp. 9-10), and which is a typical $\delta^{13}C$-signature for terrestrial C3-plants. Factors reported to influence mangrove leaf $\delta^{13}C$ include their water use efficiency, salinity, and ambient humidity (Farquhar et al. 1982, Lin & Sternberg 1992, Kao & Chang 1998). Loneragan et al. (1997) found no seasonal differences in mangrove leaf $\delta^{13}C$. Several authors have found no significant changes in the $\delta^{13}C$ signal of mangrove leaves during decomposition (Zieman et al. 1984, Dehairs et al. 2000), so that we may assume that mangrove detritus exported into the water column also exhibits a carbon isotope signature in the same range as the measured $\delta^{13}C$ values for mangrove leaves. Although fresh mangrove leaves are reported to have C/N ratios ranging between 20 and 78 (average around 50), this ratio increases two- to threefold during senescence due to re-absorption of 50 to 80 % of the nitrogen by the plants (Rao et al. 1994, Jennerjahn & Ittekkot 1997, Lin & Wang 2001). During subsequent decomposition and bacterial colonization, however, nitrogen enrichment occurs due to nitrogen fixation (Woitchik et al. 1997) and due to immobilization, both on the forest floor (Twilley et al. 1986) and in the water column (Cifuentes et al. 1996). These processes result in much lower C/N ratios for mangrove detritus. According to Cifuentes et al. (1996), suspended mangrove detritus (defined as suspended matter having a carbon-to-chlorophyll a ratio higher than 1000) has an average POC/PN ratio of 12.1,

whereas others report C:N ratios of 24 to 51 after 45 days of decomposition for *Excoecaria agallocha* and *Avicennia marina,* respectively (Dehairs et al. 2000), C/N ratios approaching 24 after about 100 days of decomposition for *A. marina, A. corniculatum* and *Kandelia candel* (Tam et al. 1990), and values as low as 5 to 20 after 3 months of decomposition (Wafar et al. 1997).

Due to the practical difficulties in obtaining pure phytoplankton samples free from terrestrial detritus, no $\delta^{13}C$ data specifically for phytoplankton are available. It is generally accepted, however, that marine phytoplankton from tropical regions shows a $\delta^{13}C$ signal between –18 to –22 ‰ (Fontugne & Duplessy 1981, Goericke & Fry 1994), whereas estuarine and freshwater phytoplankton may be more depleted in ^{13}C due to the uptake of isotopically light DIC (dissolved inorganic carbon) resulting from the bacterial respiration of terrestrial organic matter (Mook & Tan 1991, Hellings et al. 1999). Phytoplankton C/N ratios are reported to range from 6.6 to 8.7 under natural conditions (Redfield et al. 1963, Holligan et al. 1984).

Due to light limitation and inhibition by soluble tannins, benthic microalgal production in mangrove forests is usually rather low (Alongi 1994 and references therein). In the following discussion only phytoplankton and terrestrial (including mangrove) detritus will thus in first instance be considered as major components of suspended matter.

In Kakinada Bay, suspended matter from stations K_2, K_3, and K_4 was significantly enriched in ^{13}C relative to all mangrove waterway stations (paired t-test), but values were generally more depleted than those reported for typical tropical marine phytoplankton. Several POC/PN ratios at these stations were relatively high (i.e. between 9 and 17.3) compared to typical phytoplankton C/N ratios (6.6), which leads to the conclusion that a certain amount of terrestrial detritus is present at these locations. In view of the relative proximity to the mangrove waterways (e.g. about 4 km from K_4 to the Coringa mouth, fig. 1), it may be assumed that mangrove detritus constitutes at least a part of this terrestrial matter. Suspended matter $\delta^{13}C$ values at these stations also exhibited a fairly wide range (-21.7 to –25.8 ‰ at K_2, -19.2 to –26.3 ‰ at K_3, and –20.7 to –26.4 ‰ at K_4). This variability may have been caused simply by a variable contribution of terrestrial material to the local phytoplankton, but some samples which, judging from their low POC/PN ratios (< 7) were dominated by phytoplankton, had $\delta^{13}C$ values ranging between –21.6 and –26.3 ‰, indicating that

phytoplankton at these stations may also exhibit variations in its $\delta^{13}C$ signal, e.g. due to the uptake of isotopically light DIC (e.g. Hellings et al. 1999), variability in growth rate (e.g. Fry & Wainright 1991, Burkhardt et al. 1999a,b), or variability in ambient dissolved CO_2 concentrations (Hinga et al. 1994, Burkhardt et al. 1999a,b). Seasonal variations in $\delta^{13}C_{DIC}$ have indeed been shown to occur in the entire Bay region (Chapter 4), and values as low as -7 ‰ may even be found.

Suspended matter $\delta^{13}C$ values from all Kakinada Bay stations did not seem to show any distinct seasonal pattern (Figure 2), although it is clear that all stations usually followed the same trend. Remarkably, the northernmost station (K_1) which is located in the opening of the Bay into the Bay of Bengal, exhibited the most depleted average $\delta^{13}C_{POC}$ value, indicating a larger terrestrial influence than the central Bay stations. It is unclear, however, whether this is the result of circulation patterns in the Bay (Sreenivas 1998) which could direct the water flowing out of the mangrove waterways along a clockwise route to the Bay opening (K_1), or because of a more direct influence by the Kakinada Canal (see Figure 1), which opens into the western side of the Bay on the south end of Kakinada town and carries substantial amounts of domestic waste. Satellite data show that the outflow of the Kakinada Canal is directed towards the Bay opening, supporting the latter hypothesis. Either way, it seems that terrestrial detritus, possibly including mangrove-derived material, comprises a variable and detectable fraction of suspended matter in Kakinada Bay, several km from the outlets of the mangrove creeks.

At all three Coringa stations, suspended matter had average $\delta^{13}C$ of –25.5 ‰, which were the lowest average values encountered in this study. Of all the sites considered, Coringa is clearly least influenced by the saline Bay water, so the $\delta^{13}C_{POC}$ values at these stations (especially at C_3 which had an average salinity of 4.2 ppt; Table 1) can be considered to be representative of the freshwater end members of suspended matter $\delta^{13}C$.

In Gaderu, suspended matter exhibited the lowest average $\delta^{13}C$ at the central G_3 station, and it became more enriched in ^{13}C towards both its marine ends (Table 1). This gradient may be caused by (a combination of) two factors, i.e. a lesser admixture of marine phytoplankton with terrestrial material from the outer stations towards G_3, or a depletion in ^{13}C in local phytoplankton in the central Gaderu station compared to the other stations. Contrary to the expectation that POC/PN ratios would have been

largest at G_3 and lower towards the open water because of a possibly elevated contribution of mangrove detritus to suspended matter, the reverse pattern was observed (Table 1), suggesting that the observed trend in $\delta^{13}C_{POC}$ was not due solely to a larger contribution of terrestrial material. In addition, phytoplankton counts and chlorophyll measurements indicated that in Gaderu, phytoplankton was most abundant at G_3 and diminished towards G_1 and G_5 (Rohini 1997). Thus, in Gaderu, a larger contribution of phytoplankton to suspended matter (at G_3) was accompanied by more depleted $\delta^{13}C_{POC}$ values, suggesting that -on average- phytoplankton here may have been more ^{13}C-depleted than the nearby bay phytoplankton. The latter can also be derived from (later) measurements of $\delta^{13}C_{DIC}$ (see Chapter 4) which show markedly lower $\delta^{13}C$ values for Gaderu (on average ~ - 8 ‰) than in the Bay (on average ~ - 2 ‰).

If we consider $\delta^{13}C_{POC}$ data from all locations, it is clear that the stable carbon isotope composition of suspended matter was very variable, and that seasonal variability was more pronounced than average spatial differences. Based on the wide range of POC/PN ratios encountered (3.9 to 42.4), part of this variation may have been caused by a variable contribution of terrestrial and autochthonous material to the total suspended organic matter load. However, the wide range of $\delta^{13}C$ values (e.g. -21.6 ‰ at K_4 to –29.5 ‰ at G_3) in samples with low POC/PN ratios (POC/PN < 7, suggesting a substantial phytoplankton contribution), suggests that there was some spatial and temporal variation in phytoplankton $\delta^{13}C$, which was obscured or masked in samples where the terrestrial contribution was high. Especially for the mangrove creeks, we expect local phytoplankton to have been relatively depleted in ^{13}C, due to the uptake of isotopically light DIC, which results from the degradation of the large amounts of mangrove litter. Direct evidence for this comes from two relatively pure (visually assessed) phytoplankton samples (10<<50 μm) collected in Coringa in February 1999, which showed a $\delta^{13}C$ of –28.9 ‰ (at C_3) and –26.9 ‰ (at C_1), i.e. they were depleted in ^{13}C relative to the average $\delta^{13}C_{POC}$ at these sites, and were falling in the same range as $\delta^{13}C$ values reported for mangrove leaves. $\delta^{13}C_{DIC}$ values of surface water samples collected simultaneously with these showed a significant ^{13}C-depletion of the DIC pool, with $\delta^{13}C$ values between –10.5 ‰ at C_3 and –10.0 ‰ at C_1. The existence of a sustained and strongly ^{13}C-depleted DIC pool was later confirmed over a longer time period (see Chapter 4).

$\delta^{13}C$ values of POC collected during a 24 hour period at G_3 in November 1995, showed substantial variations with the stage of the tide, with suspended matter being most depleted (-28.3 ‰) during low tide, and most enriched (-26.5 ‰) at high tide (Figure 4). The amplitude $\delta^{13}C_{POC}$ variations observed is smaller than that noted in the same creek in June 2001 (range of approximately 4 ‰, with salinity fluctuations of merely 4 ppt). Similar observations in tidal mangrove ecosystems were made by Rezende et al. (1990), and tidal variations in $\delta^{13}C_{POC}$ of an even greater magnitude (about 5 ‰) were observed by Cifuentes et al. (1996), even though the salinity fluctuations they encountered (Δ sal = 1.7) were much smaller than those recorded in our study (Δ sal = 7.5). $\delta^{13}C_{POC}$ values were well correlated with salinity ($R^2 = 0.62$; $p = 0.012$) but not with POC/PN ratios ($R^2 = 0.14$). These POC/PN ratios are within the same range as most other data reported from other mangrove ecosystems (e.g. Cifuentes et al. 1996).

ZOOPLANKTON $\delta^{13}C$ AND ITS RELATION TO POC $\delta^{13}C$.

Very little information exists on the trophic pathways associated with zooplankton in mangrove ecosystems, but Grindley (1984) suggested that the abundant particulate organic matter (i.e. detritus) in mangrove estuaries constitutes the major food source for zooplankton in these ecosystems, and similar conclusions have been made in temperate estuaries (e.g. Hummel et al. 1988). Camillieri & Ribi (1986) showed experimentally that several species of small crustaceans are able to survive when offered flakes formed from DOC (dissolved organic carbon) leached from *Rhizophora* leaves. The species they investigated included some harpacticoid copepods and amphipods (i.e. benthic organisms), but no calanoid copepods, which usually form the bulk of the pelagic zooplankton in the study area (Chandra Mohan et al. 1997). Moreover, the fact that these organisms are able to survive on this food source does not imply that they would utilise it under natural conditions, when more nutritious algal material is also present.

Careful comparison of the zooplankton and suspended matter $\delta^{13}C$ data revealed several patterns which suggest that zooplankton were not feeding indiscriminately on bulk suspended matter, but selected components of the suspended matter pool that showed a more pronounced spatial and seasonal variability in $\delta^{13}C$ than POC.

Firstly, the overall range of $\delta^{13}C$ values for zooplankton ($\delta^{13}C_{ZP}$) collected at the four selected stations (-30.1 to –16.5 ‰) was much larger than the range of $\delta^{13}C_{POC}$ values from those locations (-29.5 to –21.7 ‰; Table 1 and 3). If zooplankton were feeding indiscriminately on suspended organic matter (and assuming a constant $\delta^{13}C$ trophic shift), the seasonal fluctuations of their $\delta^{13}C$ values would have been of the same magnitude as those observed in POC. If, however, they were feeding selectively on either terrestrial detritus (which should have a fairly constant $\delta^{13}C$) or phytoplankton (which may have a more variable $\delta^{13}C$), the fluctuations of their $\delta^{13}C$ signal should have been either smaller or larger than those of POC, respectively.

Secondly, the average zooplankton $\delta^{13}C$ of the four sampling locations followed the same trend in ^{13}C-depletion as did the suspended matter from these stations (i.e. $K_2>G_6>G_3>C_1$), but the $\delta^{13}C$ gradient was more pronounced in the zooplankton (Figure 5). If we assume a constant and small fractionation in ^{13}C between zooplankton and their diet (0-1 ‰; DeNiro & Epstein 1978), this would suggest that at K_2 and G_6, zooplankton were feeding on a fraction enriched in ^{13}C relative to the total suspended matter, but on a fraction that was ^{13}C-depleted relative to POC at G_3 and C_1 (see Figure 5). Del Giorgio & France (1996) found from a compilation of literature data that there is a trend in the mean difference between $\delta^{13}C_{ZP}$ and $\delta^{13}C_{POC}$ going from the open ocean (+ 2.7 ‰), coastal (+ 1.8 ‰) and estuarine (+ 0.8 ‰) ecosystems, to freshwater lakes, where zooplankton is depleted relative to POC by an average of 2.7 ‰. The most likely explanation for this trend is that zooplankton feeds selectively on phytoplankton which, in freshwater and sometimes in estuarine systems, is isotopically lighter than the total suspended matter (del Giorgio & France 1996).

A third argument for selectivity in zooplankton feeding comes from a comparison of the average difference in $\delta^{13}C_{POC}$ and the average difference in $\delta^{13}C_{ZP}$ between different stations, as shown in Figure 7. Although the spatial differences in $\delta^{13}C_{POC}$ are often significant (paired t-test), they are relatively small (0.3 to 2.1 ‰) when compared to the difference in the zooplankton $\delta^{13}C$ signal between these locations (1.4 to 6.0 ‰). If zooplankton would have been feeding indiscriminately on suspended organic matter, these between-site differences would be expected to be of equal magnitude for both POC and zooplankton.

Although these data do not allow us to quantitatively determine the exact contribution of phytoplankton or terrestrial carbon to zooplankton nutrition, our results clearly indicate that local aquatic primary production provides a more important carbon source for zooplankton, despite the high inputs of terrestrial (including mangrove) carbon in the aquatic system.

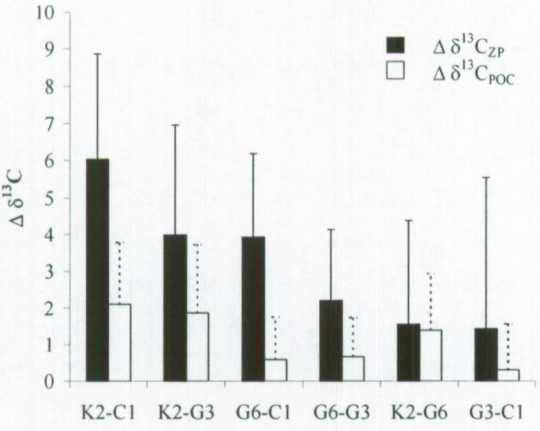


Figure 7 : Average difference in zooplankton $\delta^{13}C$ (black bars) and average difference in POC $\delta^{13}C$ (white bars) for different pairs of locations. Error bars = 1 s.d.

POSSIBLE MECHANISMS INFLUENCING THE SPATIO-TEMPORAL VARIATIONS IN POC AND ZOOPLANKTON $\delta^{13}C$

The selective feeding of zooplankton on phytoplankton (discussed above) implies that the $\delta^{13}C_{ZP}$ will provide us with a better parameter than $\delta^{13}C_{POC}$ for elucidating possible mechanisms influencing the carbon stable isotopic signal of the phytoplankton in the study area. Some important factors influencing the $\delta^{13}C$ of

phytoplankton have been found to include the $\delta^{13}C$ of the DIC pool and the phytoplankton growth rate (e.g. Fry & Wainright 1991, Hellings et al. 1999). To our knowledge, no studies have attempted to analyse the seasonal variability of phytoplankton $\delta^{13}C$ in tropical, monsoon-influenced estuaries. Much of our earlier speculations on the factors underlying the spatial and seasonal $\delta^{13}C_{ZP}$ variations (i.e. as reported in Bouillon et al. 2000) have in the mean time been confirmed by the monthly sampling of DIC for $\delta^{13}C$ analysis in the study area (see Chapter 4). Briefly, we speculated that :

(1) The remarkable spatial variability, i.e. the clear trend from more depleted $\delta^{13}C$ values for zooplankton in the most freshwater parts (Coringa), and a gradual increase towards more estuarine (G_3, G_6) and near-marine (K_2) locations, could have been the result of an accompanying gradient in $\delta^{13}C_{DIC}$, which might have been more negative in the mangrove sites due to the microbial respiration of the higher amounts of terrestrial and mangrove POC available. Indeed, it was later found that the DIC pool is consistently and markedly more depleted in the mangrove creeks relative to the Bay area (see Chapter 4).

(2) Seasonal variations in $\delta^{13}C_{ZP}$ might have been the result of an increased importance of bacterial mineralization of POC during the monsoon when the river discharge imports large quantities of terrestrial POC. Bearing in mind possible effects of tidal amplitude and year-to-year variations in the climatic pattern on the stable carbon isotopic composition of POC, the following trends seemed to be a general feature in the $\delta^{13}C_{ZP}$ signal (Figure 6) :

- During the pre-monsoon period (i.e. March-April to May-June), when salinity is high in the entire area and the suspended organic matter load is minimal (Dehairs et al. 2000), zooplankton is enriched in ^{13}C relative to its average $\delta^{13}C$ signal. The small amount of data from the first half of the monsoon period (July-August) seem to suggest that the $\delta^{13}C_{ZP}$ remains high during this period (figure 6). This seasonal trend in zooplankton $\delta^{13}C$ values was confirmed by Rao (unpublished data) for zooplankton collected at various sites in the study area during 1996/1997.

- Minimal values of $\delta^{13}C_{ZP}$ are observed between the middle of the monsoon period and the middle of the dry season (i.e. between September and February).

Again, this seasonal pattern can be clearly identified in the DIC pool, which shows markedly lower $\delta^{13}C$ values during and shortly after the monsoon period (see Chapter 4 for a more detailed discussion).

ESTIMATING SPATIO-TEMPORAL PHYTOPLANKTON $\delta^{13}C$ VARIATIONS

Although our data show conclusively that local aquatic primary production is the main carbon source for the zooplankton community, it remains difficult to make a quantitative estimate of the relative contribution of phytoplankton and terrestrial (or mangrove) carbon sources. One of the main causes is that phytoplankton could not be analysed for $\delta^{13}C$ as such because it is difficult if not impossible to separtate from the mixture of suspended matter. Although direct proxies to estimate phytoplankton $\delta^{13}C$ values have recently become feasible, e.g. by measuring specific algal fatty acid $\delta^{13}C$, most studies have used the $\delta^{13}C$ of the DIC pool in order to estimate phytoplankton $\delta^{13}C$, either assuming either a constant fractionation factor (Cai et al. 1988) or taking into account additional factors such as CO_2 concentrations (Hellings et al. 1999). In this study, no concurrent $\delta^{13}C_{DIC}$ data are available, but more recent spatio-temporal data from the same study area can be used for a comparison (see Chapter 4).

As a second approach, we described a simple two-end mixing model (see Appendix for details) to estimate the relative contribution of phytoplankton and mangrove (or other terrestrial) detritus to the POC pool based on the POC/PN ratio of the suspended matter, and hence, to derive an estimate for the $\delta^{13}C$ of the phytoplanktkon component assuming a constant and known $\delta^{13}C$ for the terrestrial/mangrove fraction and assigning a constant C/N ratio to local primary production and mangrove/terrestrial detritus. Although evidently, such a simplified model has severe limitations and should not be used to derive absolute phytoplankton $\delta^{13}C$ values to be used in e.g. mixing models, this approach was shown to result in a very plausible spatio-temporal pattern of phytoplankton $\delta^{13}C$.

First, when comparing the estimated seasonal $\delta^{13}C_{PHYTO}$ pattern with monthly rainfall distribution (Figure 8), it can be seen that a decrease in the estimated phytoplankton $\delta^{13}C$ values occurs after, or during, the two peaks of heavy rainfall (May 1995 and

October 1995). Discharge rates usually show a fairly similar pattern (albeit usually with a monomodal peak - unfortunately discharge data are not available for the studied period) but peaks of discharge may come slightly earlier than rainfall peaks in the study area, as the large Godavari drainage area includes more western regions where the monsoon period preceeds the rainfall along the east coast. Thus, we hypothesize that the phytoplankton $\delta^{13}C$ in our study area may be more strongly depleted by the input of terrestrial organic matter during periods of heavy rainfall or discharge, as the microbial respiration of this material will result in an depletion of the DIC pool in ^{13}C, thus causing phytoplankton to exhibit lower $\delta^{13}C$ values. When discharge is low or absent, only local mangrove carbon entering the tidal creeks (as POC, DOC, or DIC) can be held responsible for the decreased $\delta^{13}C_{DIC}$ values relative to the marine environment (see also Chapter 4).

Secondly, seasonal variations in $\delta^{13}C_{PHYTO}$ were larger in each of the three regions than the $\delta^{13}C_{POC}$ variations, and show a better correspondence with zooplankton $\delta^{13}C$ data (an example is given in Figure 9, using the data on samples collected at station K_2). The fact that zooplankton and estimated phytoplankton $\delta^{13}C$ data do not entirely match does not necessarily imply that the method is not producing reliable results, since other effects such as the degree of selectivity and the turnover time will influence the zooplankton $\delta^{13}C$.

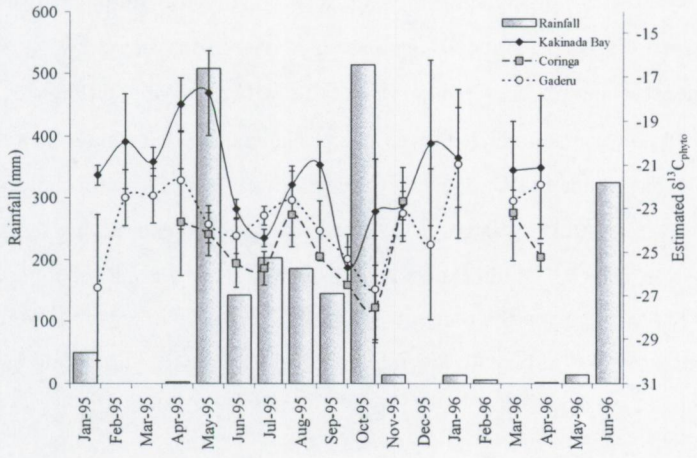


Figure 8 : Rainfall pattern (bars) and estimated seasonal variations of the stable carbon isotope composition ($\delta^{13}C$) of phytoplankton in Kakinada Bay (diamonds), Gaderu (circles), and Coringa (squares). Error bars indicate ± 1 s.d.

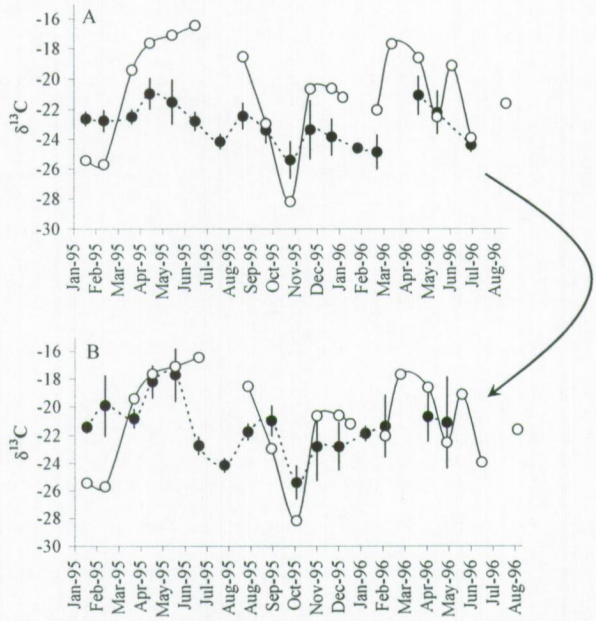


Figure 9 : (A) $\delta^{13}C$ of POC (full circles) in Kakinada Bay and zooplankton (open circles) at station K_2, and (B) $\delta^{13}C$ of zooplankton at station K_2 (open circles) and estimated $\delta^{13}C$ of phytoplankton in Kakinada Bay (full circles). Error bars indicate ± 1 s.d.

Overall, the results of the proposed simple two-source mixing model were largely confirmed by later analysis of $\delta^{13}C_{DIC}$, i.e. (1) the suspected seasonal pattern in $\delta^{13}C_{DIC}$ was also largely confirmed, i.e. lower $\delta^{13}C$ values during and shortly after the monsoon discharge, gradually increasing to overall maximun $\delta^{13}C_{DIC}$ values during premonsoon period (see Chapter 4), and (2) the larger spatial differences in $\delta^{13}C_{DIC}$ as in $\delta^{13}C_{POC}$ were as predicted (even though the magnitude is larger than expected). As for the magnitude of the spatial $\delta^{13}C$ trend, however, $\delta^{13}C_{DIC}$ data show a significantly larger variation than was predicted by our simple two-end mixing model, e.g. based on $\delta^{13}C_{DIC}$ data we would expect phytoplankton to show a shift of approximately 7 ‰ between Coringa and the northern Kakinada Bay (i.e. similar to the observed shift in zooplankton and in benthic invertebrates, see Chapter 6), but the mixing model only accounts for a 4.5 ‰ shift.

ZOOPLANKTON $\delta^{15}N$ VARIABILITY

Zooplankton $\delta^{15}N$ values exhibited much less seasonal variation compared to the $\delta^{13}C_{ZP}$ variations (Table 3). Although the few data appear to suggest that Coringa zooplankton had lower $\delta^{15}N$ values (+ 4.8 and + 5.2 ‰, n=2) than did zooplankton at the three other stations (which showed relatively similar average $\delta^{15}N$ values of 7.5 ‰ at G_3, 7.9 ‰ at K_2, and 8.4 ‰ at G_6), $\delta^{15}N$ values of zooplankton collected in 1996/1997 did not differ between Coringa (6.3 ± 1.9 ‰) and several side creeks of Gaderu (6.0 ± 1.4 ‰ and 6.4 ± 1.3 ‰, A.V.V.S. Rao, unpublished data). Due to the small amount of $\delta^{15}N$ data, it is difficult to detect any clear seasonal trend in zooplankton $\delta^{15}N$ in our dataset. For zooplankton collected in 1996/1997 (A.V.V.S. Rao, unpublished data), however, an apparent decrease in $\delta^{15}N$ values is noted when freshwater conditions set in at the start of the monsoon period, although the pattern is not as clear as for $\delta^{13}C$. As no concurrent nutrient data for Rao's sampling locations are available, it is currently impossible to relate the observed $\delta^{15}N$ variations to specific processes. It is well known that marine invertebrates, including zooplankton, are usually more ^{15}N-enriched than freshwater invertebrates (e.g. France 1994) and this has been ascribed to the ^{15}N-enriched inorganic N-pool that remains due to selective uptake of ^{14}N by phytoplankton (e.g. Altabet & Francois 1994) or when intense bacterial N processing takes place (nitrification, denitrification, e.g. Mariotti et al. 1984, Montoya et al. 1990). Thus, if inorganic N nutrients are imported into the ecosystem during monsoon discharge, we may expect a gradual enrichment of the DIN pool in ^{15}N towards the pre-monsoon period, and a parallel increase in consumer $\delta^{15}N$ values. Benthic invertebrates (Chapter 6) and fish (own unprocessed data, see Chapter 10 for a brief discussion) also show a clear enrichment in ^{15}N between the mangrove areas and Kakinada Bay of about 2 -3 ‰, and we hypothesize that differences in DIN sources and availability, and processing by microbial and plankton communities are the main determinants for the $\delta^{15}N$ variations observed in zooplankton. However, as no concurrent nutrient and zooplankton $\delta^{15}N$ data are available, it is impossible to confirm such coinciding trends.

CONCLUDING REMARKS

The data presented in this study clearly demonstrate that zooplankton communities in mangrove ecosystems may be sustained predominantly by local aquatic primary production, and that mangrove or other terrestrial carbon sources may be quantitatively less important. Major questions remain unresolved, however :

(1) A quantitative estimate of the importance of both sources is difficult to make, however, and it is not clear to which extent seasonal and spatial variations in the selectivity occur. Even when the phytoplankton component would be better characterized isotopically, the relatively small difference in $\delta^{13}C$ between phytoplankton in the mangrove creeks and terrestrial sources might preclude an accurate estimate of their relative importance. Results of $\delta^{13}C_{DIC}$ and $\delta^{13}C$ and $\delta^{15}N$ data of size-fractionated suspended matter and zooplankton from a more elaborate sampling effort (2000-2001, samples await analysis) will hopefully provide some more detailed insights in this.

(2) Secondly, the role of heterotrophic bacteria as trophic intermediates is unknown, as our data only demonstrate that local autotrophs are at the *basis* of the foodweb sustaining zooplankton. One possible approach of answering such a complex question is the use of *in situ* enrichment experiments with ^{13}C-labeled compounds to label either autotrophs or heterotrophs (similar to the approach of Wylie & Currie (1991) with ^{14}C) and to trace the distribution of the label in zooplankton.

(3) Thirdly, the general mechanisms underlying the selectivity are not known : is it the result of merely size-selective feeding (e.g. particles of a different size have a different composition, see e.g. Chapter 6), or is there active particle selection and/or rejection ?

(4) Finally, detailed studies in other (estuarine and non-estuarine) mangrove ecosystems would be required in order to determine the extent to which our results can be generalized.

APPENDIX : ESTIMATION OF PHYTOPLANKTON $\delta^{13}C$ VALUES BASED ON POC/PN AND $\delta^{13}C_{POC}$ DATA (See Bouillon & Dehairs (2000) for a more detailed discussion)

The first step comprises the estimation of the contribution of phytoplankton to the POC pool. This was done using the measured POC/PN ratios of the suspended matter samples, and assuming constant values for the C and N content of phytoplankton and terrestrial organic matter, according to the following non-linear equation (1) :

$$X_{phyto} = \frac{C_{terr} - CN_{POC} * N_{terr}}{CN_{POC} * N_{phyto} - CN_{POC} * N_{terr} + C_{terr} - C_{phyto}}$$

Where :
X_{phyto} = fraction of phytoplankton in the suspended matter sample ($0 \leq X_{phyto} \leq 1$)
CN_{POC} = the measured POC/PN ratio of the suspended matter sample
C_{terr} , N_{terr} = the C and N content of the terrestrial end-member [g/ g dry weight]
C_{phyto}, N_{phyto} = the C and N content of the phytoplankton component [g / g dry weight]

We used the following values for the transformation of our dataset : $C_{terr} = C_{phyto} =$ 0.45 g/g dry weight ; $N_{terr} = 0.018$ g/g dry weight; and $N_{phyto} = 0.068$ g/g dry weight so that C/N ratios of terrestrial organic matter and phytoplankton were 25 and 6.6 (Redfield et al. 1963), respectively. A value of 25 for the C /N ratio of terrestrial/mangrove detritus was chosen as this is intermediate between the values suggested by Cifuentes et al. (1996) for terrestrial organic matter in a mangrove estuary and those reported for degraded mangrove leaves (see Dehairs et al. 2000 and references therein).

When the measured POC/PN ratio of suspended matter was smaller than the proposed value of 6.6 for phytoplankton (this occurred in 19 out of 195 samples), X_{phyto} was assigned a value of 1, and when the measured CN_{POC} was larger than the proposed value of 25 for terrestrial detritus (this occurred in 6 out of 195 samples), X_{phyto} was assigned a value of 0.
Once the phytoplankton fraction had been estimated and was found to be > 0, the carbon isotopic composition of this component was calculated as (equation (2)) :

$$\delta^{13}C_{phyto} = \frac{\delta^{13}C_{POC} - (1 - X_{phyto}) * \delta^{13}C_{terr}}{X_{phyto}}$$

Where $\delta^{13}C_{phyto}$ = the carbon isotopic composition of phytoplankton [‰]
$\delta^{13}C_{POC}$ = the measured carbon isotopic composition of the POC [‰]
$\delta^{13}C_{terr}$ = the carbon isotopic composition of terrestrial organic matter [‰]

Note that when $X_{phyto} = 1$, the measured $\delta^{13}C_{SPOM}$ becomes the estimate for $\delta^{13}C_{phyto}$. A value of –26.5 ‰ was used for $\delta^{13}C_{terr}$, within the range of $\delta^{13}C$ values of terrestrial C3 vegetation and close to the average $\delta^{13}C$ of suspended matter with high POC/PN ratios (> 20, n = 10) in the study area (see higher).

CHAPTER 6 : Do mangroves provide carbon to subtidal benthic invertebrates in an estuarine mangrove ecosystem ? A case study in Andhra Pradesh, India.

Foreword

The question whether mangrove primary production -once exported to the adjacent aquatic environment- sustains benthic and pelagic faunal communities has long been an issue of debate in the literature. This dependancy, however, is often quoted in the scientific literature and is frequently used as a strong argument for the conservation of mangrove forests. In this chapter, we discuss the results of stable isotope analyses conducted on samples of various biological components collected during the pre-monsoon and post-monsoon period in the mangrove ecosystem located in the Gautami Godavari estuary (Andhra Pradesh, India) in order to gain insight into trophic dependancies of the benthic invertebrate fauna.

This chapter is based to a certain extent on the following publication, to which the data from the post-monsoon season of 1999 have been added, and which has been updated with more recent literature :

Bouillon S, Raman AV, Dauby P, & Dehairs F (2002) Carbon and nitrogen stable isotope ratios of subtidal benthic invertebrates in an estuarine mangrove ecosystem (Andhra Pradesh, India). Estuar Coast Shelf Sci 54 : 901-913.

Abstract

In order to assess the relative trophic importance of mangrove litterfall and aquatic primary production in the mangrove creeks of the Coringa Wildlife Sanctuary (Andhra Pradesh, India) and the adjacent semi-enclosed Kakinada Bay, carbon and nitrogen stable isotope ratios were determined in a variety of benthic invertebrate species collected at 22 sites during the pre-monsoon period (May-June) of 1997 and 1999, and at 8 sites during the post-monsoon period of 1999. During both seasons, $\delta^{13}C$ values showed little interspecific variation at any given location. During the pre-monsoon season, there was a distinct spatial gradient in consumer $\delta^{13}C$ values of about 7 ‰, with more depleted values in the mangrove creeks (-23.6 ± 0.6 ‰), and gradually increasing in the mangrove outlets (-21.5 ± 0.9 ‰), a relatively restricted zone in the south-eastern part of Kakinada Bay adjacent to the mangroves (-18.8 ± 0.8 ‰), and the central and northern part of the Bay (-16.7 ± 1.4 ‰) which opens into the Bay of Bengal. During the post-monsoon period, this spatial gradient was even more pronounced (spanning ~ 9 ‰), but $\delta^{13}C$ values of consumers were generally lower by 1-3 ‰ than during pre-monsoon. These gradients are much larger than those observed in bulk suspended organic matter (maximum about 2.7 ‰) and in sediment organic matter (about 1.5 - 2.5 ‰). The observed $\delta^{13}C$ signatures therefore suggest a marked selectivity of the benthic invertebrate community for pelagic and benthic microalgal food sources and indicate that mangrove-derived and other terrestrial carbon is not a significant food source for benthic invertebrate communities in this ecosystem during both pre- and post-monsoon season. Furthermore, $\delta^{13}C$ values of sediment organic matter (SOM) suggest that terrestrial carbon is not a major contributor to the SOM-pool in this ecosystem. Evidence for seaward migration of penaeid prawns during pre-monsoon was provided by some individuals caught in the North Bay which displayed low $\delta^{13}C$ values characteristic of fauna found in the mangrove creeks or outlets. $\delta^{15}N$ values were found to be a useful indicator of trophic level, even though there remained some overlap between $\delta^{15}N$ of presumed low and higher trophic levels. Benthic invertebrates showed a $\delta^{15}N$ gradient of about 3.2 ‰ between the mangrove creeks and the Central and North Bay whereas sediments showed a smaller spatial gradient of about 1.6 ‰, which is hypothesized to reflect differences in inorganic nitrogen sources and availability.

Introduction

The degree of 'outwelling' of mangrove carbon to adjacent aquatic environments depends to a large degree on the geomorphology and tidal characteristics of the ecosystem (Lee 1995, 1999a). If mangrove-derived material is exported to the aquatic environment, either as dissolved or particulate organic carbon, the question arises whether it forms a substantial contribution in sustaining the pelagic and benthic foodwebs, and to what geographical extent (Robertson et al. 1992). The possibly limited importance of mangrove detritus in sustaining nearshore communities has previously been suggested based on mass-balance restrictions (e.g. Li & Lee 1998). Wafar et al. (1997), for instance, compared the phytoplankton productivity in a western Indian mangrove estuary with the potential contribution of mangrove carbon, and concluded that mangrove production is mainly important for the microbial food web, but not for the particulate. Daniel & Robertson (1990) found a positive correlation between the amount of mangrove macrodetritus and epibenthos biomass and density in an Australian mangrove estuary, but stressed that different factors such as reduction of predation, increased food availability and increased living space, may explain this pattern. In contrast, Lee (1999b) found no positive effect of mangrove detritus enrichment on benthic faunal biomass and even found a decrease in species diversity.

Stable isotope analysis offers one of the possible approaches to study the incorporation of different carbon sources into foodwebs on the condition that there is a sufficiently large difference in the isotopic composition of the different primary carbon sources (terrestrial material, phytoplankton, benthic microalgae), and this method has been used to study benthic foodwebs in a variety of ecosystems (e.g. Dauby 1990, Riera et al. 1999, Yoshii et al. 1999, Lepoint et al. 2000). Several stable isotope studies (e.g. Rodelli et al. 1984, Newell et al. 1995, Loneragan et al. 1997, Marguillier et al. 1997, Dehairs et al. 2000, Bouillon et al. 2000, Lee 2000, Bouillon et al. 2002a, Chong et al. 2001) have recently been carried out in mangrove ecosystems and have substantially increased the knowledge on mangrove foodwebs since the publication of the work of Odum & Heald (1975). The general conclusion resulting from many of these studies concerning the benthic communities in the aquatic environment adjacent to mangrove forests is that mangrove carbon is only used in a very restricted zone in and near mangrove forests but that its role is rapidly

taken over by phytoplankton, even though mangrove detritus was present in suspended and sediment organic matter (Rodelli et al. 1984, Zieman et al. 1984, Fleming et al. 1990, Chong et al. 2001). One major drawback of the latter studies is that their conclusions were based on the distribution of $\delta^{13}C$ values in invertebrates when compared to the $\delta^{13}C$ of mangrove leaves and typical marine phytoplankton, but did not take into account the possibility of ^{13}C-depleted phytoplankton in the mangrove creeks and near-mangrove aquatic environment. A ^{13}C-depleted dissolved inorganic carbon (DIC) pool is characteristic of many estuarine and freshwater environments (e.g. Mook & Tan 1991, Chanton & Lewis 1999, Hellings et al. 1999), and significant spatial trends in the isotopic composition of the DIC pool are known to occur in mangrove environments as well, as evidenced by direct $\delta^{13}C_{DIC}$ measurements (e.g. Dehairs et al. 2000, Bouillon et al. 2000, see data presented in Chapter 4, and S. Marguillier unpublished data) and by the spatial distribution in seagrass $\delta^{13}C$ values (Lin et al. 1991, Hemminga et al. 1994, France & Holmquist 1997, Marguillier et al. 1997). As this DIC becomes incorporated by phytoplankton and other local aquatic primary producers, the use of a typical 'marine' $\delta^{13}C$ reference value for phytoplankton becomes inappropriate and will result in a significant overestimation of the importance of mangrove detritus. This mechanism can even cause an overlap in the $\delta^{13}C$ signal of these two sources and could make the interpretation of consumer stable isotope data problematic if not carefully considered. Even though the hypothesis that mangrove litter sustains or contributes to aquatic secondary production is often quoted as one of the arguments for the conservation of these ecosystems, there is as yet little or no unambiguous evidence that such a dependency exists, as results from some studies may need to be interpreted cautiously. On the other hand, results obtained in one site cannot simply be generalized due to the large environmental variability found in mangrove ecosystems and their carbon dynamics (e.g. see Dittmar & Lara 2001, Bouillon et al. in review i.e. Chapter 7).

In this study, we analysed carbon and nitrogen stable isotope ratios of subtidal benthic invertebrates and sediments at a wide variety of locations in an estuarine mangrove ecosystem in Andhra Pradesh (India) and used baseline information of primary producer stable isotope ratios from previous studies in this area (Dehairs et al. 2000; Bouillon et al. 2000; Bouillon et al. 2002a), in an effort to determine whether mangrove carbon was assimilated by benthic fauna in different zones of this

ecosystem. As this estuary is strongly monsoon-influenced, we also wanted to assess whether we could find evidence for seasonal differences in the relative importance of different carbon sources. Finally, we wanted to assess whether the spatial trend in $\delta^{15}N$ values reported earlier (Dehairs et al. 2000) would be confirmed and could be related to sewage inputs (e.g. McKinney et al. 1999, Risk & Erdmann 2000), or to other processes.

Study area

The sampling sites (Fig 1, 2, 3) are located the area between Kakinada Bay and the Gautami branch of the Godavari, the second largest river in India, and are located in the Southeastern state of Andhra Pradesh (between 82°15' and 82°22' E, 16°43' and 17°00' N). The Godavari has a mean annual discharge of 11.1 x 10^{14} l, of which 93-96 % occurs during the wet monsoon season, and is listed as one of the largest POC (particulate organic carbon) transporting rivers in the world (Gupta et al. 1997). The Gautami Godavari opens into the Bay of Bengal, but has several branches into Kakinada Bay, the largest and most important being Coringa (total length of 26 km) and Gaderu (total length of 11 km). The area between the river and Bay is dominated by extensive mangrove forests and tidal mudflats. The shallow Kakinada Bay (depth ranging from 3 to 8 meters at high tide) which covers approximately 150 km^2, opens into the Bay of Bengal on its northern side, and is bordered along most of its eastern length by a narrow sand bar (Fig 1). Tides are semidiurnal, and tidal amplitude in the Bay is around 0.5 to 2 meters. Monsoon rainfall in the area usually occurs between July and September, and causes near-freshwater conditions in the southern part of the study area during this period. Estuarine conditions re-establish thereafter, and aquatic primary production increases towards the pre-monsoon period (April-June), during which turbidity reaches its lowest values in the entire region.

Benthic fauna in this area has witnessed a significant decrease in species diversity over the last 50 years (Deepti 1997), presumably due to the increased human pressure in Kakinada, a large city which currently hosts about 500,000 inhabitants and is located on the western shore of Kakinada Bay. The Bay and creeks are important fishing areas and in addition, molluscs are harvested on a large scale for lime production.

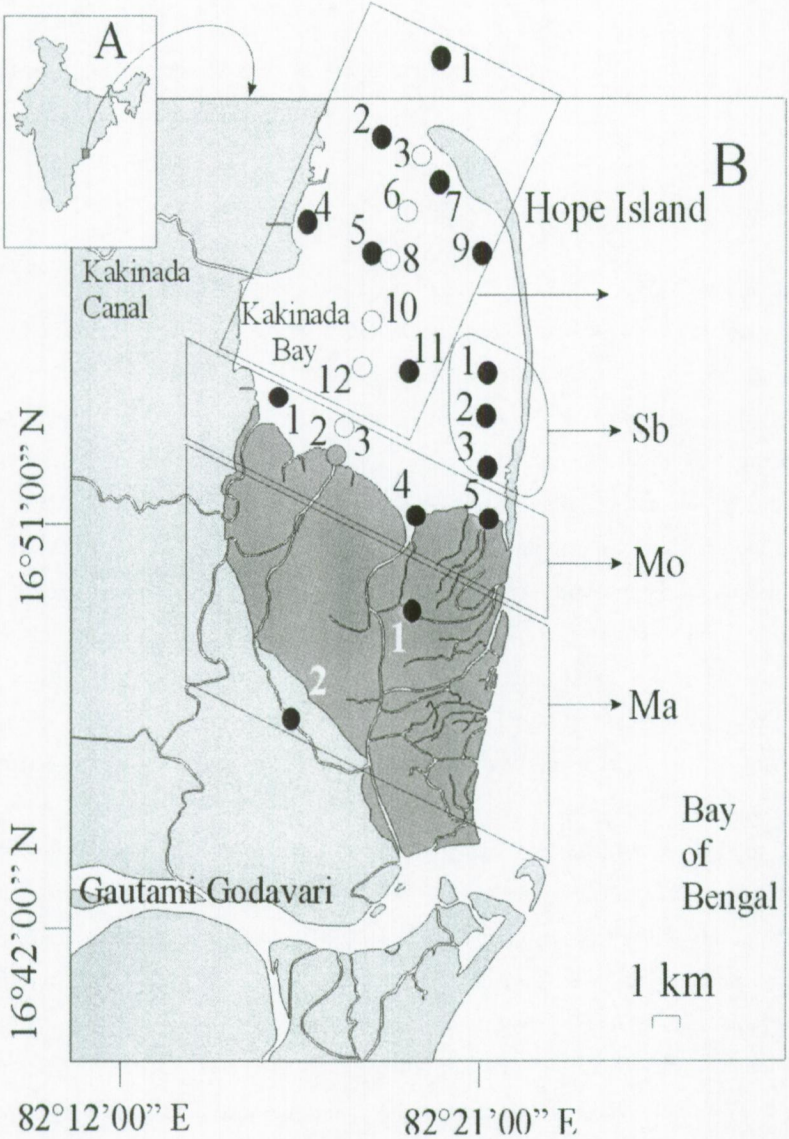


Figure 1 : Location of the study area and sampling locations for benthic fauna during the pre-monsoon surveys. Darkest areas indicate mangrove-covered regions. **Ma** : mangrove creek stations, **Mo** : mangrove creek outlet stations, **SEb** : South-east Bay stations, **CNb** : Central and North Bay stations. Open circles indicate sampling locations of the June 1997 survey, black circles the May-June 1999 sampling location. Station Mo2 (in grey) was sampled during both surveys.

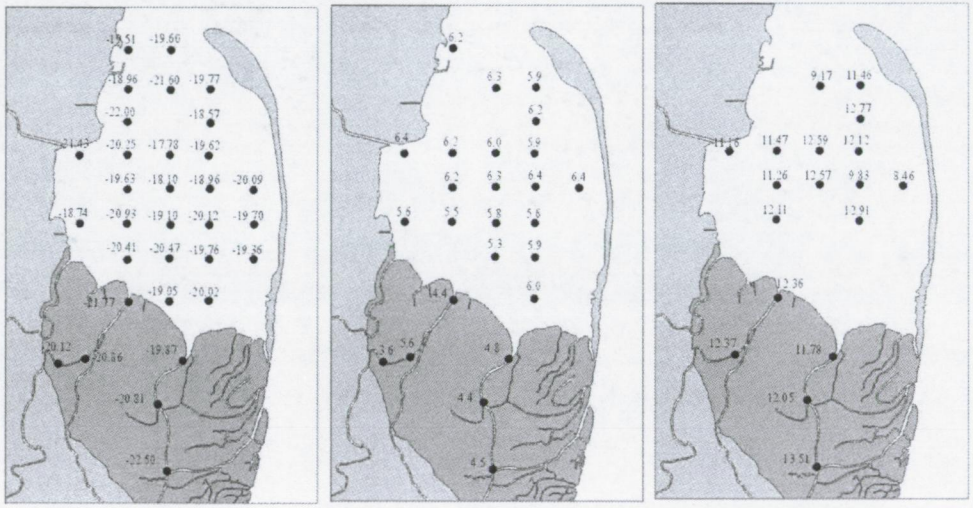


Figure 2 : Spatial distribution of (A) $\delta^{13}C$ values, (B) $\delta^{15}N$ values, and (C) elemental ratios of organic matter in sediments of the Coringa-Kakinada estuarine ecosystem during July 1995.

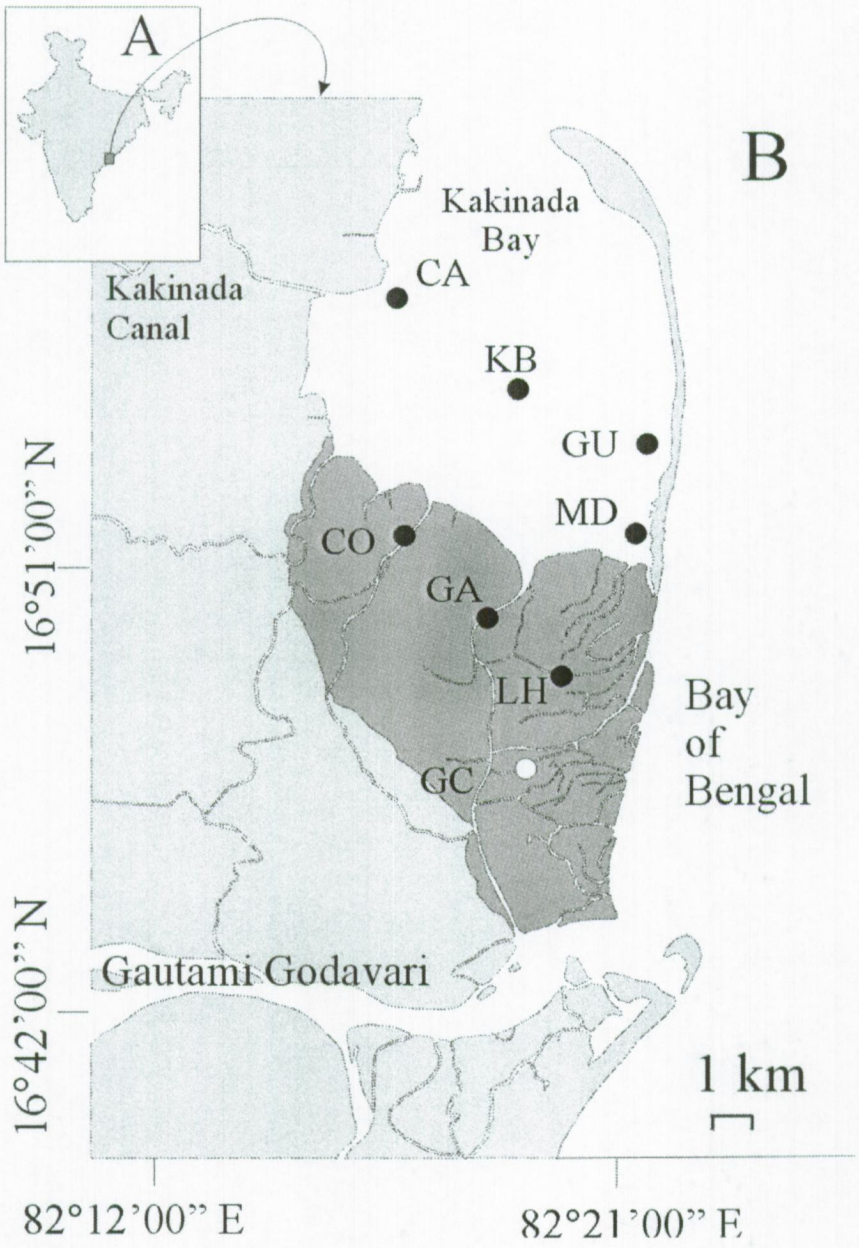


Figure 3 : Sampling locations for benthic fauna, size-fractionated POC, sediments and DIC during for post-monsoon period (December 1999).

Materials and methods

SAMPLE COLLECTION AND PREPARATION

Benthos samples representing the pre-monsoon period were taken along a linear transect from the mouth of Coringa Creek to the tip of Hope Island in the northern part of Kakinada Bay in June 1997 (open circles on Figure 1), and a variety of other sites were sampled in May-June 1999 (full circles) by the Marine Biology Department (Andhra University). Sediment samples were taken during surveys in July 1995 throughout the area (see Figure 2), and at eight other stations (Figure 3) during the post-monsoon (December 1999). The latter stations were concurrently sampled for invertebrates, dissolved inorganic carbon (DIC), and different size-fractions of suspended matter. Benthic fauna and sediments were collected using a dredge and Van Veen grab, and were kept in a cool box on board. DIC was collected by gently overfilling a glass bottle with surface water, poisoning with a saturated $HgCl_2$ solution, and gas tight capping with an rubber cap and aluminium plug. Different size fractions of suspended matter were collected as described elsewhere (Chapter 3). After transportation to the field laboratory, all faunal samples were washed and dried at 60 °C for at least 24 hours. Samples were later ground to a fine powder, and subsamples for $\delta^{13}C$ analysis were either washed with dilute HCl (fauna, sediments, some suspended matter size fractions) or kept in acid fumes (filters) to remove possible carbonates, and were redried. Subsamples for $\delta^{15}N$ analysis did not receive this treatment as this has been reported to affect $\delta^{15}N$ values (Goering et al. 1990, Bunn et al. 1995, Pinnegar & Polunin 1999).

MEASUREMENT OF STABLE ISOTOPE AND ELEMENTAL RATIOS

Samples for stable isotope analysis were combusted in a Carlo Erba NA-1500 Elemental Analyser and the resulting gases (CO_2 and N_2) were cryogenically separated with a manual extraction line. DIC was extracted from water samples (5 ml) by acidification in a vacuum line, and cryopurification of the resulting CO_2 (see chapter 3 for details). Stable isotope ratios were then determined on a Delta E Finnigan Mat isotope ratio mass spectrometer and are expressed relative to the

conventional standards, i.e. PDB limestone for carbon (Coplen 1996) and atmospheric N_2 for nitrogen (Mariotti 1983) as δ values, defined as :

$$\delta X = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] \times 10^3 \qquad [‰]$$

where X = ^{13}C or ^{15}N, and R = $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The normal working standard for carbon was CO_2 produced from Carrara marble, and high-purity tank N_2 was used as the working standard for nitrogen. Internal reference materials used were ammonium sulphate (IAEA-N1, IAEA-N2) and ammonium nitrate (IAEA-NO3) for $\delta^{15}N$, and sucrose (IAEA-C6) and polyethylene (IAEA-CH-7) for $\delta^{13}C$. Standard deviations on ten aliquots of the same sample were lower than 0.2 ‰ for both $\delta^{13}C$ and $\delta^{15}N$. Nitrogen stable isotope ratios of sediments were determined with a continuous-flow IRMS system (Micromass Optima coupled to a Carlo Erba CNS Analyser) with an analytical precision of ± 0.2 ‰ for $\delta^{15}N$. Elemental (C, N) analysis of sediment organic matter was performed by combusting pre-weighed and HCl-treated sediment samples in a Carlo Erba NA-1500 Elemental Analyser, similar to the method described by Nieuwenhuize et al. (1994).

Results

SEDIMENTS

Sediment organic matter during the 1995 survey had overall $\delta^{13}C$ values between -24.2 and -17.8 ‰, with overall averages of -21.3 ± 1.0 ‰ (n=5, mangrove creeks), -20.2 ± 1.1 ‰ (n=4, mangrove outlets), -19.7 ± 0.4 ‰ (n=3, South-east Bay) and -19.7 ± 1.2 ‰ (n=19, Central and North Bay) (Figure 2 A). In the Bay, however, the three most depleted values (all < -21 ‰) were observed near the outfall of Kakinada Canal draining the sewage systems of Kakinada town, and in a northeastern direction from that point (Figure 2 A). $\delta^{13}C$ values of sediments collected during post-monsoon (range : -23.1 to -21.4 ‰ in mangrove creeks, (-23.0 to -20.8 ‰ in the Bay locations) confirmed this pattern of limited spatial variability (see Table 1). $\delta^{15}N$ values of sediments (1995 survey only, Figure 2 B) also showed a spatial gradient, with

relatively low values in the mangrove creeks (+ 4.4 ± 0.8 ‰, n = 4), but higher values in the mangrove outlets (+ 5.1 ± 0.8 ‰, n = 3), South-east Bay (+ 6.4 ‰, n = 1) and the rest of the Bay (+ 6.0 ± 0.3 ‰, n = 16). Organic carbon content of all samples was relatively low (0.40 – 1.42 % dry weight), and C/N ratios varied between 8.5 and 13.5 with no apparent differences between regions, although some Bay stations showed remarkably low values (8.5, 9.2, 9.8) compared to other Bay stations (average 12.0 ± 0.7, n = 10, Figure 2 C).

SUSPENDED ORGANIC MATTER (SPOM)

$\delta^{13}C$ values for bulk suspended matter (i.e. total SPOM, Figure 7A) were taken from Dehairs et al. (2000) and Bouillon et al. (2000, i.e. Chapter 5). During the post-monsoon survey, concurrent samples of different size fractions of suspended matter were collected. $\delta^{13}C$ values for these different size fractions of SPOM ranged overall between -29.2 and -19.5 ‰, and significant differences were found between different size fractions (Table 1, Figure 5), but not between locations (single-factor ANOVA). Whereas the total SPOM and the < 10 µm fraction were relatively depleted in ^{13}C in all sampling locations with similar and fairly uniform $\delta^{13}C$ values between of -27.5 ± 1.2 ‰ and -27.3 ± 1.2 ‰, respectively, the intermediate fractions (10 << 50 µm and 50 << 118 µm) were spatially more variable with generally more depleted values in the mangrove creeks (Figures 4 and 5, Table 1). In general, $\delta^{13}C$ values increased markedly from the < 10 µm fraction over the 10 << 50 µm fraction to the 50 << 118 µm fraction for samples from the Bay region, but this trend was much less pronounced in the creek locations (Figure 5). POC/PN ratios of suspended matter were generally low (range : 4.5 to 9.4), being most variable in the 50<<118 µm fraction (Figure 4). POC/PN ratios (Table 2) of total suspended matter (6.6 ± 0.6) were significantly lower than those of the < 10 µm fraction (7.9 ± 0.8) and the 10 << 50 µm fraction (8.1 ± 0.5), but no significant between-site differences were detected. Whereas $\delta^{13}C$ values indicated similarities between the < 10 µm and total SPOM fractions and between the 10<<50 and 50 << 118 µm fractions, POC/PN ratios were similar in the < 10 µm and 10 <<50 µm fractions and in the 50<<118 µm and total SPOM fractions (single factor ANOVA). Note that our data (in particular those from the mangrove creeks) suggest that an additional fraction should be taken into account

in order to explain the POC/PN ratios of the total suspended matter pool as a combination of the three fractions mentioned (see Figure 4 and Table 2), i.e. our data suggest the existence of a relatively ^{13}C-depleted fraction with low a POC/PN ratio.

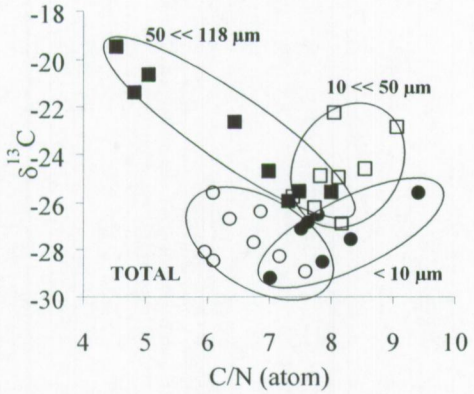


Figure 4 : Elemental composition (C/N, atom) *versus* $\delta^{13}C$ of total and size-fractionated suspended organic matter. Open circles : total SPOM, open squares : 10 << 50 µm, black circles : < 10 µm, and black squares : 50 << 118 µm. Note that the ellipses merely serve to group data of the same size class.

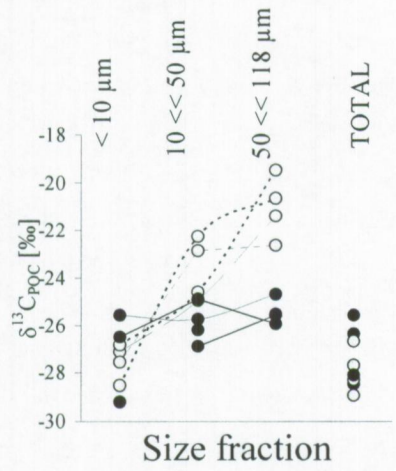


Figure 5 : $\delta^{13}C$ differences between SPOM size classes. white symbols : bay locations (MD, GU, KB, and CA), black symbols : mangrove creek locations (LH, GA, CO, and GC).

Table 1 : Carbon stable isotope composition ($\delta^{13}C$, in ‰) of different size-fractions of suspended matter and sediments from 8 locations within the Coringa – Kakinada Bay system in December 1999. n.d. : not determined.

	MANGROVE CREEKS				BAY LOCATIONS			
	LH	CO	GA	GC	MD	GU	KB	CA
SUSPENDED ORGANIC MATTER SIZE FRACTIONS								
< 10 µm	-26.5	-25.6	-29.2	n.d.	-27.6	-28.5	-26.8	-27.1
10 << 50 µm	-24.9	-25.7	-26.2	-26.9	-22.9	-22.3	-24.6	-24.9
50 << 118 µm	-25.9	-24.7	-25.5	-25.6	-22.6	-20.6	-19.5	-21.4
Total	-28.1	-25.6	-26.4	-28.5	-26.7	-28.9	-28.3	-27.7
SEDIMENTS								
Total	-21.4	-23.1	-22.5	n.d.	-23.3	-21.4	-20.8	-21.5

Table 2 : Elemental ratios (C/N, atom) of different size-fractions of suspended matter at 8 locations within the Coringa – Kakinada Bay system in December 1999. n.d. : not determined.

Fraction	MANGROVE CREEKS				BAY LOCATIONS			
⇓	LH	CO	GA	GC	MD	GU	KB	CA
< 10 µm	7.8	9.4	7.0	n.d.	8.3	7.9	7.6	7.5
10 << 50 µm	7.8	7.4	7.7	8.2	9.1	8.1	8.6	8.1
50 << 118 µm	7.3	7.0	7.5	8.0	6.4	5.1	4.5	4.8
Total	6.0	6.1	6.9	6.1	6.4	7.6	7.2	6.7

DIC

$\delta^{13}C$ values of the DIC pool (December 1999) varied between -10.6 and -2.6 ‰, with significantly lower values (-10.6 to -8.9 ‰) in the mangrove creeks compared to those in the Bay region (-4.3 to -2.6 ‰). There was, however, no clear relationship between $\delta^{13}C_{DIC}$ and salinity (Figure 6).

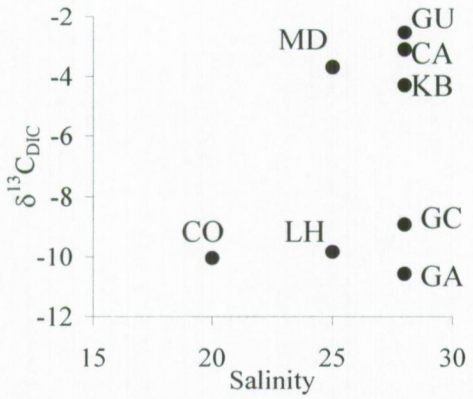


Figure 6 : Relationship between salinity (in ppt) and the carbon stable isotope composition of the dissolved inorganic carbon pool ($\delta^{13}C_{DIC}$, in ‰). Sampling locations as in Figure 3.

BENTHIC INVERTEBRATES

Pre-monsoon period

Overall, $\delta^{13}C$ values of benthic invertebrates (see Appendix I) ranged between -24.7 ‰ (for an individual of the bivalve *Tellina* sp.1 at Ma 2) and -13.2 ‰ (for an individual of the crab *Typhlocarcinus* sp. at CNb 2), while $\delta^{15}N$ values ranged from + 4.1 ‰ (for *Tellina* sp. 2 at CNb 4) to + 14.5 ‰ (for a *Metapenaeus monoceras* at CNb 1).

Stable carbon isotope ratios for different species sampled at a particular location were usually quite consistent and, with only three (*ex* 22) exceptions, showed a range of less than 4 ‰. Thus, average $\delta^{13}C$ values of all invertebrates at a given location were calculated and were found to be similar in spatially adjacent locations, allowing us to distinguish different zones on the basis of invertebrate $\delta^{13}C$ values (Table 3). Stations were thus characterised as Mangrove creek locations (Ma, average $\delta^{13}C$ values around -23.5 ‰), Mangrove outlets (Mo, average $\delta^{13}C$ values around -21.5 ‰), South-east Bay stations (SEb, average $\delta^{13}C$ values around -18.5 ‰), and Central and North Bay stations (CNb, average $\delta^{13}C$ values around -16.5 ‰). Stations for which only one or two data were available (i.e. Mo5, CNb7, CNb9) were included in the group most adjacent to them geographically. In general, there appears to be a shift in benthic invertebrate $\delta^{13}C$ values of about 7 ‰ between the mangrove creeks and the North & Central Bay regions (Figure 7 C). Two penaeid prawns caught in the North Bay,

however, were very depleted in ^{13}C ($\delta^{13}C$ = -22.7 and -21.5 ‰, see Fig 7 C) relative to other invertebrates from this zone, and their carbon isotopic signature was similar to that of organisms found in the mangrove creeks or outlets. Their $\delta^{13}C$ data were consequently not used in calculations of station-averaged $\delta^{13}C$ values (see above).

Species were classified as 'lower' or 'higher' trophic level species when data on their trophic status were available. Thus, all bivalves, the gastropod *Cerithidea cingulata*, the brachiopod *Lingula* sp., and the deposit-feeding crabs *Dorippe facchino*, *Macrophthalmus* sp., and *Typhlocarcinus* sp. were initially grouped as low trophic level species, and all penaeid prawns, the predatory or scavenging gastropods *Babylonia spirata*, *Volema cochlidium*, *Murex trapa*, *Thais lacera*, and *Nassarius* spp., the crabs *Leucosia* sp., *Charybdis* sp., *Portunus sanguinolentus*, and *Phylira* sp., and the polychaete *Diopatra neapolitana* were considered to occupy higher trophic levels. The bivalves *Meretrix meretrix* and *Pinctada radiata,* however, were then re-classsified as 'unknown' trophic level species based on their intermediate $\delta^{15}N$ values (see discussion). All other species were considered to occupy an unknown trophic level. According to this classification, it appeared that higher trophic levels showed, on average, higher $\delta^{15}N$ values (by 2.1 to 3.8 ‰), and that there was also a marked spatial $\delta^{15}N$ gradient between the mangrove creeks and the Central and North Bay of about 3.2 ‰ which could be observed in both lower and higher trophic levels (Figure 7 C).

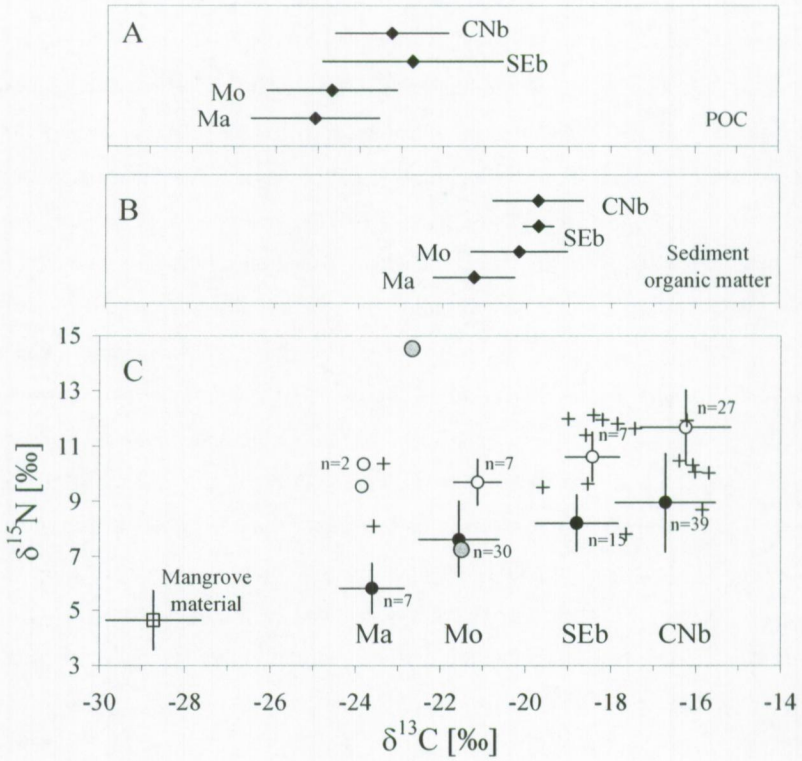


Figure 7 : Average $\delta^{13}C$ of (A) suspended particulate organic carbon (POC, data from Bouillon et al. 2000 and Dehairs et al. 2000) and (B) sediment organic matter, and (C) $\delta^{13}C$-$\delta^{15}N$ plot for mangrove litter and benthic invertebrates collected in the mangrove creeks (Ma), mangrove outlets (Mo), South-east Bay (SEb), and Central and North Bay (CNb). Closed symbols refer to species presumed to occupy a low trophic level, open symbols refer to species of higher trophic levels, and '+' indicate species of unknown trophic level from all zones. Two penaeid prawns collected in the North Bay with distinctly low $\delta^{13}C$ values (see discussion) are shown as grey circles. Error bars indicate 1 s.d.

Post-monsoon period

$\delta^{13}C$ values of invertebrates during this survey (Table 4, Figure 8, Appendix II) showed a marked spatial trend, with generally depleted values in the three mangrove creeks (LH : -27.6 ‰, CO : -27.3 ‰, and GA : -25.6 ‰), intermediate values in the southeast Bay locations (MD : -20.7 ‰, GU : -20.5 ‰) and most enriched values in the central Bay locations (KB : -18.2 ‰ for lower trophic levels, -16.3 ‰ for high trophic level species, CA : -18.8 ‰). Invertebrates from the three mangrove creek

locations (which were all classified as lower trophic levels, see higher) had comparable $\delta^{15}N$ values (averages GA : +6.2 ‰, LH : +5.9 ‰, and CO : +6.2 ‰), which were about 3 ‰ lower than those found in low trophic level invertebrates from the Bay locations (average KB : +8.8 ‰, CA : +8.9 ‰, MD : +9.0 ‰, GU : +9.2 ‰, Fig 5). The two higher trophic level species from KB showed a distinct enrichment in both $\delta^{13}C$ and $\delta^{15}N$ (Figure 8). Although invertebrates in Gaderu were found to be on average slightly enriched compared to those in other mangrove creeks, this may be due to the small amount of individuals analysed : *Tellina* sp. from the three mangrove creeks were isotopically similar (Figure 9), the only additional species from Gaderu was relatively enriched (*Macrophthalmus* sp.) whereas other species collected in CO and LH were more depleted (e.g. *Solen pecten*, *Typhlocarcinus* sp.).

Table 3 : Average $\delta^{13}C$ values (expressed in ‰) of all invertebrates sampled at each of the sampling locations. Also indicated are the standard deviation on the mean $\delta^{13}C$, the number of samples, and the minimum and maximum $\delta^{13}C$ at each location.

Location	**Average $\delta^{13}C$**	**Minimum $\delta^{13}C$**	**Maximum $\delta^{13}C$**	**n**
Ma1	-23.6 ± 0.2	-23.8	-23.3	3
Ma2	-23.6 ± 0.7	-24.7	-22.4	8
Mo1	-21.8 ± 0.9	-23.1	-20.5	8
Mo2	-21.5 ± 1.0	-23.0	-19.9	10
Mo3	-21.1 ± 0.9	-21.6	-20.0	3
Mo4	-21.5 ± 0.8	-22.5	-19.7	14
Mo5	-20.5 ; -20.2	-	-	2
SEb1	-18.4 ± 0.7	-19.6	-17.8	8
SEb2	-18.6 ± 1.0	-20.2	-16.2	10
SEb3	-19.0 ± 0.6	-20.1	-18.0	10
CNb1*	-17.1 ± 0.9	-18.7	-15.9	10
CNb2	-16.3 ± 1.9	-17.9	-13.2	7
CNb3	-16.5 ± 1.0	-17.3	-15.3	4
CNb4	-16.2 ± 0.5	-17.3	-15.7	10
CNb5	-16.3 ± 1.2	-18.0	-14.4	14
CNb6	-16.4 ± 0.6	-17.0	-15.6	4
CNb7*	-15.1	-	-	1
CNb8	-16.7 ± 1.0	-18.2	-15.4	7
CNb9	-18.4 ; -17.7	-	-	2
CNb10	-16.6 ± 1.2	-18.9	-15.1	7
CNb11	-15.9 ± 1.2	-16.9	-13.8	5
CNb12	-17.1 ± 1.5	-19.2	-14.9	7

* : One low $\delta^{13}C$ value measured for a penaeid prawn was excluded (see discussion)

Table 4 : Average carbon and nitrogen stable isotopic composition (in ‰, ± 1 s.d) of benthic invertebrates (low trophic levels, unless otherwise specified) at different sampling locations in December 1999.

	average $\delta^{13}C$	range $\delta^{13}C$	average $\delta^{15}N$	range $\delta^{15}N$	n
Mangrove creeks					
LH	-27.6 ± 1.5	-30.2 to -25.9	+ 5.9 ± 1.2	+ 4.4 to + 7.7	9
CO	-27.3 ± 0.9	-28.8 to -26.1	+ 6.2 ± 1.6	+ 4.5 to + 8.6	8
GA	-25.6 ± 0.9	-26.1 to -24.2	+ 6.2 ± 0.6	+5.4 to + 6.9	4
Bay locations					
MD	-20.7 ± 1.0	-21.8 to -19.6	+ 9.0 ± 0.8	+ 8.3 to + 9.7	4
GU	-20.5 ± 0.8	-21.8 to -19.5	+ 9.2 ± 0.8	+ 8.5 to + 10.7	8
KB[a]	-18.2	-18.3 to -18.1	+ 8.8	+ 8.8 to + 8.8	5
KB[b]	-16.3 ± 1.5	-17.8 to -14.7	+ 11.6 ± 0.6	+ 10.8 to + 12.2	2
CA	-18.8 ± 1.4	-20.5 to -17.0	+ 8.9 ± 0.5	+ 8.2 to +9.6	5

[a] : lower trophic level species ; [b] : higher trophic level species

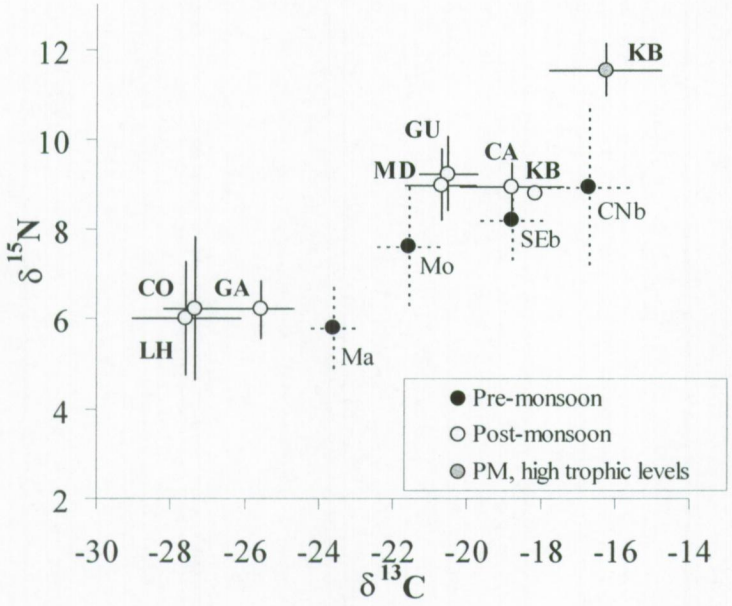


Figure 8 : Plot of $\delta^{13}C$ and $\delta^{15}N$ data for benthic invertebrates collected during post-monsoon period (open symbols : lower trophic levels, grey symbol : higher trophic level species), and a comparison with pre-monsoon data (only data for lower trophic level species are shown, black symbols). Abbreviations as in Figures 1 and 3. Error bars = 1 s.d.

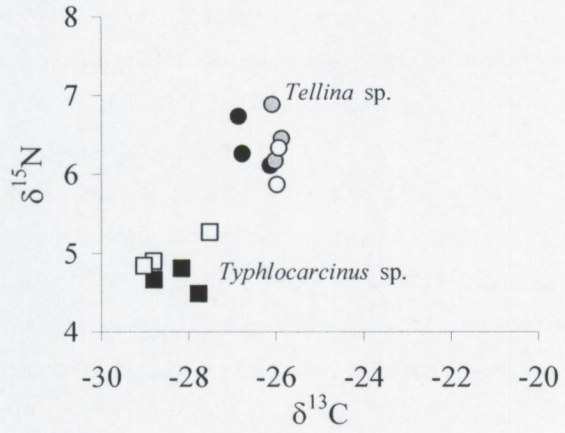


Figure 9 : Carbon and nitrogen isotopic composition of individual *Tellina* sp. (circles) and *Typhlocarcinus* sp. (squares) from the three mangrove creek locations. Black symbols : CO, grey symbols : GA, open symbols : LH.

Discussion

SEDIMENTS

Sediment organic matter showed a shift in $\delta^{13}C$ values between the mangrove creeks (-21.3 ‰) and the South-east and North Bay, where a zone of maximum $\delta^{13}C$ values between -17.8 and -19.1 ‰ can be found in the centre of the Bay (Figure 2 A). In the Bay, most depleted values (< -21 ‰) can be found in the region where satellite data indicate the plume of the Kakinada Canal, and are thus thought to be a reflection of larger inputs of ^{13}C-depleted terrestrial or sewage material. The magnitude of the overall $\delta^{13}C$ gradient is only slightly smaller than that found in suspended organic matter, but suspended matter was found to be on average about 3-4 ‰ more ^{13}C-depleted than sediment organic matter (Bouillon et al. 2000) (Figure 7 A, B). Such a discrepancy between suspended matter and sediment $\delta^{13}C$ values has also been found by Middelburg et al. (1998) in the Scheldt Estuary, with sediment $\delta^{13}C$ being enriched relative to the suspended matter in the upper estuary, but depleted in the lower estuary. C/N ratios of sediments in this study (Figure 2 C) are also higher than the average values found in suspended matter (between 8.5 and 10, see Dehairs et al. 2000). These results indicate first of all that mangrove-derived carbon (with an

average $\delta^{13}C$ of -28.7 ‰, Bouillon et al. 2002a) and other terrestrial carbon sources (~ -26.5 ‰, e.g. Hellings et al.1999), do not appear to contribute substantially to the sediment organic matter pool of the mangrove creeks and adjacent Bay. This is more or less consistent with the results of Kuramoto & Minagawa (2001) who found mangrove carbon to contribute ~ 20 % to the organic matter pool in sediments adjacent to a mangrove forest in Thailand. Furthermore, the discrepancy in C/N ratios and $\delta^{13}C$ values between suspended and sediment organic matter indicate different relative contributions of carbon sources in these two pools. However, while the higher C/N ratios in sediments would suggest a larger contribution by terrestrial sources, the higher $\delta^{13}C$ values in SOM indicate the opposite. A marked spatial shift of about 1.6 ‰ can also be observed in the sedimentary $\delta^{15}N$ record (Figure 2 B), and will be discussed in conjunction with the parallel shift in consumer $\delta^{15}N$ values below.

$\delta^{13}C$ VALUES OF BENTHIC INVERTEBRATES : IMPORTANCE OF DIFFERENT PRIMARY PRODUCERS

Pre-monsoon

The overall distribution of $\delta^{13}C$ values for benthic invertebrates collected in this period (Table 3 and Appendix I, Figure 7C) shows that, considering a trophic enrichment of ~ 1 ‰, benthic invertebrates in the South-eastern, Central and Northern part of Kakindada Bay did not rely substantially on mangrove (-28.7 ‰, see Chapter 8) or other terrestrial carbon sources (~ -26.5 ‰, e.g. Hellings et al. 1999) during the study period. In fact, the $\delta^{13}C$ values of benthic invertebrates in these areas are typical for a marine, phytoplankton-based benthic food web, and some of the more ^{13}C-enriched values (> -15 ‰) also suggest some input of ^{13}C-enriched carbon sources, such as benthic microalgae (France 1995c). We have no direct measurements of the isotopic signature of these algae from the Bay or Creek bottoms due to the practical difficulties in sampling them in this environment, but benthic microalgae from the intertidal mangrove flats in this area have been found to have an isotopic signature of around –17.3 ‰ ($\delta^{13}C$) and between + 0.5 and + 4.5 ‰ ($\delta^{15}N$) (Bouillon et al. 2002a i.e. Chapter 8), whereas SPOM from the adjacent waters during the pre-monsoon period typically has $\delta^{13}C$ values of -23 to -20 ‰ (Bouillon et al. 2000, i.e.Chapter 5).

Benthic microalgae have been found to occur throughout the study area (C. Kalavati, unpublished data), despite the high turbidity levels which may be encountered.

More depleted $\delta^{13}C$ values for invertebrates were found in the mangrove outlets (-21.5 ± 0.9 ‰, n = 37) and creeks (-23.6 ± 0.6 ‰, n = 11). However, phytoplankton $\delta^{13}C$ values in this dynamic ecosystem have been suggested to be spatially and seasonally variable (Dehairs et al. 2000, Bouillon et al. 2000, Bouillon & Dehairs 2000) and are thought to exhibit a $\delta^{13}C$ gradient between the mangrove creeks (depleted values) and the North Bay (enriched values). The magnitude of the $\delta^{13}C$ gradient observed in benthic invertebrates (~ 7 ‰) is much larger than that observed in suspended organic matter (~ 2.5 ‰) or sediment organic matter (~1.5 ‰) but is quite similar to the average difference in zooplankton $\delta^{13}C$ between the mouth of Coringa (see Fig 1) and the North Bay (~ 6 ‰, Bouillon et al. 2000 i.e. Chapter 5). Benthic invertebrates in the mangrove creeks and outlets were observed to be more ^{13}C-depleted relative to the sediment organic matter, whereas those in the South-east, Central and North Bay were enriched relative to the sediment organic carbon pool. In contrast, compared to the average $\delta^{13}C$ values for suspended organic matter (Bouillon et al. 2000), benthic invertebrates were enriched at all locations, although markedly more so in the Bay environment than in the mangrove creeks (Figure 7A, B, C).

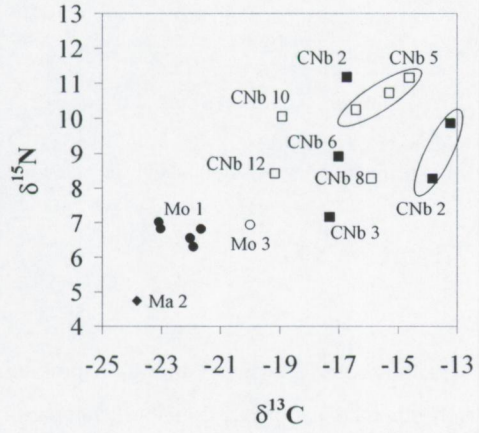
The magnitude of the observed $\delta^{13}C$ gradient in benthic invertebrates and a comparison with $\delta^{13}C$ data of suspended and sediment organic matter thus indicate a marked selectivity for pelagic and benthic microalgal carbon sources. Phytoplankton and benthic microalgae are expected to exhibit a larger $\delta^{13}C$ gradient because of a more ^{13}C-depleted DIC-pool (dissolved inorganic carbon) in and near the mangrove creeks, where bacterial respiration of ^{13}C-depleted vascular plant material will result in a dilution of the DIC-pool with isotopically light CO_2 (e.g. Marguillier et al. 1997, Bouillon et al. 2000, see Chapter 4 and below). It is also conceivable that there are spatial differences in the importance of carbon sources, i.e. mangrove carbon (and other terrestrial sources) could be more important in the mangrove creeks yet be fully replaced by algal sources towards the marine end, in which case we would also expect to find a gradient of increasing $\delta^{13}C$ values towards the northern Bay. However, the discrepancy between benthic invertebrate $\delta^{13}C$ values and the mangrove $\delta^{13}C$ signature (Figure 7 C) and the fact that phytoplankton $\delta^{13}C$ values are expected to be more ^{13}C-depleted in the mangrove creeks relative to marine phytoplankton and thus

presumably overlap with the $\delta^{13}C$ values observed in benthic invertebrates, suggest that this is not the case. A similar steeper gradient in clam $\delta^{13}C$ values compared to suspended matter $\delta^{13}C$ was found by Canuel et al. (1995) in San Francisco Bay, and was also interpreted as selectivity for phytoplanktonic sources. It thus appears that during the pre-monsoon period, when turbidity is least and the numerical abundance of phytoplankton is at a maximum, pelagic and benthic microalgal sources are the dominant primary producers sustaining the benthic community in this ecosystem. Whether this situation is representative of other seasons remains to be determined.

When comparing $\delta^{13}C$ data from the Central and North Bay and the mangrove regions, it appears that the two $\delta^{13}C$ distributions are entirely non-overlapping, except for two rather negative values (-21.5 and -22.7 ‰) found in the North Bay (Figure 7 C, shown as grey-filled circles). These two negative values were found in 2 species of penaeid prawns (*Penaeus merguiensis* and *Metapenaeus monoceros*, respectively), i.e. mobile species which are expected to migrate during this season from the mangrove creeks towards the marine environment. Thus, as the tissues of these organisms require some time to equilibrate with the isotopically distinct new diet (Riera et al. 2000), these negative values are hypothesised to indicate that these individuals had only recently migrated from the mangrove regions (e.g. *Macrobrachium rosenbergii* collected at Coringa mouth was found to have a $\delta^{13}C$ of about -21 ‰) to the North Bay, whereas some other penaeids captured in the North Bay (including other individuals of the same species) had 'normal' values of -15 to -17 ‰. The use of carbon stable isotopes as a tracer of shrimp migration has been reported earlier (e.g. Fry 1983, Fry et al. 1999, Riera et al. 2000). The $\delta^{15}N$ values of these two specimens were among the highest and lowest recorded in this study (Figure 7 C, Appendix I). Large variations in penaeid $\delta^{15}N$ values have been reported earlier (Riera et al. 2000), and we currently do not have a convincing explanation for this.

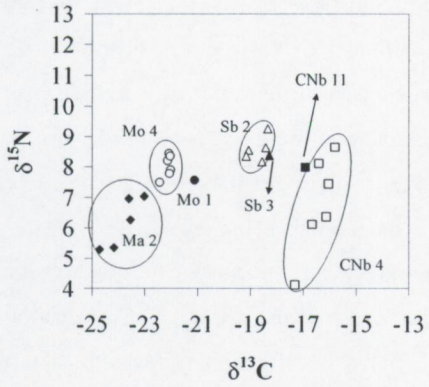
Finally, some common species were sampled at different sites, and examples of the spatial variability in their stable isotopic signatures are given in Figure 10. These data show three quite different patterns and thus indicate that species-specific differences in relative contributions of carbon sources also occur. For *Typhlocarcinus* sp. (Figure 10 A), the general trend of Figure 7 C is confirmed, i.e. an enrichment in ^{13}C and ^{15}N is found when going from the mangrove creeks to the Central and North Bay but in addition, the Central and North Bay data also display some variability, suggesting that

Typhlocarcinus sp. feeds in a highly selective way (i.e. the variability in stable isotope signatures is much larger than that observed in sediments or suspended matter). For *Tellina* spp. (Figure 10 B), the $\delta^{13}C$ trend is also confirmed, but the specimens from station CNb 4, near the outfall of Kakinada Canal, are depleted in ^{15}N relative to the expected pattern. For *Paphia undulata* (Figure 10 C), no data are available for Ma or Mo stations, but it can be seen that within the Central and North Bay, $\delta^{13}C$ values are relatively uniform, suggesting less selective feeding (but : note the rather high variability in $\delta^{15}N$, which is less straightforward to interpret).



Typhlocarcinus sp.

Figure 10 A (legend on following page)



Tellina sp.

Figure 10 B (legend on following page)

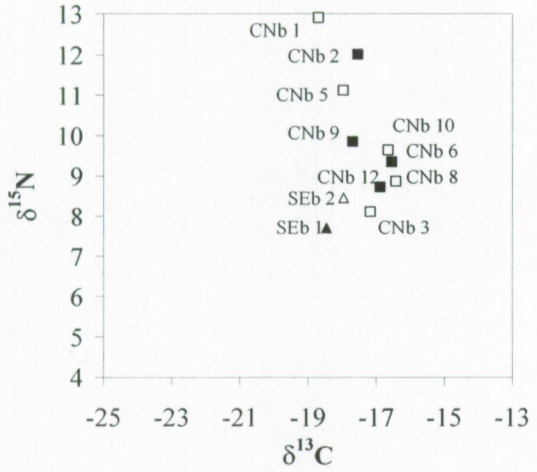


Figure 10 (see also previous page): $\delta^{13}C$-$\delta^{14}N$ plot for (A) *Typhlocarcinus* sp., (B) *Tellina* spp., and (C) *Paphia undulata* sampled at different locations throughout the study area (see Fig 1 for location of stations).

Post-monsoon

Although the general trend in stable isotope signatures found during the pre-monsoon period was confirmed in our post-monsoon data, there were 2 major differences : (1) a tendency for $\delta^{13}C$ values to be more depleted than during the pre-monsoon season by 1-3 ‰ throughout the area, and (2) the overall spatial gradient in $\delta^{13}C$ (~ 9 ‰) was even more pronounced than during the pre-monsoon season (~ 7 ‰). No seasonal change in invertebrate $\delta^{15}N$ was evident. Although the focus during this survey was to collect low-trophic level species, the isotope data for *Murex trapa* and *Nassarius* sp. from KB confirm the higher $\delta^{15}N$ values found in these scavengers/predators during pre-monsoon. The $\delta^{15}N$ data show two very distinct distributions, with invertebrates from mangrove creeks and those from the Bay regions being separated by ~ 3 ‰ with hardly any overlap (Figure 8). This clear segregation confirms the limited exchange of material between these two regions which was evident from the $\delta^{13}C_{DIC}$ distribution (Figure 6), or it could indicate that substantial transformation processes take place before N-pools from the mangrove creeks reach the Bay.

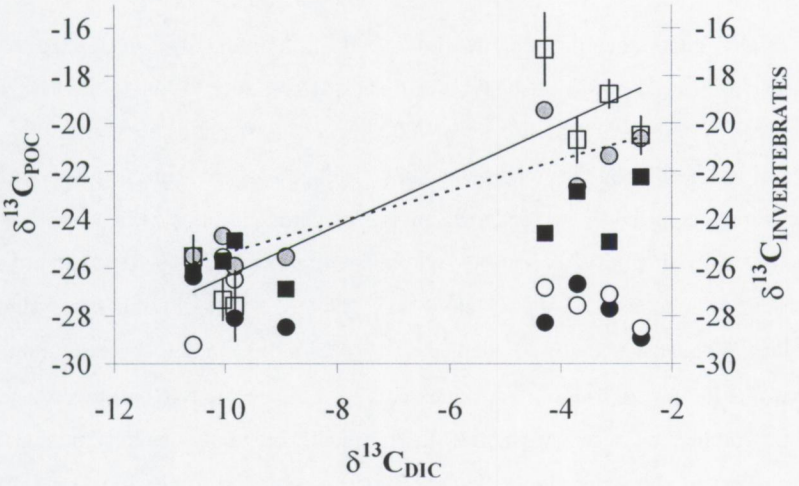


Figure 11 : $\delta^{13}C$ of different SPOM size fractions (left Y-axis) and of benthic invertebrates (open squares, right Y-axis) versus $\delta^{13}C$ of dissolved inorganic carbon. Black circles : total SPOM, open circles : < 10 µm, grey circles : 10 << 50 µm, black squares : 50 << 118 µm Error bar = 1 s.d.

The $\delta^{13}C$ values of benthic invertebrates from the creeks show a partial overlap with those of mangrove litter (see Bouillon et al. 2002a), but there are a number of arguments which strongly suggest that these depleted values are not related to direct utilization of mangrove litter by invertebrates. The wide range of $\delta^{13}C$ values (> 10 ‰) in invertebrates is in sharp contrast with the limited spatial variability in bulk sediment and suspended matter $\delta^{13}C$ values. This indicates the selectivity of the invertebrate community for components that are spatially more variable in $\delta^{13}C$ than the bulk of the available organic matter. Invertebrate $\delta^{13}C$ values were well correlated with $\delta^{13}C_{DIC}$ values (Fig 11), and as the low $\delta^{13}C_{DIC}$ are expected to result in phytoplankton $\delta^{13}C$ values which are significantly depleted relative to typical marine plankton (between -32.9 and -27.9 ‰), there is a good agreement between $\delta^{13}C$ values for local plankton and invertebrates. It is worth mentioning that initial results of microscopical examinations of different size fractions of suspended matter (April and May 2001, C. Kalavati & A.V. Raman, Andhra University, pers. comm.) indicate major differences in the biological composition of these fractions, with a dominance

of photosynthetic organisms (diatoms, flagellates) in the 10 << 50 μm and 50 <<118 μm classes.

The limited importance of mangrove litter, both in the mangrove creeks and in the adjacent waters, is in agreement with results from several other studies (e.g. Primavera et al. 1997, Bouillon et al. 2000, Lee 2000) but is in contrast to the conclusions of other studies employing stable isotope analysis that mangrove carbon significantly contributes to foodwebs in the mangrove creeks, with a decreasing importance towards the open marine environment (e.g. Rodelli et al. 1984, Fleming et al. 1990, and notably Chong et al. 2001). However, none of the latter studies considered the existence of a ^{13}C-depleted DIC pool in the mangrove creeks and used typical marine phytoplankton $\delta^{13}C$ signatures to evaluate the relative importance of aquatic production and mangrove litter, thus potentially overestimating the contribution of the latter. In particular, Chong et al. (2001), citing Hayase et al. (1999), even provided some indirect evidence for the existence of ^{13}C-depleted phytoplankton in the mangrove creeks of their study by noting that $\delta^{13}C$ values of total suspended organic matter showed a large spatial gradient between the mangrove creeks and the marine environment (-25.6 to -17.9 ‰, i.e. more than 8 ‰) whereas the estimated contribution of phytoplankton (based on Chl a measurements) changed very little over the same gradient (from 17 to 25 %), a discrepancy strongly suggesting that phytoplankton in the creeks was significantly depleted in ^{13}C. In other mangrove ecosystems, both direct measurements of $\delta^{13}C_{DIC}$ (Dehairs et al. 2000, Bouillon et al. 2000, S. Marguillier unpublished data : between -8.9 and +0.2 ‰ in Gazi Bay, Kenya, see also Chapter 4) and indirect evidence based on the $\delta^{13}C$ of seagrasses or macroalgae (e.g. Hemminga et al. 1994) indicate that the inorganic carbon pool (and thus, local phytoplankton) is depleted in ^{13}C compared to the marine environment.

Finally, it should be noticed that $\delta^{13}C$ (and $\delta^{15}N$) signatures of consumers of similar trophic levels showed relatively little variability within a certain station or region. Such a situation was also found by Lee (2000) and suggests that the consumer assemblage was using (a) common carbon source(s), i.e. there was limited segregation of food sources. This is in marked contrast with the situation in the intertidal zone in mangrove forests (see Bouillon et al. 2002a, i.e. Chapter 8), where different species of

invertebrates were found to display widely varying stable isotope signatures corresponding to a fairly limited degree of resource overlap.

$\delta^{15}N$ Values of Sediments And Benthic Invertebrates

When species in each zone were grouped according to their assumed or known trophic status (with a distinction made between 'lower' or 'higher' trophic levels, see 'Results' for details on the species in each group), it appeared that higher trophic levels showed on average higher $\delta^{15}N$ values (by 2.1 to 3.8 ‰), and that there was also a marked spatial $\delta^{15}N$ gradient between the mangrove creeks and the Central and North Bay of about 3.2 ‰ which could be observed in both low and high trophic levels (Fig 7 C, Fig 8). By comparing the $\delta^{15}N$ values of species of unknown trophic status with the average $\delta^{15}N$ values of species of known low or high trophic level from that zone, we can tentatively classify *Oratosquilla* sp. and *Harpiosquilla* sp. as 'higher' trophic level species, whereas *Meretrix meretrix* and *Acaudina molpaidoides* had intermediate $\delta^{15}N$ values. For *Meretrix meretrix* this is confirmed by gut content analysis which indicated the presence of animal tissues (C. Kalavati, unpublished data). For the bivalve *Pinctada radiata* and the sponge *Tetilla dactyoloidea*, however, insufficient data are available to assess its trophic status. Overall, the $\delta^{15}N$ signature appears to be a useful indicator of trophic level, if the local baseline $\delta^{15}N$ values are taken into account. However, in each of the zones, there remained some overlap in the $\delta^{15}N$ signatures of the two proposed trophic levels. The degree of ^{15}N-enrichment between two trophic levels and the mechanisms causing it are still not yet fully understood (Ponsard & Averbuch 1999) and the enrichment factor has been found to be quite variable (e.g. Adams & Sterner 1999), but is assumed to be on average about 2.6 to 3.4 ‰ (Owens 1987, Minagawa & Wada 1984).

The spatial $\delta^{15}N$ gradient could also be noticed in the sediment organic matter (Fig 2 B), but was less pronounced with a difference of about 1.6 ‰ between the mangrove creeks and the Central and North Bay. Contrary to our expectations, the distribution of sedimentary $\delta^{15}N$ values was relatively uniform throughout the Bay and was not indicative of major sewage impact from the Kakinada Canal. Such a $\delta^{15}N$ gradient was also noted in this area in zooplankton (Bouillon et al. 2000 i.e. Chapter 5) and fish (see Chapter 10). Thus, whereas low trophic level species in the mangrove creeks

had $\delta^{15}N$ values about 1.5 ‰ higher than sediment organic matter, this difference increased to almost 3 ‰ in the Central and North Bay. Several factors may be responsible for this $\delta^{15}N$ trend, which is ultimately related to $\delta^{15}N$ differences in primary producers. First, the source nitrogen for the primary producers in the different regions may have a variable $\delta^{15}N$ signal. For example, NO_3^- from sewage waste has been found to have significantly higher $\delta^{15}N$ values than other NO_3^- sources (Heaton 1986, Macko & Ostrom 1994), and thus ecosystem $\delta^{15}N$ has been found to increase with the degree of urbanization of the watershed (e.g. Fry 1999, McClelland et al. 1997, McClelland & Valiela 1998). Risk & Erdmann (2000) found higher $\delta^{15}N$ values in invertebrates in sewage-impacted coral reef invertebrates than in non-impacted reef invertebrates. On the other hand, sewage effluent organic matter has been found to have low $\delta^{15}N$ values (e.g. Sweeney & Kaplan 1980, Macko & Orstom 1994) causing invertebrates to exhibit lower $\delta^{15}N$ values in the vicinity of sewage outfalls than in nearby unpolluted marine locations (e.g. Rogers 1999, Thornton & McManus 1994, Tucker et al. 1999). Several bivalves collected near to the outfall of Kakinada Canal (station CNb4) did show relatively low $\delta^{15}N$ values compared to other low trophic level species in the Bay (Fig 10 B, Appendix I), but their high $\delta^{13}C$ values (~ -17 ‰) are not indicative of direct utilization of sewage-derived matter.

Secondly, the load and the phytoplankton demand for these nutrients (NO_3^- and NH_4^+) is an important factor controlling primary producer $\delta^{15}N$ values. It has been shown that $\delta^{15}N$ values of particulate (and sediment) organic matter increase as NO_3^- concentrations decrease, either along a spatial gradient or during the course of a phytoplankton bloom, and this is due to the selective assimilation of $^{14}NO_3^-$ resulting in an isotopically heavier DIN pool and subsequently newly produced biomass (see Altabet & Francois, 1994 and references therein), and a similar situation holds for NH_4^+ assimilation (Cifuentes et al. 1988). Thus, spatial and seasonal variations in the DIN concentration and speciation will affect primary producer $\delta^{15}N$ values and these will in turn be reflected in consumer tissue isotopic composition. Other processes which have been shown to increase $\delta^{15}N$ values locally or seasonally are nitrification and denitrification, which cause an enrichment in the residual DIN pool, and subsequently in all ecosystem compartments (e.g. Mariotti et al. 1984, Montoya et al. 1990).

In the study area, ammonium concentrations (AV Raman, unpublished data) have been found to be highest (average values of 0.6, 1.3, 8.9 and 13.1 µM for the North Bay, South Bay, Gaderu and Coringa, respectively) during the monsoon period (July – September), and afterwards decrease until values of < 0.1 µM are reached by the end of the pre-monsoon period (i.e. the sampling period). Thus, it appears that NH_4^+ consumption depletes the NH_4^+ pool and this should lead to an enrichment of the remaining pool in ^{15}N. In a similar way, there is a spatial gradient with NH_4^+ generally being a more important constituent of the DIN pool in the mangrove creeks and outlets, and nitrate taking over this role in the Bay waters. As Cifuentes et al. (1988) mention that no NO_3^- uptake by phytoplankton takes place as long as the NH_4^+ concentration remains > 2 µM, for the present study this would imply that NO_3^- uptake only occurs towards the end of the pre-monsoon period, for the whole area. We thus hypothesise that uptake by DIN, imported via the mangrove creeks and other freshwater sources, enriches the remaining DIN pool in the Bay and results in the observed $\delta^{15}N$ gradient in sediments and consumers.

Mass-balance considerations

Besides the evidence provided by stable isotopes (e.g. Newell et al. 1995, Dehairs et al. 2000, this study), several authors have recently questioned the importance of mangrove-derived carbon to estuarine or nearshore aquatic secondary production based on mass-balance considerations. Wafar et al. (1997) estimated that the total potential C-flux of mangroves in a western Indian estuary was only 37 % of the measured average phytoplankton C production, and this number dropped to 3-4 % in terms of N and P. Similarly, Li & Lee (1998) estimated mangrove carbon to contribute only 1.8 % to the total available carbon pool in Deep Bay, China. Using the litter fall measurements made by Dehairs et al. (2000) (weighted average of 1.2 g C m^{-2} d^{-1}) and phytoplankton primary production rates (from 1.1 to 3.3 g C m^{-2} d^{-1}) when assuming a depth of 1.5 meters with photosynthetic activity, AV Raman, unpublished data), it becomes clear that the potential contribution of mangrove carbon to the system is much less than that from phytoplankton (by a factor of ~ 5), considering the relative surface areas of aquatic and mangrove habitats. It should be stressed that this is a very rough estimate which did not take into account e.g. the fact

that part of the litter fall will be stored, consumed, and respired in the intertidal areas, and that a major part of the mangrove C-flux might be in the form of DOC (see Lee 1995) or be directed towards the Bay of Bengal on the eastern edge of the forest. It also does not include potential contributions from benthic microalgae and from other terrestrial sources (e.g. via the Kakinada Canal, and from the Gautami Godavari), and thus no doubt overestimates the potential contribution mangrove litterfall makes to the particulate organic carbon pool.

Concluding Remark

Overall, our results indicate a strong selectivity of the benthic invertebrate community for local algal sources and a limited trophic dependancy on mangrove or other terrestrial carbon sources, during both pre-monsoon and post-monsoon seasons. In contrast to the wide range of rescources used by intertidal invertebrates (Bouillon et al. 2002a i.e. Chapter 8), benthic fauna in the subtidal regions appear to show much less diversity in their carbon sources, as evidenced by the relative uniformity of $\delta^{13}C$ values at each location (see also Lee 2000). The stable isotope composition of sediments furthermore suggest that burial of mangrove and terrestrial carbon in sediments is limited. Although the still often-quoted (e.g. Holguin et al. 2001) hypothesis that exported mangrove litter supports local (and possibly adjacent) aquatic foodwebs will no doubt continue to be an issue of debate, we feel that there is currently little or no unambiguous evidence to support this view. The generation of more studies using stable isotopes, mass balance equations, and/or other tracer techniques such as fatty acid analysis from a variety of mangrove ecosystems would certainly benefit our understanding of the possible contribution of mangrove primary production to adjacent aquatic faunal communities.

Appendix I : Carbon and nitrogen stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$, expressed in ‰) of benthic invertebrates collected in the Coringa-Kakinada Bay complex, during pre-monsoon season 1997 (June, indicated by *) and 1999 (May-June).

Location	Species	$\delta^{13}C$	$\delta^{15}N$	n
Ma 1	*Diopatra neapolitana*	-23.8	+ 10.4	1
	Meretrix meretrix	-23.6, -23.3	+ 8.1, + 10.4	2
Ma 2	*Diopatra neapolitana*	-23.9	+ 9.5	1
	Macrophthalmus sp.	-22.4	+ 5.1	1
	Typhlocarcinus sp.	-23.8	+ 4.7	1
	Tellina sp. 1	-23.8 ± 0.7	+ 6.2 ± 0.8	5
Mo 1	*Tellina* sp. 1	-21.1	+ 7.6	1
	Typhlocarcinus sp.	-22.4 ± 0.7	+ 6.7 ± 0.3	5
	Cerithidea cingulata	-21.1, -20.5	+ 10.8, + 10.2	2
Mo 2	*Diopatra neapolitana**	-21.2	+ 9.0	1
	Dorippe facchino	-21.7 ± 1.5	+ 6.4 ± 0.5	4
	Macrophthalmus sp.	-22.2, -21.9	+ 4.7, + 5.2	2
	Macrobrachium rosenbergii	-21.5, -20.9	+ 10.3, + 10.6	2
	Metapenaeus dobsoni	-20.3	+ 9.4	1
Mo 3	*Typhlocarcinus* sp.*	-20.0	+ 6.9	1
	*Anadara granosa**	-21.6	+ 8.0	1
	Macoma sp.*	-21.6	+ 8.5	1
Mo 4	*Cerithidea cingulata*	-21.2 -19.7	+ 9.1, + 8.4	2
	Dorippe facchino	-21.3, -20.8	+ 8.9, + 6.9	2
	Penaeus merguiensis	-21.1 ± 0.6	+ 9.5 ± 1.1	3
	Tellina sp. 1	-22.1 ± 0.2	+ 8.0 ± 0.4	6
Mo 5	*Placuna placenta*	-20.5, -20.2	+ 8.7, + 9.1	2
SEb 1	*Paphia undulata*	-18.0	+ 8.5	1
	Placuna placenta	-19.6, -19.2	+ 9.5, + 9.3	2
	Echiuroides (unid.)	-17.8	+ 11.8	1
	Thais lacera	-17.9	+ 11.0	1
	Metapenaeopsis stridulans	-17.9, -18.2	+ 10.8, + 4.8	2
	Metapenaeus brevicornis	-18.5	+ 10.8	1

Appendix I (continued)

Location	Species	$\delta^{13}C$	$\delta^{15}N$	n
SEb 2	*Paphia undulata*	-18.5	+ 7.7	1
	Tellina sp. 1	-18.8 ± 0.4	+ 8.4 ± 0.2	4
	Tellina sp. 2	-18.4	+ 9.3	1
	Diplodonta sp.	-20.2	+ 8.0	1
	Macrophthalmus sp.	-16.2	+ 6.5	1
	Echiuroides (unid.)	-19.0	+12.0	1
	Metapenaeus brevicornis	-18.2	+ 11.8	1
SEb 3	*Meretrix meretrix*	-19.6	+ 9.5	1
	Tellina sp. 1	-18.3	+ 8.4	1
	Lingula sp.	-20.1	+ 9.3	1
	Anadara granosa	-19.3, -19.2	+ 7.2, + 6.1	2
	Acaudina molpaidioides	-18.5	+ 9.6	1
	Diopatra neapolitana	-19.4	+ 11.2	1
	Oratosquilla sp.	-18.1	+ 11.4	1
	Volema cochlidium	-18.0	+ 9.6	1
	Penaeus merguiensis	-19.2	+ 9.3	1
CNb 1	*Paphia undulata*	-18.7	+ 12.9	1
	Leucosia sp.	-18.0	+ 11.4	1
	Dorippe facchino	-16.7	+ 10.7	1
	Nassarius olivaceus	-17.5	+ 11.9	1
	Portunus sanguinolentus	-16.8	+ 12.9	1
	Harpiosquilla sp.	-17.6	+ 7.8	1
	Metapenaeopsis sp.	-15.9	+ 13.4	1
	Metapenaeus monoceros	-22.7, -16.1	+ 14.5, + 11.9	2
	Charybdis sp.	-17.0, -16.2	+ 11.4, + 11.7	2
CNb 2	*Paphia undulata*	-17.5	+ 12.0	1
	Pinctada radiata	-17.4	+ 11.6	1
	Macrophthalmus sp.	-17.9, -17.3	+ 9.5, + 8.0	2
	Typhlocarcinus sp.	-14.6 ± 1.9	+ 9.8 ± 1.5	3

Appendix I (continued).

Location	Species	$\delta^{13}C$	$\delta^{15}N$	n
CNb 3	*Paphia undulata* *	-17.2	+ 8.1	1
	Nassarius sp. *	-15.3	+ 10.5	1
	Murex trapa *	-16.0	+ 9.9	1
	Typhlocarcinus sp. *	-17.3	+ 7.2	1
CNb 4	*Meretrix meretrix*	-16.0 ± 0.3	+ 9.8 ± 0.8	4
	Tellina sp. 2	-16.4 ± 0.5	+ 6.8 ± 1.6	6
CNb 5	*Paphia undulata*	-18.0, -16.9	+ 11.1, n.d.	2
	Anadara granosa	-17.3, -16.8	+ 10.0, + 10.4	2
	Charybdis sp.	-17.1	+ 13.4	1
	Macrophthalmus sp.	-16.7, -15.5	+ 7.5, + 5.9	2
	Murex trapa	-14.5, -14.4	+ 13.9, + 13.9	2
	Nassarius olivaceus	-17.1, -16.9	+ 13.2, + 12.0	2
	Typhlocarcinus sp.	-15.5 ± 0.9	+ 10.7 ± 0.5	3
CNb 6	*Paphia undulata* *	-16.6	+ 9.4	1
	Anadara natalensis *	-16.6	+ 8.3	1
	Babylonia canaliculata *	-15.6	+ 12.2	1
	Typhlocarcinus sp. *	-17.0	+ 8.9	1
CNb 7	*Penaeus merguiensis*	-21.5	+ 7.3	1
	Parapenaeopsis stylifera	-15.1	+ 12.6	1
CNb 8	*Paphia undulata* *	-16.4	+ 8.9	1
	Typhlocarcinus sp. *	-15.9	+ 8.3	1
	Murex trapa *	-15.4	+ 10.9	1
	Anadara granosa *	-17.1	+ 10.2	1
	Meretrix meretrix *	-18.2	+ 12.0	1
	Nassarius sp. *	-17.4	+ 11.1	1
	Philyra sp. *	-16.8	+ 8.3	1
CNb 9	*Paphia undulata*	-17.7	+ 9.9	1
	Tetilla dactyoloidea	-18.4	+ 12.1	1

Appendix I (continued)

Location	Species	$\delta^{13}C$	$\delta^{15}N$	n
CNb 10	*Paphia undulata* *	-16.7	+ 9.6	1
	Typhlocarcinus sp. *	-18.9	+ 10.1	1
	Murex trapa *	-15.7	+ 11.3	1
	Nassarius olivaceus *	-17.0	+ 11.5	1
	Nasssarius sp. *	-15.1	+ 10.9	1
	Charybdis sp. *	-16.5, -16.1	+ 9.6, + 9.4	2
CNb 11	*Charybis* sp.	-15.7	+ 13.0	1
	Harpiosquilla sp.	-16.2	+ 11.9	1
	Murex trapa	-16.7	+ 11.9	1
	Tellina sp. 2	-16.9	+ 8.0	1
	Penaeus semisulcatus	-13.8	+ 10.6	1
CNb 12	*Paphia undulata* *	-16.9	+ 8.7	1
	Typhlocarcinus sp. *	-19.2	+ 8.4	1
	Nassarius olivaceus *	-18.7	+ 10.9	1
	Thais lacera *	-14.9	+ 9.0	1
	Macoma sp. *	-17.1	+ 8.9	1
	Siliqua albida *	-16.5	+ 7.6	1
	Harpiosquilla sp. *	-16.1	+ 10.3	1

Appendix II : Carbon and nitrogen stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$, expressed in ‰) of benthic invertebrates collected in the Coringa-Kakinada Bay complex, during the post-monsoon season (December 1999). For sampling locations, see Figure 3.

Location	Species	$\delta^{13}C$	$\delta^{15}N$	n
CA	*Dorippe facchino*	-20.5; -19.9	+ 8.2; + 9.1	2
	Unidentified nudibranch	-18.4	+ 9.6	1
	Typhlocarcinus sp.	-17.0; -18.1	+ 8.9; + 8.8	2
KB	*Macrophthalmus* sp.	-18.1	+ 8.8	1
	Murex trapa [a]	-15.3; -14.7	+ 11.7; +12.2	2
	Nassarius sp. [a]	-17.8; -17.3	+ 10.8; +11.6	2
	Typhlocarcinus sp.	-18.3	+8.8	1
GU	*Anadara granosa*	-21.4	+ 9.0	1
	Placuna placenta	-20.8	+ 8.9	1
	Tellina sp.	-20.1 ± 0.4	+ 8.8 ± 0.2	4
	Typhlocarcinus sp.	-21.8; -20.0	+ 10.7; + 10.3	2
MD	*Meretrix meretrix*	-20.3; -19.6	+ 9.6; + 9.7	2
	Tellina sp.	-21.8; -21.1	+ 8.4; + 8.3	2
CO	*Dorippe facchino*	-27.1; -27.0	+ 8.6; + 8.3	2
	Tellina sp.	-26.6 ± 0.4	+ 6.4 ± 0.3	3
	Typhlocarcinus sp.	-28.2 ± 0.5	+ 4.7 ± 0.2	3
GA	*Macrophthalmus* sp.	-24.2	+ 5.4	1
	Tellina sp.	-26.0 ± 0.1	+ 6.5 ± 0.4	3
LH	*Anadara granosa*	-27.0; -26.7	+ 7.3; +7.5	2
	Dorippe facchino	-27.1	+ 7.7	1
	Solen pecten	-30.2	+ 4.4	1
	Tellina sp.	-26.0; -25.9	+ 5.9; + 6.3	2
	Typhlocarcinus sp.	-28.5 ± 0.8	+ 5.0 ± 0.2	3

CHAPTER 7 : Sources of organic carbon in mangrove sediments : variability and possible ecological implications

Foreword

In the preceding chapter, we have shown that sediments in the bay adjacent to the mangrove forest in the Gautami Godavari estuary show little evidence of storage of terrestrial and/or mangrove-derived organic carbon. Naturally, the question arises whether the intertidal sediments, i.e. below the mangrove canopy, store significant amounts of mangrove-derived material, and if so, under which conditions. In this chapter, we will show that both the sources and the stocks of organic carbon in intertidal sediments in mangrove ecosystems vary widely between different mangrove ecosystems and within a certain ecosystem, and we will discuss some of the consequences this may have for our current view on mangrove ecosystem functioning. In addition, the similarities observed between mangroves and salt marshes provide a good opportunity to present a short comparison of some aspects of carbon dynamics between these two ecosystem types.

The results and ideas expressed in this chapter are partially derived from the following publication, which was updated with recent literature :

Bouillon S, Koedam N, Rao AVVS, Dahdouh-Guebas F, & Dehairs F (2002c) Sources of organic carbon in mangrove sediments : variability and some possible implications for ecosystem functioning. In review for Hydrobiologia.

Abstract

Mangrove sediments from three different mangrove forests (Coringa Wildlife Sanctuary in the Godavari Delta (Andhra Pradesh, India) and in Galle and Pambala (south-west Sri Lanka)) were analysed for their organic carbon content, elemental ratios (C/N, atom) and carbon stable isotope composition ($\delta^{13}C$). Organic carbon content (0.6 – 31.7 % dry weight), C/N ratios (7.0 – 27.3) and $\delta^{13}C$ (between -29.4 and -20.6 ‰) showed a wide range of values. Lower stocks of organic carbon coincided with low C/N ratios and less negative $\delta^{13}C$ values, indicating import of marine or estuarine particulate suspended matter. High organic carbon stocks coincided with high C/N ratios and $\delta^{13}C$ values close, but not equal, to those of the mangrove vegetation. The variations observed in this study and published literature data could be adequately described by a simple two-end mixing model, whereby marine/estuarine suspended matter and mangrove litter were taken as end members. Thus, while in some mangrove ecosystems or vegetation zones, organic carbon stocks can be very high and are almost entirely of mangrove origin, there also appear to be cases in which deposited estuarine or marine suspended matter is the dominant source of organic carbon and nitrogen in mangrove sediments. A compilation of literature data and data gathered in this study indicates that the majority of mangrove sediments show low concentrations of organic carbon (< 5 %), and intermediate C/N ratios (10 << 20) and $\delta^{13}C$ values (usually -27 ‰ << -21 ‰), illustrating the influence of imported carbon sources. The observed variability is remarkably similar to that found in temperate salt marsh ecosystems where the importance of local vascular plant production to the sediment organic carbon pool shows an equally wide range. It is suggested that the high variability in the origin of organic matter in mangrove sediments may significantly influence the overall carbon pathways in these ecosystems.

Introduction

Intertidal mangrove ecosystems are an important interface for the carbon cycle in some tropical coastal environments. The most extensive areas of mangrove forests occur on sedimentary shorelines, where large rivers discharge in low gradient coastlines. They can have high net primary production rates, and under certain conditions may export organic carbon to the adjacent aquatic environment either as leaf litter, particulate or dissolved organic matter (reviewed by Lee 1995). On the other hand, mangroves enhance sedimentation of suspended matter during flooding and thus may act as a sink for allochtonous material (e.g. Furukawa et al. 1997). Sedimentation rates in mangrove forests are difficult to measure, and although in some cases rates of up to 10 mm/yr have been reported, they are estimated to be usually less than 5 mm/yr (Twilley et al. 1992, Ellison 1998). Although a number of studies have recently investigated the -possible- outwelling of organic matter (e.g. Dittmar et al. 2001) and its potential fate in the aquatic environment (e.g. Bouillon et al. 2000, 2002a, i.e. Chapters 5 and 6) or in the sedimentary record of adjacent ecosystems (Kuramoto & Minagawa 2001, see also Chapter 6), very little attention has been given to possible 'inwelling' of organic matter, even though some authors have suggested that this might be one of the sources of the nitrogen enrichment observed in many mangrove sediments (Morell and Corredor 1993, Kazungu 1996, Middelburg et al. 1996).

Mangrove ecosystems are able to store large amounts of organic carbon (e.g. Matsui 1998, Fujimoto et al. 1999) and in some mangrove ecosystems organic-rich sediments of several meters depth have been found (e.g. Twilley et al. 1992, Lallier-Verges et al. 1998). The sources of organic carbon stocks in mangrove sediments have rarely been studied in detail, although this should be an important factor when constructing any carbon budget of mangrove ecosystems.

A recent study we conducted in an east Indian mangrove forest indicated that mangrove leaf litter was not the dominant carbon source for most benthic invertebrate species in the intertidal zone (Bouillon et al. 2002b, i.e. Chapter 8). It was suggested that this may not be a general feature of mangrove ecosystems yet might be related to e.g. the sources of organic matter in the sediment available for higher consumers. Also, Lee (1999) recently argued that more research attention should focus on the interplay between physical and biotic influences in the ecology of mangrove

ecosystems. A prime example of this interaction is provided by sediment organic carbon dynamics, as the amount and origin of organic carbon in mangrove sediments should be influenced by both physical (e.g. tidal amplitude) and biological (e.g. consumption, removal, degradation) factors, and may in turn influence the quality and availability of food sources for benthic faunal communities. In this paper, we discuss the variabiltity of sedimentary organic carbon sources in different mangrove ecosystems for which we expected to find large differences in the stocks and sources of organic carbon, and argue that this may be a key factor in some aspects of mangrove ecosystem functioning which deserves further research. In addition, a literature compilation of data related to the sources and stocks of organic matter in mangrove sediments provides some insights into the relative occurrence of the different conditions encountered.

Materials and Methods

Study areas

Surface sediment samples were collected in three different vegetation zones in the Coringa Wildlife Sanctuary (hereafter referred to as CWS) located in the Godavari Estuary along the Bay of Bengal coast (between 82°15' and 82°22' E, 16°43' and 16°52' N), i.e. an *Avicennia officinalis* fieldplot, an *Excoecaria agallocha* fieldplot (both sampled at approximately monthly intervals during 1996 and early 1997), and a mixed *Avicennia-Excoecaria* zone (sampled in November 1999). More details on these sites and a general description of the area can be found in Dehairs et al. (2000) and in Chapters 3 and 8. Briefly, the mangroves in this area are located in the estuary of the Gautami Godavari, the northern branch of India's second largest river which opens into the Bay of Bengal on the east coast of India in the state of Andhra Pradesh. Tidal amplitude in the coastal zone varies between 0.5 and 2 meters.

Two sites along the south-west southwestern coast of Sri Lanka were also selected for sampling of sediments in November 1999 : the basin/riverine forest in Unawatuna-Galle (06°01'N – 80°14'E), covering an area of about 1.5 km², and the fringing mangroves (~3.5 km²) at Pambala-Chilaw lagoon (07°35'N – 79°47'E). In Galle, sediments were taken from a mixed *Rhizophora mucronata* - *R. apiculata* zone and from an *E. agallocha* zone, whereas in Pambala, both *Rhizophora* spp. and *A. officinalis* zones were sampled. Tidal amplitude at both sites is very low (< 1 m) and

rarely exceeds 15 cm in a 7-day period. More detailed descriptions of these sites can be found in Dahdouh-Guebas et al. (2000) and Dahdouh-Guebas (2001).

Sampling and analytical techniques

All surface sediment samples (up to 5 cm depth) were collected by hand and were cleared from large debris and shell remains. Sediments were dried at 60 °C for 24-48 hours and ground to a fine powder using a mortar and pestle. All samples were acidified with dilute (5 %) HCl before analysis to remove carbonates, as described by Nieuwenhuize et al. (1994). Mangrove leaves were collected by hand, washed, and dried at 60 °C for 48-72 hours. Leaf samples contain 1 leaf/sample, but as the inter-leaf variability showed to be relatively small, pooled samples of 10 leaves were chosen in some cases.

Concentrations of organic carbon, total nitrogen, and elemental ratios (C/N) were determined by combusting preweighed samples in a Carlo Erba NA-1500 Elemental Analyser, and acetanilide (Merck) was used for calibration. All samples for carbon stable isotope analysis were combusted in a Carlo Erba NA-1500 Elemental Analyser, and the resulting CO_2 was cryogenically separated using a manual extraction line. Stable isotope ratios were determined on a Finnigan Mat Delta E Isotope Ratio Mass Spectrometer, and are expressed relative to the conventional standard (PDB limestone) as δ values, defined as :

$$\delta^{13}C = \frac{X_{sample} - X_{standard}}{X_{standard}} * 10^3 \qquad [‰]$$

where $X = {}^{13}C/{}^{12}C$. Internal reference materials included IAEA-C6 (sucrose) and IAEA-CH-7 (polyethylene). The standard deviation of $\delta^{13}C$ for ten aliquots of the same sample was lower than 0.2 ‰.

Results

Elemental and stable isotope composition

Data on organic carbon content (% OC), elemental ratios (C/N, atom), and carbon stable isotopic composition ($\delta^{13}C$) of sediments from the three study sites are shown in Fig 1 and 2. Overall, the organic carbon content of mangrove sediments was found to vary over almost two orders of magnitude (0.6 to 31.7 %), and C/N ratios varied between 7.0 and 27.3. Carbon stable isotope ratios showed a ^{13}C-enrichment relative to the average mangrove leaf material of the specific sites (Figure 1, Table 1), and varied between -29.4 and -20.6 ‰. Sediments under *Rhizophora* spp. showed a much higher OC content than under *Excoecaria agallocha* (in Galle) or *Avicennia* spp. (in Pambala). Organic carbon content in sediments from the Coringa area was much lower than that found in the two Sri Lankan mangrove forests. Lower concentrations of organic carbon and low C/N ratios coincided with less negative $\delta^{13}C$ values, whereas sediments rich in organic carbon and with higher C/N ratios had $\delta^{13}C$ values which are much closer to those of the mangrove vegetation (Figure 1A, B).

Differences in leaf $\delta^{13}C$ between sites and species were also found, with *Rhizophora* spp. from Galle being most ^{13}C-depleted with an average value of -31.5 ± 1.4 ‰ (Table 1).

Table 1 : Carbon isotopic composition of mangrove leaves from the different study sites (average ± 1 s.d.). Number of samples are indicated between brackets.

Site/species	$\delta^{13}C$
CORINGA WILDLIFE SANCTUARY	
Various species (n=27)	-28.5 ± 1.5 ‰*
GALLE	
Rhizophora apiculata (n=9)	-31.5 ± 1.4 ‰
Excoecaria agallocha (n=4)	-28.1 ± 2.0 ‰
PAMBALA	
Avicennia officinalis, pooled leaves (n=10)	-30.5 ‰
Rhizophora apiculata, pooled leaves (n=10)	-29.3 ‰
Rhizophora apiculata (n=4)	-29.1 ± 1.2 ‰
Rhizophora mucronata, pooled leaves (n=10)	-31.0 ‰
Rhizophora mucronata (n=4)	-31.3 ± 0.9 ‰

* : see Chapter 8.

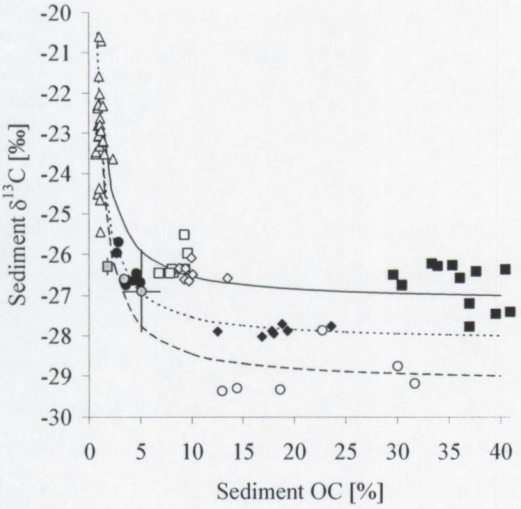


Figure 1 A : $\delta^{13}C$ (in ‰) of organic carbon versus organic carbon content (% dry weight) of surface sediments from various mangrove ecosystems. Open triangles represent data from the Coringa Wildlife Sanctuary, full circles : *Excoecaria agallocha* zone (Galle), open circles : *Rhizophora* spp. zone (Galle), open diamonds : *Avicennia* spp. zone (Pambala), full diamonds : *Rhizophora* spp. zone (Pambala), open squares : data from Kazungu (1996), grey square : data from Dittmar & Lara (2001), and black squares : data from Lallier-Verges et al. (1998), grey-filled circles : data from Jennerjahn & Ittekkot (2002). Error bars : 1 s.d. Different curves correspond to different assumptions for $\delta^{13}C$ and organic carbon content for the two end-members (see text for details).

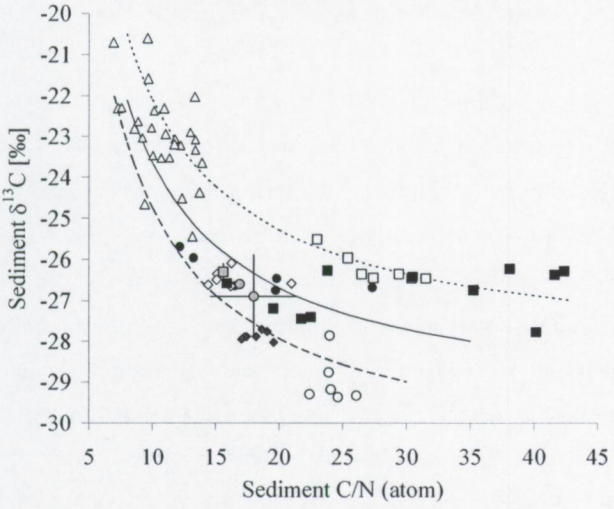


Figure 1 B : $\delta^{13}C$ (in ‰) of sediment organic carbon versus C/N (atom) ratios of sediments from various mangrove ecosystems. Symbols as in Fig 1A. Error bars : 1 s.d. Different curves correspond to different assumptions for $\delta^{13}C$, organic carbon content, and C/N ratios for the two end-members (see text for details).

Discussion

$\delta^{13}C$ values of organic carbon in 'peaty' mangrove sediments (such as those in the *Rhizophora* zones at the two Sri Lankan sites) were relatively similar to that of the mangrove vegetation and showed high C/N ratios between 17 and 25, whereas organic matter in 'mineral' sediments such as those from the Coringa area is enriched in ^{13}C by up to 8.5 ‰ and showed C/N ratios of on average about 10 but sometimes as low as 7.0 (Figure 1B). Other organic carbon-rich sediments such as those described by Lallier-Verges et al. (1998) and McKee et al. (2002) have also been shown to display high C/N ratios (up to 43) and $\delta^{13}C$ values close to that of the mangrove vegetation. The organic matter stocks in these systems can be extremely high : when assuming a carbon content of 40 % (dry weight) for mangrove organic matter (e.g. Lallier-Verges et al. 1998), some of the *Rhizophora* sediments from Galle (Figure 1A) can be estimated to consist of up to 75 % organic matter. On the other extreme, Machiwa (2000) found a distinct gradient in $\delta^{13}C$ in a mangrove ecosystem in Zanzibar, where sediments on the marine fringe showed $\delta^{13}C$ values of -17.6 ± 0.8 ‰, but lower values of -24.3 ± 1.1 ‰ in the landward zones. The more enriched values were attributed to inwelling of marine organic matter, including relatively ^{13}C-enriched seagrass material. An enrichment in ^{13}C of the sediment organic matter has also been recorded in other mangrove sediments (e.g. Hemminga et al. 1994, Kazungu 1996).

When combining the data from the three study sites, it appears that there is an inverse relationship between the organic carbon content and the corresponding $\delta^{13}C$ values (Fig 1A) and between the sediment C/N ratios and the corresponding $\delta^{13}C$ values (Fig 1B). Middelburg et al. (1997) found a similar OC % - $\delta^{13}C$ relationship in sediments from temperate salt marsh ecosystems, with sediments low in organic carbon reflecting allochtonous sources and organic-rich sediments having $\delta^{13}C$ values close to the dominant vegetation (Fig 2, note that in the case of saltmarshes the vegetation - seagrasses- is enriched in ^{13}C relative to allochtonous sources). Following the approach of Middelburg et al. (1997), two-end mixing curves were constructed to describe the relationship between sediment $\delta^{13}C$ values and the corresponding OC % and C/N values, and these are represented in Figure 1 by the full and dotted curves (the different curves represent different values for the input parameters).

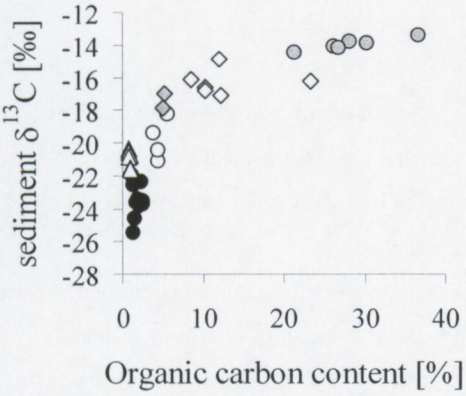


Figure 2 : $\delta^{13}C$ (in ‰) of organic carbon versus organic carbon content (% dry weight) of surface sediments from various salt marsh ecosystems. Adapted from Middelburg et al. (1997).

By defining an autochtonous component, i.e. mangrove litter, and an allochtonous component (suspended particulate matter), we can calculate the $\delta^{13}C$ values of sediments for a given OC % or C/N ratio as follows (see Appendix for details). First, we calculate the fraction of the *organic carbon*, $X_{mangroveC}$, as :

$$X_{mangroveC} = \left(\frac{C_{mangrorve}}{C_{sediment}}\right) * \left(\frac{C_{sediment} - C_{allocht}}{C_{mangrove} - C_{allocht}}\right) \qquad 0 < X_{mangroveC} < 1 \qquad [1]$$

Where $C_{sediment}$, $C_{allocht}$, and $C_{mangrove}$ are the organic carbon content of the sediment, the allochtonous component, and mangrove-derived organic matter, respectively (in g/g dry weight).

Secondly, we calculate the expected $\delta^{13}C$ of the sediment organic matter, $\delta^{13}C_{sediment}$ (expressed in ‰), as :

$$\delta^{13}C_{sediment} = X_{mangroveC} * \delta^{13}C_{mangrove} + (1-X_{mangroveC}) * \delta^{13}C_{allocht} \quad [2]$$

where $\delta^{13}C_{mangrove}$ and $\delta^{13}C_{allocht}$ are the carbon isotopic composition of mangrove-derived organic matter and the allochtonous component, respectively. Similar equations were derived for the relationship between sediment C/N (atom) ratios and sediment $\delta^{13}C$ values (see details in Appendix).

Some of the parameters used in constructing these two-source mixing curves are, of course, subject to significant variability. C/N ratios of mangrove leaf litter (and other components) are variable, and will depend on factors such as the nutrient status, the degradation stage and the species considered (e.g. Twilley et al. 1986, Dehairs et al. 2000). The suspended organic matter in mangrove creeks and nearshore waters may have a wide range of $\delta^{13}C$ signatures and C/N ratios (Cifuentes et al. 1996, Bouillon et al. 2000), but is on average more ^{13}C-enriched than the mangrove-derived carbon. In our mixing curves (Figure 1), we have used a value between -23.0 and -20.5 ‰ in order to account for the observed variability, and although $\delta^{13}C$ are expected to be lower in some cases (e.g. Bouillon et al. 2000, 2002a), this would not change the general trend of the mixing curves and its consistence with the data – except for the samples with the most enriched $\delta^{13}C$ values. C/N ratios of suspended particulate organic matter are usually much lower than those of mangrove litter, e.g. in the Coringa area suspended matter was shown to have C/N ratios of on average 8-10 (Dehairs et al. 2000). The suspended matter usually consists of a large, but variable, fraction of inorganic material (e.g. Twilley et al. 1992, Wolanski et al. 1998, Tanaka et al.1998). Using the data of Dehairs et al. (2000) and Murthy (1997), the POC contribution to suspended matter in our study area in the CWS is estimated to be -on average- between 1.8 and 3.7 %. As sedimentation results in the preferential deposition of inorganic material, we have used slightly lower values to construct our mixing curves.

Notwithstanding these sources of variability in our end-members, the general trend of the curve remains similar when the values of the end-member parameters are slightly modified, as represented by the different curves in Figures 1A and 1B ($\delta^{13}C_{allocht}$

between -23.0 and -20.5 ‰, $\delta^{13}C_{mangrove}$ between -29.0 and -27.0 ‰, sediment OC between 0.8 and 1.5 %, $C/N_{mangrove}$ between 30 and 43). Thus, the two-source mixing model appropriately describes our dataset, and the available literature data (Kazungu 1996, Lallier-Verges et al. 1998, Dittmar & Lara 2001, Jennerjahn & Ittekkot 2002) also fit in this pattern, confirming the validity of the model. Note, however, that one group of data have not been included in Figure 1, i.e. the data for *Ceriops* sediments presented by Kazungu (1996) from Gazi Bay (Kenya), as *Ceriops* at this site has markedly higher $\delta^{13}C$ values (~ -24.1 ‰, see e.g. Kazungu 1996 and Middelburg et al. 1997) than the average for mangrove litter. Therefore, these data plot out above the proposed mixing curves. Similarly, if seagrass litter is an important component of the suspended organic matter pool, the end-member values used for imported organic matter sources will need to be adapted.

Although organic carbon in sediments from some intertidal mangrove ecosystems, such as in the *Rhizophora* zones of the two Sri Lankan sites studied and the one described by Lallier-Verges et al. (1998), must be almost entirely of mangrove origin, our data show that this is clearly not a general feature. In fact, the data from the Coringa area indicate that organic matter in the sediments originates mainly from the water column suspended matter (a tentative estimate of $\geq$ 80 % is made in Chapter 10, p. 295-296), and phytoplankton-derived matter is presumably a major fraction of this material (Bouillon & Dehairs 2000, i.e. Chapter 5). In other words, there appear to be large differences in carbon dynamic between 'flow-through' systems where exchange of organic carbon (both import and export) between the intertidal regions and the adjacent aquatic environment is possible, and more closed 'accumulation' systems where local mangrove production accumulates in the underlying sediments. When considering the relatively high tidal amplitude in the Coringa area, and the very low tidal amplitude in the two Sri Lankan sites and the Guadeloupan site studied by Lallier-Verges et al. (1998), it becomes clear that this may be an important factor determining the stocks and sources of organic carbon in intertidal mangrove sediments. Naturally, other factors may also play a major role, e.g. the removal rate of litter by crabs, and the microbial degradation rate. With respect to the latter, it is noteworthy that in the case of the CWS, microbial degradation rates have been shown to be relatively high compared to most literature data, whereas litter fall rates are

within the normal range for this latitude (see Chapter 2, Figure 3 and discussion thereof).

One last factor to consider is that organic matter of mangrove origin has not explicitly been specified in the above discussion. Although it may be tempting to ascribe the accumulation of mangrove-derived organic matter to leaf litter inputs, Middleton & McKee (2001) recently stressed the importance of root material in the formation of mangrove peat, due to the much more refractory nature of the latter.

Very little information exists on the contribution of bacterial biomass or local primary producers such as benthic microalgae and cyanobacteria to the sediment organic matter pool. Gillan & Hogg (1984) estimated the bacterial carbon stock in Hinchinbrook Island (Australia) at 23-81 μg g^{-1} (46-162 μg of biomass). In combination with the organic carbon data of Alongi (1996) and Alongi et al. (1999) from the same region, the contribution of bacterial and diatom carbon to the total sediment organic carbon pool can be estimated roughly at 1.0 and 0.2 %, respectively. Interestingly, both total OC stocks (Alongi 1996) and bacterial carbon stocks (Gillan & Hogg 1984) appeared to increase to a similar degree from the creek banks to the high intertidal (note that this trend of higher organic carbon stocks in the high intertidal is also consistent with our mixing model, as less suspended matter with a low carbon content will reach the upper shore levels).

For the CWS, some preliminary concentration data of phospholipid-derived fatty acids (PLFA) gathered in the framework of this study (not presented in detail) resulted in an estimated live bacterial carbon stock of ~ 45 μg C g^{-1}, which is within the range reported by Gillan & Hogg (1984) and which suggests that live bacterial biomass accounts for approximately 0. 5 % of the total organic carbon content of the sediment in the CWS (note, however, that the method used by Gillan & Hogg to estimate bacterial standing stocks from the PLFA profile was different than the one used by us, i.e. as in Middelburg et al. 2000).

Due to the limited number of studies which have simultaneously reported $\delta^{13}C$ values and OC and/or C/N data from mangrove sediments, Figure 1 holds little information on the relative occurrence of the different situations encountered. However, $\delta^{13}C$ alone or a combination of the latter two parameters (i.e. OC and C/N data) have been much more frequently measured in mangrove ecosystems, and the distribution of these data (compiled from literature sources and this study) have been compiled in

Figure 3 ($\delta^{13}C$), 4 (organic carbon content), and 5 (C/N, atom). Although such compilations hold the potential to be biased towards those types of ecosystems or those geographical regions where more research has been undertaken, we believe that both the number of studies and the number of data compiled should result in a fairly representative distribution of data.

Thus, Figure 3 shows that approximately half of the $\delta^{13}C$ data are lower than -26 ‰, and thus suggest a predominant input of mangrove litter (although other ^{13}C-depleted sources may exist). On the other hand, a significant amount of data are relatively high (> -23, up to -17.3 ‰) and indicate significant inputs of imported (phytoplankton, seagrasses in some ecosystems) and possibly local (microphytobenthos) carbon sources. Figure 4 reveals a somewhat unexpected pattern. Although mangrove ecosystems are usually considered as being major sites for belowground carbon storage, the number of mangrove ecosystems with a markedly high content of organic carbon appears to be fairly limited (e.g. data from Lallier-Verges et al. 1998, Chen & Twilley 1999a,b, Fujimoto et al. 1999, this study), with the vast majority of data showing a low carbon content (e.g. 47 % of samples have less than 2.5 % organic carbon, a further 29 % have values between 2.5 and 7.5 %). This is in agreement with the general observation that most mangrove forests (or, at least, the largest surface areas) occur on sedimentary coastlines in large estuaries and deltas. In such cases, deposition of suspended matter (mainly inorganic, but containing non-local organic matter sources) brought in by tides or rivers is a general feature. Thus, although the situation observed in the CWS (Figure 1A) appears to be an extreme one, such a situation might actually be quite widespread, if we take the data distribution presented in Fig 4 to be relatively unbiased.

The distribution of C/N (atom) ratios (Figure 4) shows approximately half the data have C/N ratios lower than 17, with the majority of all data between 5 and 30. Assuming that C/N ratios lower than 10 are a strong indication for a major contribution of non-mangrove sources, this is found in 34 % of the data. On the other hand, very high C/N ratios (> 30, only a limited number of sites show such values) clearly indicate that the sediment organic matter (SOM) pool consists entirely or almost entirely of mangrove litter. The intermediate C/N ratios (15-25), however, are difficult to interpret and might reflect either pure mangrove litter in an advanced stage of decomposition, or a variable contribution by other carbon sources.

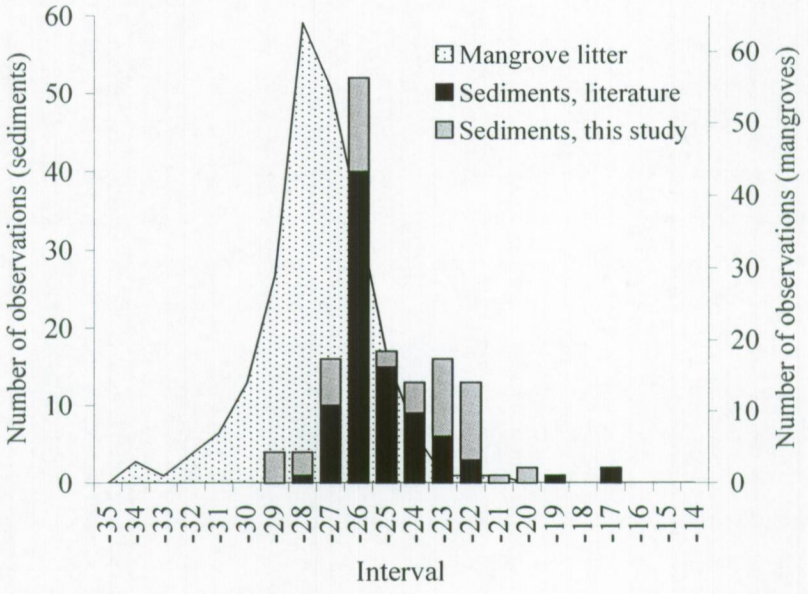


Figure 3 : Distribution of $\delta^{13}C$ data of mangrove leaves (right axis, updated from Bouillon et al. 2002b i.e. Chapter 8) and intertidal mangrove sediments (left axis) from published literature sources (black bars) and this study (grey bars). Indicated $\delta^{13}C$ value on X-axis corresponds to the upper level of the interval. Total number of sediment $\delta^{13}C$ data is 141. Literature sources for sediment $\delta^{13}C$ data : Fry (1984), Rodelli et al. (1984), Lacerda et al. (1986), Ambler et al. (1994), Hemminga et al. (1994), Kazungu (1996), Dittel et al. (1997), Loneragan et al. (1997), France (1998), Lallier-Verges et al. (1998), Machiwa (2000), McKee et al. (2002), Dittmar & Lara (2001c), Hsieh et al. (2002), Jennerahn & Ittekot (2002), E. Olaffsón & M. Skov (unpublished data).

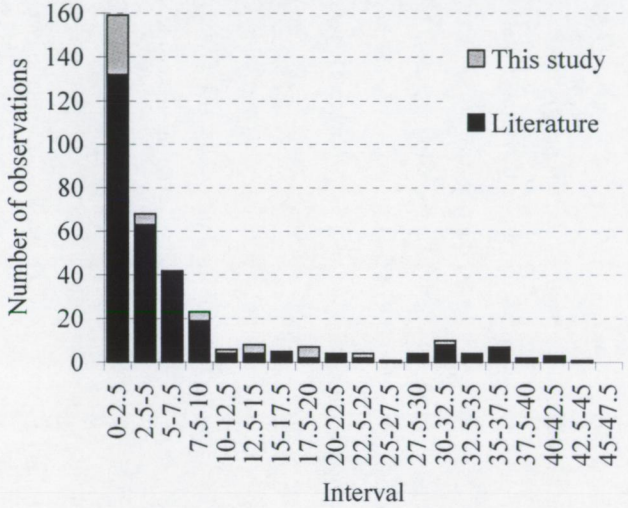


Figure 4 : Distribution of data on the organic carbon content (% on dry weight basis) of intertidal mangrove sediments from published literature (black bars) and this study (grey bars). Total number of data is 358. Literature sources, in alphabetical order : Alongi (1996), Alongi et al. (1993, 1999, 2000a, b, 2001), Chen & Twilley (1999), Dittmar & Lara (2001), Gillikin (2001), Hemminga et al. (1994), Jennerjahn & Ittekot (1997, 2002), Kazungu (1996), Kristensen et al. (1988, 1992, 2000), Lacerda et al. (1995), Lallier-Verges et al. (1998), Matsui (1998), McKee et al. (2002), Middelburg et al. (1996), Mfilinge et al. (2002), E. Olaffsón & M. Skov (unpublished data), Perrussel et al. (1999), Twilley et al. (1997), Holmer et al. (2001), Woodroffe (1985).

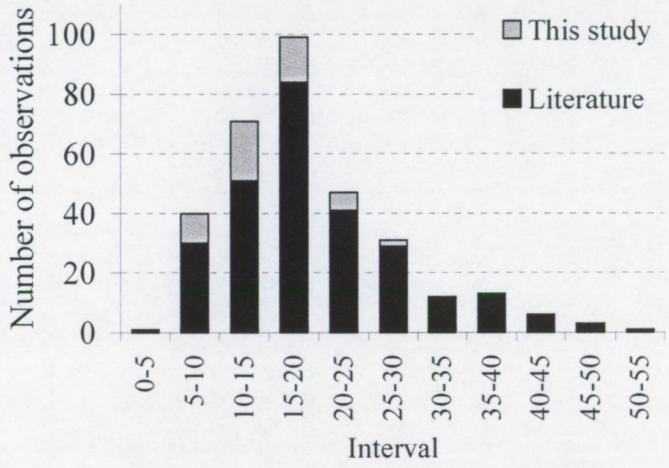


Figure 5 : Distribution of data on the elemental composition (C/N, atom) of organic matter in intertidal mangrove sediments from published literature (black bars) and this study (grey bars). Total number of data is 324. Literature sources, in alphabetical order : Alongi (1996), Alongi et al. (1993, 1999, 2000a, b), Chen & Twilley (1999), Dittmar & Lara (2001), Gillikin (2001), Jennerjahn & Ittekot (1997, 2002), Kazungu (1996), Kristensen et al. (1988, 1992, 2000), Lacerda et al. (1995), Lallier-Verges et al. (1998), McKee et al. (2002), Middelburg et al. (1996), Mfilinge et al. (2002), E. Olaffsón & M. Skov (unpublished data), Perrussel et al. (1999), Twilley et al. (1997), Holmer et al. (2001), Woodroffe (1985).

Such large variations in availability and sources of organic matter can be expected to have major consequences for the overall carbon pathways in intertidal mangrove forests. For instance, Boschker et al. (1999) showed that the contribution of local plant material to bacterial production in sediments was of little importance in 'mineral' salt marshes (i.e. those with low organic carbon content), but dominant in 'organic' salt marshes (i.e. systems where local plant production accumulated to form organic-rich sediments). It thus appears that carbon sources used by bacteria in intertidal ecosystems do not necessarily originate from the dominant local vegetation (Boschker et al., 2000), but that algal sources are preferred when available. Although there is as yet no direct evidence, it is possible that a similar situation occurs in mangrove sediments. Some circumstantial evidence for the latter was recently provided by Alongi et al. (2001), who found a correlation between the rate of total carbon mineralization with sediment accumulation rates, but not with mangrove primary productivity, suggesting that selective degradation of imported carbon sources may take place. Many invertebrates in mangrove environments feed -selectively or not- on the sediment organic matter (e.g. Bouillon et al. 2002b i.e. Chapter 8, Skov & Hartnoll 2002), and the often assumed close link between mangrove primary production and the invertebrate community may not be valid in flow-through ecosystems where mangrove litter is not a major component of sediment organic matter. A recent study on resource utilisation by benthic invertebrates in the Coringa area using on carbon and nitrogen stable isotope ratios as natural tracers (see following Chapter) showed that incorporation of mangrove-derived carbon was detectable in only a limited number of species, whereas the majority of invertebrates did not show significant assimilation of mangrove-derived carbon. In this context, it is worth noting that several authors have mentioned that organic matter should have a C/N ratio lower than 17 in order to be of nutritional use to invertebrates (Russel-Hunter 1970). As can be seen in Figure 1B, this would imply that bulk sediment organic matter can only be of importance where allochtonous sources contribute to the sediment pool. Several authors have drawn attention to the fact that mangrove leaf litter is of little nutritional value due to its high C/N ratios -even after considerable degradation- (e.g. Micheli 1993a,b, Lee 1997) and the relatively N-rich material deposited during high tides may offer some invertebrates an easily accessible N-source. In addition, high C/N ratios are not conducive to microbial degradation (a C/N ratio of 10 is often quoted as necessary for growth) but despite this, recent

experimental studies showed that bacterial acitivities in mangrove (and salt marsh) sediments were largely unaffected by nutrient (ammonium, phosphate) additions (Holmboe et al. 2001). Although this may appear to suggest that ammonium and phosphate released during decomposition were adequate to meet the growth requirements of the microbial population (Holmboe et al. 2001), the significant DIN fluxes towards the sediment at the interface found in most studies suggest that assimilation during microbial degradation results in the net uptake of DIN and a rapid and efficient DIN cycling (see Kristensen et al. 2000). Thus, other elements than N or P may have been responsible for the absence of any effects on bacterial activities in the experiments of Holmboe et al. (2001).

MANGROVES AND SALT MARSHES : SOME SIMILARITIES AND DIFFERENCES IN CARBON DYNAMICS

> *'Marshes and mangroves fulfill nearly identical roles, but [...] the differences in their structural and functional attributes outweigh their similarities.'* (Alongi 1998)

Whereas mangrove forest are entirely restricted to the tropical and subtropical zones, their place in the temperate regions is taken in by salt marsh ecosystems. The most obvious difference between the two is that mangroves are mostly trees which can attain considerable height, whereas salt marsh vegetation is dominated by grasses and small shrubs, often only a few centimetres high and only exceptionally above 2 meters high. As both occur in the intertidal on the interface between land and sea and are characterized by the visual dominance of vascular plants, many basic ecological questions on ecosystem functioning and the interaction with the adjacent aquatic environment are similar and have been a longstanding issue of debate. Both ecosystems are also an extremely important component of the coastal zone, as they protect agains coastal erosion, and may form an important habitat or nursery ground for a variety of aquatic lifeforms.

• BIOMASS AND PRODUCTIVITY

Although standing stocks of biomass in salt marshes are about an order of a magnitude lower than those of most mangroves, their above-ground productivity is strikingly comparable despite the variability found in both ecosystems (e.g. see Twilley et al. 1992, Middelburg et al. 1997, Bouchard et al. 1998). As with mangroves, there is a tendency for productivity to decline with increasing latitude, and with salinity (Hogarth 1999).

• FATE OF VASCULAR PLANT PRODUCTION

Lee (1995) points out some important characteristics of mangrove and salt marsh ecosystems which may influence the proportion of the local production available for export, and according to Duarte & Cebrián (1996) the fate of salt marsh production differs from that of mangroves, in the sense that in salt marsh ecosystems, direct herbivory generally is more important, a larger proportion local production is retained within the ecosystem and less exported, as shown in Table 2. However, as the data presented in Duarte & Cebrián (1996) are based on a limited number of studies, in which not all parameters discussed were concurrently estimated, they may be severely biased – considering the variability we can expect in both ecosystems (e.g. in the export rates, the degree of litter removal by crabs, etc...)

Alongi et al. (2000a) suggested that the variable, but relatively low ratios of total sediment respiration to forest net primary production (T_{COX}/NPP between 3 and 28 %) they found in several mangrove ecosystems indicate that mangrove forests are highly efficient in sequestering labile carbon in sediment pools. They compared T_{COX}/NPP ratios with a limited number of data from 4 North American salt marsh ecosystems (T_{COX}/NPP between 40 and 89 %), and concluded that mangroves are more efficient at immobilizing and conserving organic carbon. However, the salt marshes along the American coastline differ strongly from their European counterparts in the proportion of local vascular plant production that is retained in the sediments (see Middelburg et al. 1997 and Boschker et al. 1999), and our data show that mangroves may show an equal variability in the contribution of mangrove carbon in the SOM pool. Therefore, the suggestion of Alongi et al. (2000a) may not be universally valid. Indeed, Middelburg et al. (1996) measured total CO_2 fluxes in the sediments of Gazi Bay (Kenya), and found average fluxes of 192.6 and 92.6 mmol C m^{-2} d^{-1} for

Table 2 : Some major differences and similarities between mangroves and salt marsh ecosystems. SOM : sediment organic matter pool.

	MANGROVES	SALT MARSHES
• Biomass	high	lower (1 order of magnitude)
• Productivity	similar	
FACTORS INFLUENCING EXPORT POSSIBILITIES		
• Fate of senescent plant biomass [A]	abscised, thus higher chance of export	retained, decomposed *in situ*
• Turnover of component which can be exported [A]	high, higher export possible	lower, lower degree of export possible
• Tidal regime [A]	usually stronger tidal energy	mostly with weak tidal energy, lower export
• Litter quality [A]	high levels of secondary compounds, low utilization by detritivores	lower level of secondary compounds, easier utilization by detritivores
RELATIVE FATE OF LOCAL VASCULAR PLANT PRODUCTION		
• Eaten by herbivores [B]	9.1 %	31.3 %
• Exported [B]	29.5 %	18.6 %
• Decomposed within the system [B]	40.1 %	51.2 %
• Stored in sediments [B]	10.4 %	16.7 %
MISCELLANEOUS		
• Relative importance of local production in the SOM pool [C]	very variable	very variable
• Stocks and nutritive quality of SOM [C]	very variable	very variable
• Relative importance of local production to intertidal foodwebs [D]	contradictory results, but contribution by microaglae appears important	contradictory results, but contribution by microaglae appears important
• Bacterial biomass on plant detritus [E]	minimal (< 1 mg g^{-1})	minimal (< 1 mg g^{-1})
• Fungal biomass on plant detritus [E]	minimal (< 5 mg g^{-1})	significant, up to 200 mg g^{-1}

[A] : adapted from Lee (1995)

[B] : adapted from Duarte & Cebrián (1996). As the data on the relative fate of vascular plant production are percentages which are an average of several independent estimates, they do not necessarily total 100 %. See also Chapter 10 for estimates by Jennerjahn & Ittekot (2002).

[C] : see Middelburg et al. (1997) and this chapter

[D] : see Chapter 8 for a detailed discussion

[E] : see Newell (1996). Note, however, that for mangroves, most data are from submerged litter -not from intertidal litter- and the situation in the latter case may be quite different.

Ceriops and *Rhizophora* sediments, respectively. If we compare these with the litterfall estimates provided by Slim et al. (1996) for the same area (average of results for rainy season and dry season : 1.05 and 2.51 g m^{-2} day^{-1}, which amounts to 39.4 and 94.1 mmol C m^{-2} d^{-1} for *Ceriops* and *Rhizophora*, respectively), it becomes apparent that for the *Ceriops* sediments, the total CO_2 flux from the sediments appear to exceed substantially (> 450 %) the litter inputs, whereas for *Rhizophora* the total sediment respiration is as large as 98 % of the total litterfall. Although it should be noted that the different results may in part have been caused by the different methods used to measure CO_2 fluxes (see Kristensen et al. 1991), the latter estimates clearly suggest that the choice of study sites may have biased the suggestion of Alongi et al. (2000a). Jennerjahn & Ittekkot (2002), however, recently estimated that mangrove carbon accumulating in mangrove sediments was ~ 23 x 10^{12} g C y^{-1}, which would amount to about 15 % of the organic carbon accumulating in modern marine sediments. As the latter authors based their estimates on the fact that (1) mangroves have low T_{COX}/NPP ratios, (2) that leaves are the dominant source of carbon to the SOM pool in mangrove sediments, and (3) that an estimated 25 % of mangrove production accumulates in the sediment, we feel this estimate may be somewhat high (see Chapter 10 for a more detailed discussion).

The isotopic evidence provided by this study and by Middelburg et al. (1997) is also in contradiction with the generalised hypothesis that mangroves store a larger amount of their production in sediments than salt marsh ecosystems : in both types of ecosystems, there are cases in which local production forms the bulk or the SOM pool (thereby at least suggesting that sediment burial is a substantial sink of local production), but there are also cases in which local production represents only a minor contributor to the SOM pool, indicating that storage of plant production in sediments is only a minor fate.

In the literature compilation by Cebrián (2002), the plots of primary production data *verus* accumulation rate (Fig 2h in Cebrián 2002) for mangroves and salt marhes are nearly identical, suggesting that overall, the proportion of primary production being stored in the sediment is generally not very different. Note, however, that the analysis by Cebrián (2002) should be interpreted with care, as the log-transformed data used in his study can be somewhat misleading, i.e. it is suggested that carbon preservation (i.e. accumulation rates) are dependent on primary production rates although this is not evident from the raw data set (http://www.aslo.org/lo/toc/vol_47/0011a1.pdf) and the number of concurrent data might be too limited to draw conclusions on such relationships.

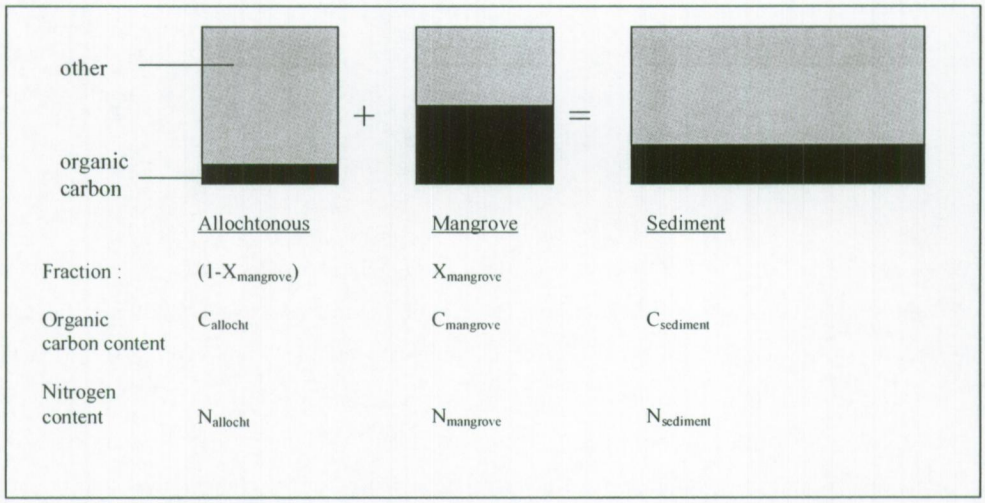
Finally, a number of stable isotope studies have shown convincing evidence that the trophic significance of local vascular plant production in salt marsh ecosystems appears to be more limited than initially thought (e.g. Sullivan & Moncreiff 1990, Currin et al. 1995, France 1995, Page 1997, Créach et al. 1997, Riera et al. 1999, Kharlamenko et al. 2001, Kurata et al. 2001), and benthic microalgae and possibly imported phytodetritus were shown to be important food sources for many intertidal invertebrates. Similarly, the relative role of mangrove litter and other primary producers may need to be re-evaluated (see Bouillon et al. 2002a, i.e. Chapter 8 for a more detailed discussion).

• GAPS IN THE CURRENT KNOWLEGDE

In conclusion, many of the processes involved in organic carbon cycling appear to show a number of striking similarities (and similar variability) in mangrove ecosystems and salt marhes. However, much of the work on microbial aspects of carbon cycling in intertidal habitats (e.g. biomass & productivity of fungi, carbon sources used by bacterial populations) have only been carried out in salt marsh ecosystems, and comparative data from a variety of mangrove ecosystems would certainly be valuable. Also, direct comparative studies (i.e. similar methodologies employed in similar settings) may help to elucidate underlying factors which influence the relative pathways of carbon processing and the relative importance of different carbon sources in the SOM pool, as a substrate for microbial growth, and as a food source for invertebrate consumers.

APPENDIX I : TWO-SOURCE MIXING MODEL

We here describe in some more detail the derivation of the equations used to construct the two-source mixing curves.



If we assume that sediments are formed by the contribution of two sources (see scheme), i.e. (1) allochtonous matter imported from the sea or from tidal creeks with a low organic carbon content, and (2) mangrove-derived organic matter with a high organic carbon content, we can describe the organic carbon content of the resulting sediment as :

$$C_{sediment} = X_{mangrove} * C_{mangrove} + (1-X_{mangrove}) * C_{allocht} \qquad [A]$$

Where $C_{sediment}$, $C_{allocht}$, and $C_{mangrove}$ are the organic carbon content of the sediment, the allochtonous component, and mangrove-derived organic matter, respectively (in g/g dry weight). $X_{mangrove}$ is the fraction of the *bulk sediment* which is from mangrove origin.

This rearranges to :

$$X_{mangrove} = \frac{C_{sediment} - C_{allocht}}{C_{mangrove} - C_{allocht}} \qquad [B]$$

Note that :
(1) the fraction $X_{mangrove}$ calculated here is only an intermediate parameter and has little ecological meaning, and
(2) when $C_{sediment}=C_{mangrove}$, then $X_{mangrove} = 1$; when $C_{sediment}=C_{allocht}$, then $X_{mangrove} = 0$.

Once the contribution of mangrove litter to the total sediment pool is known, we can calculate the fraction of the organic *carbon* which is of mangrove origin :

$$X_{mangroveC} = \frac{Amount\_of\_mangrove-derived\_C}{Total\_amount\_of\_sediment\_C} \qquad [C]$$

or :

$$X_{mangroveC} = \frac{X_{mangrove} * C_{mangrove}}{X_{mangrove} * C_{mangrove} + (1 - X_{mangrove}) * C_{allocht}} \qquad [D]$$

Substituting equation [B] into equation [D] results in :

$$X_{mangroveC} = (\frac{C_{mangrorve}}{C_{sediment}}) * (\frac{C_{sediment} - C_{allocht}}{C_{mangrove} - C_{allocht}}) \qquad [E]$$

The latter is then used to calculate the expected $\delta^{13}C$ values of the sediment organic matter (see Discussion, equation [2]) :

$$\delta^{13}C_{sediment} = X_{mangroveC} * \delta^{13}C_{mangrove} + (1\text{-}X_{mangroveC}) * \delta^{13}C_{allocht} \qquad [F]$$

For the mixing model based on C/N ratios and $\delta^{13}C$ ratios of sediments, the equations are derived from :

$$\frac{C_{sediment}}{N_{sediment}} = \frac{X_{mangrove} * C_{mangrove} + (1 - X_{mangrove}) * C_{allocht}}{X_{mangrove} * N_{mangrove} + (1 - X_{mangrove}) * N_{allocht}} \qquad [G]$$

(whereby symbols are as in equation [A], N refers to nitrogen)
Equation [G] rearranges to :

$$X_{mangrove} = \frac{C_{mangrove} - (C/N)_{sediment} * N_{mangrove}}{(C/N)_{sediment} * N_{allocht} - (C/N)_{sediment} * N_{mangrove} - C_{allocht} + C_{mangrove}} \qquad [H]$$

Where $(C/N)_{sediment}$ is the measured C/N ratio of the sediment organic matter.

Subsequently, we derive the fraction of *organic carbon* which is of mangrove origin, i.e. by using equation [C] or [D], and finally the $\delta^{13}C$ values is calculated (equation [F]).

CHAPTER 8 : Primary producers sustaining macro-invertebrate communities in intertidal mangrove forests : unexpected results from stable isotope analysis

Foreword

In the preceding chapters, we have discussed the limited trophic importance of mangrove litter to fauna in the mangrove creeks of the Coringa Wildlife Sanctuary (Andhra Pradesh, India) and the adjacent aquatic ecosystem. We have also pointed out that mangrove carbon was hardly present in subtidal sediments in the Indian study site, and that organic carbon in intertidal surface sediments showed wide variations in the contribution of mangrove litter between different mangrove ecosystems. The following questions therefore arise :

(1) are mangroves a significant source of carbon for the invertebrate communities inhabiting the *intertidal* mangrove habitats (which have a more direct access to mangrove litter) ?

(2) do different species of mangrove invertebrates show significant (trophic) resource overlap, or are there major differences in the food preferences of species ?

This chapter is an attempt to provide some preliminary answers to these questions and is to a large extent based on the following publication :

Bouillon S, Koedam N, Raman AV, & Dehairs F (2002) Primary producers sustaining macro-invertebrate communities in intertidal mangrove forests. Oecologia 130 : 441-448

As a significant amount of additional data were collected after its publication, these data have been integrated here. For reasons of clarity, the limited number of data collected in Sri Lanka will not be discussed in detail but are included as part of the compilation of $\delta^{13}C$ data.

Abstract

In contrast to the large number of studies on the trophic significance of mangrove primary production to the aquatic foodweb, there have been few attempts to provide an overview of the relative importance of different primary carbon sources to invertebrates in the intertidal mangrove habitats. We determined carbon and nitrogen stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) in sediments, primary producers, and 29 invertebrate species from an intertidal mangrove forest located along the southeast coast of India in order to determine the contribution of mangrove leaf litter and other carbon sources to the invertebrate community. Invertebrates in this site were found to display a wide range of $\delta^{13}C$ values, most being 3-11 ‰ enriched relative to the average mangrove leaf signal. Unusually low $\delta^{13}C$ values (between -43.3 and -35.2 ‰) were found in the sacoglossan *Elysia coringaensis* sp. nov., and remarkably low $\delta^{15}N$ values were found for a microepiphyte crust on *Excoecaria* stems (-8.2 ‰) and for the pulmonate gastropod *Onchidium* sp. (-8.7 to -2.7 ‰) which is possibly related to feeding on such epiphytes. Overall, the data suggest a fairly limited use of mangrove litter, and the remarkably wide range of $\delta^{13}C$ and $\delta^{15}N$ signatures indicate a fairly limited degree of resource overlap. A compilation of $\delta^{13}C$ values from various sources confirm that significant assimilation of mangrove-derived carbon is only detectable in a limited number of species, and suggests that local and imported algae are a major source of carbon for benthic invertebrate communities in intertidal mangrove forests. These results provide some new insights into carbon utilization patterns in vegetated tropical intertidal habitats and show a striking similarity with results from temperate salt marsh ecosystems where local plant production has often been found to contribute little to intertidal foodwebs.

Introduction

Tropical mangrove forests may attain high net primary production rates (Clough 1992), and although there remains some uncertainty on the fate of the leaf litter and its role in sustaining adjacent aquatic secondary production, it has become clear that this role has been overestimated in the past (e.g. Lee 1995, 1999, Dehairs et al. 2000, Bouillon et al. 2000, Bouillon et al. 2002a, i.e. Chapters 4-5). For the macro-invertebrate fauna inhabiting the intertidal regions, however, most studies assume or conclude that mangroves are the dominant primary producers sustaining these communities (e.g. Camilleri 1992, Fratini et al. 2000), which are usually dominated - both in terms of numbers and biomass- by brachyuran crabs and gastropods (e.g. Sasekumar 1974, Wells 1984). Few studies have attempted to provide an overall evaluation of different primary carbon sources to the intertidal mangrove invertebrate community, despite the potential importance of these faunal communities in ecosystem carbon dynamics (Robertson et al. 1992) and as food sources for foraging fish during high tide (Sasekumar et al. 1984, Wilson 1989, Sheaves & Molony 2000). Stable isotope analysis can offer valuable insights into the relative importance of different primary producers, but such studies have only rarely been done on mangrove-inhabiting invertebrates (Rodelli et al. 1984, Newell et al. 1995), or have been limited to one or more specific invertebrate species (Slim et al. 1997 for *Terebralia palustris*, France 1998 for *Uca vocator*, Christensen et al. 2001 for three species of *Littoraria*, Hsieh et al. 2002 for *Uca* spp. and 2 polychaetes). The stable isotope approach is based on the assumptions that (i) different primary producers (can) have different $\delta^{13}C$ values because of e.g. different photosynthetic pathways or different inorganic carbon sources, and (ii) a consistent degree of fractionation occurs between the isotopic signature of the diet and that of the consumer. For $\delta^{13}C$, a small or negligible enrichment of on average 0 to 1 ‰ has been found to occur (DeNiro & Epstein 1978, see Vander Zanden et al. 2001). For $\delta^{15}N$, a higher fractionation of on average 2.6 ‰ (Owens 1987) to 3.4 ‰ (Minagawa & Wada 1984) is usually assumed, but the actual degree of fractionation may vary considerably, and several processes have been found to result in deviations from this general pattern (e.g. Scrimgeour et al. 1995).

Sesarmid crabs are known to have a high impact on leaf litter dynamics as they can remove large amounts of leaf litter from the sediment surface and carry it into their burrows (e.g. Twilley et al. 1997, Lee 1998). On the other hand, it appears that many sesarmids are more likely to be omnivores than strict herbivores (e.g. Dahdouh-Guebas et al. 1999). Ocypodid crabs from mangrove forests such as *Uca* spp. have been considered as either bacteria feeders (e.g. Dye & Lasiak 1986, 1987) or microalgal (including cyanobacteria) feeders (Rodelli et al. 1984, France 1998, Hsieh et al. 2002 who also suggested a C_4 plant to contribute locally), and even less is known about the feeding habits of mangrove-dwelling gastropods which are often referred to as 'deposit-feeders' (Plaziat 1984), with little information on their selectivity for mangrove detritus or algal food sources (e.g. Yipp 1980, Rodelli et al. 1984).

Benthic microalgal production in mangrove forests is often low due to light limitation and/or inhibition by soluble tannins (e.g. Alongi 1994, see also Chapter 2, Table 1), but they have been found to be an important component of foodwebs in other intertidal ecosystems such as salt marshes (e.g. Sullivan & Moncreiff 1990, Currin et al. 1995, Page 1997), and several authors have suggested that their potential role in mangrove ecosystems deserves further study (e.g. Micheli 1993, Newell et al. 1995). The potential trophic importance of imported organic matter such as phytoplankton from tidal creeks (Bouillon et al. in review, i.e. Chapter 7) has also not been investigated. In an attempt to evaluate the importance of different primary producers to mangrove-inhabiting fauna, we analysed carbon and nitrogen stable isotope ratios of 29 species of invertebrates from a mangrove forest on the east coast of India, near the mouth of the Gautami Godavari River, along with sediments and primary producers. In addition, a limited number of specimens collected in a basin/riverine mangrove forest in Galle, Sri Lanka, have been included in a compilation of $\delta^{13}C$ data from both literature sources and this study.

Materials and Methods

Study areas

Samples were collected in the Coringa Wildlife Sanctuary (Figure 1), which is part of the mangrove-covered area between Kakinada Bay and the Gautami branch of the Godavari (between 82°15' and 82°22' E, 16°43' and 17°00' N). The Godavari is India's second largest river and opens into the Bay of Bengal in the south-eastern state of Andhra Pradesh. The Gautami Godavari also has several branches into Kakinada Bay, the most important of these being Coringa and Gaderu. The Sanctuary is dominated by mangrove forests and tidal mudflats, the most abundant mangrove species being *Avicennia marina, A. officinalis, Excoecaria agallocha, Sonneratia apetala, Rhizophora mucronata* and *R. apiculata* (Satyanarayana et al. 2002). Tides are semidiurnal and tidal amplitude in the Bay is about 0.5 to 2 meters. Samples were collected during a two-week period in November and December 1999 at three sites within the Sanctuary, located along the Gaderu creek and one of its side creeks (Fig 1). In order to determine whether spatial and seasonal variations in stable isotope signatures were important and in order to collect data on some additional species, samples were collected within a two-week period in May-June 2001 at Site 1 and at an additional site (4) along Matlapalem creek. Additionally, *Elysia coringaensis* sp. nov., *Uca urvillei*, and *Parasesarma plicatum* were collected at a fifth site (site 5, located along Gulla Kalava, a small side creek of Matlapalem creek). At all sites, vegetation was dominated by *A. officinalis, A. marina* and *E. agallocha*, but Site 3 was near to a patch of non-mangrove species, *Suaeda maritima* and *S. monoica.*

Sample collection and preparation

All samples of vegetation, surface sediments and fauna were collected mostly by hand, while benthic microalgae were obtained by gently scraping them off the sediment where they formed a conspicuous layer. Lichens growing on *Excoecaria* stems were gently scraped off with a knife. All floral and faunal samples were kept in a cool box, transported to the field laboratory, washed and dried at 60 °C for at least 48 hours. For the smaller *Uca* spp. and *Metaplax* spp., the gut and intestinal system were first removed and muscle tissue of the body was used, for larger crab species

muscle tissue was taken from the chelae. For the small *Assiminea* sp., four individuals were pooled as one sample. These tissues were ground to a fine powder, and subsamples for $\delta^{13}C$ and elemental (C:N) analysis were treated with dilute HCl to remove possible carbonates and redried. As this treatment has been reported to affect $\delta^{15}N$ values (e.g. Bunn et al. 1995), subsamples for $\delta^{15}N$ analysis were not acidified.

Measurement of elemental and stable isotope ratios

Elemental ratios (C:N) of sediments were determined with a Carlo Erba NA-1500 Elemental Analyser, following dilute acid treatment to remove carbonates (Nieuwenhuize et al. 1994). Samples for stable isotope analysis were similarly combusted, and the resulting gases (CO_2 and N_2) were separated by cryopurification using a manual extraction line. Stable isotope ratios were then measured on a Delta E Finnigan Mat isotope ratio mass spectrometer, and are expressed relative to the conventional standards, i.e. PDB limestone for carbon and atmospheric air for nitrogen, as δ values, defined as :

$$\delta R = \left[\frac{X_{sample} - X_{standard}}{X_{standard}} \right] * 10^3 \qquad [‰]$$

where $R = {}^{13}C$ or ${}^{15}N$, and $X = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$. Internal reference materials used were ammonium sulphate (IAEA-N1, IAEA-N2) and ammonium nitrate (IAEA-NO-3) for $\delta^{15}N$, and sucrose (IAEA-C6) and polyethylene (IAEA-CH-7) for $\delta^{13}C$. The standard deviation on ten aliquots of the same sample was lower than 0.2 ‰ for both $\delta^{13}C$ and $\delta^{15}N$.

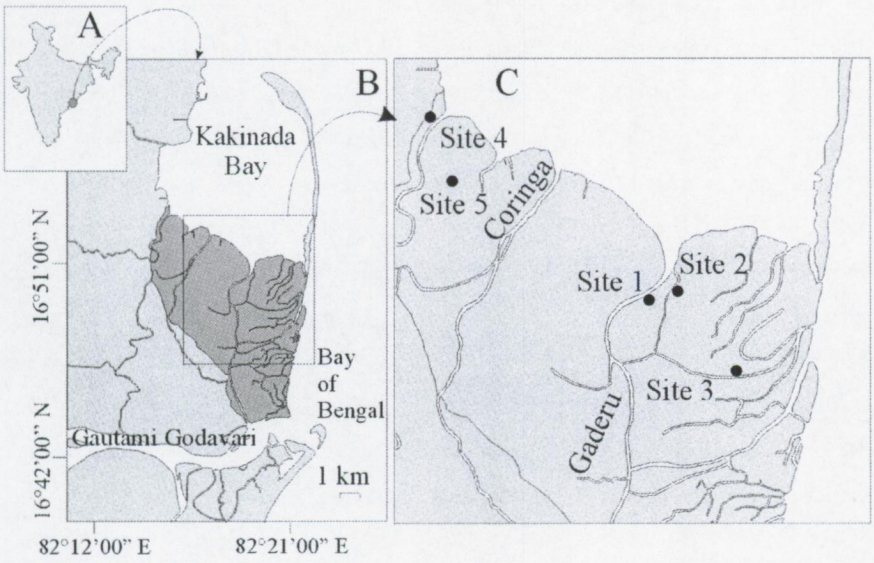


Figure 1 : Location of the sampling sites. Darkest areas in panel B indicate the most important mangrove-covered areas north of the Gautami Godavari.

Results

Primary producers and sediments

NOVEMBER-DECEMBER 1999

Leaves of *Avicennia officinalis* and *Excoecaria agallocha* showed an average $\delta^{13}C$ of –27.9 ‰ (n = 5), close to the overall value for mangrove leaves from this area (-28.5 ± 1.5 ‰, n = 27). Nitrogen stable isotope ratios for these leaves averaged + 4.1 ‰ (n = 5) (Figure 2A). *Suaeda* sp. showed similar values of -27.5 ‰ and + 3.7 ‰ for carbon and nitrogen, respectively. Carbon stable isotope ratios of benthic microalgae scraped off the sediment were much more enriched, averaging -17.3 ± 1.7 ‰ (n = 5), but $\delta^{15}N$ values were lower than those for mangroves ($\delta^{15}N$ + 1.7 ± 1.7 ‰, n = 5) (Figure 2A). Three different macroalgae which were found only in very small quantities at Site 1 had the highest $\delta^{15}N$ values of all primary producers sampled (+ 7.5 ‰ for red algae, + 9.1 ‰ for green algae, and + 11.5 ‰ for unidentified filamentous algae on *Avicennia* pneumatophores), but had intermediate $\delta^{13}C$ values of –26.0 ‰, -20.0 ‰, and –20.9 ‰ respectively. Sediments under the mangrove vegetation had a low organic carbon content (0.8 to 1.2 %), low C:N ratios (7.0 to 8.5), and a carbon isotope composition ($\delta^{13}C$ = -22.8 to – 20.7 ‰, Figure 2A) enriched by 6-8 ‰ relative to the dominant vegetation.

MAY-JUNE 2001

The three mangrove species collected at Site 4 had $\delta^{13}C$ values characteristic of those found previously, but two species had markedly higher $\delta^{15}N$ values (*A. marina* : + 8.9, n=1, and *E. agallocha* : + 8.8 ± 0.3, n=5). Sediment at this location was slightly depleted in ^{13}C ($\delta^{13}C$ = -24.9 ‰) relative to sediments at sites 1-3, but still significantly enriched relative to the average mangrove $\delta^{13}C$ signature. A pooled sample of lichens growing on *Excoecaria* stems at site 2 was found to show a relatively high $\delta^{13}C$ value (-21.4 ‰), but an extremely low $\delta^{15}N$ signature (-8.2 ‰). A dead *Avicennia* log containing *Teredinidae* ('shipworms') at site 4 had a signature of -25.7 ‰ and + 5.1 ‰ ($\delta^{13}C$ and $\delta^{15}N$, respectively).

Stable isotope composition of invertebrates

NOVEMBER-DECEMBER 1999

Overall, invertebrates exhibited a remarkably wide range of values, between -37.8 and -16.6 ‰ for $\delta^{13}C$ and between -6.6 and + 12.3 ‰ for $\delta^{15}N$ (Figure 2A and 2 B), and all invertebrates (except *Elysia coringaensis* sp. nov.) showed average $\delta^{13}C$ values at least 3 ‰ enriched relative to the mangrove $\delta^{13}C$ signal. The sacoglossan *Elysia coringaensis* sp. nov. showed highly depleted $\delta^{13}C$ signature (-36.2 ± 0.8 ‰, n=10). For all other invertebrates, most depleted $\delta^{13}C$ values were found in the gastropods *Melampus fasciatus* ($\delta^{13}C$ = -25.5 ± 0.4, n=6), *Cassidula mustelina* ($\delta^{13}C$ = -25.4 and -25.8, n=2), and *Pythia plicata* ($\delta^{13}C$ = -25.2 and -26.9, n=2) and in the sesarmid *Parasesarma asperum* ($\delta^{13}C$ = -25.5 ± 0.6, n=5) (Figure 2 A and B). The omnivorous sesarmids *Episesarma versicolor* and *E. tetragonum* were characterized by more enriched $\delta^{13}C$ values (-24.2 to -21.9 ‰, Figure 2B), the latter showing highly variable $\delta^{15}N$ values (+ 4.9 to + 10.1 ‰). Two other large brachyurans, *Cardisoma carnifex* and *Scylla serrata* had $\delta^{13}C$ values within the same range, but *C. carnifex* had markedly higher $\delta^{15}N$ values (+ 9.3 ± 2.2 ‰, n=8). $\delta^{13}C$ values comparable to those of the sediment organic matter were found in the surface grazing gastropods *Telescopium telescopium* ($\delta^{13}C$ = -22.0 ± 1.5, n=6) and *Neritina violacea* ($\delta^{13}C$ = -22.6 ± 0.7, n=6). A large number of invertebrate species had $\delta^{13}C$ values in between those of the sediment organic matter and benthic microalgae, including the fiddler crabs *Uca rosea* (-20.1 ± 0.5 ‰, n=3, at site 1, -17.3 ± 1.0, n=3, at site 3) and *U. triangularis* (-20.9 ± 0.8, n=7, at site 1 and -18.9 ‰ (n=1) at site 3), the grapsids *Metaplax distinctus* (-18.7 ± 1.7, n=9) and *M. elegans* (-18.4 ± 1.1, n=12), and the gastropods *Cerithidea obtusa* (-19.3 ± 0.7, n=6) and *Assiminea* sp. (-18.7 ± 0.5, n=6). Unusually depleted $\delta^{15}N$ values (-5.6 ± 0.9 ‰, n = 7) were found in the pulmonate gastropod *Onchidium* sp., and 3 species of the genus *Littoraria* showed relatively low $\delta^{15}N$ values between –1.7 and + 2.6 ‰. No differences were found between the isotopic signatures of specimens collected at site 1 or site 2, but some species which were collected at both site 1 and site 3 (*E. versicolor, U. rosea*, and *U. triangularis*) were enriched in ^{13}C at site 3 (Figure 2B).

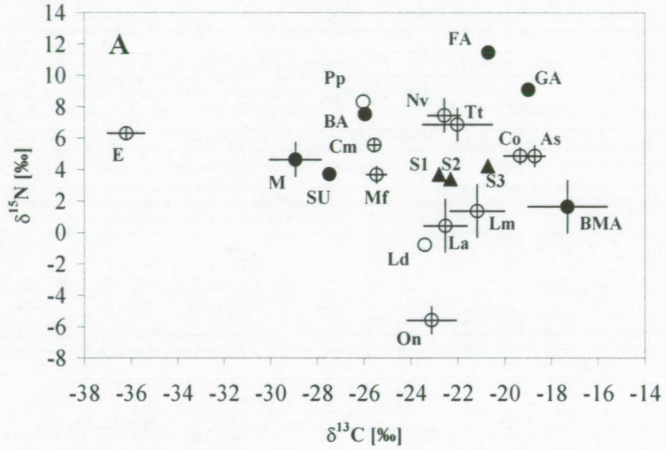


Figure 2 A : Plot of $\delta^{15}N$ versus $\delta^{13}C$ for different primary producers, sediments, and gastropods collected in the intertidal mangrove forest of the Coringa Wildlife Sanctuary in Nov-Dec 1999. Error bars indicate 1 s.d.. As: *Assiminea* sp. (6), BA: brown macroalgae (1), BMA: benthic microalgae (5), Cm: *Cassidula mustelina* (2), Co: *Cerithidea obtusa* (6), E : *Elysia coringaensis* sp. nov. (10), FA: filamentous algae (1), GA: green macroalgae (1), La: *Littoraria articulata* (5), Ld: *Littoraria delicatula* (2), Lm: *Littoraria melanostoma* (6), M: mangrove leaves (17), Mf: *Melampus fasciatus* (6), Nv: *Neritina violacea* (6), On: *Onchidium* sp. (7), Pp: *Pythia plicata* (2), S: Sediment, SU: *Suaeda* sp. (1), Tt: *Telescopium telescopium*. (n) : number of individuals/samples; numbers on figure refer to sampling sites, if not from site 1 or 2.

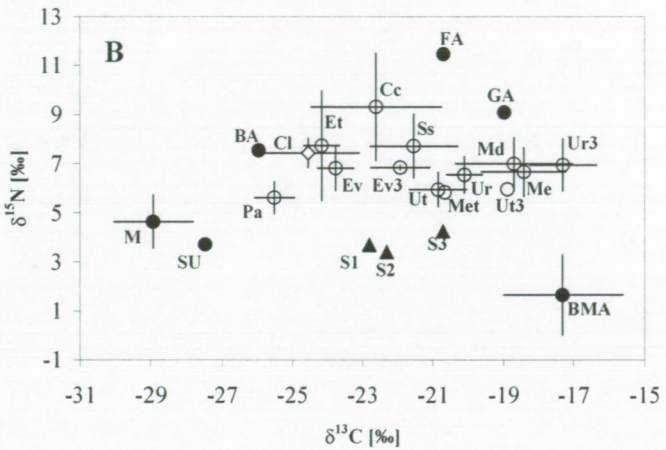


Figure 2 B : Plot of $\delta^{15}N$ versus $\delta^{13}C$ for different primary producers, sediments, and crustaceans collected in the intertidal mangrove forest of the Coringa Wildlife Sanctuary in Nov-Dec 1999. Error bars indicate 1 s.d. BA : brown macroalgae (1), BMA : benthic microalgae (5), Cc : *Cardisoma carnifex* (8), Cl : *Clibanarius longitarsis* (6), Et : *Episesarma tetragonum* (6), Ev : E. *versicolor* (5 at site 1, 3 at site 3), FA : filamentous algae (1), GA : green macroalgae (1), M : mangrove leaves (17), Md : *Metaplax distinctus* (9), Me : *M. elegans* (12), Met : *Metopograpsus messor* (1), S : Sediment, Pa : *Parasesarma asperum* (5), Ss : *Scylla serrata* (7), Su : *Suaeda* sp. (1), Ur : *Uca rosea* (3 at each site), Ut : *U. triangularis bengali* (7 at site 1, 1 at site 3). (n) : number of individuals/samples; numbers on figure refer to sampling sites, if not from site 1 or 2.

MAY-JUNE 2001

The sacoglossan *Elysia coringaensis* sp. nov. (site 5) showed even more negative $\delta^{13}C$ signatures (-42.1 ± 0.2 ‰) than individuals of this species collected during postmonsoon (Figure 5, see Chapter 9 for a more detailed discussion). Sesarmids showed a wide range of $\delta^{13}C$ values (Figure 3), although most were quite depleted, with average $\delta^{13}C$ values of -25.4 (*Perisesarma* sp. nov. adults and *E. versicolor*), -24.0 (*Perisesarma* sp. nov. juveniles), -23.8 (*Parasesarma asperum*), and -19.5 ‰ (*Parasesarma plicatum* juveniles). The *Teredinidae* ($\delta^{13}C$: -20.6 ‰, $\delta^{15}N$: + 5.8 ‰) collected in an *Avicennia* log were enriched in ^{13}C by 1.1 % relative to the wood tissue, and by ~ 0.7 ‰ for $\delta^{15}N$ (Figure 3). Several species collected at site 1 during both sampling periods showed little change in stable isotope signatures (*Pythia plicata, Onchidium* sp., and *U. triangularis*). However, specimens from Site 4 (May-June) had markedly different stable isotope signatures than those collected at Site 1 (mostly November-December) : *Uca triangularis*, *U. rosea*, *Parasesarma asperum*, *Episesarma versicolor* and *Metaplax distinctus* all showed more depleted $\delta^{13}C$ signatures and higher $\delta^{15}N$ values at Site 4 relative to Site 1 (Table 1).

Table 1 : Comparison of $\delta^{13}C$ and $\delta^{15}N$ signatures of some species collected at different sites (1 and 4) and/or seasons (N/D : November-December 1999, M/J : May-June 2001). (n) : number of individuals.

	$\delta^{13}C$			$\delta^{15}N$		
	Site 1, N/D	Site 1, M/J	Site 4, M/J	Site 1, N/D	Site 1, M/J	Site 4, M/J
Uca rosea	-20.1 ± 0.5 (3)		-20.7 (1)	6.5 ± 0.7 (3)		6.9 (1)
U. triangularis	-20.9 ± 0.8 (7)	-20.7 ± 0.3 (7)	-21.7 (2)	6.0 ± 0.7 (7)	4.8 ± 0.4 (7)	7.8 (2)
M. distinctus	-18.7 ± 1.7 (9)		-22.7 (2)	7.0 ± 1.1 (9)		7.0 (2)
Onchidium sp.	-23.1 ± 1.0 (7)	-22.2 ± 0.8 (4)		-5.6 ± 0.9 (7)	-5.0 ± 2.6 (4)	
P. plicata	-26.0 (2)	-25.3 ± 0.3 (4)		8.3 (2)	3.9 ± 1.8 (4)	
E. versicolor	-23.8 ± 0.5 (5)		-25.4 ± 0.5 (4)	6.8 ± 0.9 (5)		6.7 ± 2.1 (4)
P. asperum	-25.5 ± 0.6 (5)		-23.8 ± 2.0 (4)	5.6 ± 0.6 (5)		7.3 ± 0.7 (4)

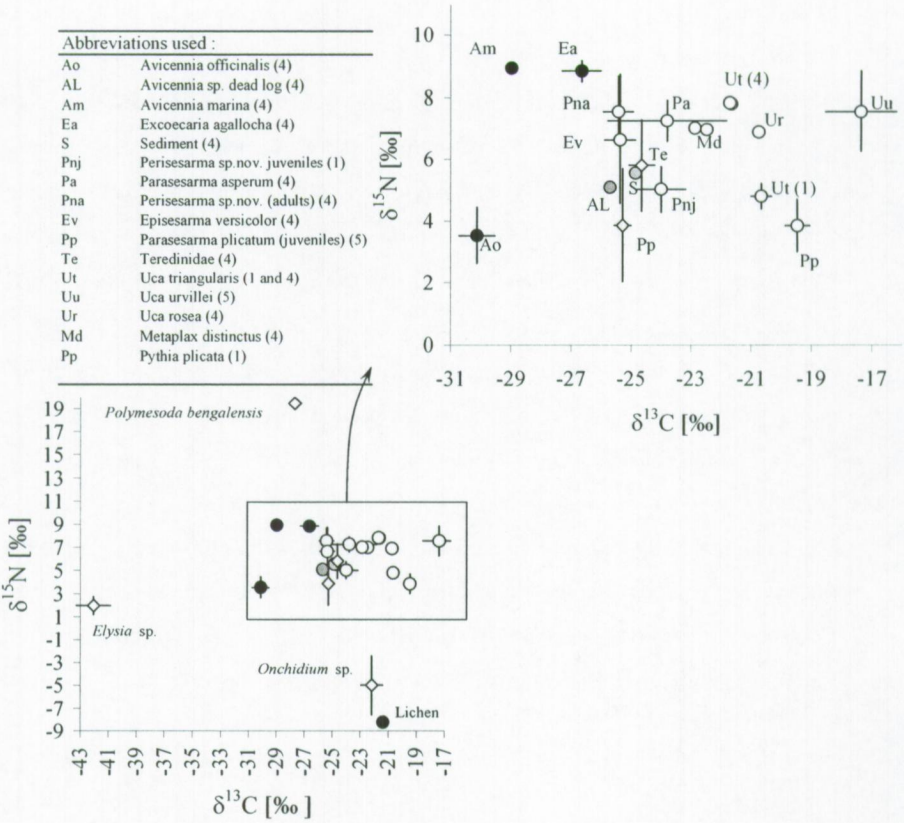


Figure 3 : Plot of $\delta^{15}N$ versus $\delta^{13}C$ for different primary producers, sediments, crustaceans and gastropods collected at different sites the intertidal mangrove forest of the Coringa Wildlife Sanctuary in May-June 2001. Abbreviations as in legend. Numbers between brackets refer to sampling sites, see Figure 1.

Discussion

Primary Producers and Sediments

The $\delta^{13}C$ values found for mangrove leaves are typical for terrestrial C_3-plants and are within the range reported for leaves of various mangrove species by others (e.g. Rao et al. 1994, Newell et al. 1995, Loneragan et al. 1997, Marguillier et al. 1997, see also Chapter 1, pp. 9-10). The $\delta^{13}C$ signature of the benthic microalgae (-17.3 ± 1.7 ‰) was very different from the mangrove leaves and similar to that reported earlier for

benthic algae from mangroves and other intertidal ecosystems (e.g. Newell et al. 1995 and references therein, Dittel et al. 1997, Page 1997, Wainright et al. 2000, Lee 2000). Although a more appropriate technique than the one used has been described to collect these algae (e.g. Couch 1989), experimentation with this technique was found to result in insufficient material in our study. The close correspondence of our $\delta^{13}C$ data to values reported in the literature and with the most enriched $\delta^{13}C$ data for invertebrates allows us to conclude that our results for microalgae are likely to be representative. The microepiphytes scraped off the stems of *Excoecaria* was characterized by an extremely low $\delta^{15}N$ value. To our knowledge, this has not been reported previously. A large discrepancy was observed between the $\delta^{13}C$ values of mangrove leaves (average -28.6 ‰, Figure 2A) and the underlying sediment (-22.8 ‰ at site 1 to –20.7‰ at site 3, Figure 2A). Such an enrichment in ^{13}C in mangrove sediments has been reported in earlier studies (e.g. Rodelli et al. 1984, Stoner & Zimmerman 1988, Hemminga et al. 1994, Dittel et al. 1997, Lallier-Verges et al. 1998, Machiwa 1999), although the discrepancy was usually less pronounced than that found in this study. This enrichment, in combination with the low organic carbon content and low C/N ratios found in sediments in this area, indicates substantial inputs of suspended matter from the mangrove creeks and adjacent Bay (Bouillon et al. in review, i.e. Chapter 7). Suspended particulate organic matter in these creeks and in the adjacent bay, has been found to have a highly variable $\delta^{13}C$ (between –19.2 and –30.9 ‰ in the study area, see Bouillon et al. 2000 i.e. Chapter 5) and was estimated to contain a large contribution by phytoplankton (Bouillon & Dehairs 2000, i.e. Chapter 5). There are thus three major types of primary carbon sources available for invertebrates on the sediment surface : mangrove litter, imported phytodetritus, and microphytobenthos (note that for tree-dwellers, the lichen are an additional isotopically distinct food source).

Macro-invertebrates

Only a limited number of species showed evidence for significant assimilation of mangrove-derived carbon. The gastropods *Melampus fasciatus*, *Cassidula mustelina*, and *Pythia plicata* had some of the most depleted $\delta^{13}C$ values encountered in this study (averages between -26 and -25 ‰, Figure 2A), and these data suggest that mangrove-derived carbon and sediment organic matter could contribute in roughly

equal proportions to their diet, although the large differences in their $\delta^{15}N$ signature suggest that their trophic position may be more complex. Sesarmid crabs are often a dominant feature of mangrove invertebrate communities, and although most experimental studies on their feeding habits only include mangrove leaf material (e.g. Steinke et al. 1993, Kwok & Lee 1995), several authors have suggested that they exploit a wider range of food sources under natural conditions (e.g. Micheli 1993a,b, Lee 1997, Skov & Hartnoll 2002). Of the five sesarmid species sampled in the Coringa area, four were the most ^{13}C-depleted brachyurans in this study (Figure 2B, Figure 3). Of these, *Parasesarma asperum* had the lowest $\delta^{13}C$ and $\delta^{15}N$ values (Figure 2A), but the discrepancy with the mangrove $\delta^{13}C$ signature (about 3.2 ‰) indicates that other sources also contributed to its diet. Feeding off the sediment surface has been noted frequently in several sesarmid species (e.g. Micheli 1993, Lee 2000, Skov & Hartnoll 2002), including *P. asperum*, *P. plicatum*, and *Perisesarma* sp. nov. (personal observation), and we hypothesize that the $\delta^{13}C$ data for this species reflect extensive use of this source as a food source. The wide range of $\delta^{13}C$ and $\delta^{15}N$ values found in *Episesarma tetragonum* and *E. versicolor* and the large difference of their $\delta^{13}C$ values and the mangrove $\delta^{13}C$ signature (on average 4.6 to 6.8 ‰ in November/December, Figure 2B, but less in May/June, Figure 3) suggest a heterogenous and mixed diet which included mangrove litter to some extent but not as the major food source. Their higher (post-monsoon) and more variable (pre- and post-monsson) $\delta^{15}N$ values compared to *P. asperum* suggest that other invertebrates or carrion contributed to their diet. The low N content of mangrove leaves has led several authors to suggest that these can not be sufficient to meet the sesarmids' N-demand (e.g. Micheli 1993a,b, Kwok & Lee 1995, Lee 1997), and our data confirm that other sources can constitute an important contribution to the diet of sesarmids. Especially in the case of the juvenile *Parasesarma plicatum* specimens which showed highly enriched $\delta^{13}C$ values (-19.5 ± 0.4 ‰, Figure 3), the influence of local phytobenthic production or imported microalgae is obvious. When combining our data with those from the literature (Rodelli et al. 1984) and some data on *Chiromanthes* sp. from a Sri Lankan mangrove (S. Bouillon, unpublished data), a significant correlation between the $\delta^{13}C$ of sediment organic matter and of sesarmids (Figure 4) is apparent, confirming the contribution of sediment organic matter in the diet of some sesarmids. *Cardisoma carnifex* stable isotope ratios (Figure 2B) suggest

an omnivorous and heterogeneous diet with only a minor contribution of assimilated mangrove leaf litter, contrary to previous reports of a mainly herbivorous diet (Micheli et al. 1991, Dahdouh-Guebas et al. 1999).

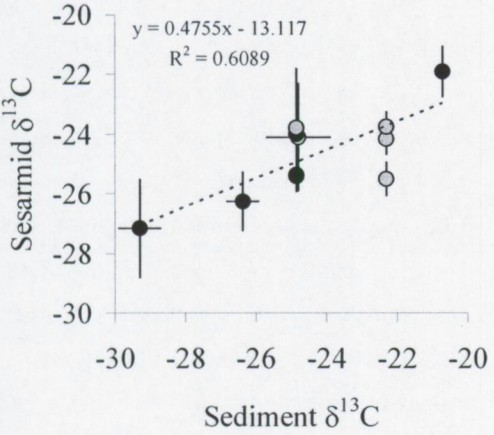


Figure 4 : Relationship between $\delta^{13}C$ values of sediment organic matter and those of different species of sesarmid crabs ($R^2 = 0.61$, $p < 0.05$). Black symbols : this study, grey symbols : data from Rodelli et al. (1984). Sediment data for Galle (Sri Lanka) were taken from Bouillon et al. (in review, i.e. Chapter 7). Error bars indicate 1 s.d.

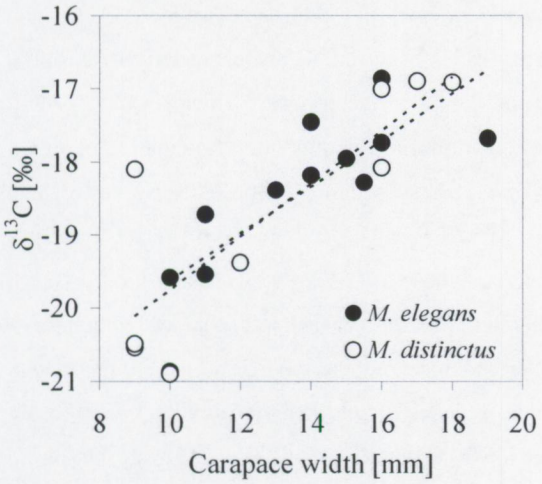


Figure 5 : Relationship between the carbon stable isotopic composition ($\delta^{13}C$, expressed in ‰) and carapax width (mm) for *Metaplax distinctus* (open circles, $R^2 = 0.70$, $p < 0.01$) and *M. elegans* (black circles, $R^2 = 0.66$, $p < 0.01$).

Two surface-grazing gastropods, *Telescopium telescopium* and *Neritina violacea*, had $\delta^{13}C$ values slightly enriched relative to that of the sediment on which they were found to forage (Figure 2A) and their $\delta^{15}N$ signatures (+ 6.9 ± 1.0 ‰ and + 7.5 ± 1.1 ‰, respectively) were higher by about 3.2 to 3.7 ‰ relative to this substrate. Our data suggest that these species feed rather indiscriminately on sediment organic matter, which is in turn comprised to a large extent of deposited phytoplankton/detritus (see Chapter 7). The pulmonate gastropod *Onchidium* sp. also had $\delta^{13}C$ values (-23.1 ± 1.1 ‰, n=7) close to that of the sediment it was usually found on (-22.8 ‰), but it exhibited remarkably low $\delta^{15}N$ values (-5.6 ± 0.9 ‰ during post-monsoon sampling, ranging widely between -8.7 and -2.7 ‰ during the pre-monsoon sampling). Such low $\delta^{15}N$ values have so far mainly been reported for organisms with endosymbiotic chemoautotrophic bacteria from hydrothermal vent systems, 'cold seeps' and reducing sediments (e.g. Fisher 1990, Conway et al. 1994), but almost similarly low values have recently been reported for several species of littorinids from Thai mangroves (Christensen et al. 2001). The latter authors proposed several hypotheses for these remarkably low values, including the possibility of an overlooked and very ^{15}N-depleted food source. Although no conclusive explanation can be given for these remarkably low values, the low $\delta^{15}N$ value found for microepiphyte crusts (-8.2 ‰) scraped off the bark of *Excoecaria* stems during this survey suggests that extensive feeding on such a food source (which is incompletely characterized as only one pooled sample was taken) could result in the observed stable isotope pattern of *Onchidium* sp. It should be noted that littorinids in this study exhibited fairly low $\delta^{15}N$ values (see below) and that *Pythia plicata* specimens collected in Galle (Sri Lanka) showed negative $\delta^{15}N$ values as well (-2.4 ± 0.7 ‰, n=6). This suggests that microepiphytes (e.g. cyanobacteria, lichen, ...) can be a significant food source for a number of mangrove invertebrates, and further isotopic characterization of such epiphytes and invertebrates might provide a more refined view on their importance.

The three species of *Littoraria*, typically found on mangrove leaves and stems, exhibited a fairly wide range of $\delta^{13}C$ values (-24.7 to -20.5 ‰), but were all characterized by their low $\delta^{15}N$ values (-1.7 to + 2.6 ‰, Figure 2A). Although it has sometimes been suggested that *Littoraria* spp. feed on the hairs of *Avicennia* leaves, it is generally accepted that they graze the surface layers of trunks and roots where they

feed on microepiphytes (Reid 1986a, Blanco & Cantera 1999, and Christensen et al. 2001 who also mention fungi and cork cells as dietary components). Our data support the latter hypothesis, as the $\delta^{13}C$ are within the range of those reported for e.g. cyanobacterial crusts (Ziegler & Luttge 1998), and the low $\delta^{15}N$ values of *Littoraria* spp. may suggest that the epiphytes are N_2-fixing, as the process of nitrogen fixation has been reported to result in a fractionation of 0 to 4 ‰ (Kohl & Shearer 1980) relative to atmospheric N_2 ($\delta^{15}N_{air}$ = 0 ‰, Mariotti 1983). Nitrogen fixation by such cyanobacterial crusts on mangrove stems has also been demonstrated in other studies (Sheridan 1991). Also, the inclusion of microepiphytes (with extremely low $\delta^{15}N$ values, see Figure 3) in the diet of the *Littoraria* spp. would be consistent with their stable isotope signatures.

A large number of suface grazers and deposit feeders had $\delta^{13}C$ signatures intermediate between those of sediment organic carbon and benthic microalgae, reflecting different degrees of selectivity for the latter and indicating little or no assimilation of mangrove carbon. These include the abundant gastropods *Assiminea* sp. and *Cerithidea obtusa*, for which $\delta^{13}C$ data indicate selective assimilation or ingestion of benthic microalgae. Consistent with this hypothesis, their $\delta^{15}N$ values (+ 4.8 ± 0.7 ‰ and + 4.9 ± 0.5 ‰, respectively) were higher by about 3 ‰ than those of benthic microalgae (Figure 2A). Kurata et al. (2001) found two species of assiminaeid gastropods in a Japanese estuarine marsh to consume mostly deposited organic matter, including phytoplankton and benthic diatoms. Their $\delta^{13}C$ values were thus markedly different from the dominant local vegetation (reed).

The three species of fiddler crabs (*Uca tringularis*, *U. rosea,* and *U. urvillei*) and the grapsids *Metaplax elegans* and *M. distinctus* collected in this study had significantly more enriched $\delta^{13}C$ values than most sesarmids, *S. serrata* or *C. carnifex* (Figure 2B and Figure 3). Although there continues to be some ambiguity on the importance of different food sources for fiddler crabs, our data confirm results from previous stable isotope studies (e.g. Rodelli et al. 1984, France 1998) that at least some species select for microphytobenthos such as diatoms and cyanobacteria. For both *Metaplax* species, $\delta^{13}C$ values increased with increasing carapace width, indicating a higher selectivity for benthic microalgae in larger individuals (Figure 5). Similar to the findings of France (1998), no such ontogenetic shift was found for fiddler crabs, or for any other of the invertebrates sampled. In contrast to the situation observed in sesarmids (Figure

4), no relation between sediment $\delta^{13}C$ values and fiddler crab stable isotope ratios is apparent in a literature compilation (Figure 6), confirming the selectivity fiddler crabs exhibit when feeding off the sediment surface. When only data from this study are considered, there did appear to be some trend between sediment and *Uca* spp. $\delta^{13}C$ values (black symbols in Figure 6), but in view of the importance of imported phytoplankton/detritus with low C/N ratios (see also Chapter 7) in this particular ecosystem, this is not in contrast with their selectivity for more nutritious components fo the SOM pool.

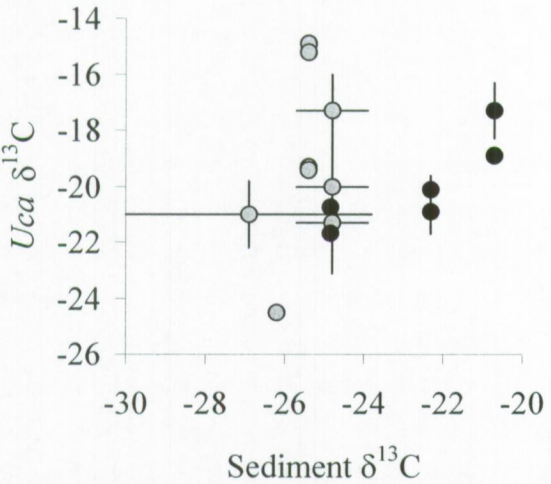


Figure 6 : Relationship between $\delta^{13}C$ values of sediment organic matter and those of different species of fiddler crabs, *Uca* spp. Black symbols : this study, grey symbols : data from literature sources (Fry 1984, Rodelli et al. 1984, France 1998, Hsieh et al. 2002). Error bars indicate 1 s.d.

Only one specimen of *Metopograpsus messor* was sampled in this study, and although it is not possible to draw definite conclusions on its diet, it clearly does not rely heavily on mangrove carbon, and its stable isotope composition is consistent with extensive feeding on littorinids in this genus (Reid 1986b), although others have found a large contribution of mangrove leaves and macroalgae in the diet of *Metopograpsus* species. (Dahdouh-Guebas et al. 1999). *Metopograpsus messor* was most frequently observed on tree trunks, or occasionally feeding off the sediment surface.

The predatory crab *Scylla serrata,* which feeds almost exclusively on animal matter (e.g. Williams 1978, Hill 1979, Jones 1984) is usually considered to be the top

predator of the mangrove benthic community. Although its carbon isotope composition corresponds well with this hypothesis, its $\delta^{15}N$ values (+ 7.7 ± 1.3 ‰, n=7) are lower than might be expected from the $\delta^{15}N$ signatures of potential prey items (Figure 2B). A possible explanation could be that *Onchidium* sp., which exhibits very low $\delta^{15}N$ values, contributes to the diet of *S. serrata*. The fact that local fishermen collect *Onchidium* sp. as bait for the capture of *S. serrata* in the mangrove creeks provides circumstantial evidence for this hypothesis.

The anomuran *Clibanarius longitarsis* had variable but depleted $\delta^{13}C$ values consistent with its filter-feeding habit (Manjulatha & Babu 1991), as suspended matter in the mangrove creeks during the sampling season is relatively depleted in ^{13}C (Bouillon et al. 2000 i.e. Chapter 5).

Most of the -scarce- previously published stable isotope data for bivalves from intertidal mangrove habitats (Rodelli et al. 1984) point towards microalgal food sources, yet the stable isotope signature for the single *Polymesoda bengalensis* ($\delta^{13}C$: -27.7 ‰, $\delta^{15}N$: + 19.5 ‰, Figure 3) sampled in the Coringa Wildlife Sanctuary does not immediately comply with this. Furthermore, the remarkably high $\delta^{15}N$ signature is also not consistent with mangrove litter as its major source, unless microbial action had altered the $\delta^{15}N$ signal substantially (e.g. see De Brabandere et al. 2002) or unless a high degree of selectivity for bacteria (either heterotrophic or chemoautotrophic) exists. A second species of bivalves sampled are the *Teredinidae* collected in a dead *Avicennia* log. These remarkable bivalves (often referred to as 'shipworms') are known to harbour populations of symbiotic cellulolytic bacteria capable of N_2-fixation and thus serving as a potential N-input for the bivalves. Our $\delta^{13}C$ data (-24.6 ± 0.4 ‰) are consistent with the *Avicennia* wood ($\delta^{13}C$: -25.7 ‰) being the major C source, but the $\delta^{15}N$ signatures of the *Teredinidae* (+ 5.8 ± 0.5) are only slighty higher than those of the log ($\delta^{15}N$: + 5.1 ‰) in which they were collected, indeed suggesting an additional input of N_2-fixation to the N-requirements of these bivalves. The large uncertainty associated with the trophic enrichment factor for ^{15}N makes it difficult to use these data quantitatively to assess the relative inputs of N_2 from wood or from dinitrogen fixation.

Finally, the sacoglossan *Elysia coringaensis* sp. nov. showed unusually depleted $\delta^{13}C$ values (Figure 2A, Figure 3), which will be discussed in detail in Chapter 9.

A broader perspective

A striking feature of Figures 2 and 3 is the diversity in stable isotope signatures found in co-occuring mangrove invertebrates, indicating a fairly limited overlap in resource utilization. Overall, the data show that although mangrove carbon was assimilated by some invertebrate species (e.g. some gastropods and sesarmid crabs), other sources formed a major part of these species' diet. For the majority of the species studied, freshly deposited phytodetritus, benthic microalgae, and microepiphytes were found to be dominant carbon sources. The distribution of $\delta^{13}C$ data of some important mangrove-inhabiting invertebrate groups from this study and several published studies have been compiled in Figure 8, whereby our own unpublished data for *Neosarmatium meinerti* and *N. smithi* from Gazi Bay (Kenya) and on *Chiromanthes* sp., *Terebralia palustris, Pythia plicata,* and *Polymesoda* sp. from Galle (Sri Lanka) have also been included. The usefulness of such compilations is immediately evident when considering the distinct distribution of $\delta^{13}C$ signatures for mangrove litter on the one hand, and micro- and macroalgal sources on the other hand (Figure 7). Note that imported carbon sources (e.g. phytoplankton or -in some ecosystems- seagrasses; not included in Figure 7) may show very variable $\delta^{13}C$ values. A similar approach was lined out for (amongst others) salt marsh ecosystems by France (1995).

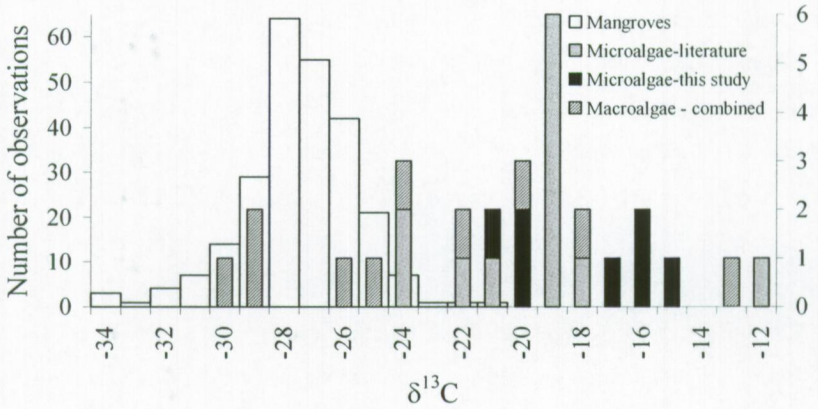


Figure 7 : Frequency distribution of $\delta^{13}C$ values of mangrove leaves (both literature data and data gathered in this study, left-hand Y-axis) and $\delta^{13}C$ values of micro- and macroalgae (right-hand Y-axis). See legend for details. Data sources for algae : M. Skov (unpublished data), Rodellli et al. (1984), Ambler et al. (1994), Newell et al. (1995), Primavera (1996), Dittel et al. (1997), Lee (2000), Machiwa (2000), Sheaves & Molony (2000).

The distribution patterns of invertebrate $\delta^{13}C$ values confirm that substantial amounts of mangrove carbon are assimilated only by a limited number of invertebrate groups (such as sesarmid crabs, and some of the gastropods), but even in these cases there is only a limited overlap in the $\delta^{13}C$ distributions. The fairly large discrepancy found between the distribution of mangrove $\delta^{13}C$ values and other invertebrate groups (e.g. *Uca* spp., *Metaplax* spp., most of the gastropod species) clearly demonstrates the important role of imported organic matter and microphytobenthos for the macro-invertebrate community in intertidal mangrove habitats. The overall average $\delta^{13}C$ value of all invertebrates presented in Figure 8 (excluding the data for *Elysia coringaensis* sp. nov.) is around –22.2 ‰, i.e. approximately 6 ‰ enriched relative to the average mangrove litter signature. These results show a remarkable similarity with those obtained in temperate salt marsh ecosystems, where a number of recent studies (Sullivan & Moncreiff 1990, Currin et al. 1995, France 1995, Page 1997, Créach et al. 1997, Riera et al. 1999, Kurata et al. 2001) have demonstrated the trophic importance of imported phytoplankton and local microalgal sources. Although standing stocks of salt marsh vegetation are about an order of magnitude lower than those of mangroves, their above-ground productivity is comparable (e.g. see Twilley et al. 1992 and Middelburg et al. 1997). Mangrove ecosystems and saltmarhes have also been found to show analogous patterns of variability in the sources of organic carbon in surface sediments (Middelburg et al. 1997, Bouillon et al. in review i.e. Chapter 7), which suggests that carbon pathways and utilization patterns in these two types of vegetated intertidal ecosystems may be quite similar. Many aspects of mangrove intertidal foodwebs remain virtually unknown, however : there is as yet very little information on the carbon sources for many infaunal organisms, notably meiofauna, nor on the role of microheterotrophs as trophic intermediates. Until more studies are undertaken in a variety of mangrove ecosystems, regional differences and the influence of the availability of carbon sources (*sensu* Bouillon et al. in review, i.e. Chapter 7) in structuring mangrove foodwebs also remain to be determined.

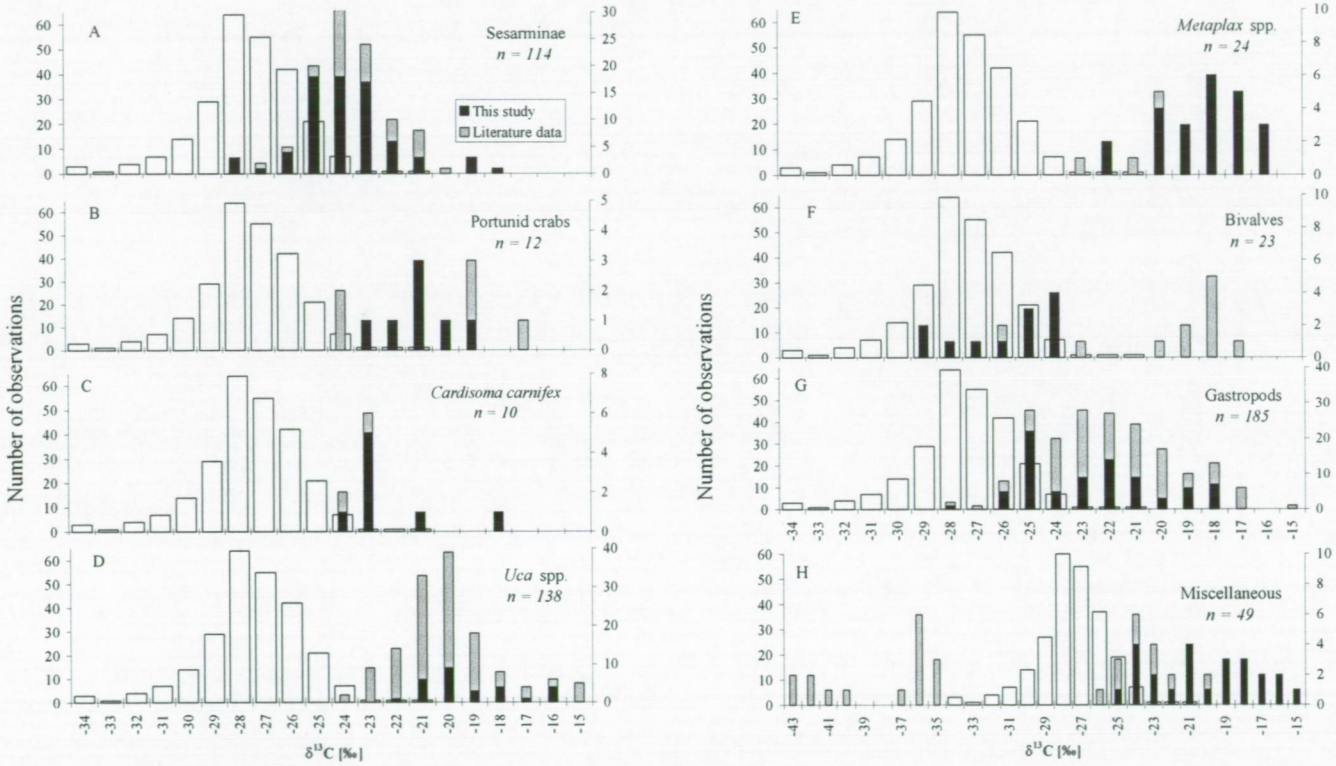


Figure 8 (legend on following page).

Figure 8 (previous page) : Frequency distribution of $\delta^{13}C$ values of mangrove leaves (white columns, this study and literature data, n=250) and $\delta^{13}C$ values of different invertebrate groups form intertidal mangrove forests. The $\delta^{13}C$ value indicates the upper (i.e. least negative) value of the interval. Black bars correspond to data from this study, grey bars refer to published data. A : sesarmid crabs, B : portunid crabs, C : *Cardisoma carnifex*, D : *Uca* spp., E : *Metaplax* spp, F : bivalves, G : gastropods (excluding *Elysia corignaensis* sp. nov. which is included in 'miscellaneous'), and H : miscellaneous taxa. *n* : number of data.
Panel H (miscellaneous taxa) includes data of the following species : *Alpheus* sp., anemone (unidentified), *Clistocoeloma merguiensis*, *Eurycarcanius natalensis*, Laonome albicingillum (polychaete), *Metopograpsus messor*, *M. latifrons*, *M. thukuhar*, *M. oceanicus*, Nemertines (unidentified), *Neanthes glandicincta* (polychaete), *Nereis* sp., *Clibanarius* sp., *Clibanarius longitarsis*, flatworm (unidentified), and *Elysia coringaensis* sp. nov.
Literature sources used in alphabetical order : Ambler et al. (1994), Boon et al. (1997), Christensen et al. (2001), Dehairs et al. (2000), Dittmar & Lara (2001), Ellison et al. (1996), Fleming et al. (1990), France (1998), Fry (1984), Harrigan et al. (1989), Hayase et al. (1999), Hemminga et al. (1994), Hsieh et al. (2002), Jennerjahn & Ittekkot (2002), Kao & Chang (1998), Kuramoto & Minagawa (2001), Kazungu (1996), Lacerda et al. (1986, 1991), Lee (2000), Lee et al. (2002), Lin & Sternberg (1992), Loneragan et al. (1997), Machiwa (2000), Marguillier et al. (1997), Medina & Fransisco (1997), Newell et al. (1995), Primavera (1996), E. Ólafsson & M. Skov (unpublished data), Rao et al. (1994), Rao (1998), Rezende et al. (1990), Rodelli et al. (1984), Schwamborn et al. (2002), Sheaves & Molony (2000), Slim et al. (1997), and Stoner & Zimmerman (1988).

Results of litter removal experiments and stable isotope results : how compatible are they ?

Much of the earlier work on intertidal mangrove foodwebs has stressed the importance of crabs in the removal of leaf litter from the forest floor (estimates range widely, but are as high as >90 % in some systems, see Lee 1998). This observation, and the fact that some of the best-known other mangrove invertebrates such as the gastropod *Terebralia palustris* have been observed to feed on mangrove leaves, has nourished the still prevalent view that 'the great majority of the mangrove macrobenthos relies directly on the high production of the mangroves themselves, consuming either leaf litter or detritus composed of decaying leaves' (Fratini et al. 2000b). This view appears to contrast sharply with the stable isotope results presented and compiled in this study, which have demonstrated that -from a community perspective- only a limited number of species appear to rely substantially on mangrove carbon, and that a range of other carbon sources are used by the invertebrate community. There are several points which can be raised to reconcile these 2 superficially contrasting viewpoints :

- First, the fact that a large proportion of the shedded leaf litter is removed and/or consumed by the local crab fauna does not necessarily imply that mangrove

leaves are the dominant item in their diet, as the population of sesarmids may consume even more of 'something else'. In this respect, the study of Skov & Hartnoll (2002) is particularly enlightening, as their field observations clearly demonstrate that sesarmids may spend considerably more time feeding off the sediment surface than collecting or eating leaves (which is suggested or confirmed by stable isotope data, e.g. see Lee 2000 and this study). Evidently, the sources of organic matter present in the sediment and the degree of selectivity with which sesarmids feed on it (both of which may be highly variable) will determine which carbon sources contribute to their diet and in which proportions.

- Secondly, much of the work on the trophic significance of different sources in mangrove ecosystems has focussed on a limited number of invertebrate groups or species, notably sesarmids and a disproportionate amount of studies on *Terebralia palustris* (e.g. Nishihira 1983, Slim et al. 1997, Fratini et al. 2001a). In order to have a *community perspective*, however, this may severely bias our view of the importance of mangrove litter, as the often rich and diverse invertebrate community apparently displays a wide variety of feeding specializations which are rarely the subject of more detailed studies.
- Lastly, it should also be noted that in view of the significant differences in elemental ratios between different food sources available to intertidal consumers (e.g. mangrove leaves have a very low N content, microphytobenthos is much richer in N, etc), the contribution of C and N from any dietary source to a specific organism is not necessarily equal. In the case of sesarmid crabs, for example, this may imply that although $\delta^{13}C$ data indicate that some (but not all) species clearly rely on mangrove carbon as a significant part of their diet, the contribution of mangrove-derived nitrogen may be much less (see also Chapter 2 for examples on how different C/N ratios of food sources may affect interpretation of combined $\delta^{13}C$ and $\delta^{15}N$ data).

CHAPTER 9 : Unusually low $\delta^{13}C$ values in the sacoglossan *Elysia coringaensis* sp. nov. from an east-Indian mangrove forest

Foreword

The unusual $\delta^{13}C$ results obtained for *Elysia coringaensis* sp. nov. (presented earlier in Chapter 8) are discussed here separately as much of the discussion remains speculative and does not directly relate to the rest of this thesis.

Abstract

In the framework of a study aiming to assess the relative importance of different carbon sources to the invertebrate community in an east Indian mangrove forest, an undescribed sacoglossan *Elysia coringaensis* sp. nov. (Mollusca : Gastropoda : Ophistobranchia) was found locally, but in large numbers, in shallow tidal pools under *Avicennia* spp. This species was found to have unusually depleted $\delta^{13}C$ signatures (ranging between -43.3 and -35.2 ‰ in samples collected in different seasons and sites) previously unrecorded in any kleptoplastidic or other algae-invertebrate symbiosis. It is hypothesized that strong internal recycling of CO_2, i.e. the fixation of host-respired CO_2 by the functional kleptoplastids, in combination with a ^{13}C-depleted external DIC pool, are responsible for the observed $\delta^{13}C$ values. Further research is needed to assess the importance of the two processes and to determine the dependency on external food sources for *E. coringaensis* sp. nov. The functionality of the plastids was shown experimentally by the enrichment in ^{13}C observed in animals kept in a ^{13}C-bicarbonate spiked solution. Significant uptake of ^{13}C was demonstrated after 2 hours of exposure under light conditions, and after 36 hours for animals kept in the dark. In contrast to the expectation, bulk lipids were not significantly ^{13}C-depleted relative to whole tissues. Further research under laboratory and field conditions is needed to further unravel the mechanisms leading to these highly unusual $\delta^{13}C$ signatures.

Introduction

Sacoglossans are herbivorous marine ophistobranchs (Mollusca : Gastropoda) which feed mainly on green or red algae, but an often encountered phenomenon in this group is the occurrence of kleptoplasty, i.e. the intercellular retention of chloroplasts obtained from the algae. These chloroplasts often remain functional for prolonged periods (up to 10 months in the case of the most intensively studied species, *Elysia chlorotica*, Rumpho et al. 2000) and may provide a varying proportion of the hosts' carbon requirements. Few studies have attempted to estimate the contribution of kleptoplasty in the overall dietary requirements of sacoglossans, and the few available estimates vary widely between species or according to the appraoch used (see Raven et al. 2001 for a recent overview). However, from the evidence available, it would appear that no somatic growth is possible without external food sources, suggesting that kleptoplasty can sustain the animals -for several months-, but not their growth.

An undescribed sacoglossan (which will be described under the tentative name *E. coringaensis* sp. nov. by Dr. C. Swennen, Netherlands Institute for Sea Reseach), was found in large numbers expanded on the sediment surface in small shallow pools during low tide in the mangrove ecosystem of the Coringa Wildlife Sanctuary (Andhra Pradesh, India). These conditions are similar to those in which the 2 other *Elysia* species known from mangrove forests are found (*E. bangtawaensis* from Thailand -see Swennen 1997- and *E. leucolegnote* from Hong Kong, C. Swennen pers. comm.). For *E. bangtawaensis*, it was shown that they suck out the cytoplasm of a small green algae, *Derbesia* cf. *marina*, which occured above mean high tide level and to which the animals did not have access during dry periods. Swennen (1997) showed that the animals were able to survive without the food algae for several months, with one specimen still alive after almost 6 months, although their size decreased. Only after supplying it with *Derbesia* did the last animal regain growth.

In one study (Raven et al. 2001), $\delta^{13}C$ values of food algae and sacoglossans were measured in an attempt to quantify the contribution of algal sources and kleptoplasty to a number of sacoglossans. The underlying idea was that carbon isotope fractionation by kleptoplastids (i.e. algal plastids in the sacoglossan host) may be different from that by the plastids in the food algae, as the overall fractionation in algae is mainly dependant on the transport mechanisms of inorganic carbon and to

processes affecting carbon losses after C fixation. However, all $\delta^{13}C$ values in the study of Raven et al. (2001) were much more enriched (-20.0 to -10.5 ‰) than those found in our study, and published $\delta^{13}C$ for more 'traditional' algae-invertebrate symbioses are also much higher (e.g. Muscatine et al. 1989, Johnston et al. 1995) than those found in this study, and we will therefore point out some possible mechanisms leading to the extremely low $\delta^{13}C$ values for *E. coringaensis* sp. nov.

Materials & Methods

E. coringaensis sp. nov. were collected along Gaderu (mixed *Avicennia* spp. and *Excoecaria agallocha*) in December 1999 (i.e. post-monsoon season), and in an *Avicennia*-dominated zone several hundreds of meters inward from Gulla Kalava, a side creek of Matlapalem Canal in June 2001 (see Chapter 3, Figure 1 for location of study site). Samples were taken to the field lab where they were dried at 60 °C for a minimum of 24 hours.

In June 2001, a simple experiment was set up to establish the functionality of the kleptoplasty. Water from the collection sites was transported to the field lab where it was filtered on a 0.7 µm glass fibre filtre (Whatman GF/F) and 23.5 mg of $NaH^{13}CO_3$ was added to approximately 200 ml of the filtrate (i.e. corresponding to ~ 1.4 mM of added DIC). This was partitioned between 2 opaque recipients, in which 7 and 11 specimens of *E. coringaensis* sp. nov. were placed; the first recipient covered in aluminium foil in order to keep the animals in the dark, the latter was kept open so that the animals remained exposed to either natural light (daytime) or artificial light (nighttime). Specimens from both treatmens were collected after 2, 4, 6, and 36 hours, placed on pre-combusted Whatman GF/F filters and dried at 60 °C for at least 24 hours. Field-collected specimens were taken to represent initial conditions.

Lipids from two specimens collected in December 1999 were extracted following the procedures outlined in McKenzie et al. (2000). Briefly, 15 ml of chloroform and 30 ml of methanol were added to a known amount of ground sample material, the mixture was shaken for several minutes, and 15 ml of distilled H_2O was added. The mixture was shaken, and after settling, the lower fraction (chloroform, containing the lipid fraction) was drawn off. 15 ml of chloroform was added to the remaining methanol/water mixture and the procedure was repeated. Both chloroform extracts

were combined and evaporated in a fume cupboard. The lipids were then scraped off the bottom of the glass vial, placed in decontaminated tin cups, and analysed for $\delta^{13}C$. All tissues were ground to a fine powder, and subsamples for $\delta^{13}C$ and elemental analysis were treated with dilute HCl to remove possible carbonates and redried. Elemental ratios (C:N) were determined with a Carlo Erba NA-1500 Elemental Analyser, and samples for stable isotope analysis were similarly combusted, after which the resulting gases (CO_2 and N_2) were separated by cryopurification using a manual extraction line. Stable isotope ratios were then measured on a Delta E Finnigan Mat isotope ratio mass spectrometer, and are expressed relative to the conventional standards, i.e. PDB limestone for carbon and atmospheric air for nitrogen, as δ values, defined as :

$$\delta X = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] * 10^3 \qquad [‰]$$

where X = ^{13}C or ^{15}N, and R = $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Reproducibility was better than 0.2 ‰ for both $\delta^{13}C$ and $\delta^{15}N$.

Results

Field-collected *E. coringaensis* sp. nov. from December 1999 showed $\delta^{13}C$ values ranging between -37.8 and -35.2 ‰ (average -36.2 ± 0.8 ‰, n=10), whereas specimens collected in June 2001 had even more negative $\delta^{13}C$ values between -43.3 and -40.1 ‰ (average -42.2 ± 1.2 ‰, (n=6) (Table 1)). $\delta^{15}N$ values averaged + 6.3 ± 0.3 ‰ (n=6) in December 1999, but were markedly lower at + 2.1 ± 0.2 ‰ (n=2) in June 2001. Elemental ratios (C:N, atom) of specimens collected in Dec 1999 were remarkably high (Table 1) at 8.4 ± 0.8 (n=4). For the two specimens collected in Dec 1999, the lipid fraction was found to have nearly identical, or even slightly enriched, $\delta^{13}C$ values than the bulk tissue (Table 1).

During the incubation experiment, uptake of ^{13}C from the external DIC pool was apparent in all specimens kept in the light, already after 2 hours ($\delta^{13}C$ = -24.6 ‰, n=2) (Figure 1). No marked changes in the uptake occurred between 2 and 6 hours, but specimens harvested after 36 hours were markedly more enriched in ^{13}C, with

$\delta^{13}C$ values around + 350 ± 64 ‰. Specimens kept in the dark showed no signs of uptake of ^{13}C-labeled HCO_3^- after 2, 4, or 6 hours, but the one specimen remaining in this treatment after 36 hours showed clear evidence of dark fixation ($\delta^{13}C$ = + 25.0 ‰).

Table 1 : $\delta^{13}C$ of bulk tissue and lipid fraction, and elemental ratios ($C:N_{atom}$) of *Elysia coringaensis* sp. nov. collected in the Coringa Wildlife Sanctuary, Andhra Pradesh, India.

Individual nr.	$\delta^{13}C_{bulk}$	$\delta^{13}C_{lipid\ fraction}$	$\delta^{15}N$	**C:N (atom)**
DECEMBER 1999, ALONG GADERU				
1	-36.3		+ 6.5	8.9
2	-35.2		+ 5.8	9.1
3	-37.8		+ 6.0	7.3
4	-35.3		+ 6.7	8.4
5	-36.6		+ 6.5	
6	-35.4		+ 6.3	
7	-36.5			
8	-36.8			
9	-36.0	-35.2		
10	-36.2	-36.1		
AVERAGE ± 1 S.D.	**-36.2 ± 0.8**		**6.3 ± 0.3**	**8.4 ± 0.8**
JUNE 2001, GULLA KALAVA				
1	-42.2		+ 1.9	
2	-42.5		+ 2.2	
3	-40.1		+ 3.0	
4	-43.1		+ 1.1	
5	-41.1		+ 2.5	
6	-43.3		+ 1.2	
AVERAGE ± 1 S.D.	**-42.1 ± 1.2**		**2.0 ± 0.8**	

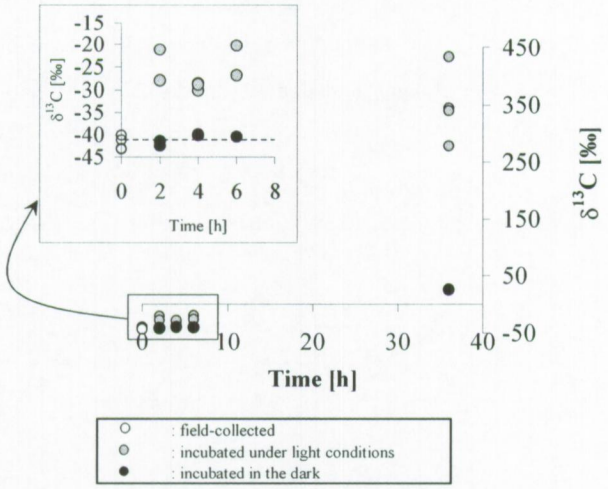


Figure 1 : $\delta^{13}C$ values of field-collected *Elysia coringaensis* sp. nov.(June 2001), and evolution of $\delta^{13}C$ during incubation under light or dark conditions in the presence of ^{13}C-labeled $NaHCO_3$.

Discussion

The $\delta^{13}C$ values obtained for field-collected *E. coringaensis* sp. nov. in our study (Table 1) are remarkably negative for any invertebrate, and in particular when compared to published $\delta^{13}C$ data for other sacoglossans and algae-invertebrate symbioses (Table 2). We will briefly examine some possible factors leading to these unexpected $\delta^{13}C$ signatures.

(1) One major difference with the abovementioned published $\delta^{13}C$ data is the fact that *E. coringaensis* sp. nov. were collected in intertidal pools in mangroves, where the DIC pool can be expected to be more depleted in ^{13}C than in a marine environment (i.e. where all data shown in Table 2 were obtained). Although unfortunately, we have no direct measurements of $\delta^{13}C_{DIC}$ from the intertidal pools in which the animals were collected (note that these were not small puddles left over at low tide, but rather areas that remained inundated at low tide, with a water depth of ~ 30 cm), $\delta^{13}C_{DIC}$ in the mangrove creeks during the second sampling period were indeed relatively depleted in ^{13}C (see Chapter 4) the lowest value of -10 ‰ during the latter period, which was recorded at the highest salinity

(37 ppt) is thought to reflect best the composition of the porewater draining the intertidal areas. Small intertidal pools in mangroves of Sri Lanka have also been found to show very negative $\delta^{13}C_{DIC}$ values (usually ~ -10 ‰, but in small standing puddles as low as -24 ‰; unpublished data). Considering the huge difference (average 20 to 26 ‰) between our $\delta^{13}C$ values and those observed for other sacoglossans by Raven et al. (2001), we believe that the ^{13}C-depleted DIC-pool, although obviously an important contributor, is an insufficient explanation for the observed $\delta^{13}C$ signatures.

Table 2 : Overview of published $\delta^{13}C$ values for algae-invertebrates symbioses.

Species	$\delta^{13}C$	C/N	Source
GASTROPODA (SACOGLOSSANS)			
Elysia australis	-19.3; -20.0	6.96	Raven et al. (2001)
Elysia expansa	-15.7; -16.6	5.55	Raven et al. (2001)
Elysia maoria	-16.1 ± 0.9	6.74	Raven et al. (2001)
Elysiella pusilla	-18.4	5.25	Raven et al. (2001)
Oxynoe viridis	-13.8	6.92	Raven et al. (2001)
Placida dendritica	-19.0 ± 0.18	6.02	Raven et al. (2001)
Stiliger aureomarginatus	-10.5 ± 0.2	7.74	Raven et al. (2001)
BIVALVIA			
Tridacna gigas	-15.8		Johnston et al. (1995)
Tridacna maxima	-23		Black & Bender (1976)*
ZOOXANTHELLATE CORALS			
Different species, animals or algae	-19.64 to -9.63		Muscatine et al. (1989)
Different species, animal tissues	-15.1 to -12.1		Yamamuro et al. (1995)
MEDUSAE			
Mastigias sp.	-24.1		Muscatine et al. (1989)

*: cit. in Muscatine et al. (1989)

(2) We therefore hypothesize that the very negative $\delta^{13}C$ values are a reflection of the combination of two factors :

(a) a large dependancy on kleptoplasty (this certainly appears plausible, as macroalgae are uncommon in the study area, whereas most sacoglossans such as those studied by Raven et al. (2001) are found in systems where the host plant is abundant), and

(b) a significant part of the CO_2 fixed by the plastids is host-respired (metabolic) CO_2, which should have approximately the same isotopic composition as the host tissue. Such 'internal recycling' of respired CO_2 has been proposed for other, more traditional algae-invertebrate symbioses, such as those found in foraminifera (Rink et al. 1998), sea anemones (Harland & Davies 1995), and

coral zooxanthellae (Muscatine et al. 1989), and may be a process enhancing the photosynthetic rate of the endosymbionts by ensuring a supply of CO_2 which may otherwise be limiting due to diffusion resistance (Harland & Davies 1995, Rink et al. 1998). The fact that the plastids occur *inter*cellularly makes this a likely process to occur in sacoglossans, but it is unclear why this mechanism is not pronounced in other sacoglossans (i.e. those studied by Raven et al. (2001) where no extremely negative $\delta^{13}C$ values were found).

In any case, if metabolic CO_2 contributes (and this seems likely), an equilibrium should exist between the fixation of CO_2 from the external medium and metabolic CO_2.

A quick back-of-the-envelope calculation does not conflict with the proposed hypothesis leading to such low $\delta^{13}C$ values :

Assuming that the animals have been deprived of their host algae for some time, and thus, that their stable isotope composition is mainly determined by the carbon fixed by kleptoplasty, we can estimate that (taking a fractionation of -20 ‰ *versus* the inorganic carbon species used pool) for an individual which derives 60 % of the carbon fixed by kleptoplastids from its external environment, and 40 % as host-respired CO_2 :

$\delta^{13}C_{Elysia} = 0.6*(\delta^{13}C_{DIC} - 20) + 0.4 * (\delta^{13}C_{Elysia} - 20)$

(assuming $\delta^{13}C_{DIC} = -10$ ‰) results in : $\delta^{13}C_{Elysia} = -43.3$ ‰

The functionality of the kleptoplasty was shown experimentally by keeping individuals of *E. coringaensis* sp. nov. in filtered water spiked with ^{13}C-enriched bicarbonate (see Figure 1). Uptake of labelled CO_2 or bicarbonate was rapid (within 4 hours) and significant (~ 20 ‰ enrichment, whereas control animals kept in the dark did not show any enrichment during this time period). Remarkably, however, evidence for dark fixation of CO_2 was noticed after 36 hours, with an enrichment of the only animal remaining in the dark of ~ 60 ‰. Relatively high rates of dark fixation were also noted for a shelled sacoglossan from Florida (K. Jensen, pers. comm.), and is known to occur in a variety of macro-algae (e.g. Gomez et al. 1995).

Another further unexplained phenomenon is related to the stable isotope composition of the lipid fraction of *E. coringaensis* sp. nov. Lipids are usually strongly depleted in ^{13}C relative to other compounds (e.g. McKenzie et al. 2000) due to the kinetic isotope

effect associated with pyruvate dehydrogenase during lipid biosynthesis. Individuals of *E. coringaensis* sp. nov., however, were found to show similar $\delta^{13}C$ values for bulk tissue and for the total lipid fraction (see Table 1). Only one study has to our knowledge reported a similar situation: Johnston et al. (1995) found similar $\delta^{13}C$ values for lipids and bulk tissue in the giant clam *Tridacna gigas* (an algae-invertebrate symbiosis). In their study, zooxanthellae were found to have an extremely high lipid content (51 % of total dry weight), and the authors hyptothesized the lack of depletion in ^{13}C for lipids to be caused by either (1) very low pyruvate concentrations, thereby eliminating the kinetic isotope effect normally associated with pyruvate dehydrogenase, or (2) an alternative source of acetyl-CoA such as acetate. Some evidence for the latter hypothesis is provided by the results of Blanquet et al (1979, cited in Johnston et al. 1995) who found that zooxanthellae incorpored ^{14}C-labeled acetate into some of their fatty acids (16:0 and 18:1).

Concluding remarks

Much of the above discussion remains speculative. Additional field and laboratory work is needed to elucidate the mechanisms leading to the unusually low $\delta^{13}C$ values for *E. coringaensis* sp. nov. In particular the following information could provide useful insights into the functioning of this remarkable algae-invertebrate asssociation :

1. Of primary importance is the identification of the host algae from which the kleptoplastids are derived, and its carbon isotopic characterization. Additionally, it needs to be established whether the organisms have permanent access to their food algae (see Swennen 1997).
2. Secondly, the overall 'fractionation' between organisms and the DIC pool should be established in the field and under laboratory conditions. The evaluation of the time trend in $\delta^{13}C$ of specimens kept under aquarium conditions (with characterized $\delta^{13}C_{DIC}$) and deprived of their food algae could be useful to find out if the $\delta^{13}C$ of *Elysia* finds an equilibrium, which can then be directly related to the fixation of carbon by kleptoplastids.
3. Tracer experiments with ^{13}C-labeled acetate could indicate whether lipid synthesis occures via an alternative pathway than through the traditional pyrovate dehydrogenase pathway as the initial source of acetyl-CoA, and whether the dark fixation observed here is confirmed after an adaptation period.

CHAPTER 10 : General Discussion

This final chapter is intended to provide :

(1) an evaluation of the usefulness of stable isotopes, in particular of carbon and nitrogen, as natural tracers in this study - we here refer to the general introduction for a brief overview of the initial aims of this work. [this section will include a brief presentation of $\delta^{13}C$ and $\delta^{15}N$ data of fishes collected in the study area during the post-monsoon of 1999];

(2) an integrated overview of the results presented in previous chapters, in order to present an overall image of the importance of different carbon sources to faunal communities in the estuarine mangrove ecosystem of the Coringa Wildlife Sanctuary;

(3) some considerations on the fate of mangrove production in the study area considered and in general;

(4) and finally, some gaps in the current knowledge will be pointed out where relevant, along with suggestions for future research.

I. AN EVALUATION OF THE USE OF STABLE ISOTOPES AS NATURAL TRACERS OF ORGANIC MATTER SOURCES AND UTILIZATION PATTERNS IN MANGROVE ECOSYSTEMS

Although it is unquestionable that many, if not most, of the recent insights into the sources of organic carbon contributing to foodwebs in mangrove ecosystems (as well as a variety of other ecosystems) have been the result of the application of stable isotope techniques, it is imperative to make a critical evaluation of the possibilities and limitations of this approach in studying the sources and utilization of organic matter in mangrove ecosystems. For some more general considerations on the application of stable isotopes as tracers of organic matter sources and utilization, we refer to Chapter 1 (pp. 26-38).

Stable carbon isotopes of carbon are clearly powerful tracers of the sources of organic carbon sustaining consumer communities, provided that the primary carbon sources are adequately characterized and differ in their $\delta^{13}C$ signatures. The latter conditions, however, are not always met under the dynamic estuarine conditions in which

mangroves are usually found. Most importantly, phytoplankton is a difficult component to characterize isotopically, as it is practically infeasible to separate it from the suspended matter pool for stable isotope analysis. Its carbon isotope composition is thus often masked by the terrestrial component of the suspended matter pool (see e.g. Chapter 5), and if we want to estimate its actual $\delta^{13}C$ value, we need to revert to e.g. $\delta^{13}C_{DIC}$ values (see Chapter 4) which can be converted into estimated $\delta^{13}C$ values for phytoplankton. Even when such data are available, the uncertainty associated with such estimates and the relatively small difference between estuarine phytoplankton $\delta^{13}C$ values and those of terrestrial organic matter usually do not allow their use in making reliable *quantitative* estimates of the relative contribution of these 2 components to an organism's diet. As we have mentioned on several occasions (Chapters 5 and 6), the variations in the $\delta^{13}C$ signature of aquatic primary producers are expected to be substantial in many mangrove ecosystems due to the often strong gradients in $\delta^{13}C_{DIC}$ (e.g. Chapter 4, Lin et al. 1991, Hemminga et al. 1994, France & Holmquist 1997, Marguillier et al. 1997, S. Marguilier unpublished data). As nearly all published stable isotope studies in mangrove ecosystems (e.g. Rodelli et al. 1984, Newell et al. 1995, Loneragan et al. 1997, Chong et al. 2001, Schwamborn et al. 2002) have not taken this variation into account but have rather taken typically marine phytoplankton $\delta^{13}C$ values as an end-member, an inherent overestimate of the importance of mangrove carbon for consumers is made, and some of the results of the abovementioned papers should thus be carefully (re-)interpreted.

The large spatial and seasonal variations that can be expected in the stable isotope signatures of aquatic primary production in a dynamic environment (and hence, the large sampling & analysis effort that would be required to describe these variations in detail) indeed make the interpretation of stable isotope data of consumers or organic matter pools not always straightforward, and hampers their direct quantitative use in mixing models. On the other hand, a comparison of the spatial and/or seasonal variations in stable isotope ratios between potential food sources and consumers (e.g. see Chapter 5 and 6) has been shown to be rewarding and may give qualitative and semi-quantitative (see this Chapter, pp. 292-293) information on the selectivity with which faunal communities use different primary carbon sources, and therefore on their relative importance.

When using $\delta^{13}C$ values as indicators of the contribution of different sources to the suspended organic matter pool (e.g. Chapter 5) or the sedimentary organic matter pool (e.g. Chapter 7), it was also clear that use of additional parameters (e.g. organic carbon content, elemental ratios, $\delta^{13}C_{DIC}$, but also POC/Chl a ratios, data on the distribution of lignin-related compounds etc.) can be extremely valuable if not indispensable for a correct interpretation.

Stable isotopes of nitrogen usually have little value as an indicator of the primary nitrogen source of a consumers' diet, but have been proven to be an indicator of the trophic level of an organism, due to the more pronounced fractionation that occurs between trophic levels. However, potential drawbacks in its application remain that (1) the degree of fractionation shows a rather large variability and may be dependent on the N content of the food source (as an indicator of its nutritive quality), and (2) that the mechanisms underlying the fractionation of ^{15}N are still poorly understood (see Chapter 1 for a more thorough discussion). Therefore, when detailed information on the trophic position of a specific organism is required, it may be needed to first determine the actual degree of fractionation in laboratory or controlled field conditions (e.g. see Webb et al. 1998, Gorokhova & Hansson 1999, Oelbermann & Scheu 2001, Schwamborn et al. 2002). In many cases, however, such detailed information is not required, and (average) $\delta^{15}N$ data of consumers can still provide useful information. In our dataset on subtidal benthic invertebrates, for example, a consistent difference in $\delta^{15}N$ values was clearly seen between 'higher' and 'lower' trophic level species (see Chapter 6) when different species and individuals were grouped as such. Based on this segregation for species on which information on their feeding habits are available, $\delta^{15}N$ values of less well known invertebrate species can be used to infer their approximate trophic position.

Under certain conditions, $\delta^{15}N$ values can also provide source information. In our study, this was the case in the intertidal mangrove areas (see Chapter 8) where some inconspicuous producers (epiphytic crusts) showed highly depleted $\delta^{15}N$ signatures (~ -8.2 ‰, although further characterization is needed), i.e. markedly different from the other major primary producers (mangroves, microphytobenthos, imported seston). These unusual values were reflected in the $\delta^{15}N$ signatures of several consumers, i.e. 3 species of *Littoraria* and in *Onchidium* sp. It is worth mentioning that Christensen et al. (2001) recently also found remarkably negative $\delta^{15}N$ values in several *Littoraria*

species from a Thai mangrove forest. Furthermore, we observed lower $\delta^{15}N$ values than expected in the top predator *Scylla serrata*, which might be explained when *Onchidium* sp. represents a significant (~10 %) proportion of its diet (see Chapter 8 for details). Finally, it should be stressed that $\delta^{15}N$ values of primary producers (and hence, of consumers) in the aquatic environment are also influenced by a variety of biogeochemical processes (nitrification, denitrification, uptake by phytoplankton) in addition to source and trophic level effects (see Chapter 1 and 6).

The analysis of stable isotope signatures in consumers can offer much more information than merely indications on the primary C sources and their trophic position. One particular example which will be discussed in more detail here is that in environments where spatial trends are known to occur in the stable isotope ratios of primary carbon and/or nitrogen sources (and therefore, of local consumers of these sources), the natural abundance of these isotopes in mobile consumers can be used as tracers of short-term or long-term movements (e.g. diurnal feeding migrations or migration from freshwater to the marine environment, respectively). One example given in this study was the seaward migration of penaeid prawns, as several specimens collected in the northern Kakinada Bay had $\delta^{13}C$ signatures which reflected their origin in the vicinity of the mangroves (see Chapter 6), and several similar cases are described in the literature (e.g. Fry 1983, Fry et al. 1999, Riera et al. 2000, see also Hobson 1999). As a second example, the potential of $\delta^{13}C$ and $\delta^{15}N$ to determine the main feeding habitats of benthic invertebrate feeding fish will be briefly illustrated based on our own unpublished stable isotope data of fish collected in the study area during Nov-Dec1999. A variety of fish species were collected at 7 locations, and background data on the stable isotope composition of sediments, suspended matter, and benthic invertebrates collected from these sites were discussed previously (Chapter 6). The rationale behind our approach was that :

(i) there are distinct spatial patterns in $\delta^{13}C$ values (and to a lesser extent in $\delta^{15}N$) of primary producers and consumers in this ecosystem (see Chapters 5, 6),

(ii) stable isotope ratios in benthic invertebrates from a single location show little interspecific variations, at least during a specific season (Chapter 6), and

(iii) macro-invertebrates from the intertidal areas, in contrast, show very diverse stable isotope signatures which are on average distinct from those found in creek invertebrates (Chapter 8)

Thus, when stable isotope ratios of benthic invertebrate feeding fish (hereafter referred to as BIF fish) are not consistent with those of the local benthos, this can result from either the use of specific feeding areas (which are different from the collection sites) or from their recent migration from areas in which their food sources are isotopically different. Although the data processing is ongoing and will require the integration of data from gut content analyses and on the seasonal distribution of the relevant fish species in the area (such data are collected by the Katholieke Universiteit Nijmegen in the framework of the EU-INCO project by which this work was funded, and will shortly be available), some general observations are worth mentioning. First, if we compare the stable isotope signatures of assumed BIF fish (preliminarily categorized as such based on data from Froese & Pauly 2000) at each of the sampling locations (Figure 1), several patterns are noticed : (1) in the three true mangrove creek locations (Figure 1A, B, C) many of the BIF fish show $\delta^{13}C$ values significantly more enriched than would be expected if they fed mainly on creek benthic invertebrates. In Kakinada Bay (Figure 1D) and to a lesser extent in the vicinity of Kakinada Canal (Figure 1E), in contrast, many BIF fish were depleted in ^{13}C relative to their assumed local food sources. Finally, stable isotope signatures of BIF fish in Mukanali Dibba and Guticada (Figure 1F, G) were consistent with local feeding. It is worth mentioning that sampling in the latter two sites was performed with block nets along Hope Island, and fish (collected at low tide) at these extensive mudflats can indeed be expected to have been feeding locally on invertebrates.

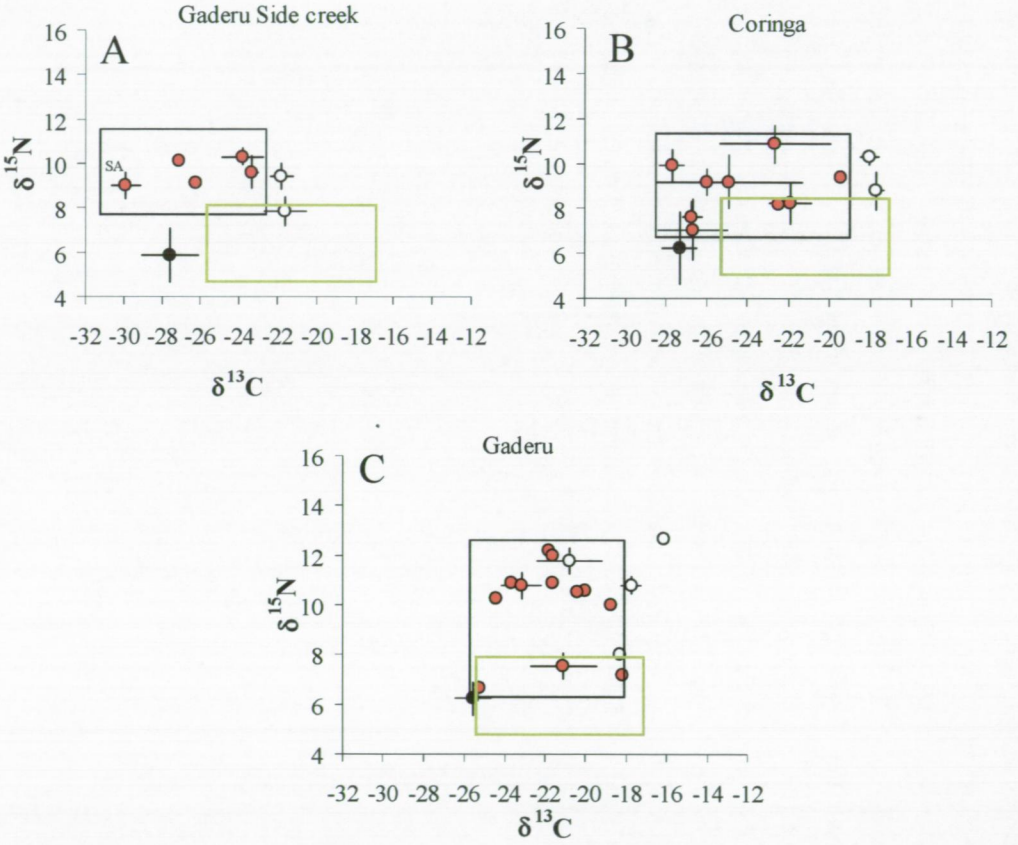


Figure 1 : $\delta^{13}C$ - $\delta^{15}N$ plot of fish species collected at various locations in the Coringa Wildlife Sanctuary and adjacent Kakinada Bay during post-monsoon of 1999 (see Chapter 6 for location of sites). Black symbols : lower trophic level benthic invertebrates sampled during the same period at the specified site (data from Chapter 6), red symbols : benthic invertebrate feeding fish, and open symbols : fish with other or unknown feeding habits. The green square represents the stable isotope signature for most intertidal invertebrates (see Chapter 8). SA : *Scatophagus argus*. Error bars = 1 s.d.

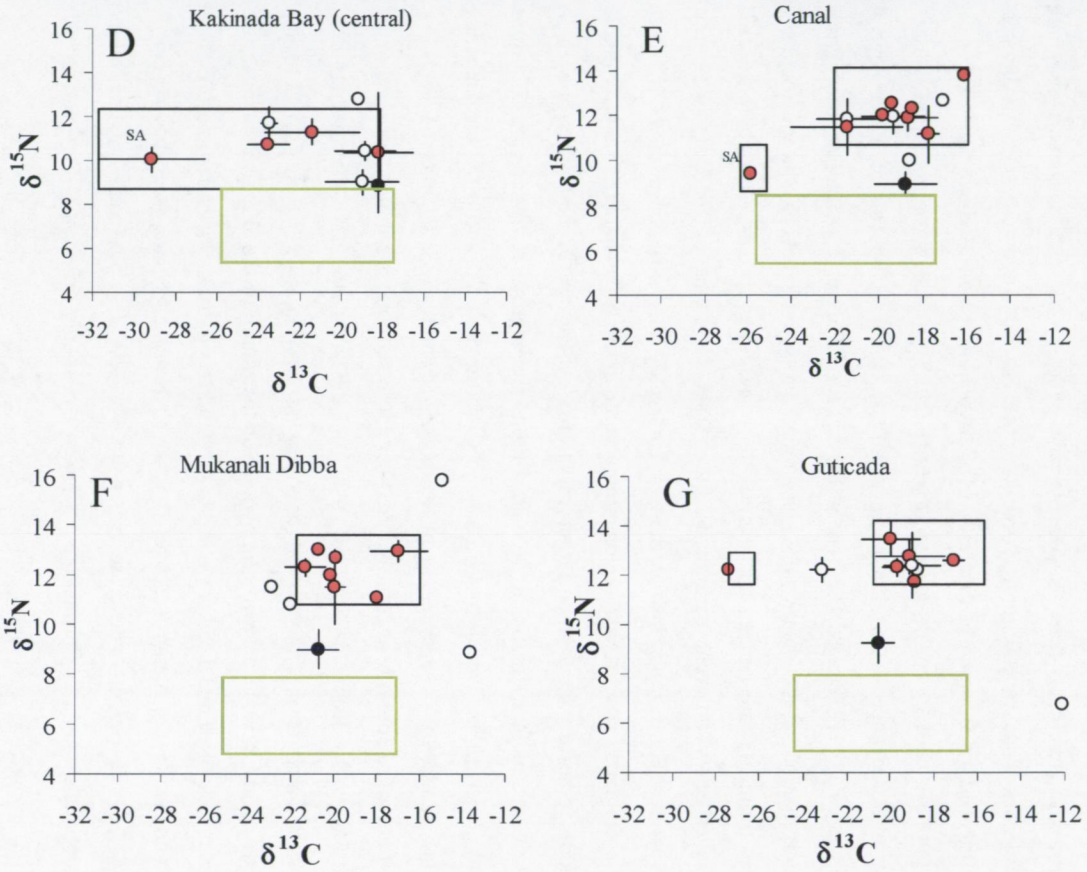


Figure 1 (continued): $\delta^{13}C$ - $\delta^{15}N$ plot of fish species collected at various locations in the Coringa Wildlife Sanctuary and adjacent Kakinada Bay during post-monsoon of 1999 (see Chapter 6 for location of sites). Black symbols : lower trophic level benthic invertebrates sampled during the same period at the specified site (data from Chapter 6), red symbols : benthic invertebrate feeding fish, and open symbols : fish with other or unknown feeding habits. The green square represents the stable isotope signature for most intertidal invertebrates (see Chapter 8). SA : *Scatophagus argus*. Error bars = 1 s.d.

The data from the mangrove creeks may suggest that fish make extensive use of the intertidal mangrove areas as feeding grounds, whereas the more negative than expected $\delta^{13}C$ signatures of fish in the central Bay may have resulted from recent immigration from the mangrove creeks or freshwater areas, or from more short-term movements whereby fish residing the Bay can use the extensive mud flats along Hope Island or the intertidal mangrove areas as important feeding grounds. In the case of the Kakinada Bay samples, this is also suggested by the generally low $\delta^{15}N$ values of BIF fish (i.e. not markedly higher than in the mangrove creeks, and clearly lower than in Mukanali Dibba and Guticada), which is in contrast with the $\delta^{15}N$ trend observed in benthic invertebrates (see also Chapter 6). At least one species shows convincing evidence of its recent immigration into the Bay area from a more freshwater-influenced environment : juveniles of *Scatophagus argus* (indicated as 'SA') on Figure 1A, D, E are consistently more depleted in ^{13}C than any available food source.

As a second approach, we have presented data for three species of which several individuals were caught throughout the area in Figure 2. Although a rigorous interpretation of the data will require more background data on the ecology and feeding habits (gut content analysis) of these and other species, these three selected species show different patterns in the spatial variations of their stable isotope signatures. For *Terapon jarbua*, there is remarkably little variation in the $\delta^{13}C$ values of specimens from different regions (remarkable in the sense that the locally available food sources *do* show much larger variations), whereas $\delta^{15}N$ values do show large variations and are significantly lower in the two mangrove creek locations (Coringa and Gaderu). For *Pomadasys kaakan*, in contrast, the $\delta^{13}C$ and $\delta^{15}N$ variations are quite similar to those observed in benthic invertebrates (see Chapter 6), with one important exception being that whereas benthic invertebrates are most enriched in the central part of Kakinada Bay, BIF fish from the same area have intermediate $\delta^{13}C$ values. The latter is also observed for e.g. *Leiognathus equulus* (Figure 2, final panel), and would be consistent with the hypothesis that many of the BIF fish caught in the central Bay area make extensive use of the mudflats in the south-eastern part of Hope Island and/or the mangrove-covered areas as feeding grounds (see above). For *L. equulus*, the general pattern described for *P. kaakan* is observed, but one of the individuals caught in Coringa creek showed a markedly different $\delta^{13}C$ signature than

the rest of the individuals from this location (see Figure 2, last panel), suggesting its non-local origin.

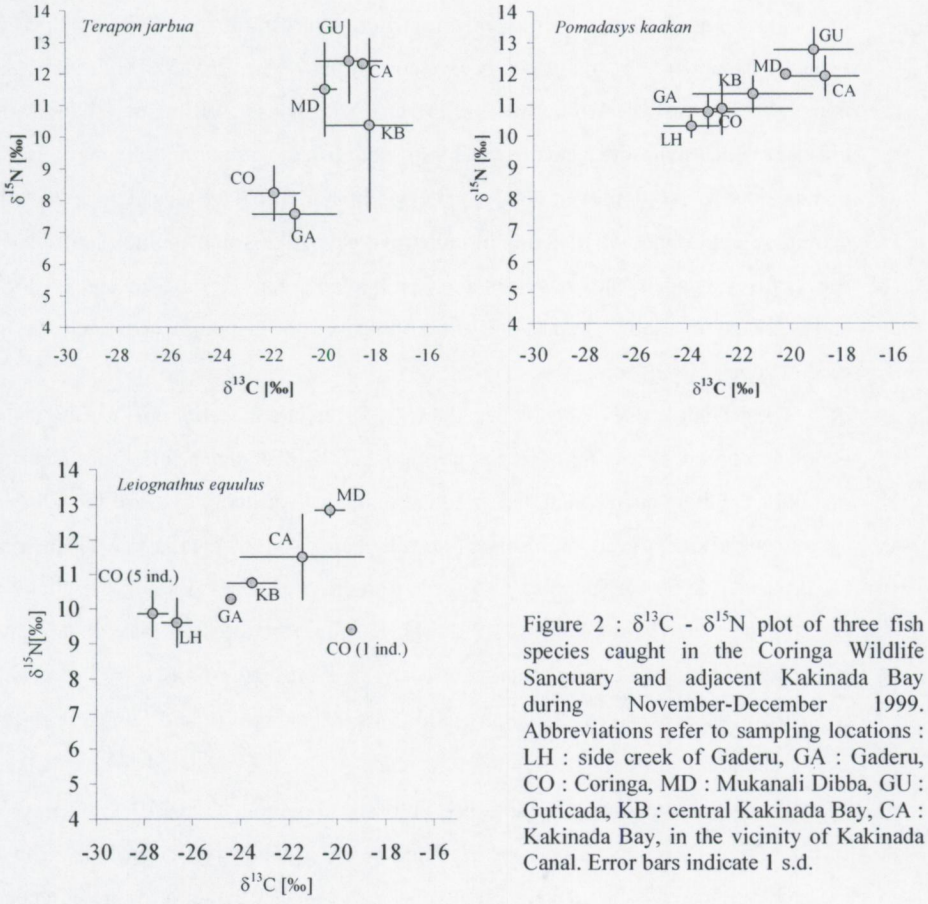


Figure 2 : $\delta^{13}C$ - $\delta^{15}N$ plot of three fish species caught in the Coringa Wildlife Sanctuary and adjacent Kakinada Bay during November-December 1999. Abbreviations refer to sampling locations : LH : side creek of Gaderu, GA : Gaderu, CO : Coringa, MD : Mukanali Dibba, GU : Guticada, KB : central Kakinada Bay, CA : Kakinada Bay, in the vicinity of Kakinada Canal. Error bars indicate 1 s.d.

II. IMPORTANCE OF DIFFERENT CARBON SOURCES FOR CONSUMERS

Since the publication of the work of Odum & Heald (1972, 1975) on the outwelling of organic matter from mangroves, there have been numerous studies on the importance of mangrove and salt marsh primary production as a carbon source for benthic and pelagic consumers. For mangrove ecosystems in particular, it was hypothesized that mangrove litterfall fuels much of the system, and that a 'detritus-based foodweb' exists in which plant litter is converted into more palatable microbial biomass, which in turn acts as the dominant food source for higher trophic levels. In view of the economic importance of fisheries in mangrove ecosystems and the adjacent waters, such a trophic dependency has been an often-quoted argument for their conservation, and is almost invariably cited as one of the 'functions' of mangrove ecosystems in the coastal zone (e.g. Ellison 2000).

With the advent of new techniques (and in particular, the common use of stable isotope techniques) to study the sources and fate of different primary producers, a number of authors have concluded that the trophic role of mangroves for the adjacent aquatic environment is either minimal (Newell et al. 1995, Primavera 1997, Dehairs et al. 2000, Lee 2000) or spatially restricted (Rodelli et al. 1984, Fleming et al. 1990, Loneragan et al. 1995, Chong et al. 2001). It should be stressed that all the latter studies may need to be interpreted cautiously, as their conclusions were based on a comparison of consumer $\delta^{13}C$ values with those of mangroves and typically marine phytoplankton, without taking the existence of a ^{13}C-depleted phytoplankton population in the vicinity of mangroves into consideration. A spatial trend in $\delta^{13}C$ values of aquatic production can be expected in mangrove ecosystems (and was even indirectly indicated by the data in Chong et al. 2001 – see Chapter 6 for more details), and can be very pronounced (as e.g. in our study area, see Chapter 4), which implies that any interpretation of the data in the abovementioned papers (and others, e.g. Schwamborn et al. 2002) remains speculative. Seasonal variations in $\delta^{13}C$ may also not always have been properly taken into account, e.g. the findings of Loneragan et al. (1997) that $\delta^{13}C$ values of juvenile penaeids in a mangrove estuary were lower during the wet season may have resulted from changes in the ^{13}C content of the DIC pool, rather than from a larger contribution of mangrove detritus.

In our study, we found that on an annual basis, zooplankton in the mangrove creeks of the CWS and the adjacent Kakinada Bay were clearly more dependent on local aquatic primary production than on terrestrial (which here includes mangrove-derived) carbon sources (Chapter 5). Although our dataset does not allow us to make reliable quantitative estimates of the relative contribution of both (see below), a clear selectivity for local production was evident, i.e. the higher contribution of local production was not merely the result of its larger availability. This selectivity was not immediately evident from a comparison of absolute $\delta^{13}C$ values of zooplankton and suspended matter, but from a more detailed look into the spatial and seasonal variations, which were much more pronounced in zooplankton than in bulk suspended matter. Although a number of detailed stable isotope studies have recently focused on the nutrition of zooplankton in freshwater ecosystems (e.g. Gu et al. 1996a, Jones et al. 1999, Grey et al. 2000, 2001), studies in estuarine ecosystems are scarce. Our data are in general agreement with the recent results of Schwamborn et al. (2002) who found that the contribution of mangrove litter to selected zooplankton species (note that bulk zooplankton was analyzed in our study) in a Brazilian mangrove estuary was almost negligible. If we consider the (potential) importance of zooplankton as a trophic link to larger pelagic consumers (e.g. certain shrimp and fish species), these findings are clearly significant in demonstrating that an important trophic link between mangroves and the latter consumers appears unlikely.

For subtidal benthic invertebrates in the same area, aquatic (and presumably benthic) primary production was shown to be the dominant primary carbon source, both during pre-monsoon and post-monsoon season (Chapter 6). In order to be able to correctly interpret consumer stable isotope signatures in such a dynamic ecosystem, (semi-) quantitative and/or qualitative data on the variability (spatial and seasonal) of primary producers were shown to be indispensable. Even though the evidence for selectivity is unquestionable (see Chapter 6) and the observed $\delta^{13}C$ data are consistent with a dominance of phytoplankton and benthic microalgae at the foodweb basis, any attempt at quantification of the relative contribution of different sources remains difficult and prone to error.

We can exemplify this by attempting a quick calculation of the overall selectivity of benthic invertebrates for local production using the pre-monsoon and post-monsoon dataset provided in Chapter 6. As described in more detail elsewhere, the sediment

organic matter pool and the suspended POC pool show an average spatial difference (between the mangrove creeks and the adjacent Kakinada Bay) of about 2.5 and 2.7 ‰, respectively. This variability is much smaller than that expected in phytoplankton and benthic microalgae, as the DIC pool exhibits a much larger variability of –on an annual basis- approximately 6.8 ‰ (see Chapter 4). Benthic invertebrates were found to display a spatial gradient of approximately 6.9 and 8.8 ‰ during pre- and post-monsoon, respectively.

We can formulate the overall selectivity (i.e. assuming that the degree of selectivity is similar in the whole region – no doubt an oversimplification) as :

$$\text{Selectivity} = \left(\frac{\Delta\delta^{13}C_{\text{invertebrates}} - \Delta\delta^{13}C_{\text{POC}}}{\Delta\delta^{13}C_{\text{DIC}} - \Delta\delta^{13}C_{\text{POC}}}\right) * 100 \qquad [\%]$$

where :

$\Delta\delta^{13}C_{\text{invertebrates}}$: the overall gradient in invertebrate $\delta^{13}C$ values

$\Delta\delta^{13}C_{\text{DIC}}$: the overall gradient in DIC $\delta^{13}C$ values

$\Delta\delta^{13}C_{\text{POC}}$: the overall gradient in POC $\delta^{13}C$ values (note that we might similarly have taken sediment organic carbon)

Thus, if $\Delta\delta^{13}C_{\text{invertebrates}} = \Delta\delta^{13}C_{\text{POC}}$, no selectivity occurs (i.e. local aquatic production and terrestrial sources are used in the proportions in which they occur in the POC pool), whereas $\Delta\delta^{13}C_{\text{invertebrates}} = \Delta\delta^{13}C_{\text{DIC}}$ implies a selectivity of 100 %. This immediately shows that a selectivity of approximately 100 % (pre-monsoon) or even > 100 % (post-monsoon) occurs. Note that the same approach used on the average zooplankton data (Chapter 5) also results in a calculated selectivity higher than 80 %. The example above shows the problems associated with such an approach :

(1) despite the large amount of $\delta^{13}C_{\text{DIC}}$ data, how appropriate is the annual average used (6.8 ‰) ? The spatial trend is fairly consistent throughout the year, but the slightest error on this value has a major impact on the calculated selectivity. The same line of thought holds for the POC value used.

(2) The described calculation no longer holds if the degree of selectivity varies spatially, or if the relative role of benthic and pelagic microalgae varies. Both assumptions cannot be ruled out.

Could we reliably estimate the selectivity at a single station using the benthic invertebrate data gathered in this study ? For several reasons, such an attempt is precluded. First, the $\delta^{13}C$ values of primary producers in such a dynamic environment will be variable even at a single location, over very short time periods (e.g. tidal variations, see Chapter 4) and over several months (e.g. Chapters 4 and 5) - and the consumer $\delta^{13}C$ values represent an integration over time of these variations. Thus, a correct characterization of the phytoplankton or microphytobenthos $\delta^{13}C$ at a given site remains problematic. Secondly, as the difference between $\delta^{13}C$ signatures of terrestrial sources and local production can become minimal inside the creeks (since monthly averaged $\delta^{13}C_{DIC}$ values for mangrove creeks vary widely between -12.4 and -5.8 ‰, see Chapter 4, Figure 10), the errors that arise when two-end mixing models are employed to calculate their relative contribution become unacceptable (see Phillips 2001 and Ben-David & Schell 2001).

In conclusion, the role of mangrove carbon in sustaining aquatic faunal communities (both benthic and pelagic) appears to be minimal, and any potential role (for which, in our view there is currently little direct convincing evidence) is most likely to be spatially restricted. In this respect, there is currently no evidence to assume that benthic and pelagic foodwebs in estuarine mangrove ecosystems function in a substantially different way than those in non-mangrove estuaries (e.g. see Chanton & Lewis 2002).

The above discussion only applies to the subtidal aquatic ecosystem, but not for the intertidal. In the latter, the role of mangrove carbon has been much less debated (and much less studied) and this is no doubt to a certain extent due to the fact that consumption of leaf litter by crabs is an often conspicuous feature in mangrove forests, and that the role of leaf litter therefore appears obvious. Nevertheless, we showed that at least for the mangrove forest in our main study area, the intertidal invertebrate community showed a remarkably wide range of stable isotope signatures (and hence, of the resources used), and mangrove-derived carbon itself was overall (*sensu* at the community level) not at all dominant (note that in view of the low N-content of mangrove litter compared to other available sources, the importance of mangroves as an N source is expected to be even more limited). The few studies which have used a stable isotope approach to study the dietary sources for specific intertidal mangrove invertebrates (e.g. France 1998, Christensen et al. 2001, Hsieh et

al. 2002, Lee et al. 2002) came to similar conclusions. Although the compilation of $\delta^{13}C$ data on intertidal mangrove invertebrates from the literature and from this study resulted in a relatively large dataset (see Chapter 8), the number of sites in which a community-level evaluation of the carbon sources sustaining these communities has been made is currently much too small to obtain a more refined view on the generality of our conclusions and on the possible environmental factors which may influence the importance of different C sources for intertidal invertebrates in a given site (e.g. the availability of imported carbon sources, e.g. see Chapter 7).

Moreover, there are as yet no studies for which data on more than a few different species are available from the African continent, the whole Indo-Pacific from Indonesia to Australia, nor from Central or South-America, and we therefore propose that a number of comparable studies from a range of (geographically and environmentally) different mangrove forests are required. We have also demonstrated (see also Christensen et al. 2001) that a number of more inconspicuous primary producers in mangrove ecosystems are as yet insufficiently characterized, and their inclusion in stable isotope studies may be particularly important.

One additional question which has been ignored in all studies on intertidal mangrove foodwebs so far is what carbon sources sustain more inconspicuous consumers, in particular meiofauna (which in these habitats is usually dominated by nematodes, harpacticoid copepods and foraminiferans) and infaunal groups such as polychaetes (see Hsieh et al. 2002). Although it has been suggested (Alongi 1987a, c, Tietjen & Alongi 1990) that mangrove litter may be an inappropriate food substrate for some species of nematodes, the relative importance of local microphytobenthic production, imported carbon sources, or mangrove-derived carbon has not been assessed in any mangrove ecosystem, nor are there specific data on the role of microbial heterotrophs (bacteria, fungi) as trophic intermediates. It was recently found that local production by microphytobenthos and imported phytodetritus are the main carbon sources for the nematode communities of intertidal flats and salt marshes in the Westerschelde (Moens et al. 2002). The role of meiofauna in channelling primary production (regardless of its source(s)) in mangrove ecosystems remains unknown.

If the importance of mangrove litter in sustaining invertebrate communities in intertidal mangrove forests will prove to be relatively minor in a variety of other sites (i.e. as found in our study area), one obvious question which arises is how we can

(re)define the role of mangroves in sustaining these communities. Clearly, the main importance of mangroves then appears to be in providing a suitable habitat (structural complexity, shade, substrate, and food sources such as benthic, epiphytic, and deposited algae).

One final important remark concerning the relative importance of mangroves and other primary producers in sustaining faunal communities is that most of the above discussion relates to the relative contributions of different primary *carbon* sources. If we were to evaluate the relative importance of mangroves and other producers in ensuring the N requirements of faunal communities, the role of mangroves would in most cases be significantly lower, due to the low N content of mangrove biomass compared to most other available sources. Due to the often small differences in $\delta^{15}N$ values between primary producers, the inherently larger uncertainty regarding the trophic fractionation of ^{15}N (see Chapter 1), and the impact of major biological processes such as nitrification, denitrification and DIN uptake by phyotoplankton on baseline $\delta^{15}N$ signatures, the natural abundance of ^{15}N is usually of not much direct use to distinguish between different N sources (see discussion in this chapter, pp. 3-4)

Sources of organic carbon in the intertidal sediment pool

The origin of carbon in intertidal mangrove sediments collected from a variety of mangrove forests was found to be highly variable (Chapter 7), with strongly different proportions of locally produced (mangrove) carbon and imported carbon sources (e.g. from aquatic primary production by phytoplankton or seagrasses). Evidently, the tidal influence was proposed to be a major factor influencing the relative importance of these two major contributors (see also Twilley 1985). As for the contribution of mangrove-derived carbon, the relative importance of leaf litter inputs and other components (wood, roots) deserves further study (e.g. see Middleton & McKee 2001). Furthermore, the contribution of *live* microbial (fungi, bacteria) and microphytobenthic biomass was shown to be minor in the total sediment organic carbon pool by analysis of polar-lipid derived fatty acids (see Chapter 7), a phenomenon which appears to be quite universal (e.g. Findlay et al. 2002). Whether or not bacterial and microphytobenthic production are preserved to a significant extent in the sediment organic matter pool as *dead* biomass remains unresolved. As discussed in Chapter 7, the variability observed in the stocks and origin of organic

carbon may have a significant impact on the overall carbon dynamics (e.g. on the utilization patterns of carbon sources by invertebrates), but any relationship remains speculative until further studies are undertaken.

III. THE FATE OF MANGROVE CARBON : SOME CONSIDERATIONS

In previous chapters, we have shown that mangrove detritus contributes overall little to aquatic foodwebs, and that its utilization even by intertidal communities appears much more limited than expected. Both intertidal (Chapter 7) and subtidal (Chapter 6) sediment organic matter also appears to contain much less mangrove-derived carbon than might was expected. The obvious question which then arises is 'where does all the carbon fixed by mangroves end up ?'. Are there other pathways in which mangrove carbon is lost from the ecosystem, or do the relatively small contributions by mangrove carbon to the abovementioned pools or destinations add up to the total mangrove primary production ? Although we will not be able to provide a definitive answer the latter question due to the lack of quantitative data on C fluxes, the following discussion will focus on evaluating the different potential fates for mangrove-derived carbon, rather than evaluating its role in comparison with other carbon sources (for the latter, see this Chapter, first section). As a general outline, it may be instructive to revert to the scheme presented earlier in Chapter 2 which provides an overview of the possible fate of mangrove carbon (Figure 3).

First, **production** by mangroves is known to be high compared to other ecosystems (see Chapter 2) and varies with latitude. In the CWS (at ~16 °N), litterfall rates for *Avicennia marina* and *Excoecaria agallocha* reported by Dehairs et al. (2000) are within the range expected for its latitude (see Twilley et al. 1992), and amount to an estimated (i.e. assuming the average litterfall rate of both species is representative of the whole area, and assuming an approximate areal cover of 150 km² for the CWS) total production of 151,000 t DW y^{-1}, i.e. ~ 63,400 t C y^{-1}. It is important to stress that this is a very rough estimate in that the assumptions (areal cover, averaged litterfall rate) are prone to large errors, and that it only takes litterfall into account and not e.g. belowground production. By contrast, aquatic primary production by phytoplankton can be *very* roughly estimated at 178,000 t C y^{-1} for the entire mangrove creek system and Kakinada Bay, using the data presented in Murthy (1997) and Raman

(2000) and converting these to an annual basis (taking 1.5 meter water depth at which photosynthesis occurs, averaging available primary production data for North Bay, South Bay, and mangrove creeks and assuming surface areas of 70 km², 70 km², and

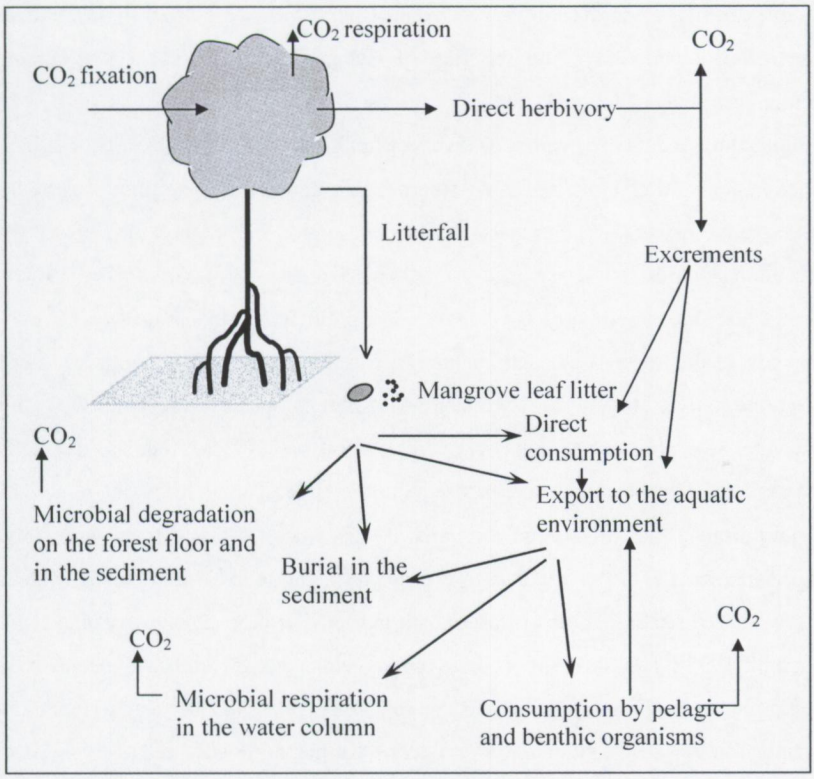


Figure 3 : Schematic overview of the potential fate of mangrove litterfall.

10 km², respectively). Although it is tempting to directly compare these two estimates (mangrove carbon then represent ~ 20 % of the total production for the CWS-Kakinada Bay), it may be safer to state that the carbon inputs by phytoplankton and mangroves appear to be of the same order of magnitude. Quantification of the production, stocks and fluxes of different carbon sources in this ecosystem is at this stage impossible, because the complexity of the area and the seasonal dynamics would require high-resolution (spatial, seasonal) data on microphytobenthic production (currently no data available, whereas stable isotope data do indicate their importance, e.g. Chapter 8), pelagic production (few data available, but highly

variable which makes the estimated annual areal production uncertain), mangrove production (one-year litterfall data available for two species), and the inputs of terrestrial (and other) carbon sources by the Gautami Godavari and other freshwater sources (Matlapalem Canal, Kakinada Canal) are also entirely unknown. The complexity of such a system and its connectivity with freshwater inputs, the semi-enclosed Kakinada Bay, and the Bay of Bengal would make such an attempt a challenging study of its own.

No quantitative data are available on **direct herbivory** for the study area, but in most other systems where this has been studied, this appears to be minimal (Lee 1986, Robertson & Duke 1987, Farnsworth & Ellison 1991, 1993, Saur et al. 1999, although exceptional cases do exist e.g. Anderson & Lee 1995). In theory, however, quantifying direct herbivory is relatively straightforward albeit time-consuming : as only part of the leaves are usually eaten (i.e. not removed whole), it suffices to collect a representative amount of leaves from different species of mangroves and to calculate (e.g. by image analysis) the proportion of leaf damage by grazing (references). **Direct consumption** of mangrove litter (or at least, its removal and burial by fauna) has often been estimated to account for a major fraction of the total litter fall (see Lee 1998 for a review), in particular in the Indo-Pacific where the importance of sesarmid crabs is larger than in the New World mangroves (see McIvor & Smith 1995). The observation that some conspicuous invertebrate species feed on mangrove leaves and propagules and that in some ecosystems, they are able to remove a major fraction of the litter fall (see Lee 1998), has no doubt fuelled the apparently evident hypothesis that mangrove litter is the dominant carbon source for intertidal invertebrates. Nevertheless, our results (Chapter 8) show that, from a community perspective, mangrove litter appears not to be of dominant importance, at least not for the area studied. Here, it is important to distinguish that these two seemingly paradoxical conclusions -(1) that large amounts of litter can be removed by fauna, and (2) that other sources may be more important as a carbon source for invertebrates- are not necessarily mutually exclusive. If a small number of species which have mangrove litter as a substantial part of their diet (but not necessarily as the dominant source) dominate the total biomass of invertebrates (or rather, their production or consumption), than both can go hand in hand and that it is merely a question of looking "from the tree's point-of-view" or "from the invertebrate communities' point-of-view". Testing such a hypothesis could actually be very rewarding, and requires

the combination of a community-level study of the sources of carbon sustaining each species and good knowledge of each species' consumption rates and their relative abundance. As the latter data are entirely lacking for our study area, it is impossible to estimate the actual amount of mangrove carbon (as a percentage of mangrove production) that is lost through consumption by intertidal fauna.

Mineralization of mangrove litter and sediment organic carbon on the forest floor or in the sediment organic matter pool is unquantified, but a comparison of litterfall rates and degradation constants of mangrove litter measured by Rao (1998) in the study area, and data from the literature (see Chapter 2, pp. 22-24) suggest that degradation of leaf litter in the study area is comparably fast and may therefore be an important pathway for mangrove carbon to be lost from the ecosystem. Although it has sometimes been suggested that sediment respiration represents only a minor fate of mangrove carbon, this does not appear to be generally valid, as discussed in more detail in Chapters 2 and 7.

The **burial** and storage of mangrove carbon in the sedimentary organic matter pool is also the subject of discussion. The generally high efficiency attributed to the storage of mangrove carbon in sediments (e.g. Alongi 1998) is in our opinion unlikely to be generally valid (see Chapters 2 & 7 for a more detailed discussion), and a compilation of data gathered in this study and from the literature shows a whole spectrum of sources and stocks of organic matter in mangrove sediments. Again, the assessment of the proportion of mangrove carbon that is stored in mangrove sediments is not straightforward and the data needed for such an estimate are not available for the study area, but a rough calculation will be made to constrain this proportion. If we assume an accretion rate of 5-10 mm y^{-1} (which is no doubt an overestimate, see e.g. Ellison 1998), and a specific gravity of the deposited material of 1.5 g cm^{-3} (a 'normal' value for estuarine sediments, but in more organic-rich sediments this may be much lower, e.g. McKee & Faulkner 2001), this amounts to the deposition of 7,500 - 15,000 g m^{-2} y^{-1}, of which (on a dry weight basis), approximately 1 % is organic carbon, i.e. 75 - 150 g of organic carbon per m^2 (note that the latter is again *a priori* an overestimate as it is calculated from the wet weight, not dry weight, of the deposited material). Our $\delta^{13}C$ data for sediment organic matter (-23.0 ± 1.1n n = 28) and C/N data (10.9 ± 2.1, n = 27) suggest that the contribution of mangrove carbon (average for the study area : -28.5 ± 1.5, n = 27) is unlikely to be higher than 20 %

(assuming suspended matter as the second important source, with a $\delta^{13}C$ of ~ -22 ‰, which might also be an overestimate, see e.g. Chapter 4 and 5). This rough calculation would constrain the *maximal* amount of mangrove carbon accumulating in the sediment at 15-30 g m^{-2} y^{-1}, i.e. ~ 3 - 6 % of the litterfall (average for *Avicennia officinalis* and *Excoecaria agallocha* of ~ 1000 g DW m^{-2} y^{-1}) as reported by Dehairs et al. (2000). Although the data in this calculation should not be taken too strictly, it does suggest that burial in the intertidal sediments is only a minor fate of mangrove primary production in the study area.

As for the **export** of mangrove-derived carbon, it should first of all be mentioned that again, no quantitative data on export (or rather, exchange) rates of organic carbon are available for the study area (as indeed, due to the complexity of the system, reliable data on the exchange of carbon would be nearly impossible to generate). Nevertheless, some of our results give us some indications on the relative importance of export as a fate of mangrove carbon and the subsequent processes that may happen to it. First, the $\delta^{13}C_{POC}$ and POC/PN data of suspended matter in the mangrove creeks and Kakinada Bay (Chapter 4) do indicate that terrestrial organic matter is present in the POC pool, and it is safe to assume that mangrove carbon is a significant component of this terrestrial matter - at least during non-monsoon seasons. We also have some indications that the DOC pool may have been seriously overlooked (Chapter 4), and that a closer examination of the sources and dynamics of DOC might give us more insight into the export of mangrove carbon. It is therefore unquestionable that export of mangrove carbon occurs in the study area (which is also expected as it appears to be a relatively unexploited food source in the intertidal areas, and as only a minor part of it appear to be stored in intertidal sediments, see discussion above). The obvious question is then : what happens to the exported mangrove carbon, i.e. what is the relative importance of (1) its consumption by fauna, (2) its burial in the sediment pool, and (3) its mineralization in the water column ?

As for its **consumption** by pelagic and benthic fauna, our data have shown that (at least for the particular area under study) mangrove carbon contributes very little to the carbon requirements of benthic invertebrates and zooplankton (and therefore, to higher trophic level species which use these as a food source) and that these communities are able to make very selective use of other primary carbon sources, i.e. local microalgal production. However, as mentioned before for the intertidal faunal

communities, our data do not allow us to make an estimate of the total amount of mangrove carbon that is ultimately taken up by these faunal communities, but as the contribution of mangrove carbon was estimated to be very small (see Chapters 5 and 6 and this Chapters, pp. 3-4), we hypothesize that this represents only a minor fate for mangrove production. Considering the fact that intertidal sediments were shown to store surprisingly little mangrove-derived carbon (Chapter 7), it is not entirely surprising that $\delta^{13}C$ values of surface organic matter in subtidal **sediments** of the adjacent Kakinada Bay were quite high (generally between -21 and -18 ‰) and are not indicative of a large terrestrial influence (with the exception of some locations in the plume of the Kakinada Canal effluent, see Chapter 6). However, during the fieldwork campaign in May-June 2001, several southern Bay stations were sampled (by AV Raman and F Dehairs) with a suction hose equipped with a relatively large-mesh sieve (1 mm) and were found to contain a larger plant debris. These fractions were analyzed for their elemental and carbon isotope composition and were found to have an organic carbon content between 9.3 and 33.9 %, C/N ratios between 9.5 and 26.7 and $\delta^{13}C$ ratios between -27.6 and -24.7 ‰ (with low $\delta^{13}C$ values coinciding with high C/N ratios), indicative of an important contribution of terrestrial debris to this size fraction. Although we have no indication of the origin of this debris (terrestrial *vs.* mangrove), it is not unlikely that at least part of this material is of mangrove origin (it should be kept in mind, however, that the Gautami Godavari had its main discharge into Kakinada Bay until quite recently, see Chapter 3, pp. 85-88). It would certainly be worth investigating further the origin and contribution of this size fraction to the total sediment organic carbon pool.

Finally, one potential fate of mangrove carbon which has received very little attention in the literature and has, in fact, not been quantified for a single mangrove ecosystem, is the **mineralization** of mangrove-derived carbon in the water column. In the Coringa Wildlife Sanctuary, however, the data gathered in the framework of this thesis and those collected by the Dept. of Oceanography (ULg, see Chapter 4) demonstrate the importance of the tidal creek network as sites of intense mineralization of organic matter. This was shown from the consistently low $\delta^{13}C_{DIC}$ values, low pH, and high pCO_2 observed in the tidal creeks, while these characteristics rapidly fade towards the adjacent Kakinada Bay. Although the short time frame of the pCO_2 data and the uncertainties associated with converting them to actual CO_2 fluxes

do not allow us to make an estimate of the quantitative importance of CO_2 efflux as a fate of mangrove carbon, we hypothesized (see Chapter 4) that this pathway may be very important. Its quantification in several mangrove ecosystems clearly deserves more research attention. In the latter context, several additional questions arise :

(1) To what extent can the markedly different biogeochemistry observed (cfr. Chapter 4) be related to the presence of mangroves itself, i.e. would the same pattern have resulted if the estuary had been cleared of mangrove vegetation and replaced by e.g. more extensive aquaculture ? Although we have shown evidence that some processes can be directly linked to the presence of mangroves (e.g. the higher mineralization of organic matter, which must have been of mangrove origin during the pre-monsoon period), it must also be kept in mind that physico-chemical conditions in the creeks may differ due to changes in water flow, sedimentation rate, ... and that these may influence biogeochemical processes. Although distinguishing such effects is not straightforward, a number of comparable studies in temperate and tropical river systems, with and without large vegetated intertidal areas (salt marshes and mangroves, respectively) in their estuarine zone, would no doubt be instructive.

(2) Our dataset also points out that the composition and dynamics of the dissolved organic carbon (DOC) pool deserves much more attention. It is well known that a major fraction of mangrove biomass may be leached as DOC (e.g. see Chapter 2), but the stocks and composition of DOC in mangrove ecosystems have rarely been studied, let alone be compared with that in adjacent ecosystems. The combination of several techniques for the characterization of DOC (e.g. lignin derivatives, see Dittmar et al. 2001, ^{13}C and ^{14}C composition, see Raymond & Bauer 2001) and for studying its dynamics (e.g. see repeated diurnal cycles over longer time periods, e.g. Lara & Dittmar 1999, Dittmar et al. 2001, long-term flux studies e.g. Davis et al. 2001a,b) would be useful to gain more insights into the sources and fate of DOC and its importance as a pathway for the removal of mangrove carbon. Similarly, the application of relatively recent approaches and techniques, such as the experimental *in situ* labelling of autotrophic production or heterotrophs with ^{13}C (e.g. as bicarbonate and glucose, respectively) and the follow-up of the applied label in various components of the aquatic system (POC, DOC, DIC, autotrophs and

heterotrophs) through various stable isotope techniques could provide important clues into the dynamics of the DOC pool and its interaction with other components of the aquatic system.

With respect to the role of mangrove carbon on a worldwide scale, Twilley et al. (1992) and, more recently, Jennerjahn & Ittekkot (2002) provided the first detailed estimates of the amount of mangrove carbon accumulating in (mangrove) sediments at ~ 20 to 23 x 10^{12} g C y^{-1} respectively, which would amount to approximately 15 % of the organic carbon accumulating in modern marine sediments (Berner 1982, cited in Jennerjahn & Ittekkot 2002). In addition, Jennerjahn and Ittekkot estimated that the export of mangrove carbon makes up ~ 11 % or the total global organic carbon inputs into the oceans (whereas Twilley et al. 1992 estimated this contribution at a slightly higher 14 %). Jennerjahn & Ittekkot (2002) thereby assumed :

(1) that the high productivity of mangroves and the low ratio of sediment respiration to net primary production make mangroves highly efficient in the sequestration of carbon into sediments

(2) that leaves are the major source of the carbon accumulating in mangrove sediments, and

(3) that most carbon is exported from mangrove systems as leaves.

Evidently, the reliability of such an estimate is dependent on the underlying assumptions and the estimated contributions of mangrove carbon might have to be considered cautiously. Below we have listed some considerations which currently hamper a more refined budget of the contribution of mangrove carbon to global carbon export and burial, and which call for more basic research to provide the data needed for a correct evaluation.

(1) it is unclear whether the low T_{COX} / NPP ratios (i.e. the ratio of total carbon oxidation rate in the sedment to net forest primary production) observed in the few studies that examined them are generally valid, see discussion on this matter in Chapter 2 pp. 25-27

(2) the assumption that leaves are the major source of carbon accumulating in mangrove sediments does not appear to be generally valid. Our results show that the sources of organic carbon in mangrove sediments may be very variable, and there are even arguments to suggest that in general, non-local sources might on average make

up a substantial part of organic carbon in mangrove sediments, as the majority of mangroves are located in large deltas and estuaries, where sedimentation of allochtonous material is important (see Chapter 7 for a more detailed account). Jennerjahn & Ittekkot (2002) further estimate that 25 % of the (aboveground) production accumulates in mangrove sediments (and 50 % is exported, 25 % is remineralized inside the system). This estimate can also induce considerable bias in the estimated contribution of mangrove carbon, as e.g. Duarte & Cebrián (1996) estimated the proportion of mangrove production that accumulates at 10.4 %, i.e. less than half the estimate of Jennerjahn & Ittekkot (2002). As the estimate by Duarte & Cebrián (1996) is based on actual literature studies, the latter may appear more likely. For the CWS, we have constrained the proportion of litterfall that enters the sediment organic matter pool (by overestimating each of the parameters used in its calculation, see this Chapter, p. 11) at *maximum* 3 to 6 %.

(3) the estimate of the contribution of *exported* mangrove carbon to the total organic carbon accumulating in the ocean is substantial (~11%), and one of the prime underlying estimates is that on average 50 % of the litterfall is exported, and assuming a worldwide average for litterfall of 460 g C m^{-2} y^{-1}. Here, two aspects deserve some consideration:

(1) The average number of 50 % (similar to the 40 % estimate by Duarte & Cebrián 1996) is based on a variety of studies, most of which have assessed or estimated the flux of organic carbon (DOC, POC, or both) either by actual flux measurements (e.g. Twilley 1985, Dittmar & Lara 2001a,b, but usually without distinction between the origin of the organic matter which was imported or exported) or by equalling export of mangrove carbon as the difference between production and other accounted losses (e.g. burial, consumption, ...). As other sources (terrestrial and/or local aquatic primary production) obviously do contribute -no doubt in a highly variable proportion- the estimate of Jennerjahn & Ittekkot (2002) is *a priori* an overestimate, but there are insufficient data available to make a reasonable correction for this bias.

(2) Secondly, it is inherently assumed that all the organic carbon exported will accumulate in coastal sediments. Although it is difficult to define the boundaries between the mangrove ecosystem itself and the coastal environment, (an unknown but potentially important) part of the exported

carbon will be mineralized in the aquatic environment (e.g. see Chapter 4) before it can enter the coastal sediment pool. Although it is currently impossible to estimate this loss for any mangrove ecosystem, this restriction again makes the estimate of Jennerjahn & Ittekkot *a priori* an overestimate.

Finally, it should be taken into consideration that the literature estimates of e.g. the global riverine transport of organic carbon also show some variability (see e.g. Degens et al. 1991, Ludwig et al. 1996a,b) – note, for example, that Twilley et al. (1992) used an estimate of 350.10^{12} g C y^{-1}, whereas Jennerjahn & Ittekkot (2002) used a value of 429.10^{12} g C y^{-1}. In conclusion, the estimates by Twilley et al. (1992) and Jennerjahn & Ittekkot (2002) suggest that mangroves might play an important role in the coastal carbon cycle at a global scale, but perhaps most importantly indicate the need for much more data in order to reliably estimate this contribution.

CARBON DYNAMICS IN MANGROVE ECOSYSTEMS : A MANAGEMENT PERSPECTIVE.

The incentives to study the trophic role of mangroves and the fate of their often high production in the aquatic ecosystem are not only of a fundamental nature, but in view of their prominence in tropical coastal regions and their fast disappearance, there is a need to predict the changes in the aquatic biogeochemistry and ecology that will occur when the mangrove cover in a certain area would be lost (e.g. due to clearcutting and conversion to aquaculture ponds). Such a question will evidently be highly site-specific and dependent on what replaces the lost mangrove cover (e.g. shrimp ponds, bare mud flats, ...). Possible effects (often mutually counter-acting) include :

(1) The loss of carbon inputs from mangrove production
(2) The potential release of carbon stocks in mangrove sediments, which may become prone to erosion
(3) A decrease in sedimentation if the vegetation is not replaced
(4) A decrease in sedimentation, and an increased erosion can be expected to result in increasing turbidity levels, which in turn may lead to decreased aquatic production
(5) If mangroves are replaced by aquaculture activities, there are additional effects of nutrients in wastewater effluents to consider.

Moreover, there is a certain need to describe the carbon dynamics for a 'normal' ecosystem functioning in undisturbed mangrove forests, to allow an evaluation of such functioning for restored sites. The question whether replanted or naturally restored mangrove forests (can) resume their initial functions is not new (see Ellison 2000 for a recent overview), but there are very few studies which have compared the biogeochemistry of natural and clear-cut or replanted field sites (Kaly et al. 1997, Mc Kee & Faulkner 2000) or replanted sites of different ages (e.g. Alongi et al. 1998a, 2000b, 2001). McKee & Faulkner (2000) noted significantly lower concentrations of organic carbon in replanted mangrove sediments, and similar differences were found in the study by Alongi et al. (1998a), but do not appear to be general (Alongi et al. 2000b, 2001). Alongi et al. (1998a) also found no significant differences in the rates of decomposition between Malaysian *Rhizophora apiculata* stands of different age (2, 15, and 60 years), although there were differences in the relative importance of diagenetic pathways, with sulphate reduction being less important in the youngest stand. In a subsequent study in a *R. apiculata* forest in Vietnam, however, Alongi et al. (2000b) found that oxidation rates were lowest in an 8 yr old stand, and significantly higher in a 6 yr old and a 35 yr old stand. Oxidation pathways were similar in the 8 and 35 yr old stands, but oxic respiration was more important in the 6 yr old stand. With so few studies available, it is difficult to make general conclusions on how the biogeochemical functioning of restored mangrove forests differs from that in undisturbed sites, and if restoration can be successful in that context. The generation of considerably more studies from different regions will be needed to be able to eliminate effects of e.g. differences in environmental factors (see McKee & Faulkner 2000), and to gain a more refined view of the factors determining the successful restoration of mangrove ecosystem functioning.

References

Abraham WR, Hesse C, & Pelz O (1998) Ratios of carbon isotopes in bacterial lipids as an indicator of substrate usage. Appl Environ Microbiol 54 : 4202-4209

Abril G, Nogueira M, Etcheber H, Cabeçadas G, Lemaire E, & Brogueira MJ (2002) Behaviour of organic carbon in nine contrasting European estuaries. Estuar Coast Shelf Sci 54 : 241-262

Adams TS, & Sterner RW (2000) The effect of dietary nitrogen content on trophic level ^{15}N enrichment. Limnol Oceanogr 45 : 601-607

Aizpuru M, Achard F, & Blasco F (2000) Global assessment of cover change of the mangrove forest using satellite imagery at medium to high resoution. In : EEC research project (n° 15017-1999-05 FIED ISP FR, Joint research centre, Ipra.

Alongi DM (1987a) Inter-estuary variation and intertidal zonation of free-living nematode communities in tropical mangrove systems. Mar Ecol Prog Ser 40: 103-114

Alongi DM (1987b) Intertidal zonation and seasonality of meiobenthos in tropical mangrove estuaries. Mar Biol 95: 447-458

Alongi DM (1987c) The influence of mangrove-derived tannins on intertidal meiobenthos in tropical estuaries. Oecologia 71: 537-540

Alongi (1988) Bacterial productivity and microbial biomass in tropical mangrove sediments. Microb Ecol 15 : 59-79

Alongi DM (1990) Abundances of benthic microfauna in relation to outwelling of mangrove detritus in a tropical coastal region. Mar Ecol Prog Ser 63 : 53-63

Alongi DM (1991) The role of intertidal mudbanks in the diagenesis and export of dissolved and particulate materials from the Fly River Delta, Papua New Guinea. J Exp Mar Biol Ecol 149 : 81-107

Alongi DM, & Sasekumar A (1992) Benthic communities. In : Robertson AI, & Alongi DM (eds) Tropical mangrove ecosystems. Coastal and estuarine studies n° 41. American Geophysical Union, 1992. 329 pp

Alongi DM, Christoffersen P, & Tirendi F (1993) The influence of forest type on microbial-nutrient relationships in tropical mangrove sediments. J Exp Mar Biol Ecol 171 : 201-223

Alongi DM (1994) Zonation and seasonality of benthic primary production and community respiration in tropical mangrove forests. Oecologia 98 : 320-327

Alongi DM (1996) The dynamics of benthic nutrient pools and fluxes in tropical mangrove forests. J Mar Res 54 : 123-148

Alongi DM (1998) Mangroves and salt marshes. In : Alongi DM. Coastal ecosystem processes. CRC Press, 419 pp.

Alongi DM, Ayukai T, Brunskill GJ, Clough BF, & Wolanski E (1998a) Sources, sinks, and export of organic carbon through a tropical, semi-enclosed delta (Hinchinbrook Channel, Australia). Mangroves and Salt Marshes 2 : 237-242

Alongi DM, Sasekumar A, Tirendi F, & Dixon P (1998b) The influence of stand age on benthic decomposition and recycling of organic matter in managed mangrove forests of Malaysia. J Exp Mar Biol Ecol 225 : 197-218

Alongi DM, Tirendi F, Dixon P, Trott LA, & Brunskill GJ (1999) Mineralization of organic matter in intertidal sediments of a tropical semi-enclosed delta. Estuar Coast Shelf Sci 48 : 451-467

Alongi DM, Tirendi F, & Clough BF (2000a) Below-ground decomposition of organic matter in forests of the mangroves *Rhizophora stylosa* and *Avicennia marina* along the arid coast of Western Australia. Aquat Bot 68 : 97-122

Alongi DM, Tirendi F, Trott LA, & Xuan TT (2000b) Benthic decomposition rates and pathways in plantations of the mangrove *Rhizophora apiculata* in the Mekong delta, Vietnam. Mar Ecol Prog Ser 194 : 87-101

Alongi DM, Wattayakorn G, Pfitzner J, Tirendi F, Zagorskis I, Brunskill GJ, Davidson A, & Clough BF (2001) Organic carbon accumulation and metabolic pathways in sediments of mangrove forests in southern Thailand. Mar Geol 179 : 85-103

Altabet MA, & Francois R (1994) Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Global Biogeochem Cycles 8 : 103-116

Amarasinghe MD, & Balasubramaniam S (1992) Net primary productivity of two mangrove forest stands on the northwestern coast of Sri Lanka. Hydrobiologia 247 : 37-47

Ambler JW, Alcala-Herrera J, & Burke R (1994) Trophic roles of particle feeders and detritus in a mangrove island prop root ecosystem. Hydrobiologia 292/293 : 437-446

Anderson C, & Lee SY (1995) Defoliation of the mangrove *Avicennia marina* in Hong-Kong : cause and consequences. Biotropica 27 : 218-226

Ashton EC, Hogarth PJ, & Ormond R (1999) Breakdown of mangrove leaf litter in a managed mangrove forest in Peninsular Malaysia. Hydrobiologia 413 : 77-88

Aucour AM, Sheppard SMF, Guyamar O, & Wattelet J (1999) Use of ^{13}C to trace origin and cycling of inorganic carbon in the Rhone river system. Chem Geol 159 : 87-105

Ayukai T, Miller D, Wolanski E, & Spagnol S (1998) Fluxes of nutrients and dissolved and particulate organic carbon in two mangrove creeks in northeastern Australia. Mangroves and Salt Marshes 2 : 223-230

Azariah J, Azariah H, Gunasekaran S, & Selvam V (1992) Structure and species distribution in Coringa mangrove forest, Godavari Delta, Andhra Pradesh, India. Hydrobiologia 247 : 11-16

Baird ME, Emsley SM, & McGlade JM (2001) Using a phytoplankton growth model to predict the fractionation of stable carbon isotopes. J Plankt Res 23 : 841-848

Balesdent J, Girardin C, & Mariotti A (1993) Site-related $\delta^{13}C$ of tree leaves and soil organic matter in a temperate forest. Ecology 74 : 1713-1721

Bano N, Nisa MU, Khan N, Saleem M, Harrison PJ, Ahmed SI, & Azam F (1997) 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

Baran E, & Hambrey J (1998) Mangrove conservation and coastal management in Southeast Asia : what impact on fish resources ? Mar Poll Bull 37 : 431-440

Bates NR, & Merlivat L (2001) The influence of short-term wind variability on air-sea CO_2 exchange. Geophys Res Lett 28 : 3281-3284

Bauch D, Carstens J, Wefer G, & Thiede J (2000) The imprint of anthropogenic CO_2 in the Arctic Ocean : evidence from planktonic $\delta^{13}C$ data from watercolumn and sediment surfaces. Deap-Sea Res II 47 : 1791-1808

Ben-David M, & Schell DM (2001) Mixing models in analyses of diet using stable isotopes : a response. Oecologia 127 : 180-184

Benedict CR, Wong WWL, & Wong JHH (1980) Fractionation of the stable isotopes of inorganic carbon by seagrasses. Plant Physiol 65 : 512-517

Benner R, Fogel ML, & Sprague EK (1991) Diagenesis of belowground biomass of *Spartina alterniflora* in salt-marsh sediments. Limnol Oceanogr 36 : 1358-1374

Bidigare RR, Kennicutt II MC, Keeney-Kennicutt WL, & Macko SA (1991) Isolation and purification of chlorophylls a and b for the determination of stable carbon and nitrogen isotope composition. Anal Chem 63 : 130-133

Bidigare RR et al. (1997) Consistent fractionation of ^{13}C in nature and in the laboratory : growth-rate effects in some haptophyte algae. Glob Biogeochem Cyc 11 : 279-292

Boon PI, & Bunn SE (1994) Variations in the stable isotope composition of aquatic plants and their implications for food web analysis. Aquat Bot 48 : 99-108

Boon PI, Bird FL, & Bunn E (1997) Diet of the intertidal callianassid shrimps *Biffarius arenosus* and *Trypea australiensis* (Decapoda : Thalassinidae) in Western Port (southern Australia), determined with multiple stable-isotope analyses. Mar Freshwater Res 48 : 503-511

Boschker HTS, de Brouwer JFC, & Cappenberg TE (1999) The contribution of macrophyte-derived organic matter to microbial biomass in salt-marsh sediments : stable carbon isotope analysis of microbial biomarkers. Limnol Oceanogr 44 : 309-319

Boschker HTS, Wielemaker A, Schaub BEM, & Holmer M (2000) Limited coupling of macrophyte production and bacterial cycling in the sediments of *Zostera* spp. meadows. Mar Ecol Prog Ser 203 : 181-189

Boschker HTS, & Middelburg JJ (2002) Stable isotope analysis of biomarkers in microbial ecology. FEMS Microb Ecol 40 : 85-95

Bosley KL, & Wainright SC (1999) Effects of preservatives and acidification on the stable isotope ratios ($^{15}N:^{14}N$, $^{13}C:^{12}C$) of two species of marine animals. Can J Fish Aquat Sci 56 : 2181-2185

Boto KG, & Bunt JS (1981) Tidal export of particulate organic matter from a northern Australian mangrove forest. Estuar Coast Shelf Sci 13 : 247-255

Boto KG, & Wellington JT (1988) 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

Boto KG, & Robertson AI (1990) The relationship between nitrogen fixation and tidal exports of nitrogen in a tropical mangrove system. Estuar Coast Shelf Sci 31 : 531-540

Bouchard V, Creach V, Lefeuvre JC, Gertru G, & Mariotti A (1998) Fate of plant detritus in a European salt marsh dominated by *Atriplex portulacoides* (L.) Aellen. Hydrobiologia 373/374 : 75-87

Bouillon S, & Dehairs F (2000) Estimating spatial and seasonal phytoplankton $\delta^{13}C$ variations in an estuarine mangrove ecosystem. Isot Environ Health Stud 36 : 273-284

Bouillon S, Chandra Mohan P, Sreenivas N, & Dehairs F (2000) 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

Bouillon S, Koedam N, Raman AV, & Dehairs F (2002a) Primary producers sustaining macro-invertebrate communities in intertidal mangrove forests. Oecologia 130 : 441-448.

Bouillon S, Raman AV, Dauby P, & Dehairs F (2002b) Carbon and nitrogen stable isotope ratios of subtidal benthic invertebrates in an estuarine mangrove ecosystem (Andhra Pradesh, India). Estuar Coast Shelf Sci 54 : 901-913

Bouillon S, Koedam N, Rao AVVS, Dahdouh-Guebas F, & Dehairs F (2002c) Sources of organic carbon in mangrove sediments : variability and some possible implications for ecosystem functioning. Hydrobiologia, in review.

Bowen R (1991) Isotopes and Climate. Elsevier Applied Science, London. 483 pp.

Boyce MC, Lavery P, Bennett IJ, & Horwitz P (2001) Spatial variation in the $\delta^{13}C$ signature of *Ruppia megacarpa* (Mason) in coastal lagoons of southwestern Australia and its implications for isotopic studies. Aquat Bot 71 : 83-92

Branstrator DK, Cabana G, Masumder A, & Rasmussen JB (2000) Measuring life-history omnivory in the opossum shrimp, *Mysis relicta*, with stable nitrogen isotopes. Limnol Oceanogr 45 : 463-467

Buhl D, Neuser RD, Richter DK, Riedel D, Roberts B, Strauss H, & Veizer J (1991) Nature and nurture – environmental isotope story of the river Rhine. Naturwissenschaften 78 : 337-346

Bunn SE, Loneragan NR, & Kempster MA (1995) Effects of acid washing samples on stable isotope ratios of C and N in penaeid shrimps and seagrasses : implications for food web studies using stable isotopes. Limnol Oceanogr 40 : 622-625

Bunt JS, Boto KG, & Boto G (1979) Survey methods for estimating potential levels of mangrove forest primary production. Mar Biol 52 : 123-128

Burkhardt S, Riebesell U, & Zondervan I (1999a) Stable carbon isotope fractionation by marine phytoplankton in response to daylength, growth rate, and CO_2 availability. Mar Ecol Prog Ser 184 : 31-41

Burkhardt S, Riebesell U, & Zondervan I (1999b) Effects of growth rate, CO_2 concentration, and cell size on the stable carbon isotope fractionation in marine phytoplankton. Geochim Cosmochim Acta 63 : 3729-3741

Cai DL, Tan FC, & Edmond JM (1988) Sources and transport of particulate organic carbon in the Amazon River and estuary. Estuar Coast Shelf Sci 26 : 1-14

Cai WJ, & Wang Y (1998) The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha rivers, Georgia. Limnol Oceanogr 43 : 657-668

Camilleri JC (1989) Leaf choice by crustaceans in a mangrove forest in Queensland. Mar Biol 102 : 453-459

Camilleri JC (1992) Leaf-litter processing by invertebrates in a mangrove forest in Queensland. Mar Biol 114 : 139-145

Camilleri JC, & Ribi G (1986) 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

Cannicci S, Fratini S, & Vannini M (1999) Life on a mangrove trunk : use of time, space and food rescources in *Selatium elongatum* (*Grapsidae*; *Sesarminae*). Mar Biol 135 : 335-339

Cannicci S, Ruwa RK, Giuggioli M, & Vannini M (1998) Predatory activity and spatial strategies of *Epixanthus dentatus* (Decapoda : Oziidae), an ambush predator among the mangroves. J Crust Biol 18 : 57-63

Canuel EA, Cloern JE, Ringelberg DB, Guckert JB, & Rau GH (1995) Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San Fransisco Bay. Limnol Oceanogr 40 : 67-81

Caraco NF, Lampman G, Cole JJ, Limburg KE, Pace ML, & Fisher D (1998) Microbial assimilation of DIN in a nitrogen rich estuary : implications for food quality and isotope studies. Mar Ecol Prog Ser 167 : 59-71

Carini S, Weston N, Hopkinson C, Tucker J, Giblin A, & Vallino J (1996) Gas exchange rates in the Parker river estuary, Massachsetts. Biol Bull 191 : 333-334

Cebrián J (2002) Variability and control of carbon consumption, export, and accumulation in marine communities. Limnol Oceanogr 47 : 11-22

Chandra Mohan P, Sreenivas N, Prasad NV, & Rao AVVS (1997) Zooplankton diversity and seasonal fluctuations in Kakinada Bay with special reference to the mangrove habitat. In : An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of European Community INCO-DC contract CI1*CT930320, Part II, pp. 1-21

Chanton JP, & Lewis FG (1999) Plankton and dissolved inorganic carbon isotopic composition in a river-dominated estuary : Apalachicola Bay, Florida. Estuaries 22 : 575-583.

Chanton JP, & Lewis FG (2002) Examination of coupling between primary and secondary production in a river-dominated estuary : Apalachicola Bay, Florida, USA. Limnol Oceanogr 47 : 683-697

Chapman VJ (1984) Mangrove biogeography. In : Por FD, & Dor I (eds) Hydrobiology of the mangal. The ecosystem of the mangrove forests. Developments in hydrobiology 20 Dr. W. Junk Publishers, The Hague. 260 pp

Checkley DM Jr, & Entzeroth LC (1985) Elemental and isotopic fractionation of carbon and nitrogen by marine, planktonic copepods and implications to the marine nitrogen cycle. J Plankton Res 7 : 553-568

Chen R, & Twilley RR (1998) A gap dynamic model of mangrove forest development along gradients of soil salinity and nutrient resources. J Ecol 86 : 37-51

Chen R, & Twilley RR (1999a) A simulation model of organic matter and nutrient accumulation in mangrove wetland soils. Biogeochemistry 44 : 93-118

Chen R, & Twilley RR (1999b) Patterns of mangrove forest structure and soil nutrient dynamics along the Shark River estuary, Florida. Estuaries 22 : 955-970

Cheng IJ, & Chang PC (1999) The relationship between surface macrofauna and sediment nutrients in a mudflat of the Chuwei mangrove forest, Taiwan. Bull Mar Sci 65 : 603-616

Chong VC, Sasekumar A, & Wolanski E (1996) The role of mangroves in retaining penaeid prawn larvae in Klang Strait, Malaysia. Mangroves and Salt Marshes 1 : 11-22

Chong VC, Low CB, & Ichikawa T (2001) Contribution of mangrove detritus to juvenile prawn nutrition: a dual stable isotope study in a Malaysian mangrove forest. Mar Biol 138 : 77-86

Christensen JT, Sauriau PG, Richard P, & Jensen PD (2001) Diet in mangrove snails : preliminary data on gut contents and stable isotope analysis. J Shellfish Res 20 : 423-426

Cifuentes LA, Sharp JH, & Fogel ML (1988) Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. Limnol Oceanogr 33 : 1102-1115

Cifuentes LA, Coffin RB, Solorzano L, Cardenas W, Espinoza J, & Twilley RR (1996) Isotopic and elemental variations of carbon and nitrogen in a mangrove estuary. Estuar Coast Shelf Sci 43 : 781-800

Cifuentes LA, & Salata GG (2001) Significance of carbon isotope discrimination between bulk carbon and extracted phospholipid fatty acids in selected terrestrial and marine environments. Org Geochem 32 : 613-621

Clough B (1998) Mangrove forest productivity and biomass accumulation in Hinchinbrook Channel, Australia. Mangroves and Salt Marshes 2 : 191-198

Clough B, Tan DT, Phuong DX, & Buu DC (2000) Canopy leaf area index and litter fall in stands of the mangrove *Rhizophora apiculata* of different age in the Mekong Delta, Vietnam. Aquat Bot 66 : 311-320

Clough B (1992) Primary productivity and growth of mangrove forests. In : Robertson AI, & Alongi DM (eds) Tropical Mangrove Ecosystems. Coastal and estuarine studies 41. 329 pp

Coffin RB, & Cifuentes LA (1999) Stable isotope analysis of carbon cycling in the Peridido estuary, Florida. Estuaries 22 : 917-926

Conway NM, Keniicutt II MC, & Van Dover CL (1994) Stable isotopes in the study of marine chemosynthetic-based ecosystems. In : Lajtha K, & Michener RH (eds) Stable isotopes in ecological and environmental science. Blackwell Scientific Publications, 1994

Cole JJ, & Caraco NF (2001) Carbon in catchments : connecting terrestrial carbon losses with aquatic metabolism. Mar Freshwater Res 52 : 101-110

Cooksey KE, Cooksey B, Evans PM, & Hildebrand EL (1975) Benthic diatoms as contributors to the carbon cycle in a mangrove community. In: Persoone G, & Jaspero E (eds) 10th European Marine Biology Symposium, pp. 165-178. Universa Press, Welteren

Coplen TB (1996) New guidelines for the reporting of stable hydrogen, carbon, and oxygen isotope ratio data. Geochim Cosmochim Acta 60 : 3359-3360

Couch CA (1989) Carbon and nitrogen stable isotopes of meiobenthos and their food rescources. Estuar Coast Shelf Sci 28 : 433-441

Coull BC (1999) Role of meiofauna in estuarine soft-bottom habitats. Austr J Ecol 24 : 327-343

Cox EF, & Allen JA (1999) Stand structure and productivity of the introduced *Rhizophora mangle* in Hawaii. Estuaries 22 : 276-284

Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim Cosmochim Acta. 12 : 133-149

Créach V, Schrike MT, Bertru G, & Mariotti A (1997) Stable isotopes and gut content analyses to determine feeding relationships in saltmarsh macroconsumers. Estuar Coast Shelf Sci 44 : 599-611

Cullen JT, Rosenthal Y, & Falkowski PG (2001) The effect of anthropogenic CO_2 on the carbon isotope composition of marine phytoplankton. Limnol Oceanogr 46 : 996-998

Currin CA, Newell SY, & Paerl HW (1995) The role of standing dead *Spartina alterniflora* and benthic microalgae in salt marsh food webs : considerations based on multiple stable isotope analysis. Mar Ecol Prog Ser 121 : 99-116

Dahdouh-Guebas F, Giuggioli M, Oluoch A, Vannini M, & Cannicci S (1999) Feeding habits of non-ocypodid crabs from two mangrove forests in Kenya. Bull Mar Sci 64 : 291-297

Dahdouh-Guebas F, Verheyden A, De Genst W, Hettiarachchi S, & Koedam N (2000) Four decade vegetation dynamics in Sri Lankan mangroves as detected from sequential aerial photography : a case study in Galle. Bull Mar Sci 67 : 741-759

Dahdouh-Guebas F (2001) Mangrove vegetation structure and dynamics. PhD thesis, Vrije Universiteit Brussel, Brussels, Belgium. Abstracts available at the follwing URL : http://www.vub.ac.be/APNA/staff/FDG/PhD/PhD.html

Daniel PA, & Robertson AI (1990) Epibenthos of mangrove waterways and open embayments : community structure and the relationship between exported mangrove detritus and epifaunal standing stocks. Estuar Coast Shelf Sci 31 : 599-619

Dauby P (1990) The stable carbon isotope ratios in benthic food webs of the Gulf of Calvi, Corsica. Cont Shelf Res 9 : 181-195

Dauby P, Khomsi A, Bouquegneau JM (1998) Trophic relationships within intertidal communities of the Brittany coast: a stable carbon isotope analysis. J Coast Res 14 : 1202-1212

Davis III SE, Childers DL, Day JW, Rudnick DT, & Sklar FH (2001a) Nutrient dynamics in vegetated and unvegetated areas of a southern Everglades mangrove creek. Estuar Coast Shelf Sci 52 : 753-768

Davis III SE, Childers DL, Day JW, Rudnick DT, & Sklar FH (2001b) Wetland-water column exchanges of carbon, nitrogen, and phosphorus in a southern Everglades dwarf mangrove. Estuaries 24 : 610-622

Day JW, Connor WH, Leylou F, Day RH, & Navarro AM (1987) The productivity and composition of mangrove forests, Laguna de Terminos, Mexico. Aquat Bot 27 : 267-284

de Boer WF (2000) Biomass dynamics of seagrasses and the role of mangrove and seagrass vegetation as different nutrient sources for an intertidal ecosystem. Aquat Bot 66 : 225-239

Deepti R (1997) Benthic macrofauna. In : Dehairs F (ed) An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of contract CI1*CT930320.

Dehairs F, Rao RG, Chandra Mohan P, Raman V, Marguillier S, & Hellings L (2000) Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami-Godavari Delta, Bay of Bengal (India). Hydrobiologia 431 : 225-241

Dehairs F (ed) An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of contract CI1*CCT930320. Vrije Universiteit Brussel, 1999.

del Giorgio PA, & France RL (1996) Ecosystem-specific patterns in the relationship between zooplankton and POM or microplankton $\delta^{13}C$. Limnol Oceanogr 41 : 359-365

DeMott WR (1988) Discrimination between algae and detritus by freshwater and marine zooplankton. Bull Mar Sci 43 : 486-499

DeMott WR (1995) Food selection by calanoid copepods in response to between-lake variation in food abundance. Freshwat Biol 33 : 171-180

DeNiro MJ, & Epstein S (1978) Influence of diet on the distribution of carbon isotopes in animals. Geochim Cosmochim Acta 42 : 495-506

Descolas-Gros C, & Fontugne MR (1990) Dynamics of carbon assimilation by St-Lawrence estuary phytoplankton at the end of summer. Hydrobiologia 207 : 227-232

Dham VV, Heredia AM, Wafar S, & Wafar M (2002) Seasonal variations in uptake and *in situ* regeneration of nitrogen in mangrove waters. Limnol Oceanogr 47 : 241-254

Dick TM, & Osunkoya OO (2000) Influence of tidal restriction floodgates on decomposotion of mangrove litter. Aquat Bot 68 : 273-280

Dick RM, & Streever WJ (2001) Decomposition of *Avicennia marina* on an iron-smelting slag substrate. Austr Ecol 26 : 127-131

Dittel AI, Epifiano CE, Cifuentes LA, & Kirchman DL (1997) Carbon and nitrogen sources for shrimp postlarvae fed natural diets from a tropical mangrove system. Estuar Coast Shelf Sci 45 : 629-637

Dittel AI, Epifiano CE, Schwalm SM, Fantle MS, & Fogel ML (2000) Carbon and nitrogen sources for juvenile blue crabs *Callinectes sapidus* in coastal wetlands. Mar Ecol Prog Ser 194 : 103-112

Dittmar T, Lara RJ, & Kattner G (2001) River or mangrove ? Tracing major organic matter sources in tropical Brazilian coastal waters. Mar Chem 73 : 253-271

Dittmar T, & Lara RJ (2001a) Driving forces behind nutrient and organic matter dynamics in a mangrove tidal creek in North Brazil. Estuar Coast Shelf Sci 52 : 249-259

Dittmar T, & Lara RJ (2001b) 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

Dittmar T, & Lara RJ (2001c) Molecular evidence for lignin degradation in sulphate-reducing mangrove sediments (Amazonia, Brazil). Geochim Cosmochim Acta 65 : 1417-1428

Dor I (1984) Epiphytic blue-green algae (Cyanobacteria) of the Sinai mangal: considerations on vertical zonation an morphological adaptations. In: Por FD, & Dor I (eds) Hydrobiology of the mangal. The ecosystem of the mangrove forests. Developments in hydrobiology 20 Dr. W. Junk Publishers, The Hague. 260 pp.

Duarte CM, & Cebrián J (1996) The fate of marine autotrophic production. Limnol Oceanogr 41 : 1758-1766

Duke NC, Bunt JS, & Williams WT (1981) Mangrove litterfall in northeastern Australia. I. Annual totals by component in selected species. Austr J Bot 29 : 547-553

Duke NC, Bunt JS, & Williams WT (1984) Observations on the floral and vegetative phenologies of northeasterns Australian mangroves. Austr J Bot 32 : 87-99

Duke NC (1992) Mangrove floristics and biogeography. In: Robertson AI, & Alongi DM (eds) Tropical mangrove ecosystems. Coastal and estuarine studies n° 41. American Geophysical Union, 1992. 329 pp

Dye AH, & Lasiak TA (1986) Microbenthos, meiobenthos and fiddler crabs : trophic interactions in a tropical mangrove sediment. Mar Ecol Prog Ser 32 : 259-267

Dye AH, & Lasiak TA (1987) Assimilation efficiencies of fiddler crabs and deposit-feeding gastropods from tropical mangrove sediments. Comp Biochem Physiol 87A : 341-344

Ehleringer JR (1991) $^{13}C/^{12}C$ fractionation and its utility in terrestrial plant studies. In : Coleman DC, & Fry B (eds) Carbon isotope techniques. Academic Press, San Diego. pp. 187-201

Ehleringer JR, Buchmann N, & Flanagan LB (2000) Carbon isotope ratios in belowground carbon cycle processes. Ecol Appl 10 : 412-422

Ekblad A, Nyberg G, & Högberg P (2002) ^{13}C-discrimination during microbial respiration of added C_3-, C_4- and ^{13}C-labelled sugars to a C_3-forest soil. Oecologia 131 : 245-249

Ellison AM, Farnsworth EJ, & Twilley RR (1996) Facultative mutualism between red mangroves and root-fouling sponges in Belizean mangal. Ecology 77 : 2431-2444

Ellison JC (1998) Impact of sediment burial on mangroves. Mar Poll Bull 37 : 420-426

Ellison AM, Farnsworth EJ, & Merkt RE (1999) Origins of mangrove ecosystems and the mangrove biodiversity anomaly. Glob Ecol Biogeogr 8 : 95-115

Ellison AM (2000) Mangrove restoration : do we know enough ? J Ecol 8 : 219-229

Ellison AM, Mukherjee BB, & Karim A (2000) Testing patterns of zonation in mangroves: scale dependence and environmental correlates in the Sundarbans of Bangladesh. J Ecol 88 : 813-824

Ellison AM, & Farnsworth EJ (2001) Mangrove communities. In : Bertness MD, Gaines S, & Hay ME (eds) Marine Community Ecology. Sinauer Press, Sunderland, Massachusetts, USA. pp 423-442

Erskine PD, Bergstrom DM, Schmidt S, Stewart GR, Tweedie GE, & Shaw JD (1998) Subantarctic Macquarie Island – a model ecosystem for studying animal-derived nitrogen sources using ^{15}N natural abundance. Oecologia 117 : 187-193

Evans RD (2001) Physiological mechanisms influencing plant nitrogen isotope composition. Trends Plant Sci 6 : 121-126

Ewel KC, Twilley RR, & Ong JE (1998) Different kinds of mangrove forests provide different goods and services. Glob Ecol Biogeogr Lett 7 : 83-94

Faganeli J, Malej A, Pezdic J, & Malacic V (1988) C-N-P ratios and stable C isotopic ratios as indicators of sources of organic matter in the Gulf of Trieste (Northern Adriatic). Oceanol Acta 11 : 377-382

Falkowski PG (1991) Species variability in the fractionation of ^{13}C and ^{12}C by marine phytoplankton. J Plankt Res 13 : 21-28

Fantle MS, Dittel AI, Schwalm SM, Epifiano CE, & Fogel ML (1999) A food web analysis of the juvenile blue crab, *Callinectes sapidus*, using stable isotopes in whole animals and individual amino acids. Oecologia 120 : 416-426

Farnsworth EJ, & Ellison AM (1991) Patterns of herbivory in Belizean mangrove swamps. Biotropica 23 : 555-567

Farnsworth EJ, & Ellison AM (1993) Dynamics of herbivory in Belizean mangal. J Trop Ecol 9 : 435-453

Farnsworth EJ, & Ellison AM (1997) The global conservation status of mangroves. Ambio 26 : 328-334

Farquhar GD, Ball MC, van Caemmerer S, & Roksandic Z (1982) Effect of salinity and humidity on $\delta^{13}C$ value of halophytes – evidence for diffusional isotope fractionation determined by the ratio of intercellular/atmospheric partial pressure of CO_2 under different environmental conditions. Oecologia 52 : 121-124

Farquhar GD, Ehleringer JR, & Hubick KT (1989) Carbon isotope discriminatrion and photosynthesis. Annu Rev Plant Phys 40 : 503-537

Feng X (1999) Trends in intrinsic water-use efficiency of natural trees for the past 100-200 years : a response to atmospheric CO_2 concentration. Geochim Cosmochim Acta 63 : 1891-1903

Fenton GE, & Ritz DA (1988) Changes in carbon and hydrogen stable isotope ratios of macroalgae and seagrasses during decomposition. Estuar Coast Shelf Sci 26 : 429-436

Findlay S, Tank J, Dye S, Mulholland PJ, McDowell WH, Johnson SL, Hamilton SK, Edmonds J, Dodds WK, & Bowden WB (2001) A cross-ecosystem comparison of bacterial and fungal biomass in detritus pools of headwater streams. Microb Ecol, in press.

Finlay JC, Power ME, & Cabana G (1999) Effects of water velocity on algal carbon isotope ratios : implications for river food web studies. Limnol Oceanogr 44 : 1198-1203

Fisher CR (1990) Chemoautotrophic and methanotrophic symbioses in marine invertebrates. Rev Aquat Sci 2 : 399-436

Flanagan LB, Cook CS, & Ehleringer JR (1997) Unusually low carbon isotope ratios in plants from hanging gardens in southern Utah. Oecologia 111 : 481-489

Flanagan LB, Brooks JR, Varney GT, Berry SC, & Ehleringer JR (1996) Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO_2 in boreal forest ecosystems. Glob Biogeochem Cyc 10 : 629-640

Fleming M, Lin G, & Sternberg LDSL (1990) Influence of mangrove detritus in an estuarine ecosystem. Bull Mar Sci 47 : 663-669

Flores-Verdugo FJ, Day JW, & Briseno-Duenas R (1987) Structure, litter fall, decomposition, and detritus dynamics of mangroves in a Mexican coastal lagoon with an ephemeral inlet. Mar Ecol Prog Ser 35 : 83-90

Focken U, & Becker K (1998) Metabolic fractionation of stable carbon isotopes : implications of different proximate compositions for studies of the aquatic food webs using $\delta^{13}C$ data. Oecologia 115 : 337-343

Fogel ML, & Tuross N (1999) Transformation of plant biochemicals to geological macromolecules during early diagenesis. Oecologia 120 : 336-346

Fontugne MR, & Duplessy JC (1978) Carbon isotope ratio of marine plankton related to surface water masses. Earth Planet Sci Lett 41 : 365-371

Fontugne MR, & Duplessy JC (1981) Organic carbon isotopic fractionation by marine plankton in the temperature range -1 to 31 °C. Oceanol Acta 4 : 85-90

France R (1995a) Source variability in $\delta^{15}N$ of autotrophs as a potential aid in measuring allochthony in freshwaters. Ecography 18 : 318-320

France R (1995b) Stable nitrogen isotopes in fish : literature synthesis on the influence of ecotonal coupling. Estuar Coast Shelf Sci 41 : 737-742

France RL (1995c) Carbon-13 enrichment in benthic compared to planktonic algae : foodweb implications. Mar Ecol Prog Ser 124 : 307-312

France RL (1995d) Stable isotopic survey of the role of macrophytes in the carbon flow of aquatic foodwebs. Vegetatio 124 : 67-72

France RL, & Holmquist JG (1997) $\delta^{13}C$ variability of macroalgae : effects of water motion via baffling by seagrasses and mangroves. Mar Ecol Prog Ser 149 : 305-308

France R (1998) Estimation the assimilation of mangrove detritus by fiddler crabs in Laguna Joyuda, Puerto Rico, using dual stable isotopes. J Trop Ecol 14 : 413-425

France R, Holmquist J, Chandler M, & Cattaneo A (1998) $\delta^{15}N$ evidence for nitrogen fixation associated with macroalgae from a seagrass-mangrove-coral reef system. Mar Ecol Prog Ser 167 : 297-299

Frankignoulle M (1994) A complete set of buffer factors for acid/base CO_2 system in water. J Mar Syst 5 : 111-118

Frankignoulle M, Elskens M, Biondo R, Bourge I, Canon C, Desgain S, & Dauby P (1996) Distribution of inorganic carbon and related parameters in surface seawater of the English Channel during spring 1994. J Mar Syst 7 : 427-434

Frankignoulle M, Abril G, Borges A, Bourge J, Canon J, DeLille B, Libert E, & Theate JM (1998) Carbon dioxide emissions from European estuaries. Science 282 : 434-436

Fratini S, Cannicci S, & Vannini M (2000a) Competition and interaction between *Neosarmatium smithi* (Crustacea : Grapsidae) and *Terebralia palustris* (Mollusca : Gastropoda) in a Kenyan mangrove. Mar Biol 137 : 309-316

Fratini S, Cannici S, Abincha LM, & Vannini M (2000b) Feeding, temporal and spatial preferences of *Metopograpsus thukuhar* (Decapoda; Grapsidae) : an opportunistic mangrove dweller. J Crust Biol 20 : 326-333

Frenkiel L, Gros O, & Mouënza M (1996) Gill structure in *Lucina pectinata* (Bivalvia : Lucinidae) with reference to hemoglobin in bivalves with symbiotic sulphur-oxidizing bacteria. Mar Biol 125 : 511-524

Frith DW, Tantanasiriwong R, & Bhatia O (1979) Zonation and abundance of macrofauna on a mangrove shore, Phuket Island. Phuket Mar Biol Centre Res Bull 10 : 1-37

Froese R, & Pauly D (eds) (2002) FishBase. World Wide Web electronic publication. Available at http://www.fishbase.org

Frusher SD, Giddins RL, & Smith TJ (1994) Distribution and abundance of grapsid crabs (Grapsidae) in a mangrove estuary : effects of sediment characteristics, salinity tolerances, and osmoregulatory ability. Estuaries 17 : 647-654

Fry B, & Arnold C (1982) Rapid $^{13}C/^{12}C$ turnover during growth of brown shrimp (*Penaeus aztecus*). Oecologia 54 : 200-204

Fry B (1983) Fish and shrimp migrations in the Northern Gulf of Mexico analyzed using stable C, N, and S isotope ratios. Fish Bull 81 : 789-801

Fry B, & Sherr EB (1984) $\delta^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystems. Contrib Mar Sci 27 : 13-47

Fry B (1984) $^{13}C/^{12}C$ ratios and the trophic importance of algae in Florida *Syringodium filiforme* seagrass meadows. Mar Biol 79 : 11-19

Fry B, & Wainright SC (1991) Diatom sources of ^{13}C-rich carbon in marine food webs. Mar Ecol Prog Ser 76 : 149-157

Fry B (1996) $^{13}C/^{12}C$ fractionation by marine diatoms. Mar Ecol Prog Ser 134 : 283-294

Fry B, Mumford BL, & Robblee MB (1999) Stable isotope studies of pink shrimp (*Farfantepenaeus duorarum* Burkenroad) migrations on the southwestern Florida shelf. Bull Mar Sci 65 : 419-430

Fuhrmann R, & Zirino A (1988) High-resolution determination of the pH of the seawater with a flow-through system. Deep-Sea Res 35 : 197-208

Fujimoto K, Imaya A, Tabuchi R, Kuramoto S, Utsugi H, & Murofushi T (1999) Belowground carbon storage of Micronesian mangrove forests. Ecol Res 14 : 409-413

Gannes LZ, O'Brien DM, & del Rio CM (1997) Stable isotopes in animal ecology: Assumptions, caveats, and a call for more laboratory experiments. Ecology 78 : 1271-1276

Gattuso JP, Frankignoulle M, & Wollast R (1998) Carbon and carbonate metabolism in coastal aquatic ecosystems. Annu Rev Ecol Syst 29 : 405-434

Gee JM, & Somerfield PJ (1997) Does mangrove diversity and leaf litter decay promote meiofaunal diversity ? J Exp Mar Biol Ecol 218 : 13-33

Gervais F, & Riebesell U (2001) Effects of phosphorus limitation on elemental composition and stable carbon isotope fractionation in a marine diatom growing under different CO_2 concentrations. Limnol Oceanogr 46 : 497-504

Ghosh S, Jana TK, Singh BN, & Choudhury A (1987) Comparative study of carbon dioxide system in virgin and reclaimed mangrove waters of Sundarbans during freshet. Mahasagar 20 : 155-161

Giddins RL, Luscas JS, Neilson MJ, & Richards GN (1986) Feeding ecology of the mangrove crab *Neosarmatium smithi* (Crustacea : Decapoda : Sesarmidae). Mar Ecol Prog Ser 33 : 147-155

Gillan FT, & Hogg RW (1984) A method for the estimation of bacterial biomass and community structure in mangrove-associated sediments. J Microbiol Meth 2 : 275-293

Gillikin DP (2000) Factors controlling the distribution of Kenyan brachyuran mangrove crabs : salinity tolerance and ecophysiology of two Kenyan *Neosarmatium* species. MSc thesis, Vrije Universiteit Brussel, 151 pp.

Goedkoop W, Sonesten L, Ahlgren G, & Boberg M (2000) Fatty acids in profundal benthic invertebrates and their major food resources in Lake Erken, Sweden : seasonal variation and trophic indications. Can J Fish Aquat Sci 57 : 2267-2279

Goericke R, & Fry B (1994) Variations of marine plankton $\delta^{13}C$ with latitude, temperature, and dissolved CO_2 in the world ocean. Glob Biogeochem Cy 8 : 85-90

Goericke R, Montoya JP, & Fry B (1994) Physiology of isotopic fractionation in algae and cyanobacteria. In : Lajtha K, & Michener JD (eds) Stable isotopes in ecology and environmental science. Blackwell Scientific Publications, 1994. 316 pp

Goering J, Alexander V, & Haubenstock N (1990) Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific bay. Estuar Coast Shelf Sci 30 : 239-260

Gomez I, Wiencke C, & Weykam G (1995) Seasonal photosynthetic characteristics of *Acoseira mirabilis* (Acoseirales, Phaeophyceae) from King George Island, Antartica. Mar Biol 123 : 167-172

Gong WK, & Ong JE (1990) Plant biomass and nutrient flux in a managed mangrove forest in Malaysia. Estuar Coast Shelf Sci 31 : 519-530

González-Farias F, & Mee LD (1988) Effect of mangrove humic-like substances on biodegradation rate of detritus. J Exp Mar Biol Ecol 119 : 1-13

Gorokhova E, & Hansson S (1999) An experimental study on variations in stable carbon and nitrogen isotope fractionation during growth of *Mysis mixta* and *Neomysis integer*. Can J Fish Aquat Sci 56 : 2203-2210

Grey J, Jones RI, & Sleep D (2000) Stable isotope analysis of the origins of zooplankton carbon in lakes of differing trophic state. Oecologia 123 : 232-240

Grey J, Jones RI, & Sleep D (2001) Seasonal changes in the importance of the source of organic matter to the diet of zooplankton in Loch Ness, as indicated by stable isotope analysis. Limnol Oceanogr 46 : 505-513

Grindley JR (1984) The zooplankton of mangrove estuaries. In : Por FD, & Dor I (eds) Hydrobiology of the mangal. The ecosystem of the mangrove forests. Developments in hydrobiology 20 Dr W Junk Publishers, The Hague. 260 pp

Gu B, Schelske CL, & Brenner M (1996a) Relationship between sediment and plankton isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) and primary productivity in Florida lakes. Can J Fish Aquat Sci 53 : 875-883

Gu B, Schelske CL, & Hoyer MV (1996b) Stable isotopes of carbon and nitrogen as indicators of diet and trophic structure of the fish community in a shallow hypereutrophic lake. J Fish Biol 49 : 1233-1243

Guerreiro J, Freitas S, Pereira P, Paula J, & Macia A (1996) Sediment macrobenthos of mangrove flats at Inhaca Island, Mozambique. Cah Biol Mar 37 : 309 - 327

Gupta LP, Subramanian V, & Ittekkot V (1997) Biogeochemistry of particulate organic matter transported by the Godavari River, India. Biogeochemistry 38 : 103-128

Hamilton SK, & Lewis WM (1992) Stable carbon and nitrogen isotopes in algae and detritus from the Orinoco river floodplain, Venezuela. Geochim Cosmochim Acta 56 : 4237-4246

Handley LL, & Raven JA (1992) The use of natural abundance of nitrogen isotopes in plant physiology and ecology. Plant Cell Environ 15 : 965-985

Handley LL, Odee D, & Scrimgeour CM (1994) $\delta^{15}N$ and $\delta^{13}C$ patterns in savanna vegetation : dependance on water availability and disturbance. Funct Ecol 8 : 306-314

Handley LL, Austin AT, Robinson D, Scrimgeour CM, Raven JA, Heaton THE, Schmidt S, & Stewart GR (1999) The 15-N natural abundance ($\delta^{15}N$) of ecosystem samples reflects measures of water availability. Austr J Plant Physiol 26 : 185-199

Hansson I, & Jagner D (1973) Evaluation of the accuracy of Gran plots by means of computer calculations. Anal Chim Acta 65 : 363-373

Harland AD, & Davies PS (1995) Symbiont photosynthesis increases both respiration and photosynthesis in the symbiotic sea anemone *Anemonia viridis*. Mar Biol 123 : 715-722

Harrigan P, Zieman JC, & Macko SA (1989) The base of nutritional support for the grey snapper (*Lutjanus griseus*) : an evaluation based on a combined stomach content and stable isotope analysis. Bull Mar Sci 44 : 65-77

Harrison PJ, Khan N, Yin K, Saleem M, Bano N, Nissa M, Ahmed SI, Rizvi N, & Azam F (1997) Nutrient and phytoplankton dynamics in two mangrove tidal creeks of the Indus River delta, Pakistan. Mar Ecol Prog Ser 157 : 13-19

Hayase S, Ichikawa T, & Tanaka K (1999) Preliminary report on stable isotope ratio analysis for samples from Matang mangrove brackish water ecosystems. Japan Agricultural Research Quarterly 33 : 215-221

Heaton THE (1986) Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere : a review. Chem Geol 59 : 87-102

Hellings L, Dehairs F, Tackx M, Keppens E, & Baeyens W (1999) Origin and fate of organic carbon in the freshwater part of the Scheldt Estuary as traced by stable carbon isotopic composition. Biogeochemistry 47 : 167-186

Hellings L (2000) Origin and fate of dissolved inorganic and particulate organic carbon in a highly polluted estuary (The Scheldt) as traced by stable carbon isotopes. PhD dissertation, Vrije Universiteit Brussels. 210 pp.

Hellings L, Dehairs F, Van Damme S, & Baeyens W (2001) Dissolved inorganic carbon in a highly polluted estuary (the Scheldt). Limnol Oceanogr 46 : 1406-1414

Hemminga MA , Slim FJ, Kazungu J, Ganssen GM, Nieuwenhuize J, & Kruyt NM (1994) Carbon outwelling from a mangrove forest with adjacent seagrass beds and coral reefs (Gazi Bay, Kenya). Mar Ecol Prog Ser 106 : 291-301

Hemminga MA, & Mateo MA (1996) Stable carbon isotopes in seagrasses : variability in ratios and use in ecological studies. Mar Ecol Prog Ser 140 : 285-298

Henn MR, & Chapela IH (2000) Differential C isotope discrimination by fungi during decomposition of C_3 and C_4-derived sucrose. Appl Environ Microb 66 : 4180-4186

Henn MR, & Chapela IH (2001) Ecophysiology of ^{13}C and ^{15}N isotopic fractionation in forest fungi and the roots of the saprophytic-mycorrhizal divide. Oecologia 128 : 480-487

Hill BJ (1979) Aspects of the feeding strategy of the predatory crab *Scylla serrata*. Mar Biol 55 : 209-214

Hinga KR, Arthur MA, Pilson MEQ, & Whitaker D (1994) Carbon isotope fractionation by marine phytoplankton in culture : the effects of CO_2 concentration, pH, temperature, and species. Glob Biogeochem Cy 8 : 91-102

Hobbie EA, Maco SA, & Shugart HH (1999) Insights into nitrogen and carbon dynamics of ectomycorrhizal and saprophytic fungi from isotopic evidence. Oecologia 118 : 353-360

Hobbie JE, Dayley RJ, & Jasper S (1977) Use of Nucleopore filters for counting bacteria by epifluorescence microscopy. Appl Environ Microbiol 33: 1225-1228

Hobson KA, & Clark RG (1992) Assessing avian diets using stable isotopes II : factors influencing diet-tissue fractionation. Condor 94 : 189-197

Hobson KA, & Clark RG (1993) Turnover of ^{13}C in cellular an plasma fractions of blood : implications for nondestructive sampling in avian dietary studies. Auk 110 : 638-641

Hobson KA, Alisauskas RT, & Clark RG (1993) Stable nitrogen isotope enrichment in avian tissues due to fasting and nutritional stress : implications for isotopic analysis of diet. Condor 95 : 388-394

Hobson KA, Schell DM, Renouf D, & Noseworthy E (1996) Stable carbon and nitrogen isotopic fractionation between diet and tissues of captive seals : implications for dietary reconstructions involving marine mammals. Can J Fish Aquat Sci 53 : 528-533

Hobson KA (1999) Tracing origins and migration of wildlife using stable isotopes : a review. Oecologia 120 : 314-326

Hoch MP, Fogel ML, & Kirchman DL (1992) Isotope fractionation associated with ammonium uptake by a marine bacterium. Limnol Oceanogr 37 : 1447-1459

Hogarth PJ (1999) Biology of mangroves. Oxford University Press, Oxford. 238 pp

Högberg P, Plamboeck AH, Taylor AFS, & Fransson PMA (1999) Natural ^{13}C abundance reveals trophic status of fungi and host-origin of carbon in mycorrhizal fungi in mixed forests. Proc Natl Acad Sci USA 96 : 8534-8539

Holligan PM, B alch WM, & Yentsch CM (1984) The significance of subsurface chlorophyll, nitrite and ammonium maxima in relation to nitrogen for phytoplankton growth in stratified waters of the Gulf of Maine. J Mar Res 42 : 1051-1073

Holmboe N, Kristensen E, & Andersen FO (2001) Anoxic decomposition in sediments from a tropical mangrove forest and the temperate Wadden Sea : implications for N and P addition experiments. Estuar Coast Shelf Sci 53 : 125-140

Holmer M, Anderson FO, Holmboe N, Kristensen E, & Thongtham N (2001) Spatial and temporal variability in benthic processes along a mangrove-seagrass transect near the Bangrong Mangrove, Thailand. Wetlands Ecology and Management 9 : 141-158

Hsieh HL, Chen CP, Chen YG, & Yang HH (2002) Diversity of benthic organic matter flows through polychaetes and crabs in a mangrove estuary : $\delta^{13}C$ and $\delta^{34}S$ signals. Mar Ecol Prog Ser 227 : 145-155

Hummel H, Moerland G, & Bakker C (1988) The concommitant existence of a typical coastal and a detritus food chain in the Westerschelde estuary. Hydrobiol Bull 22 : 35-41

Igamberdiev AU, Ivlev AA, Bykova NV, Threlkeld C, Lea PJ, & Gardeström P (2001) Decarboxylation of glycine contributes to carbon isotope fractionation in photosynthetic organisms. Photosynthesis Res 67 : 177-184

Ish-Shalom-Gordon N, Lin G, & Sternberg LDSL (1992) Isotopic fractionation during cellulose synthesis in two mangrove species : salinity effects. Phytochemistry 31 : 2623-2626

Ittekkot V, & Laane RWPM (1991) Fate of riverine particulate organic matter. In : Degens ET, Kempe S, & Richey JE (eds) Biogeochemistry of major world rivers. Wiley, U.K. 466 pp

Ivlev AA, Bykova NV, & Igamberdiev AU (1996) Fractionation of carbon ($^{13}C/^{12}C$) isotopes in glycine decarboxylase reaction. FEBS Lett 386 : 174-176

Jayatissa LP, Dahdouh-Guebas F, & Koedam N (2002) A review of the floral composition and distribution of mangroves in Sri Lanka. Bot J Linn Soc 138 : 29-43

Jennerjahn TC, & Ittekkot V (1997) Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil : I. Amino acids and hexosamines. Oceanol Acta 20 : 359-370

Jennerjahn TC, & Ittekkot V (2002) Relevance of mangroves for the production and deposition of organic matter along tropical continental margins. Naturwissenschaften 89 : 23-30

Jiang JX, & Li RG (1995) An ecological study of the Mollusca in mangrove areas in the estuary of the Jiulong River. Hydrobiologia 295 : 213-220

Johnston M, Yellowlees D, & Gilmour I (1995) Carbon isotopic analysis of the free fatty acids in a tridacnid-algal symbiosis : interpretation and implications for the symbiotic association. Proc R Soc Lond B 260 : 293-197

Jones DA (1984) Crabs of the mangal ecosystem. In : Por FD, & Dor I (eds) Hydrobiology of the mangal. Dr W Junk Publishers, The Hague.

Kaehler S, & Pakhomov EA (2001) Effects of storage and preservation on the $\delta^{13}C$ and $\delta^{15}N$ signatures of selected marine organisms. Mar Ecol Prog Ser 219 : 299-304

Kaly UL, Eugelink G, & Robertson AI (1997) Soil conditions in damaged North Queensland mangroves. Estuaries 20 : 291-300

Kao WY, & Chang KW (1998) Stable carbon isotope ratio and nutrient content of the *Kandelia candel* mangrove populations of different growth forms. Bot Bull Acad Sin 39 : 39-45

Kao W, Tsai HC, & Tsai TT (2001) Effect of NaCl and nitrogen availability on growth and photosynthesis of seedlings of a mangrove species, *Kandelia candel* (L.) Druce. J Plant Physiol 158 : 841-846

Kathiresan K (2000) A review of studies on Pichavaram mangrove, southeast India. Hydrobiologia 430 : 185-205

Kazungu JM (1996) Nitrogen-transformational processes in a tropical mangrove ecosystem (Gazi Bay, Kenya). PhD dissertation, Free University of Brussels

Keeley JE (1990) Photosynthetic pathways in freshwater aquatic plants. TREE 5 : 330-333

Kharlamenko VI, Kiyashko SI, Imbs AB, & Vyskkvartzev DI (2001) Identification of food sources of invertebrates from the seagrass *Zostera marina* community using carbon and sulfur stable isotope ratios and fatty acid analyses. Mar Ecol Prog Ser 220 : 103-117

Kitheka JU (1997) Coastal tidally-driven circulation and the role of water exchange in the linkage between tropical coastal ecosystems. Estuar Coast Shelf Sci 45 : 177-187

Kitheka JU, Ohowa BO, Mwashote BM, Shimbira WS, Mwaluma JM, & Kazungu JM (1996) Water circulation dynamics, water column nutrients and plankton productivity in a well-flushed tropical bay in Kenya. J Sea Res 35 : 257-268

Koch MS, & Madden CJ (2001) Patterns of primary production and nutrient availability in a Bahamas lagoon with fringing mangroves. Mar Ecol Prog Ser 219 : 109-119

Kohl PL, & Shearer G (1980) Isotopic fractionation associated with symbiotic N_2 fixation and uptake of NO_3^- by plants. Plant Physiol 66 : 51-56

Kohzu A, Yoshioka T, Ando T, Takahashi M, Koba K, & Wada E (1999) Natural ^{13}C and ^{15}N abundance of field-collected fungi and their ecological implications. New Phytol 144 : 323-330

Kondolarao B, & Ramana Murty KV (1988) Ecology of intertidal meiofauna of the Kakinada Bay (Gautami-Godavari estuarine system), East coast of India. Ind J Mar Sci 17 : 40-47

Korol RL, Kirschbaum MUF, Farquhar GD, & Jeffreys M (1999) Effects of water status and soil fertility on the C-isotope signature in *Pinus radiata.* Tree Physiol 19 : 551-562

Krishnamurthy K, Sultan Ali MA, & Prince Jeyaseelan MJ (1984) Structure and dynamics of the aquatic food web community with special reference to nematodes in mangrove ecosystem. Proc As Symp Mangr Env – Res & Manag : 429-452

Kristensen E, Andersen FO, & Kofoed LH (1988) Preliminary assessment of benthic community metabolism in a south-east Asian mangrove swamp. Mar Ecol Prog Ser 48 : 137-145

Kristensen E, Holmer M, & Bussarawit N (1991) Benthic metabolism and sufate reduction in a south-east Asian mangrove swamp. Mar Ecol Prog Ser 73 : 93-103

Kristensen E, Devol AH, Ahmed SI, & Saleem M (1992) Preliminary study of benthic metabolism and sulfate reduction in a mangrove swamp of the Indus Delta, Pakistan. Mar Ecol Prog Ser 90 : 287-297

Kristensen E, Andersen FO, Holmboe N, Holmer M, & Thongtham T (2000) Carbon and nitrogen mineralization in sediments of the Bangrong mangrove area, Phuket, Thailand. Aquat Microb Ecol 22 : 199-213

Kristensen E, & Pilgaard R (2001) The role of faecal pellet deposition by leaf-eating sesarmid crabs on litter decomposition in a mangrove sediment (Phuket, Thailand). In press.

Kroopnick P (1974) Correlations between ^{13}C and $\sum CO_2$ in surface and atmospheric CO_2. Earth Planet Sci Lett 22 : 397-403

Kuo SR, Lin HJ, & Shao KT (1999) Fish assemblages in the mangrove creeks of northern and southern Taiwan. Estuaries 22 : 1004-1015

Kuramoto T, & Minagawa M (2001) Stable carbon and nitrogen isotopic characterization of organic matter in a mangrove ecosystem on the south-western coast of Thailand. J Oceanogr 57 : 421-431

Kurata K, Minami H, & Kikuchi E (2001) Stable isotope analysis of food sources for salt marsh snails. Mar Ecol Prog Ser 223 : 167-177

Kwok PW, & Lee SY (1995) The growth performance of two mangrove crabs, *Chiromanthes bidens* and *Parasesarma plicata* under different leaf litter diets. Hydrobiologia 295 : 141-148

Lacerda LD, Rezende CE, Martinelli LA, Ovalle ARC, Mozeto A, Nogueira F, Victoria RL, Aragon GT, Da Cunha CT, & Souza CAR (1986) Composição isotópica de carbono em componentes de um ecossistema manguezal na Baía de Sepetiba, Rio de Janeiro. Ciência e cultura 38 : 1714-1717

Lacerda LD, Silva SAR, Rezende CE, & Martinelli LA (1991) Food sources for the mangrove tree crab *Aratus pisonii* : a carbon stable isotopic study. Rev Brasil Biol 51 : 685-687

Lacerda LD, Ittekkot V, & Patchineelam SR (1995) Biogeochemistry of mangrove soil organic matter : a comparison between *Rhizophora* and *Avicennia* soils in south-eastern Brazil. Estuar Coast Shelf Sci 40 : 713-720

Laegdsgaard P, & Johnson C (2001) Why do juvenile fish utilise mangrove habitats ? J Exp Mar Biol Ecol 257 : 229-253

Lancaster J, & Waldron S (2001) Stable isotope values of lotic invertebrates : sources of variation, experimental design, and statistical interpretation. Limnol Oceanogr 46 : 723-730

Lallier-Verges E, Perrussel BP, Disnar J-R, & Baltzer F (1998) Relationships between environmental conditions and the diagenetic evolution of organic matter derived from higher plants in a modern mangrove swamp system (Guadeloupe, French West Indies). Org Geochem 29 : 1663-1686

Lara RJ, & Dittmar T (1999) Nutrient dynamics in a mangrove creek (North Brazil) during the dry season. Mangroves and Salt Marshes 3 : 185-195

Lajtha K, & Marshall JD (1994) Sources of variation in the stable isotopic composition of plants. In : Lajtha K, & Michener JD (eds) Stable isotopes in ecology and environmental science. Blackwell Scientific Publications, 1994. 316 pp

Laws EA, Popp BN, Bidigare RR, Kennicutt MC, & Macko SA (1995) Dependence of phytoplankton carbon isotopic composition on growth rate and $[CO_2]_{aq}$: theoretical considerations and experimental results. Geochim Cosmochim Acta 59 : 1131-1138

Lee SY (1986) The intensity and consequences of herbivory on *Kandelia kandel* (L.) Druce leaves at the Mai Po marshes, Hong Kong. Proceedings of the second international marine biological workshop : the marine flora and fauna of Hong Kong and southerns China, Hong Kong. pp 717-725

Lee SY (1989) The importance of sesarminae crabs *Chiromanthes* spp. and inundation frequency on mangrove (*Kandelia candel* (L.) Druce) leaf litter turnover in a Hong Kong tidal shrimp pond. J Exp Mar Biol Ecol 131 : 23-43

Lee SY (1990) Primary productivity and particulate organic matter flow in an estuarine mangrove wetland in Hong Kong. Mar Biol 106 : 453-463

Lee SY (1995) Mangrove outwelling : a review. Hydrobiologia 295 : 203-212

Lee SY (1997) Potential trophic importance of the faecal material of the mangrove sesarmine crab *Sesarma messa*. Mar Ecol Prog Ser 159 : 275-284

Lee SY (1998) Ecological role of grapsid crabs in mangrove ecosystems : a review. Mar Freshwater Res 49 : 335-343

Lee SY (1999a) Tropical mangrove ecology : physical and biotic factors influencing ecosystem structure and function. Austr J Ecol 24 : 355-366

Lee SY (1999b) The effect of mangrove leaf litter enrichment on macrobenthic colonization of defaunated sandy substrates. Estuar Coast Shelf Sci 49 : 703-712

Lee SY (2000) Carbon dynamics of Deep Bay, eastern Pearl River estuary, China. II : Trophic relationship based on carbon and nitrogen stable isotopes. Mar Ecol Prog Ser 205 : 1-10

Lee OHK, Williams GA, & Hyde KD (2001) The diets of *Littoraria ardouiniana* and *L. melanostoma* in Hong Kong mangroves. J Mar Biol UK 81 : 967-973

Leggett MF, Servos MR, Hesslein R, Johannsson O, Millard ES, & Dixon DG (1999) Biogeochemical influences on the carbon isotope signatures of Lake Ontaria biota. Can J Fish Aquat Sci 56 : 221-2218

Leh DMU, & Sasekumar A (1986) The food of sesarmid crabs in Malaysian mangrove forests. Malayan Nature Journal 39 : 135-145

Lepoint G, Nyssen F, Gobert S, Dauby P, & Bouquegneau JM (2000) Relative impact of seagrass beds and its adjacent epilithic algal community in consumer diets. Mar Biol 136 : 513-518

Lewis WM, Hamilton SK, Rodriguez MA, Saunders JF, & Lasi MA (2001) Foodweb analysis of the Orinoco floodplain based on production estimates and stable isotope data. J N Am Benthol Soc 20 : 241-254

Ley JA, McIvor CC, & Montague CL (1999) Fishes in mangrove prop-root habitats of northeastern Florida Bay: Distinct assemblages across an estuarine gradient. Estuar Coast Shelf Sci 48 : 701-723

Li MS (1997) Nutrient dynamics of a Futian mangrove forest in Shenzhen, South China. Estuar Coast Shelf Sci 45 : 463-472

Li MS, & Lee SY (1998) Carbon dynamics of Deep Bay, eastern Pearl River Estuary, China. I: A mass balance budget and implications for shorebird conservation. Mar Ecol Prog Ser 172 : 73-87

Lin G, Banks T, & Sternberg LO (1991) Variation in $\delta^{13}C$ values for the seagrass *Thalassia testudinum* and its relations to mangrove carbon. Aquat Bot 40 : 333-341

Lin G, & Sternberg L da SL (1992a) Effect of growth form, salinity, nutrient and sulfide on photosynthesis, carbon isotope discrimination and growth of red mangrove (*Rhizophora mangle* L.) Aust J Plant Physiol 19 : 509-517

Lin G, & Sternberg LDSL (1992b) Differences in morphology, carbon isotope ratios, and photosynthesis between scrub and fringe mangroves in Florida, USA. Aquat Bot 42 : 303-313

Lin P, & Wang WQ (2001) Changes in the leaf composition, leaf mass and leaf area during senescence in three species of mangroves. Ecol Engin 16 : 415-424

Loneragan NR, Bunn SE, & Kellaway DM (1997) Are mangroves and seagrasses sources of organic carbon for penaeid prawns in a tropical Australian estuary ? A multiple stable-isotope study. Mar Biol 130 : 289-300

Longinelli A, & Edmond JM (1983) Isotope geochemistry of the Amazon basin - a reconaissance. J Geophys Res 88 : 3703-3717

Lu CY, & Lin P (1990) Studies on litter fall and decomposition of *Bruguiera sexangula* (Lour) Poir, community on Hainan Island, China. Bull Mar Sci 47 : 139-148

Lugo AE, & Snedaker SC (1974) The ecology of mangroves. Annu Rev Ecol Syst 5 : 39-64

Lyman J (1957) Buffer mechanism of seawater, Ph.D. thesis, University of California, Los Angeles, 186 pp.

Maberly SC, Raven JA, & Johnston AM (1992) Discrimination between ^{12}C and ^{13}C by marine plants. Oecologia 91 : 481-492

Machiwa J (1999) Fate of organic carbon in a tropical mangrove ecosystem. PhD dissertation, Stockholm University.

Machiwa JF (2000) $\delta^{13}C$ signatures of flora, macrofauna and sediment of a mangrove forest partly affected by sewage wastes. Tanz J Sci 26 : 15-28

Mackey AP, & Smail G (1996) The decomposition of mangrove litter in a subtropical mangrove forest. Hydrobiologia 332 : 93-98

Macko SA, Lee WY, & Parker PL (1982) Nitrogen and carbon isotope fractionation by two species of marine amphipods : laboratory and field studies. J Exp Mar Biol Ecol 63 : 145-149

Macko SA, & Estep MLF (1984) Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. Org Geochem 6 : 787-790

Macko SA, & Ostrom NE (1994) Pollution studies using stable isotopes. In : Lajtha K, & Michener RH (eds) Stable isotopes in ecology and environmental science. Blackwell Scientific Publications, 1994. 316 pp.

MacLeod NA, & Barton DR (1998) Effects of light intensity, water velocity, and species composition on carbon and nitrogen stable isotope ratios in periphyton. Can J Fish Aquat Sci 55 : 1919-1925

Mahedevan C, & Rao RP (1958) Causes of the growth of sand spit north of Godavari confluence. Andhra University Memoirs in Oceanography, Volume II, pp.69-74 (+ 7 plates)

Malej A, Faganeli J, & Pezdic J (1993) Stable isotope and biochemical fractionation in the marine pelagic food chain : the jellyfish *Pelagia noctiluca* and net zooplankton. Mar Biol 116 : 565-570.

Manjulatha C, & Babu DE (1991) Functional organisation of mouth parts, and filter feeding, in *Clibanarius longitarsus* (Crustacea : Anomura). Mar Biol 109 : 121-127

Marguillier S, van der Velde G, Dehairs F, Hemminga MA, & Rajagopal S (1997) Trophic relationships in an interlinked mangrove-seagrass ecosystem as traced by $\delta^{13}C$ and $\delta^{15}N$. Mar Ecol Prog Ser 151 : 115-121

Marguillier S (1998) Stable isotope ratios and food web structure of aquatic ecosystems. PhD dissertation, Vrije Universiteit Brussels. 208 pp.

Marino R, & Howarth RW (1993) Atmospheric oxygen exchange in the Hudson River : dome measurements and comparison with other natural waters. Estuaries 16: 433-445

Mariotti A (1983) Atmospheric nitrogen is a reliable standard for natural ^{15}N abundance measurements. Nature 303 : 685-687

Mariotti A (1984) Natural ^{15}N abundance measurements and atmospheric nitrogen standard calibration. Nature 311 : 251-252

Mariotti A, Lancelot C, & Billen G (1984) Natural isotopic composition as a tracer of origin for suspended matter in the Scheldt estuary. Geochim Cosmochim Acta 48 : 549-555

Martinelli LA, Piccolo MC, Townsend AR, Vitousek PM, Cuevas E, McDowell W, Robertson GP, Santos OC, & Treseder K (1999) Nitrogen stable isotopic composition of leaves and soil : tropical versus temperate forests. Biogeochemistry 46 : 45-65

Matsui N (1998) Estimated stocks of organic carbon in mangrove roots and sediments in Hinchinbrook Channel, Australia. Mangroves and Salt Marshes 2 : 199-204

May JD (1999) Spatial variation in litter production by the mangrove *Avicennia marina* var. *australasica* in Rangaunu Harbour, Northland, New Zealand. New Zealand J Mar Freshwater Res 33 : 163-172

McClelland JW, & Valiela I (1998) Linking nitrogen in estuarine producers to land-derived sources. Limnol Oceanogr 43 : 577-585

McClelland JW, Valiela I, & Michener RH (1997) Nitrogen-stable isotope signatures in estuarine food webs : a record of increasing urbanization in coastal watersheds. Limnol Oceanogr 42 : 930-937

McIvor CC, & Smith TJ III (1995) Differences in the crab fauna of mangrove areas at a Southwest Florida and a Northeast Australia location : implications for leaf litter processing. Estuaries 18 : 591-597

McKee KL, & Faulkner PL (2000) Restoration of biogeochemical function in mangrove forests. Restoration Ecology 8 : 247-259

McKee KL, Feller IC, Popp M, & Wanek W (2002) Mangrove isotopic ($\delta^{15}N$ and $\delta^{13}C$) fractionation across a nitrogen vs. phosphorus limitation gradient. Ecology 83 : 1065-1075

McKenzie JD, Black KD, Kelly MS, Newton LC, Handley LL, Scrimgeour CM, Raven JA, & Henderson RJ (2000) Comparison of fatty acid and stable isotope ratios in symbiotic and non-symbiotic brittlestars from Oban Bay, Scotland. J Mar Biol Ass UK 80 : 311-320

McKinney RQ, Lake JL, Allen M, & Ryba S (1999) Spatial variability in Mussels used to assess base level nitrogen isotope ratios in freshwater ecosystems. Hydrobiologia 412 : 14-24

McMillan C, Parker PL, & Fry B (1980) $^{13}C/^{12}C$ ratios in seagrasses. Aquat Bot 9 : 237-249

Medina E, & Francisco M (1997) Osmolality and $\delta^{13}C$ of leaf tissues of mangrove species from environments of contrasting rainfall and salinity. Estuar Coast Shelf Sci 45 : 337-344

Mehrbach C, Culberson CH, Hawley JE, & Pytkowicz RM (1973) Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol Oceanogr 18 : 897-907

Meier-Augustein W (1999) Applied gas chromatography coupled to isotope ratio mass spectrometry. J Chromatogr A 842 : 351-371

Meziane T, & Tsuchiya M (2000) Fatty acids as tracers of organic matter in the sediment and food web of a mangrove/intertidal flat ecosystem, Okinawa, Japan. Mar Ecol Prog Ser 200 : 49-57

Micheli F (1993a) Effect of mangrove litter species and availability on survival, moulting, and reproduction of the mangrove crab *Sesarma messa*. J Exp Mar Biol Ecol 171 : 149-163

Micheli F (1993b) Feeding ecology of mangrove crabs in North Eastern Australia : mangrove litter consumption by *Sesarma messa* and *Sesarma smithii*. J Exp Mar Biol Ecol 171 : 165-186

Middelburg JJ, Nieuwenhuize J, Slim FJ, & Ohowa B (1996) Sediment biogeochemistry in an East African mangrove forest (Gazi Bay, Kenya). Biogeochemistry 34 : 133-155

Middelburg JJ, Nieuwenhuize J, Lubberts RK, & van de Plassche O (1997) Organic carbon isotope systematics of coastal marshes. Estuar Coast Shelf Sci 45 : 681-687

Middelburg JJ, & Nieuwenhuize J (1998) Carbon and nitrogen isotopes in suspended matter and sediments from the Schelde Estuary. Mar Chem 60 : 217-225

Middelburg JJ, Barranguet C, Boschker HTS, Herman PMJ, Moens T, & Heip CHR (2000) The fate of intertidal microphytobenthos carbon : an in situ ^{13}C-labelling study. Limnol Oceanogr 45 : 1224-1234

Middleton BA, & McKee KL (2001) Degradation of mangrove tissues and implications for peat formation in Belizean island forests. J Ecol 89 : 818-828

Millero FJ (1979) The thermodynamics of the carbonate system in seawater. Geochim Cosmochim. Acta 43 : 1651-1661

Millero FJ, Hiscock WT, Huang F, Roche M, & Zhang JZ (2001) Seasonal variation of the carbonate system in Florida Bay. Bull Mar Sci 68 : 101-123

Minagawa W, & Wada E (1984) Stepwise enrichment of ^{15}N along food chains : further evidence and the relation between δ^{15}N and animal age. Geochim Cosmochim Acta 48 : 1135-1140

Mfilinge PL, Atta N, & Tsuchiya M (2002) Nutrient dynamics and leaf litter decomposition in a subtropical mangrove forest at Oura Bay, Okinawa, Japan. Trees 16 : 172-180

Moens T,

Monteiro PMS, James AG, Sholto-Douglas AD, & Field JG (1991) The δ^{13}C trophic position isotope spectrum as a tool to define and quantify carbon pathways in marine food webs. Mar Ecol Prog Ser 78 : 33-40

Montoya JP, Horrigan, SG, & McCarthy JJ (1990) Natural abundance of ^{15}N in particulate nitrogen and zooplankton in the Chesapeake Bay. Mar Ecol Prog Ser 65 : 35-61

Montoya JP, & McCarthy JJ (1995) Isotopic fractionation during nitrate uptake by phytoplankton grown in continuous culture. J Plankton Res 17 : 439-464

Mook WG, & Tan FC (1991) Stable carbon isotopes in rivers and estuaries. In : Degens ET, Kempe S, & Richey JE (eds) Biogeochemistry of major world rivers. SCOPE, John Wiley and sons Ltd. pp 245-264

Moore DJ, Nowak RS, & Tausch RJ (1999) Gas exchange and carbon isotope discrimination of *Juniperus occidentalis* across environmental gradients in the Great Basin of western North America. Tree Physiol 19 : 421-433

Moran MA, Wicks RJ, & Hodson RE (1991) 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

Morell JM, & Corredor JE (1993) Sediment nitrogen trapping in a mangrove lagoon. Estuar Coast Shelf Sci 37 : 203-212

Mueller H, & Ayukai T (1998) Concentration and molecular weight distribution of dissolved organic carbon in a mangrove creek in the Hinchinbrook area, Australia. Mangroves and Salt Marshes 2 : 231-235

Murthy NVSS (1997) Hydrography. In : An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of European Community INCO-DC contract CI1*CT930320, Part III, pp. 16-25

Murty AS, & Rao MB (1977) Studies on the ecology of Mollusca in a South Indian mangrove swamp. J Moll Stud 43 : 223-229

Muscatine L, Porter JW, & Kaplan IR (1989) Resource partitioning by reef corals as determined from stable isotope composition. I. δ^{13}C of zooxanthellae and animal tissue vs depth. Mar Biol 100 : 185-193

Nagelkerken I, van der Velde G, Gorissen MW, Meijer GJ, van 't Hof T, & den Hartog C (2000) Importance of mangroves, seagrass beds and the shallow coral reef as a nursery for important coral reef fishes, using a visual census technique. Estuar Coast Shelf Sci 51 : 31-44

Nedwell DB, Blackburn TH, & Wiebe WJ (1994) Dynamic nature of the turnover of organic carbon, nitrogen and sulfur in the sediments of a Jamaican mangrove forest. Mar Ecol Prog Ser 110 : 223-231

Neilson MJ, & Richards GN (1989) Chemical composition of degrading mangrove leaf litter and changes produced after consumption by mangrove crab *Neosarmatium smithi* (Crustacea : Decapoda : Sesarmidae). J Chem Ecol 15 : 1267-1283

Newell SY (1996) Established and potential impacts of eukaryotic mycelial decomposers in marine/terrestrial ecotones. J Exp Mar Biol Ecol 200 : 187-206

Newell RIE, Marshall N, Sasekumar A, & Chong VC (1995) Relative importance of benthic microalgae, phytoplankton, and mangroves as sources of nutrition for penaeid prawns and other coastal invertebrates from Malaysia. Mar Biol 123 : 595-606

Nieuwenhuize J, Maas YEM, & Middelburg JJ (1994) Rapid analysis of organic carbon and nitrogen in particulate materials. Mar Chem 45 : 217-224

Nobbs M, & McGuinness MA (1999) Developing methods for quantifying the apparent abundance of fiddler crabs (Ocypoda : Uca) in mangrove habitats. Austr J Ecol 24 : 43-49

Norland S (1993) The relationship between biomass and volume of bacteria. In : Kemp PF, Sherr EB, Sherr EB, Cole JJ (eds.) Current methods in aquatic microbial ecology. pp. 303-307. Lewis publihers.

Odum WE, & Heald EJ (1972) Trophic analysis of an estuarine mangrove community. Bull Mar Sci 22 : 671-737

Odum WE, & Heald EJ (1975) The detritus-based food web of an estuarine mangrove community. In : Estuarine Research, by Cronin, L.E. (ed.), Ac. Press New York pp. 265-286

Oelbermann K, & Scheu S (2001) Stable isotope enrichment ($\delta^{15}N$ and $\delta^{13}C$) in a generalist predator (*Pardosa lugubris*, Araneae : Lycosidae) : effects of prey quality. Oecologia 130 : 337-344

Ogawa N, & Ogura N (1997) Dynamics of particulate organic matter in the Tamagawa estuary and inner Tokyo bay. Estuar Coast Shelf Sci 44 : 263-273

O'Leary MH (1981) Carbon isotope fractionation in plants. Phytochemistry 20 : 553-567

O'Leary MH, Madhavan S, & Paneth P (1992) Physical and chemical basis of isotope fractionation in plants. Plant Cell Environ 15 : 1099-1104

Osmond CB, Valaane N, Haslam SM, Uotila P, & Roksandic Z (1981) Comparison of $\delta^{13}C$ values in leaves of aquatic macrophytes from different habtitats in Britain and Finland; some implications for photosynthetic processes in aquatic plants. Oecologia 50 : 117-124

Ostrom PH, Colunga-Garcia M, & Gage SH (1997) Establishing pathways of energy flow for insect predators using stable isotope ratios : field and laboratory evidence. Oecologia 109 : 108-113

Ovalle ARC, Rezende CE, Lacerda LD, & Silva CAR (1990) Factors affecting the hydrochemistry of a mangrove tidal creek, Sepetiba Bay, Brazil. Estuar Coast Shelf Sci 31 : 639-650

Ovalle ARC, Rezende CE, Carvalho CEV, Jennerjahn RC, & Ittekkot V (1999) Biogeochemical characteristics of coastal waters adjescent to small river-mangrove systems, East Brazil. Geo-Marine Lett 19 : 179-185

Owens NJP (1987) Natural variations in ^{15}N in the marine environment. Adv Mar Biol 24 : 389-451

Padmavathi D, & Satyanarayana D (1999) Distribution of nutrients and major elements in riverine, estuarine and adjoining coastal waters of Godavari, Bay of Bengal. Ind J Mar Sci 28 : 345-354

Page HM (1997) Importance of vascular plant and algal production to macro-invertebrate consumers in a southern California salt marsh. Estuar Coast Shelf Sci 45 : 823-834

Palmer SM, Hope D, Billet MF, Dawson JJC, & Bryant CL (2001) Sources of organic and inorganic carbon in a headwater stream : evidence from carbon isotope studies. Biogeochemistry 52 : 321-338

Pérez FF, & Fraga F (1987) The pH measurements in seawater on the NBS scale. Mar Chem 21 : 315-327

Peterson BJ, & Fry B (1987) Stable isotopes in ecosystem studies. Ann Rev Ecol Syst 18 : 293-320

Phillips DL (2001) Mixing models in analyses of diet using multiple stable isotopes : a critique. Oecologia 127 : 166-170

Phillips DL, & Gregg JW (2001) Uncertainty in source partitioning using stable isotopes. Oecologia 127 : 171-179

Phillips DL, & Koch PL (2001) Incorporating concentration dependance in stable isotope mixing models. Oecologia 130 : 114-125

Pinnegar JK, & Polunin NVC (1999) Differential fractionation of $\delta^{13}C$ and $\delta^{15}N$ among fish tissues : implications for the study of trophic interactions. Funct Ecol 13 : 225-231

Pinnegar JK, Campbell N, & Polunin NVC (2001) Unusual stable isotope fractionation patterns observed for fish host-parasite trophic relationships. J Fish Biol 59 : 494-503

Plaziat JC (1984) Mollusk distribution in the mangal. In : Por FD, & Dor I (eds) Hydrobiology of the mangal, pp. 113-143

Ponsard S, & Averbuch P (1999) Should growing and adult animals fed on the same diet show different $\delta^{15}N$ values ? Rapid Comm Mass Spectrom 13 : 1305-1310

Popp BN, Laws EA, Bidigare RR, Dore JE, Hanson KL, & Wakeham SG (1998) Effect of phytoplankton cell geometry on carbon isotope fractionation. Geochim Cosmochim Acta 62 : 69-77

Price HJ (1988) Feeding mechanisms in marine and freshwater zooplankton. Bull Mar Sci 43 : 327-343

Primavera JH (1996) Stable carbon isotope ratios of penaeid juveniles and primary producers in a riverine mangrove in Guimeras, Phillipines. Bull Mar Sci 58 : 675-683

Primavera JH (1997) Fish predation on mangrove-associated penaeids. The role of structures and substrate. J Exp Mar Biol Ecol 215 : 205-216

Raman AV (ed) GIS based study for Coringa mangroves. Final report of ICMAM project. Andhra University, 2000.

Rao RG, Woitchik AF, Goeyens L, van Riet A, Kazungu J, Dehairs F (1994) Carbon, nitrogen contents and stable isotope abundance in mangrove leaves from an east African coastal lagoon (Kenya). Aquat Bot 47 : 175-162

Rao RG (1998) Tracing carbon flow in the mangrove ecosystem of Godavari Delta, India. Ph.D. thesis, Vrije Universiteit Brussel, Brussels, Belgium. 142 pp.

Rao GMN (1995) Seasonal growth, biomass, and reproductive behavior of three species of red algae in Godavari Estuary, India. J Phycol 31 : 209-214

Rau GH, Takahashi T, Des Marais DJ, Repeta KJ, & Martin JH (1992) The relationship between $\delta^{13}C$ of organic matter and $[CO_2(aq)]$ in ocean surface water : data from a JGOFS site in the northeast Atlantic Ocean and a model. Geochim Cosmochim Acta 56 : 1413-1419

Raven JA, Walker DI, Jensen KR, Handley LL, Scrimgeour CM, & McInroy SG (2001) What fraction of the organic carbon in sacoglossans is obtained from photosynthesis by kleptoplastids? An investigation using the natural abundance of stable carbon isotopes. Mar Biol 138 : 537-545

Raymond PA, Bauer JE, & Cole JJ (2000) Atmospheric CO_2 evasion, dissolved inorganic carbon production, and net heterotrophy in the York river estuary. Limnol Oceanogr 45 : 1707-1717

Raymond PA, & Bauer JE (2001) DOC cycling in a temperate estuary : a mass balance approach using natural ^{14}C and ^{13}C isotopes. Limnol Oceanogr 46 : 655-667

Raymond PA, & Cole JJ (2001) Gas exchange in rivers and estuaries : choosing a gas transfer velocity. Estuaries 24 : 312-317

Raymond PA, & Bauer JE (2001) Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine and coastal DOC and POC sources and cycling : a review and synthesis. Org Geochem 32 : 469-485

Reid DG (1986a) Intense predation by crabs on mangrove littorinids. Am Malacol Bull 4 : 112

Reid DG (1986b) The Littorinid molluscs of mangrove forests in the Indo-Pacific region. British Museum (Natural History)

Reinfelder JR, Kraepiel AML, & Morel FMM (2000) Unicellular C_4 photosynthesis in a marine diatom. Nature 407 : 996-999

Rezende CE, Lacerda LD, Ovalle ARC, Silva CAR, & Martinelli LA (1990) Nature of POC transport in a mangrove ecosystem : a carbon stable isotopic study. Estuar Coast Shelf Sci 30 : 641-645

Riebesell U, Burkhardt S, Dauelsberg A, & Kroon B (2000) Carbon isotope fractionation by a marine diatom : dependance on the growth-rate-limiting rescource. Mar Ecol Prog Ser 193 : 295-303

Riebesell U (2000) Carbon fix for a diatom. Nature 407 : 959-960

Riera P, Stal LJ, Nieuwenhuize J, Richard P, Blanchard G, & Gentil F (1999) Determination of food sources for benthic invertebrates in a salt marsh (Aiguillon Bay, France) by carbon and nitrogen stable isotopes : importance of locally produced sources. Mar Ecol Prog Ser 187 : 301-307

Riera P, Montagna PA, Kalke RD, & Richard P (2000) Utilization of estuarine organic matter during growth and migration by juvenile brown shrimp *Penaeus aztecus* in a South Texas estuary. Mar Ecol Prog Ser 199 : 205-216

Rink S, Kühl M, Bijma J, & Spero HJ (1998) Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer *Orbulina universa*. Mar Biol 131 : 583-595

Risk MJ, & Erdmann MV (2000) Isotopic composition of nitrogen in stomatopod (Crustacea) tissues as an indicator of human sewage impacts on Indonesian coral reefs. Mar Poll Bull 40 : 50-58

Rivera-Monroy VH, & Twilley RR (1995) The relative role of denitrification and immobilization in the fate of inorganic nitrogen in mangrove sediments (Terminos Lagoon, Mexico). Limnol Oceanogr 41 : 284-296

Robertson AI (1986) Leaf-burying crabs : their influence on energy flow and export from mixed mangrove forests (Rhizophora spp.) in northeastern Australia. J Exp Mar Biol Ecol 102 : 237-248

Robertson AI (1987) The determination of trophic relationships in mangrove-dominated systems : areas of darkness. In : Field CD, & Dartnall AJ (eds) Mangrove ecosystems of Asia and th Pacific : status, exploitation and management. AIMS and the ACMR, Townsville, Australia, pp. 292-304.

Robertson AI (1988) The decomposition of mangrove leaf litter in tropical Australia. J Exp Mar Biol Ecol 116 : 235-247

Robertson AI, & Daniel PA (1989) The influence of crabs on litter processing in high intertidal mangrove forests in tropical Australia. Oecologia 78 : 191-198

Robertson AI, & Blaber SJM (1992) Plankton, epibenthos and fish communities. In : Robertson AI, & Alongi DM (eds) Tropical mangrove ecosystems. Coastal and estuarine studies n° 41. American Geophysical Union, 1992. 329 pp

Robertson AI, Alongi DM, & Boto KG (1992) Food chains and carbon fluxes. In : Robertson AI, & Alongi DM (eds) Tropical mangrove ecosystems. Coastal and estuarine studies n° 41. American Geophysical Union, 1992. 329 pp

Robinson D (2001) $\delta^{15}N$ as an integrator of the nitrogen cycle. Trends Ecol Evol 16 : 153-162

Rodelli MR, Gearing JN, Gearing PJ, Marshall N, & Sasekumar A (1984) Stable isotope ratios as a tracer of mangrove carbon in Malaysian ecosystems. Oecologia 61 : 326-333

Rodriguez C, & Stoner AW (1990) The epiphyte community of mangrove roots in a tropical estuary : distribution and biomass. Aquat Bot 36 : 117-126

Rogers KM (1999) Effects of sewage contamination on macro-algae and shellfish at Moa Point, New Zealand using stable carbon and nitrogen isotopes. New Zeal J Mar Freshwater Res 33 : 181-188

Rohini T (1997) Phytoplankton. In : An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of European Community INCO-DC contract CI1*CT930320, Part III, pp. 26-32

Rönnbäck P (1999) The ecological basis for economic value of seafood production supported by mangrove ecosystems. Ecol Econ 29 : 235-252

Rosing MN, Ben-David M, & Barry RP (1998) Analysis of stable isotope data : a K nearest-neighbours randomization test. J Wildlife Manag 62 : 380-388

Rumpho ME, Summer EJ, & Manhart JR (2000) Solar-powered sea slugs. Mollusk/algal chloroplast symbiosis. Plant Physiol 123 : 29-38

Russell-Hunter WD (1970) Aquatic productivity: an introduction to some basic aspects of biological oceanography and limnology. Macmillan, New York

Saenger P, & Snedaker SC (1993) Pantropical trends in mangrove aboveground biomass and annual litterfall. Oecologia 96 : 293-299

Sagers CL, Ginger SM, & Evans RD (2000) Carbon and nitrogen isotopes trace nutrient exchange in an ant-plant mutualism. Oecologia 123 : 582-586

Sarma VVSS, Kumar MD, & Marerikar M (2001) Emission of carbon dioxide from a tropical estuarine system, Goa, India. Geophys Res Lett 28 : 1239-1242

Sasekumar A (1974) Distribution of mangrove fauna on a Malayan mangrove shore. J Anim Ecol 43 : 51-64

Sasekumar A, Ong TL, & Thong KL (1984) Predation of mangrove fauna by marine fishes. Proc As Symp Mangr Env – Res & Manag : 378-384

Sasekumar A, Chong VC, Leh MU, & D'Cruz R (1992) Mangroves as a habitat for fish and prawns. Hydrobiologia 247 : 195-207

Satyanarayana B (1997) Biology of mangroves. In : An assessment of the ecological importance of mangroves in the Kakinada area, Andhra Pradesh, India. Final report of European Community INCO-DC contract CI1*CT930320, Part III, pp. 13-15

Satyanarayana B, Raman AV, Dehairs F, Kalavati C, & Chandramohan P (2002) Mangrove floristic and zonation patterns of Coringa, Kakinada Bay, East coast of India. Wetlands Ecology and Management 10 : 25-39

Saur E, Imbert D, Etienne J, & Mian D (1999) Insect herbivory on mangrove leaves in Guadeloupe : effects on biomass and mineral content. Hydrobiologia 413 : 89-93

Schell DM (2000) Declining carrying capacity in the Bering Sea : isotopic evidence from whale baleen. Limnol Oceanogr 45 : 459-462

Schell DM (2001) Carbon isotope ratio variations in Bering Sea biota : the role of anthropogenic carbon dioxide. Limnol Oceanogr 46 : 999-1000

Schrijvers J, Fermon H, & Vincx M (1996) Resource competition between macrobenthic epifauna and infauna in a Kenyan *Avicennia marina* mangrove forest. Mar Ecol Prog Ser 136 : 123-135

Schrijvers J, Okondo J, Steyaert M, & Vincx M (1995) Influence of epibenthos on meiobenthos of the *Ceriops tagal* mangrove sediment at Gazi Bay, Kenya. Mar Ecol Prog Ser 128 : 247-259

Schubert CJ, & Nielsen (2000) Effects of decarbonation treatments on $\delta^{13}C$ values in marine sediments. Mar Chem 72 : 55-59

Schwamborn R, Voss M, Ekau W, & Saint-Paul U (1999) Stable isotope composition of particulate organic matter and zooplankton in North-East Brazilian shelf waters. Arch Fish Mar Res 47 : 201-210

Schwamborn R, Ekau W, Voss M, & Saint-Paul U (2002) How important are mangroves as a carbon source for decapod crustacean larvae in a tropical estuary ? Mar Ecol Prog Ser 229 : 195-205

Schweizer M, Fear J, & Cadish G (1999) Isotopic (^{13}C) fractionation during plant residue decomposition and its implications for soil organic matter studies. Rapid Commun Mass Spectrom 13 : 1284-1290

Scrimgeour SM, Gordon SC, Handley LL, & Woodford JAT (1995) Trophic levels and anomalous $\delta^{15}N$ of insects on raspberry (*Rubus idaeus* L.). Isot Environ Health Stud 31 : 107-115

Selvam V, Azariah J, & Azariah H (1992) Diurnal variation in physical-chemical properties and primary production in the interconnected marine, mangrove and freshwater biotopes of Kakinada coast, Andhra Pradesh, India. Hydrobiologia 247 : 181-186

Sheaves M, & Molony B (2000) Short-circuit in the mangrove food chain. Mar Ecol Prog Ser 199 : 97-109

Sheridan RP (1991) Epicaulous, nitrogen-fixing microepiphytes in a tropical mangal community, Guadeloupe, French West Indies. *Biotropica* 23 : 530-541

Sheridan RP (1992) Nitrogen fixation by epicaulous cyanobacteria in the Pointe de la Saline mangrove community, Guadeloupe, French West Indies. Biotropica 24 : 571-574

Sherman RE, Fahey TJ, & Howarth RW (1998) Soil-plant interactions in a neotropical mangrove forest : iron, phosphorus and sulfur dynamics. Oecologia 115 : 553-563

Sherr EB (1982) Carbon isotope composition of organic seston and sediments in a Georgia salt marsh estuary. Geochim Cosmochim Acta 46 : 1227-1232

Shunula JP, & Whittick A (1999) Aspects of litter production in mangroves from Unguja Island, Zanzibar, Tanzania. Estuar Coast Shelf Sci 49 : 51-54

Simpson JH, Gong WK, & Ong JE (1997) The determination of the net fluxes from a mangrove estuary system. Estuaries 20 : 103-109

Siqueiros-Beltrones DA & Castrejón ES (1999) Structure of benthic diatom assemblages from a mangrove environment in a Mexican Subtropical Lagoon. Biotropica 31 : 48-70

Sivasothi N (2000) Niche preferences of tree-climbing crabs in Singapore mangroves. Crustaceana 73 : 25-38

Skov MW, & Hartnoll RG (2002) Paradoxical selective feeding on a low-nutrient diet : why do mangrove crabs eat leaves ? Oecologia 131 : 1-7

Slim FJ, Gwada PM, Kodjo M, & Hemminga MA (1996) Biomass and litterfall of *Ceriops tagal* and *Rhizophora mucronata* in the mangrove forest of Gazi Bay, Kenya. Mar Freshwater Res 47 : 999-1007

Slim FJ, Hemminga MA, Ochieng C, Jannick NT, Cocheret de la Morinière E, & van der Velde G (1997) Leaf litter removal by the snail *Terebralia palustris* (Linneaus) and sesarmid crabs in an East African mangrove forest (Gazi Bay, Kenia). J Exp Mar Biol Ecol 215 : 35-48

Somayajulu BLK, Martin JM, Eisma D, Thomas AJ, Borole DV, & Rao KS (1993) Geochemical studies in the Godavari estuary, India. Mar Chem 43 : 83-93

Sonnerup RE, Quay PD, McNichol AP, Bullister JL, Westby TA, & Anderson HL (1999) Reconstructing the oceanic ^{13}C Suess effect. Glob Biogeochem Cycles 13 : 857-872

Spitzy A, & Leenheer J (1991) Dissolved organic carbon in rivers. In : Degens ET, Kempe S, & Richey JE (eds) Biogeochemistry of major world rivers. Wiley, U.K. 466 pp

Sreenivas NV (1998) Zooplankton composition and distribution in mangrove habitats of the Godavari Estuary – Kakinada. PhD thesis, Andhra University

Steinke TD, & Ward CJ (1987) Degradation of mangrove leaf litter in the St-Lucia estuary as influenced by season and exposure. South Afr J Bot 53 : 323-328

Steinke TD, Rajh A, & Holland AJ (1993) The feeding behaviour of the red mangrove crab *Sesarma meinerti* de Man, 1887 (Crustacea : Decapoda : Grapsidae) and its effect on the degradation of mangrove leaf litter. S Afr J mar Sci 13 : 151-160

Stoner AW, & Zimmerman RJ (1988) Food pathways associated with penaeid shrimps in a mangrove-fringed estuary. Fish Bull 86 : 543-551

Striegl RG, Kortelainen P, Chanton JP, Wickland KP, Bugna GC, & Rantakari M (2001) Carbon dioxide partial pressure and C-13 content of north temperate and boreal lakes at spring ice melt. Limnol Oceanogr 46 : 941-945

Subramanian P, Prince Jeyaseelan MJ, & Krishnamurthy K (1984) The nature of biodegradation of vegetation in mangrove ecosystem. Chem Ecol 2 : 47-68

Sullivan MJ, & Moncreiff CA (1990) Edaphic algae are an important component of salt marsh food webs : evidence from multiple stable isotope analysis. Mar Ecol Prog Ser 62 : 149-159

Sweeney RE, & Kaplan IR (1980) Natural abundance of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. Mar Chem 9 : 81-94

Swennen C (1997) Two new gastropods, *Elysia bangtawaensis* and *E. siamensis* from southern Thailand (Ophistobranchia, Sacoglossa, Elysiidae). Bull Zool Mus Univ Amsterdam 16 : 33-39

Tam NFY, Vrijmoed LLP, & Wong YS (1990) Nutrient dynamics associated with leaf decomposition in a small subtropical mangrove community in Hong Kong. Bull Mar Sci 47 : 68-78

Tam NFY, Wong YS, Lan CY, & Wang LN (1998) Litter production and decomposition in a subtropical mangrove swamp receiving wastewater. J Exp Mar Biol Ecol 226 : 1-18

Tanaka K, Sugahara K, Ohwaki Y, & Choo P-S (1998) C, N, P composition of suspended matter in Matang mangrove estuary, Malaysia. Japan Agricultural Research Quarterly 32 : 153-158

Thornton SF, & McManus J (1994) Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems : evidence from the Tay Estuary, Scotland. Estuar Coast Shelf Sci 38 : 219-233

Tieszen LL, Boutton TW, Tesdahl KG, & Slade NA (1983) Fractionation and turnover of stable carbon isotopes in animal tissues : implications for $\delta^{13}C$ analysis of diet. Oecologia 57 : 32-37

Tietjen JH, & Alongi DM (1990) Population growth and effects of nematodes on nutrient regeneration and bacteria associated with mangrove detritus from northeastern Queensland (Australia). Mar Ecol Prog Ser 68 : 169-179

Tomlinson PB (1986) The botany of mangroves. Cambridge University Press, London. 413 pp.

Tortell PD, Rau GH, & Morel FMM (2000) Inorganic carbon acquisition in coastal Pacific phytoplankton communities. Limnol Oceanogr 45 : 1485-1500

Turner JT, & Tester PA (1989) Zooplankton feeding ecology : non-selective grazing by the copepods *Acartia tonsa* Dana, *Centropages velificatus* De Oliveira, and *Eucalanus pileatus* Giesbrecht in the plume of the Mississippi river. J Exp Mar Biol Ecol 126 : 21-43

Twilley RR (1985) The exchange of organic carbon in basin mangrove forests in a southwest Florida estuary. Estuar Coast Shelf Sci 20 : 543-557

Twilley RR, Ejdung G, Romare P, & Kemp WM (1986) A comparative study of decomposition, oxygen consumption and nutrient release for selected aquatic plants occuring in an estuarine environment. Oikos 47 : 190-198

Twilley RR, Chen RH, & Hargis T (1992) Carbon sinks in mangrove forests and their implications to the carbon budget of tropical coastal ecosystems. Water Air Soil Pollut 64 : 265-288

Twilley RR, Poro M, Garcia VH, Rivera-Monroy VH, Zambrano R, & Bodero A (1997) Litter dynamics in riverine mangrove forests in the Guayas River Estuary, Ecuador. Oecologia 111 : 109-122

Underwood GJC, & Kromkamp J (1999) Primary production by photoplankton and microphytobenthos in estuaries. Adv Ecol Res 29 : 93-153

Vander Zanden MJ, & Rasmussen JB (1999a) Primary consumer $\delta^{13}C$ and $\delta^{15}N$ and the trophic position of aquatic consumers. Ecology 80 : 1395-1404

Vander Zanden MJ, Shuter BJ, Lester N, & Rasmussen JB (1999b) Patterns of food chain length in lakes : a stable isotope study. Am Nat 154 : 406-416

Vander Zanden MJ, & Rasmussen JB (2001) Variation in $\delta^{15}N$ and $\delta^{13}C$ trophic fractionation : implications for aquatic food web studies. Limnol Oceanogr 46 : 2061-2066

Velimirov B, Valenta-Simon M (1992) 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

Verardo DJ, Froelich PN, & McIntyre A (1990) Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer. Deep-Sea Res 37 : 157-165

Vidy G (2000) Estuarine and mangrove ecosystems and the nursery concept : which is which ? The case of the Sine Saloum system (Senegal). Wetlands Ecology and Management 8 : 37-51

Vijayakumar R, Ansari SA, & Parulkar AH (1991) Benthic fauna of Kakinada bay and backwaters, East coast of India. Ind J Mar Sci 20 : 195-199

Wada E, & Hattori A (1978) Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. Geomicrobiol J 1 : 85-101

Wada E, Shibata R, & Torii T (1981) N-15 abundance in Antartica : origin of soil-nitrogen and ecological implications. Nature 292 : 327-329

Wada E, Mizutani H, & Minagawa M (1991) The use of stable isotopes for food web analysis. Crit Rev Food Sci Nutr 30 : 361-371

Wada K, & Wowor D (1989) Foraging on mangrove pneumatophores by ocypodid crabs. J Exp Mar Biol Ecol 134 : 89-100

Wafar S, Untawale AG, & Wafar M (1997) Litter fall and energy flux in a mangrove ecosystem. Estuar Coast & Shelf Sci 44 : 111-124

Wainright SC, & Fry B (1994) Seasonal variation of the stable isotopic compositions of coastal marine plankton from Woods Hole, Massachusetts and Georges Bank. Estuaries 17 : 552-560

Wainright SC, Weinstein MP, Able KW, & Currin CA (2000) Relative importance of benthic microalgae, phytoplankton and the detritus of smooth cordgrass *Spartina alterniflora* and the common reed *Phragmites australis* to brackish-marsh food webs. Mar Ecol Prog Ser 200 : 77-91

Wallander H, Nilsson LO, Hagerberg D, & Baath E (2001) Estimation of the biomass and seasonal growth of external mycelium of ecotmycorrhizal fungi in the field. New Phytol 151 : 753-760

Waser NAD, Harrison PJ, Nielsen B, Calvert SE, & Turpin DH (1998) Nitrogen isotope fractionation during the uptake and assimilation of nitrate, nitrite, ammonium, and urea by a marine diatom. Limnol Oceanogr 43 : 215-224

Waser NA, Yu ZM, Yin KD, Nielsen B, Harrison PJ, Turpin DH, & Calvert SE (1999) Nitrogen isotopic fractionation during a simulated diatom spring bloom : importance of N-starvation in controlling fractionation. Mar Ecol Prog Ser 179 : 291-296

Waterbury JB, Calloway CB, & Turner RD (1983) A celllulotytic nitrogen-fixing bacterium cultured from the gland of Deshayes in shipworms (Bivalvia, Teredinidae). Science 221 : 1401-1403

Wattayakorn G, Wolanski E, & Kjerfe B (1990) Mixing, trapping, and outwelling in the Klong Ngao mangrove swamp, Thailand. Estuar Coast Shelf Sci 31 : 667-688

Webb SC, Hedges REM, & Simpson SJ (1998) Diet quality influences the $\delta^{13}C$ and $\delta^{15}N$ of locusts and their biochemical components. J Experim Biol 201 : 2903-2911

Wedin DA, Tieszen LL, Dewey B, & Pastor J (1995) Carbon isotope dynamics during grass decomposition and soil organic matter formation. Ecology 76 : 1383-1392

Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar Chem 2 : 203-215

Wells FE (1984) Comparative distribution of macromolluscs and macrocrustaceans in a North-western Australian mangrove system. Aust J Mar Freshw Res 35 : 591-596

Williams MJ (1978) Opening of bivalve shells by the mud crab *Scylla serrata* Forskål. Aust J Mar Freshwater Res. 29 : 699-702

Williams MJ (1982) Natural food and feeding in the commercial sand crab *Portunus pelagicus* Linnaeus, 1766 (Crustacea : Decapoda : Portunidae) in Moreton Bay, Queensland. J Exp Mar Biol Ecol 59 : 165-176

Wilson KA (1989) Ecology of mangrove crabs : predation, physical factors and refuge. Bull Mar Sci 44 : 263-273

Woitchik AF, Ohowa B, Kazungu JM, Rao RG, Goeyens L, & Dehairs F (1997) Nitrogen enrichment during decomposition of mangrove litter in an east African coastal lagoon (Kenya) : relative importance of biological nitrogen fixation. Biogeochemistry 39 : 15-35

Wolanski E, Jones M, & Bunt JS (1980) Hydrodynamics of a tidal mangrove swamp system. Austr J Mar Freshwat Res 31 : 431-450

Wolanski E, Spagnol S, & Ayukai T (1998) Field and model studies of the fate of particulate carbon in mangrove-fringed Hinchinbrook Channel, Australia. Mangroves and Salt Marshes 2 : 205-221

Woodroffe CD, & Moss TJ (1984) Litter fall beneath *Rhizophora stylosa* Griff, Vaiputu, Tuvalu, South Pacific. Aquat Bot 18 : 249-255

Woodroffe CD (1985) Studies of a mangrove basin, Tuff Crater, New Zealand : I. Mangrove biomass and production of detritus. Estuar Coast Shelf Sci 20: 265-280

Woodroffe CD, Bardsley KN, Ward PJ, & Hanley JR (1988) Production of mangrove litter in a macrotidal embayment, Darwin Harbour, N.T., Australia. Estuar Coast Shelf Sci 26 : 581-598

Wylie JL, & Currie DJ (1991) The relative importance of bacteria and algae as food sources for crustacean zooplankton. Limnol Oceanogr 36 : 708-728

Yamamuro M, Kayanne H, & Minagawa M (1995) Carbon and nitrogen stable isotopes of primary producers in coral reef ecosystems. Limnol Oceanogr 40 : 617-621

Yang C, Telmer K, & Veizer J (1996) Chemical dynamics of the "St Lawrence" riverine system : δD_{H_2O}, $\delta^{18}O_{H_2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{sulphate}$, and dissolved $^{87}Sr/^{86}Sr$. Geochim Cosmochim Acta 60 : 851-866

Yipp MW (1980) The distribution of ground-dwelling gastropods in a small mangrove stand in Hong Kong. In : Morton BS, & Tseng CK (eds) Proceedings of the first international marine biological workshop : the marine flora and fauna of Hong Kong an Southern China, Hong Kong. pp. 705-720

Yoshii K, Melnik NG, Timoshkin OA, Bondarenko NA, Anoshko PN, Yoshioka T, & Wada E (1999) Stable isotope analysis of the pelagic food web in Lake Baikal. Limnol Oceanogr 44 : 502-511

Yoshioka T, Wada E, & Hayashi H (1994) A stable isotope study on seasonal food web dyamics in a eutrophic lake. Ecology 75 : 835-846

Ziegler H, & Luttge U (1998) Carbon isotope discrimination in cyanobacteria of rocks of inselbergs and soils of savannas in the neotropics. Bot Acta 111 : 212-215

Zieman JC, Macko SA, & Mills L (1984) Role of seagrasses and mangroves in estuarine food webs : temporal and spatial changes in stable isotope composition and amino acid content during decomposition. Bull Mar Sci 35 : 380-392

Zohary T, Erez J, Gophen M, Berman-Frank I, & Stiller M (1994) Seasonality of stable carbon isotopes within the pelagic food web of Lake Kinneret. Limnol Oceanogr 39 : 1030-1043

GLOSSARY

$[CO_2]_{aq}$: concentration of dissolved CO_2
µ : phytoplankton growth rate
C/N : ratio of carbon content to nitrogen content. Can be expressed in molar terms (mol/mol) or atom (g/g).
Chl a : chlorophyll-a
Depletion : the term depletion is used here to refer to the process whereby the stable isotope ratio of an element decreases, i.e. whereby the end product is depleted in the 'heavy' isotope (^{13}C or ^{15}N).
DIC : Dissolved inorganic carbon, i.e. the sum of the concentrations of dissolved CO_2 (referred to as $[CO_2]_{aq}$), HCO_3^-, and CO_3^{2-}.
DIN : dissoved inorganic nitrogen
Discrimination : the relative change in stable isotope ratios between the end product of a reaction and the initial product.
DOC : dissolved organic carbon
Enrichment : the term enrichment is used here to refer to the process whereby the stable isotope ratio of an element increases, i.e. whereby the end product is enriched in the 'heavy' isotope (^{13}C or ^{15}N).
Euhaline : zone with salinity ranging between 30 and 40 ppt
Fractionation : the process whereby the end product of a reaction has a different stable isotope composition than the initial product
Isotope : isotopes are atoms of the same element having different numbers of neutrons; i.e. isotopes of a certain element have different masses (mass number = number of protons + number of neutrons).
Mesohaline : zone with salinity ranging between 5 and 18 ppt
Oligohaline : zone with salinity ranging between 0.05 and 5 ppt
pCO_2 : the partial pressure of CO_2
PN : particulate nitrogen, see POC
POC : particulate organic carbon, often defined operationally as the organic carbon which is retained on e.g. 0.7 µm pore size glassfibre filters.
POC/PN : the ratio of particulate organic carbon concentrations to particulate nitrogen concentrations, can be expressed as molar (mol/mol) or atom (g/g)
Polyhaline : zone with salinity ranging between 18 and 30 ppt
SOM : sediment organic matter, or soil organic matter
SPOM : suspended particulate organic matter
TAlk : Total Alkalinity
TSM : total suspended matter
TSS : total suspended solids (note : identical to TSM)