VRIJE UNIVERSITEIT BRUSSEL

FACULTY OF SCIENCE
LABORATORY OF ANALYTICAL CHEMISTRY
ACADEMIC YEAR: 1995 - 1996

Nitrogen - Transformational Processes in a Tropical Mangrove Ecosystem (Gazi Bay, Kenya)

By

Johnson Michael Kazungu

Promotor : Prof. Dr. F. Dehairs
Co-promotor : Dr. L. Goeyens

A dissertation presented to the faculty of science, in fulfilment for the degree of Doctor of Philosophy (Science)

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Dedicated to Azimio

ABSTRACT

In order to understand and assess the role of mangrove sediments in the overall nitrogen budget of a tropical mangrove ecosystem, the following was investigated: (1) granulometry and pore-water chemistry; (2) main nitrogen transformational processes - organic nitrogen mineralization (regeneration and assimilation rates), nitrification (both potential and actual) and (3) sediment - water column nutrient fluxes, for sediments underlying stands of the two most predominant species of mangrove vegetation (i.e. *Rhizophora mucronata* and *Ceriops tagal*) in Gazi bay. These processes were investigated and related to both; possible sources of the remineralized sedimentary organic material and the concentrations of dissolved inorganic nitrogenous compounds found in the overlying water column.

Though senescent leaves of both, *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) species were found to have a C/N atom ratio of about 200, the sedimentary organic matter indicated a C/N atom ratio of between 19 and 30 for the upper 6 cm depth. This tremendous reduction of the C/N ratio in mangrove sediments in comparison to the mangrove leaf litter (expected to be the main source of organic matter) indicates a high possibility of another (perhaps more important) external supply of organic nitrogen into the sediments. Though this could come from nitrogen fixation, the maximum possible nitrogen addition into both Rm and Ct sediments through N_2 fixation and mangrove litterfall is relatively low when compared to the observed remineralization rates implying that without a constant external supply of organic nitrogen, the system would not be self-sustaining. Using a simple conservative mass balance model, this study has demontrated the likelyhood of organic material in mangrove sediments to be composed of two main parts; (1) a pool of highly refractory organic material from mangrove vegetation which is very poor in organic nitrogen and; (2) a pool of labile organic nitrogen, most likely marine POM of phytoplankton origin. However, when compairing the actual fluxed CO_2 (Middelburg et al., in press) and the observed nitrogen remineralization rates in the sediments, the remineralized organic matter is observed to have a C/N atom ratio of between 3 and 8. This implies that another source of organic matter whose C/N is < 6.6 is actively involved in the mineralization process. Since bacterial biomass has a C/N atom ratio of between 3 and 7, it is very likely that this biomass could be the major souce of the regenerated NH_4^+ in mangrove sediments. The marine PON therefore possibly acts as the easily available source of the labile organic nitrogen pool for bacterial utilization supporting the high bacterial productivities observed in most mangrove sediments. Upon death, these bacterial cells are then remineralized becoming the main source of the ammonium in mangrove sediments.

It is furthermore observed that between 44 % and 60 % of the ammonium mineralized is again taken up during bacterial growth. The remaining fraction of ammonium produced is then available for (1) nitrification; (2) outflux to the overlaying water column and (3) uptake by roots. When excluding the effect of O_2 supplied by roots, nitrification appears essentially limited to the first cm of the sediment column and represents only between 25 % (Rm sediment) and 3 % (Ct sediment) of the net ammonification rate found at the upper 1 cm of the sediment. These low nitrification rates are ascribed to low oxygen availability for Rm sediments and toxic conditions found in Ct sediments as a result of relatively high temperatures and salinities coupled with extreme acidic conditions lowering the pH of the pore water out of the limiting range (6.0 - 9.5) of most nitrifying bacteria.
The possible strength of the mangrove sediments as a source of dissolved inorganic nitrogen to the overlying water column was also investigated, both by measuring field epibenthic fluxes and by calculating fluxes based on measured concentration gradients across the sediment - water column interface. Nitrate (+ nitrite) fluxes were generally much lower and amounted only to about 10 to 15 % of the observed ammonium outflux. Ammonium outflux represents at most 0.7 % (Rm sediments) and 1.1 % (Ct sediments) of the ammonium regenerated stressing the minor role of epibenthic fluxes in the sedimentary nitrogen budget of these mangrove ecosystems.

It is estimated that periodic tidal resuspension of the upper 1.5 mm of sediment is necessary in order to add the required extra $\sum$ N (NH_4^+ + NO_3^- + NO_2^-) necessary to support the observed primary productivity in Gazi mangrove creeks. From these results, bacterial ammonium production and uptake appear to be the main processes affecting the organic nitrogen pool while nitrification, denitrification and nitrogen fixation represent relatively minor processes. Between 35 % (Rm) and 55 % (Ct) of the regenerated ammonium is found to be taken up by the trees themselves.

It thus appears that nitrogen introduced into the mangrove sedimentary compartment is mainly left for (I) recycling through an active bacterial production system; (II) uptake by the mangrove root system and (III) accumulation as refractory nitrogen. These different observations indicate that mangrove ecosystems, at least those similar to the system present in Gazi bay, are probably not important exporters of organic nitrogen and dissolved inorganic nutrients to the coastal ecosystem. Instead, they function as rather efficient traps and appear to efficiently recycle nitrogen in order to primarily satisfy nitrogen requirements of the mangrove trees themselves.

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CHAPTER 1

1.0 INTRODUCTION

1.1 General background

Ever since nutrients - nitrogen (organic and inorganic), phosphorus (organic and inorganic), silicone, and trace elements, e.g iron and copper, were cited as the major limiting factors in primary productivity in both fresh water and marine systems, a lot of research on them has been conducted. Of the indicated nutritional elements, nitrogen emerged as the most important - acting mostly as the major limiting element (Ryther and Dunstan, 1971; Eppley et al., 1979; McCarty and Goldman, 1979), hence it has currently enjoyed relatively higher attention than the other two. Nitrogen in marine environment can exist in five different oxidation states: +5 (NO_3^-), +3 (NO_2^-), +2 (N_2O), 0 (N_2) and -3 (NH_4^+). However, the biologically active states in marine systems are NO_3^-, NO_2^- and NH_4^+. Table 1.10 below (adapted from Sharp, 1983) gives an indication of some of the values expected for NO_3^-, NO_2^- and NH_4^+ in oceanic and coastal (including estuarine) water systems.

Table 1.10: Major dissolved inorganic nitrogen species in the sea. Approximate average values (μM).

Species		Surface oceanic (0 -100 m)	Deep oceanic (> 100 m)	Coastal	Estuarine
Nitrate	(NO_3^-)	0.2	35	0 - 30	0 - 350
Nitrite	(NO_2^-)	0.1	< 0.1	0 - 2	0 - 30
Ammonium	(NH_4^+)	< 0.5	< 0.1	0 - 25	0 - 600

The above indicated surface oceanic values are mostly for oligotrophic systems. Dynamic systems like those found in upwelling areas would tend to have relatively higher nutrient levels at the surface. In estuaries and shallow coastal systems

relatively higher nutrient levels are also observed. These nutrients are supplied by different allochtonous sources such as river input, seepage and anthropogenic inputs. Once in the estuaries, organic load brought about by the river input and vegetation within the coastal system can also undergo microbial degradation which would eventually release NH_4^+ into the system. This production is usually referrred to as regenerated production since it is produced in situ within the system. Dugdale and Goering (1967), introduced the concept of "new" and "regenerated" production when they partitioned the primary production of oceanic waters according to the nitrogen sources. New production is associated with nitrogen input to the photic zone mainly from upwelling nitrate, land run-off, nitrogen fixation and precipitation while regenerated production is associated with input mainly from nitrogen nutrients remineralized within the euphotic zone (mainly regenerated ammonium). In the absence of allochtonous supply of nutrients in oceanic waters this regenerated ammonium production has been proved to be very essential in maintaining oceanic productivity (McCarty, 1972; McCarty et al., 1977; Glibert, 1982; Owens et al., 1993).

Apart from these allochtonous and autochtonous supplies, ambient concentrations of these nutrients would also very much depend on the nutritional demand by primary producers (McCarty et al., 1977; El-Sayed et al., 1983; Jennings et al., 1984). It has been demonstrated that phytoplankton assimilates nitrogenous compounds preferentially (Glibert et al., 1982; Ronner et al., 1983; Henriksen and Kemp, 1988), always preferring NH_4^+ to other forms of nitrogen. According to McCarty et al. (1977), all nitrogen sources would be used simultaneously and in proportion to their concentrations at ammonium concentration less than 0.5 μM. Above this, the demand for nitrogen by the phytoplankton would be fully satisfied by ammonium and urea. This clearly demonstrates the crucial position NH_4^+ plays in nutrient dynamics in these systems.

Of the three major oceans of the world, namely; Pacific, Atlantic and Indian ocean, the latter has received less attention in terms of oceanographic research than the other two. The main reason is simply that Pacific and Atlantic are bordered by countries with old and active oceanographic institutions while fewer countries bordering the Indian ocean have any established oceanographic institutes. Most of the oceanographic research conducted in the Indian Ocean has been based on periodic international expeditions (Angel, 1984) which have mainly focused on the upwelling region off the Somali and the Arabian coasts (Leetmaa, 1972; Smith and Bothero, 1977; Leetmaa et al., 1982; Somasundra et al., 1990; Schott et al., 1990).

1.2 Circulation pattern of the Indian Ocean (neighbouring Kenyan coastline)

The circulation pattern of the Indian ocean very much depends on the monsoonal wind pattern observed in the area (McClanahan, 1988). The winds, which are the key to the physical forcing of the cycling in the Indian Ocean, blow from the northeast (NE) during the period of December - March producing the NE monsoon. In May, the winds reverse direction and start blowing from the southwest (SW). Wind velocity increases sharply in late May creating the SW monsoon which blows during the period between June and September. Inter-monsoon transitions occur during March - May and October - November and coincide with the rainy seasons in the east African regions. Long rainy seasons in Kenya are experienced mainly in April to June while short rainy period is mostly between November and December. The period between January and March is usually the most dry period with hardly any rainfall.

Figures 1.1 and 1.2 (adapted from Swallow et al., 1991) display the surface circulation pattern observed between 0^0 and 12^0 S off the eastern African coastline (Kenya coastline lies approximately between 1^0 and 5^0 S). Between 10^0 and 12^0 S we see the South Equatorial Current (SEC) moving from east towards the African continent. Near the African continent, it splits into two with one branch - the East African Coastal Current (EACC) going north. In the northern winter the EACC meets the southward flowing Somali Current (SC) near 3^0 S (fig. 1.1) and together they form the Equatorial Counter Current (ECC) at the surface (Swallow et al., 1991). During the northern summer due to the reversing of the monsoon winds the Somali Current (SC) reverses direction and flows northwards hence getting reinforcement from the East African Coastal Current (fig. 1.2). The waters off the Kenyan coast are therefore seen to be always under the influence of strong currents.

1.3 Nutrient regimes in the Indian Ocean

Apart from the upwelling regions off the Somali coast and the Arabian sea, the Indian ocean is mostly described as oligotrophic (Mantoura et al., 1993). During the southwest monsoon period upwelling develops at the northwestern part of the Indian Ocean as a result of the northward flowing Somali current turning east close to the Arabian sea. This upwelled water results in high nutrient levels off the northern part of the Somali coast (Smith and Codispoti, 1980; Sen Gupta and Naqvi, 1984). Nitrate values as high as 20 μM are sometimes found in these upwelling regions resulting in very high primary production (Smith and Codispoti, 1980). South of this upwelling zone, primary productivity is low (0.3 g C m^{-2} d^{-1}: Smith and Codispoti, 1980; Owens et al., 1993) being very much similar to those found in oligotrophic regions.

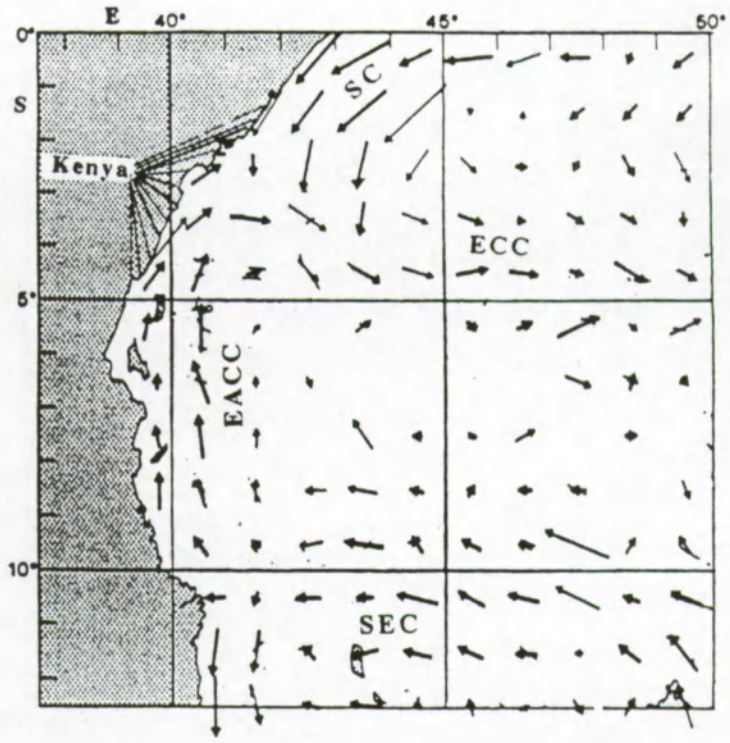


Fig. 1.1: Surface circulation pattern off the eastern African coastline between January and March during the Northeast (NE) monsoon period. (Adapted from Swallow et al., 1991).

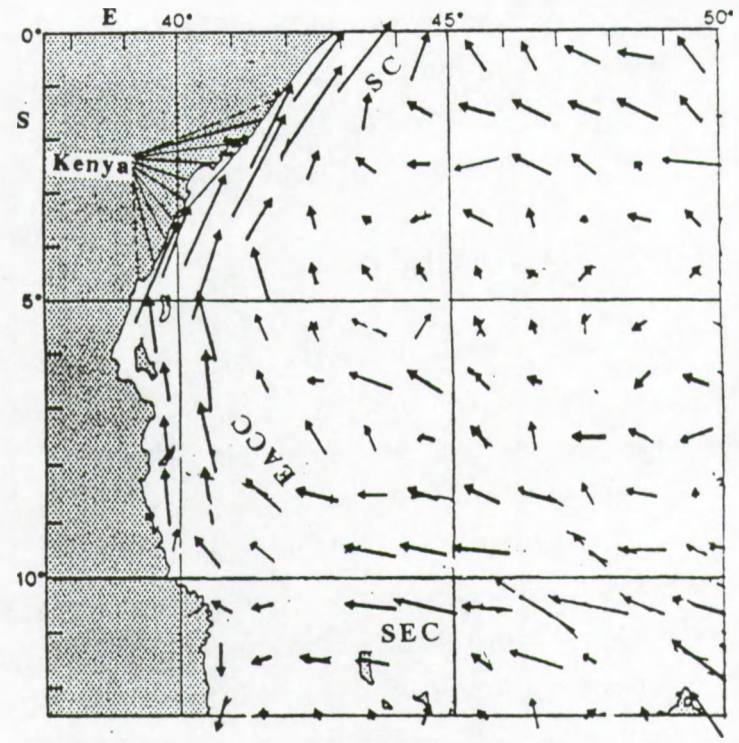


Fig. 1.2: Surface circulation pattern off the eastern African coastline between July and September during the southwest monsoon (SW) period. (Adapted from Swallow et al., 1991).

A most recent survey carried out in the tropical western Indian Ocean (Kenyan coast) during two cruises on board R.V. Tyro in 1992 confirmed the oligotrophic nature of the waters off the Kenyan coast (Semeneh et al., submitted). From this latest observation the average total surface inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$) concentrations found off the Kenyan coast during the northeast and southeast monsoons were 0.16 ± 0.13 and 0.29 ± 0.23 μM respectively. The slightly elevated values found during the SW monsoon period are attributed to riverine discharge coinciding with the long rainy seasons (McClanahan, 1988; Semeneh et al., submitted). The average observed C/N atom ratio for the particulate organic material off the Kenyan coast during the NE monsoon period was found to be ca. 6.40 reflecting mostly phytoplanktonic POM while during the SW monsoon this value was ca. 7.87 indicating the possibility of addition of terrigeneous particulate organic material poorer in nitrogen.

1.4 Estuaries and shallow coastal regions

Apart from rivers Tana and Sabaki in the northern part of Kenya (fig. 1.3) most of the rivers emptying their waters into the Indian Ocean off the Kenyan coastline are seasonal. These two major rivers (Tana and Sabaki) are known to have relatively high nutrient values (McClanahan, 1988). Measurements from Sabaki river show average phosphorus and nitrate concentrations of about 42 μM and 12 μM respectively (Giesen and Van de Kerkhof, 1984). Discharges of these rivers into the Indian ocean were found to be highest during the rainy seasons with Sabaki river discharging an average of about 0.3 x 10^9 m^3 per month while the Tana discharges upto 0.9 x 10^9 m^3 per month during the rainy period (McClanahan, 1988). During the southwest monsoons the northbound currents are stronger (fig. 1.2) and inputs from these discharges are washed northward while during the NE monsoon the currents are relatively weaker keeping discharged effects localised around discharge points (Brakel, 1984).

Generally, not much work on nutrients distribution has been done on the seasonal rivers emptying their waters into the Indian ocean apart from those done at Tudor estuary in Mombasa. Kazungu et al. (1989), observed that Tudor creek in Mombasa exhibited estuarine characteristics only during the rainy season due to the seasonal riverine supply from river Kombeni upstream. Nitrate values as high as 22 μM were associated with this riverine input and conservative - mixing persisted during the rainy period. However, during dry period the riverine effect was not noticed. These authors concluded that during rainy period, the Tudor creek could be defined as a "low nutrient estuary" with nitrate values at the fresh water end ranging between

10 and 30 μM and decreasing linearly to about 0 μM in the full salt end of the estuary while in dry period, the creek behaved just as an extended arm of the ocean with no significant nutrient variation.
If this could be taken as a pointer (in the absence of data from other seasonal rivers) the other seasonal rivers emptying into the Indian Ocean are expected to act the same with varying nutrients range in the fresh water end depending on the agricultural (or industrial, if any) activities found on each particular river.

However, though most nutrient work in Kenya has been focused on dissolved inorganic nutrients within the water column it is now well known that, globally, benthic nitrogen regeneration in shallow coastal ecosystems is very essential since it sometimes contributes more than 30 % of the nitrogen needed to sustain nitrogen production in the overlying water (Blackburn, 1988). Degradable material enters these systems as a result of terrestrial, littoral, pelagic and occasionally in situ production. Organic substances from all but the latter of these sources undergo considerable recycling prior to deposition. Once deposited on the bottom sediment, the organic-N is again acted upon by various heterotrophic organisms having ammonium as a by-product.
This NH_4^+ ion, can eventually undergo various transformational processes (Klump and Martens, 1983). Sediment mineralization and bacterial synthesis occur in zones dominated by different electron-acceptors. Organic carbon is first oxidized by oxygen and subsequently by nitrate and sulphate. As carbon is oxidized in these different zones, organic nitrogen is also mineralized to ammonium ions (Blackburn, 1988). The produced NH_4^+ accumulates in lower, anoxic sediment layers from where it diffuses up to the oxic surface. It is mostly at the sediment surface that nitrification (ammonium oxidation) can occur. Part of this ammonium is hence nitrified (McCarty et al., 1980; Henriksen et al., 1981; Henriksen and Kemp, 1988) while the remaining part diffuses into the water column (flux) across the sediment - water interface (Kemp et al., 1990; Iizumi et al, 1982; Blackburn and Henriksen, 1983). Apart from local consumption by benthic microorganisms, the nitrate produced as a result of nitrification has three fates: (1) reduction to NH_4^+ through the nitrate ammonification process (Koike and Sorensen, 1988), (2) lost as nitrogen gas through the denitrification process (Andersen et al., 1984), or (3) diffusion out into the water column (nitrate flux). The extent at which these processes occur in an ecosystem, depends on the biogeochemistry of the sediments in relation with the overlying water column.

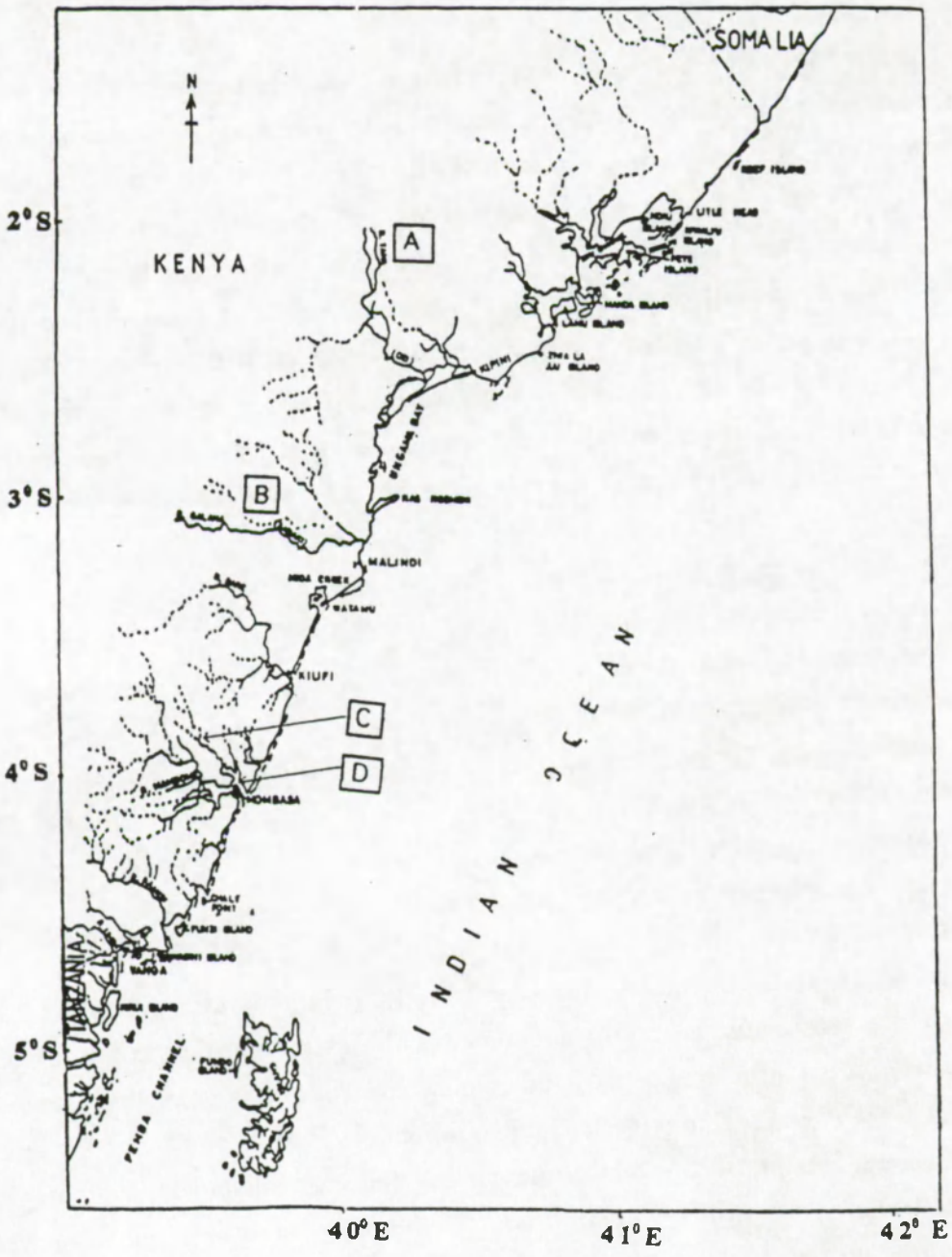


Fig. 1.3: Permanent and seasonal rivers discharging into the Indian ocean off the Kenyan coastline; A: river Tana, B: river Sabaki, C: river Kombeni and D: Tudor creek.

1.5 Mangrove ecosystems

"Mangrove" is an ecological term referring to a taxonomically diverse association of woody trees and shrubs that form the dominant vegetation in tidal, saline wetlands along tropical and subtropical coasts (Ball, 1988). Although specific patterns vary locally and regionally a major characteristic of mangrove forest structure is the zonation of species across the intertidal zone. Many abiotic and biotic factors vary with elevation and distance from the open water and create a continuum of contrasting conditions for mangrove survival and growth (Smith, 1992; McKee, 1993). This ecosystem offers a suitable shelter for many different types of marine species with fish and many types of Crustacea using mangrove streams for spawning and as nursery grounds. Other direct benefits of mangroves have been itemized as;

- protects the coast from erosion
- supports bird life
- supports fishing activities
- supports mariculture activities
- provides fuel
- provides building material
- a source of traditional medicines
- traps, concentrates and recycles nutrients

However, despite the many indicated benefits a large proportion of the global mangrove resource is currently threatened with destruction due to the increase of human-induced influences. Unlike natural disturbances due to events like, storm-wind damage for example, the effect of human influences is often to change the intertidal environment so that subsequent recolonization and reestablishment of the vegetation is prevented. Apart from the direct destructive human actions on mangrove vegetation (e.g. tree cutting for charcoal or building), in south-east Asia and many parts of Africa water diversions (e.g. for irrigation or drought) are severely disturbing mangrove ecosystems by deminishing fresh water flow, increasing soil salinities hence affecting the distribution pattern of the vegetation (IUCN report, 1983).

Though these ecosystems are known to be very beneficial to mankind, relatively far less research on them has been conducted compared to other systems like the salt marsh in temperate regions (Boto, 1982). Some reasons for this lack of data are obvious. Mangroves are essentially tropical or subtropical plants with a marked inability to withstand cold winters. Hence most of the developed countries with the

capacity to support marine research have little or no mangrove forests on their coastline.

Mangrove swamps are highly productive marine ecosystems and are believed to enhance near-shore primary and secondary productivity (Wattayakorn et al., 1990). Despite this knowledge relatively little is known about the nutrients dynamics therein. The litter generated by mangrove vegetation acts as an additional input of organic matter in a mangrove ecosystem (Jagtap, 1987; Steinke and Ward, 1987; Lee, 1990; Rezende et al., 1990). Again, this organic material can undergo microbial degradation resulting in the increase of nitrogenous compounds into the ecosystem (Alongi, 1990). Tidal currents can ultimately transport the organic material and nutrients into the open sea making the open coastal waters next to a mangrove vegetation very productive (Wolanski et al., 1986; Alongi et al., 1989; Wattayakorn et al., 1990).

CHAPTER 2

2.0 RATIONALE OF THE STUDY

Most of the studies done on mangroves within the east African coast have mainly been focussed on zonation patterns (Ruwa, 1987; Galin et al., 1989; Ruwa, 1993). Due to the present collaboration between European and east African scientists on several aspects of marine research, a number of interesting articles are now appearing on macroalgae (Coppejans and Galin, 1989) and organic matter distribution (Rao et al., 1993; Hemminga et al., 1994; Hemminga et al., 1995) in east African mangrove ecosystems. However, very little has been reported on the fluctuation of dissolved inorganic nutrients within the water column in relation to nutrient stocks and the organic-N remineralization process in these sediments. Alongi et al., 1992, in their extensive review work on mangrove ecosystems, pointed out the need of detailed study of nitrogen regeneration and sustainment in mangrove ecosystems worldwide to enable a full description of the same to be made.

In their study, Rao et al. (1993) found that between 50 to 60 % of the nitrogen is resorbed by the trees before a mangrove leaf falls (senescence). The senescent mangrove leaves were therefore found to be very poor in nitrogen having very high C/N atom ratios (*Rhizophora mucronata* : 193 ± 45; *Ceriops tagal* : 218± 26). Stable carbon isotope-13 signature of the mangrove sediment indicated the possibility of the mangrove vegetation to be the main source of the organic carbon found in mangrove sediments. However, examination of the mangrove sediment showed relatively very low C/N values (*Rhizophora* : 21; *Ceriops* : 18; Rao et al., 1993) indicating enrichment of nitrogen in these sediments. Hemminga et al. (1994) attributed this increase of nitrogen to seagrass from the neighbourhood. However, the question that has to be answered is: "Is seagrass the main cause of the sudden drop of C/N in mangrove sediments or does it just help, when available, to lower the C/N value of the sedimentary organic material ?" Examination of past work done on most mangrove sediments (even those not having seagrass neighbourhood) indicates relatively low C/N values (between 20 and 40 for the upper 12 cm depth) as compared to the C/N value associated with mangrove vegetation (Hatcher, et al,. 1982; Shaiful et al., 1986; Blackburn, et al., 1987; Jagtap, 1987; Kristensen, et al., 1988; Kristensen et al., 1992). Blackburn (1986), demonstrated that organic matter with C/N atom ratio of ≤ 20 would favour remineralization while that with C/N ratio of ≥ 20 would favour immobilization with no significant net ammonium production. In this case mangrove sediments are expected to favour immobilization with no

significant net production of ammonium. However, past work on mangrove sediments has indicated significant net ammonium production in these sediments (Shaiful, et al., 1986: Blackburn et al., 1987: Nedwell et al., 1994) implying the possibility of having a refractory and labile pool of the sedimentary organic nitrogen content.

This particular study which was undertaken concurrently with that reported by Rao et al. (1993) and Hemminga et al. (1994), will focus more on the dissolved inorganic nitrogen within the mangrove streams in relation to; (1) the sediment nutrient loads, (2) sedimentary organic nitrogen stock (and its transformational processes) - in sediments colonized by two dominant mangrove species (*Rhizophora mucronata* and *Ceriops tagal*) in Gazi bay.

This study was initiated under the Kenya-Belgium project in marine sciences and funded by the European Community under two projects titled: (1) Dynamics and assessment of Kenyan mangrove ecosystems and (2) Interlinkages on the eastern African coastal ecosystems. Part of the data was also collected under the Kenyan - Netherlands Indian Ocean Research Expedition (Land based programme, 1992).

2.1 Main objective

To investigate nitrogen transformational processes and their seasonal variations (dry and wet seasons) within mangrove biotopes in order to assess their relative importance in the overall supply of nitrogenous compounds into the ecosystem.

In order to be able to achieve the goals of the main objective, a number of specific objectives were made.

2.1.1 Specific objectives

(I) Analysis of the sources and stocks of the suspended and sedimentary organic material in the system in order to identify the origin and distribution of the same in the ecosystem.

(II) Analysis of the sedimentary organic matter deamination process to evaluate ammonium regeneration and bacterial assimilation rates giving rise to the net ammonium production in the ecosystem.

(III) Analysis of potential and actual nitrification rates in different mangrove sediments in order to assess the importance of nitrate (+ nitrite) production in these sediments.

(IV) Analysis of sediment - water column epibenthic fluxes in mangrove sediments in order to relate them to ambient concentrations both in the sediments and the water column.

(V) Analysis of seasonal distribution of dissolved inorganic nitrogenous compounds (NH_4^+, NO_3^- + NO_2^-) within the water column of the mangrove bay and relate the same with the epibenthic fluxes.

Figure 2.1 below gives a schematic representation of some of the nitrogen transformational processes that will be discussed, partly to answer the main objective.

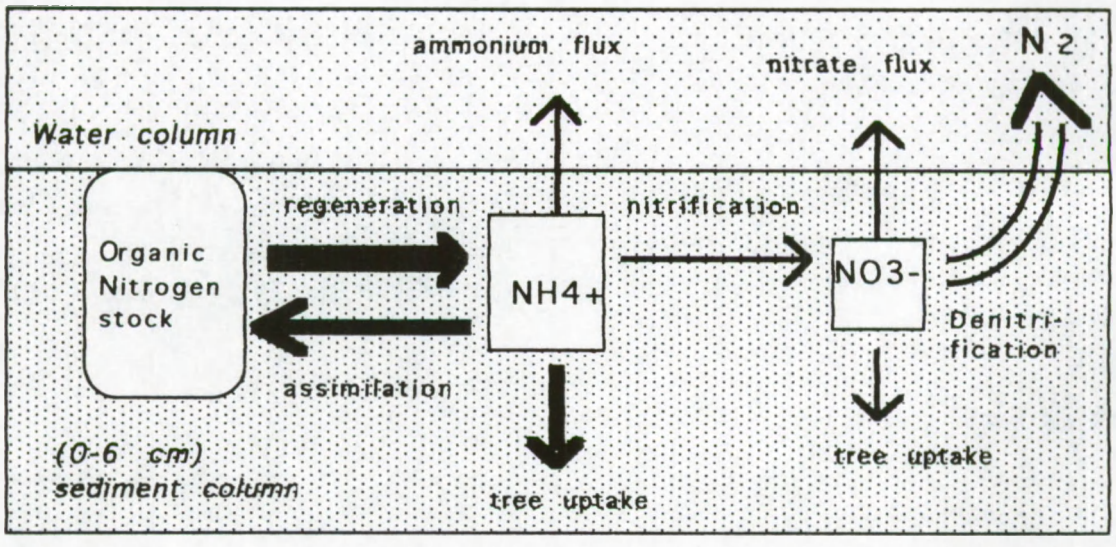


Fig. 2.1 : Schematic representation of nitrogen transformational processes in mangrove sediments.

CHAPTER 3

3.0 MATERIAL AND METHODS

3.1 Study site

3.1.1 Background information on Gazi bay

Gazi bay is situated 50 km south of Mombasa at approximately 39° 30' E and 4° 22' S. The bay is a shallow semi-enclosed coastal water system whose total area excluding the mangrove swamp is about 10 km^2 (Kitheka, 1995). The mangrove forest surrounding the bay covers an area of approximately 6.61 km^2 (Hemminga et al., 1994). The main documented species (Rao et al., 1993) found within this mangrove forest are:

Avicennia marina (Forssk) Viesh.
Bruguiera gymnorrhiza (L.) Lamarck
Ceriops tagal (Perr.) C.B. Rob
Heritiera littoralis (Dryand) A.t.
Lumnitzera racemosa Van Steems
Rhizophora mucronata Lamarck
Sonneratia alba J. Smith
Xylocarpus granatum Koenig

Additionally, Middelburg et al. (in press), using median elevation values reported by van Speybroek (1992) concluded that the relative elevation at which the most common species occur in Gazi bay is;

Sonneratia ≈ **creek-type** ***Avicennia*** < ***Rhizophora*** ≈ ***Bruguierra*** < ***Ceriops*** ≤ **basin shrub-type** ***Avicennia***

Because of the difference in elevation, the low lying species e.g. *Sonneratia*, creek-type *Avicennia* and *Rhizophora mucronata* are mostly inundated twice a day (during both spring and neap high tides) while the rest are inundated only during spring high tide. These two different flooding rates are bound to reflect different physico-chemical patterns in the sediments of these vegetations.

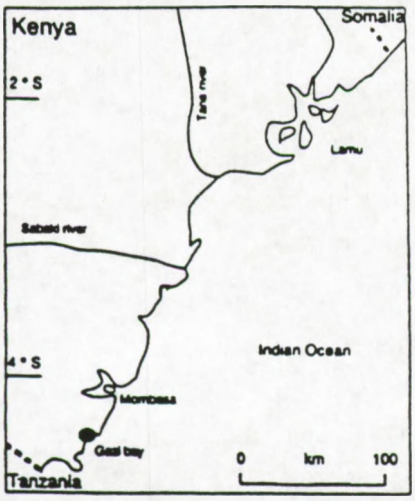
In this study two different sediment types were selected for the investigation of the nitrogen transformational processes in the mangrove sediments. The selected sediment biotopes

were those colonized by monospecific stands of *Rhizophora mucronata* (inundated twice a day) and *Ceriops tagal* species (inundated only during spring high tides). These two species occupy about 70 % of the entire vegetation found in Gazi mangrove forest and as mentioned earlier, formed the main area of study during two EEC funded projects.

Figure 3.1 shows a map of Gazi displaying the thick mangrove forest. Within the bay are found two major tidal creeks which penetrate the thick mangrove forest. These two are Kidogoweni in the western part and Kinondo in the east. Kidogoweni creek has a total length of about 4.5 km and forms the mouth of river Kidogoweni which is a seasonal river. Kinondo creek is shorter and has no direct river connection. Run-off volumes in river Kidogoweni are only significant during rainy seasons with average discharge of $(2.02 \pm 1.76) \times 10^5 m^3 d^{-1}$ during peak rainy periods while during most periods of the year the discharge is mostly less than $0.02 \times 10^5 m^3 d^{-1}$ (Kitheka, 1995).

The intertidal and subtidal areas found in the central part of the bay are covered by seagrass vegetation which from visual observation appears to be more densely packed in the eastern part than in the west. To the south, the bay is connected to the Indian ocean through a wide entrance (about 5 km) of which the depth varies between 3.0 and 8.0 m depth (Kitheka, 1995).

During spring low tide most parts of the bay are exposed with water only being found in the channels. The average water column height at the central part of the bay during spring high tide is about 4 meters decreasing gradually northward. The average tidal height at the *Rhizophora* and *Ceriops* study plots (fig. 3.1) during spring high tide was about 2.0 m and 1 m respectively. During neap tide, the average tidal height at the *Rhizophora* plot is about 1.5 m while the *Ceriops* plot is not covered by water during this period.



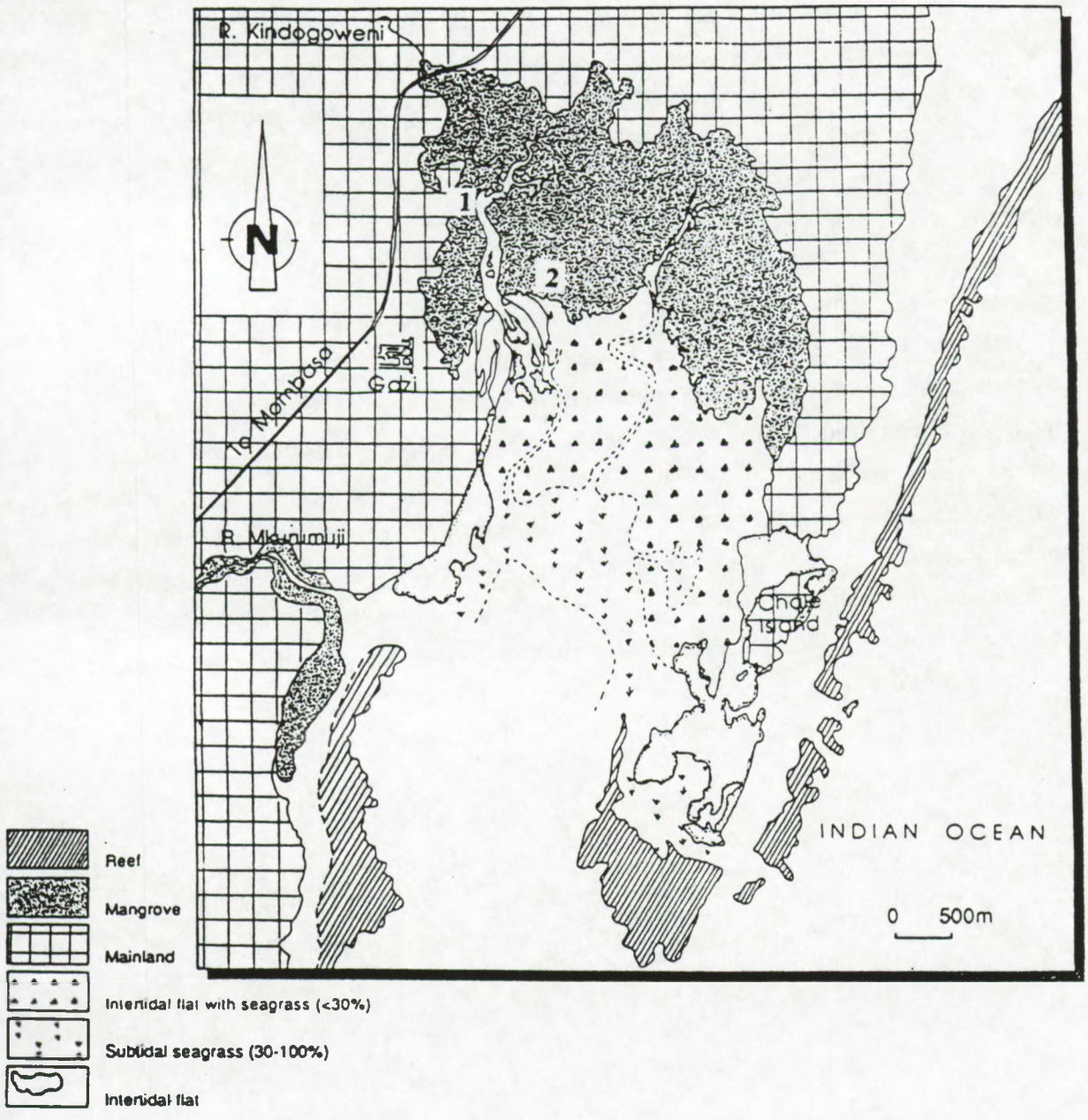


Fig. 3.1: Map of Gazi displaying the bay and the thick mangrove vegetation. Stations marked **1** and **2** represent the *Ceriops tagal* and *Rhizophora mucronata* fied plots.

Salinity distribution within the bay

Extensive work on salinity distribution within the bay has been reported by Kitheka, 1995. Due to seasonal run-off of river Kidogoweni which directly empties its riverine water into the upper part of the bay, the salinity regime of the bay during wet season is slightly different from that observed during dry season. Figure 3.2 gives a vertical cross section of salinity profiles as observed in Gazi bay during wet season while figure 3.3 shows the same during dry period (Kitheka, 1995). Station K1 is located towards the river mouth while St. G1 is towards the open sea (these stations will be described in detail in the next section). While the riverine effect is clearly noticed during the rainy season, it is hardly noticed during dry period. The slightly higher salinity values seen in the deeper parts of the Kidogoweni creek during the dry periods have been attributed to evapotranspiration since the creek is very shallow ($\leq$ 1 m) in the inner channels.

Currents within the bay

Astronomical tide is the main forcing function driving water circulation in Gazi bay. The tide generates strong reversing currents in the deep and narrow tidal channels within the mangrove creeks with slightly weaker currents observed at the central part of the bay. The strength and magnitude of the tidal currents in Gazi bay vary depending on the cross-sectional area of the channel, depth and tidal regime. The peak current speed in the creeks are found to reach as high as 0.6 m s^{-1} while at the central part of the bay these currents are found to slacken to about 0.3 m s^{-1} (Kitheka et al., 1995). Another detailed investigation on the circulation pattern of Gazi bay was made in 1992 during the Kenya - Dutch Indian ocean expedition. Figure 3.4 (adapted from Hemminga et al., 1994) gives a summarized version of the tidal currents as observed at the entrance of the Kinondo creek. Again the currents were seen to be mainly responding to a semi-diurnal tidal regime.

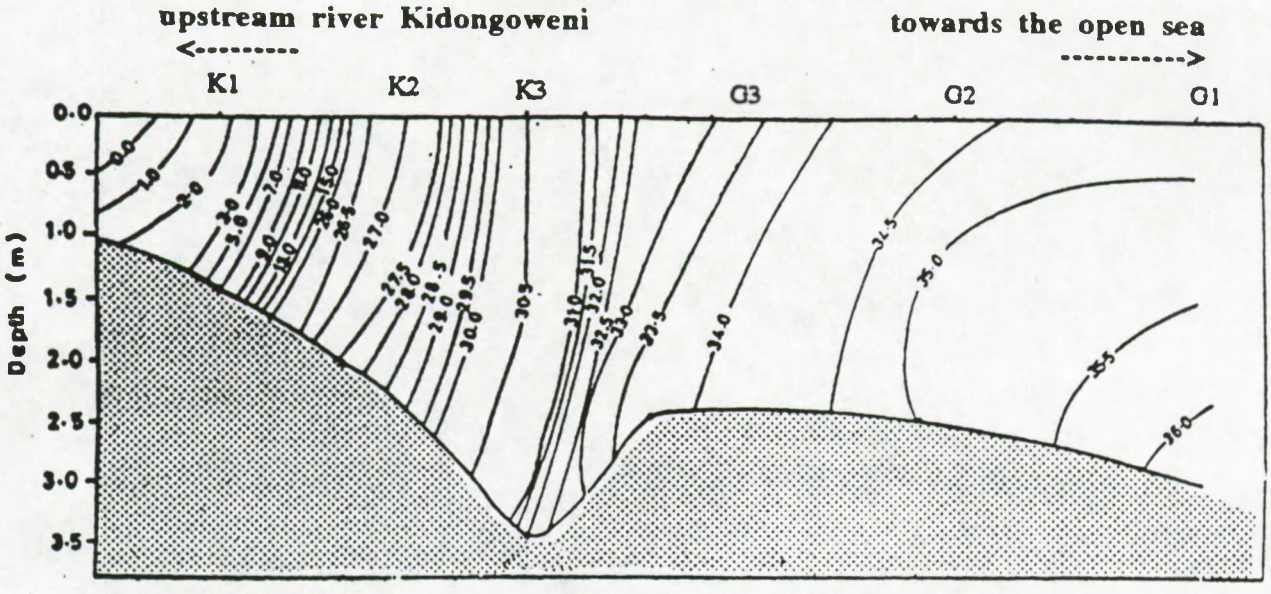


Fig.3.2: General features of vertical cross section of salinity profiles in Gazi bay during rainy season (April - June). Station K1 is upstreem river Kidogoweni while station G1 is towards the open sea. Adapted from Kitheka (in press).

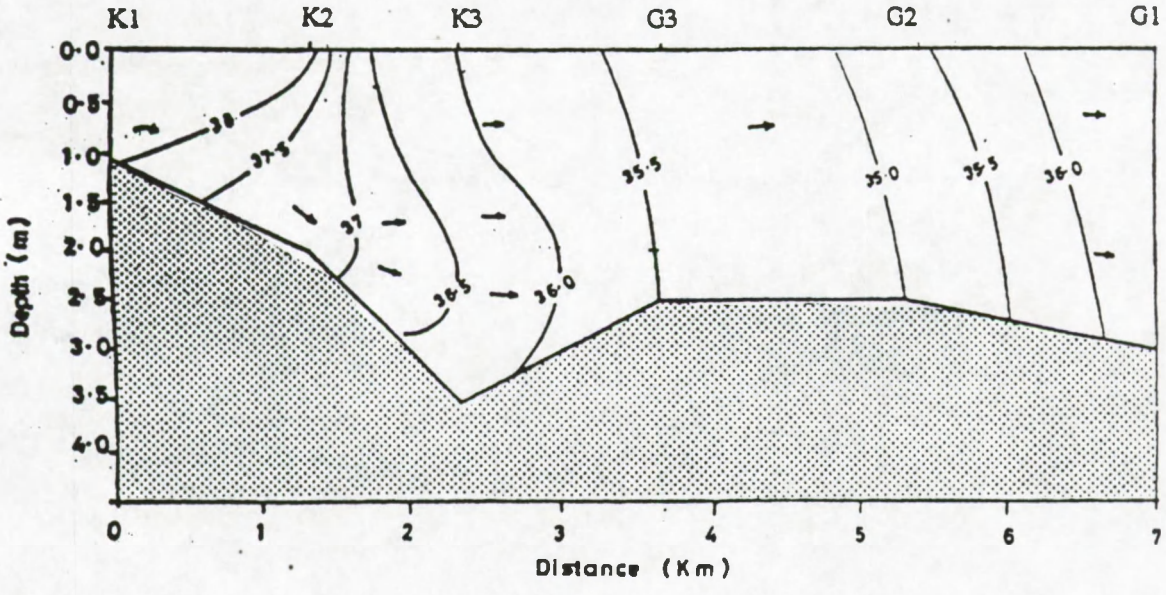


Fig.3.3: General features of vertical cross section of salinity profiles in Gazi bay during dry season (January - March). Station K1 is upstreem river Kidogoweni while station G1 is towards the open sea. Adapted from Kitheka (in press).

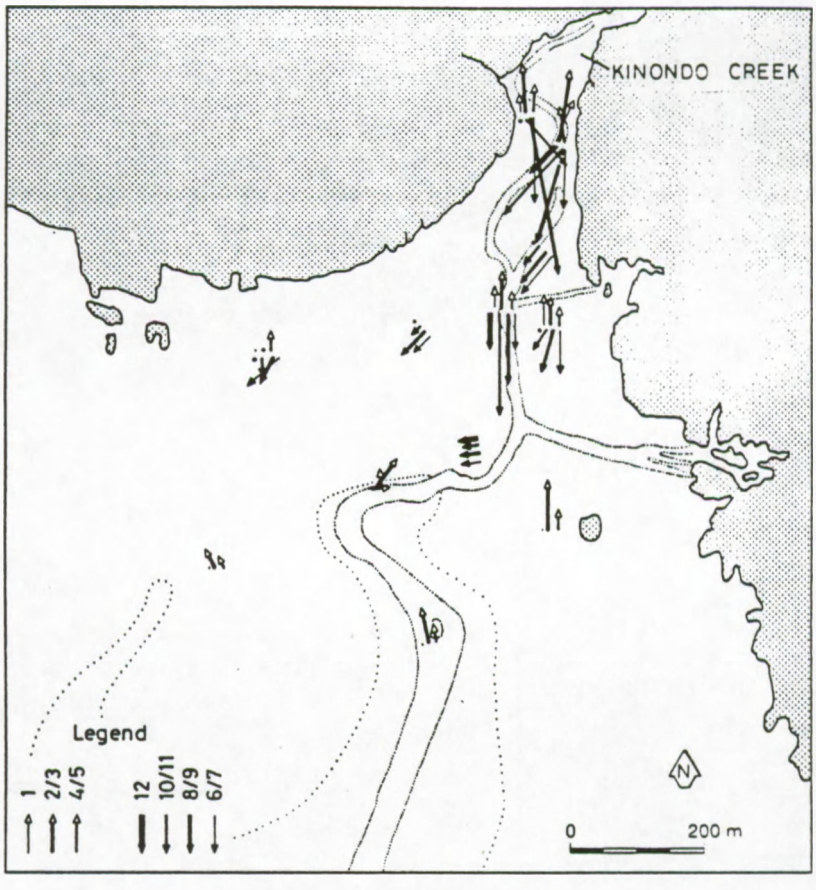


Fig. 3.4: Tidal regulated circulation pattern in the study area near Kinondo creek. Arrow length corresponds to the transformed current velocity. Different arrow styles indicate average flow characteristics measured during 1st hour, 2nd and 3rd, and 4th and 5th hour of flood tide, and during the ebb tide after the 6th hour. Adapted from Hemminga et al., 1994.

3.1.2 Sampling stations

3.1.2.1 Water column samples

(i) Sampling sites

Sampling for dissolved inorganic nutrients (DIN) and particulate organic material (POM) within the water column was started in 1991 by establishing the seven sampling stations displayed in figure 3.5a. Stations G1 to G4 were established within the creek to monitor the seasonal fluctuation of dissolved inorganic nutrients (DIN) and particulate organic material (POM) while K1, K2 and K3 were selected to monitor the nutrient levels from river Kidogoweni. In 1992 and 1993, seventeen more stations (at about 150 m apart) were added between station G3 and K1, to check on the conservative or non-conservative nature of the mixed water within the creek leading to river Kidogoweni. These stations were marked as RK1 to RK 17 where RK1 coincided with station K1 while RK 17 coincided with station G3 (fig. 3.5a). Additional to the above observations a special survey was also conducted in 1992 to establish, among others, the fate of outwelled mangrove organic material from the mangrove vegetation. For these observations, four stations - marked as MM (to represent a station within mangrove zone), MS (representing a station between mangroves and seagrass zone), CS (station between seagrass and coral reef zone) and CC (representing coral reef zone) were established (fig. 3.5b) within the bay.
In 1993 and 1994, sixteen more stations were established at the central part of the bay (fig. 3.5c) to monitor seasonal distributions of DIN at mid-tide during ebb and flood tides. These stations were marked as M1 to M16.

Sampling for dry season was mostly done between January and March while rainy season sampling was done between May and July. Fig. 3.6 gives the rainfall pattern obtained from an observation station close to the study site during the study period.

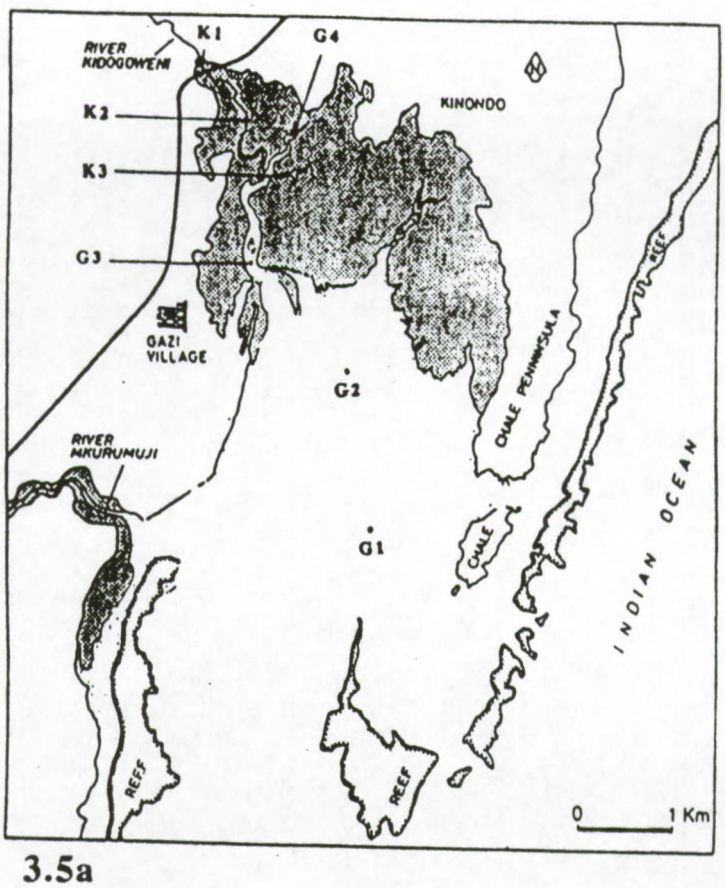


Fig. 3.5a

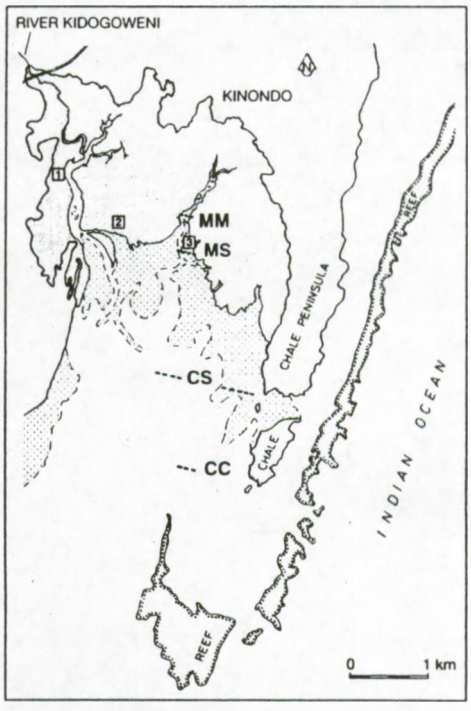


Fig. 3.5b

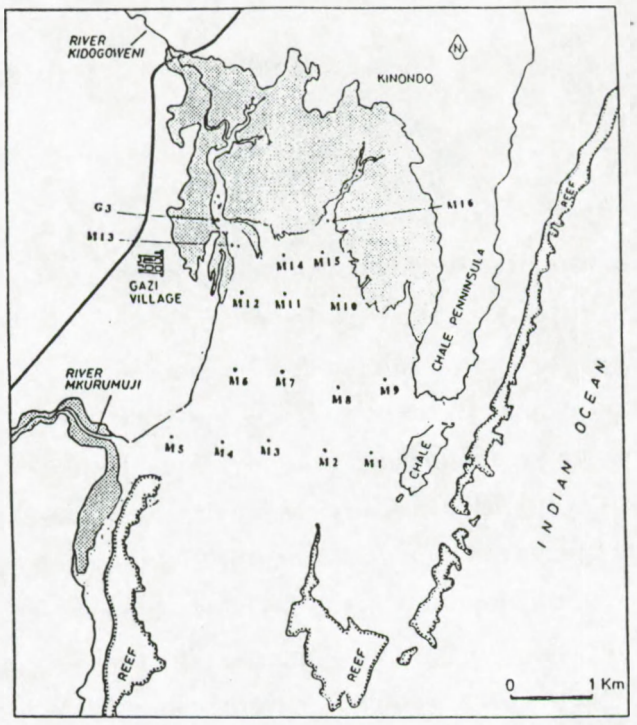


Fig. 3.5(a - c): Various sampling stations established in Gazi Bay for nutrient and particulate organic carbon studies.

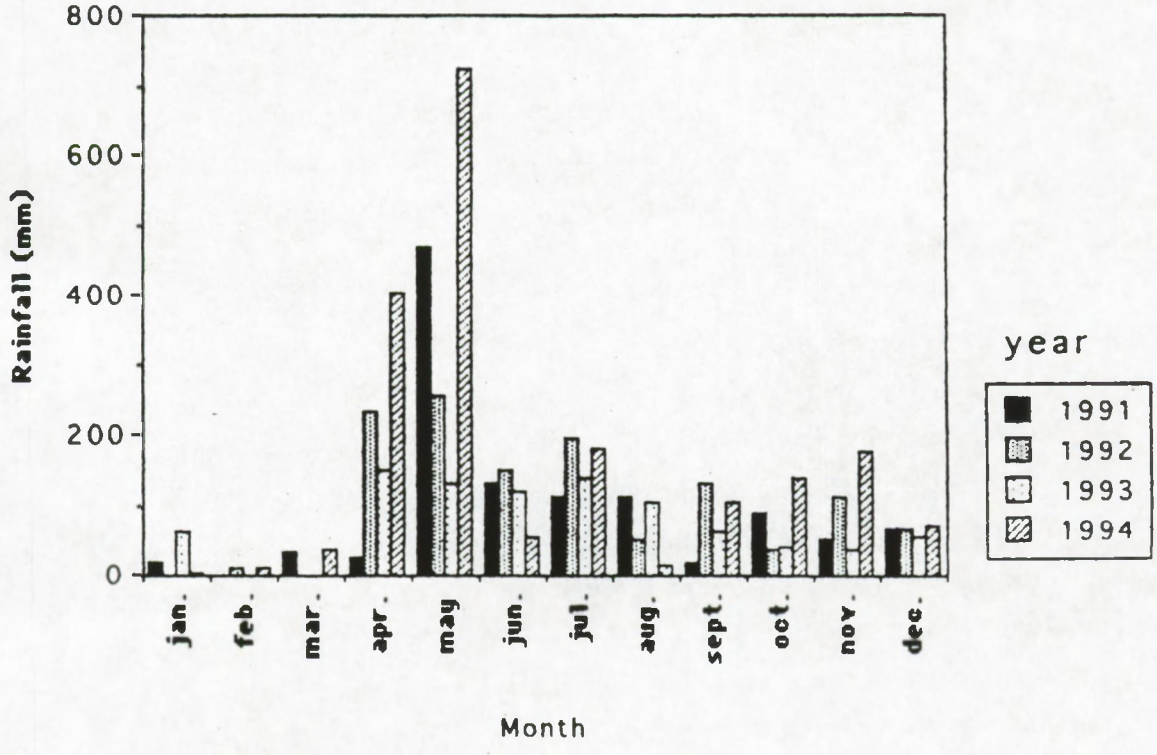


Fig. 3.6: Rainfall pattern covering the study site between 1991 and 1994. Data from Msambweni Agricultural Office.

(ii) Sample collection

Since the bay and the creeks were generally shallow (≤ 4 m depth) samples for water column determinations were taken at about 40 cm from the surface by hand in clean acid-washed polyethylene bottles. Samples for nutrients and POM determinations were immediately stored in the coolbox after collection pending transportation to the laboratory (about 2 hours drive from the study site). At the laboratory, samples for ammonium determinations were analyzed immediately on arrival while nitrate (+ nitrite) samples were deep-frozen and analyzed later (usually within the same week). Samples for POM determinations were filtered through a Whatman GF/F filters (usually about 2 liters) and the filters dried in an oven for 24 hours at 105 °C. These samples were then put in clean petri-dishes and stored in dessicators pending transportation to Vrije Universiteit, Brussels, where the organic carbon, nitrogen and $\partial^{13}C$ determinations were done.

3.1.2.2 Mangrove sediment samples

(i) Sampling sites

A study plot measuring 20 x 20 m^2 was established at each of the two selected study biotopes (*Rhizophora mucronata* and *Ceriops tagal* sediments). Depending on the experiments to be conducted, specific subplots were established within these study plots and various cores taken for different analysis.

(ii) Sample collection

All the sediment samples were collected by hand using clear perspex tubes of i.d. 3.6 cm and length ca. 30 cm. Sampling was mostly done during flood tide when the water column above the plots was about 30 cm high. The sampled tubes were then kept in a big plastic container and taken to the laboratory for processing. Within three hours of collection, these samples were sectioned into 0-1, 1-2, 2-4, 4-6, 6-8, 8-10 and 10-12 cm segments which were eventually processed depending on the analysis required.

A special observation to monitor daily fluctuation of nitrogenous nutrients, and salinity in the upper 4 cm depth of the sediments was also made during the dry (January/February) and rainy seasons (May/June) of 1993 and 1994. For these observations sediment samples (5 tubes) were collected after every other day and taken to the laboratory where they were

sectioned and the upper 4 cm depth squeezed for pore water using N_2 gas under pressure. The pore water was eventually analyzed for salinity, ammonium and nitrate (+ nitrite) concentrations. Salinity determination was done using a hand-refractometer with an error of ± 1 psu. Temperatures from the study plots were determined by a thermometer dipped into the upper 1 cm of the sediment. An average of 5 readings from different parts of the plot was used as a representative temperature of the whole plot.

3.2 Experimental protocols

3.2.1 Nutrient stocks

3.2.1.1 Analysis of nitrogenous nutrients

(a) Ammonium determination

The most common method for ammonium determination is the indophenol blue photometric determination (Koroleff, 1969). The blue colour-forming reaction, called the Berthelot reaction, was discovered more than a century ago and adapted to seawater analysis after a method was found to avoid precipitates of magnesium and calcium hydroxides at high pH. Basically, the ammonium is converted into monochloramine by hypochlorite, and after addition of phenol in alkaline conditions, the indophenol blue complex is formed. Usually nitroprusside is used as catalyst (Patton & Crouch, 1977; Lesage, 1984). Precipitation of hydroxides is hindered by metal-complexing sodium citrate.
The Berthelot reaction does not proceed rapidly enough to achieve adequate colour formation in a short time, but the final complex remains stable for over 24 hours. Therefore, samples are stored at ambient temperature for nearly one day after addition of the reagents. The absorbance is measured at a wavelength of 640 nm. A Shimadzu UV-150-02 Double Beam Spectrophotometer was used for the absorbance measurements.

(b) Nitrate determination

A comprehensive summary of different analytical procedures for the determination of nitrogenous nutrients in fresh and saline water is given by D'Elia (1983). Presently, the most widely accepted method of nitrate determination typically relies on the reduction of nitrate to nitrite by cadmium (Grasshoff, 1964), the subsequent diazotation of nitrite and the coupling of the diazocompound with N-(1-naphtyl)-ethylene diamine (Bendschneider

and Robinson, 1952) in order to produce pink coloured compound. Its absorbance is measured at a wavelength of 550 nm; calibration is usually carried out in a series of standards.

Nitrate was analyzed by an autoanalyzer system. By means of an automatic sampler, sea water (the samples) and rinse water are alternatively introduced into the system (fig. 3.7) in order to separate between the consecutive samples. A peristaltic pump, the heart of the system, maintains a continuous and constant flow of reagents and sample in the manifold. Flow rates and residence times, determined by the diameter of the tubes as well as by the length of delay and mixing coils are properly chosen for an optimal reaction. Reaction products generally constitute dyes and their detection is spectrophotometrically performed by a colorimeter with adapted flow-through cell. The automatic analytical procedures have been particularly welcomed for three reasons (D'Elia, 1983). In first instance the samples pass through the same reduction column, precluding column-to-column standardization problems. Secondly, the reproducibility of the reduction and hence the precision of the measurement is increased by an accurate control of the flow rate through the column. And finally, the automation of the nitrate (and other nutrients) determination represents a considerable relief to the scientist by reducing intensive sample handling and time involved especially when analyzing many samples. Automated procedures for nutrients determination have been revised and published by Tréguer and Le Corre (1975) and Elskens and Elskens (1989).

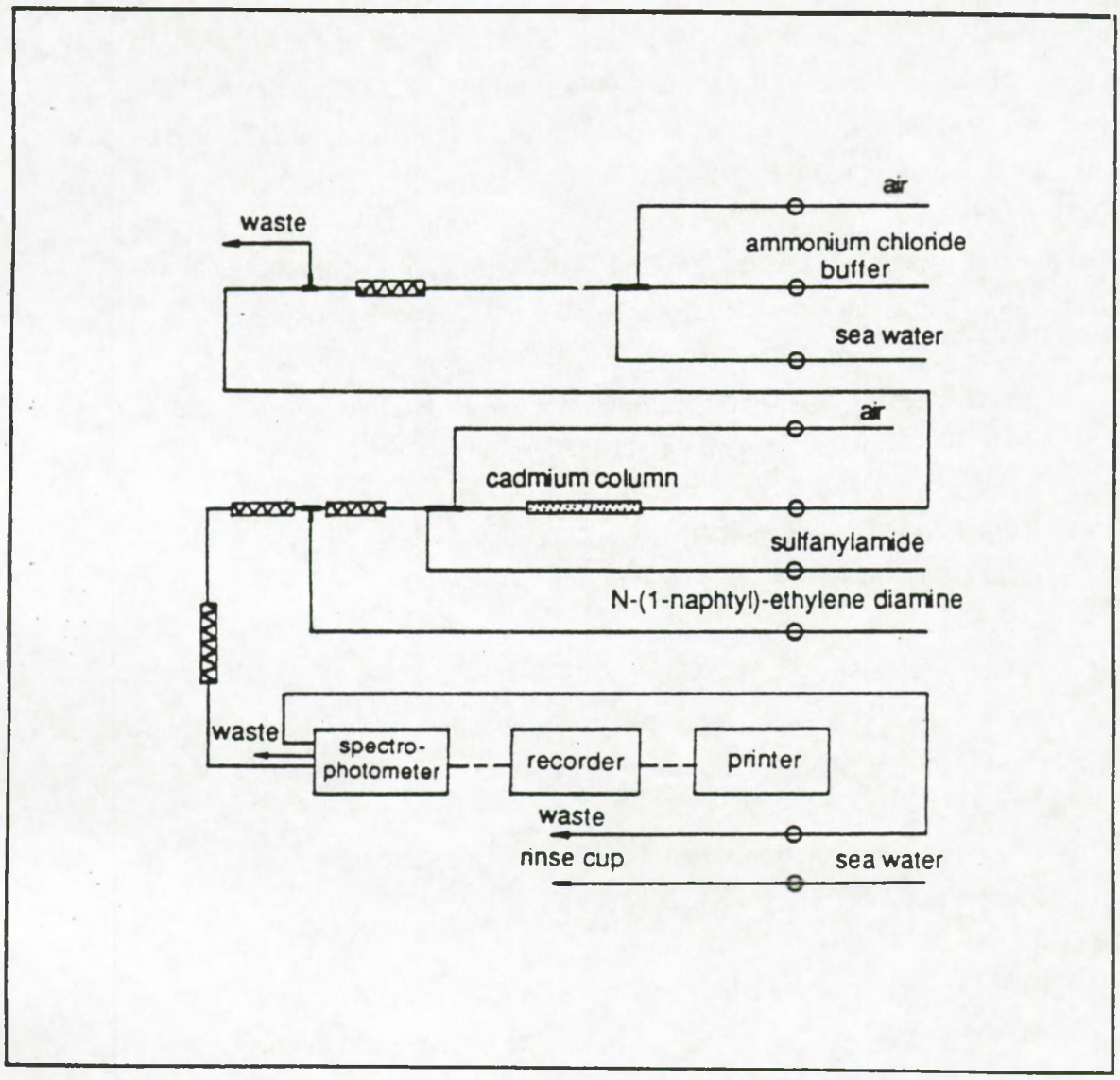


Fig. 3.7: Schematic view of the manifold for nitrate analysis, according to Trguer and Le Corre (1995).

3.2.1.2 General sample handling protocol

(I) KCl extractions

Most sediments or soils possess negative charge that holds cations dissolved in the soil solution. NH_4^+ ion being positively charged, could therefore get itself adsorbed on the surfaces of the sediment / soil particles. Potassium chloride solution is one of the most common extractants used for extracting the adsorbed NH_4^+ (Blackburn, 1979; Mackin and Aller, 1980; Iizumi et al., 1982; Hansen and Blackburn, 1991; Blackburn and Henriksen, 1993) in sediments. In order to determine total ammonium (free + ionically - bound) in Gazi mangrove sediments, we also used 1 N KCl solution and the following procedure was followed immediately the sediment core tubes arrived to the laboratory;

(i) The sediments from the perspex tubes were sectioned into 0-1, 1-2, 2-4, 4-6, 6-8, 8-10, 10-12 cm sections and weighed into serum vials.

(ii) Potassium chloride (solution) was then added to each sample at corresponding volumes (for every 10 g wet weight , 40 ml of 1 N KCl used for extraction).

(iii) All the samples in the serum vials were then flushed with N_2 gas (about 3 minutes per sample) before they were placed on a shaker table (1 hour) followed by centrifugation at 2000 x g r.p.m. for 10 minutes.

(iv) The supernatant solution was then filtered through a Whatman GF/F filter and collected into acid washed polyethylene bottles.

(v) Determination of ammonium concentration was then immediately performed by phenol-hypochlorite method (Koroleff, 1969) after the dilutions of the samples (usually 10 times dilutions). 1 cm cuvettes were used for sediment's pore water NH_4^+ determination while for the water column samples, 10 cm cuvettes were used.

(vi) A part of the collected samples were immediately deep-frozen (after removing the aliquotes for ammonium determination before dilution) for eventual nitrate+nitrite determinations.

(II) N_2 (gas) pressure extractions

Interstitial water from some samples was also obtained using a special cylindrical aluminium device. Sectioned segments from corresponding depths were put into this devise and nitrogen gas pressure applied at one end. The pore water filtered through a Whatman GF/F filter fitted at the other end of the aluminium device and was collected into acid washed polyethylene bottles. These samples were used for salinity determinations and occasionally (depending on the experiment) also for DIN determination.

3.2.2 Determination of the physico-chemical parameters

3.2.2.1 Density and porosity

An average of 5 perspex tubes was used (collected randomly from the study plot) each time density and porosity of the sediment was to be determined. The sediment tubes were sectioned as outlined in section 3.2.1.1. The corresponding segments were then pooled together and mixed thoroughly. The mixed slurries were eventually put into small 10 ml beakers (to the 10 ml mark), weighed and left in an oven at 105 °C for 24 hours (or till constant weight). Porosity was then calculated from the loss of water content in a known volume of sediment. Density was calculated as the wet weight of the sediment in a known volume.

3.2.2.2 Salinity determinations

The sediment's pore water was used for salinity determinations. Because of the small quantities of pore water obtained from these sediments an Atago hand-held refractometer (with an error of ± 1 ppt) was used for this determination. Salinity determination on water column samples was done using the Knudsen titration method where the chlorinity of the water sample is titrated against standard silver nitrate solution (Strickland and Parsons, 1968).

3.2.2.3 Redox potential determination

Redox potential determination was done using a platinum electrode with a calomel electrode as the reference cell. Zobell solution (0.0987g potassium ferricyanide + 0.0127g potassium ferrocyanide - in 100ml of 0.1 N KCl) was used for calibration. The platinum electrode was specifically designed to be able to penetrate the sediment with less force.

3.2.3 Organic matter determination

3.2.3.1 Loss on Ignition (LOI) organic matter content

Organic content was determined as the Ignition loss of dried sediment after 24 hours at 450 °C. In most cases the sediments used for porosity determination were the same used for LOI determination. After grinding the dry sediments thoroughly about 10 g was then weighed for this determination. Loss in weight at 450 °C was calculated to reflect the LOI organic matter content.

3.2.3.2 Determination of organic carbon and organic nitrogen content

Total organic carbon (TOC) and organic nitrogen (TON) were analyzed after preliminary carbonate elimination with HCl and conversion of the bound C and N into carbon dioxide and molecular nitrogen. Preliminary tests were initially done to determine the right weight of the dried sediment sample which could give enough molecular nitrogen for detection. Eventually about 10 and 50 mg of dried sediment of *Rhizophora* and *Ceriops* sediments respectively were used for organic carbon and nitrogen determinations. These samples were weighed into small silver cups after which the cups were placed on a hot plate at a temperature of ca. 100 °C. Small drops of HCl were then added, few at a time, to eliminate the carbonates. After this the samples were folded and transferred to a Carlo Erba NA-1500 CN analyzer. In this analyzer, the samples are completely combusted with excess oxygen in a quartz reactor, filled with chromium (III) oxide and heated to 1010 °C. On the bottom of this reactor, we have cobalt-oxide coated with silver to retain sulpher oxides and halogen compounds produced. The main reaction products of the oxidative combustion are carbon dioxide and molecular nitrogen together with H_2O and nitrogen oxides. In a second reactor the excess oxygen and the nitrogen oxides (N_xO_y) in the gas mixture are reduced on metallic copper. Final water is trapped by anhydrone. Only dinitrogen, carbon dioxide and

carrier gas (He) are swept into the detection system. Carbon dioxide and nitrogen are seperated by means of a gas chromatographic column (Porapak QS) and measured by thermal conductivity detection.

A calibration was carried out with an organic standard: Acetanilide (71.09 % C, 10.36 % N). The relative error for 10 replicate measurements of this standard is ≤ 2 %.

Determinations for particulate organic carbon and nitrogen on POM samples from the water column were also done using the Carlo Erba NA-1500 CN analyzer. However, after elimination of carbonates using HCl vapour (held under vacuum) in a dessicator, small filters were cut from the filters obtained in the field and put in tin cups and transferred to the analyzer for carbon and nitrogen measurements.

For stable carbon isotope ratio measurements the Carlo Erba NA-1500 Element analyzer was placed in line with a Finnigan Mat delta E isotope ratio mass spectrometer interfaced with a Finnigan Mat trapping box CT-NT. Carbon-13 abundancy was expressed in ∂ units where;

$$\partial^{13}C \text{ ‰} = \left\{ \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right\} \times 1000$$

UGS-24 (graphite) was used as the working standard. Final results were expressed against the Pee Dee Belemnite (PDB) carbonate reference. Ten measurements on same sample gave a standard deviation of 0.04 ‰ while several aliquotes of te same sample gave a standard deviation of < 0.2 ‰.

3.2.4 Transformational processes

3.2.4.1 Regeneration and assimilation studies using the nitrogen-15 isotope dilution techniques.

The present knowledge about regeneration and assimilation of nitrogen compounds is based largely on recent studies using isotope tracer techniques. The increasing number of scientists from different disciplines currently involved in the ^{15}N methodology, and the large number of literature references (Faust, 1981; Harrison, 1983) is evidence for the actual interest for stable isotope techniques (Goeyens, 1993). Though a number of radio isotopes (e.g. ^{13}N) have been used, stable ^{15}N isotope remains the most widely used tracer (Harrison, 1983).

The stable isotopes, ^{14}N and ^{15}N, have a relative abundance of 99.635 % and 0.365 % respectively, in natural conditions. Any departure of this natural abundance, mostly by increasing the concentration of the rare isotope, labels this element as well as its compounds, which are called tracers. In addition to the definition of ^{15}N abundance, the definition of ^{15}N atom percent excess is used to indicate the ^{15}N enrichment in comparison with its natural abundance.

General principles - Labelling reagents of reaction products of any process in the nitrogen cycle can prove advantageous in the study of this particular process. The introduction and use of the stable isotope ^{15}N (Dugdale and Dugdale, 1965; Dugdale and Goering, 1967) was very significant for our present knowledge about utilisation and recycling of nitrogen compounds in aquatic ecosystems.

A general experimental design for studies dealing with the assimilation of dissolved nitrogen by marine phytoplankton consists of: (1) confinement of the sea water sample, usually in a glass or polycarbonate bottle, (2) inoculation with the labelled nutrient, (3) incubation, (4) collection of the particulate organic material, normally by filtration and (5) measurement of the incorporated label (Dugdale and Goering, 1967). In regeneration studies a variation of this protocol is employed with one additional step added: (6) the isolation of ammonium from its sea water matrix in order to determine its isotopic dilution. The decrease of the relative abundance of the tracer, or the isotopic dilution, is used to determine the production rate of unlabelled substrate during remineralization process (Blackburn, 1979; Caperon et al., 1979; Glibert et al., 1982-b).

In studies of regeneration and assimilation processes in sediments , the experimental design commonly used is;

(i) Confinement of a sediment slurry usually in a serum vial

(ii) Inoculation with a labelled nitrogen compound (e.g. $^{15}NH_4Cl$)

(iii) Incubation

(iv) Collection of final ammonium pool after incubation (usually by extraction using 1N KCl)

(v) Isolation of the labelled NH_4^+ from its sea water matrix for isotopic determination (This is usually done by microdiffusion technique (Blackburn, 1979; Kazungu and Goeyens, 1989) discussed later in this section.

(vi) Measurement of isotopic tracer incorporation of the sample. This is usually done by either isotope ratio mass or emission spectrometry.

After the sample isolation, its isotopic analysis generally follows two steps:

1. Conversion of the bound Nitrogen: - **N** - —> N_2 (gas)

2. Optical measurement of ^{15}N: usually by emission spectrometer

Conversion of the bound Nitrogen — For the emission spectrophotometric determinations of the ^{15}N abundance, conversion of all nitrogen atoms present in the sample into dinitrogen gas is commonly effected by use of various combustion techniques. Although adapted methods are available for the conversion of a restricted category of nitrogen containing compounds into dinitrogen (Faust, 1976), three main techniques, originally developed for the conversion of particulate material, are commonly used (Fiedler and Proksch, 1975; Harrison, 1983). These methods are:

1) $$\mathbf{PON} \xrightarrow{\text{Kjeldahl}} \mathbf{NH_4^+} \xrightarrow{\text{Rittenberg}} \mathbf{N_2}$$

(Kjeldahl - Rittenberg method)

2) $$PON \xrightarrow[CaO\ (>500\ ^{\circ}C)]{Cu/CuO} N_2$$

(Dumas combustion method)

3) $$PON \xrightarrow{Kjeldahl} NH_4^+ \xrightarrow{CuO} N_2$$

(Modified Dumas method)

The Kjeldahl - Rittenberg method combines a Kjeldahl digestion, to transform the particulate nitrogen into ammonium, with the subsequent liberation of dinitrogen by oxidation of ammonium with sodium hypobromite:

$$2\ NH_4^+ + 2\ OH^- + 3\ BrO^- \rightarrow N_2 + 3\ Br^- + 5\ H_2O$$

The second method is less laborious. It involves a dry combustion of the particulate nitrogen with CuO to oxidize the bound nitrogen into nitrogen gas:

$$2\ NH_4Cl + 4\ CuO \rightarrow N_2 + 2\ CuCl + 2\ Cu + 4\ H2O$$

However, incomplete combustion was sometimes experienced with this method (McCarthy, 1980) hence the eventual development of a method combining the first two methods resulting in the modified Dumas method. In the so called modified Dumas method the nitrogen compound is first transformed into ammonium by the classical Kjeldahl technique and subsequently oxidized to molecular nitrogen by the Dumas combustion.

For our ^{15}N dilution experiments, the extracted ammonium (extracted and trapped by using a microdiffusion technique described in section 3.2.4.1.1) was converted into dinitrogen by means of oxidation with CuO. The conversion was performed in small quartz discharge tubes at a temperature of 750 °C. In order to eliminate atmospheric nitrogen (the main source of contamination in the preparation phase), the tubes were evacuated to pressures $< 10^{-3}$ Torr with a vacuum system, consisting of an oil rotation (Balzer DUO 400-B) and oil diffusion pump (DAIA model DPF-2Z). Interfering gases as carbon dioxide and water were absorbed into calcium oxide brickets.

The optical measurement of ^{15}N — The determination of the ^{15}N concentration (%) by emission spectrometry is based on an isotope shift (Kumazawa, 1973; Fiedler and Proksch, 1975; Müller, 1976): the masses of the nitrogen molecules affect the wavelength of light emission, in this case in the ultraviolet region. When excited by an external energy source, the dinitrogen molecules in the discharge tubes incorporate energy by: (1) raising one or more electrons to a higher energy state, (2) by increased vibration of the atoms along the internuclear axis, and (3) by increased rotation of the molecules. Each electronic energy level is therefore seperated in definite vibrational sublevels and each of them in discrete rotational sublevels. When electrons transit from a high energy level to a low energy level light is emitted with an energy content equal to the sum of the changes in electronic, vibrational and rotational energy:

$$E = E^e + E^v + E^r, \text{ and } \Delta E = h\nu$$

Isotope effects occur in dinitrogen molecules, since the mass differences between isotopic molecules affect the vibrational and rotational energy, and therefore the corresponding wavelength of the emitted light. A wavelength shift is induced according to the difference in quantum number. As the effect of the rotational energy levels are minor in comparison with the vibrational ones the isotope effect is approximately proportional to the difference in vibrational quantum numbers (Kumazawa, 1973; Müller, 1976).

Practically, out of a large number of emission band spectra obtained when the N_2 molecules are excited, the best compromise between emission intensity and wavelength resolution is a measurement at wavelengths of 297.7, 298.3 and 298.9 nm for $^{14}N\ ^{14}N$, $^{14}N\ ^{15}N$ and $^{15}N\ ^{15}N$ respectively. The instrument used is a JASCO Model NIA-1 N-15 Analyzer, with a high energy source (a high frequency oscillator) of 13.56 MHz, 30 W output.

The ^{15}N percentage is deduced from the emission intensities at two of the three wavelengths by means of formulas common in mass spectrometric analysis, and these emission spectrometric readings are corrected to real ^{15}N percentages by standardization (Goeyens et al., 1985).

The ^{15}N concentration, as a percentage, equals per definition 100 times the ratio of the total number of ^{15}N isotopes to the total number of nitrogen atoms:

$$\% \ ^{15}N = \frac{\textbf{all } ^{15}\textbf{N atoms}}{\textbf{sum of all N atoms}} \times 100$$

This can be rewritten as:

$$\% \ ^{15}N = \frac{\frac{1}{2}\left[^{15}N\ ^{14}N\right] + \left[^{15}N_2\right]}{\left[^{15}N_2\right] + \left[^{14}N\ ^{15}N\right] + \left[^{14}N_2\right]} \times 100$$

Assuming that the binding probability is the same for each isotope the reaction between them can be expressed by the equation:

$$2\ ^{14}N^{15}N <\!\!-\!\!> {}^{14}N_2 + {}^{15}N_2$$

The equilibrium constant, Keq, is determined following the general rule of the law of mass action:

$$K_{eq} = \frac{\left[^{14}N\ ^{15}N\right]^2}{\left[^{14}N_2\right]\left[^{15}N_2\right]} = 4$$

With the definition of the atom % ^{15}N at one hand and the equilibrium constant at the other it is possible to express the ^{15}N concentration as a function of the concentrations in $^{14}N\ ^{14}N$ and $^{14}N\ ^{15}N$ or as a function of the concentrations in $^{15}N\ ^{15}N$ and $^{14}N\ ^{15}N$:

$$\% \ ^{15}N = \frac{100}{2R + 1} \quad \textbf{(i)}, \text{ and}$$

$$\% \ ^{15}N = \frac{100}{R' + 1} \quad \textbf{(ii)}, \text{ with}$$

$$R = \frac{\left(^{14}N\ ^{14}N\right)}{\left(^{14}N\ ^{15}N\right)} \quad \text{and} \quad R' = \frac{1}{2}\frac{\left(^{14}N\ ^{15}N\right)}{\left(^{15}N\ ^{15}N\right)} \quad \text{respectively.}$$

By this approach a determination can be carried out by measuring the emission intensity of only two molecule types instead of three. It must be stressed, however, that the calculated percentages are corrected by a calibration against certified standards (Goeyens et al., 1985). It is difficult to evaluate the ^{15}N abundance directly from the peak intensities, because in actual spectra there is a little interaction among the respective emissions: slight overlapping between the emission peaks can induce erratic values and generally it is most practical to compare empirical data with the ones of certified standards. The coefficient of variation for ^{15}N abundance measurements with standards or with laboratory prepared discharge tubes amounted to ≤ 3.5 % (Goeyens et al., 1985).

As in many applications lower enrichments in ^{15}N (between natural abundance and 10 % ^{15}N) are usually used in these studies.

3.2.4.1.1 Optimization of the microdiffusion technique for isolation of NH_4^+ from sea water matrix for isotope analysis

As seen from the previous section, one of the steps within the overall experimental protocol of ^{15}N isotope dilution studies is isolation of labelled compound $^{15}NH_4^+$ from the sea water matrix for isotopic determination. This has been one of the most common problems in isotope studies. In the Kjeldahl-Rittenberg conversion method, the NH_4^+ is steam-distilled and converted to N_2 gas by reaction with sodium hypobromide (Harrison, 1983; Caperon et al., 1979). While this remains a common procedure, Blackburn (1979) used a diffusion process to isolate the NH_4^+ ions. With addition of a strong base to a sample (in a diffusion vial) the NH_4^+ ion was transformed into ammonia gas and diffused onto a glass capillary tube coated with a thin layer of sulphuric acid (Blackburn, 1979). Blackburn left the diffusion process to take place overnight before performing isotope analysis on the trapped ammonia. In order to optimize this microdiffusion process, the time factor for the diffusion process and possibilities of isotope discrimination during diffusion were investigated.

Experimental design

Using unlabelled and labelled ammonium sulphate (97.5 % ^{15}N), a solution of 4.0 mmol $N\text{-}NH_4\ l^{-1}$ with 10 % ^{15}N was prepared. 10 ml of this solution was then put into a 100 ml diffusion vial (fig. 3.9) and 0.5 ml of 50 % KOH solution was added and the vial stoppered immediately. The stopper had a long syringe needle which passed through a plastic holder holding a small tin cup with about 0.1 g Al_2O_3 and 10 μl sulphuric acid

(0.25 N). The OH^- transforms the NH_4^+ to NH_3 gas which diffuses into sulphuric acid coated on the aluminium oxide.

Six diffusion vials were used. After 3, 6, 12, 30, 48 and 72 hours the tin cups were removed (carefully to prevent contamination), closed and folded ready for the ^{15}N analysis. For the ^{15}N isotope analysis, the Dumas combustion method was used (Harrison, 1983; Goeyens et al., 1985). The samples were put into thin pre-conditioned (pre-conditioned by being left in an oven at 750 °C for 8 hours) glass tubes. Copper oxide (approx. 1.50 g) and calcium oxide (approx. 1.50 g) were put into the tubes (fig. 3.10). The long ends of the tubes were then sealed with a hot flame. The open short ends were then connected to a vacuum system (Edwards Dirani -14 vacuum pump) for air evacuation while heating the calcium oxide. The tubes were evacuated to pressures $< 10^{-3}$ Torr before sealing the open end making the sample ready for the ^{15}N determinations.

The isotope measurements were performed using the JASCO NIA-1 ^{15}N analyzer. Correct % ^{15}N values were then obtained by getting the corresponding % ^{15}N values from a standard calibration graph with certified ^{15}N standards (Goeyens et al., 1985). To check on reproducibility, the experiments were done in triplicate.

Since we started with a labelled ammonium solution which had 10 % ^{15}N, addition of a strong base (OH^-) would have generated ammonia whose ^{15}N percentage is 10. From fig. 3.11 the maximum ^{15}N recovered is shown to be 9.75 ± 0.06 % ^{15}N. This confirms that the diffusion process for isolating NH_4^+ ion is very effective since approximately 97.5 % of the original labelled nitrogen used is recovered.

These results also indicate that isotope discrimination takes place during the diffusion process. Since % ^{15}N measurements are governed by monitoring the ^{15}N / (^{14}N + ^{15}N) isotope ratio (Caperon et al., 1979) the relatively low % ^{15}N values obtained initially (i.e. 3, 6, 12 and 30 hrs.) mean that more ^{14}N was being diffused. This could be attributed to the mass difference of the two nitrogen isotopes. ^{14}N being lighter, is released more easily. In this case, in order to be sure of complete diffusion, a time factor is essential. From the results obtained, 48 hrs is suggested as the minimum time to be allowed for the microdiffusion process before the samples are transfered for optical measurements.

$Pa\,Aa + Pb\,Ab = Pm\,Am$ $\quad Am = \frac{Pa\,Aa + Pb\,Ab}{Pm}$

Am calculated
Am measured } identical

Mean Recovery is 36
100 % !

see discussion pages 122 and onwards

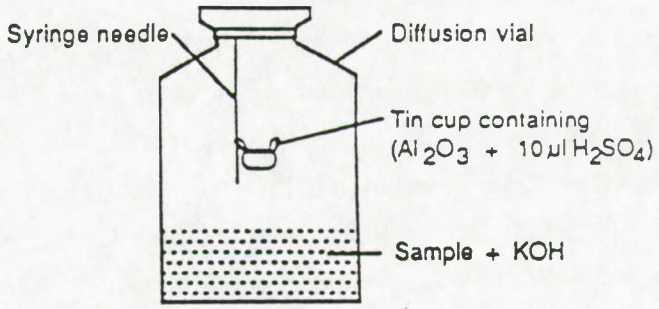


Fig. 3.9: Diffusion vial used for trapping of labeled ammonia.

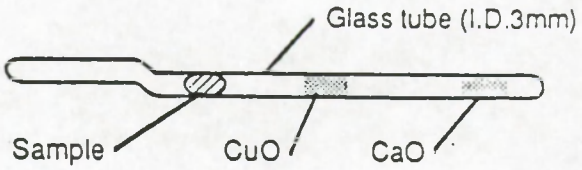


Fig. 3.10: Arrangement of sample, copper oxide, and calcium oxide in the glass tubes used for N - 15 measurements.

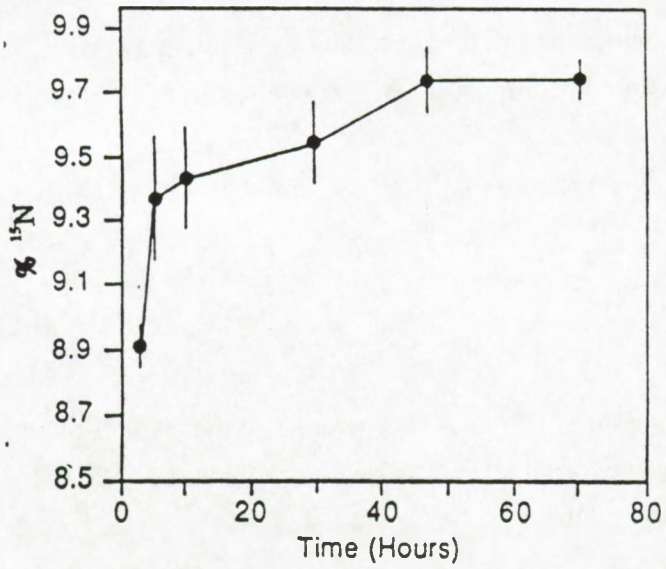


Fig. 3.11: Graph showing the efficiency of the microdiffusion trapping of labeled ammonia.

3.2.4.1.2 Calculations of regeneration and assimilation rates

Mathematical formulas for the calculation of regeneration and assimilation rates have been developed and reviewed by many scientists (Blackburn, 1979; Caperon et al., 1979; Bowden, 1984). In principle, in this isotope dilution technique, the rate of ammonium regeneration and uptake is determined by labelling the product, i.e. ammonium. The ^{15}N - labelled compound is initially added to the water sample (or sediment sample) and the dilution of the atom % ^{15}N with regenerated ammonium of only the natural background ^{15}N abundance (0.366 %) is monitored with time. By determining the initial and final ammonium concentration and atom % ^{15}N of the ammonium pool, the rate of dilution of ammonium pool (ammonium regeneration) and uptake rates of ammonium can be calculated.

In this study on regeneration and assimilation in mangrove sediment we used mathematical formulas developed by Blackburn, 1979. In Blackburn's equations, the following arguments are used;

The pool of NH_4^+, P(t), in the experiment changes through time due to a constant production rate, d, and a constant utilization (incorporation) rate, i, thus;

and $\mathbf{P(t) = P_0 + (d - i)\ t}$ ..... (1)

where $\mathbf{P_0}$ is the initial concentration.

The objective is to calculate d and i in the perturbed experimental system where P_0 changes and where the nitrogen isotope composition of the labelled NH_4^+ pool is altered.

Then,

let ^{15}N and ^{14}N be the concentrations of ^{15}N - NH_4^+ and ^{14}N - NH_4^+, respectively, and let

$$\mathbf{R = \frac{(^{14}N\ ^{14}N)}{(^{14}N\ ^{15}N)}} \quad \text{..... (2)}$$

describe the relative abundance of ^{15}N - NH_4^+, which is a measurable quantity.

Furthermore, let ^{15}n be the naturally occuring relative abundance of ^{15}N ($^{15}n = 0.0037$) and let R_0 be the initial value in a labeling experiment.

Equation (1) for the change in the pool size may be separated into two equations for the changes in ^{15}N and ^{14}N pools. As the produced NH_4^+ has the natural ^{15}N abundance and as the incorporation removes NH_4^+ within the ^{15}N abundance of the labeled pool, then

$$\frac{d\,^{15}N}{dt} = d\,^{15}n - iR \qquad \text{..... (3a)}$$

$$\frac{d\,^{14}N}{dt} = d\left(1 - {}^{15}n\right) - i\left(1 - R\right) \qquad \text{..... (3b)}$$

From equation 2 and 3, we get after simplification, an equation for the change in the relative ^{15}N abundance

$$\frac{dR}{dt} = \frac{\left({}^{15}n - R\right)}{P} d \qquad \text{..... (4)}$$

This may be integrated by using the expression (1) for P and the solution may be written as:

$$\ln\left(R - {}^{15}n\right) = \ln\left(R_0 - {}^{15}n\right) - \left(\frac{d}{dt}\right) \ln\left[\frac{(d - i)\,t + P_0}{P_0}\right] \qquad \text{..... (5)}$$

Rearranging the equation further we have;

$$\frac{d}{d - i} = \frac{\ln\left(R_0 - {}^{15}n\right) - \ln\left(R - {}^{15}n\right)}{\ln\left[\frac{(d - i)\,t + P_0}{P_0}\right]} \qquad \text{..... (6)}$$

Now since we know that $d - i = (P(t) - P_0) / t$ from equation (1) the equation can be simplified to;

$$\frac{d}{d - i} = \frac{\ln \frac{R_0 - {}^{15}n}{R - {}^{15}n}}{\ln \frac{P_{(t)}}{P_0}}$$

or to;

$$\frac{d}{d-i} = \frac{\ln \frac{A_i}{A_f}}{\ln \frac{P_f}{P_i}} \qquad \text{..... (7)}$$

where $A_i = R_o - {}^{15}n$ = excess % ^{15}N initial

$A_f = R - {}^{15}n$ = excess % ^{15}N final

$P_f = P(t)$ = final NH_4^+ pool concentration

$P_i = P_0$ = initial NH_4^+ pool concentration

Equation (7) can be rearranged and we have:

$$d = \left(\frac{P_f - P_i}{t}\right) \cdot \left(\frac{\ln \frac{A_i}{A_f}}{\ln \frac{P_f}{P_i}}\right) \qquad \text{..... (8)}$$

$$i = d - \left(\frac{P_f - P_i}{t}\right) \qquad \text{..... (9)}$$

From these equations, if we know the ammonium pool concentration initially (Pi) and finally (Pt) after incubation time t and we also know the excess % ^{15}N atom for the initial pool (A_i, immediately after spiking) and of the excess % ^{15}N atom for the final pool (A_f), then regeneration and assimilation rates can easily be calculated.

In this study, the ammonium pools were determined by the Indo-phenol method (Korolef, 1969) while the % ^{15}N atom measurements were made as explained earlier.

In principle, the initial % ^{15}N atom can be calculated from the following dilution equation;

$$P_a A_a + P_b A_b = P_m A_m$$

in which P_a and P_b are the nitrogen pools (or quantities) of the ^{15}N labelled compounds **a** and **b** respectively, A_a and A_b the corresponding ^{15}N abundances, P_m is the amount of the mixture ($P_m = P_a + P_b$) and A_m its corresponding ^{15}N abundance. However, in our case, actual measurements were made to determine the initial % ^{15}N.

3.2.4.2 Determination of nitrification rates

Two methods were used for the investigation of nitrification process in Gazi mangrove sediments. Potential nitrification method was used to compare the potential abilities of the *Rhizophora* and *Ceriops* sediments to nitrify ammonium if excess ammonium and oxygen were supplied. Differences in potential nitrification in the two sediment types reflected differences in numbers (or activity) of nitrifying bacteria (Henriksen et al., 1981; Henriksen et al., 1993).

The actual nitrification process was also investigated to give the in situ nitrification processes existing in the sediments. The methods applied are described below.

(a) Potential nitrification

Potential nitrification rates in sediments were assessed using the technique described by Henriksen et al. (1981) and Caffrey and Kemp (1990). The sediment samples for this determination were sectioned into the following 7 depth intervals: 0-1, 1-2, 2-4, 4-6, 6-8, 8-10 and 10-12 cm. A number of cores (between 5 and 10 collected randomly from the plots) were used and corresponding segments pooled together and mixed thoroughly. Duplicate samples (2 g wet weight) from the different depths were then incubated (in serum vials) on a shaker table in 50 ml of filtered sea water (from the water overlying the sediment station) for 24 hrs under aerobic conditions at ca. 25 °C. The sea water used was enriched with NH_4Cl (0.5 mmol l^{-1}) and KH_2PO_4 (0.1 mmol l^{-1}). Incubations of these samples were done in the dark and at t = 2 hrs. and t = 26 hrs., replicate samples were centrifuged (2000 x g r.p.m. for 10 min.) and the water filtered (Whatman GF/F filters) and analyzed for NO_3^- + NO_2^-. Potential nitrification rates of the different depths were then calculated from the accumulation of NO_3^- + NO_2^- determined according to the previously explained analytical procedure.

(b) Actual nitrification

Actual nitrification was performed using the procedure described by Hall, 1984, with minor variation of the volumes of the nitrification inhibitor compound - allylthiourea (ATU), used. A prior experiment was conducted to find out exact concentration of ATU effective for stopping the nitrification process. ATU of different volumes was added to sets of samples prepared for potential nitrification process (as described above using only the 0-1 cm sediment) and the concentrations of ATU required to stop this process was determined.

A stock solution of ATU (5 g/l) was prepared and different volumes were used. The ATU volumes were added to the samples (2 g wet sediment + 50 ml of filtered sea water spiked with the NH_4Cl and KH_2PO_4) to have final concentrations of 1, 3, 5, 7 and 9 mg/l. After this initial experiment, the effective ATU concentration was found to lie between 5 and 8 mg/l. Eventually other experiments were done focusing on final ATU concentrations of 4 to 8 mg/l. Table 3.5 gives a summary of the results obtained while figure 3.12 gives the overall results observed. From figure 3.12 it is seen that the final concentration of 7 mg/l of ATU was the most effective in blocking the nitrification process.

Experimental protocol for actual nitrification process

1. The sediment samples were collected with perspex cores (i.d. 3.6 cm, height 18 cm) and adjusted to about 5 cm depth. These cores had silicone filled ports at 1 cm intervals at the sides. In each experiment, 8 cores were used with four of these being controls. (The 5 cm depth was found to be a desirable depth since an earlier experiment on potential nitrification rates in *Rhizophora* sediments indicated possible active nitrification process upto 4 cm depth).
2. At the laboratory, the overlying water was removed and replaced with 40 ml of filtered sea water, from the sampling locality.
3. To half of the cores (usually about 4 cores) each cm of the sediment was injected with 12 μl of the stock ATU (5 g/l). To insure maximum distribution of the inhibitor within the 1 cm segment each port was injected with 6 μl of the inhibitor diagonally (upwards and down). Since the water volume in each cm in *Rhizophora* sediment was about 8 ml (average weight of each cm segment was about 12 g with water content being averagely 65 %), these additions insure a final ATU concentration of about 7 mg/l in the interstitial water in the sediment.

4. For *Ceriops* sediments the average volume of the interstitial water was about 4 ml per cm segment and so we used 6 μl of the stock ATU (5 g/l) for each cm segment.
5. The overlying water was also spiked with 60 μl of ATU to bring the final concentration to about 7 mg/l. This overlying water was also continuously gently stirred with a small magnetic stirrer to maintain oxygen gradients.
6. After 24 hrs, these cores were sectioned into 0-1, 1-2, 2-3 and 3-4 and each sediment extracted with 60 ml of 1 N KCl.
7. A similar exercise was done with the control cores except - instead of using ATU, distilled water was used.
8. After the experiment the overlying water was also filtered and determined for NH_4^+ concentration.
9. Nitrification rate was then calculated as the difference in ammonium concentrations between inhibited and uninhibited cores.

Table 3.5: A table showing four experiments done on different times to determine the concentration of Allythiourea effective to block nitrification in *Rhizophora* sediments. The rates are in μg - at N / l /day.

ATU (mg/l)	Exp. 1 $\Delta(NO^{-3} + NO^{-2})$	Exp. 2 $\Delta(NO^{-3} + NO^{-2})$	Exp. 3 $\Delta(NO^{-3} + NO^{-2})$	Exp. 4 $\Delta(NO^{-3} + NO^{-2})$	Average $\Delta(NO^{-3} + NO^{-2})$
0	119.63 ± 10.88	127.14 ± 33.09	128.17 ± 7.69	108.37 ± 14.20	120.83 ± 16.80
1	114.38 ± 14.98	129.01 ± 18.60	117.18 ± 45.00	119.68 ± 11.68	120.06 ± 20.61
2	-	-	-	-	-
3	87.89 ± 9.12	87.32 ± 5.69	-	-	86.61 ± 6.21
4	-	-	30.76 ± 12.82	44.04 ± 8.70	37.40 ± 11.78
5	14.15 ± 7.38	7.93 ± 4.22	10.79 ± 7.63	23.87 ± 5.67	12.29 ± 8.80
6	-	-	5.28 ± 1.29	1.58 ± 0.58	3.43 ± 2.29
7	0.63 ± 0.36	0.28 ± 0.21	1.27 ± 1.19	0.37 ± 0.11	0.64 ± 0.63
8	-	-	0	0.35 ± 0.04	0.18 ± 0.21
9	0	0	0	0	0

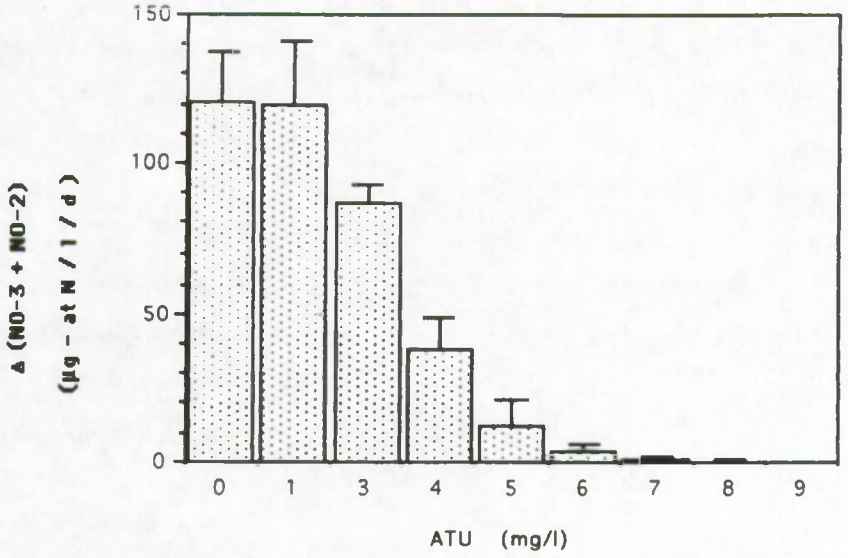


Fig. 3.12: A bar graph displaying effective ATU concentration required to block potential nitrification in Rhizophora sediments.

3.2.4.3 Determination of epibenthic fluxes

The sediment - water nutrient fluxes were investigated using two methods;

1. Plexiglass incubation chambers
2. Intact core incubations

The experimental design for the two methods was as described below.

3.2.4.3.1 Sediment - water fluxes using plexiglass chambers

Cylindrical plexiglass chambers of diameter 30 cm and height 30 cm were constructed for the sediment - water interface flux studies. These chambers were also fitted with a thermometer, a sampling port and a stirrer whose speed could be controlled by a small motor . At the field these chambers were forced into the sediment gently with the top cover removed. These experiments were usually done at the beginning of flood tides when the water column above the study plot was about 40 cm high. Once the jars were secure, the

top lid would be returned and the water left for about 30 minutes to equilibrate. The first sample was therefore taken after 30 minutes and thereafter samples were taken at 1 hour intervals. However, due to the short residence time for the water at the *Ceriops* plot at high tide, samples at this plot were taken after every 45 minutes (sometimes less).

A 50 ml syringe was used for collecting the samples through the sampling ports. The proper stirring speed had been obtained by prior experiments in the laboratory by monitoring the mixing of drops of ink put into the jar chambers filled with water.

3.2.4.3.2 Intact core incubations

Intact core (i.d. 3.6 cm, length 30 cm) incubation for the investigation of sediment - water interface fluxes were done using a technique similar to that described by Henriksen et al. (1981). The NH_4^+ and NO_3^- fluxes between sediment and water column were measured in short term incubations (4 to 6 h) in undisturbed sediment cores (3.6 cm i.d.). In each case, about 12 cm of sediment depth was used. In the laboratory, the overlying water in each core was replaced by 80 ml of filtered sea water collected from the respective sampling plots. During incubation this water was aerated by continuous bubbling with clean air (which had been passed through sulphuric acid). At each time, about five sediment cores were used with an additional two empty cores, which were filled with the same filtered sea water and used as control. The increase (or decrease) of NH_4^+ and NO_3^- over incubation time was used to reflect the flux rates.

CHAPTER 4

4.0 DISSOLVED INORGANIC NITROGEN (NH_4^+, NO_3^-+NO_2^-) IN THE WATER COLUMN AND SEDIMENTS OF GAZI MANGROVE BAY:CONCENTRATIONS, STOCKS AND FLUXES

4.1 RESULTS AND DISCUSSION

4.1.1 Dissolved inorganic nitrogen (DIN) concentrations in the water column of Gazi bay

A detailed description of the study stations is given in chapter 3. Figures 3b and 3c display some of these stations whose DIN results are discussed in this chapter. Seasonal observations of the discharge rates of river Kidogoweni indicated that this river could play a significant role in the supply of dissolved inorganic nitrogen into Gazi bay. Station K1 which was established at the extreme end of the mangrove vegetation close to the entrance of river Kidogoweni was therefore ment for detailed investigation on discharge rates and supply of riverine nutrients into the bay while st. G1 (next to the open sea) was used to monitor the fluctuations of DIN into and out of the bay.

Tables 4.10 and 4.11 below give results of the average concentration of NH_4^+ and NO_3^- + NO_2^- observed at the two stations at high and low tides of the dry and rainy seasons respectively. Discharge rates of river Kidogoweni were found to be averagely (0.02 ± 0.01) x 10^5 m^3 and (2.02 ± 1.76) x 10^5 m^3 per day (table 4.12) during dry and rainy seasons respectively (Kitheka et al., 1995). The high standard deviations noticed are mainly due to the day to day rainfall pattern observed within the season since the riverine discharge is highly rainfall dependant. At the observed discharge rates this riverine water would supply an average DIN contribution of (1.6 ± 1.3) x 10^3 mmol N-NH_4^+ and (8.0 ± 5.7) x 10^3 mmol N - NO_3^- per day during dry season while in rainy season when the river discharge rate is relatively higher, this riverine contribution would be (1.1 ± 1.1) x 10^6 mmol N - NH_4^+ and (1.0 ± 1.0) x 10^6 mmol N - NO_3^- per day (table 4.12). Nitrate - nitrogen therefore forms about 83 % of the total dissolved inorganic nitrogen supplied by the river in dry season while in rainy season both nitrate - nitrogen and ammonium - nitrogen are supplied almost in equal proportions. However, due to the relatively low riverine discharge rates in dry periods, the riverine nutrients supply is much reduced compared to the supply observed in rainy season. The average supplied total dissolved inorganic nitrogen Σ N (Σ N = NH_4^+ + NO_3^- + NO_2^-) in wet season is therefore

$(2.1 \pm 1.5) \times 10^{6}$ mmol N d^{-1} while in dry season it is reduced to about $(9.6 \pm 5.8) \times 10^{3}$ mmol N d^{-1}.

Table 4.10: Ammonium, nitrate (+ nitrite) and salinity at stations K1 (next to river Kidogoweni) and st. G1 (next to the open sea) during dry seasons (January/February) of 1991 to 1994. n = 27 : number of observations.

Station	High tide n = 27			Low tide n = 27		
	NH_4^+ (μM)	NO_3^- (μM)	salinity (psu)	NH_4^+ (μM)	NO_3^- (μM)	salinity (psu)
K1	0.2 ± 0.2	0.2 ± 0.1	37 ± 2	0.8 ± 0.5	4.0 ± 2.0	1 ± 1
G1	0.1 ± 0.1	0.2 ± 0.1	36 ± 1	0.1 ± 0.1	0.1 ± 0.1	36 ± 1

Table 4.11: Ammonium, nitrate (+ nitrite) and salinity at stations K1 (next to river Kidogoweni) and st. G1 (next to the open sea) during rainy seasons (May/June) of 1991 to 1994. n = 32 : number of observations.

Station	High tide n = 32			Low tide n = 32		
	NH_4^+ (μM)	NO_3^- (μM)	salinity (psu)	NH_4^+ (μM)	NO_3^- (μM)	salinity (psu)
K1	3.5 ± 1.5	3.5 ± 2.0	13 ± 6	5.5 ± 3.0	5.0 ± 2.0	0
G1	0.2 ± 0.2	0.2 ± 0.1	35 ± 1	0.2 ± 0.2	0.2 ± 0.1	36 ± 1

Table 4.12 : Discharge rate of river Kidogoweni and the expected discharged DIN during dry and rainy seasons.

Season	River discharge* ($\times 10^5$ m^3 d^{-1})	NH_4^+ ($\times 10^3$ mmol N d^{-1})	$NO_3^- + NO_2^-$ ($\times 10^3$ mmol N d^{-1})	Σ N ($\times 10^3$ mmol N d^{-1})
Dry season	0.02 ± 0.01	1.6	8.0	9.6
Rainy season	2.02 ± 1.76	1100 ± 1100	1030 ± 990	2130 ± 1480

* River discharge data adapted from Kitheka et al., 1995

At the station next to the open waters (G1), no significant change in salinity (36 ± 1 psu) is noticed during both flood and ebb tides in dry seasons. All nutrient concentrations are also found to be very low (< 0.3 μM) at this station (tables 4.10 and 4.11).

Nutrient profiles for 17 stations covering the central part of the bay during mid-flood tide of rainy period of 1993 (May) indicated that fresh water from river Mkurumuji (fig. 3.1) with slightly elevated nutrients concentrations also enters the bay through the western part of the bay (fig. 4.10). At this time nitrate and ammonium concentrations are found to be relatively higher to the west as compared to the eastern end. This effect is not pronounced to the east of station G1 and at high tide the bay is well mixed with average concentrations of 0.2 ± 0.2 and 0.2 ± 0.2 μM for the NH_4^+ and $NO_3^- + NO_2^-$ respectively observed at the central part of the bay (table 4.13). A progressive increase of the nutrient concentration is however noticed upwards - towards river Kidogoweni (fig. 4.11). This increase is more pronounced in the creek reaching peak concentrations of 3 ± 2 and 3.5 ± 1.5 μM for NH_4^+ and $NO_3^- + NO_2^-$ respectively at station K1 (figure 4.11).

Profiles of nutrients versus salinity during rainy season (figures 4.12A and 4.12B) indicate conservative mixing at the upper end of the western creek leading to river Kidogoweni.

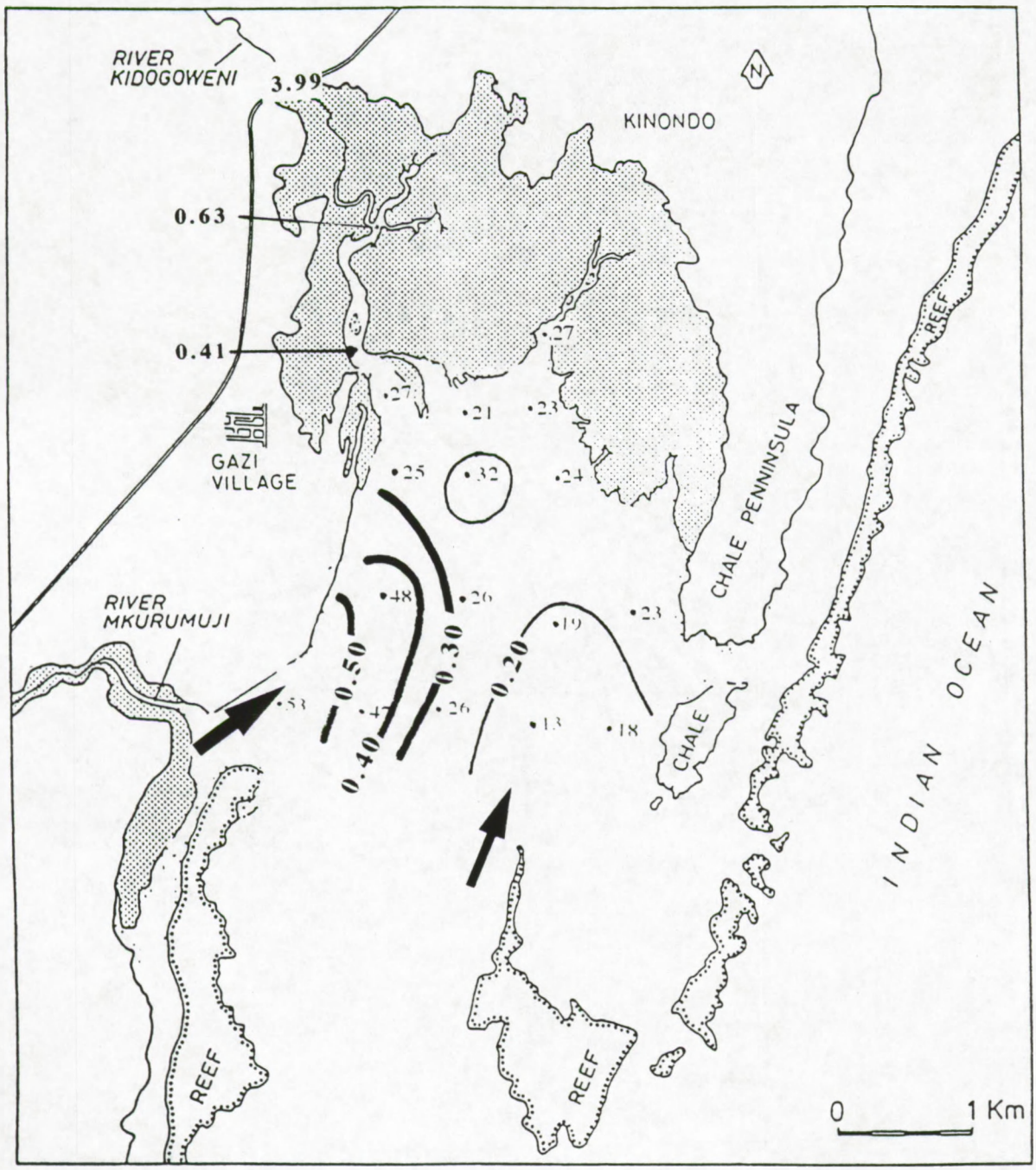


Fig. 4.10 (B): Surface profiles of nitrate (+ nitrite) (μM) within Gazi bay between 2 and 3 hours before spring high tide (flood tide). Observations made during rainy season (May. 1993). Arrows indicate flow direction.

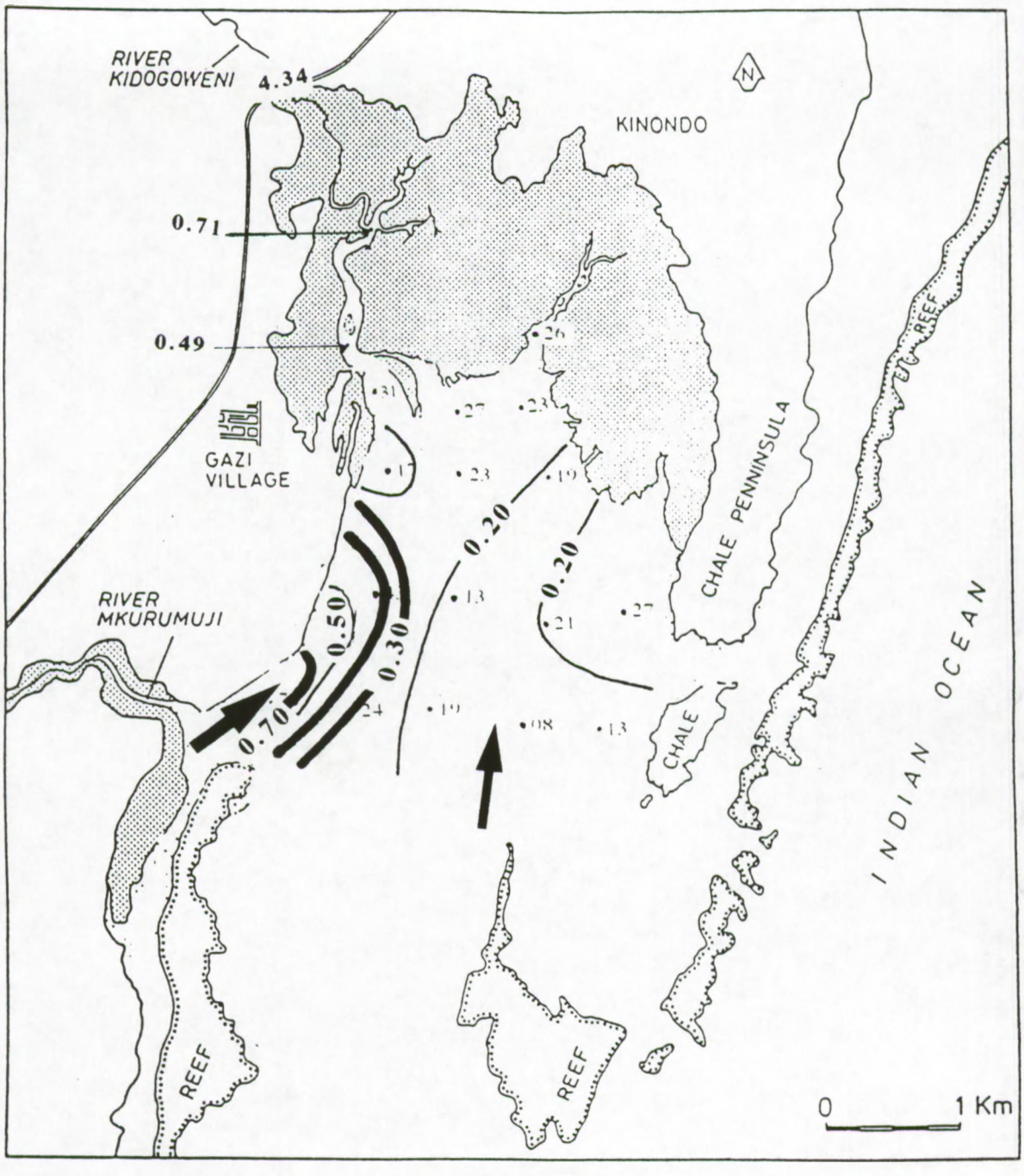


Fig. 4.10 (A): Surface profiles of ammonium (μM) within Gazi bay between 2 and 3 hours before spring high tide (flood tide). Observations made during rainy season (May, 1993). Arrows indicate flow direction.

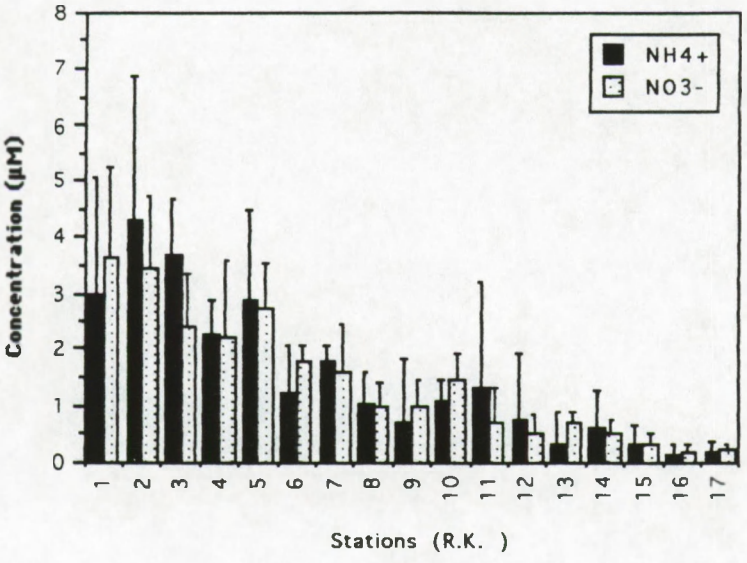
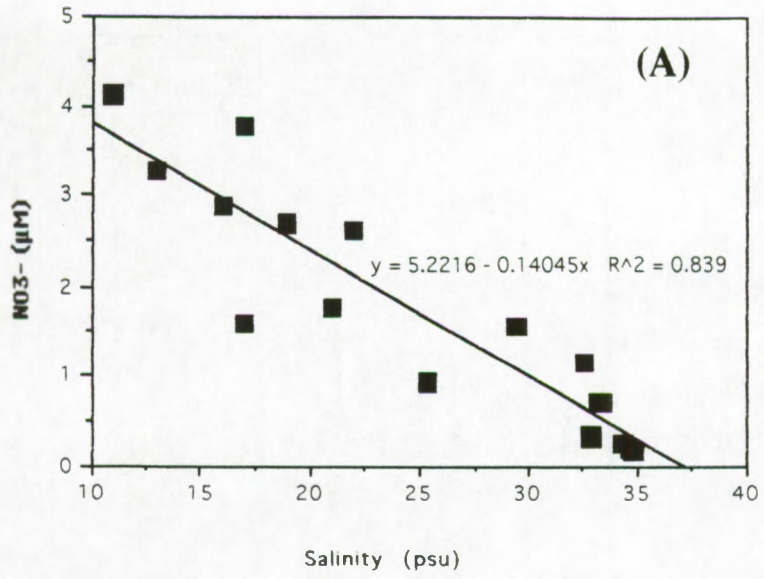


Fig. 4.11: Ammonium and nitrate (+ nitrite) concentrations for stations RK1 to RK17 along Kidogoweni creek. Observations made in the rainy seasons of 1993 and 1994. n = 9 (no. of observations). Stations RK1 to RK 17 are 17 stations established between stations K1 and G3 shown in fig. 3.5a with RK1 and RK2 coinciding with K1 and G3, respectively.

Table 4.13 : Ammonium and nitrate (+ nitrite) concentrations (at high tide) in central Gazi bay and Kidogoweni creek in dry and rainy seasons of 1992, 1993 and 1994. n = number of observations. The concentrations indicated for Kidogoweni creek during rainy season denote the observed average range between st. RK1 to RK17.

Nutrient	Dry season		Rainy season	
	Central Bay st. (M1 - M16) n = 4	Kidogoweni creek st. (RK1 - RK17) n = 13	Central Bay st. (M1 - M16) n = 5	Kidogoweni creek st. (RK1 - RK17) n = 9
NH_4^+ (μM)	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.2 - 3.6
$NO_3^- + NO_2^-$ (μM)	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.2	0.2 - 3.4



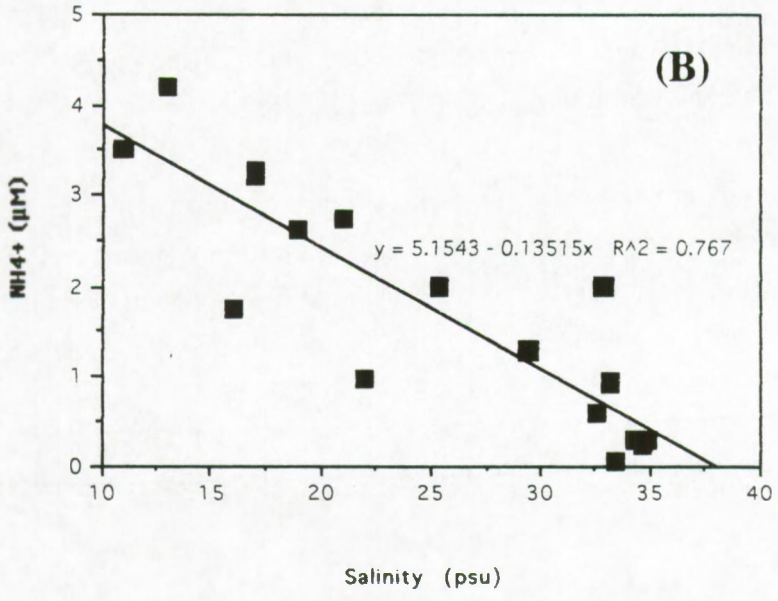
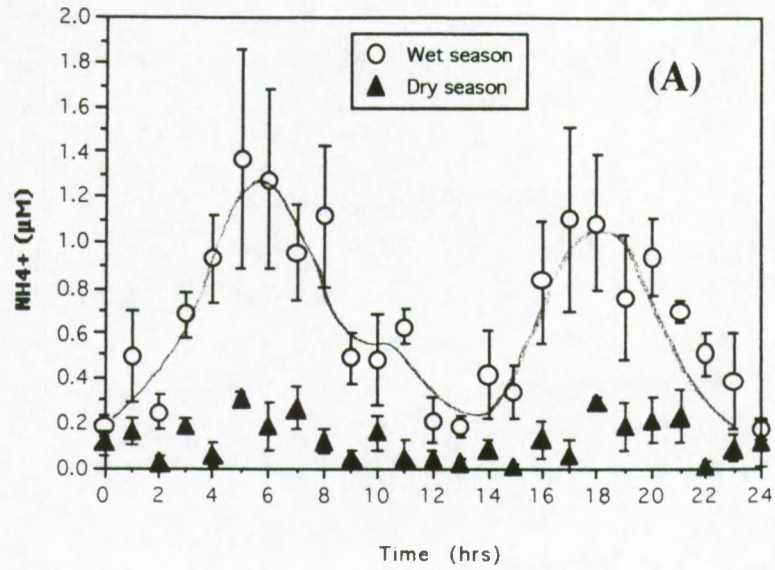


Fig. 4.12 (A - B): Ammonium (fig. **A**) and nitrate (+ nitrite) (fig. **B**) concentrations versus salinity between st. K1 and G1 in rainy season of 1993 (May).

24-hr time series observations at station G3 indicate that part of this riverine contribution observed in the creek during rainy season, is washed into the open bay during ebb flow. At this station, ammonium and nitrate (+ nitrite) values were found to increase from ≤ 0.2 μM at high tide to about 1.4 ± 0.3 and 0.9 ± 0.2 μM, respectively at low tide (fig. 4.13 and 4.14). However, due to the large volume of oceanic water, these nutrient increases associated with river Kidogoweni were hardly noticed at st. G1 offshore during ebb flow.

During dry season, nitrate concentrations at st. G3 remained at 0.2 ± 0.1 μM and hardly changed with changing tides (fig. 4.14B). However, NH_4^+ concentrations increased significantly (ANOVA: $p < 0.05$) from about 0.1 ± 0.1 μM at high tide to 0.3 ± 0.2 μM at low tide (fig. 4.13B). In the absence of significant riverine contributions in dry season, this slight increase in NH_4^+ concentration with ebb flow could be attributed to contributions from within the mangrove vegetation. However, simultaneous 6-hr time series observations at st. G3 and K3 during flood tides indicated that an experimental oyster farm between st. G3 and K3 could have been responsible for this elevated NH_4^+ concentrations observed at st. G3 during low tide. At low tides, ammonium concentrations at st. G3 and K3 were found to be averagely 0.24 ± 0.16 and 0.28 ± 0.15 μM (from 5 observations). However, it was observed that as the oceanic waters entered the bay, NH_4^+ concentrations at G3 decreased from 0.28 ± 0.15 μM to about 0.1 ± 0.1 μM at high tide (fig. 4.15) while at K3, ammonium increased to a peak of 0.5 ± 0.3 μM (after 2 hrs.) but decreased sharply to about 0.1 ± 0.1 μM at maximum high tide. This may imply that as the first high tide water passes through the farm, during flood tide, they pick high concetrations of excreted NH_4^+ (oyster NH_4^+ excretions) raising the average NH_4^+ concentrations at st. K3. However, as the volume of the oceanic water increases with increasing tide, this localized effect fades away and NH_4^+ concentrations decreases again to 0.1 ± 0.1 μM at maximum high tide. This trend was not noticed for NO_3^- + NO_2^- (table 4.14). An experiment conducted at the oyster farm using flow through tunnels with oysters indicated a significant increase of NH_4^+ concentration as the tide waters passes through the tunnels (Bollen, pers. comm.). This confirms that the oyster experimental farm is a possible localized source of NH_4^+ in Kidogoweni creek.



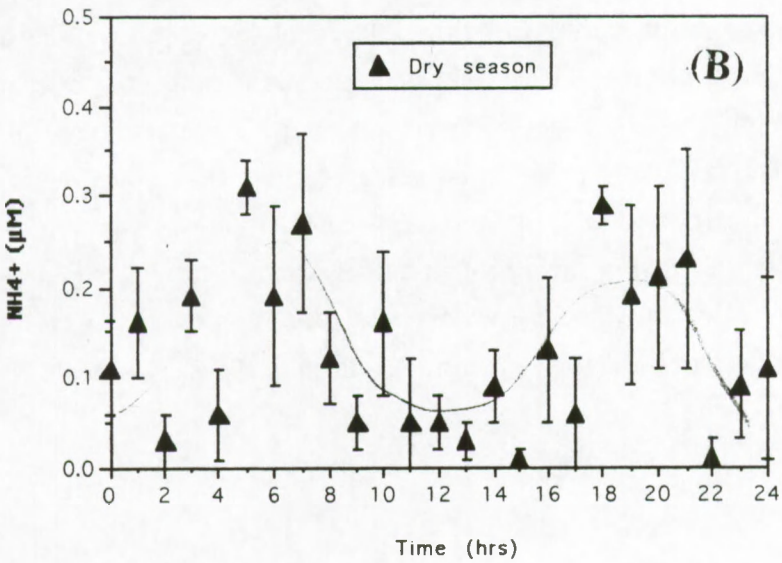
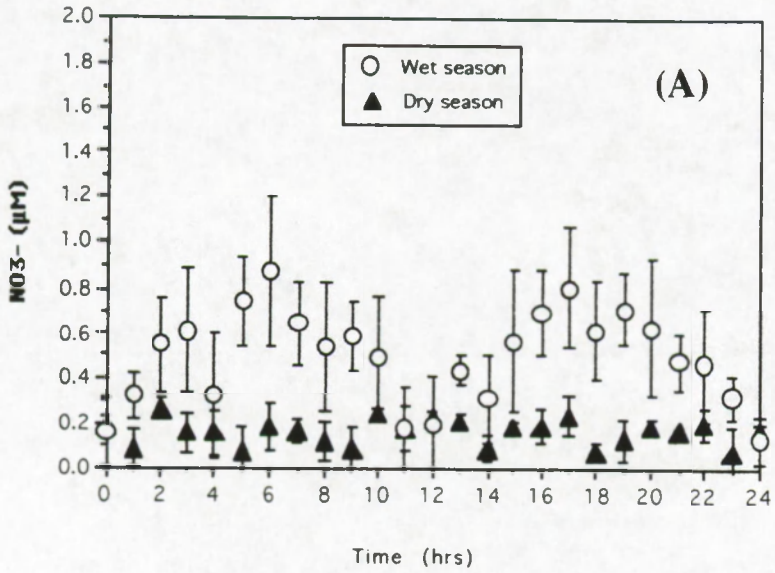


Fig. 4.13 (A & B): Ammonium observations during various 24 - hr. time series conducted at st. G3 during dry and rainy seasons (fig. A) between 1992 and 1994. Fig. 4.13B displays the dry seasons observations on an expanded scale. No. of observations: n = 9 and 7 (rainy and dry seasons respectively).



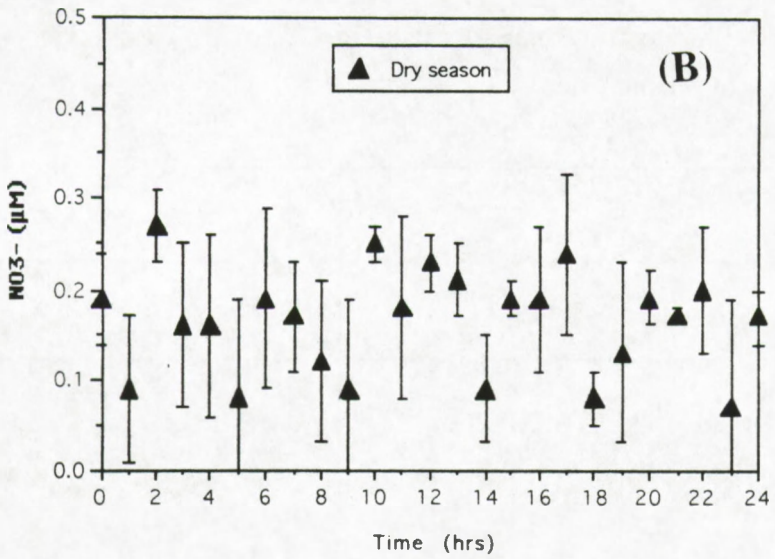


Fig. 4.14 (A & B): Nitrate (+ nitrite) observations during various 24 - hr. time series conducted at st. G3 during dry and rainy seasons (fig. A) between 1992 and 1994. Fig. 4.14B displays the dry seasons observations on an expanded scale. No. of observations: n = 9 and 7 (rainy and dry seasons respectively).

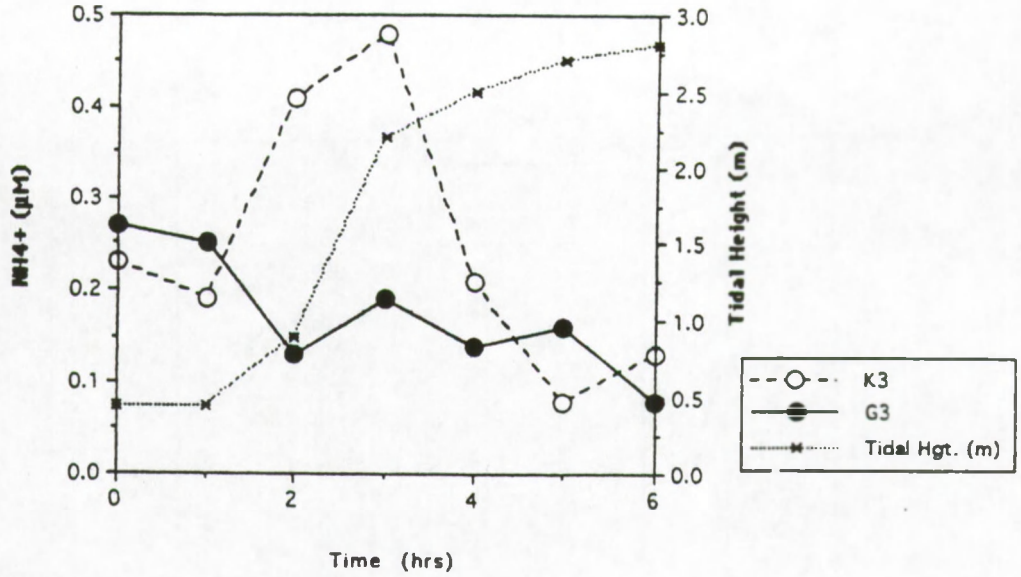


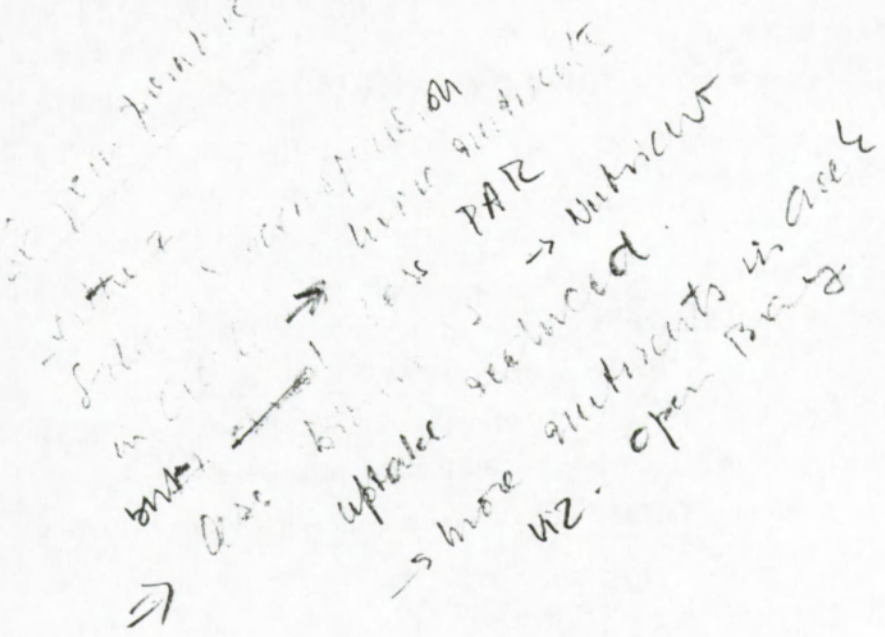
Fig. 4.15: Ammonium profiles at st. G3 and K3 during flood tide. Time t = 0 hrs. coincides with low tides while t = 6 hrs is high tide. Samples were taken within ± 5 minutes of the indicated times. n = 5 (no. of observations).

Table 4.14: NH_4^+ and $NO_3^- + NO_2^-$ concentrations at stations G3 and K3 during flood spring tide of September and October 1995. n = 5 (no. of observations). time t = 0 hr. corresponds to low waters. Samples were taken within ± 5 minutes of the indicated times.

Tidal time (hrs.)	NH_4^+ (μM)		$NO_3^- + NO_2^-$ (μM)	
	G3	K3	G3	K3
0	0.3 ± 0.2	0.2 ± 0.2	0.2 ± 0.1	0.1 ± 0.1
1	0.3 ± 0.2	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
2	0.1 ± 0.1	0.4 ± 0.2	0.2 ± 0.1	0.2 ± 0.1
3	0.2 ± 0.1	0.5 ± 0.3	0.2 ± 0.1	0.1 ± 0.1
4	0.1 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.2 ± 0.1
5	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
6	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

Ammonium profile across a transect between st. K1 and G1 at neap high tide (samples taken within 1 hr. duration by four groups positioned across the transect) confirms the low NH_4^+ concentrations observed in the creek and bay (fig. 4.16A: given as an example for observation made on January 25th, 1994 during a dry period). However, three subregions (A, B and C) are identified. During neap tide, oceanic water does not reach st. K1, so though the discharge rate is very low, salinity is zero while the nutrients concentrations are relatively high. This riverine effect is only noticed at the upper 300 meters (from st. K1) downstream the river. After this point, NH_4^+ concentrations are more-or-less uniform at 0.10 ± 0.05 μM upto about 5 km outward (within the central part of the bay after st. G2). Ammonium concentrations then drop to ≤ 0.05 μM between the central part of the bay and the the open sea station (G1). This trend was also noticed for nitrate (fig. 4.16B) and phosphate (not shown). Though this trend was established for a number of observations (7 out of a total of 11) conducted during dry period of 1993 and 1994, statistical treatment of all the data obtained from these two last subregions (B and C) indicated no significant difference (analysis of variance: $p > 0.05$). However, it is not clear as to why a decrease in all the three nutrients was noticed towards the open waters. One observation is that the nutrient levels observed in Gazi bay are so low that the slightly elevated (?) values observed from the central bay into the creeks could be due to resuspension of bottom surface sediments during flood and ebb tides. Comparison of chlorophyl-a biomass and the mean gross primary production (Kitheka et al., 1995) within the mangrove creek and the open waters (fig. 4.17) reveals that there is a relatively higher rate of carbon fixation per unit chlorophyl biomass in the open sea than in the creeks. This may imply a different assemblage of primary producers in the mangrove creek - perhaps surface benthic primary producers brought into the water column from the shallow bottom surface by tidal resuspension while at station G1 this assemblage may be typical of offshore waters. The mean gross primary production at st. G1 in dry season is averagely 230 mg C m^{-3} d^{-1} while the standing chlorophyl-a biomass is averagely 0.2 μg/l. In this case, we have a carbon fixation of about 1200 g C per unit gram chlorophyl-a biomass while for the mangrove station (G3) we calculate a carbon fixation of about 270 g C per unit gram chlorophyl biomass. If the assemblage of primary producers in the two stations would be the same, the carbon fixation rate per unit chlorophyl biomass would not be very different. Comparison of the molar C/N ratio and $\partial^{13}C$ isotope signature of particulate organic material (POM) at the open sea station (G1) and that within the mangroves (G3), indicates that at high tide, POM at the open sea station is purely of phytoplanktonic origin with a C/N molar ratio of 7.0 ± 0.63 and a $\partial^{13}C$ isotope signature of -19.37 ± 0.63 ‰ (chapter 5: table 5.10A). It is

known that POM of marine origin mainly consists of phytoplankton with an average molar C/N ratio of 6.6 and a $\partial^{13}C$ isotope signature varying between -18.76 and -21.6 ‰ (Fontugne & Duplessy, 1978; Fry & Sherr, 1984; Fontugne & Duplessy, 1991). On the other hand, POM of the water column within the mangrove creek (st. G3) was found to have C/N and $\partial^{13}C$ isotope signatures (9.3 ± 2.4 and -22.78 ± 1.84 ‰, respectively; chapter 5: table 5.10A) which were significantly different (ANOVA: $p < 0.05$) from those observed at the open sea station. The increase of the molar C/N ratio and the $\partial^{13}C$ isotope signature reflect the mangrove POM effect which may be brought about by tidal resuspension of the surface sediments which may also include surface benthic primary producers. Alternatively, in a system where we have seagrass vegetation close to a mangrove forest, the seagrass traps the outwelled detritus from the mangrove forest (Hemminga et al., 1994). The water therefore becomes less turbid towards the open sea (Osore, 1994). This situation could therefore encourage more favourable conditions for uptake of nutrients hence slightly lowering the concentrations towards the open sea to low values typical for waters offshore the Kenyan coast (Semeneh et al., submitted). These concentrations are however very low almost boardering our detection limits (NH_4^+ : 0.05 μM, NO_3^- : 0.1 μM) so the differences noticed are not significant but discussed to indicate possible nutrients contribution due to tidal disturbance of the shallow surface sediments within the bay.



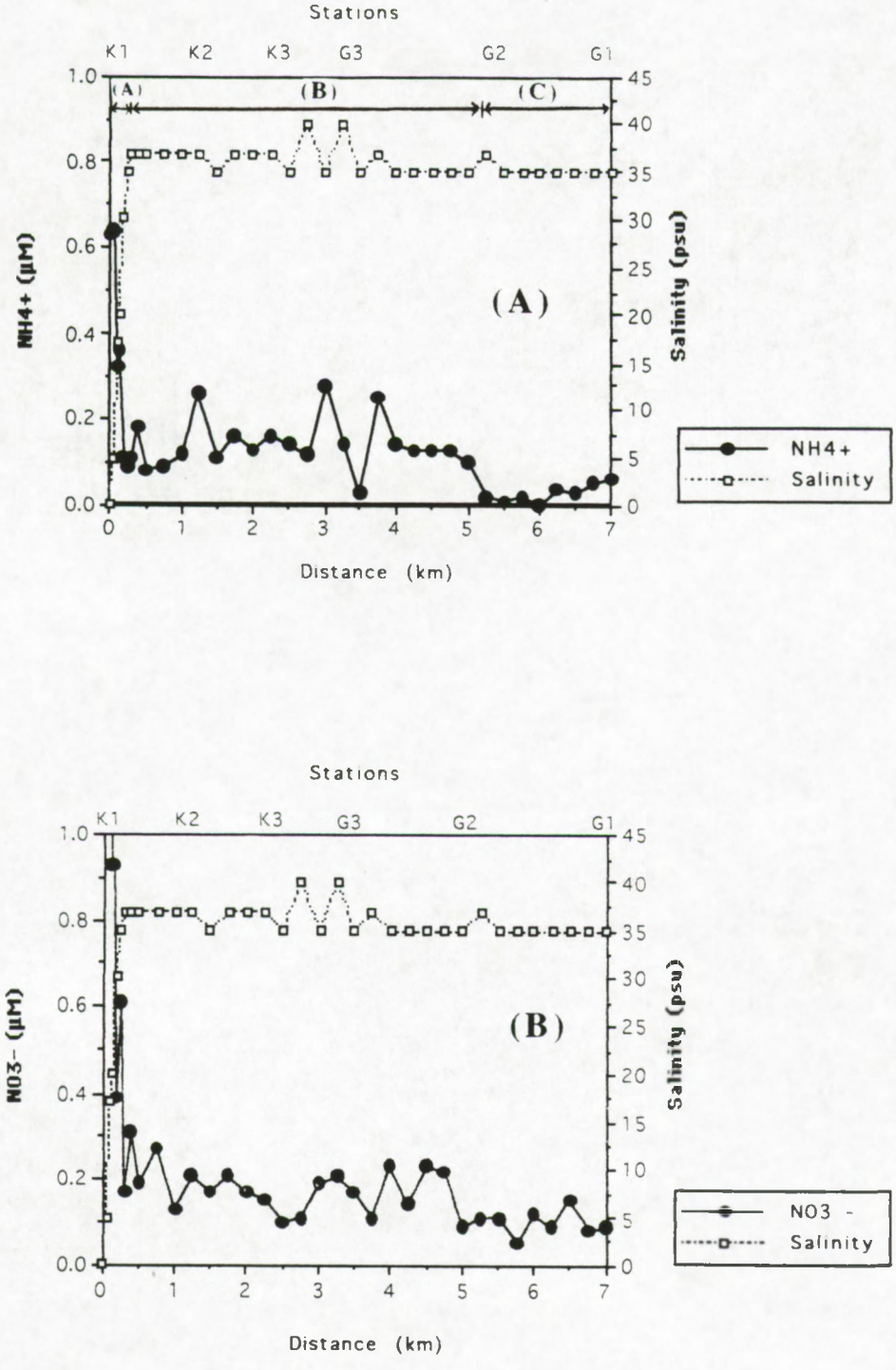


Fig. 4.16 (A & B): Ammonium (fig. **A**) and nitrate (+ nitrite) (fig. **B**) profiles between the open sea (st. G1) and the inner part of Kidogoweni creek (st. K1) during dry season (January 25th, 1994).

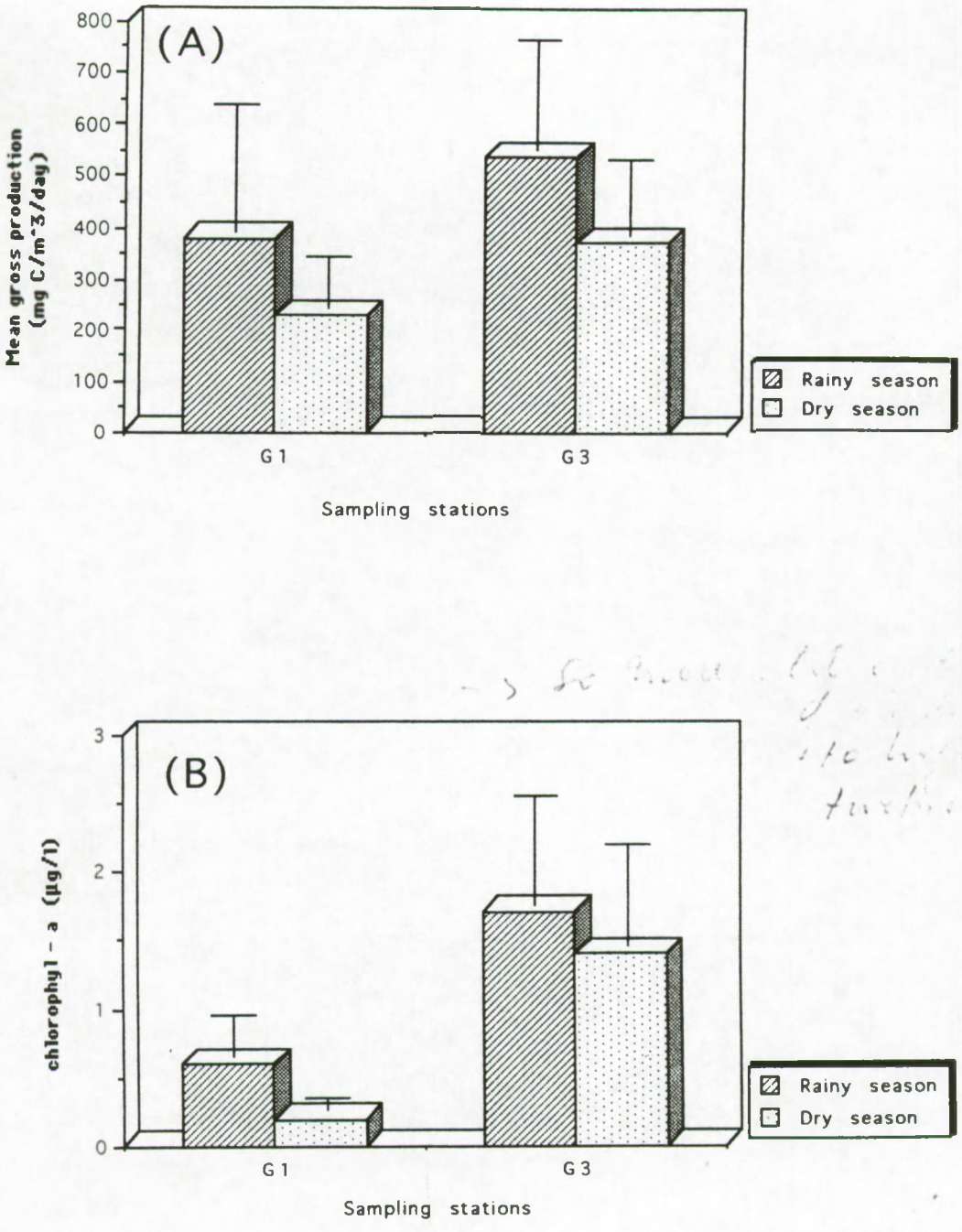


Fig 4.17 (A & B): Mean gross production (**A**) and chlorophyl - a biomass (**B**) at the mangrove station (G3) and open sea station (G1) for the dry and rainy season at Gazi bay. (Adapted from Kitheka et al., 1995).

In conclusion, dissolved inorganic nitrogen (Σ N) in the water column of central Gazi bay is very low and hardly goes above 0.2 μM. In dry season NH_4^+ and NO_3^- + NO_2^- concentrations within the bay and the creeks are averagely 0.1 ± 0.1 μM. This situation is somehow different in rainy season due to riverine discharges from river Mkurumuji to the western part of the bay and river Kidogoweni in the north. Because of its position, river Kidogoweni is found to have direct effect on nutrient fluctuations within the creek leading to the bay during rainy season. This river is found to supply ca. (2.1 ± 1.5) x 10^6 mmol N of Σ N (Σ N = NH_4^+ + NO_3^- + NO_2^-) per day during rainy season compared to (9.6 ± 5.8) x 10^3 mmol N d^{-1} during dry period. However, this observed difference in supply rates of the Σ N by the river is only relative and its overall effect in the entire bay is minimal due to the large volume of oceanic water that covers the bay during high tides. Kitheka et al. (1995), estimated that discharged riverine water in Gazi bay forms less than 1 % of the total volume of water in the bay during high tide. The main effect of this discharged riverine water (and elevated Σ N concentrations) is therefore only noticed along the creek leading to the river where NH_4^+ and NO_3^- + NO_2^- concentrations are found to range averagely between 0.2 μM (towards the bay) and 5.0 μM (towards the river side) during rainy season. During dry season, the riverine discharge is negligable and NH_4^+ concentrations in the entire bay (both within the central part of the bay and along Kidogoweni creek) are found to be ca. 0.1 ± 0.1 μM while that of NO_3^- + NO_2^- is found to be 0.2 ± 0.1 μM. An experimental oyster farm at the Kidogoweni creek is found to be an additional source of ammonium in the creek. However this supply which is localized and relatively small is hardly noticed during high tide. In general, in the absence of the riverine contribution, no clear evidence was noticed for a net export of dissolved inorganic nitrogen from the Gazi mangrove forest. Boto and Wellington (1988) found mean NH_4^+ and NO_3^- concentrations of 0.1 - 0.65 and 0 - 0.22 μM, repectively in mangrove creeks of Hinchinbrook Island, Australia which are similar to those found at Gazi bay during dry season. These observed nutrient levels are quite low and comparable to the levels reported by Alongi et al. (1992) for other tropical bays.

4.1.2 Dissolved inorganic nitrogen (DIN) concentrations in mangrove sediments inhabited by *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) species

4.1.2.1 Physico-chemical characteristics of Rm and Ct sediments

4.1.2.1.1 Mud / Sand contents of Rm and Ct sediments

Determination of mud and sand contents for the surface (0 - 10 cm) and bottom (10 - 20 cm) sediment for the two field study plots indicated slight differences. Ct sediments had a percentage mud level of ca. 48 % (by volume) for the surface which increased to ca. 78% (by volume) at 20 cm depth while for Rm the surface mud portions was ca. 70 % and increased to ca. 98 % at 20 cm depth (fig. 4.18). The largest portion of the sediment's sand (both for *Ceriops* and *Rhizophora*) were found to have grain size of ca. 0.18 mm (fig. 4.19). Though the sand's grain sizes were similar, the diferences in sand and mud contents indicated above for the two sediment types lead to different sediment porosities.

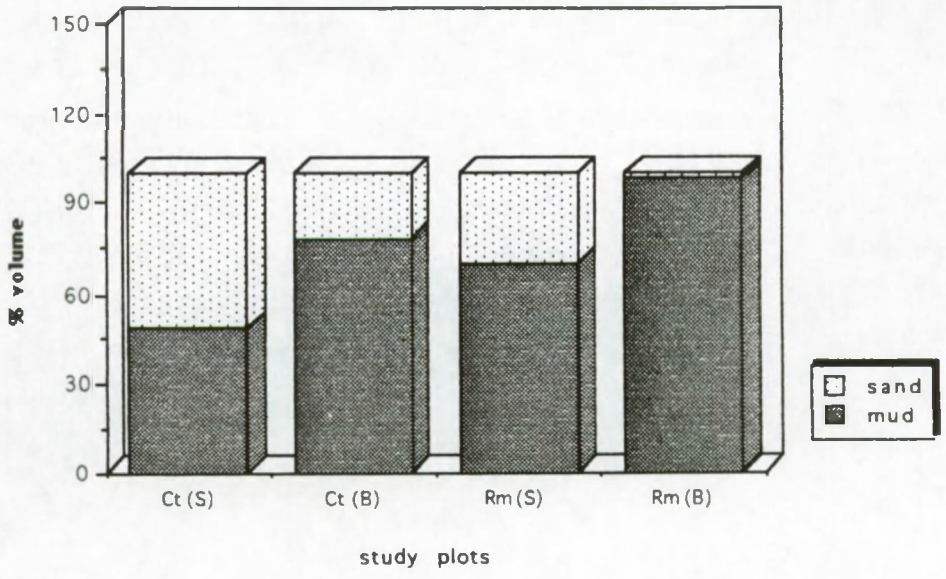


Fig. 4.18: A bar graph showing mud and sand contents (by volume) for the surface (S: 0 - 10 cm) and bottom (B: 10 - 20 cm) sediments of Ct and Rm plots.

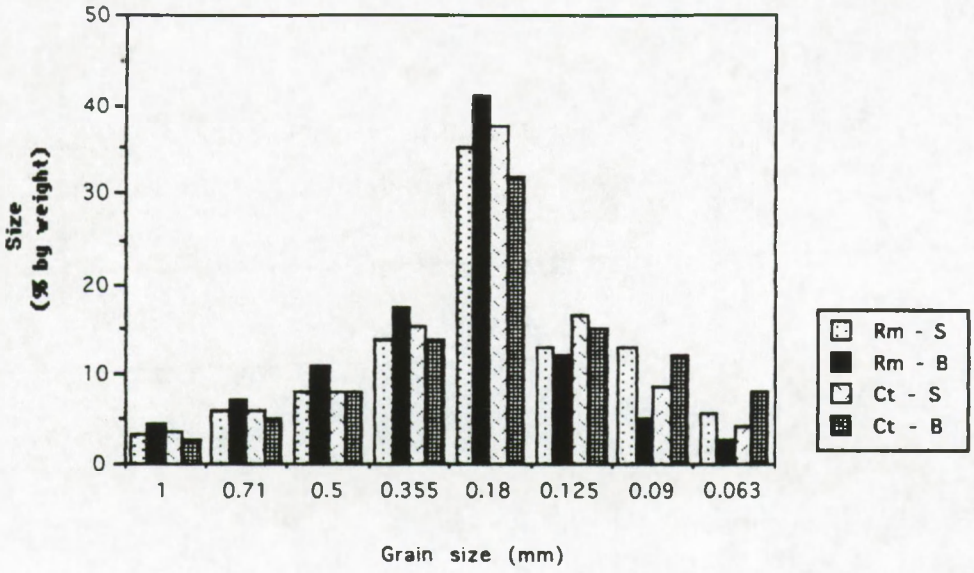


Fig.4.19: Histograms showing percentages by weight of various grain sizes of surface (S: 0 - 10 cm) and bottom (B: 10 -20 cm) sediments from the Rm and Ct plots.

4.1.2.1.2 Density and Porosity

Density (wet sediments) for Rm sediments increased slightly from 1.35 ± 0.05 g cm^{-3} at the surface to ca. 1.48 ± 0.05 g cm^{-3} at 12 cm depth while for Ct sediments it was slightly higher, being 1.91 ± 0.14 g cm^{-3} at the surface decreasing to ca. 1.48 ± 0.07 g cm^{-3} at 12 cm depth (table 4.15). Porosity determination indicated different porosity levels for the two sediments types. The surface porosity for the Rm sediment was 0.92 ± 0.04 (v/v) and decreased to ca. 0.74 ± 0.02 (v/v) at 12 cm depth while for Ct, it was 0.46 ± 0.05 for the surface and increased gradually to 0.65 ± 0.02 at 12 cm depth (table 4.17). Due to the differences in porosity, *Rhizophora mucronata* (Rm) sediments were found to have a higher water content than that of *Ceriops tagal* (Ct). The 0 - 1 cm sections of the Rm sediments had a water content of ca. 68 % (porosity/wet density) which decreased gradually to ca. 50 % at 12 cm depth. For Ct sediments the surface (0 - 1 cm) had a water content of ca. 24 % which increased gradually to ca. 48 % at 12 cm depth. Samples for these determinations were always taken during flood tide when the overlying water column was about 30 cm high. No significant (analysis of variance gives $p > 0.05$ for results of all

corresponding sections) differences of the water content were noticed between dry (February / March) and rainy (May / June) seasons and the density and porosity values shown in table 4.15 represent mean values.

Table 4.15: Mean (± S.D.) values of wet density and porosity of *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) sediments of Gazi bay. n = 48 (no. of observations).

Depth (cm)	Rm sediment		Ct sediment	
	Density g cm^{-3}	Porosity (vol. / vol.)	Density g cm^{-3}	Porosity (vol. / vol.)
0 - 1	1.35 ± 0.05	0.92 ± 0.04	1.91 ± 0.14	0.46 ± 0.05
1 - 2	1.33 ± 0.07	0.85 ± 0.05	1.80 ± 0.12	0.50 ± 0.04
2 - 4	1.36 ± 0.05	0.82 ± 0.03	1.74 ± 0.16	0.55 ± 0.05
4 - 6	1.42 ± 0.03	0.78 ± 0.02	1.63 ± 0.16	0.57 ± 0.07
6 - 8	1.49 ± 0.03	0.78 ± 0.01	1.62 ± 0.05	0.66 ± 0.04
8 - 10	1.48 ± 0.01	0.78 ± 0.02	1.57 ± 0.05	0.66 ± 0.02
10 - 12	1.48 ± 0.03	0.74 ± 0.02	1.48 ± 0.07	0.65 ± 0.02

4.1.2.1.3 Salinity and Temperature

(i) Salinity

The lowest salinity recorded at the water column above the Rm study plot during rainy season was about 32 psu while the highest recorded in dry season was about 36 psu (table 4.16). During dry season (February/March) pore water salinity at the 0 - 1 cm depth was ca. 38.0 ± 2 psu and did not change much with depth while in wet season it was 34.0 ± 4.0 psu at the surface and increased slightly with depth. For Ct sediments the surface salinities were found to be ca. 46 ± 5 psu and increased to ca. 58 ± 3 psu at 12 cm depth (table 4.16) during dry period. During rainy season, the surface salinities were found to be slightly lower (ca. 42 ± 6 psu) but also increased to ca. 57 ± 2 psu at 12 cm depth. The relatively high standard deviation noticed for the 0 - 1 and 1 - 2 cm depth during rainy

season reflects the variability of the salinity with sampling time. Heavy down pour on exposed (low tide) sediment had an effect of lowering the surface pore water's salinity. These samples were taken during spring flood tide when the water column height was about 30 cm. Fig. 4.20 displays a daily (samples were taken every other day at low tide) salinity profile of the upper 4 cm depth of Rm sediments during dry (14th January to 12th February 1994) and wet (10th May to 9th June 1994). While no significant (ANOVA: $p = 0.0001$) difference in salinity was noticed between spring and neap tides in Rm sediments, average salinity observed on the exposed sediments during wet season was slightly lower than those for dry season. However, the mean difference between the two seasons was hardly above 3 psu.

Table 4.16: Average salinity values observed for the water column and sediments at the Rm and Ct study plots in dry (Feb./Mar.) and rainy seasons (May/June) between 1992 and 1994. n = no. of observations.

Depth (cm)	**Rm plot salinity (psu)**		**Ct plot salinity (psu)**	
	Dry season (n = 13)	**Rainy season** (n = 17)	**Dry season** (n = 15)	**Rainy season** (n = 14)
water column	35 ± 1	34 ± 2	36 ± 1	33 ± 3
0 - 1	38 ± 2	34 ± 4	46 ± 5	42 ± 6
1 - 2	39 ± 1	36 ± 3	46 ± 4	45 ± 4
2 - 4	40 ± 1	38 ± 3	49 ± 5	47 ± 5
4 - 6	40 ± 2	40 ± 1	54 ± 3	49 ± 4
6 - 8	40 ± 1	39 ± 1	56 ± 3	54 ± 5
8 - 10	40 ± 1	40 ± 1	57 ± 2	57 ± 3
10 - 12	40 ± 1	40 ± 1	58 ± 3	57 ± 2

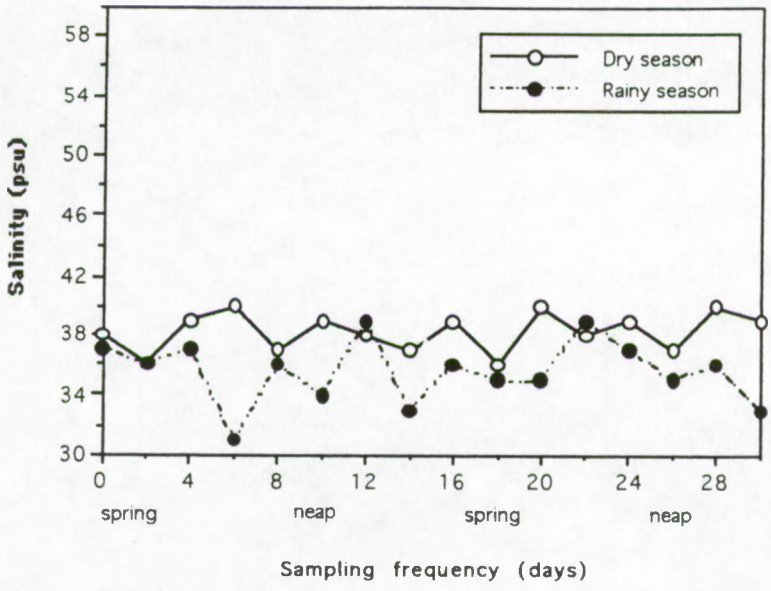


Fig.4.20: Daily salinity fluctuations on Rm sediments (upper 4 cm depth) during dry 14th Jan. to 12th Feb.) and rainy (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and rainy periods respectively.

Fig. 4.21 also displays a daily (samples taken every other day at low tide) salinity profile of the upper 4 cm Ct sediments in both dry and wet seasons of 1994. These samples were taken on the same days as the Rm sediment samples.

Unlike the Rm sediments, a very clear tidal influence on salinity profile is noticed for the Ct sediments. This influence is more pronounced during dry season than in wet (rainy) season. During spring low tide of the dry season, the salinity of the upper 4 cm of Ct sediments varies between 42 and 47 psu and increases gradually to about 58 psu at neap tide. During wet season, the salinity is found to lie between 37 and 47 psu (fig. 4.21). Rainfall profile covering the same sampling period (fig. 4.22) at Gazi indicates that the relatively low salinities observed in the first two weeks of the rainy period, were mainly due to the heavy down-pour on exposed (more pronounced during neap tide) sediments.

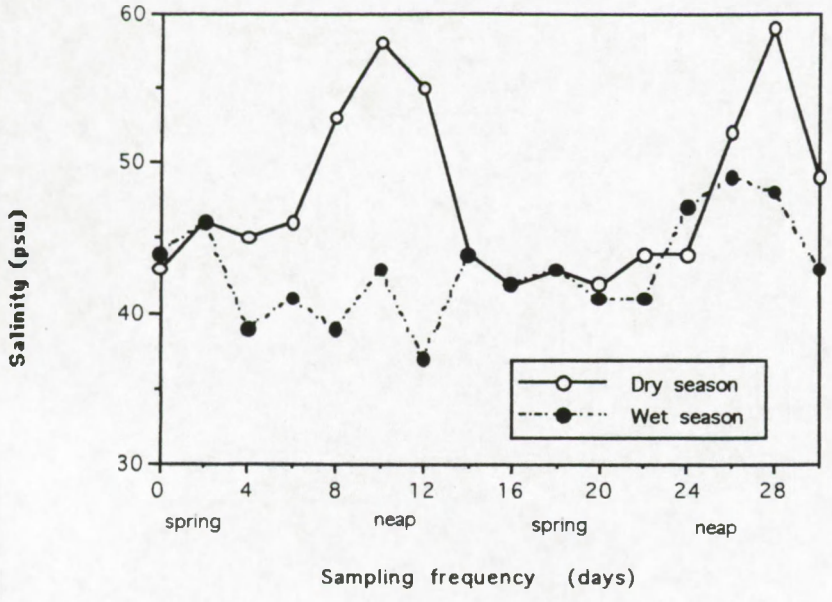


Fig. 4.21: Daily salinity fluctuations on Ct sediments (upper 4 cm depth) during dry (14th Jan. to 12th Feb.) and wet (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/04/94 and 10/05/94 for the indicated dry and wet seasons.

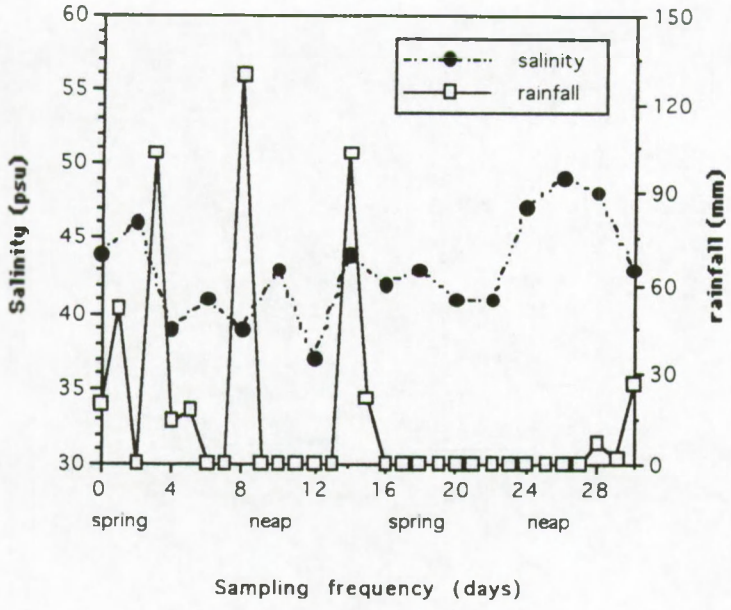


Fig. 4.22: Daily salinity fluctuations of Ct sediments ploted against rainfall pattern covering the study plots during the wet season (May 10th to June 9th, 1994).

(ii) Temperature

Temperature profiles for both the Rm and the Ct sediments gave a more or less similar variation pattern as that observed for salinity. No tidal influence was noticed for the temperature of the upper 1 cm depth of Rm sediments both in dry and wet season. However, while the temperature in dry period was averagely about 25 ± 1°C, that of the wet season was slightly lower at an average value of 23 ± 1 °C(fig.4.23A).

For Ct sediments, a marked difference of temperature was noticed between spring and neap tides in dry season. While the temperature during spring low tides was averagely 29 ± 3 °C,at neap tide temperatures as high as 39 ± 3 °C were recorded (fig. 4.23B). However, the high temperatures observed during neap tide depended on: (1) at what time of the day the temperature measurements were made and (2) whether the temperatures were taken under the Ct trees or in areas not covered by the tree shade. In order to note possible maximum temperature differences, all our Ct sampling for this experiment was done at

between 13:00 and 15:00 hours when the sun's radiation was expected to be at its maximum. These temperature readings were also taken from 5 randomly selected points covering area's under the tree shades and those exposed to direct sun rays.

No clear temperature pattern was observed for the Ct sediment during wet season except that the temperatures were lower than those observed during dry season (fig. 4.23B). These low temperatures are mainly due to the cool atmosphere created as a result of periodic rainfall and cloudy conditions during the wet period.

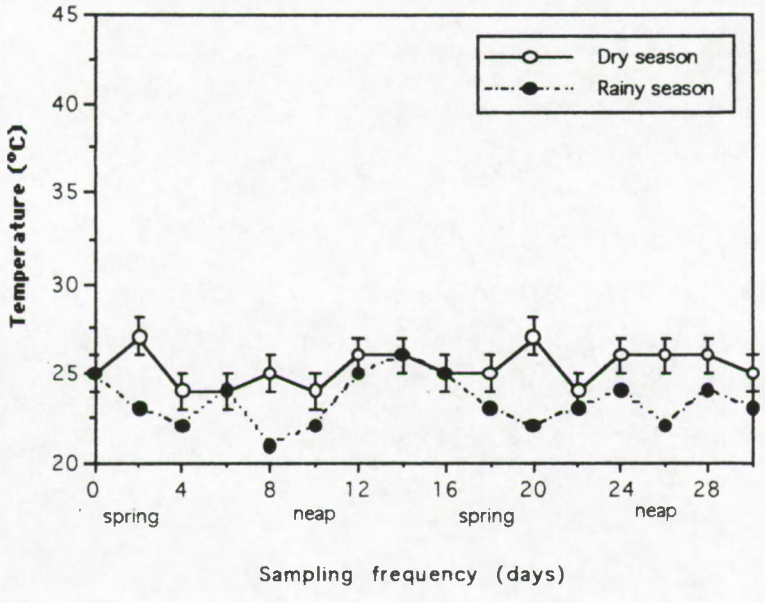


Fig. 4.23A: Daily temperature fluctuations on Rm sediments (upper 1 cm depth) during dry (14th Jan. to 12th Feb.) and wet (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and wet seasons.

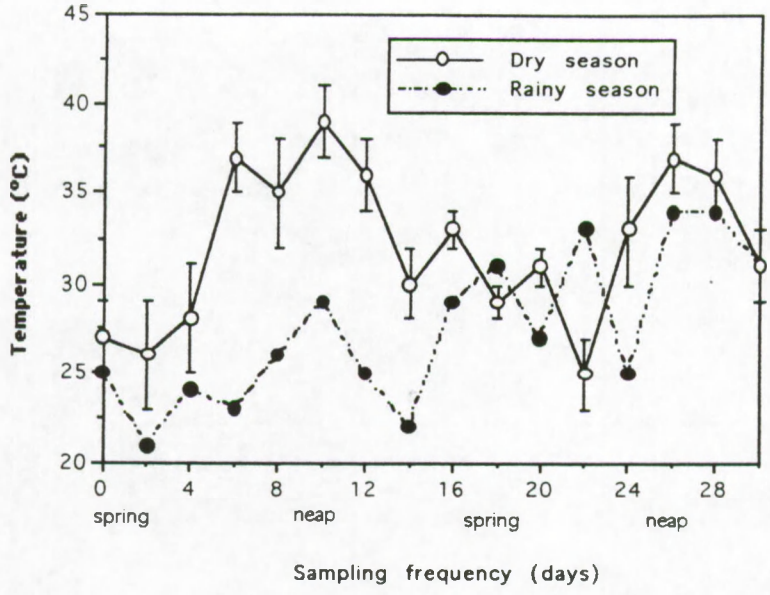


Fig. 4.23B: Daily temperature fluctuations on Ct sediments (upper 1 cm depth) during dry (14th Jan. to 12th Feb.) and wet (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and wet seasons.

4.1.2.1.4 NH_4^+ adsorption capacity in Rm and Ct mangrove sediments

Most sediments or soils possess net negative charge that attracts and holds cations dissolved in soil solution. In general cations are held and displace one another in the sequency;

$$Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+$$

on cation exchange sites (Schlesinger, 1991).

NH_4^+ ion being positively charged, would therefore have a tendency of being adsorped on the surfaces of sediment particles hence becoming unavailable for diffusing out into the water overlaying these sediments (Blackburn & Henriksen, 1993).

It has also been shown that because NH_4^+ is a minor cation in marine sediments, its ion-exchange behaviour simplifies to a linear adsorption isotherm over natural concentration

ranges (Rosenfield, 1979; Berner, 1980) and that adsorbed ammonium is always in equilibrium with the pore water ammonium. Blackburn and Henriksen (1993) found out that when the exchange capacity was high (implying higher adsorption rate) very little ammonium was transferred to the water column and when the exchange capacity was low more NH_4^+ fluxed out. This implies that the binding of NH_4^+ to solid sediment substrate reduces its concentration in the pore water and may decrease its rate of loss from sediment by diffusional and flushing processes.

Mackin and Aller (1984), on their investigation of ammonium adsorption in different marine sediments, found a very constant ratio of 1:1.3 between free and ionically-bound ammonium. Blackburn and Henriksen (1983) found a much wider variation in ratio (1: 5 to 17). However, they had no explanation for their wide variations (Blackburn, 1986).

In order to know the adsorption capacity of the Rm and Ct sediments both during the dry and rainy season, a specific experiment was done a number of times during the dry and rainy season of 1992. This experiment was aimed to give us the exact volume of 1N KCl necessary to extract maximum adsorbed NH_4^+. From the total ammonium pool (which includes free and adsorbed NH_4^+) and the interstitial ammonium pool obtained by sediment squeezing using nitrogen gas (refer chapter 3) we calculated percent adsorbed NH_4^+ as;

$$\% \text{ adsorbed } NH_4^+ = \frac{NH_4^+ (ex)}{NH_4^+ (total)} \times 100$$

where NH_4^+ (total) = total NH_4^+ extracted at 40 ml 1 N KCl (for 10 g wet sediment)

NH_4^+ (ex) = NH_4^+ (total) - free pore water NH_4^+

In this text, free NH_4^+ is defined as that ammonium which is dissolved in pore water and not adsorbed onto sediment particles, while ionically-bound NH_4^+ is adsorbed ammonium.

Experimental set-up

10 core samples were taken (using plexiglass cores; i.d. 3.6 cm; length ca. 30 cm) randomly from our 20 m x 20 m sampling plot described in chapter 3. These samples were taken to the laboratory (within 3 - 4 hours) where the upper 6 cm depth were pooled and mixed together (under N_2 gas) in a plastic bag before the following two steps were performed;

Step 1

Three 50 g subsamples were weighed from the mixed sediment and transferred separately into a stainless steel extraction devise (refer to chapter 3). Nitrogen gas was then passed through the devise under pressure and the resultant pore water collected through a GF/F whatman filter into a 50 ml acid washed polyethylene container. These samples were analyzed (in duplicate) for NH_4^+ immediately using the Indophenol blue procedure as described in chapter 3. A 1:20 dilution (with de-ionised water) was made on the sample before the NH_4^+ determination. The obtained ammonium concentration represented the pore water (free NH_4^+) concentration.

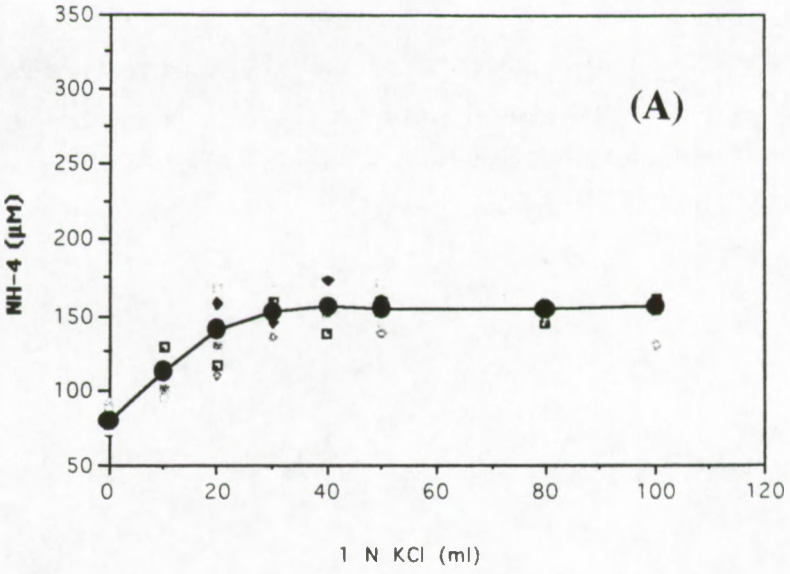
Step 2

Sixteen 10 g subsamples were weighed into separate glass serum vials and varying volumes (10 ml, 20 ml, 30 ml, 40 ml, 50 ml, 60 ml, 80 ml, 100 ml) of 1N KCl added (in duplicate) to the vials. These vials were then stoppered gas tightly with rubber stoppers (and aluminium clips) and flushed with N_2 gas (3 minutes) before being placed on a shaker table for 1 hour. They were then centrifuged at 2000 r.p.m. for 10 minutes before filtering the supernatant liquid through a GF/F whatman filter into acid washed polyethylene bottles and the NH_4^+ concentration determined as in step 1. The different KCl volumes used were put into consideration when making the necessary calculations for NH_4^+ concentrations. This concentration represents total (free + ionically-bound) NH_4^+ concentrations as obtained by the different volumes of KCl. This experiment was repeated 12 times (7 times in dry period and 5 times in rainy season) for both the Rm and Ct sediments.

Figures 4.24A and 4.24B give the adsorption curves as observed for Rm sediments in both dry season (January 1992) and rainy season (May 1992). In both cases, it is demonstrated that we need a minimum of 30 ml 1N KCl to extract the adsorbed NH_4^+ pool from a 10 g wet sediment sample. At 40 ml 1 N KCl, all adsorbed pool was extracted. ANOVA statistical analysis of the total ammonium concentration at 40 ml 1 N KCl indicated no significant difference in concentrations ($p = 0.405$) for dry and wet period. The average total NH_4^+ concentration for the Rm sediment at 40 ml KCl volume for dry and wet period was 156 ± 10 and 150 ± 12 μM respectively while for the pore water it was 80 ± 8 μM and 68 ± 7 μM respectively. From these results the average adsorbed NH_4^+ in Rm sediment is

about 51.6 % of the total NH_4^+ concentration. The actual observed results are given in the appendix.

The adsorbed NH_4^+ fraction for Ct sediments was found to be relatively low as compared to the Rm sediments. A maximum of about 10 ml 1N KCl was found to be enough for total extraction of NH_4^+ . In both seasons the adsorbed fractions (figures 4.25A and 4.25B) were found to be only about 15 % implying that 85 % of the total NH_4^+ in Ct sediments existed as free ammonium.



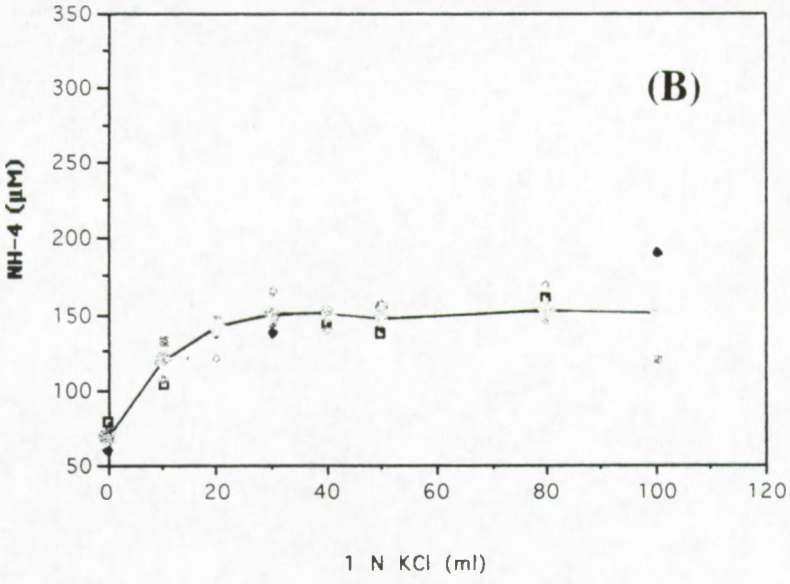
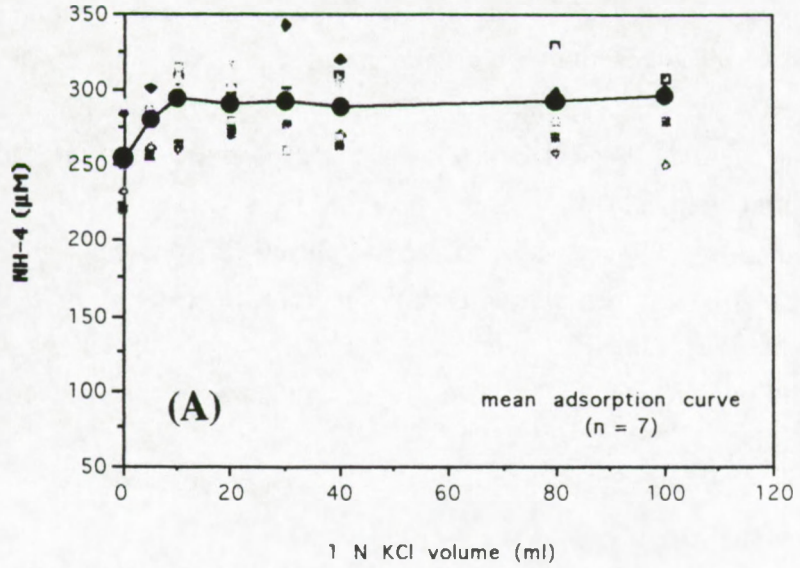


Fig. 4.24 (A & B): Adsorption curve for Rm sediments during dry (Jan., 1992: n = 7) and rainy (May, 1992: n = 5) seasons. The full line gives the average values from all the experiments conducted in that season. Ammonium concentrations at 0 ml KCl corresponds to free interstitial NH_4^+ obtained by squeezing the sediments.



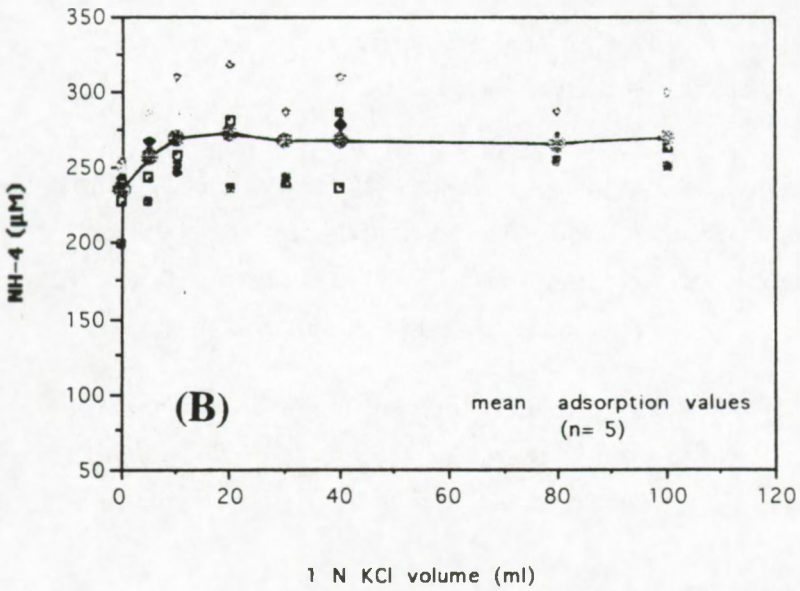


Fig. 4.25 (A & B): Adsorption curve for Ct sediments during dry (Jan., 1992: n = 7) and rainy (May, 1992: n = 5) seasons. The full line gives the average values from all the experiments conducted in that season. Ammonium concentrations at 0 ml KCl corresponds to free interstitial NH_4^+ obtained by squeezing the sediments.

4.1.2.1.5 Redox potential (Eh) in Rm and Ct sediments

Redox reactions in sediments very seldom reach equilibrium and are seldom reversible due to the continuous biological activity. The redox state of a natural environment is the result of a variable number of redox reactions which may proceed independently of each other. What is therefore measured in a natural environment is of little value for quantitative chemical calculations (Stumm, 1966). However, the redox potential gives information on the kind of chemical and biological reactions that take place. Therefore the redox state of a sediment is a valuable measurement when characterising an environment for ecological purposes. In coastal marine sediments, usually only the uppermost layer of the sediment exhibits oxidizing conditions while the rest is reduced (Henriksen, 1980; Hall, et al., 1989; Hallberg, 1992). The thickness of the oxidized layer and the reducing capacity of the sediment below depend on;

1. The concentration of oxygen in the overlying water
2. The rate of oxygen penetration into the sediment
3. The accessibility of utilizable organic matter for the bacterial activity.

Though the inflection point of the redox gradient, constituting the boundary between oxidising and reducing environments in sediments lies at around +250 mV, Hallberg (1992) suggested a range of +250 ± 50 mV would be more correct due to natural variations. This implies that soils whose redox potential values lie below +200 mV, should be considered to have reducing capacity.

McKee et al. (1988), investigating on physico-chemical parameters of sediment colonised by mangrove vegetation observed a positive correlation between soil redox potentials and the presence of the aerial roots of mangrove trees. Soil redox potentials near the aerial roots were always found to be higher than in the adjacent sediment.

The work of Scholander et al. (1955) demonstrated that aerial roots, i.e. the pneumatophores of *Avicennia germinans* and the prop roots of *Rhizophora* mangle, serve as conduits for oxygen flow from the atmosphere to the roots growing into the anaerobic soils.

Apart from the oxygen supplied by these roots into the sediment, Kristensen et al. (1988), working on benthic community metabolism in a south-east Asian mangrove swamp, observed that diffusion rates of oxygen into sediments are higher when the sediments are exposed than when they are covered by water. Though this dissolved oxygen is usually

limited to the upper 1 cm depth, the overall oxidation effect can be detected up to about 10 cm depth (Revsbech et al., 1980).

In order to know the reducing capacity of our two mangrove sediment types (Rm and Ct), redox potential profiles were determined from 10 randomly selected cores from the two plots. The potential of a calomel reference electrode (+244 mV) was added to each value to calculate Eh.

Figure 4.26 gives the average profiles obtained from each plot. From the two redox potential profiles, Ct sediments are seen to be relatively more oxidized.

Ct sediments are covered by water only during spring tides. This means unlike the Rm sediments, these sediments are exposed to air most of the time. The relatively high redox potentials found in Ct sediments could therefore be a result of the long exposure (to air) periods of these sediments making them relatively more oxidized (Kristensen et al., 1988; Revsbech et al., 1980). Researchers at the Wetland Biogeochemical Institute, USA, are currently carrying out experiments to determine whether different mangrove species could also have different rates of oxygen leakage from their roots which could also influence the redox conditions differently (McKee, 1993).

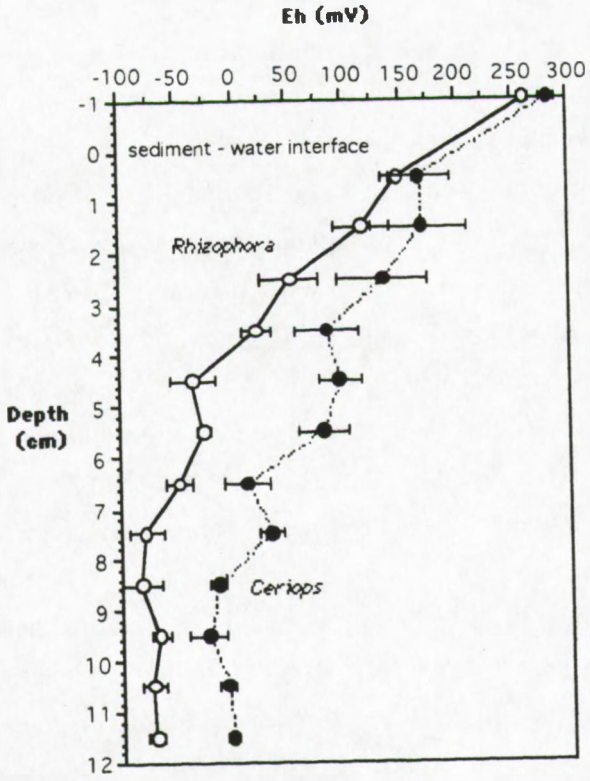


Fig. 4.26: Mean (± S.D.) redox potential values (Eh) of 10 randomly selected subplots within the Rm and Ct field plots.

4.1.2.1.6 Discussion on the physico-chemical characteristics of Rm and Ct sediments

Due to the high percentage of sand in Ct sediments these sediments have a relatively higher density (1.48 to 1.91 g cm^{-3}) than that of Rm sediments (1.34 to 1.48 g cm^{-3}) when considering the upper 12 cm depth. The water content in Rm sediment is found to be much higher (50 to 68 %) than that of Ct sediments (24 to 48 %) implying that care has to be exercised while comparing nutrient stocks in terms of mass per unit volume. The two sediment types also displayed different salinity profiles. While salinity in Rm sediments did not indicate any tidal influence, Ct sediments responded to tidal (or flooding) frequency. At neap tide when the Ct sediments are exposed for long duration without flooding, salinity and temperatures were found to rise significantly. The salinity values in Ct sediments therefore oscillated between 46 ± 5 psu (at spring tide) and 57 ± 2 psu (at neap tide) for the upper 4 cm depth during the dry season (fig. 4.21). Temperature for the same sediments (Ct) varied from 29 ± 3 °C at spring low to as high as 39 ± 3 °C at neap tide in the same season (fig. 4.23B). For the Rm sediments not much variation was noticed with the change of tides and salinity and temperature values were averagely 38 ± 1 psu (fig. 4.20) and 25 ± 1 °C (fig. 4.23A) respectively during dry period. During wet (rainy) season salinities were generally lower for both field plots with Ct sediments registering bigger difference with dry season due to a more pronounced effect of rain on exposed surface during neap tide.

Seitzinger et al. (1991) working on the effect of salinity on ammonium sorption on aquatic sediments concluded that competition for cation exchange site by ions in sea water is a factor responsible for the lower exchangable ammonium concentrations in marine sediments as compared to fresh water. Salinity fluctuation in the Rm sediments during dry and rainy season were hardly above 3 psu. This fluctuation range is probably quite low to influence changes in adsorption capacity of the sediment, hence the lack of significant differences (ANOVA: $p > 0.05$) in exchangeable ammonium concentrations observed between both seasons. In both seasons, about 52 % of the total NH_4^+ in the sediment was adsorbed on sediment. However, for Ct sediments, only about 15 % of the total NH_4^+ is adsorbed implying that a bigger percentage of the total NH_4^+ is free in pore water. Using the conclusions of Seitzinger et al. (1991), this could be explained by the slightly elevated salinity concentrations in these sediments. However, another explanation on these observed differences in adsorption capacities of the two sediments could be given based on the redox state of the sediments in question. Redox potential profiles of the two sediments indicate that Ct sediments are more oxidized than Rm sediments. Middelburg et al. (in press)

demonstrated that oxidized environments could have a net effect of increasing the acidity of mangrove sediments through the following reactions;

$CH_2O + O_2 \rightarrow H_2CO_3$ (1); respiration

$NH_3 + 2\,O_2 \rightarrow HNO_3 + H_2O$ (2a); nitrification

$H_2S + 2\,O_2 \rightarrow H_2SO_4$ (2b); sulphide oxidation

$FeS_2 + 3.75\,O_2 + 2.5\,H_2O \rightarrow FeOOH + 2\,H_2SO_4$ (2c); sulphide oxidation

Since redox potential values for Ct sediments indicate a more oxidizing environment, these sediments are therefore expected to be more acidic than the Rm sediments. Indeed Middelburg et al. (in press) observed a pH between 3 and 7 for these Ct sediments while Rm sediments had a pH of mostly between 7 and 8 and concluded that the more acidic conditions found in *Ceriops tagal* sediments are mostly due to lack of buffering effect caused by low calcium carbonate in these Ct sediments.

Since as indicated earlier, cations in sediments are held and displace one other in the sequence;

$$\mathbf{Al^{3+} > H^{+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+}}$$

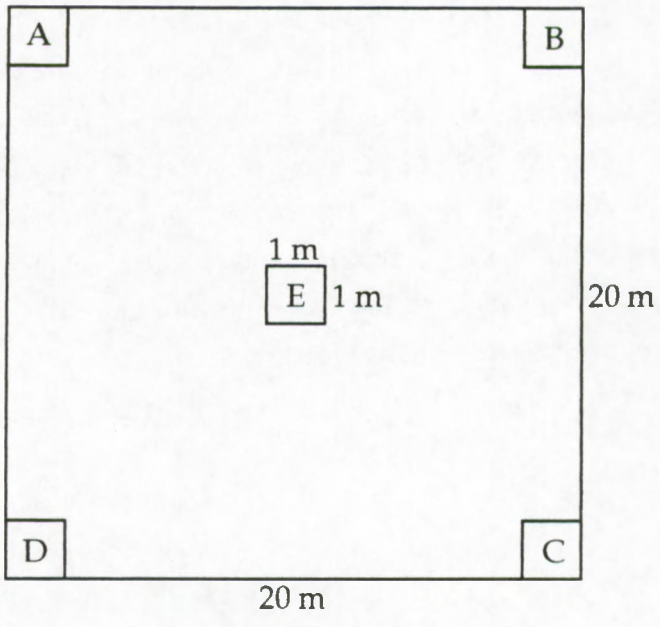
the more acidic conditions in Ct sediments would always favour displacement of the NH_4^+ ion hence possibly resulting to a lower percentage of adsorbed ammonium in the pore water of these sediments compared to that of Rm sediments.

Mackin and Aller (1984) on their investigation of ammonium adsorption in different marine sediments, found a very constant ratio of 1:1.3 between free and ionically-bound ammonium for many different sediments. Adsorbed NH_4^+ in our Rm sediments is about 52 % implying that our ratio of free to ionically - bound NH_4^+ is 1:1.08 which is close to that observed by the mentioned authors. However, our ratio of free to ionically bound NH_4^+ in Ct sediments is found to be 1:0.18 which is very different from that of Rm sediments. Blackburn and Henriksen (1983), working on sediments from Danish coastal waters found a much wider variation (1: 5 to 17) than that reported by Mackin and Aller (1984) but had no explanation for their values (Blackburn, 1986). The big variation of adsorbed NH_4^+ between Rm and Ct sediments could therefore stress on the role of acidity in regulating the stock of free NH_4^+ ions in mangrove sediments.

4.1.2.2 Nitrogenous stocks (NH_4^+, NO_3^-+ NO_2^-) in *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) sediments

4.1.2.2.1 Spatial distribution within the study plots

In order to investigate on the nutrient (NH_4^+, NO_3^- + NO_2^-) stock in our study plots, five 1m x 1m subplots were established within the two study plots. These subplots were numbered as A, B, C, D and E as shown below:



Six core samples (plexiglass cores I.D. 3.6 cm, height 25 cm) were taken randomly from each subplot. Immediately after sampling, one core from each plot was used for redox potential determination using a platinum electrode with calomel reference. This was done within two hours of sample collection. The remaining twenty five cores from the five subplots were rushed to the laboratory (two hours drive) where they were sectioned into 0 - 1, 1 - 2, 2 - 4, 4 - 6, 6 - 8, 8 - 10 and 10 - 12 cm sections. Corresponding sections of one core from each subplot were pooled together and mixed thoroughly and used for porosity and density determinations. All the other segments were extracted individually with corresponding volumes of potassium chloride (40 ml 1 N KCl : 10 g sediment) under nitrogen gas as explained in chapter 3. The ammonium pool obtained represents total ammonium (free + ionically-bound) concentrations.

Ammonium stock and its spatial distribution within the Rm sediments

Total ammonium concentrations in the Rm sediment for the upper 12 cm section were found to vary between 100 and 200 μM. Figures 4.27A to E give ammonium profiles of individual cores taken from each subplot. Cores from suplots A and D in Rm plot were taken from an area with a dense network of fine roots as compared to cores from suplots B, C and E. Based on this and the nitrate profiles, results from these cores were averaged together to form two groups; namely the A and D group and the B, C, E group.

Fig. 4.28 shows the average NH_4^+ profiles from subplot A and D and those obtained from the average of subplot B, C and E (excluding standard deviation). These two profiles were not only similar but almost coinciding. The average NH_4^+ concentration profile (including standard deviation) of all the cores sampled (20 cores) was found to fit well between the first two profiles. One clear observation noticed from these profiles was that the NH_4^+ concentrations in the upper 12 cm depth of Rm sediment varied between 100 and 200 μM with the maximum always observed between 1 and 2 cm depth followed by a gradual decrease with depth. One other characteristic noticed with the NH_4^+ profile was the high standard deviation: between 10 to 30 % of the observed concentration. This stresses on the fact that even within a one by one meter subplot standard deviation on sampled cores could be as high as 30 % of the concentration measured. On the average, the results obtained indicate that cores taken from any part of the plot would give a representative NH_4^+ profile of the general area.

Previous experiments on adsorption capacities of the Rm sediments (section 4.1.2.1.4) indicate that upto about 52 % of this total ammonium concentration (free and ionically-bound NH_4^+) is adsorbed and only about 48 % is free within the interstitial water.

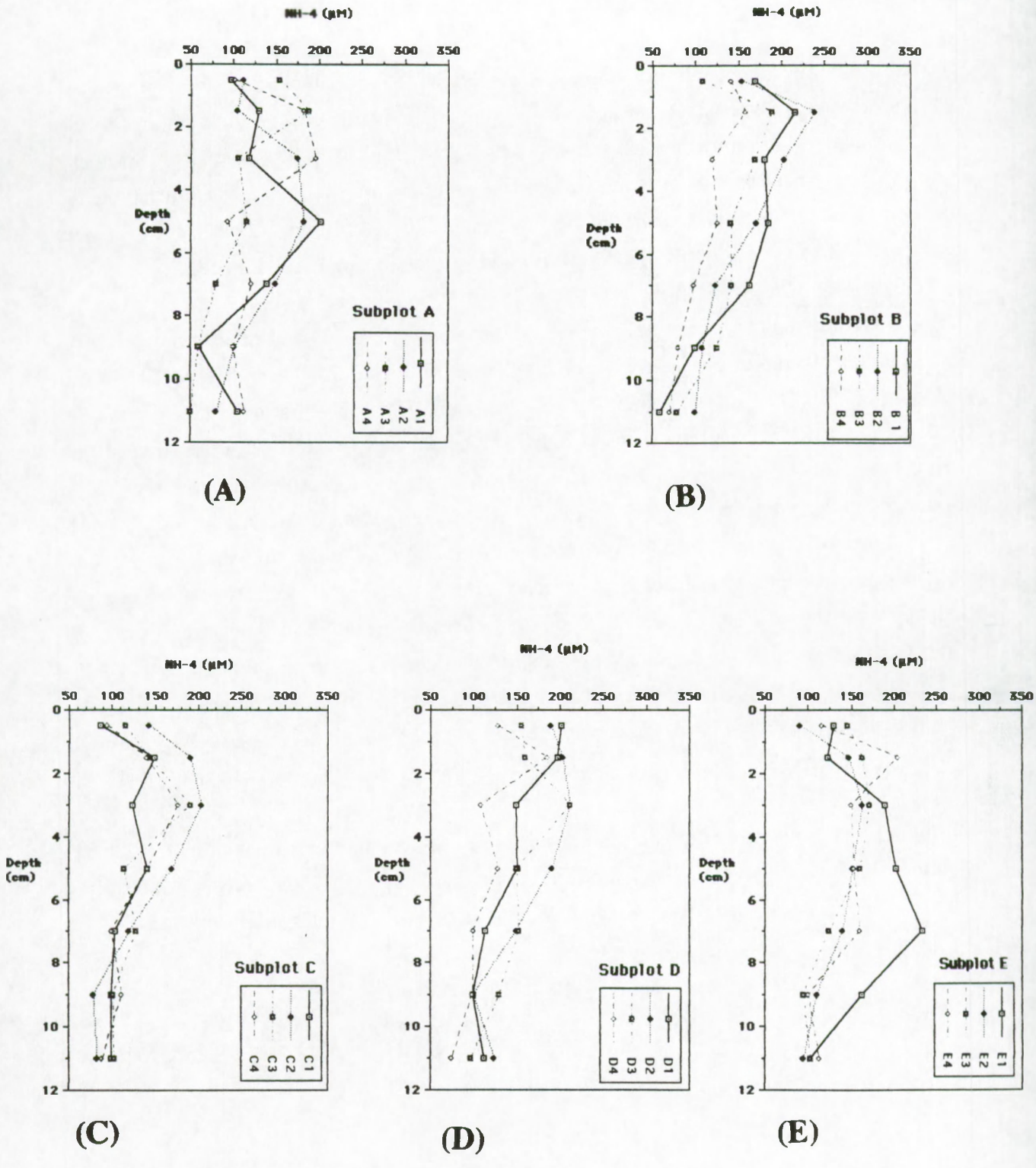


Fig. 4.27 (A - E): Vertical profiles of ammonium concentrations in subplots A, B, C, D and E observed in Rm sediments.

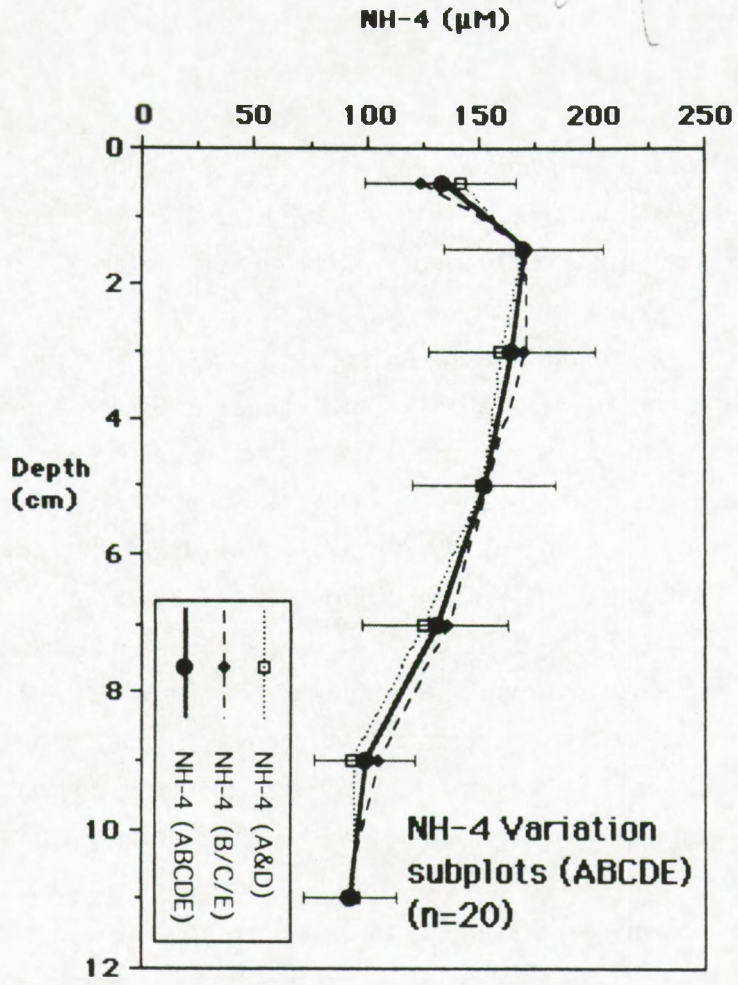


Fig. 4.28: Average total ammonium (free + adsorbed) profiles for subplots A & D and B, C and E in Rm sediments. A profile giving average values (including S.D.) for all the 20 cores analysed is also shown.

Nitrate (+ nitrite) stock and its spatial distribution within the Rm study plot

Unlike the ammonium profiles, nitrate profiles exhibited two distinct patterns. All cores taken from subplots A and D (figs. 4.29A and B) displayed a maximum at between 2 and 5 cm depth. Cores taken from subplots B, C and E (fig. 4.29C, D and E) were found to have a different type of profiles with high concentrations found at the top section and decreasing sharply with depth. As explained earlier, samples from sub-areas A and D were characterized by the presence of a dense root network as compared to sub areas B, C and E. Nitrate profiles from subplot D (fig. 4.29B) indicate that even within a one by one square meter plot, nitrate concentration might be very different despite having the same profile pattern. Core D 3 indicates a maximum peak value of ca. 7.50 μM while core D 4 has a sub-surface maximum concentration of ca. 2.0 μM at similar depth. This stresses on the fact that even on an area with roots, the biomass of the live roots or proximity of the sampling spot to the roots may result in registering different concentrations within a closeby vicinity. Figure 4.30 gives profiles for mean nitrate values for subplots B, C, E and A and D in which, apart from the surface section whose concentrations are statistically not different (ANOVA: $p = 0.051$; $n = 20$), the other concentrations of the two groups were significantly different ($p < 0.05$) at corresponding sections below the 2 cm depth. The lack of statistical difference in nitrate concentrations at the surface (0 - 1 cm) may imply that while the nitrate concentrations below the surface may depend on the presence or absence of roots to transport O_2 to the anaerobic sediment, the surface nitrate mostly depends on molecular diffusion of oxygen from the water column into the sediment hence the lack of significant statistical difference between groups A&D and B, C, E for the upper 1 cm. Figure 4.34 also displays the average nitrate profile (including standard deviation) obtained from all the twenty cores. The difference in profile patterns obtained between the cores from subplots A and D and those from B, C and E, and the high standard deviation (almost 100% between 3 and 5 cm depth) observed when pooling all the results together, confirm that, unlike the ammonium stock, a few cores taken randomly from a mangrove sediment biotope can not be used to give a general nitrate profile of the area. Since the two different profiles obtained for nitrate did not affect the general profile of ammonium pool (fig. 4.28), this may suggest that nitrification due to oxygen supply by roots is also of less magnitude and does not affect the ammonium profile significantly. However, any effect on the ammonium pool could easily be masked by the high standard deviation noticed on ammonium concentrations.

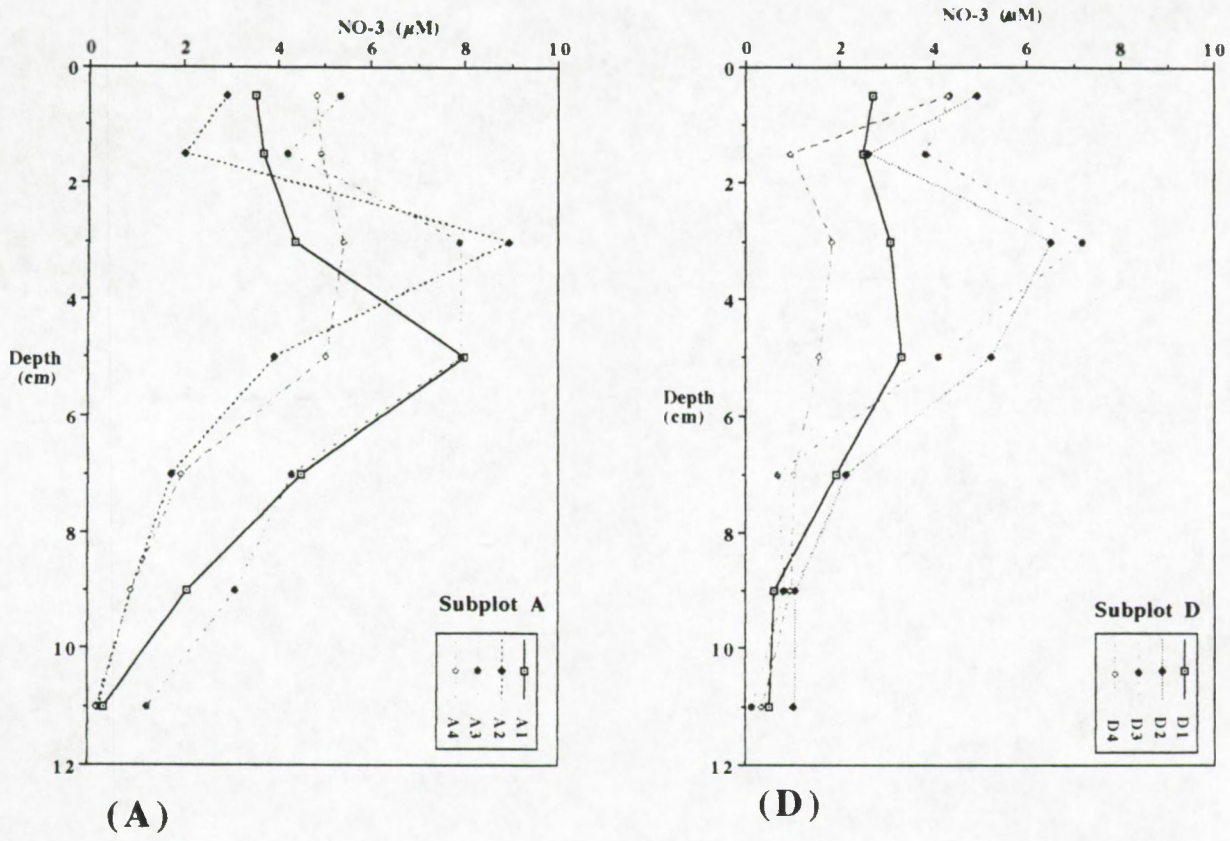


Fig. 4.29 (A & D): Nitrate (+ nitrite) profiles for Rm sediments as obtained from individual cores on subplots A and D.

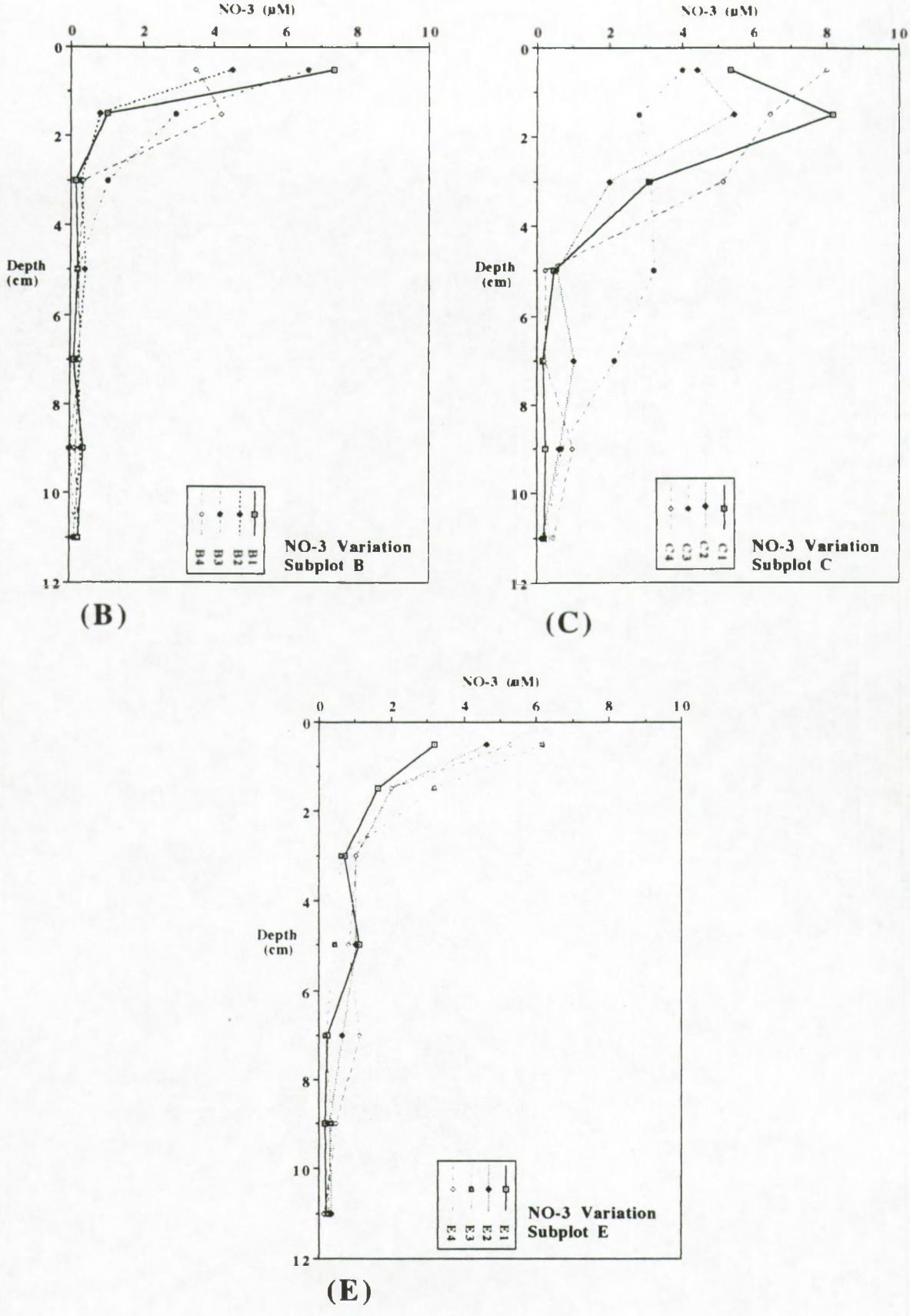


Fig. 4.29 (B, C & D): Nitrate (+ nitrite) profiles for Rm sediments as obtained from individual cores on subplots B, C and D.

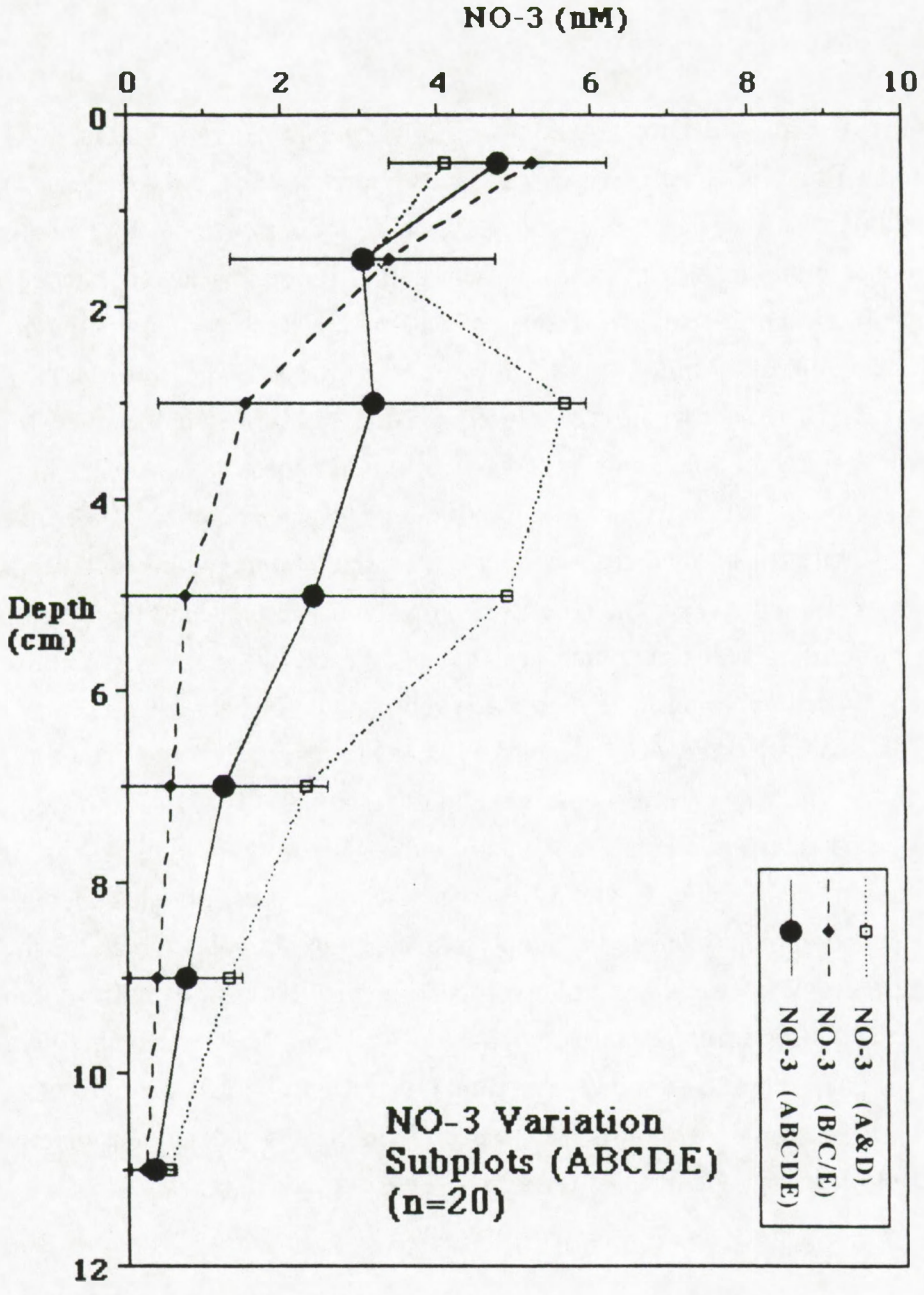


Fig. 4.30: Average nitrate (+ nitrite) profiles from subplots A & D and B, C and E. The average profile (± S.D.) for all the five subplots (ABCDE) is also displayed.

Redox potential profiles within the Rm sediment taken concurrently with nutrient stocks

Figure 4.31 displays the redox potential profiles (Eh) obtained in subplots A, B, C, D and E within the Rm plot. In all five cases, redox potential within the water column (1 cm above sediment surface) was between +250 and +300 mV indicating relatively higher oxygen concentrations. However at 0 - 1 cm depth, the redox potential dropped to about +150 mV. In all the profiles we notice a steady decrease of redox potential up to 6.5 cm depth (for profiles B, C and E) and 7.5 cm depth (for A and D profiles) where it then remains at $\leq$ -50 mV down to 12 cm depth. Note that core C displayed higher redox potential between the 1 and 4 cm depth than all the other cores despite being in the subplots considered to be roots-free as that of subplot B and E. McKee et al. (1988), investigating on physico-chemical parameters of sediment colonised by mangrove vegetation, observed a positive correlation between soil redox potentials and the presence of the aerial roots of mangrove trees. Soil redox potentials near the aerial roots were always found to be higher than in the adjacent sediment. The increase of redox potential between the 1 and 4 cm depth in core C is also most likely due to fine roots since nitrate profiles from subplot C were also slightly higher than those from subplots B and E (figs. 5.30 C & D). From figure 4.35, we find that below 1 cm depth redox potential values for cores A and D start being more positive than those of cores B and E (disregard core C profile). This increase of redox potential is most probably due to the supply of oxygen by the roots hence the higher nitrate concentrations at 2 - 5 cm depth noticed for nitrate profiles from subplots A and D. Note that while the widest difference in redox potential was found between 5 and 7 cm depth, the nitrate maxima in subplots A and D were found at a slightly upper depth (2 - 5 cm depth). Potential nitrification experiments in Rm sediments (discussed later) indicate significant reduction of nitrifiers bacterial biomass below 4 cm depth.

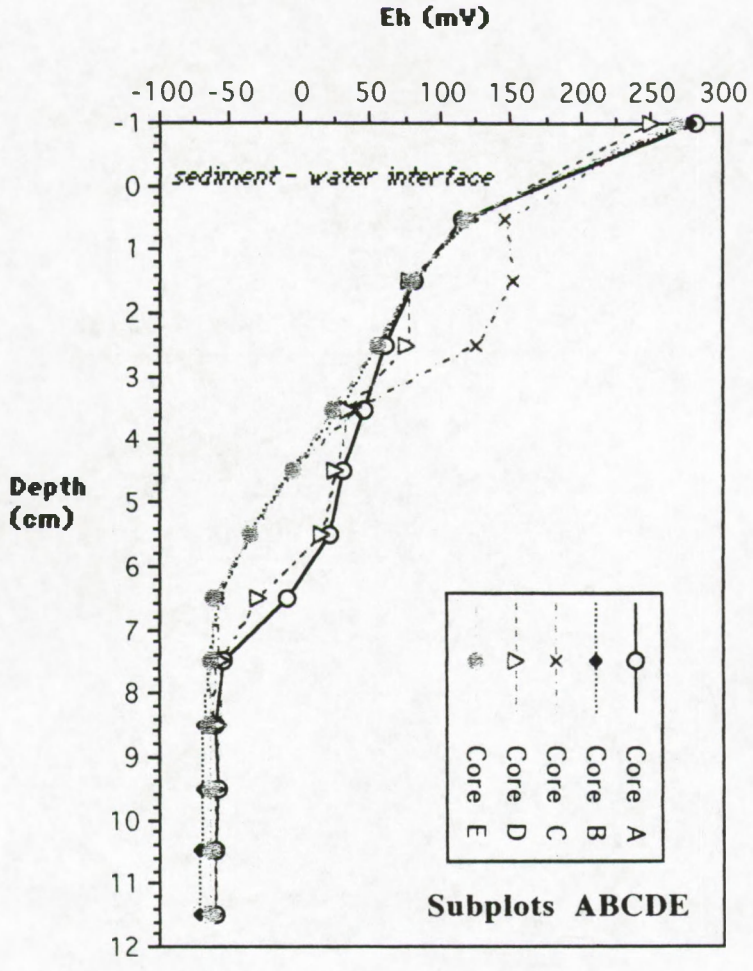


Fig. 4.31 : Redox potentials (mV) of Rm sediments as observed in subplots A, B, C, D and E.

Ammonium stock and its spatial distribution within the Ct plots

Ammonium variations in the five individual subplots within the Ct plot were more-or-less the same as those displayed for the Rm sediment. The mean vertical NH_4^+ profile (fig. 4.32) was similar to that of Rm sediment except that ammonium concentrations were higher (varying mostly between 100 and 300 μM) with an average maximum of about 260 ± 55 μM at about 2 cm depth. The adsorption capacity of Ct sediments (section 4.1.2.1.4) indicates that, unlike the Rm sediments about 85 % of this total ammonium pool is free within the interstitial pool while only ca. 15 % is adsorbed.

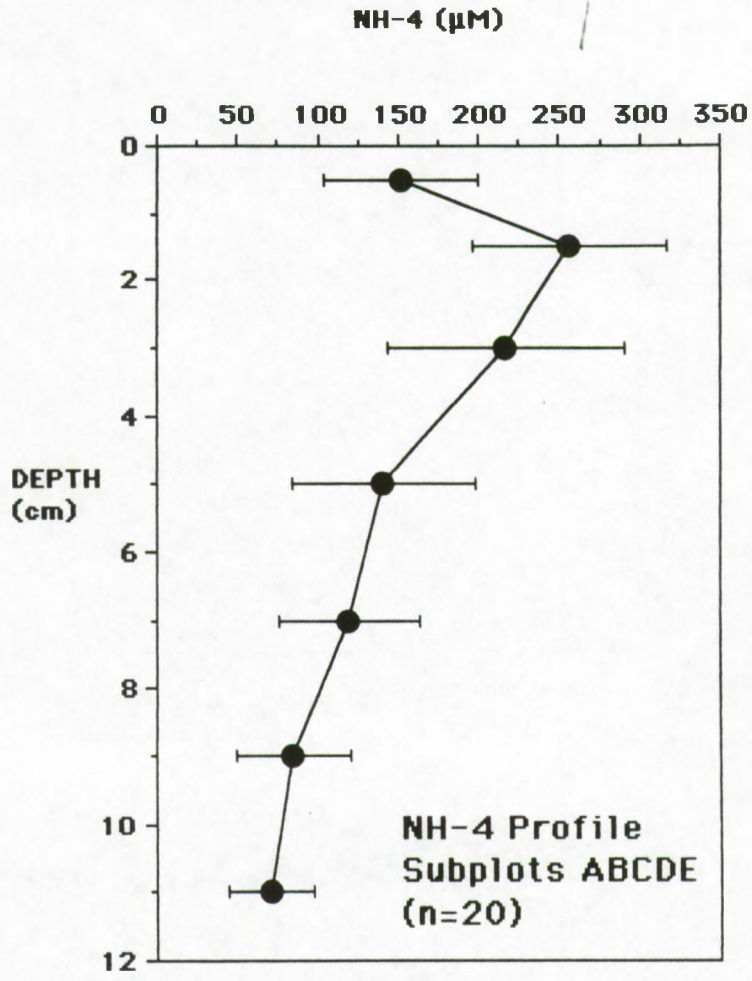


Fig. 4.32: Average (± S.D.) ammonium profile for all the 20 cores sampled at the Ct plot.

Nitrate stock and its spatial distribution within the Ct study plot

Unlike the Rm sediments, all NO_3^- + NO_2^- profiles for the Ct sediments indicated a sub-surface peak mostly between 1 and 5 cm depth (figs. 4.33 A - E). The nitrate profiles from the Ct plot displayed slightly higher concentrations with values as high as 30 μM. However, it is noted that the water contents for the two sediments are different (section 4.1.2.1.1) and so as stated earlier, direct comparisons of NH_4^+ and NO_3^- + NO_2^- can not be made without considering porosities of the two sediment types.

Fig 4.34 gives the nitrate profile (including S.D.) for all the twenty cores sampled. Maximum concentrations are found to lie between 1 and 4 cm depth. The high standard deviations noticed are also most probably due to differences in a core's proximity to a root system.

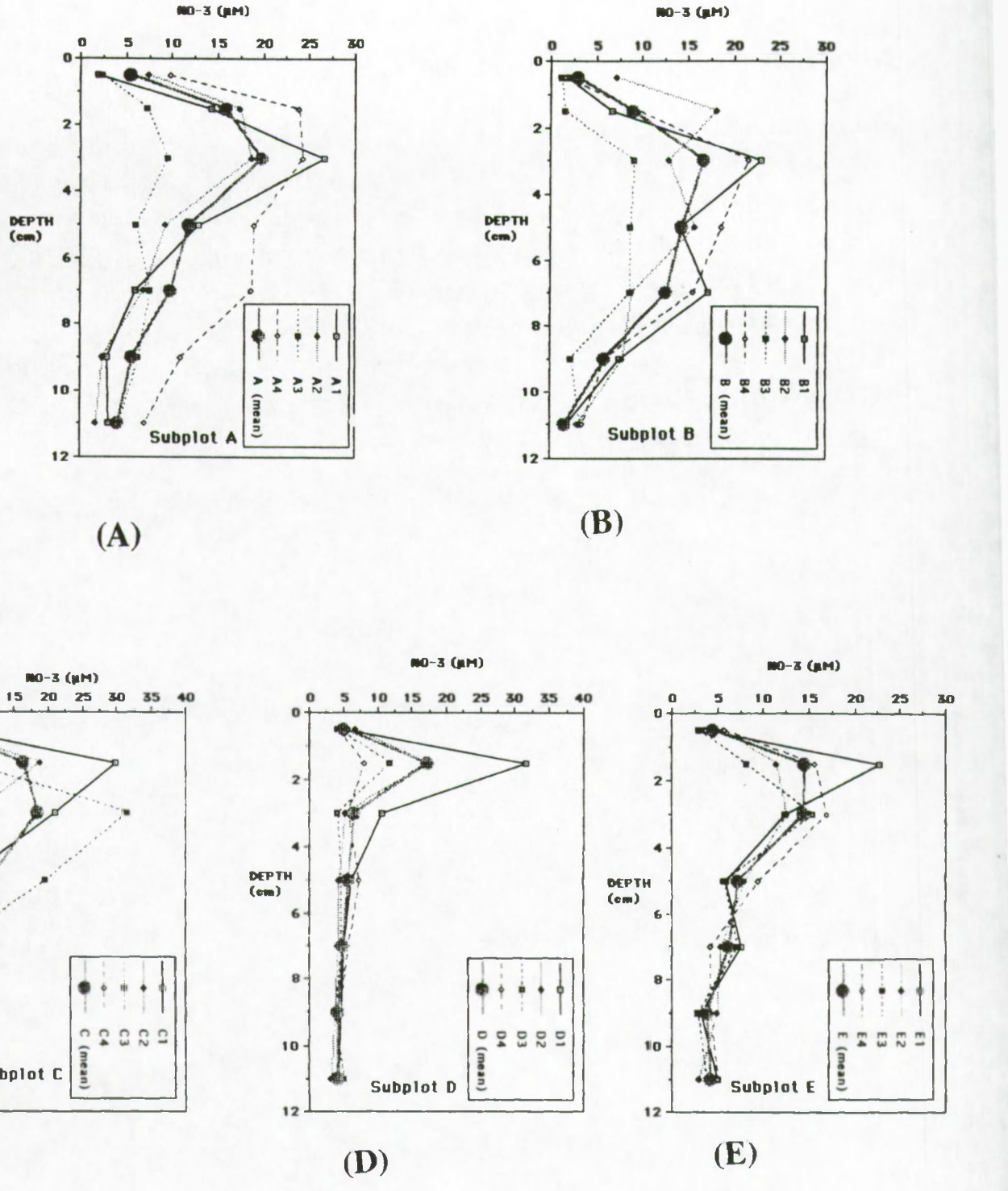


Fig. 4.33 (A - E): Nitrate (+ nitrite) profiles observed in all individual sediment cores taken from subplots A, B, C, D and E of Ct plot.

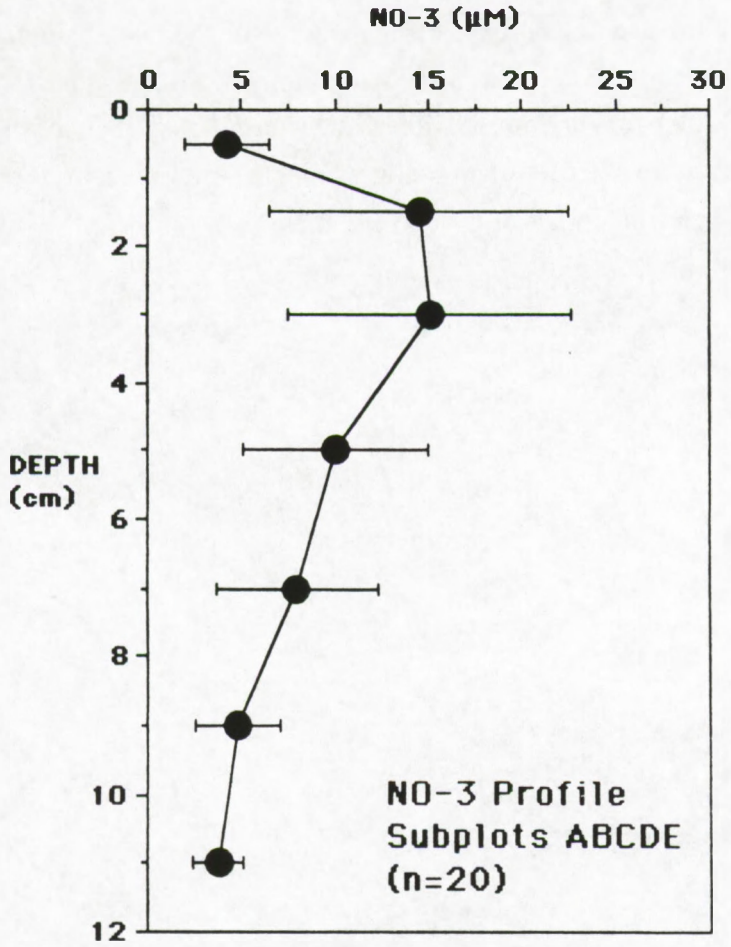


Fig. 4.34: Average nitrate (+ nitrite) profile (including S.D.) for all the 20 sediment cores sampled at the Ct plot.

Redox potential profiles in sub-plots within the Ct sediments

Redox potential values for the five sub-plots (fig. 4.35A) were again found to be higher than those found in Rm sediment indicating that the Ct sediments are more oxidizing. Fig. 4.39B again displays the average redox potential values for the two sediment types where the Ct sediments are clearly seen to be more oxidizing. An obvious question at this stage would be: If the Ct sediments are more oxidized why don't they display higher absolute nitrate concentrations compared to the Rm sediments ? This question will be addressed after examining the nitrification potentials of the two sediments.

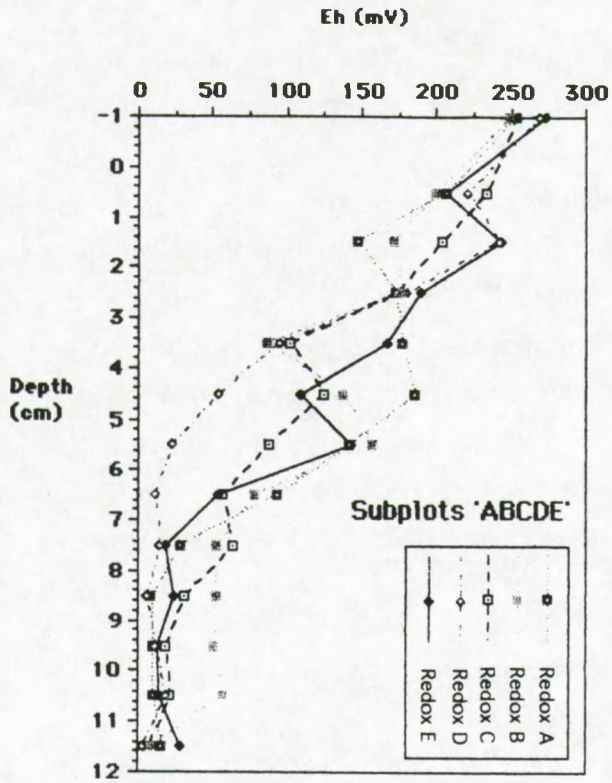


Fig. 4.39A : Redox potential values (mV) for the five sampled subplots (ABCDE) at *Ceriops tagal* plot.

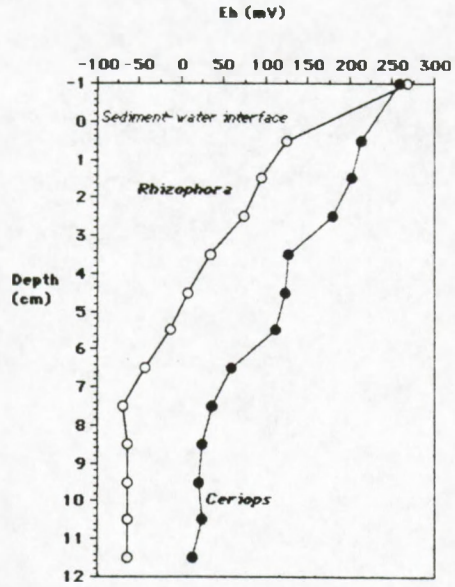


Fig. 4.39B : Average redox potential values (mV) for the Rhizophora and Ceriops sediments of Gazi Bay.

4.1.2.2.2 Seasonal (dry and wet) variations of nitrogenous stocks (NH_4^+, NO_3^- + NO_2^-) in Rm and Ct sediments

From the spatial distribution of the nitrogenous stocks in our study plots (section 4.1.2.2) it was clearly seen that profiles taken from any position within the plots gave representative NH_4^+ concentrations, while NO_3^- + NO_2^- profiles depended on proximities to a root network. In order to monitor seasonal changes of the nitrogenous stocks (NH_4^+, NO_3^- + NO_2^-) in Rm and Ct sediments, samples for the upper 4 cm depth were collected every other day from the two plots during dry (January/February) and rainy (May/June) periods of 1993 and 1994 for a duration of 30 days (each time) during low tidal periods of both spring and neap tides. Only interstitial (pore water) solutions were considered for the seasonal fluctuation studies.

Seasonal variation of NH_4^+ and NO_3^- + NO_2 in Rm sediments

Samples for the dry season of 1993 were collected for 30 days between January 5th and February 3rd while those of 1994 were collected between January 14th and February 12th. Samples for wet season were collected between May 6th to June 4th and May 10th to June 9th in 1993 and 1994 respectively. Comparison of the dry season results of 1993 (included in appendix) and those of 1994 (used for discussion) indicate no significant difference in NH_4^+ and NO_3^- + NO_2^- (ANOVA: $p > 0.05$) concentrations during the two dry periods. Comparison of the ammonium (fig. 4.36) and nitrate (fig. 4.37) results for dry and wet seasons, respectively, of 1994 also indicated no significant seasonal differences (ANOVA: NH_4^+: $p = 0.595$ and NO_3^- + NO_2^- : $p = 0.576$).

NH_4^+ concentrations in the upper 4 cm depth of Rm sediments were averagely 71 ± 10 μM during dry season and 69 ± 10 μM during wet season while NO_3^- + NO_2^- concentrations were far much less being averagely 2.5 ± 0.5 μM during both seasons.

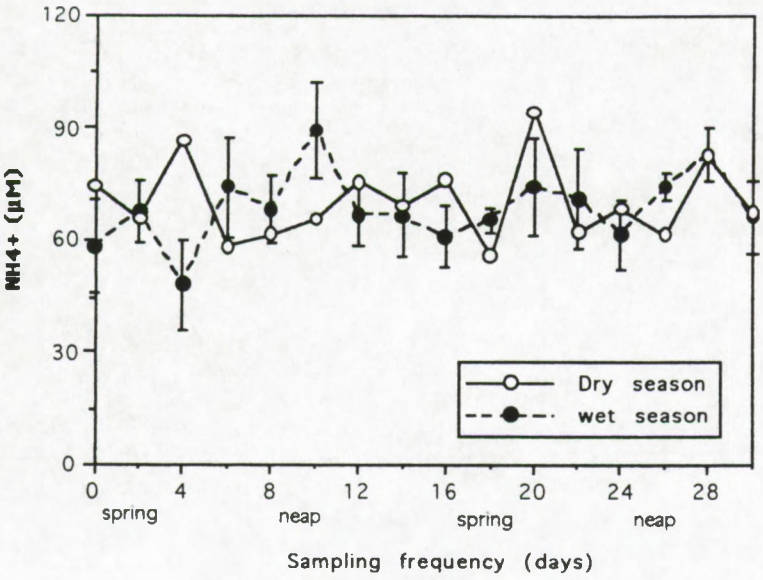


Fig. 4.36: Daily ammonium fluctuations in Rm sediments (upper 4 cm depth) during dry (14th Jan. to 12th Feb.) and rainy (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and rainy periods respectively.

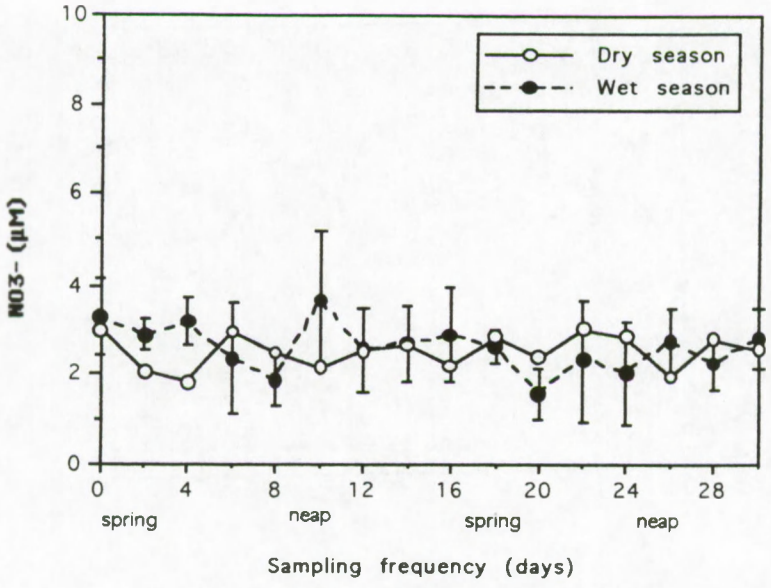


Fig. 4.37: Daily NO_3^- + NO_2^- fluctuations in Rm sediments (upper 4 cm depth) during dry (14th Jan. to 12th Feb.) and rainy (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and rainy periods respectively.

Seasonal variation of NH_4^+ and NO_3^- + NO_2^- in Ct sediments

For Ct sediments, both NH_4^+ and NO_3^- + NO_2^- were found to respond more to tidal inundation than to seasons. At spring tide, in dry season, NH_4^+ values were mainly between 150 and 200 μM but increased to about 275 μM at neap tide (fig. 4.38). For NO_3^- + NO_2^-, concentrations were between 15 and 20 μM at spring tide but increased to between 25 and 30 μM at neap tide (fig. 4.39). This increase was mainly due to evapotranspiration since salinity (fig. 4.21) also appeared to respond similarly. During rainy season, the tidal responce was not well defined due to less evapotranspiration effect.

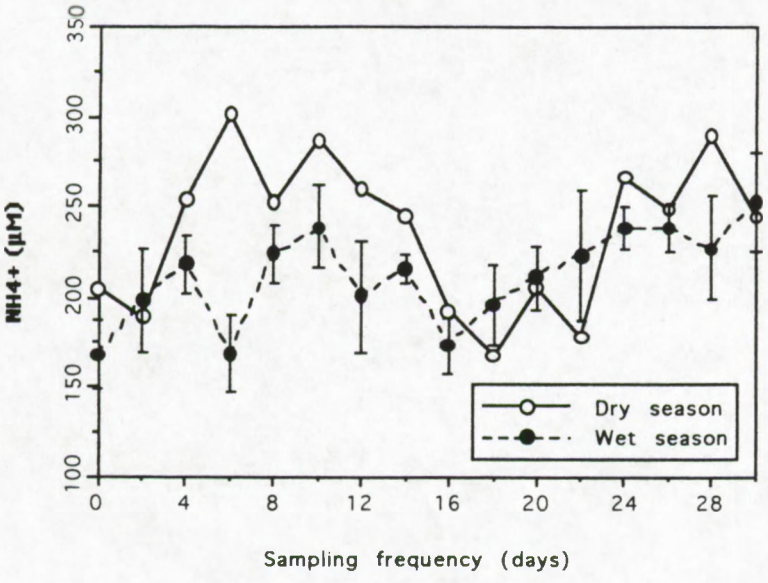


Fig.4.38: Daily ammonium fluctuations on Ct sediments (upper 4 cm depth) during dry (14th Jan. to 12th Feb.) and rainy (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and rainy periods respectively.

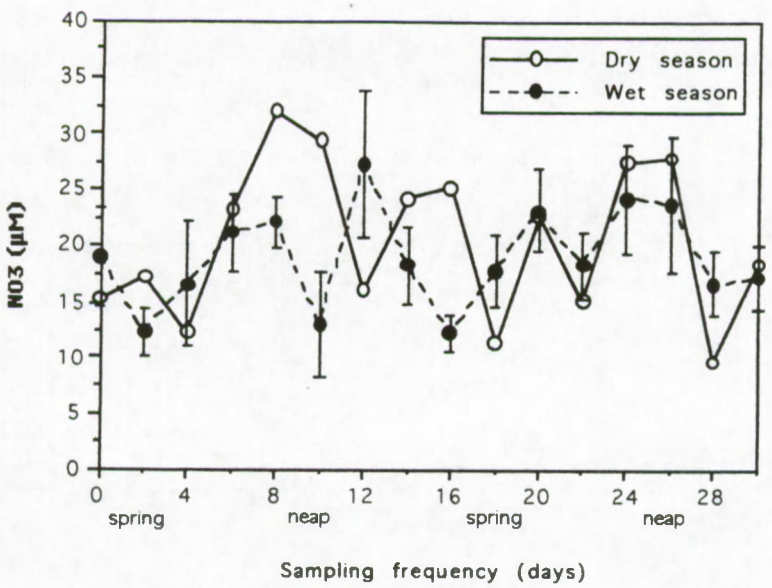


Fig. 4.39: Daily NO_3^- + NO_2^- fluctuations on Ct sediments (upper 4 cm depth) during dry (14th Jan. to 12th Feb.) and rainy (10th May to 9th June) seasons of 1994. Day 0 corresponds to sampling date 14/01/94 and 10/05/94 for the indicated dry and rainy periods respectively.

4.1.2.3 Discussion of the nitrogenous stocks in Rm and Ct sediments

Average total concentrations (free + ionically-bound) of NH_4^+ in Rm sediments were found to lie between 100 and 200 μM with a peak always observed at about 2 cm depth. The adsorption capacity of the Rm sediments indicates that about 52 % of this total ammonium pool is adsorbed giving an average value of between 48 and 96 μM as free NH_4^+ in interstitial water for the upper 12 cm depth. Investigation of seasonal variation of this stock between dry and wet (rainy) periods indicate no significant variation (ANOVA: $p > 0.05$) with seasons for the upper 4 cm sediment depth.

Concentration levels of NO_3^- + NO_2^- were found to be significantly lower than those of NH_4^+ and hardly went above 4 % of the NH_4^+ concentration. However, two types of NO_3^- + NO_2^- profiles were identified in Rm sediments. Samples taken close to a root-

network indicated sub-surface peaks of NO_3^- + NO_2^- while those taken from the same plot but away from a dense root network indicated a sharp decrease below 1 cm depth. Though significant variations (s.d. > 100 %) were noticed for NO_3^- + NO_2^- concentrations below 1 cm depth in various subplots within the Rm sediment, the surface 0 - 1 cm nitrate concentrations were not significantly different (ANOVA: $p = 0.051$). This may imply that while the sub-surface nitrate concentrations could depend on absence or presence of a root network, the surface concentrations mainly depend on the molecular diffusion from the overlaying water assuming uniform removal rates by other heterotrophic processes.

No significant (ANOVA: $p = 0.595$) seasonal variation of NO_3^- + NO_2^- stock was noticed for the upper 4 cm of the Rm sediment . The concentrations were averagely 2.5 ± 0.5 μM for both seasons.

For the Ct sediments, the total NH_4^+ concentration was found to lie between 100 and 300 μM levels for the upper 12 cm sediment with peak values found between 1 and 2 cm followed by a gradual decrease. However, unlike the Rm sediments, the adsorption capacity of the Ct sediments indicates that only about 15 % of this total NH_4^+ is adsorbed giving average values of between 85 and 255 μM as being free NH_4^+ in Ct interstitial water. The relatively low adsorption capacity of the Ct sediments, is attributed to the relatively high acidic conditions caused by poor $CaCO_3$ buffering capacity of the sediments (Middelburg et al., in press). Though the concentrations found in Ct sediments appear to be higher compared to those of Rm sediments, the water content of Ct sediment is lower, hence care has to be exercised when making direct comparisons of the absolute stock. During neap tide, the water content in Ct sediments is reduced even further due to the higher evapotranspiration process resulting in elevated nutrient concentrations. However this does not change the absolute stock of the nutrients.

CHAPTER 5

5.0 ORGANIC MATTER DISTRIBUTION IN GAZI MANGROVE BAY

Organic matter in marine environment is known to play a very important role in fuelling most of the oxidation processes in sediments. Degradable material enters the system as a result of terrestrial, littoral, pelagic and occasionally in-situ production. Organic substances from all but the latter of these sources undergo considerable recycling prior to deposition. Once deposited on the bottom sediment, the organic-N is again acted upon by various heterotrophic organisms having ammonium as a by-product. As mentioned earlier, ammonification in sediments generally depends on the quality (C/N ratio) and quantity (stock) of the organic matter (Aller, 1980; Middelburg, 1989). Blackburn (1986) demonstrated that organic matter whose C/N molar ratio is $\geq$ 20 should favour immobilisation with no significant net production of NH_4^+ while organic matter with C/N $\leq$ 20 favours mineralisation.

Calculations of relative contributions of marine and mangrove particulate organic material (POM) of mangrove bays have previously been made using simple two end-member conservative mass balance equations (Flemming et al., 1990; Rezende et al., 1990). However, the situation in Gazi bay is made difficult by the presence of a third component (seagrass) whose relative importance as a carbon and nitrogen source is still not clear. Particulate organic material of marine origin is known to mainly consist of phytoplankton with an average Redfield C/N ratio of 6.6 and $\partial^{13}C$ isotope signature varying between -18.76 and -21.6 ‰ (Fontugne & Duplessy, 1978; Fry & Sherr, 1984; Fontugne & Duplessy, 1991). On the other hand POM associated with mangroves are known to have $\partial^{13}C$ isotope signature of about -27 ± 1 ‰ (Rodelli et al., 1984; Zieman et al., 1984; Rezende et al., 1990; Rao et al.,1993). Seagrasses have been shown to have highly variable $\partial^{13}C$ isotope signature depending on their locations (McMillan et al., 1980; Hemminga et al., 1994). Fleming et al. (1990), reported a range of - 8.7 ± 0.05 to -15.3 ± 1.2 ‰ for seagrasses in south Florida fringe coastal seagrass communities. The slightly more negative values were associated with seagrasses closer to a mangrove effluent. Similar observations were also noticed for Gazi bay, where seagrass closer to the mangrove forest had a $\partial^{13}C$ isotope signature of - 19.65 ± 0.39 ‰ becoming less negative towards the open waters (Hemminga et al., 1994).

In this chapter, we shall examine possible sources of the particulate organic material in Gazi bay in relation to the observed total organic material in Gazi mangrove sediments.

5.1 RESULTS AND DISCUSSION

5.1.1 Particulate organic material (POM) within the water column of Gazi bay

In Gazi bay, particulate organic carbon of suspended material at high tide, increased from ca. 0.3 ± 0.1 mg C/l at the open sea (station G1) to about 0.7 ± 0.5 mg C /l at station K1 (closer to river Kidogoweni). This was accompanied by only a slight increase of particulate organic nitrogen from ca. 0.05 ± 0.01 mg N /l at station G1 to about 0.06 ± 0.02 mg N/l at station K1 (table 5.10A). The C/N atom ratio of POM in the water column of Gazi bay at high tide, therefore varied between about 7 ± 1 at the open sea end to about 13 ± 5 at the upper end of Gazi bay. At high tide the $\partial^{13}C$ isotope signature was also found to decrease from ca. -19.37 ± 0.63 ‰ at the open end to ca. -25.11 ± 0.62 ‰ at the upper end of Kidogoweni creek. Both the C/N molar ratio and the $\partial^{13}C$ isotope signature of the POM in the bay was found not to change significantly during rainy season (table 5.10B). Since the average $\partial^{13}C$ of mangrove leaves of all the eight mangrove species in Gazi bay is -26.66 ‰ (table 5.11), the more negative $\partial^{13}C$ isotope signature found within the creeks can be attributed to mangrove POM.

Table 5.10A: Particulate organic carbon (POC), particulate organic nitrogen (PON), C/N molar ratio and $\partial^{13}C$ isotope signature of suspended POM in Gazi bay as observed in dry season of 1991 to 1993. n = 9 (no. of observations). G1 to K1 are sampling stations indicated earlier (fig. 3.5a).

Item	G1	G2	G3	K3	K2	K1
POC (%)	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.5 ± 0.2	0.6 ± 0.3	0.7 ± 0.5
PON (%)	0.05 ± 0.01	0.05 ± 0.02	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.02	0.06 ± 0.02
C/N	7.0 ± 0.63	7.0 ± 0.59	9.3 ± 2.4	11.7 ± 2.5	11.7 ± 1.4	13.2 ± 4.5
$\partial^{13}C$ (‰)	-19.37 ± 0.63	- 21.34 ± 1.46	- 22.78 ± 1.84	- 23.94 ± 1.23	-25.07 ± 0.57	- 25.11 ± 0.62

Table 5.10B: Particulate organic carbon (POC), particulate organic nitrogen (PON), C/N molar ratio and $\partial^{13}C$ isotope signature of suspended POM in Gazi bay as observed in rainy season of 1991 to 1993. n = 11 (no. of observations). G1 to K1 are sampling stations indicated earlier in fig. 3.5a.

Item	G1	G2	G3	K3	K2	K1
POC (%)	0.3 ± 0.1	0.4 ± 0.2	0.5 ± 0.3	0.5 ± 0.2	0.9 ± 0.5	1.1 ± 0.7
PON (%)	0.05 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.05 ± 0.02	0.08 ± 0.03	0.9 ± 0.04
C/N	7.0 ± 0.72	7.8 ± 1.01	11.7 ± 1.9	11.7 ± 2.5	13.14 ± 3.7	14.25 ± 3.6
$\partial^{13}C$ (‰)	- 20.13 ± 1.01	- 22.41 ± 1.53	- 21.92 ± 1.43	- 23.36 ± 0.93	-25.04 ± 0.99	- 24.87 ± 0.73

Table 5.11: Carbon isotope signature ($\partial^{13}C$ ‰) of mangrove leaves occuring in Gazi bay. Means of 2 samples of pooled (10 to 20) leaves (adapted from Hemminga et al., 1994). And Ran et al.?

Species	$\partial^{13}C$ ‰
Rhizophora mucronata	- 28.25
Ceriops tagal	- 24.12
Sonneratia alba	- 27.15
Avicennia marina	- 26.84
Bruguiera gymnorrhiza	- 27.30
Xylocarpus granatum	- 24.86
Lumnitzera racemosa	- 26.99
Heritiera littoralis	- 27.73
Average $\partial^{13}C$ ‰	- 26.66 ± 1.42

Particulate organic material collected at st. G3 at high and low tides of dry and wet seasons (table 5.12) indicates that at high tide, C/N molar ratio is averagely 8 ± 2 while at low tide it increases to 13 ± 2. The $\partial^{13}C$ isotope signature of the POM at high tide was also found to be ca. -21.39 ± 1.43 ‰ and decreased to -23.96 ± 1.33 ‰ at low tide. No significant differences (ANOVA: $p > 0.05$) in C/N and $\partial^{13}C$ isotope signature were noticed for dry and wet seasons. Since POM associated with mangrove vegetation has a $\partial^{13}C$ isotope signature of -26.66 ‰ (table 5.11), the decrease (becoming more negative) of $\partial^{13}C$ value with ebb flow could indicate export of POM predominantly of mangrove origin. Likewise, the increase of $\partial^{13}C$ (becoming less negative) could also imply import of POM of marine (or seagrass) origin. Figure 5.10 shows a typical time series profile obtained at st. G3 for one of the 24 - hour time series experiment.

Table 5.12: Particulate organic carbon (POC), particulate organic nitrogen (PON), molar C/N ratio and $\partial^{13}C$ isotope signatures of POM at st. G3 at high and low tides of dry and rainy seasons (1991 - 1993). Mean ± S.D.

Tide	Dry season (n = 16)				Rainy season (n = 13)			
	C (%)	N (%)	C/N	$\partial^{13}C$ (‰)	C (%)	N (%)	C/N	$\partial^{13}C$ (‰)
High tide	0.42 ± 0.16	0.06 ± 0.02	8.14 ± 1.53	- 21.39 ± 1.43	0.51 ± 0.15	0.07 ± 0.02	8.50 ± 1.73	- 22.08 ± 0.87
Low tide	0.76 ± 0.27	0.07 ± 0.02	12.67 ± 1.89	- 23.96 ± 1.33	0.97 ± 0.54	0.08 ± 0.03	14.15 ± 2.24	- 24.23 ± 1.68

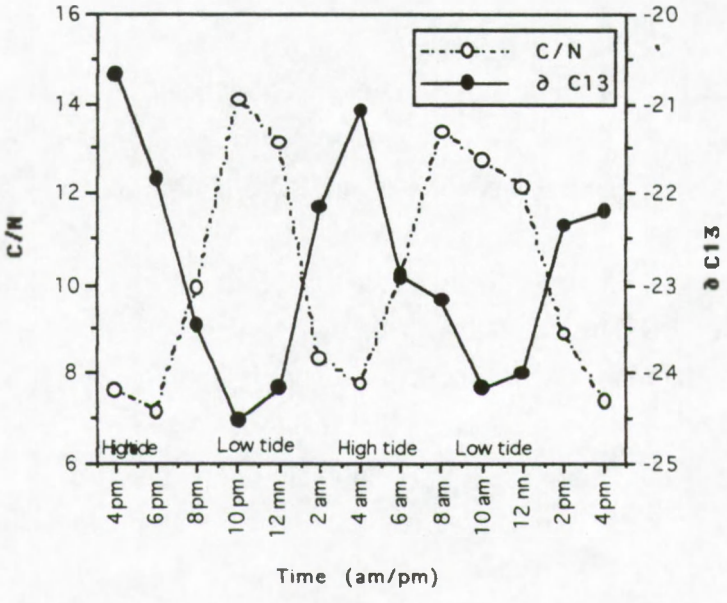


Fig. 5.10: A profile showing the C/N molar ratios and $\partial^{13}C$ isotope signature (‰) of POM at st. G3 over a 24 - hr. time series observation conducted on 6 th to 7th May 1993. Sampling was started at 4 pm on 6th May.

A specific intensive survey was carried out in June/July 1992 to find out the exact fate of the outwelled mangrove POM as it transverses the seagrass zone of Gazi bay from the mangrove forest . Descriptions of the sampling strategies and analytical manipulations have been given in detail in chapter 3. In short, 4 transects indicated as MM, MS, CS and CC were established from the opening of Kinondo creek (fig. 3.5b) to the open sea (CC). Station MM was established in the creek within the mangrove zone while station CC was established in the coral reef zone next to the open sea. Stations MS and CS were within the seagrass zone. The $\partial^{13}C$ isotope signature of the sediment at the MM transect was found to be ca. -22.94 ± 0.26 ‰ and increased gradually to -15.14 ± 0.78 ‰ at the open sea station (table 5.12). Seagrass at station MM was found to have a $\partial^{13}C$ isotope signature of -19.65 ± 0.39 ‰ which also increased towards the open sea station to -10.7 ± 0.23 ‰. While the C/N atom ratio of the sediment decreased from ca. 14.79 ± 2.11 at the creek to about 8.65 ± 1.50 at station CC, the seagrass (*Thallassodendron ciliatum*) had a more or less uniform C/N atom ratio of ca. 23 for all the transects (table 5.13).

Table 5.13: A table showing total organic carbon, total organic nitrogen, C/N molar ratios and $\partial^{13}C$ isotope signatures of sediment and seagrass at transects MM, MS, CS and CC at Gazi bay.n = 4 (no. of observations per transect).

Transect	Sediment				Seagrass			
	C %	N %	C/N	$\partial^{13}C$ ‰	C %	N %	C/N	$\partial^{13}C$ ‰
MM	3.79 ± 0.95	0.31 ± 0.01	14.8 ± 2.1	- 22.93 ± 0.24	38.67 ± 1.79	2.01 ± 0.20	22.5 ± 1.5	-19.65 ± 0.39
MS	2.36 ± 0.88	0.16 ± 0.09	17.3 ± 4.6	- 20.61 ± 1.46	39.66 ± 0.44	1.98 ± 0.17	23.37 ± 2.27	- 18.29 ± 0.46
CS	0.69 ± 0.20	0.08 ± 0.02	10.1 ± 2.0	- 18.41 ± 0.34	-	-	-	- 15.77 ± 0.47
CC	0.89 ± 0.12	0.12 ± 0.02	8.65 ± 1.5	- 15.14 ± 0.78	39.80 ± 1.19	2.00 ± 0.07	23.2 ± 0.6	-10.70 ± 0.23
Chale station	0.73 ± 0.08	0.10 ± 0.02	8.52 ± 0.02	- 14.75 ± 0.52	-	-		- 10.89 ± 0.17

The progressive decrease (becoming more negative) of the $\partial^{13}C$ isotope signature of the sediments from transect CC to MM underlines the outwelling effect of the mangrove POM. Comparison of the $\partial^{13}C$ isotope signature of sediments at station CC and that sampled at a control station (eastern part of Chale Island - with no mangrove influence) indicates that the outwelled mangrove POM is mainly trapped by seagrass in between stations MM and CC and is actually not noticed at station CC. This conclusion is arrived at by noting that the C/N and $\partial^{13}C$ isotope signatures at these two stations (st. CC and the Chale control station) are not significantly different (ANOVA: $p > 0.05$). $\partial^{13}C$ isotope signature of the seagrass at the two stations are also similar.

Atmospheric CO_2, the source of carbon for plants, has a $\partial^{13}C$ isotope signature of ca. -7.6 ‰ (Francey et al., 1985). CO_2 dissolved in water will therefore have a a $\partial^{13}C$ isotope signature close to that of atmospheric CO_2 unless significant organic matter respiration has affected the DIC pool. For submerged plants, the isotopic composition of the dissolved inorganic carbon (DIC) pool can affect the $\partial^{13}C$ value of these aquatic plants since in most cases, the DIC pool is their sole carbon source (Fleming et al., 1990). At Gazi bay, a gradual increase (becoming less negative) of $\partial^{13}C$ isotope was observed for the seagrass from the transect closer to the mangrove vegetation (st. MM) to the transect next to the open sea (CC). Since this increase is parallel to the increase noticed for the sediment, remineralization of the trapped mangrove organic material at each transect and eventually utilization of the produced CO_2 with a relatively more negative $\partial^{13}C$ signature could partly explain the observed gradient (Dehairs, pers. comm.; Hemminga et al., 1994).

Examination of the seston collected simultaneously at st. CC and MM during flood tide, indicates that more particulate organic material is picked by incoming water at the seagrass zone before the tide water enters the mangrove forest (table 5.14). Taking the average results of the 11 observations, about 3.0 mg l^{-1} of seston is found to pass through transect CC during flood tide. However, simultaneous sampling at MM indicates that averagely seston, of which the concentration is ca. 7.4 mg l^{-1}, passes transect MM into the mangrove forest during the same flood tides. Statistical treatment (analysis of variance) of these results indicates a significant ($p < 0.05$) increase of seston content between the two transects during flood tide. It is difficult to assess the exact composition of this organic material picked from the seagrass zone. The first assumption would be that this organic material is mainly of seagrass origin together with particles of mangrove detritus outwelled during previous ebb tides. However, it is observed that the average increase in organic

carbon and nitrogen between st. CC and MM is 1.12 mg C l^{-1} and 0.11 mg N l^{-1} respectively (table 5.14). This would imply that the added organic material has a C/N atom ratio of ca. 12. Since senescent mangrove leaves (whose particles are expected to form a large portion of the overall outwelled mangrove POM) of the main mangrove species (*Rhizophora mucronata* and *Ceriops tagal*) in Gazi bay are known to have C/N atom ratio of ca. 200 (table 5.15) and the C/N of the seagrass at Gazi bay is averagely 23 (table 5.13), the observed relatively low C/N ratio of the organic material picked from the seagrass zone may imply presence of another source of organic material at the seagrass zone with low C/N atom ratio. Fleming et al. (1990), while comparing $\partial^{13}C$ signatures of small organisms living in seagrass zone close to a mangrove forest and organisms living in seagrass with no terrestrial influence, concluded that marine phytoplankton could form an important additional source of particulate organic material in seagrass communities. Using a two end-member mass balance model, these authors could calculate marine POM contributions at the seagrass vegetation (without mangrove influence) of about 59 % emphasizing on the importance of marine POM in these shallow coastal lagoons.

Table 5.14: A table displaying seston content, POC, PON and $\partial^{13}C$ values of particulate organic material filtered simultaneously at the CC and MM transect in Gazi bay during flood tides.

Date	Transect	Seston mg/l	POC mg/l	PON mg/l	C/N	$\partial^{13}C$ ‰	no.of observ.
30.06.92	**CC**	3.5 ± 1.7	0.28 ± 0.13	0.049 ±0.16	6.62	- 18.22	5
	MM	6.2 ± 2.6	1.12 ± 0.39	0.123 ±0.04	10.62	- 23.46	5
01.07.92	**CC**	2.8 ± 0.1	0.35 ± 0.07	0.066 ±0.02	6.19	- 18.80	6
	MM	8.7 ± 6.6	1.76 ± 1.27	0.212 ±0.13	9.69	- 22.88	5
Average	**CC**	3.0 ± 1.3	0.32 ± 0.10	0.058 ±0.02	6.44	- 18.39	11
	MM	7.4 ± 4.9	1.44 ± 0.95	0.168 ±0.10	10.00	- 23.23	10

Table 5.15: C/N molar ratio of senescent leaves *of Rhizophora mucronata* and *Ceriops tagal* mangrove species. Adapted from Rao et al., 1993.

Species	C/N molar ratio
Rhizophora mucronata	193 ± 45
Ceriops tagal	218 ± 26

Table 5.14 indicates that the average C/N and $\partial^{13}C$ isotope signature of the particulate organic material that enters the bay during flood tides is 6.44 and - 18.39 ‰ respectively which could reflect phytoplankton POM. From the results of $\partial^{13}C$ isotope signature of sediment across the MM - CC transect, no mangrove effect is noticed at st. CC since the sediment and seagrasses at this station were found to be similar to those found at a control station to the east of Chale Island with no mangrove influence (table 5.13).

In this case, we can assume that the total organic material at station CC is mainly from seagrass POM within the locality and partly from marine POM brought by the incoming tides. If this holds true, we can then calculate relative contributions of these two sources using a two end-member model below;

$$[[\ \mathbf{POC}]_x\ (\boldsymbol{\partial}^{13}\mathbf{C})_x\ ]\ +\ [\ \mathbf{POC}]_y\ (\boldsymbol{\partial}^{13}\mathbf{C})_y] = ([\mathbf{POC}]_x + [\mathbf{POC}]_y)(\boldsymbol{\partial}^{13}\mathbf{C})_s \quad \text{----- (1)}$$

x and **y** indicate two end members with their corresponding **POC** fractions ($[POC]_x + [POC]_y = 1$) and $\boldsymbol{\partial}^{13}\mathbf{C}$ values while $(\boldsymbol{\partial}^{13}\mathbf{C})_s$ is the observed $\partial^{13}C$ value of the sediment sample at the CC transect.

We therefore have;

$$[\mathbf{POC}]_x = [\mathbf{POC}]_{SG} \quad \text{(relative seagrass POC contribution)}$$

$(\partial^{13}C)_x$ = - 10.70 ‰ (seagrass : $\partial^{13}C$ - at transect CC)

$|POC|_y$ = $|POC|_{MR}$ (relative marine POC contribution)

$(\partial^{13}C)_y$ = - 18.39 ‰ (marine: $\partial^{13}C$), and

$(\partial^{13}C)_s$ = - 15.14 ‰ (CC sediment)

If we substitute all the indicated values to equation 1 we get:

Seagrass POC contribution = 42 % and
Marine POC contribution = 58 %

As a further attempt to justify the observed contributions, we can calculate their exact fractions in the observed organic matter at transect CC and find out whether the resultant calculated C/N atom ratio fits the observed sedimentary C/N atom ratio at the transect. Table 5.13 indicates that 100 g of dry sediment at transect CC has about 0.89 g C. If 42 % of this is of seagrass origin, then we have 0.37 g C from seagrass and 0.52 g C from marine POM. It is also observed that the C/N atom ratio of the seagrass at transect CC is averagely 23 (table 5.13) while that associated with marine POM was 6.44 (table 5.14). Using these C/N molar ratios, a seagrass and marine carbon contribution of 0.37 and 0.52 g C would correspond to nitrogen contributions of 0.019 and 0.094 g N respectively. The expected calculated C/N atom ratio of the sediment at transect CC is therefore 9.17 which is within the values observed (8.65 ± 1.50) for sediments at this trasect (table 5.13). This confirms the validity of our two end - member mass balance model and clearly emphasizes on the importance of marine POM in the seagrass zone. However, this two end-member model can not be applied for the transects between stations CC and MM because of the increasing influence of the outwelled mangrove effect.

The particulate organic material picked from the seagrass zone by incoming flood waters could therefore be of either mangrove, seagrass or marine origin. The relatively low C/N molar ratio of this transported organic material may actually imply relatively more contribution from marine POM than seagrass and mangrove POM. What is the relative contributions of these POM sources to the sedimentary organic material of Gazi bay ?

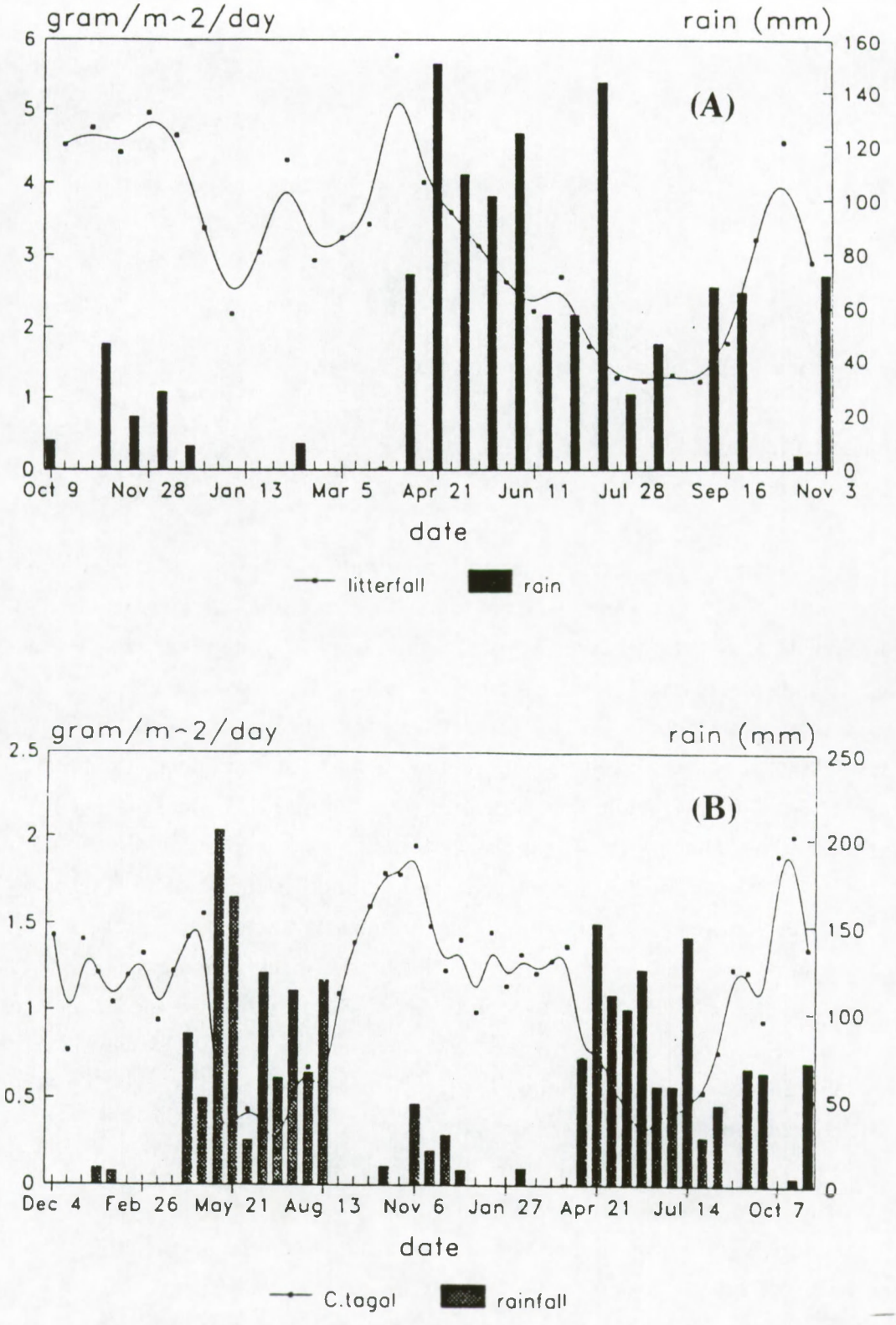
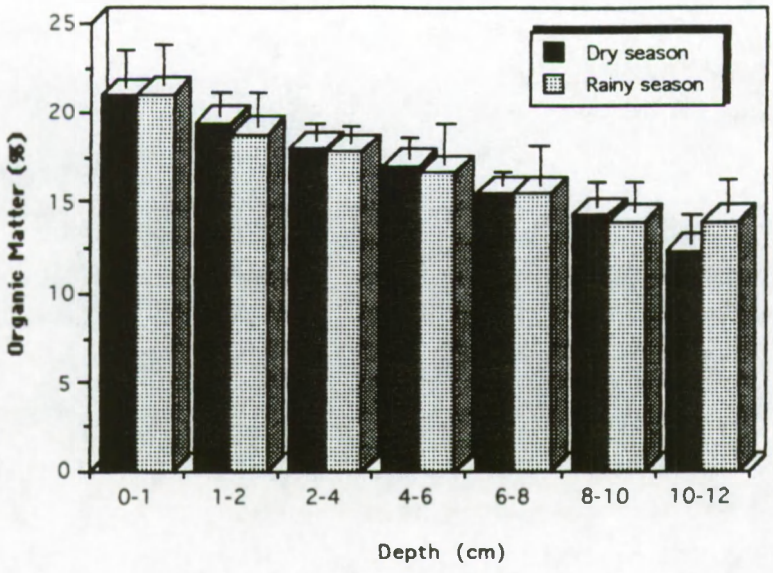


Fig. 5.12: Litterfall (g D.W.) as related to rainfall pattern in Gazi field stations. Figure (**A**) is for Rm plot while figure (**B**) is for the Ct plot. Adapted from Slim and Gwada, 1993.

5.1.2 Total organic matter content of sediment inhabited by *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) mangrove species of Gazi bay

In order to investigate possible seasonal (dry and wet seasons) variation of organic matter in mangrove sediments, sediment samples from the Rm and Ct field plots were sampled and analysed for organic matter content during both dry (February/March) and rainy (May/June) seasons of 1992, 1993 and 1994.

For Rm sediments, the highest organic matter (LOI) content (ca. 21 ± 1% $D.W._{sediments}$) was found at the surface and decreased gradually to ca. 13 ± 2% $D.W._{sediments}$ at the 12 cm depth (fig. 5.11A). Organic matter content for Ct sediment (fig. 5.11B) was much lower, being ca. 2.40 ± 0.5% $D.W._{sediment}$ at the surface and increasing to ca. 10.5 ± 1.2 % $D.W._{sediment}$ at 12 cm depth. Tables 5.16 and 5.17 show the other variables: total organic carbon (TOC), total organic nitrogen (TON), and C:N atom ratio which were determined on some of the sediment samples analyzed for organic matter content for the Rm and Ct sediments respectively. Ct sediment is seen to be poorer in organic nitrogen than the Rm sediment. The C:N ratio for the Rm sediment increased from ca. 23 ± 1 at the surface to about 30 ± 1 at 12 cm depth while for Ct, it increased from ca. 19 ± 1 at the surface to about 39 ± 2 % at 12 cm depth. A slight increase (becoming less negative) was noticed for $\partial^{13}C$ isotope signature from the bottom (12 cm) to the surface. One striking observation in both sediments is the lack of significant variation ($p > 0.05$ for all corresponding sections) of organic matter content with seasons. This is in contrast to litterfall observations for the same study plots. Slim and Gwada (1993), observed relatively higher litterfall for both the Rm (fig. 5.12A) and Ct (fig. 5.12B) study plots during dry season as compared to rainy season. The lack of seasonality (dry / wet seasons) for the sedimentary organic matter confirms the buffering capacity of the sediments. The C/N molar ratio of the falling senescent leaves was found to be about 200 (Rao et al., 1993) while that of the sediment is much lower (Rm: 23 - 30; Ct: 19 - 39). The low sedimentary C/N molar ratio implies import of organic matter richer in nitrogen. This imported organic material which lowers the sedimentary C/N atom ratio could also be responsible for buffering the observed litterfall seasonality effect.



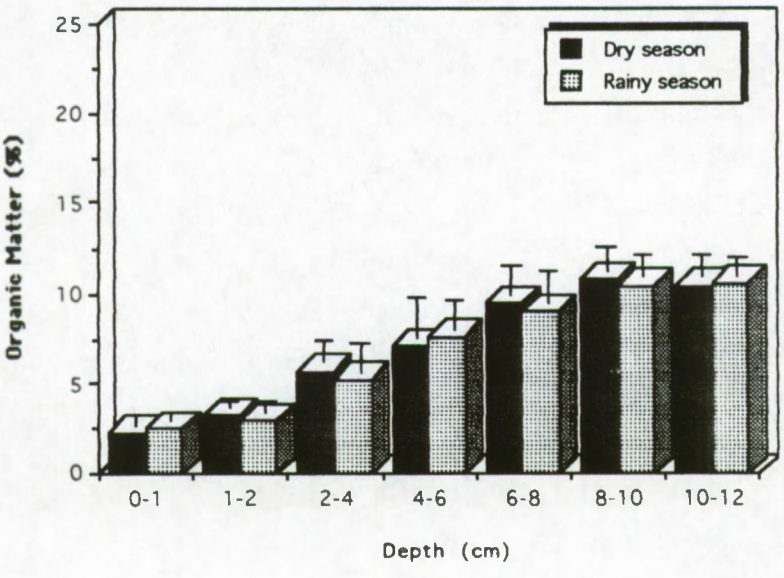


Fig. 5.11: Total organic matter content (LOI) as observed in Rm (fig. A) and Ct (fig. B) sediments during dry and rainy seasons of 1992/3/4. n = 24.

Table 5.16: A table showing mean total organic matter content (LOI), total organic carbon (TOC), total organic nitrogen (TON), C/N molar ratio and $\partial^{13}C$ isotope signature of the Rm sediments. The organic matter content is from samples collected between 1992 and 1994 (dry and rainy seasons) while TON, C/N and the $\partial^{13}C$ values are for samples of 1992.

Depth (cm)	Org. Matter LOI (%) (n = 48)	TOC (%) (n = 4)	TON (%) (n = 4)	C:N	$\partial^{13}C$ (‰) (n = 4)
0 - 1	21.08 ± 0.93	9.27 ± 0.93	0.47 ± 0.05	23.0 ± 0.8	- 25.52 ± 0.42
1 - 2	19.16 ± 1.58	9.59 ± 1.16	0.44 ± 0.05	25.4 ± 0.4	- 25.97 ± 0.25
2 - 4	17.48 ± 1.05	9.32 ± 2.25	0.41 ± 0.11	26.5 ± 1.7	- 26.36 ± 0.14
4 - 6	17.36 ± 1.72	8.22 ± 0.75	0.35 ± 0.05	27.4 ± 1.2	- 26.45 ± 0.10
6 - 8	15.55 ± 1.69	8.06 ± 0.59	0.32 ± 0.03	29.4 ± 0.9	- 26.36 ± 0.13
8 - 10	14.16 ± 1.50	7.84 ± 0.91	0.29 ± 0.03	31.5 ± 0.6	- 26.46 ± 0.06
10 - 12	13.21 ± 1.63	6.78 ± 0.60	0.26 ± 0.04	30.4 ± 0.8	- 26.46 ± 0.04

Table 5.17: A table showing total organic matter content (LOI), total organic carbon (TOC), total organic nitrogen (TON), C/N molar ratio and $\partial^{13}C$ isotope signature of the Ct sediments.

Depth (cm)	Org. Matter LOI (%) (n = 48)	TOC (%) (n = 4)	TON (%) (n = 4)	C:N	$\partial^{13}C$ (‰) (n = 4)
0 - 1	2.40 ± 0.50	0.81 ± 0.22	0.05 ± 0.01	18.9 ± 0.9	- 22.94 ± 0.53
1 - 2	3.07 ± 0.50	1.06 ± 0.31	0.05 ± 0.01	24.7 ± 2.8	- 23.49 ± 0.44
2 - 4	5.46 ± 1.31	1.77 ± 0.31	0.08 ± 0.02	25.8 ± 2.5	- 23.59 ± 0.36
4 - 6	7.34 ± 1.85	2.87 ± 0.27	0.11 ± 0.01	30.4 ± 1.7	- 24.13 ± 0.37
6 - 8	9.23 ± 1.61	3.51 ± 0.35	0.13 ± 0.01	31.5 ± 2.0	- 24.49 ± 0.40
8 - 10	10.64 ± 1.21	4.12 ± 0.44	0.13 ± 0.01	36.9 ± 1.9	- 24.37 ± 0.21
10 - 12	10.46 ± 1.20	4.66 ± 0.24	0.01 ± 0.01	38.8 ± 1.8	- 24.51 ± 0.28

Comparison of the $\partial^{13}C$ isotope signature of the Rm and Ct sediments (Rm: - 25.52 ± 0.42 and Ct: - 22.92 ± 0.53 ‰ for the upper 1 cm depth) in Gazi bay (tables 5.16 and 5.17) and those of mangrove leaves of the same species (Rm: - 28.25 and Ct: - 24.12 ‰, table 5.11) confirms that the two are very close but slightly more positive (less negative $\partial^{13}C$ values) for the sediments. However, as indicated above, while the range of C/N atom ratio of Rm and Ct sediments are found to be 23 - 30 and 19 - 39, respectively for the upper 12 cm sediment, those of mangrove leaves (senescent) of the same species are found to be 193 ± 45 and 218 ± 26 respectively (table 5.15). This decrease of C/N molar ratio in sediments may indicate that either there are strong losses of carbon relative to nitrogen, or vice versa that there are benthic nitrogen inputs. Using a simple mass balance model, Middelburg et al. (1995), ruled out the possibility of preferential decrease of carbon to be the cause of the increase of the observed sedimentary molar C/N ratio. This would then imply a tremendous increase in sedimentary organic nitrogen compared to mangrove leaves. Nedwell et al. (1994), while investigating on the turnover of organic carbon and nitrogen in the sediments of a Jamaican mangrove forest, also observed elevated stocks of organic nitrogen which they could not account for. These authors suggested that nitrogen fixation could be a possible source of this extra nitrogen stock. However, Capone (1983), had earlier concluded that N_2 fixation in mangrove sediments is generally low. Indeed N_2 fixation rates at Gazi mangrove sediments have been found to be very low compared to the sedimentary N-mineralization rates (Woitchik et al., submitted; Kazungu, et al., 1995). So we are essentially back to the same question. What is the source of this elevated stock of organic nitrogen in mangrove sediments ? Could the seagrass ($\partial^{13}C$: - 10.70 to - 19.65 ‰ and C/N ratio: averagely 23) at Gazi bay which are pushed into the mangrove zone during flood tides be the cause of the relative increase (becoming less negative) in $\partial^{13}C$ isotope signatures (relative to the mangrove leaves) and decrease of the sedimentary C/N molar ratios in the mangrove sediments ?

As a further attempt to answer some of the above questions, and also knowing the possible importance of marine POM contribution found in the seagrass zone, a number of assumptions are made in calculating relative contributions of various POM sources to the mangrove sediments of Gazi bay.

A two end-member conservative mass balance equation used earlier (and reproduced below) in assessing relative contributions of seagrass and marine POM to the sedimentary

organic material at an open sea station (transect CC) in Gazi bay is again applied for the mangrove sediments.

$$[[POC]_x (\partial^{13}C)_x] + [POC]_y (\partial^{13}C)_y] = ([POC]_x + [POC]_y) (\partial^{13}C)_s \text{ ---------- (1)}$$

x and **y** as indicated earlier are two end members with their corresponding **POC** fractions and $\partial^{13}C$ values while $(\partial^{13}C)_s$ is the observed $\partial^{13}C$ value of the mangrove sediment sample. The above mass balance equation is applied with care knowing very well that we have three possible end - members (mangrove, seagrass and marine POM) and not two as the equation pre-supposes.

Assumption 1

Since the slightly more positive sedimentary $\partial^{13}C$ values found in mangrove sediments could likely be due to the seagrass washed into the forest during ebb tide (Hemminga et al., 1994), as a first assumption, we assume that the particulate organic material at the mangrove sediments is only contributed by POM from mangroves (senescent leaves) and seagrass from the bay with the tidal waters only acting as a media of transport. This assumption therefore recognizes two end members - the mangroves and the seagrasses.

For the Rm sediments, $(\partial^{13}C)_x$ for the Rm leaves is - 28.25 ‰ (table 5.11) while the $(\partial^{13}C)_y$ for the seagrass is - 10.70 ‰ (table 5.12). The $(\partial^{13}C)_s$ for the Rm sediments (0 - 1 cm depth) is - 25.52 ‰ (table 5.16). In this case, we have:

$[POC]_x$	=	$[POC]_{MG}$	(relative Rm POC contribution)
$(\partial^{13}C)_x$	=	- 28.25 ‰	(Rm leaves: $\partial^{13}C$)
$[POC]_y$	=	$[POC]_{SG}$	(relative seagrass POC contribution)
$(\partial^{13}C)_y$	=	- 10.70 ‰	(seagrass without mangrove influence: $\partial^{13}C$)
$(\partial^{13}C)_s$	=	- 25.52 ‰	(Rm sediment: 0 - 1 cm depth)

If all these figures are substituted in equation 1 we get;

Mangrove POC contribution = 84.40 %, and
Seagrass POC contribution = 15.60 %

From table 5.16, 100 g Rm dry sediment of the 0 - 1 cm depth has 9.27 g C. If 84.40 % of this is from the mangrove contribution, then we have in this sediment, 7.82 g C from mangroves and the remaining (1.45 g C) from the seagrasses.

However, do their corresponding nitrogen contributions as end members satisfy the observed sedimentary C/N ratio ?

The C/N atom ratio of Rm senescent leaves is 193 (table 5.15) while that of seagrass is about 23 (table 5.12). This implies that the POM from the mangrove leaves which has 7.82 g C should contribute 0.047 g N while the POM from the seagrass should contribute 0.074 g N. From these values, the resultant expected C/N atom ratio of the Rm sediment will be 89. This value is quite high compared to the observed value (23 - 30 : for the upper 12 cm depth: table 5.16). Even if we assumed that the seagrass next to the mangrove vegetation (with a $\partial^{13}C$ of - 19.65 ‰) to be the second end-member instead of that next to the open sea, we get a C/N atom ratio of about 60 which is still relatively high. If the same exercise is repeated for the Ct sediments we get calculated sedimentary C/N molar ratios of above 100 while the observed values are averagely about 30 for the upper 12 cm sediment (table 5.17). This clearly indicates that the seagrasses between the open sea and the mangrove vegetation may not be the main contributor to the low sedimentary C/N ratios observed in the mangrove sediments.

Assumption 2

Like Gazi mangrove sediments, reported values for surface sedimentary C/N molar ratio of most mangrove sediments are found to be between 20 and 30 regardless of whether there is seagrass in the neighbourhood or not (Hesse, 1961; Shaiful et al., 1986; Blackburn et al., 1987; Kristensen et al., 1988; Kristensen et al., 1992). With this in mind we can again confidently assume different end-members for equation 1. Instead of the seagrass, we can assume marine POM to be our second end-member.

In this case,

$[POC]_x$ = $[POC]_{MG}$ (relative Rm POC contribution)

$(\partial^{13}C)_x$ = - 28.25 ‰ (Rm leaves: $\partial^{13}C$)

$[POC]_y$ = $[POC]_{MR}$ (relative marine POC contribution)

$(\partial^{13}C)_y$ = - 18.39 ‰ (marine: $\partial^{13}C$), and

$(\partial^{13}C)_s$ = - 25.52 ‰ (Rm sediment: 0 - 1 cm depth)

Substituting all the above figures in equation 1 we get;

Mangrove POC contribution = 72.3 % and
Marine POC contribution = 27.7 % → 2.57 g N / 100 g sediment

Again, 100 g dry sediment of the surface (0 - 1 cm) Rm sediment has 9.27 g C. Out of this, mangrove POC will be 6.70 g C while 2.57 g C will have been contributed by the marine POM.

However, since the C/N ratio of the senescent Rm leaves is averagely 193 while that of marine POM is 6.44 (table 5.14), a carbon contribution of 6.70 and 2.57 g C from the mangroves and marine POM would correspond to a nitrogen contribution of 0.04 and 0.47 g N, respectively. The resultant sedimentary C/N ratio would therefore be 21.2 which is actually within the values observed for the surface Rm sediments (table 5.16).

If we repeat the same exercise with the Ct sediments, we have;

$[POC]_x$ = $[POC]_{MG}$ (Ct POC contribution)

$(\partial^{13}C)_x$ = - 24.12 ‰ (Ct leaves: $\partial^{13}C$)

$[POC]_y$ = $[POC]_{MR}$ (marine POC contribution)

$(\partial^{13}C)_y$ = - 18.39 ‰ (marine: $\partial^{13}C$), and

$(\partial^{13}C)_s$ = - 22.92 ‰ (Ct sediment: 0 - 1 cm depth)

Again substituting all these figures in equation 1, we get;

Mangrove POC contribution = 79.1 % and
Marine POC contribution = 20.9 %

Marine contribution in Ct sediments is seen to be less than that noticed for the Rm sediments. A probable reason for this could be the infrequent tidal inundation in the Ct plot as compared to the Rm plot.

100 g Ct dry sediment (0 - 1 cm), has 0.81 g C. From the above calculated percentages, mangrove POC contribution will be 0.641 g C while 0.169 g C would be the contribution from marine POC. Corresponding nitrogen contributions from the two sources judging from their C/N ratios (Ct leaves: 218 and marine POM: 6.44), would be 0.003 and 0.031 g N, respectively. The resultant C/N ratio is therefore found to be 27.83 which is also close to the values found in Ct sediments (table 5.17). It is therefore likely that marine POM could be the organic material giving a significant contribution to the overall sedimentary C/N ratios in mangrove sediments since when used as a second end-member it satisfies both the observed sedimentary C/N and $\partial^{13}C$ isotope signatures of the mangrove sediments.

The results of the above calculations demonstrate that the reduction of the C/N molar ratio in mangrove sediments compared to the mangrove vegetation could most likely be due to import of marine particulate organic material of planktonic origin. This may therefore imply that the seagrasses in the neighbourhood play a localized role in POM distribution in Gazi bay. This conclusion is also supported by the fact that apart from the Rm and Ct sediments, Middelburg et al. (in press), found averagely a C/N ratio of about 25 for most of the Gazi mangrove sediments despite whether they were closer to the seagrass influence or not. Reported surface sedimentary C/N ratios of most mangrove sediments are also found to lie between 20 and 30 (Hesse, 1961; Shaiful et al., 1986; Blackburn et al., 1987; Kristensen et al., 1988; Kristensen et al., 1992).

These results indicate that the organic matter in mangrove sediments is most likely composed of two parts: (1) a pool of highly refractory organic material from mangrove vegetation which is very poor in organic nitrogen, and (2) a pool of labile organic nitrogen, probably of marine phytoplanktonic origin. This would then imply that mangroves are net importers of particulate organic nitrogen.

CHAPTER 6

6.0 NITROGEN - TRANSFORMATIONAL PROCESSES IN SEDIMENTS INHABITED BY *Rhizophora mucronata* (Rm) AND *Ceriops tagal* (Ct) SPECIES

Early diagenetic reactions particularly those directly or indirectly involving the decomposition of organic matter are most intense and rapid in the upper 1 m and especially in the upper 10 cm of marine sediment. It is this zone where most benthic organisms live and interact with sediments and where exchange rates of dissolved and particulate material between sediment and overlying water are largely determined (Aller, 1980). Knowledge of the diagenetic processes taking place in this zone is therefore essential for understanding the chemistry of the sediments and the water overlying the sediments. Sediment mineralization and bacterial synthesis occur in zones dominated by different electron acceptors. Organic carbon is first oxidized by oxygen and subsequently by nitrate and sulphate by different heterotrophic bacteria. Reactions (1) to (6) give the possible heterotrophic hydrolysis and oxidation of organic matter that can be found in sediments (Aller, 1980). MnO_2 and $Fe(OH)_3$, when available, are also shown to be possible electron acceptors in sediments.

(a) $(CH_2O)_x(NH_3)_y + (x + 2y)O_2 = xCO_2 + (x + y)H_2O + yHNO_3$ ..... (1)

(b) $5(CH_2O)_x(NH_3)_y + 4xNO_3^- = xCO_2 + 3xH_2O + HCO_3^- + 2xN_2 + 5yNH_3$ ..... (2)

(c) $(CH_2O)_x(NH_3)_y + 2xMnO_2 + 3xCO_2 + xH_2O = 4xHCO_3^- + 2xMn^{2+} + yNH_3$ ..... (3)

(d) $(CH_2O)_x(NH_4)_y + 4xFe(OH)_3 + 7xCO_2 = 8xHCO_3^- + 3xH_2O + 4xFe^{2+} + yNH_3$ ..... (4)

(e) $2(CH_2O)_x(NH_3)_y + SO_4^{2-} = 2xHCO_3^- + xH_2S + yNH_3$ ..... (5)

(f) $2(CH_2O)x(NH_3)y = xCO_2 + xCH_4 + 2yNH_3$ ..... (6)

As carbon is oxidized in these different zones, organic nitrogen is also mineralized to ammonium ion - a process commonly referred to as ammonification. Once produced, part of this ammonium can again be incorporated (assimilated) back into bacterial cells by the bacteria responsible for the mineralization process. Net production of ammonium hence depends very much on the quality and quantity of the organic substrate (Aller, 1980;

Middelburg et al., 1989). The produced NH_4^+ accumulates in lower, anoxic sediment layers from where it diffuses up to the oxic surface (Blackburn, 1988; Ullman and Sandstrom, 1987; Kristensen, et. al., 1992). It is mostly at the sediment surface that nitrification (ammonium oxidation) has the possibility of taking place. Part of this ammonium is hence nitrified (Henriksen and Kemp, 1988; McCarthy et al., 1980; Henriksen et al., 1981) while the remaining part diffuses out into the water column (ammonium efflux) across the sediment-water interface (Kemp et al., 1990; Iizumi et al, 1982; Blackburn and Henriksen, 1983). Apart from local consumption by benthic micro-organisms, the nitrate produced as a result of nitrification has three fates: reduction to NH_4^+ through the nitrate ammonification process (Koike and Sorensen, 1988), lost as nitrogen gas through the de-nitrification process (Andersen et al., 1984) or diffusing out into the water column (nitrate flux). All these processes depend on the micro-environment existing in a biotope.

In this chapter, results of ammonification (regeneration and assimilation) nitrification (potential and actual) and sediment - water DIN fluxes in Rm and Ct sediments of Gazi bay are discussed.

6.1 RESULTS AND DISCUSSION

6.1.1 Regeneration and Assimilation Rates (RAR) in Rm and Ct sediments

Ammonium regeneration and assimilation rates are usually investigated using the ^{15}N isotope dilution technique (Blackburn, 1979; Iizumi et al., 1982; Blackburn and Henriksen, 1983; Bowden, 1984; Selmer, 1988). This technique is described in detail in chapter 3. In principal, in this technique the rate of ammonium regeneration and uptake is determined by labelling the product, i.e. ammonium. The ^{15}N labelled is initially added to the sediment sample and the dilution of the atom % ^{15}N of the ammonium pool, the rate of dilution of ammonium pool (equal to the rate of ammonium regeneration) and uptake of the ammonium can be calculated from equations (1) and (2) below developed by Blackburn (1979) and discussed in detail in chapter 3.

$$d = \frac{P_f - P_i}{t} \cdot \frac{\ln \frac{A_i}{A_f}}{\ln \frac{P_f}{P_i}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$i = d - \left(\frac{P_f - P_i}{t}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

From the above two equations, it is apparent that correct determinations of d (regeneration) and i (incorporation or assimilation) depend on accurate determinations of ammonium pools and their corresponding ^{15}N isotopic abundances. Recent findings on recoveries of labelled ^{15}N compounds have indicated that there could be a serious problem of underestimation of the ammonium concentrations in sediments due to either; (1) incomplete extraction of total NH_4^+ in sediments by the KCl (Laima, 1993) or (2) presence of amines in sediments which may hinder colour development during NH_4^+ analysis (Ngo, et al., 1982; Laima, 1992).

In order to check whether we also have incomplete extraction of NH_4^+ from our mangrove sediment samples, specific experiments were undertaken to check on recoveries of % ^{15}N added to the mangrove sediments.

6.1.1.1 Recovery of % ^{15}N added to mangrove sediments

While the microdiffusion method was found to be very effective in trapping the labelled ammonium giving more than 97 % recovery (section 3.2.4), a specific experiment was done to check on recovery levels of added ^{15}N in mangrove sediments. For this investigation, Rm sediments were used.

Experimental design.

(a)

1. Ten sediment core samples were sectioned into 0-6 cm segments. All these segments were then pooled together and mixed thoroughly.
2. Ten 10 g subsamples were then weighed into serum vials and spiked with 0.1 ml (750 μmol) of labelled $^{15}NH_4Cl$ (99 %).
3. 40 ml of 1 N KCl was then added and the samples were flushed with N_2 and placed on a shaker table for 1 hour before centrifugation (2000 x g r.p.m.) and filtration (GF/F Whatman filter) into clean polyethylene bottles.
4. The extracts were diluted tenfold before measurement of the ammonium pool.

5. Microdiffusion was then performed to trap the NH_4^+ for ^{15}N determination.
6. Isotopic determinations were eventually done using an emmission spectrometer at Vrije Universiteit Brussel.

(b)

Using labled (99 % ^{15}N) and unlabelled NH_4Cl a solution of 10 % ^{15}N was prepared using both distilled water and 1 N KCl. Microdiffusion was also done on these solutions to trap NH_4^+ for comparison to re-check the efficiency of the trapping process and assess possibilities of contamination during transport.

Calculation of expected (theoretical) % ^{15}N in the mixture.

For the calculation of the theoretical % ^{15}N in the sediments, we used the dilution formula given in chapter 3 where;

$$P_a A_a + P_b A_b = P_m A_m$$

in which P_a, P_b, P_m are the ammonium pools and A_a, A_b and A_m are the respective % ^{15}N of the pools.

For each sample the ammonium pool (P_m) was measured after spiking and its original ammonium pool (P_a) calculated from the relationship $P_a = P_m - P_b$.

P_b was the added spike (0.1 ml of 750 μmol $^{15}NH_4Cl$). Tables 6.10, 6.11 and 6.12 below give the observed and theoretical % ^{15}N results obtained from different experiments.

Table 6.10: % recovery of ^{15}N spike in Rm sediments.

Spike : 0.1 ml $^{15}NH_4Cl$ (750.0 μM)
Sample: 10 g wet weight sediment (0 - 6 cm depth)
Extractant : 40 ml 1 N KCl
Water content: 64.99 %
Experiment : 1

P_i (μM)	A_i ^{15}N % (experimental)	A_i ^{15}N % (calculated)	% recovery
159.67	4.907	7.496	65.46
117.34	5.627	10.184	55.25
144.23	3.978	7.744	51.37
146.17	5.499	8.157	67.41
123.24	6.741	9.605	70.18
165.65	5.327	7.796	68.33
136.78	4.828	8.691	55.55
146.19	5.789	8.805	65.75
124.33	6.114	9.525	64.19
Average 140.40 ± 16.54	5.428 ± 0.80	8.667 ± 0.947	62.61 ± 6.74
prepared soln. (with dist. H_2O) 10 % ^{15}N 200.00 μM (a)	9.487	10.00	94.87
(b)	9.862		98.62
(c)	9.676		96.76
Average	9.675 ± 0.188	10.00	96.75 ± 1.88
prepared soln. (with 1 N KCl) 10 % ^{15}N 200.00 μM (a)	9.811	10.00	98.11
(b)	9.723		97.23
(c)	9.722		97.22
Average	9.752 ± 0.05	10.00	97.52 ± 0.50

Table 6.11: ^{15}N recovery in Rm sediments with 40 ml of 1 N KCl.

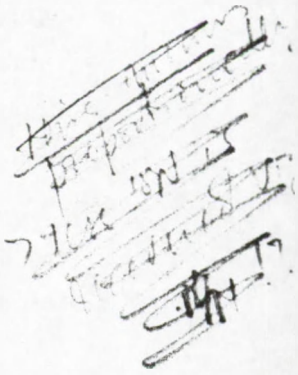
Spike : 0.1 ml $^{15}NH_4Cl$ (750.0 μM)
Sample : 10 g wet weight (0 - 6 cm depth)
Extractant : 40 ml 1 N KCl
Water content : 66 %
Experiment : 2

P_i (μM)	A_i ^{15}N % (experimental)	A_i ^{15}N % (calculated)	% recovery
Extraction with 40 ml 1 N KCl			
138.37	5.333	8.472	62.95
149.82	4.931	7.850	62.82
128.66	5.073	9.083	55.84
163.74	4.711	7.208	65.36
152.89	5.503	7.701	71.46
144.67	4.327	8.116	53.31
138.89	4.996	8.437	59.22
156.66	5.173	8.084	63.99
152.38	5.208	7.723	67.43
133.84	5.987	8.747	68.48
Average 145.99 ±11.01	5.124 ± 0.448	8.142 ± 0.556	63.08 ± 5.65

Table 6.12: ^{15}N recovery in Rm mangrove sediments with varying volumes of extractant KCl (60 ml & 80 ml of 1 N KCl)

Spike : 0.1 ml $^{15}NH_4Cl$ (750.0 μM)
Sample : 10 g wet weight (0 - 6 cm depth)
Extractant : 60 and 80 ml 1 N KCl
Water content : 66 %
Experiment : 2 (continued)

P_i (μM)	A_i ^{15}N % (experimental)	A_i ^{15}N % (calculated)	% recovery
extraction with 60 ml 1 N KCl			
162.74	5.097	7.257	70.23
137.87	4.911	8.499	57.78
157.82	4.878	7.469	65.31
128.33	5.911	9.104	64.93
134.87	5.021	8.682	57.83
159.70	5.133	7.388	69.48
163.74	5.462	7.213	75.72
129.88	4.972	9.001	55.24
Average 146.87 ± 15.48	5.173 ± 0.349	8.077 ± 0.821	64.565 ± 7.169
Extraction with 80 ml 1 N KCl			
148.86	4.661	7.895	59.04
173.84	4.931	6.819	72.31
134.66	5.273	8.691	60.67
123.97	6.033	9.413	64.09
141.38	4.042	8.299	48.69
152.14	5.491	7.738	70.96
159.74	4.372	7.384	59.21
Average 147.80 ± 16.44	4.972 ± 0.684	8.034 ± 0.857	62.14 ± 8.03



From table 6.10 it is seen that not all added % ^{15}N could be recovered. Only about 63 % of ^{15}N was recovered. It is also observed that the KCl extractant does not interfere with the NH_4^+ microdiffusion trapping since more than 97 % of the ^{15}N is recovered. No contamination was also detected since the ^{15}N percent recovery of about 97 % is similar to that established for the microdiffusion trapping technique (chapter 3). Tables 6.11 and 6.12 indicate that higher volumes of the extractant (1 N KCl) did not result in higher recoveries.

Low recoveries of ^{15}N in the KCl-extractable NH_4^+ pool have also been reported in other sediment studies (Blackburn et al., 1994; Nedwell, et al., 1994). These ^{15}N recoveries could sometimes even be lower than 50 % (Blackburn, pers. comm.).
As indicated earlier, several reasons have been given for these low recoveries. The amount of ^{15}N label recovered depends on accurate measurement of NH_4^+ and % ^{15}N in the extract (Laima, 1993). An error in the measurement of any of the two could be reflected in the calculation of the % ^{15}N recovery. It has been suggested that the presence of amines in sediments could inhibit colour development during ammonium determination using the indophenol technique (Ngo et al., 1982) leading to underestimation of the ammonium pool. Recently, another explanation given for the low ^{15}N recoveries has been atributed to the KCl as an extractant. Though KCl has been used widely as an extractant of exchangeable NH_4^+ in sediments (Blackburn, 1979; Mackin and Aller, 1984), Laima (1993) indicated that sometimes not all adsorbed NH_4^+ is able to be extacted by the KCl solution.

In this study, an attempt has been made to introduce a correction factor that will account for the undetermined NH_4^+ pool in the calculations of regeneration and assimilation rates.

If we assume that the presence of amines or incomplete extraction of NH_4^+ by KCl extractant leads us to underestimate the NH_4^+ concentration by x, this may really not change the net ammonium production since,

$$\text{net } NH_4^+ \text{ production} = \mathbf{d - i = P_f - P_i / t}$$

where as defined earlier;

d = regeneration rate
i = assimilation rate
t = incubation time

$\mathbf{P_i}$ = initial NH_4^+ pool concentration

$\mathbf{P_f}$ = final NH_4^+ pool concentration after incubation time t

and if we add x to both $\mathbf{P_f}$ and $\mathbf{P_i}$ in the above formula, we have;

$$\frac{(P_f + x) - (P_i + x)}{t} = \frac{P_f - P_i}{t}$$

However, this underestimated NH_4^+ if not corrected for, may affect the overall calculation of **d** and **i** in equations (1) and (2) since,

$$\ln \frac{P_f}{P_i} \neq \ln \frac{(P_f + x)}{(P_i + x)}$$

So it is absolutely necessary to re-estimate x and include it in regeneration and assimilation calculations.

In principal, mixing of labelled ^{15}N compound usually follows the dilution equation given earlier where,

$$\mathbf{P_a A_a + P_b A_b = P_m A_m}$$

in which $\mathbf{P_a}$ and $\mathbf{P_b}$ are nitrogen pools (or quantities) of the ^{15}N labelled compounds **a** and **b** respectively, $\mathbf{A_a}$ and $\mathbf{A_b}$ the corresponding ^{15}N abundances, $\mathbf{P_m}$ is the amount of the mixture ($\mathbf{P_m = P_a + P_b}$) and $\mathbf{A_m}$ its corresponding ^{15}N abundace. The above equation can be re-written as

$$P_m = P_b \cdot \frac{(A_b - A_a)}{(A_m - A_a)}$$

Since we know $\mathbf{P_b}$, $\mathbf{A_a}$, $\mathbf{A_b}$ and the experiment on microdiffusion technique indicated that our $\mathbf{A_m}$ recovery and measurement is about 98 % (table 6.12), accurate $\mathbf{P_m}$ which would correspond to our initial ammonium pool (immediately after the addition of the spike), can easily be calculated. The difference between this calculated value and the experimentally observed value would give an estimate of the underestimated NH_4^+ concentration. This difference was calculated and added to the initial ($\mathbf{P_i}$) and final ($\mathbf{P_f}$) ammonium pools in all our regeneration and assimilation calculations.

6.1.1.2 Regeneration and assimilation rates (RAR) in Rm sediments

Tables 6.13 and 6.14 give the results of ammonium pools and ^{15}N abundances observed in our regeneration and assimilation experiments for the Rm sediments in dry and rainy seasons respectively. Details of the exact methodology used are given in chapter 3.
Table 6.15 gives the observed and corrected NH_4^+ pools for the same sediments while tables 6.16 and 6.17 give the calculated regeneration and assimilation rates for dry and rainy seasons, respectively.

During dry season, the regeneration rate is found to be about 934 ± 82 nmol N g^{-1} d^{-1} for the upper 1 cm and averagely 485 ± 156 nmol N g^{-1} d^{-1} for the 1 - 6 cm depth, respectively. About 60 % of this is taken up (by bacteria) giving a net balance of about 399 ± 59 nmol N g^{-1} d^{-1} and 170 ± 60 nmol N g^{-1} d^{-1} for the 0 - 1 and 1 - 6 cm depth, respectively. In rainy season, the net produced NH_4^+ is found to be 410 ± 56 and 225 nmol N g^{-1} d^{-1} for 0 - 1 and 1 - 6 cm sections respectively. Statistical treatment (analysis of variance) of the regeneration rate in dry and rainy seasons indicate no significant difference ($p > 0.05$) in the two seasons. Table 6.18 gives the average results of the pooled data in which the average regeneration rate for the 0 - 1 and 1 - 6 cm depth is found to be 1036 ± 237 and 511 ± 127 nmol N g^{-1} d^{-1} respectively.

Table 6.13 : Results of the ammonium pools and their corresponding ^{15}N adundances observed during regeneration and assimilation experiments on Rm sediments in dry season between 1992 and 1993.

Date	Depth (cm)	P_o µM	P_i µM	P_f µM	A_i % ^{15}N	A_f % ^{15}N	Water content (%)
26/2/92	0 - 1	112.8 ± 11.3	123.4 ± 22.8	315.2 ± 23.5	3.871 ± 0.170	0.881 ± 0.188	67.0
t = 24 h	1 - 6	131.6 ± 10.5	128.0 ± 31.4	237.0 ± 15.0	4.201 ± 0.182	1.435 ± 0.018	60.4
spike *							
27/3/92	0 - 1	91.3 ± 5.9	94.8 ± 9.9	236.3 ± 19.4	5.233 ± 0.281	0.730 ± 0.064	67.3
t = 24	1 - 6	99.3 ± 10.9	104.7 ± 3.9	204.3 ± 49.8	4.434 ± 1.647	1.102 ± 0.185	61.4
spike*							
9/2/93	0 - 1	109.2 ± 16.7	116.3 ± 15.3	248.2 ± 27.4	6.963 ± 0.113	2.393 ± 0.086	77.1
t = 24	1 - 6	128.4 ± 15.1	143.3 ± 27.7	217.5 ± 25.1	7.395 ± 0.149	2.052 ± 0.133	65.0
spike**							
27/2/93	0 - 1	116.9 ± 8.1	137.4 ± 19.6	317.0 ± 12.7	5.849 ± 0.211	1.318 ± 0.137	67.1
t = 24	1 - 6	151.3 ± 11.9	157.7 ± 21.9	275.0 ± 31.3	5.680 ± 0.173	1.422 ± 0.029	60.7
spike**							
11/3/93	0 - 1	57.1 ± 6.9	64.4 ± 11.7	192.6 ± 19.3	10.249 ± 0.18	1.296 ± 0.199	70.0
t = 24 h	1 - 6	97.5 ± 8.4	98.2 ± 5.8	180.6 ± 9.4	8.853 ± 0.22	2.993 ± 0.084	62.3
spike**							
27/3/93	0 - 1	73.8 ± 10.4	79.37 ± 7.9	297.61	9.871 ± 0.099	1.217 ± 0.066	63.7
t = 24 h	1 - 6	95.9 ± 19.4	114.8 ± 10.1	224.78	8.970 ± 0.177	3.085 ± 0.153	56.2
spike**							

Spike*: 0.1 ml 400 µM $^{15}NH_4Cl$ **Spike**:** 0.1 ml 750 µM $^{15}NH_4Cl$

Table 6.14 : Results of the ammonium pools and their corresponding ^{15}N adundances observed during regeneration and assimilation experiments on Rm sediments in wet season between 1992 and 1993.

Date	Depth (cm)	P_o μM	P_i μM	P_r μM	A_i % ^{15}N	A_f % ^{15}N	Water content (%)
2/5/92	0 - 1	73.7 ± 8.5	79.3 ± 6.7	273.1 ± 17.8	5.247 ± 0.203	2.413 ± 0.087	68.7
t = 24 h	1 - 6	125.6 ± 10.3	127.4 ± 15.5	278.0 ± 15.9	4.396 ± 0.117	1.315 ± 0.117	58.3
spike*							
25/5/92	0 - 1	77.3 ± 14.8	83.04 ± 10.4	314.8 ± 39.6	6.141 ± 0.227	1.118 ± 0.104	65.7
t = 24 h	1 - 6	119.9 ± 23.3	136.7 ± 15.8	326.3 ± 24.7	4.185 ± 0.239	1.311 ± 0.065	62.4
spike*							
9/6/92	0 - 1	119.4 ± 13.1	121.7 ± 15.3	296.1 ± 23.9	3.590 ± 0.211	0.649 ± 0.097	72.2
t = 24	1 - 6	108.8 ± 15.7	118.9 ± 12.9	207.6 ± 19.9	5.440 ± 0.123	1.486 ± 0.121	65.4
spike*							
23/6/92	0 - 1	89.2 ± 9.3	106.7 ± 18.9	272.3 ± 31.1	6.297 ± 0.201	0.942 ± 0.127	69.2
t = 24	1 - 6	133.7 ± 22.5	139.3 ± 27.2	216.3 ± 22.1	4.901 ± 0.027	1.596 ± 0.163	62.4
spike**							
21/5/93	0 - 1	95.22 ± 5.9	95.77 ± 17.1	233.3 ± 19.4	8.769 ± 0.218	1.115 ± 0.179	71.1
t = 24	1 - 6	129.9 ± 28.8	148.6 ± 22.1	299.6 ± 29.3	6.121 ± 0.113	1.789 ± 0.219	66.3
spike**							
5/6/93	0 - 1	72.6 ± 11.1	77.83 ± 9.6	281.1 ± 25.7	9.675 ± 0.311	0.776 ± 0.086	69.3
t = 24 h	1 - 6	121.2 ± 19.4	129.7 ± 17.4	300.1 ± 47.2	5.825 ± 0.221	1.124 ± 0.111	60.3
spike**							
18/6/93	0 - 1	107.7 ± 17.8	121.6 ± 27.1	288.4 ± 23.2	7.088 ± 0.261	1.099 ± 0.100	65.8
t = 24 h	1 - 6	93.7 ± 16.4	101.4 ± 11.7	194.3 ± 27.4	9.293 ± 0.277	2.457 ± 0.177	60.2
spike**							

Spike*: 0.1 ml 400 μM $^{15}NH_4Cl$ **Spike**:** 0.1 ml 750 μM $^{15}NH_4Cl$

Table 6.15: Correction of observed ammonium pools for regeneration / assimilation calculations for Rm sediments (1992 - 1993).

Date	Depth (cm)	A_i % ^{15}N (observed)	Observed NH_4^+ pool (μM)		Corrected NH_4^+ pool (μM)	
			P_i	P_r	P_i	P_r
06.02.92	0 - 1	5.596	82.11	180.90	111.35	210.16
	1 - 6	4.858	145.9	219.40	145.90	219.37
26.02.92	0 - 1	3.871	123.43	315.69	159.88	351.69
	1 - 6	4.200	127.99	237.03	171.67	280.71
27.03.92	0 - 1	5.233	94.76	236.27	131.20	272.71
	1 - 6	4.434	104.72	204.26	173.86	273.40
02.05.92	0 - 1	5.247	79.31	273.15	111.72	305.56
	1 - 6	4.396	127.42	278.08	168.91	319.57
25.05.92	0 - 1	6.140	83.04	314.80	104.07	335.83
	1 - 6	4.185	136.72	326.28	165.66	355.22
09.06.92	0 - 1	3.590	121.66	296.10	153.99	328.43
	1 - 6	5.440	118.93	207.61	145.98	234.66
23.06.92	0 - 1	6.297	87.74	253.26	120.50	286.02
	1 - 6	4.901	139.37	216.29	171.30	248.22
09.02.93	0 - 1	6.963	116.34	248.21	145.71	277.58
	1 - 6	7.395	123.32	197.50	161.97	236.15
27.02.93	0 - 1	5.849	101.49	281.03	201.82	381.36
	1 - 6	5.680	157.69	275.00	229.38	346.69
11.03.93	0 - 1	10.250	64.37	192.62	107.32	235.57
	1 - 6	8.853	98.23	180.58	139.99	222.34
27.03.93	0 - 1	9.870	79.37	297.61	122.35	340.59
	1 - 6	8.970	114.83	224.78	153.21	263.16
21.05.93	0 - 1	8.769	95.77	233.25	133.13	270.61
	1 - 6	6.121	148.63	299.56	194.15	345.08
05.06.93	0 - 1	9.675	77.83	281.12	114.66	317.95
	1 - 6	5.825	129.69	300.11	224.77	395.19
18.06.93	0 - 1	7.088	121.63	288.37	167.32	334.06
	1 - 6	9.293	101.37	194.32	137.37	230.73

Table 6.16: Regeneration (**d**) and assimilation (**i**) rates (nmol N g^{-1} d^{-1}) in Rm sediments in dry seasons (Feb. / March) of 1992 and 1993.

Date	Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
26.02.92	0 - 1	950	560	390	59
	1 - 6	433	266	167	61
27.03.92	0 - 1	1036	724	312	70
	1 - 6	599	303	296	51
09.02.93	0 - 1	808	366	442	46
	1 - 6	522	384	138	74
27.02.93	0 - 1	1005	556	449	55
	1 - 6	710	528	183	74
11.03.93	0 - 1	901	552	349	61
	1 - 6	345	209	136	60
27.03.93	0 - 1	905	453	452	50
	1 - 6	301	142	159	47
Average	0 - 1	934 ± 82	535 ± 120	399 ± 59	57
(± S.D)	1 - 6	485 ± 155	305 ± 136	180 ± 67	63

Table 6.17: Regeneration (**d**) and assimilation (**i**) rates (nmol N g^{-1} (DW) d^{-1}) in Rm sediments in rainy seasons (May / June) of 1992 and 1993.

Date	Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
02.05.92	0 - 1	1042	617	425	59
	1 - 6	479	268	211	56
25.05.92	0 - 1	778	331	447	43
	1 - 6	440	126	315	27
09.06.92	0 - 1	1450	1002	448	69
	1 - 6	534	367	168	69
23.06.92	0 - 1	1007	577	430	57
	1 - 6	459	315	137	72
21.05.93	0 - 1	1150	814	337	71
	1 - 6	726	429	298	59
05.06.93	0 - 1	1407	949	459	67
	1 - 6	622	367	255	59
18.06.93	0 - 1	1032	710	322	69
	1 - 6	476	286	190	60
Average	0 - 1	1124 ± 237	714 ± 232	410 ± 56	63
(± S.D)	1 - 6	533 ± 104	308 ± 97	225 ± 67	58

Table 6.18: Average values of regeneration (**d**) and assimilation (**i**) rates (nmol Ng^{-1} d^{-1}) in Rm sediments in dry (Feb. / March) and rainy seasons of 1992 and 1993.n = 13 (no. of observations).

Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
0 - 1	1036 ± 201	631 ± 203	373 ± 110	61
1 - 6	511 ± 127	307± 111	204 ± 65	60

6.1.1.3 Regeneration and assimilation rates (RAR) in Ct sediments

Tables 6.19 and 6.20 give the regeneration and assimilation rates observed for the Ct sediments in dry and rainy seasons while table 6.21 is the overall average for the Ct sediments. The actual observed and calculated ammonium pools and their corresponding ^{15}N isotopic abundances are given in the appendix.

No statistical difference (analysis of variance; $p > 0.05$) in regeneration and uptake rates were noticed for the Ct sediments in dry and rainy seasons. The observed average regeneration rate for the 0 - 1 cm depth (673 nmol N g^{-1} d^{-1}) was found to be significantly smaller than that observed on Rm sediments (1036 nmol N g^{-1} d^{-1}). However, considering the fact that the difference in organic nitrogen content in the two sediment types is about ten times, this difference is relatively small. Net ammonium production in these Ct sediments was found to be about 411 and 239 nmol N g^{-1} d^{-1} for the 0 - 1 and 1 - 6 cm depth respectively.

Ammonification rate measured in anaerobic mangrove sediment of Hinchinbrook Island (Iizumi, 1986) displayed rates ranging from 60 to 260 nmol N g^{-1} (D.W) d^{-1} while Rosenfield (1979), reported net ammonium release of 76 nmol N g^{-1} (D.W) d^{-1} for Florida mangrove sediments. Our average net ammonium production rates (for the 0 - 1 cm depth) of about 400 nmol N g^{-1} (D.W) d^{-1} for the Rm and Ct Gazi mangrove sediments are therefore quite high and can only be compared to those found in Malaysian mangrove sediments which ranged between 450 and 750 nmol N g^{-1} (D.W) d^{-1} (Shaiful et al., 1986). It is important to note that in all these mangrove sediments, there is a significant net production on ammonium despite having organic matter poor in quality (C/N ratio $\geq$ 20; Blackburn, 1986).

Table 6.19: Regeneration (**d**) and assimilation (**i**) rates (nmol N g^{-1} d^{-1}) in Ct sediments in dry seasons (Feb. / March) of 1992 and 1993.

Date	Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
06.02.92	0 - 1	604	203	401	34
	1 - 6	502	184	318	34
20.02.92	0 - 1	774	251	524	33
	1 - 6	519	195	324	38
17.03.92	0 - 1	588	245	343	42
	1 - 6	392	169	223	43
08.02.93	0 - 1	757	280	475	37
	1 - 6	439	209	230	48
27.02.93	0 - 1	694	243	451	35
	1 - 6	531	334	197	61
11.03.93	0 - 1	451	171	280	38
	1 - 6	292	157	135	54
27.03.93	0 - 1	896	377	519	42
	1 - 6	402	189	212	47
Average (± S.D)	0 - 1	680 ± 146	253 ± 65	427 ± 91	37
	1 - 6	439 ± 85	205 ± 59	234 ± 67	47

Table 6.20: Regeneration (**d**) and assimilation (**i**) rates (nmol N g^{-1} d^{-1}) in sediments in rainy seasons (May / June) of 1992 and 1993.

Date	Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
02.05.92	0 - 1	562	206	356	37
	1 - 6	533	258	275	48
06.06.92	0 - 1	438	184	254	42
	1 - 6	225	79	146	35
21.05.93	0 - 1	872	414	457	48
	1 - 6	350	85	265	24
05.06.93	0 - 1	674	222	452	33
	1 - 6	592	310	282	52
16.06.93	0 - 1	771	355	416	46
	1 - 6	420	161	259	38
Average (± S.D)	0 - 1	663 ±170	276 ± 102	387 ± 85	42
	1 - 6	424 ± 146	179 ± 103	246 ± 54	42

Table 6.21: Average values of regeneration (**d**) and assimilation (**i**) rates (nmol N g^{-1} d^{-1}) in Ct sediments in dry (Feb. / March) and rainy seasons of 1992 and 1993. n = 12 (no. of observations).

Depth (cm)	d	i	d - i (Net prod.)	i/d (%)
0 - 1	673 ± 149	263 ± 79	411 ± 87	39
1 - 6	416 ± 151	188 ± 88	239 ± 60	45

6.1.2 Nitrification process in Rm and Ct sediments

Nitrification can in simple terms be defined as ammonium (or nitrite) oxidation. By this definition it is clearly seen that for nitrification to occur, we need to have NH_4^+ (or NO_2^-) and oxygen in the presence of nitrifying bacteria. Nitrifying bacteria are chemolithotrophic (Kelly, 1971) and can obtain all the energy necessary for growth and carbon assimilation from the aerobic oxidation of ammonium to nitrite or nitrite to nitrate. In the marine environment two genera of bacteria, *Nitrosomonas* and *Nitrosococcus* mediate the oxidation of NH_4^+ to NO_2^- while *Nitrobacter*, *Nitrospira* and *Nitrococcus* group oxidize NO_2^- to NO_3^- (Kaplan, 1983).

During growth by nitrifying bacteria at sea water pH, the reactions for the first step in nitrification are:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad \text{.....(1)}$$

followed by the oxidation of NO_2^-

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- \quad \text{..... (2)}$$

Rates of nitrification that have been measured in aquatic marine environments (within the water column) range from 1 to 10 nmol N l^{-1} d^{-1} over a wide range of NH_4^+ concentrations, locations and depths (Kaplan, 1983). Most coastal marine sediments are anoxic with a redox potential of less than + 200 mV below the surface. However due to abundance of nitrifying bacteria on the upper sediment layer (usually the upper 1 cm depth) nitrification in sediments could be very high depending on oxygen availability. For instance, surface sediments of Malaysian mangrove vegetation (Shaiful et al., 1986) were observed to have rates as high as 470 μmol N l^{-1} d^{-1} (2.82 mmol N m^{-2} d^{-1}) which are several orders of magnitude higher than those observed in aquatic marine environments. The rates observed by Shaiful et al. (1986) are however quite high compared to most rates observed in sediment which are mostly found to lie between 0.7 - 1.8 mmol N m^{-2} d^{-1} (Henriksen et al., 1993). Though the abundance of nitrifying bacteria in sediment is higher than in the overlaying water, the major limitation of nitrification in sediment is usually oxygen. Revsbech et al. (1980), using micro-electrodes, could not detect any oxygen below 10 mm depth in Danish estuary sediments. Most of their oxygen profiles could only extend up to 3 - 5 mm depth. In a south-east Asian mangrove swamp, Kristensen et al. (1988) found

oxygen penetration up to a maximum of only 2.5 mm depth. Due to these oxygen diffusion differences between sediments (and also differences in biomass of nitrifiers), different sediments may display different nitrification rates.

6.1.2.1 Potential Nitrification Rates (PNR) of Rm and Ct sediments

Potential nitrification (refer to chapter 3 for general methodology) is a method commonly used to compare nitrification ability of different sediments (Henriksen, et. al., 1993). In this technique ammonium and oxygen are supplied in excess to a sediment sample and nitrification rate measured as change of nitrate concentration with incubation time. In this case, nitrification rate is also assumed to be directly proportional to biomass and activity of nitrifying bacteria (Henriksen et. al., 1993).

6.1.2.1.1 Spatial and seasonal variation of PNR in Rm sediments

In order to investigate on possible spatial differences in potential nitrification in the Rm and Ct study plots, the following steps were followed.

(a) Twenty cores were taken from four randomly selected subplots (called A, B, C and D) within the study site.
(b) Each core was sectioned into 0-1, 1-2, 2-4, 4-6, 6-8, 8-10 and 10-12 cm and all corresponding segments from each subplot were pooled together and mixed thoroughly. Potential nitrification for each mixed segment was then determined as described in chapter 3. Changes in nitrate concentration between time t = 24 hours and initially (t = 0) were used in calculating the rates.

For easy comparison between the two sediment types, the results are expressed in units per gram sediment dry weight.
Table 6.22 gives the PNR rates as observed in Rm sediment in January 1993 on four randomly selected subplots.

Table 6.22: Potential nitrification rates (± S.D.) in nmol N g^{-1} $(D.W.)_{sediment}$ d^{-1} for Rm sediment in January 1993. Subplots A, B, C and D were randomly selected within the Rm study plot. Mean ± S.D (of duplicate samples).

Section (cm)	Subplot A	Subplot B	Subplot C	Subplot D
0-1	218 ± 39	277 ± 29	244 ± 35	260 ± 15
1-2	188 ± 21	251 ± 30	195 ± 24	254 ± 20
2-4	164 ± 16	150 ± 20	179 ± 30	169 ± 20
4-6	60 ± 10	34 ± 6	21 ± 3	57 ± 7
6-8	5 ± 3	2 ± 1	1 ± 1	10 ± 3
8-10	1 ± 1	1 ± 1	0	1 ± 1
10-12	0	0	0	0

No significant difference in PNR was noticed between the four subplots . This implies that considering the overall distribution of nitrification activity, there is no difference in spatial distribution of biomass of the nitrifying bacteria in the Rm study plot. Due to this, all results from the corresponding sections have been pooled together resulting in figure 6.10.

A sharp decrease of nitrification rate is noticed below 4 cm depth and hardly any nitrification process is noticed below 8 cm depth. Redox potentials taken concurrently at the four subplots (fig. 6.11) indicate slight inter-subplots variations (+200 to -50 mV) between the surface and 4 cm depth. However, below 4 cm depth the redox potentials are ≤ -50 mV.

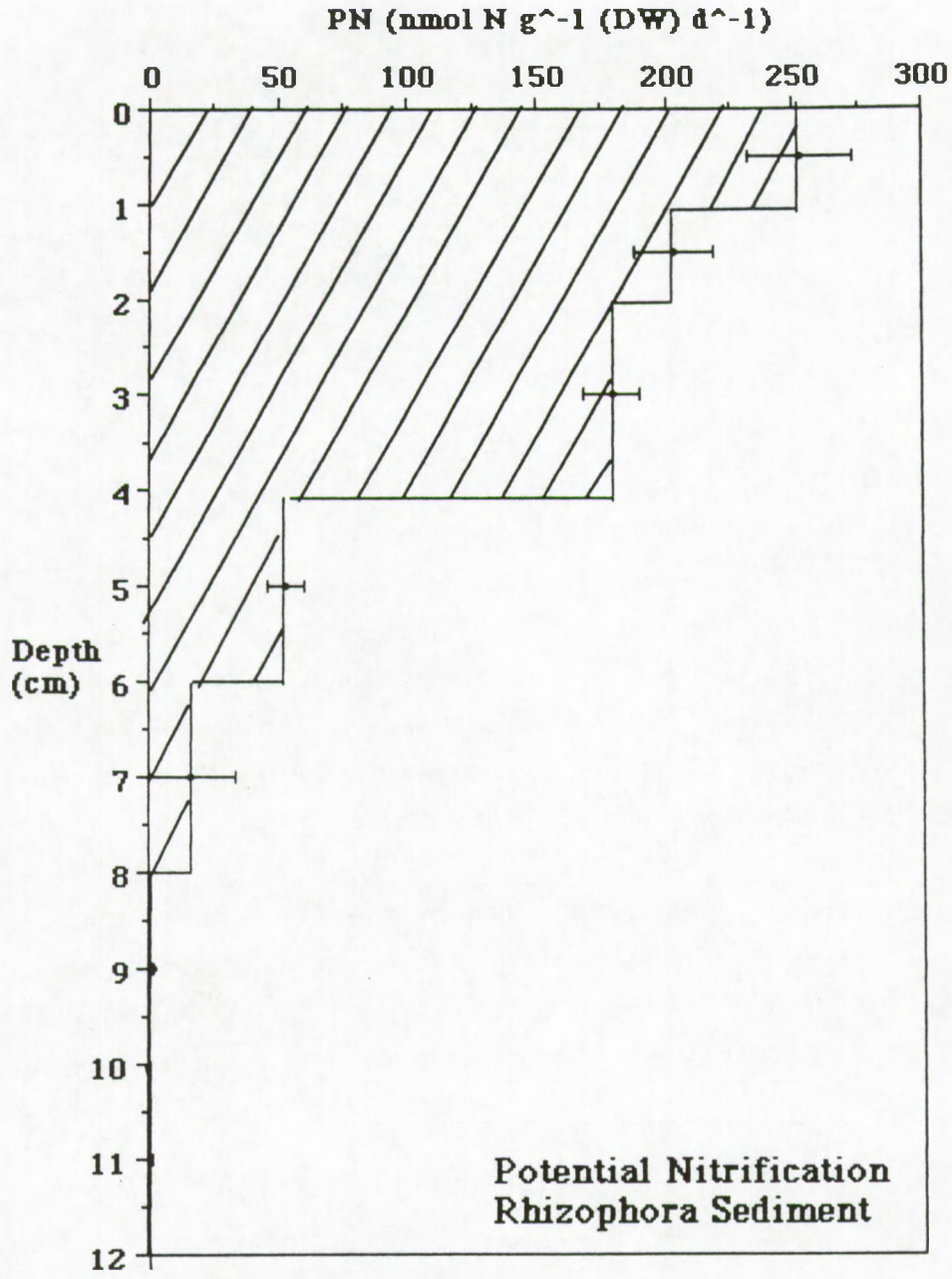


Fig. 6.10: Average potential nitrification rates (nmol N g^{-1} (D.W.)) from four randomly selected positions within the *Rhizophora mucronata* plot.

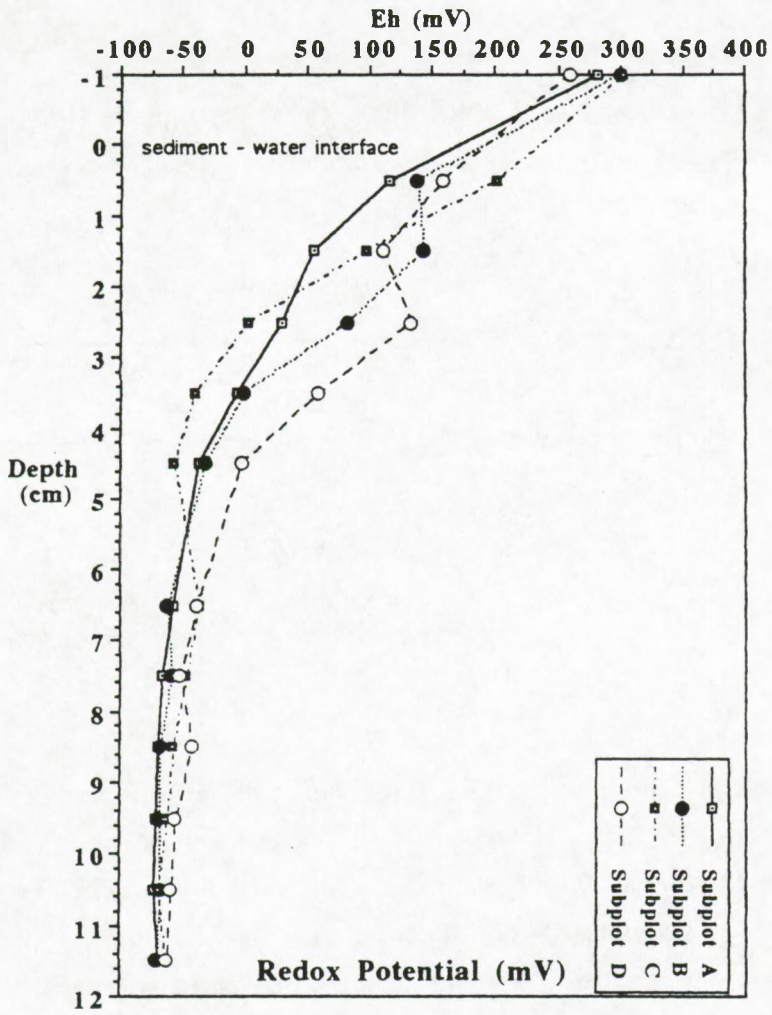


Fig. 6.11: Redox potential profiles four four subplots (A, B, C & D) used for potential nitrification experiments.

To check possible seasonal variation on potential nitrification in the Rm sediments, PNR determination was done once (or twice) a month between February, 1993 and July 1994. At each time 10 cores were taken randomly at the study plot, sectioned into 0 - 1, 1 - 2 and 2-6 cm sections and all corresponding sections pooled together and mixed thoroughly. Subsamples were then taken from these mixed slurries and used for PNR determination as outlined earlier.

Table 6.23: PNR (nmol N g^{-1} (D.W.) d^{-1}) in the upper 6 cm of the Rm sediment for dry and rainy season of 1993 and 1994. Means ± S.D. (n = number of observations).

Section (cm)	Dry Season (n = 4)	Rainy Season (n = 5)
0 - 1	264.4 ± 35.0	253.1 ± 25.1
1 - 2	227.5 ± 24.5	203.6 ± 30.2
2 - 6	128.8 ± 33.6	116.2 ± 35.5

No significant (ANOVA: $p > 0.05$) seasonal difference (table 6.23) was noticed on the potential nitrificaion rate implying lack of significant seasonal differences in activity (or biomass) of nitrifying bacteria. Henriksen et al. (1981), investigatinig on actual and potential nitrification rates in Danish sediments, observed no seasonal variations while Alongi, 1989 pointed out that bacterial distributions and densities in mangroves and adjacent sandflats in dry tropics, exhibited little or no seasonality over weekly or monthly intervals.

6.1.2.1.2 Spatial and seasonal variation of PNR in Ct sediments

Table 6.24 gives the PNR as observed in four randomly selected subplots (a total of twenty cores) within the Ct plot while table 6.25 shows results of the seasonal variations in dry and rainy periods. The Ct sediments displayed very different PNR levels as compared to the Rm sediments. Surface PNR did not exceed 20 nmol N g^{-1} (D.W) d^{-1} for any of the subplots randomly selected though a gradual decrease of PNR with depth was also noticed. Redox potential profiles for the four subplots (fig. 6.12) indicated slightly higher values than those found in Rm sediment. This would imply more oxidizing environment. The low PNR in Ct sediment implies low activity (or biomass) of nitrifying bacteria as compared to that found in Rm sediments. Again, as observed for Rm sediments, no seasonal variation of PNR was noticed. For easy comparison with actual nitrification rates, the average PNR values observed for subplots A, B, C and D in the two biotopes are given in table 6.26 in units of mmol N m^{-2} d^{-1}.

Table 6.24: Average potential nitrification rates (nmol N g^{-1} (D.W.) d^{-1}) of Ct sediment in January 1993. Subplots A, B, C and D were randomly selected within the Ct plot. Mean ± S.D. (of dublicate samples).

Section (cm)	Subplot A (PNR)	Subplot B (PNR)	Subplot C (PNR)	Subplot D (PNR)
0 - 1	17.2 ± 2.1	16.9 ± 1.7	18.3 ± 2.1	12.2 ± 1.5
1 - 2	11.7 ± 2.1	13.1 ± 1.4	22.1 ± 2.0	12.7 ± 0.8
2 - 4	10.4 ± 1.4	6.5 ± 1.1	14.1 ± 1.6	12.2 ± 1.2
4 - 6	6.5 ± 0.7	7.6 ± 0.7	8.3 ± 1.4	8.3 ± 1.2
6 - 8	6.5 ± 0.4	4.6 ± 0.3	8.6 ± 0.7	5.7 ± 0.3
8 - 10	1.9 ± 0.4	2.9 ± 0.3	1.6 ± 0.3	0.8 ± 0.3
10 - 12	3.0 ± 1.0	0.8 ± 0.4	0.7 ± 0.3	0.7 ± 0.2

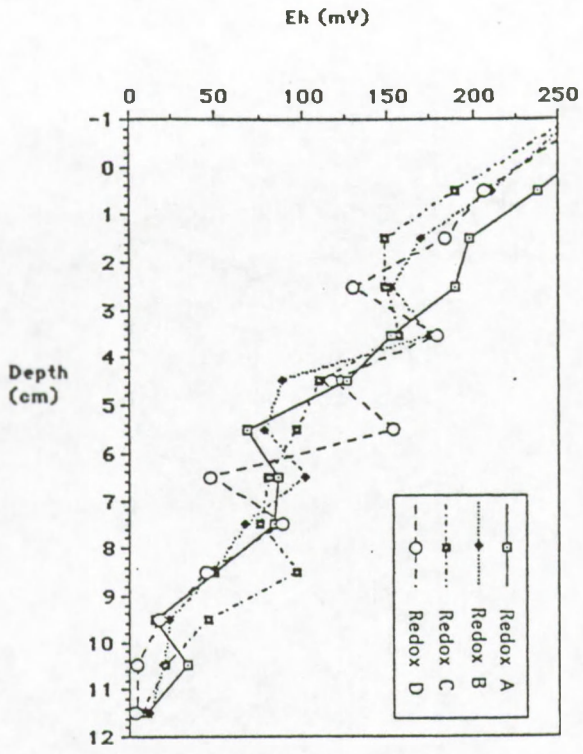


Fig 6.12: Redox potentials (Eh) taken at subplots used for PNR studies for Ct sediments.

Table 6.25: PNR (nmol N g^{-1} (D.W.) d^{-1}) in the upper 6 cm of the Ct sediment for dry and rainy season of 1993 and 1994. Means ± S.D. (n = number of observations).

Section (cm)	Dry Season (n = 6)	Rainy Season (n = 6)
0 - 1	15.5 ± 3.3	17.6 ± 3.3
1 - 2	10.1 ± 2.7	8.9 ± 3.4
2 - 6	9.0 ± 3.5	8.3 ± 2.2

Table 6.26: Average rates (without S.D.) of potential nitrification (PN) of subplots A, B, C and D in Rm and Ct sediments. The rates have been recalculated (using porosity values in table 4.17) and expressed in mmol N m^{-2} d^{-1} for easy comparison with actual nitrification rates.

Section (cm)	Rm (mmol N m^{-2} d^{-1})	Ct (mmol N m^{-2} d^{-1})
0 - 1	1.07	0.23
1 - 2	1.08	0.19
2 - 4	1.79	0.26
4 - 6	0.59	0.16
6 - 8	0.07	0.12
8 - 10	0.00	0.03
10 - 12	0.00	0.02

6.1.2.2 Actual Nitrification Rates (ANR) of Rm and Ct sediments

One of the main steps for nitrification to occur is bacterial conversion of NH_4^+ to NO_2^- ;

$$NH_4^+ + 1.5\ O_2 \text{ ----------> } NO_2^- + H_2O + 2H^+$$

It is possible to block this process by adding nitrification inhibitors which are capable of blocking the reaction (Henriksen et al., 1993). Differences in accumulation of ammonium between inhibited and uninhibited samples allow estimates of nitrifying activity (actual nitrification rate) to be determined (Hall, 1984). Two of the most commonly used nitrification inhibitors are Nitrapyrin and Allythiourea (ATU). In our study, we used ATU and the exact experimental protocol is described in chapter 3.

Another important requirement for the nitrification blocking method is to have sediments with relatively low variation in ammonium pool concentrations (Henriksen et al., 1993). This is necessary because one set is used as control with no addition of the inhibitor so it is necessary to have a more or less uniform initial NH_4^+ concentration before incubation. As discussed earlier (section 4.1.2.2), Gazi mangrove sediments exhibit high (10-30%) standard deviations of NH_4^+ profiles even for cores taken within an area of 1x1 meter square. Due to this, differences in NH_4^+ concentrations between inhibited and uninhibited cores were mainly found to lie within the standard deviation of the subsamples (implying no significant difference for the means). The actual nitrification results presented here are therefore only for those where significant differences between initial and final ammonium concentrations were found. These rates should therefore only be considered as maximum possible rates.

Tables 6.27A and 6.27B show two examples of the results obtained for nitrification experiments conducted on 7th and 23rd September 1994 respectively, while table 6.28A and 6.28B give the same for the Ct sediments. Table 6.29 gives the average (± S.D.) of all the ANR results obtained from all experiments conducted between September and October 1994 from Rm and Ct sediments.

Table 6.27A: Maximum possible nitrification rate (mmol N m^{-2} d^{-1}) in Rm sediment on 7th September 1994.

DEPTH cm	NH_4^+ t = 0 μM	NH_4^+ (+ATU) t = 24 h μM	NH_4^+ (-ATU) t = 24 h μM	NH_4^+ Net accum. μM N d^{-1}	**Max. Nitrif. rate mmol N m^{-2} d^{-1}**
0 - 1	151 ± 26	303 ± 37	239 ± 32	64	0.64
1 - 2	149 ± 19	242 ± 22	212 ± 16	30	0.30
2 - 3	158 ± 33	163 ± 23	179 ± 21	-16	0
3 - 4	123 ± 16	169 ± 29	158 ± 22	11	0

Table 6.27B: Maximum possible nitrification rate (mmol N m^{-2} d^{-1}) in Rm sediment on 23rd September 1994.

DEPTH cm	NH_4^+ t = 0 μM	NH_4^+ (+ATU) t = 24 h μM	NH_4^+ (-ATU) t = 24 h μM	NH_4^+ Net accum. μM N d^{-1}	**Max. Nitrif. rate mmol N m^{-2} d^{-1}**
0 - 1	140 ± 27	229 ± 33	184 ± 26	45	0.45
1 - 2	184 ± 30	289 ± 30	263 ± 30	24	0
2 - 3	178 ± 26	224 ± 30	224 ± 26	26	0
3 - 4	142 ± 32	190 ± 20	184 ± 22	22	0

Table 6.28A: Maximum possible nitrification rate (mmol N m^{-2} d^{-1}) in Ct sediments on 10th september 1994.

DEPTH (cm)	NH_4^+ t = 0 μM	NH_4^+ (+ATU) t = 24 h μM	NH_4^+ (-ATU) t = 24 h μM	NH_4^+ Net accum. μM N d^{-1}	**Max. Nitrif. rate mmol N m^{-2} d^{-1}**
0 - 1	157 ± 21	479 ± 33	433 ± 26	46	0.21
1 - 2	211± 29	388 ± 30	417 ± 35	-29	0
2 - 3	258 ± 36	403± 28	421 ± 39	18	0
3 - 4	244 ± 32	372 ± 35	401± 42	29	0

Table 6.28B: Maximum possible nitrification rate (mmol N m^{-2} d^{-1}) in Ct sediments on 19th September 1994.

DEPTH cm	NH_4^+ t = 0 μM	NH_4^+ (+ATU) t = 24 h μM	NH_4^+ (-ATU) t = 24 h μM	NH_4^+ Net accum. μM N d^{-1}	**Max. Nitrif. rate mmol N m^{-2} d^{-1}**
0 - 1	139 ± 21	453 ± 26	411 ± 33	42	0.21
1 - 2	215 ± 37	482 ± 19	444 ± 32	38	0.19
2 - 3	311± 15	489 ± 35	504 ± 43	- 15	0
3 - 4	229 ± 33	377 ± 28	389 ± 36	12	0

Table 6.29: Average maximum possible actual nitrification rates (mmol N m^{-2} d^{-1}) in Rm and Ct sediments.

Depth (cm)	Rm sediments n = 5	Ct sediments n = 7
0 - 1	0.43 ± 0.12	0.18 ± 0.11
1 - 2	0.06 ± 0.13	0.00
2 - 4	0.00	0.00
4 - 6	0.00	0.00

6.1.3 Benthic Fluxes (sediment - water interface) of Gazi mangrove sediments

Once produced from decaying organic matter as a result of remineralization, part of the ammonium can be incorporated back by bacteria (Blackburn, 1979), while in the presence of oxygen, part of it can be nitrified (Henriksen and Kemp, 1988; Henriksen, et al., 1993). The produced nitrate and the balance of the produced ammonium can either be taken up by trees or diffuse by molecular diffusion out into the water column. In principle, the ammonium and nitrate concentrations found in sediments are usually orders of magnitude higher than those found in the water column so the fluxes are always expected to be upward. This has led to the development of a number of mathematical models (Aller 1977; Toth and Lerman, 1977) which may be used to predict molecular diffusion of inorganic nutrients across the sediment - water interface. However, field studies conducted in different marine sediments indicate that the difference in concentration may not always lead to observable flux rates across the interface. Blackburn and Henriksen (1983) looking into nitrogen cycling in different types of Danish marine sediments, observed no significant correlation between ammonium flux and ammonium pore water gradient. These authors concluded that the ion exchange capacity of the sediment may be more important in controlling ammonium flux from sediment to the overlaying water than the mere differences in NH_4^+ concentrations in the two layers. Henriksen et al. (1983) also observed no correlation between concentration gradient of NO_3^- across the sediment - water interface and the measured NO_3^- flux. They attributed the low flux rates (despite large nitrate gradient at the interface) to the presence of benthic diatoms at the surface which create an effective filter for nutrients diffusing towards the sediment surface from below.

In mangrove sediments, nutrient concentrations are much lower than those found in most other types of sediments. While the maximum total dissolved ammonium (free and adsorbed NH_4^+) found in the Rm sediment was about 175 μM, those found in salty marsh sediments are mostly an order of magnitude higher. These low concentrations in mangrove sediments eventually result in low sediment to water column nutrient fluxes into the water column (Hines and Lyons, 1982; Kristensen et al., 1988; Alongi, 1990). It has also been reported that the nutrient flux rates observed are sometimes even much lower than those expected from the gradient between pore water and the overlaying water (Alongi et al., 1992). Several reasons have been given to explain this phenomenon apart from NH_4^+ adsorption on to the clay (Blackburn & Henriksen, 1993). Kristensen et al. (1992)

working on nutrient dynamics in a south-east Asian mangrove swamp observed the same phenomenon (low fluxes from sediment to water column than expected from the differences in NH_4^+ concentrations between the two layers) and suggested that this may be related to the nutritional status of the living or active microalgae at the sediment surface. These authors demonstrated that the microalgae may assimilate DIN from below and above the sediment - water interface despite low concentrations in the overlaying water, thereby acting as a "filter" for the DIN flux from the sediment. In this case, it is even possible to have negative flux rates despite having relatively higher nutrient concentration in sediment than in the water column.

Dissolved inorganic nitrogen flux rates between the sediment and overlaying water within the Rm and Ct sediments, were determined using jar chambers and intact core incubations techniques. The exact methodologies used for the chambers and the intact core incubations are given in chapter 3. In this section, only the results and problems encountered are discussed. In order to have an idea about the possible NH_4^+ flux rate expected, mathematical calculations (using Fick's law on molecular diffusion) were also performed using observed pore-water concentration gradients.

6.1.3.1 NH_4^+ flux rate using mathematical calculation (Fick's law).

Flux rates from sediments may be calculated from pore water concentration gradients and diffusion coefficients using diagenetic models (Aller, 1977; Toth and Lerman, 1977; Krom and Berner, 1980; Ullman and Aller, 1982) assuming that molecular diffusion follows Fick's law.

Fick's first law, as expressed by Ullman and Aller (1982), is as follows:

$$J_i = - \phi D_s^i \frac{\partial C_i}{\partial x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where
- J_i = flux rate (mass of solute · unit area sediment^{-1} . time^{-1})
- ϕ = porosity
- D_s^i = Bulk sediment diffusion coefficient of solute i (unit area . time^{-1})
- C_i = mass of solute . unit volume pore water^{-1}
- x = space co-ordinate

Ullman and Aller, 1982, further demonstrated that D_s^i is correlated to free solution diffusion coefficient of solute i (D_o^i) by the following equation:

$$D_s^i = \frac{D_o^i \phi^m}{\phi} \quad \text{..... (2)}$$

where D_o^i = free solution diffusion coefficient of solute i
m = tortuosity correction factor (m = 2 when $\phi \leq 0.7$ and 2.5 - 3 when $\phi \geq 0.7$)

The free solution diffusion coefficient D_o^i of NH_4^+ is $(19.8 + 0.4\ (T-25°)) \times 10^{-6}$ cm^2 s^{-1} as given by Krom and Berner (1980), where T is temperature in degrees Celsius.
In Gazi Rm sediment, the porosity of the 0 - 1 cm depth is 0.92 (vol:vol) as shown on table 4.17. In this case the porosity correction factor m is 3. The bulk sediment diffusion coefficient of NH_4^+ in equation 2 is therefore 16.76×10^{-6} cm^2 s^{-1} at an average Rm sediment temperature of 25 °C. For the Ct sediments, the water porosity is averagely 0.46 (table 4.17) for the upper 1 cm depth. This implies that the tortuosity correction factor, m, is 2. The free solution diffusion coefficient D_o^i of NH_4^+ is therefore 9.48×10^{-6} cm^2 s^{-1} at an average Ct sediment temperature of 27°C.

The maximum observed NH_4^+ concentration in the water column above the Rm sediment was about 0.4 μM (section 4.1.1) while that observed at the 0 - 1 cm sediment depth ca. 64 ± 16 μM (refer to section 5.2; only interstitial water considered). The maximum change in concentration between the sediment and water column (2 cm space co-ordinate) is therefore ca. 63.6 μM. When all these values are put into equation (1) the calculated NH_4^+ flux rate from the sediment into the water column is found to be ca. 0.39 mmol N m^{-2} d^{-1}.

The water column ammonium concentration above the Ct sediments also hardly exceeds 0.4 μM while the sediment's pore water NH_4^+ concentration (free NH_4^+) is averagely 129 ± 39 μM for the upper 1 cm depth. Substituting all these values to equation 1 above, we get a flux rate of 0.111 mmol N m^{-2} d^{-1} from the sediment into the water column.

6.1.3.2 NH_4^+ fluxes using plexiglass chambers

Cylindrical plexiglass chambers of diameter 30 cm and height 30 cm were constructed for sediment - water interface flux studies. These chambers were also fitted with a thermometer, a sampling port and a stirrer whose speed could be controlled by a small motor. The exact details of these chambers are given in chapter 3.

It is very unfortunate that due to the mangrove root system, it was completely impossible to use the chambers for flux studies. Any attempt of forcing the chambers into the sediment resulted in disturbance of the surface sediments making the initial ammonium concentrations very high. Also, due to the dense root system, it was difficult to have the water enclosed in the jars completely isolated from surrounding water.

A number of trials were done and most of them were unsuccessful. We therefore stopped using the chambers in mangrove sediments and concentrated on using plexiglass cores.

6.1.3.3 Benthic fluxes using intact core incubation technique

Intact core incubations for the investigation of sediment - water interface fluxes were done using a technique similar to that described by Henriksen et al. (1981). The NH_4^+ and NO_3^- fluxes between sediment and water column were measured in short term incubations (4 to 6 h) in undisturbed sediment cores (3.6 cm i.d.).

Increase of NH_4^+ and NO_2^- + NO_3^- concentrations in overlying water during incubation period were measured. At each time, about five sediment cores were used. Two empty cores were also filled with water from the same station and used as control. The exact details of the methodology are given in chapter 3. This experiment was done on routine basis in 1992, 1993 and part of 1994 and all the results obtained from each core were used in plotting frequency distribution charts. Figures 6.13A and 6.13B give the frequency distribution charts for NH_4^+ and NO_3^- + NO_2^- fluxes, respectively, across the sediment - water interface of Rm sediments while figures 6.14A and 6.14B give the same for the Ct sediments. The actual results obtained from each core are given in the appendix.

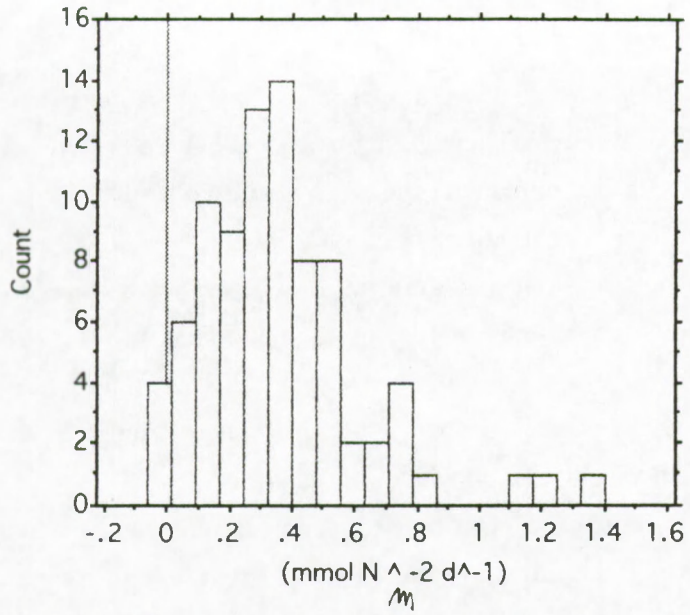


Fig. 6.13A: Frequency distribution of NH_4^+ flux rate (mmol N m^{-2} d^{-1}) across the sediment - water interface of Rm plot between 1992 and 1994. (n = 17: no.of observations).

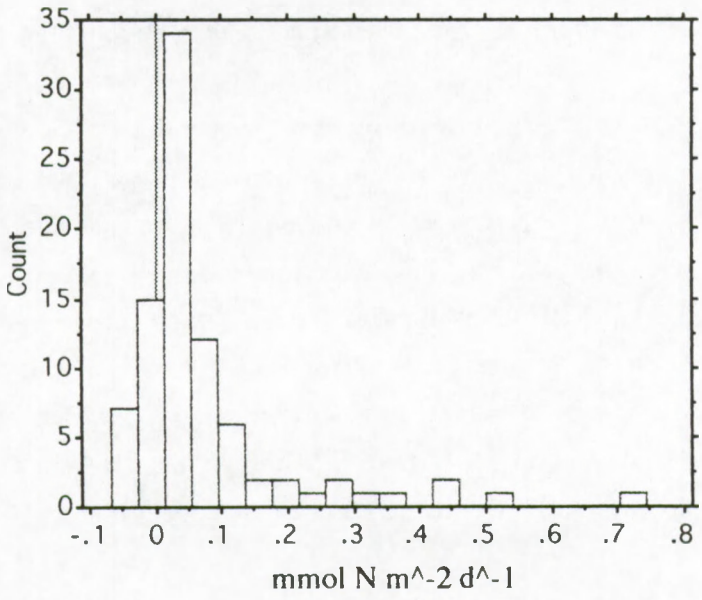


Fig. 6.13B: Frequency distribution of NO_3^- flux rate (mmol N m^{-2} d^{-1}) across the sediment - water interface of Rm plot between 1992 and 1994. (n = 17 : no. of observations)

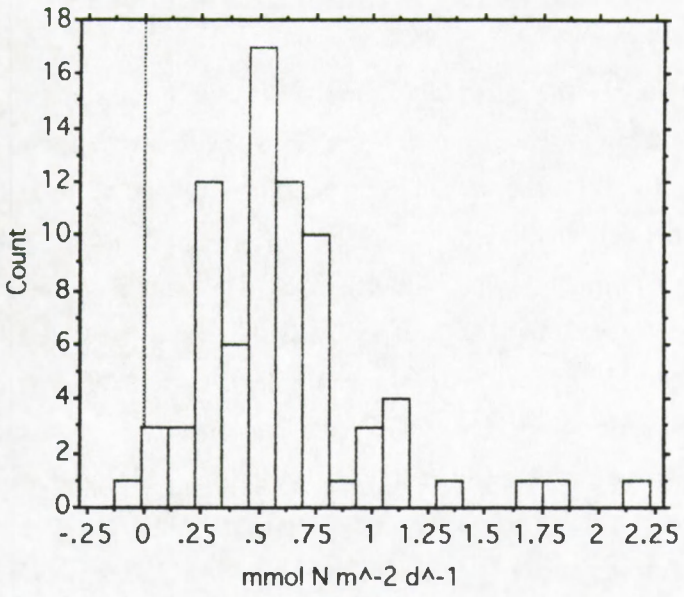


Fig. 6.14A: Frequency distribution of NH_4^+ flux rate (mmol N m^{-2} d^{-1}) across the sediment - water interface of Ct plot between 1992 and 1994. (n = 15 : no. of observations).

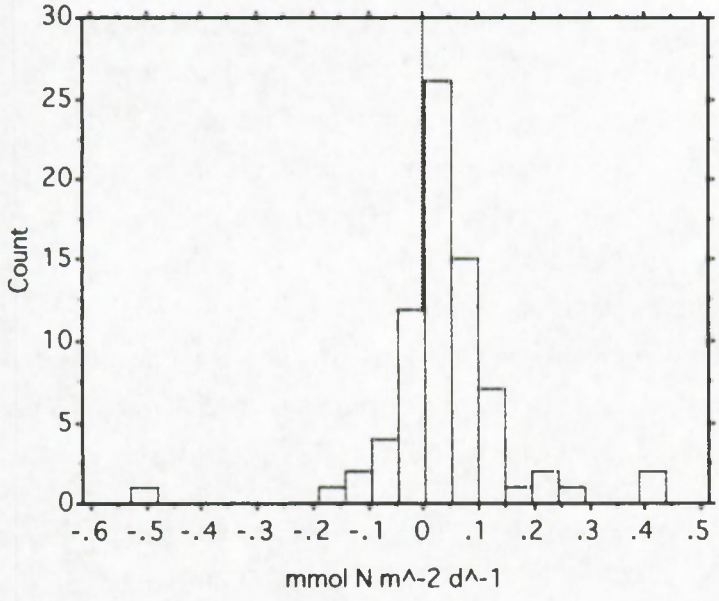


Fig. 6.14B: Frequency distribution of NO_3^- flux rate (mmol N m^{-2} d^{-1}) across the sediment - water interface of Rm plot between 1992 and 1994. (n = 14: no. of observations).

6.1.3.4 Discussion of the benthic fluxes in Rm and Ct sediments

Though jar-chamber incubation may be the best technique for the determination of nutrient flux exchanges across the sediment - water interface of most sediments, their use in mangrove sediments is made difficult by the presence of a dence network of root system within these sediments. Mathematical calculations (using Fick's law on diffusion) indicate that NH_4^+ flux rate across the sediment - water interface of Rm and Ct sediments is expected to be about 0.33 and 0.10 mmol N m^{-2} d^{-1} respectively. Due to a possible filtering effect which may be caused by benthic algae (Kristensen et al., 1992), calculated rates may be higher than actually observed. Alongi et al. (1992), also cautioned the application of these mathematical formulas in mangrove sediments and suggested that due to high bioturbation in mangrove sediments, more complex modelling may be needed to calculate these flux rates. We have therefore calculated the above rates only as indicative expected rates in our two sediment biotopes. It is however observed that for Gazi mangrove sediments, the calculated and observed flux rates are within the same order of magnitude.

Using the intact core technique, we find that, while the sediment - water column NH_4^+ flux rate is seen to vary between -1.0 to +1.4 mmol N m^{-2} d^{-1}, the highest frequency is noticed to fall at around 0.4 mmol N m^{-2} d^{-1}. For nitrate, the values are much lower. The nitrate flux rate is seen to vary between -0.06 to +0.75 mmol N m^{-2} d^{-1} with the highest frequency being at about +0.02 to +0.06 mmol N m^{-2} d^{-1}. The total flux of dissolved inorganic nitrogen ($NH_4^+ + NO_2^- + NO_3^-$) from the Rm mangrove sediments into the water column is hence ca. 0.46 mmol N m^{-2} d^{-1} if we only consider rates with the highest frequency occurence. These obtained values should also be considered as highest possible values since our experimental observation was that however careful one was in adding the filtered sea water into the cores, there was always an element of disturbing the thin sediment surface layer. The highest recorded fluxes of ammonium and nitrate (1.4 and 0.75 mmol N m^{-2} d^{-1} respectively) could therefore have been as a result of this disturbance.

For Ct sediments, the highest occurence for NH_4^+ flux is found to lie at about +0.5 mmol N m^{-2} d^{-1} while that of $NO_3^- + NO_2^-$ lies between +0.02 and +0.05 mmol N m^{-2} d^{-1}. The flux of dissolved inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$) from the Ct sediment into the water column is therefore ca. 0.55 mmol N m^{-2} d^{-1} when considering only the highest frequency occurence.

These calculated and observed flux rates are quite low, as also reported for other tropical sediments. For instance, the total nitrogen, ΣN ($\Sigma N = NH_4^+ + NO_3^- + NO_2^-$) flux from sediments of the central great barrier reef lagoon, Australia, ranged between -0.15 to +0.89 mmol N m^{-2} d^{-1} (Ullman and Sandstrom, 1987). On Phuket Island in Thailand, Kristensen et al., (1988) observed negative ΣN flux rates ranging between - 0.06 to - 0.154 mmol N m^{-2} d^{-1} on mangrove sediments. They attributed the negative rates to uptake of nutrients from both the sediments and the overlying water by microalgae at the sediment surface. Our results indicate that at Gazi mangrove sediments, despite possible uptake of the nutrients at the surface to support various benthic processes, appreciable (?) levels flux out into the water column.

6.2 DISCUSSION ON NITROGEN - TRANSFORMATIONAL PROCESSES IN Rm AND Ct MANGROVE SEDIMENTS

Ammonification rates in sediments generally depend on the quantity (stock) and quality (C/N) of the organic matter. Though Rm sediments are higher in organic nitrogen quantity as compared to the Ct sediments, both sediments are not expected to register any net production of NH_4^+ since their organic matter quality ($C/N \geq 20$) is poor. Blackburn (1986), demonstrated that organic matter whose C/N is ≥ 20 should favour immobilization with no significant net production on NH_4^+. Though Rm and Ct sediments have $C/N \geq 20$ (averagely 26 for the upper 6 cm depth), significant net production of NH_4^+ was observed in these sediments.

In order to be able to use the regeneration and assimilation rates of the Rm and Ct sediments in assessing nitrogen flux rates in these sediments, the units have been converted from nmol N g^{-1} (D.W.) d^{-1} into mmol N m^{-2} d^{-1} using the average wet density and porosity values of the sediments. Tables 6.30 and 6.31 therefore give regeneration and assimilation rates of the Rm and Ct in mmol N m^{-2} d^{-1}.

Table 6.30: Average values of regeneration (**d**) and assimilation (**i**) rates (mmol N m^{-2} d^{-1}) in Rm sediments in dry (Feb. / March) and rainy seasons of 1992 and 1993. n = 13 (no. of observations).

Depth (cm)	d	i	d - i (Net prod.)	wet density g cm^{-3}	porosity vol:vol
0 - 1	4.46 ± 0.87	2.72 ± 0.87	1.74 ± 0.47	1.35 ± 0.05	0.92 ± 0.04
1 - 6	14.05 ± 3.49	8.44 ± 3.05	5.61 ± 1.79	1.38 ± 0.06	0.83 ± 0.04
0 - 6 (Integrated)	18.51 ± 3.60	11.16 ± 3.17	7.35 ± 1.85	-	-

Table 6.31: Average values of regeneration (**d**) and assimilation (**i**) rates (mmol N m^{-2} d^{-1}) in Ct sediments in dry (Feb. / March) and rainy seasons of 1992 and 1993. n = 12 (no. of observations).

Depth (cm)	d	i	d - i (Net prod.)	wet density g cm^{-3}	porosity vol:vol
0 - 1	9.75 ± 2.16	3.81 ± 1.14	5.94 ±1.26	1.91 ± 0.14	0.46 ± 0.05
1 - 6	26.22 ± 9.51	11.85 ± 5.50	14.37 ± 3.78	1.74 ± 0.16	0.53 ± 0.05
0 - 6 (Integrated)	35.97 ± 9.75	15.66 ± 5.62	20.31 ± 9.98	-	-

It is noticed that about 18.51 ± 3.60 and 35.97 mmol N m^{-2} d^{-1} is regenerated for the Rm and Ct sediments, respectively. At an average sedimentary C/N ratio of about 26 for the 0 - 6 cm depth (section 5.1.2), this remineralization will be coupled by a corresponding carbon dioxide production of about 481 and 935 mmol C m^{-2} d^{-1} for the Rm and Ct sediments

respectively. However, in-situ measurements of CO_2 fluxes across the sediment - water interface at the Rm sediments indicated a production rate of 60.5 mmol C m^{-2} d^{-1} (Middelburg et al., in press). The organic matter which satisfies a CO_2 production rate of 60.5 mmol C m^{-2} d^{-1} and a regeneration rate of 18.51 mmol N m^{-2} d^{-1} must have a C/N ratio of about 3.3. For the *Ceriops tagal* sediments, the observed CO_2 flux rate was about 291 mmol C m^{-2} d^{-1} (Middelburg et al., in press). With our observed regeneration rate of 35.97 mmol N m^{-2} d^{-1} for the Ct sediments, the organic matter capable of giving these two rates must have a C/N ratio of about 8.1.

Our results indicate that the remineralized organic material in Gazi mangrove sediments, for the upper 6 cm depth has a C/N molar ratio of between 3 and 8 and not the observed C/N ratio of 26. This may imply three things; either, (1) the marine POM part indicated in chapter 5 to be likely present within the mangrove sediments, is remineralized or, (2) the remineralization process is mainly centered on dead bacteria in the sediments since the C/N ratio of marine bacteria ranges from 3 to 7 (Nagata, 1986; Lee and Fuhrman, 1987) or (3) remineralization involves decomposition of the imported marine POM, dead bacterial recycling and partly the refractory mangrove organic material. The third possibility appears very likely due to the fact that the C/N molar ratios of the remineralized organic material for the Rm and Ct sediments are slightly different.

Once produced, the net mineralized NH_4^+ can be nitrified into nitrite or nitrate. For nitrification to take place, NH_4^+ (and/or NO_2^-) is needed in the presence of oxygen and nitrifying bacteria. While the water column may be saturated with air, most coastal marine sediments are anaerobic with oxygen diffusion hardly going below 5 mm (Revsbech et al., 1980; Kristensen et al., 1988). Once in the sediments, part (or all) of the diffused oxygen may be used by heterotrophic bacteria for aerobic degradation of organic matter according to:

$$(CH_2O)_x (NH_3)_y + (x + 2y)\ O_2 \rightarrow x\ CO_2 + (x + y)\ H_2O + y\ HNO_3 \quad \ldots\ldots\ldots (1)$$

The remaining diffused oxygen can then be used by nitrifying bacteria for nitrate production through the following process:

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

which as indicated earlier (section 6.1.2) takes place in two steps.

From the high demand of oxygen to facilitate the two processes above, there is always a big competition for O_2 by bacteria responsible for the indicated processes. Due to the limited penetration of O_2 in sediments high biomass of nitrifying bacteria are mostly found in the upper 1 cm of sediments (Webb and Wiebe, 1975; Henriksen, et al. 1993; Jensen, et al,. 1993) . The presence of living nitrifying bacteria in deeper sediment strata can be caused either by physical down mixing or macrofaunal activity (Henriksen et al., 1983). The benthic macrofauna influences the distribution of nitrifying bacteria in two ways:

(1) Down mixing of sediment particles from the oxic surface zone (mostly by Bivalves and some Polychaetes) and

(2) Creation of aerobic surfaces in ventilated infauna burrows where active growth can take place (mostly Amphipods and Polychaetes).

The potential nitrification profile in Rm sediment indicates active transportation of nitrifying bacteria between the surface and 4 cm depth. Redox potential measurements taken from the four subsampling positions (fig 6.11) indicate a gradual decrease of redox potential till $\leq$ -35mV, at 5 cm depth where its decrease becomes less pronounced to about -70 mV at 12 cm depth. According to Stumm and Morgan (1970), considerable sulphate reduction can not occur before a redox potential of less than -51 mV at about 25°C is reached. This sulphate reduction results in sulphides which are known to be toxic to nitrifying bacteria (Norton and Thibodeau,1985; McKee, et. al., 1988). Kristensen et. al. (1991), working on benthic metabolism in an Asian mangrove swamp, noticed active sulphate reduction only at Eh values of $\leq$ -40 mV. Though sulphide concentrations were not determined in this study it is safe to assume from these previous findings that considerable sulphide concentration at the Rm sediment would start appearing from about 5 cm depth and below. So the sudden drop of bacterial population (nitrifiers) just below 4 cm depth would most probably be connected with sources responsible for the mixing and also the toxicity caused by the presence of sulphides. From this, we could conclude that most of the down-mixing caused by the burrowing infauna takes place above 4 cm and that the survival of the nitrifying bacteria below this depth is made difficult by possible presence of sulphides.

Hardly any nitrification process was noticed below 8 cm depth implying that any nitrate concentrations detected below 8 cm depth are therefore not a result of nitrification within that depth but mostly due to downward diffusion. This existence of NO_3^- concentrations below 4 cm would encourage the denitrification process (coupled to sulphide oxidation) since FeS, FeS_2 and H_2S would react very fast with NO_3^- (Middelburg, pers. comm.) releasing N_2 gas.

Unlike the Rm sediments, Ct sediments had relatively very low activity (or biomass) of the nitrifying bacteria judging from their relatively lower potential nitrification rates. While the

surface (0 - 1 cm) PNR of Rm sediments were averagely 1.07 mmol N m^{-2} d^{-1}, Ct sediments had a PNR of about 0.24 mmol N m^{-2} d^{-1} which is about a fifth of that observed for the Rm sediments.

It is very unlikely that this low activity could be due to toxicity caused by the presence of sulphides since redox potential profiles of the two sediments indicated relatively more oxidizing conditions for the Ct sediments and sulphide production can mostly be noticed at Eh ≤ - 40 mV in mangrove sediments (Kristensen et al., 1991).

While the presence of oxygen, ammonium and nitrifying bacteria have been documented to be essential for nitrification to occur (Henriksen et. al., 1981; Henriksen et. al., 1993) other factors like temperature and salinity may also affect the rate. Carlucci and Strickland (1968) isolated several nitrifiers from the northern Pacific ocean and the optimum temperature for all cultures was found to be about 28°C. Similarly Watson and Waterburg (1971) noted that the nitrite oxidizers *Nitrospina* and *Nitrococcus* both grew optimally at 25° - 30°C. Chen et al. (1976) studied the salinity effect on nitrification in a river estuary and quantitatively concluded that nitrification rate was inversely proportional to salinity implying the higher the salinity, the lower the nitrification rate. Billen (1975), also made similar observations in the Scheldt estuary.

Salinity at the Ct sediment was found to be relatively higher (ca. 46 - 55 psu for the upper 12 cm depth) than in Rm sediments (34 - 40 psu). During neap tide, the salinity in the upper 4 cm of the Ct sediments could rise upto ca. 58 ± 3 psu (refer to section 4.1.2.1) due to infrequent flooding and evapotranspiration of the surface pore water. The maximum difference in salinity between Rm and Ct could therefore occasionally be ca. 20 psu. These relatively elevated salinities are likely to affect the activity of the nitrifying bacteria in the Ct sediments. Excessive heat in the Ct sediments could be another possible reason for this big difference in nitrification activity. Mangrove trees of Rm species are usually quite big with relatively wide leaves which always cover the Rm sediments from direct sunlight while Ct species have small leaves and short trees which are not densily packed (Slim and Gwada, 1993). Since the Ct sediments are only inundated during spring tides, the prolonged absence of water during neap tide coupled with the direct sunlight on the exposed sediments would tend to raise the sediments temperature. While the temperatures at the Rm sediments were found to lie mostly between 22 and 26 °C, those at Ct plot could raise to as high as 39 °C during neap tide (refer to section 4.1.2.1).

Ct sediments which are only inundated during spring tide have their sediment surface exposed to air most of the time. Since oxygen diffusion rates on exposed sediments have been documented to be higher than on water covered sediments (Kristensen et al., 1988),

the overall effect is that the Ct sediments are relatively more oxidized than the Rm sediments. However, this aspect introduces another problem for the nitrifying bacteria. The net effect of the diffused oxygen and that introduced by mangrove roots would be an enhancement of aerobic degradation of organic matter leading to acid (H_2CO_3, H_2SO_4, HNO_3) production. This has an overall effect of lowering the pH of the interstitial solution in calcium carbonate depleted sediments like the *Ceriops tagal* sediments (Middelburg et al., in press). Indeed, Middelburg et al. (in press) working on the biogeochemistry of Gazi mangrove sediments reported pH values of between 6 and 7 for the Rm sediments while Ct sediments had pH values ranging from 3.5 to 6. The activity of nitrifying bacteria are optimal in a narrow range with a limiting range being 6 - 9.5 (Henriksen and Kemp, 1988). The acidic conditions found in the Ct sediments are therefore not favourable for nitrification activity since they lower the pH of the interstitial water out of the nitrifying bacteria's limiting range.

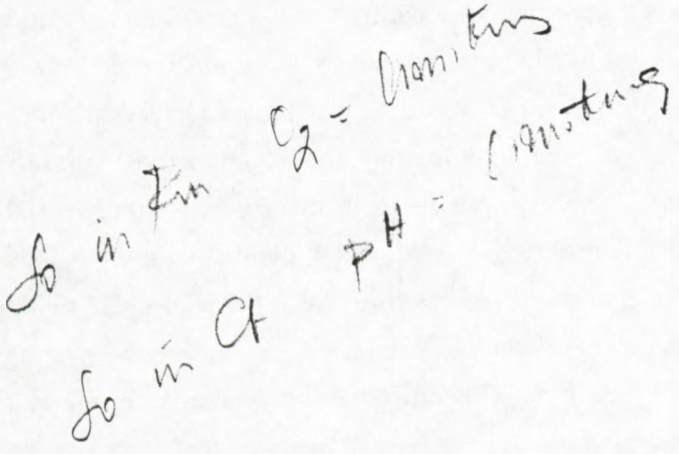
During rainy season, salinity and temperature at the Ct sediments are relatively lower than during dry period. However, PNR did not change as a result of these slightly favourable conditions observed in rainy season. This confirms that though the high salinity and temperature found in Ct sediments could lead to low nitrification activity, the low pH values observed (Middelburg et al., in press) play a major role in reducing the activity of the nitrifying bacteria.

Though PNR indicated active nitrification process in Rm sediments upto about 4 cm depth, actual nitrification rate (ANR) indicated significant nitrification rates only at the upper 1 cm depth. Below this depth, ANR was negligible. However, we should note that ANR determination techniques using core incubations preclude O_2 supply by roots.

The upper 1 cm depth of Rm sediments indicated ANR of about 0.43 mmol N m^{-2} d^{-1} which is just about 40 % of the determined potential nitrification ability (1.07 mmol N m^{-2} d^{-1}) of these sediments. The low ANR could be attributed to both low oxygen availability and relatively low standing stocks of free NH_4^+ in Rm sediments. Organic matter content found in the Rm sediments is very high compared to that found in most mangrove sediments. The LOI organic matter content at the sediment surface was found to be about 20% (dry wt.), while POC and PON were found to be about 9 % and 0.4 % respectively. In comparison, LOI organic matter content found in a south-east Asian mangrove swamp was only about 8 % while the POC and PON were ca. 2 % and 0.09 % respectively (Kristensen et al. 1988). In a mangrove swamp of the Indus delta, Pakistan, Kristensen et al. (1992), found LOI organic matter content of ca. 5 % (dry wt). Kristensen et al.(1988)

demonstrated that up to 73 % of the available oxygen in mangrove sediments could also be used to support decay of algal cells in a mangrove swamp and thus becoming unavailable for nitrification. The low actual nitrification process in Rm sediment could thus be due to high use of oxygen to support decomposition of the high organic matter stock observed, hence lowering the concentration of diffused oxygen available for nitrification. Apart from the low levels of O_2, mangrove trees seem to take up most of the net produced NH_4^+ since the stocks are found to be relatively low in these sediments. Ammonium concentrations (free) in the upper 1 cm depth of the Rm sediments had a concentration of about 64 μM (section 5.2.1.1) which is equivalent to 0.56 mmol N m^{-2} (at an average porosity of 0.92 v/v for the upper 1 cm depth). So, though the Rm potential nitrification is 1.07 mmol N m^{-2} d^{-1}, the actual available stock is about half.

For Ct sediments, the low actual nitrification rate measured is mostly due to the toxicity caused by acidic conditions since the pH found in these sediments (3.5 - 6) are out of the limiting range for nitrifying bacteria (6 - 9.5 : Henriksen and Kemp, 1988). The actual nitrification rate was found to be 0.18 ± 0.11 mmol N m^{-2} d^{-1} while the PNR was 0.23 mmol N m^{-2} d^{-1}. This implies that even when NH_4^+ and O_2 are supplied in abundance, the nitrifying bacteria are already operating at their maximum ability. Unlike the Rm sediments ammonium and oxygen are therefore not the limiting factors for the low nitrification process in Ct sediments.



CHAPTER 7

7.0 NITROGEN DYNAMICS IN GAZI MANGROVE ECOSYSTEM (General Discussion and Conclusions)

7.1 General Discussion

In order to have a detailed picture of the nitrogen transformational processes in Gazi mangrove sediments in relation to the dissolved inorganic nitrogen (DIN) pool in the ove lying water column, it is important to give the topic a general approach taking into consideration various possible sources of particulate organic material (POM) within the ecosystem. As indicated in the schematic chart (fig. 7.10), there are several possible sources of particulate organic nitrogen (PON) in Gazi mangrove bay which may include; (1) mangrove litter, (2) nitrogen fixation, (3) seagrass, and (4) marine POM associated with primary production. Detritus which essentially may include decaying particles from all the possible indicated sources, may be considered to form the fifth (5) source of POM into the mangrove ecosystem. Dissolved inorganic nitrogen (DIN) within the sediments is essentially introduced into the system by mineralization (a) of the organic material while within the water column, DIN may be introduced by diffusion through the sediment - water boundary (b), remineralization of detritus within the water column (c), direct riverine discharges and groundwater seapage (d), or resuspension of surface sediments by tidal flushing (e). Possible main removal pathways of DIN 'within' the ecosystem may include; removal by primary productivity processes within the water column (f) and on sediment surfaces (g) or direct removal by seagrass uptake (h). Higher trophic level organisms (6) may directly consume detritus (j), seagrass (k), or phytoplankton (m) and the main removal pathways of nitrogen from the ecosystem may therefore include: migration of higher trophic organisms (n), outwelling of products of primary production (p), fishing activities (q), direct harvesting of mangroves (r) or through denitrification (s). From the many different possible nitrogen pathways indicated in the schematic chart (which is still not exhaustive), it is quite clear that detailed description of nitrogen - cycling in the Gazi mangrove ecosystem is not possible without also having detailed information from different disciplines like; water hydrodynamics, mangrove management (primary production and wood harvesting) and primary and secondary production including fish migration within the ecosystem. Though a lot of data on some aspects of the above indicated desciplines have been collected at Gazi bay through two EEC funded projects, most of this data is still

being analyzed. It is therefore not the main intention of this study to provide answers and figures to all the indicated pathways but to contribute by elucidating the possible nitrogen contributions from the main sources of organic material in the ecosystem and possible transformational processes (including fluxes) in these sediments in relation to the DIN pool observed within the water column. While it is clearly seen from the chart that the C/N molar ratio of mangrove leaves (senescent) in Gazi bay varied between 70 and 200 (depending on the species), with an average $\partial^{13}C$ isotope signature of -27 ± 1 ‰ (Rao et al., 1993; Hemminga et al., 1994), the *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) sediments (0 - 6 cm depth) had a C/N ratio of between 19 and 30 with a $\partial^{13}C$ isotope signature varying between -22 and -26 ‰. The only possible sources of this tremendous increase in nitrogen resulting into the observed decrease in C/N ratio could mostly come from nitrogen fixation, marine POM, seagrasses or detritus material since all these indicated sources have relatively low C/N atom ratio with a more positive (less negative) range of $\partial^{13}C$ signature (fig. 7.10).

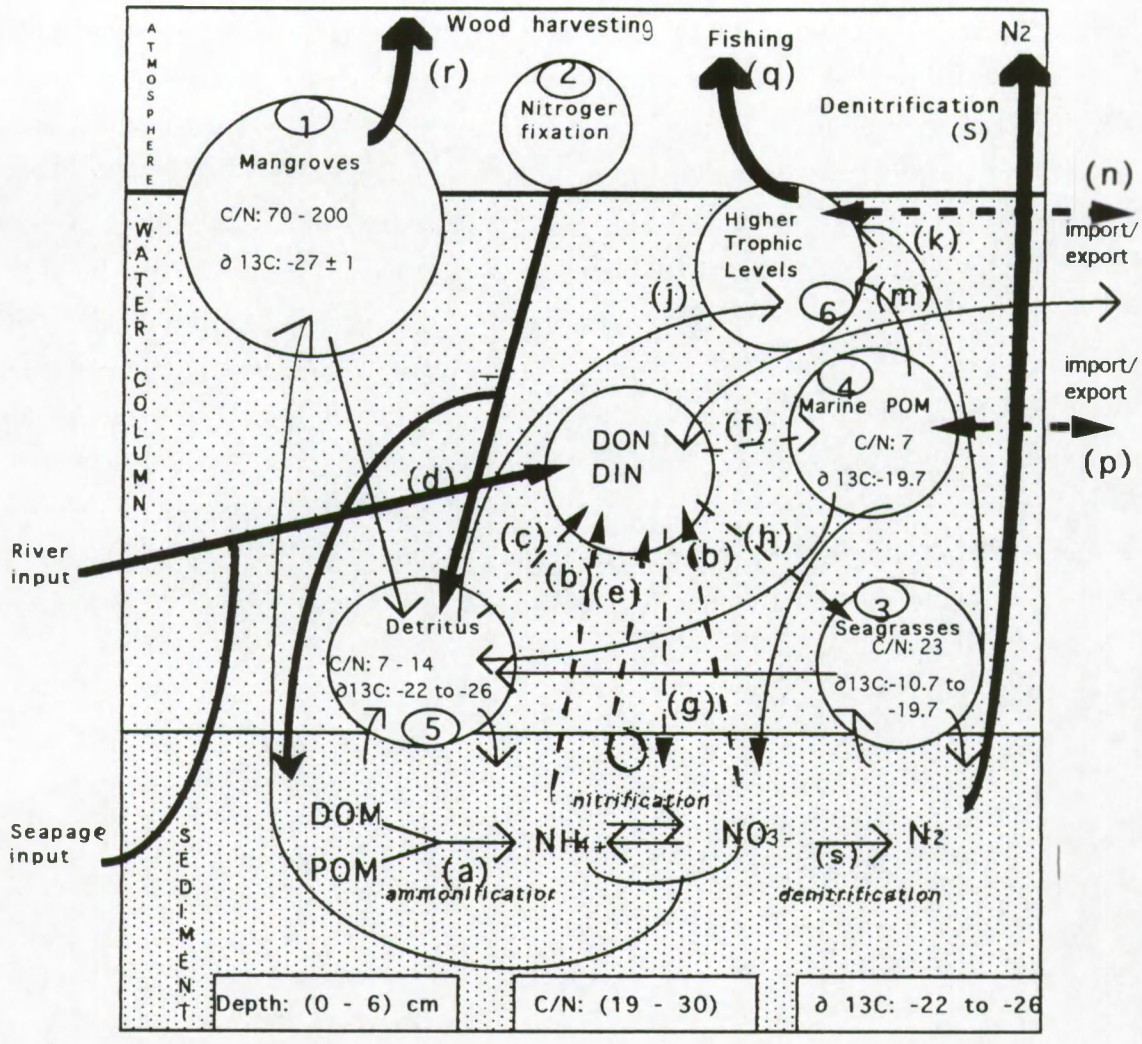


Fig. 7.10: Schematic chart showing the various possible sources of particulate organic material (POM) and their possible cycle in Gazi Bay. $\partial^{13}C$ isotope signature is expressed in ‰ units.

Since mangrove trees form the major vegetation within the forest, their litter is expected to supply a significant portion of organic material to the total organic matter found in the sediments. Indeed, the $\partial^{13}C$ isotope signature of the mangrove sediments (Rm: - 25.52 and Ct: - 22.94 ± 0.53 ‰: 0 - 1 cm depth) is found to be close (but slightly more positive) to that of the mangrove leaves (Rm: - 28.25 and Ct: - 24.16 ; Hemminga et al., 1994). However, the C/N molar ratio of the sediments (19 to 30 : for the upper 6 cm depth) was found to be very low compared to that of senescent mangrove leaves (Rm: 193 ± 45 and

Ct: 218 ± 26: Rao et al., 1993). Middelburg et al. (in press), using a conservative mass balance model, ruled out the possibility of the decrease in sedimentary C/N molar ratio to preferential loss of carbon. In this case, the decrease in molar C/N ratio, could either be due to import of organic nitrogen from one (or all) of the possible indicated sources or internal build-up due to possibly low remineralization processes. The last possibility is however very unlikely due to relatively high reported ammonification rates in different mangrove sediments (Shaiful et al., 1986; Blackburn 1987; Nedwell et al., 1994). Before looking into the mineralization processes of the sedimentary organic pool, it's important to have an inventory of the nitrogen related studies undertaken at Gazi bay with a view of trying to identify the most likely source(s) of the observed sedimentary organic nitrogen build-up. This would include mangrove biomass and litterfall studies, nitrogen fixation and denitrification, seagrass transport into the mangrove forest and possible importation of marine POM of planktonic nature into the mangrove ecosystem.

(i) Mangrove biomass and litterfall

N- additions through mangrove litterfall

Mangrove biomass and litterfall experiments covering the Rm and Ct field plots were conducted concurrently with this study at Gazi bay (Slim and Gwada, 1993; Slim et al., 1995). In conclusion, these authors found an average mangrove biomass of 24.9 ± 4.01 and 4.01 ± 0.34 kg (D.W.) m^{-2} giving a corresponding litterfall contribution of 2.51 ± 1.15 and 1.05 ± 0.49 g (D.W.) m^{-2} d^{-1} for the Rm and Ct vegetations, respectively. Since the observed C/N molar ratio of the senescent leaves of Rm and Ct species are 193 ± 45 and 218 ± 26 (Rao et al., 1993), the daily indicated litterfall input will correspond to a maximum nitrogen input of 0.5 and 0.2 mmol N m^{-2} d^{-1} respectively (table 7.11) into the sediments, assuming all litterfall is retained within the plot.

Table 7.11: Maximum possible nitrogen contribution into Rm and Ct sediments through litterfall.

Species	[1] Biomass kg (DW) m^{-2}	[1] Litterfall g (DW) $m^{-2} d^{-1}$	[2] C % DW ± ó	[2] N % DW ± ó	[2] C/N	N-input mmol N $m^{-2} d^{-1}$
Rm	24.9 ± 4.01	2.51 ± 1.15	41.2 ± 2.0	0.3 ± 0.1	193 ± 45	0.5
Ct	4.01 ± 0.34	1.05 ± 0.49	43.2 ± 2.0	0.2 ± 0.1	218 ± 26	0.2

(1) Data from Slim et al., 1995; (2) Data from Rao et al., 1993

(ii) Nitrogen fixation in Rm and Ct study plots

N-additions through N_2-fixation activity

Nitrogen fixation is an important nitrogen process in marine environment since it involves converting free nitrogen gas into a form which can easily be utilized by primary and secondary producers. In brief, biological nitrogen fixation is the reduction of dinitrogen (N_2) to NH_3. This process is catalyzed by the molybdo-iron-enzyme, nitrogenase, and the ammonium formed is subsequently incorporated into cellular material (Capone, 1985). N_2-fixation rates in mangrove sediments are low compared to other estuarine and marine habitats and a probable reason associated with this is, low light levels under the forest canopy and low standing amounts of Cyanobacteria (Capone, 1983). Alongi et al. (1992) summarized in a table form, the mean rates of nitrogen fixation in a variety of microhabitats in mangrove forests and displayed various ranges observed in these sediments. For instance, mangrove sediments of Batu Maung, Malaysia had nitrogen fixation rates of 0.09 mmol N $m^{-2} d^{-1}$ while sediments of Hinchinbrook Island, Australia had nitrogen fixation rates ranging from 0 to 0.24 mmol N $m^{-2} d^{-1}$. Nitrogen fixation studies carried out at Gazi bay (both on decaying leaf litter and sediments) also displayed low rates similar to those found in other mangrove biotopes (Kazungu et al., 1995; Woitchik et al., 1995; Woitchik et al., submitted). Table 7.12 below gives summarized details of possible nitrogen input into Rm and Ct sediments through nitrogen fixation activities.

Table 7.12: Maximum possible nitrogen input into Rm and Ct sediments through nitrogen fixation activities. Data from Woitchik et al., 1995 and Kazungu et al., 1995).

Plot / Season		N - input through N_2 fixation (decaying leaf) (mmol N m^{-2} d^{-1})	N - input through N_2 fixation (sediment) (mmol N m^{-2} d^{-1})	Total N - input through N_2 fixation (mmol N m^{-2} d^{-1})
Rm	(Dry season)	0.087	0.092	0.179
	(Wet season)	0.296	0.066	0.362
Ct	(Dry season)	0.049	0.332	0.381
	(Wet season)	0.020	0.188	0.208

From the above table, it is noticed that though there are seasonal differences, maximum possible nitrogen contribution to Rm and Ct sediments through nitrogen fixation hardly exceed 0.4 mmol N m^{-2} d^{-1}.

(iii) Denitrification process in Rm and Ct sediments

N-removal through denitrification process

Denitrification which in simple terms can be defined as conversion of nitrate into molecular nitrogen is one of the main processes of removing nitrogen from sediments (Koike and Sorensen, 1985). In Gazi bay, this process was investigated (Woitchik et al., 1995) using nitrogen isotope pairing technique (Nielsen, 1992). Table 7.13 below gives the average denitrification rate as observed for Rm and Ct sediments in Gazi bay.

Table 7.13: Denitrification rates in Rm and Ct sediments. Data from Woitchik et al., 1995 and Kazungu et al., 1995.

Sampling plot	Denitrification rate (mmol N m^{-2} d^{-1})
Rm	0.101
Ct	0.055

(iv) Seagrass transport in Gazi bay

N-addition through seagrass importation

Seagrass transport studies in Gazi bay have indicated a possibility of having a net import of seagrass into the mangrove forest (Slim et al., 1995). These authors indicated the possibility of seagrass leaves constituting between 7 to 60 % of the total dry weight of course particulate organic material (CPOM) found lying on the *Rhizophora* mangrove sediment floor. Working on possible maximum nitrogen input from this seagrass source, we can assume that the maximum of 60 % as seagrass composition on course material at the sediment floor also reflects the maximum possible seagrass contribution in the total organic material (TOM) found underlying the sediments. Since 100 g dry Rm sediment (0 - 1 cm depth) has 9.27 g C (table 5.15), if 60 % is from seagrass, this would mean a contribution of 5.56 g C from seagrass and about 3.71 g C from mangrove litter. At an average C/N ratio of 23 (table 5.12) and 193 (table 5.14) for seagrass and mangrove leaves (senescent), this would imply a nitrogen contribution of 0.282 and 0.022 g N respectively. The overall expected C/N molar ratio of the Rm sediment would therefore be about 36. Using the two end - member mass balance model discussed in section 5.1, 60 % seagrass contribution on the TOM in the Rm sediments would result in an expected sedimentary $\partial^{13}C$ isotope signature of between -17.7 and -23.1 ‰ (using $\partial^{13}C$ isotope signature of –10.7 and -19.65 ‰ of the seagrass found in Gazi bay: table 5.12). Though the calculated C/N molar ratio (36) is relatively low and could be compared to that found within the upper 12 cm depth (23 - 31) of the Rm sediments, the observed $\partial^{13}C$ isotope signature range of -17.7 and -23.1 ‰ is on the higher side (less negative) than that found in the sediments (-25.5 to -26.5 ‰: for the upper 12 cm depth). Still working on maximum possible nitrogen additions, Woitchik et al. (submitted), observed that a significant enrichment of nitrogen (reaching a maximum of 316 % of the original nitrogen content) occurred during decomposition of Rm mangrove leaves. This addition, which was partly attributed to nitrogen fixation would then lower the C/N molar ratio of the senescent mangrove leaves to about 61. If these nitrogen enriched mangrove leaves (or enriched particles of the leaves) would then be assumed to form the mangrove organic matter contribution to the sediments, the organic nitrogen corresponding to the 3.71 g C mangrove contribution would be about 0.07 g N lowering the expected sedimentary C/N molar ratio to 31. The lowest sedimentary C/N molar ratio expected from maximum contributions of seagrass and nitrogen fixation is therefore 31 with a corresponding $\partial^{13}C$ isotope signature of between -17 and - 23 ‰. Though the C/N molar ratio is found to fall within the values observed in

the upper 12 cm depth of Rm sediments, the observed $\partial^{13}C$ isotope signatures are still found to be on the more positive range. It should also be noted that the assumptions given to arrive at these values are highly theoretical since we did not only use maximum possible inputs of seagrass but also assumed that all this is retained within the mangroves. The nitrogen enrichment experiments were also done on leaves restricted within the study plot for the duration of the experiments (about 45 days) which does not reflect the actual conditions. It is therefore highly unlikely that nitrogen fixation processes and possible importation of seagrass into the mangrove ecosystem could be the main source of the observed nitrogen enrichment in mangrove sediments.

(v) Particulate organic material of phytoplanktonic origin

N-additions from marine POM

Time series observations (over tidal cycles) conducted at a station (st. G3) within the mangrove creek indicated that at high tide, C/N molar ratio of the POM (seston) was averagely 8.14 ± 1.53 while at low tide it increased to 13.66 ± 2.03. $\partial^{13}C$ isotope signature of the POM at high tide was found to be ca. - 21.70 ± 1.10 ‰ and decreased to -24.21 ± 0.62 ‰ at low tide. Since POM associated with Gazi mangrove vegetation has an average $\partial^{13}C$ isotope signature of -26.66 ± 1.42 ‰ (table 5.11), the decrease (becoming more negative) of the $\partial^{13}C$ value with ebb flow could indicate export of POM predominantly of mangrove origin. Likewise, the increase of $\partial^{13}C$ (becoming less negative) could also imply import of POM of marine (or seagrass) origin. However, since the C/N molar ratio of the seagrass within the bay was found to be averagely 23, and marine POM of phytoplanktonic origin has a C/N ratio of about 6.6 (Redfield ratio) and a $\partial^{13}C$ isotope signature value varying between -18.76 and -21.6 ‰ (Fontugne & Duplessy, 1978; Fry & Sherr, 1984; Fontugne & Duplessy, 1991), the relatively low C/N ratio (8.14 ± 1.53) observed on POM at high tide, uderlines the relative importance of marine POM of phytoplanktonic origin within the mangrove ecosystem. Hemminga et al. (1994) observed that the outwelled mangrove POM was mostly trapped within the seagrass zone and was hardly noticed at a station (st. CC) close to the open sea. Using a two end-member mass balance equation, this study has demonstrated that in the absence of mangrove POM at this station (st. CC), marine POM of phytoplanktonic origin could contribute upto 59 % of the total sedimentary organic matter while the seagrass within the locality would contribute only about 41 % which again underlines the relative importance of the marine POM. When the same conservative mass balance equation was applied to both the Rhizophora and

Ceriops sediments it was found that when marine POM was used as a second end member (with mangrove POM), it could explain both the observed increase of sedimentary $\partial^{13}C$ isotope signature (compared to mangrove leaves) and the increase in organic nitrogen resulting in the observed decrease of the sedimentary C/N molar ratio in mangrove sediments. Since reported surface sedimentary C/N molar ratios of most mangrove sediments are found to lie between 20 and 30 (Hesse, 1961; Shaiful et al., 1986; Blackburn et al., 1987; Kristensen et al., 1988; Kristensen et al., 1992) regardless on whether there is seagrass neighbourhood or not, our findings highlight the relative importance of marine POM of phytoplanktonic origin as a major contributor to the elevated organic nitrogen stocks in mangrove sediments.

As observed above, the maximum possible input of nitrogen from litterfall and nitrogen fixation at the Rm and Ct sediments is 0.862 and 0.581 mmol N m^{-2} d^{-1} while removal rate through denitrification processes is 0.101 and 0.055 mmol N m^{-2} d^{-1} respectively. Net nitrogen input in these two sediments from these processes is therefore about 0.701 and 0.526 mmol N m^{-2} d^{-1}. These input rates are very low when compared to ammonification rates observed in most mangrove sediments confirming the relative importance of import of organic nitrogen or internal build-up of nitrogen stock which is constantly produced and remineralized. Results obtained from regeneration and assimilation experiments indicate that NH_4^+ regeneration rate of Rhizophora sediment is about 18.51 ± 3.60 mmol Nm^{-2} d^{-1} for the upper 6 cm depth. However, about 60 % of this is assimilated back giving a net production of about 7.35 ± 1.85 mmol N m^{-2} d^{-1} available for nitrification or plant uptake. For Ceriops sediments, the regeneration rate was ca. 35.97 ± 9.75 while the uptake rate was 15.66 ± 5.62 mmol N m^{-2} d^{-1} giving a net production of ca. 20.31 ± 9.98 mmol N m^{-2} d^{-1} available for plant uptake or other nitrogen processes. These results seem to be similar to the rates reported in other mangrove sediments. Nedwell et al. (1994) estimated 10 mmol N m^{-2} d^{-1} to be the net ammonium produced for plant uptake in a Jamaican mangrove forest. However, while comparing rates in mmol N m^{-2} d^{-1}, it is important to take note of the depth and porosities of the sediments since these could create a difference. Before discussing other nitrogen processes in Gazi mangrove sediments, it is important to compare the observed regeneration rates with the standing stocks in order to get an idea about the turnover rates. From the total organic nitrogen (TON) contents (tables 5.15 and 5.16) and density and porosity values given in table 4.17 it is possible to calculate the organic nitrogen stock (in mmol N m^{-2} units) for the 0 - 6 cm depth. Table 7.14 below, gives the calculated organic nitrogen stocks, regeneration and turnover rates for the upper 6 cm depth for both *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) sediments.

Table 7.14: Total organic nitrogen stocks, regeneration (**d**) and turnover rates for the upper 6 cm depth of Rm and Ct sediments.

Item	Rm	Ct
Depth (cm)	6.0	6.0
TON stock (mmol N m^{-2})	9337.0	3996.0
d (mmolN m^{-2} d^{-1})	18.5	36.0
Turnover rate (yrs)	1.4	0.3
Average C/N ratio (approx.)	26.0	26.0

From the above table, very high turnover rates of organic nitrogen (Rm: 1.4 yrs and Ct: 0.3 yrs) are observed for the upper 6 cm depth of these mangrove sediments implying that without a constant supply of organic nitrogen, the system would not be self-sustaining. Since from our earlier calculations, we indicated that organic matter in mangrove sediments is most likely composed of two parts: (1) a pool of highly refractory organic material from mangrove vegetation which is very poor in organic nitrogen, and (2) a pool of labile organic nitrogen (which is probably of marine origin), it is tempting to assume that this second pool could be the main organic material responsible for the observed high turnover rates. However, remineralization rate of 18.5 and 36 mmol N m^{-2} d^{-1} for the Rhizophora and Ceriops sediments would imply a carbon mineralization rate of ca. 481 and 935 mmol C m^{-2} d^{-1} respectively at an average observed sedimentary C/N molar ratio of 26 (for the upper 6 cm depth). Direct measurements of carbon dioxide flux from the Rm and Ct sediments gave a carbon remineralization rate of ca. 60.5 and 291 mmol C m^{-2} d^{-1} (Middelburg et al., in press) implying that the organic matter responsible for this production does not have a C/N of 26 but of about 3.3 (for Rm) to 8.1 (for Ct). The C/N molar ratio of 3.3 is relatively lower than that of marine POM (phytoplankton) and therefore implies that though marine POM could be available within the sediments, a different pool of labile organic nitrogen is being remineralized. Since the C/N molar ratio of

marine bacteria ranges from 3 to 7 (Lee and Fuhrman, 1987; Nagata, 1986), the calculated C/N ratio of 3.3 to 8.1 as being responsible for the CO_2 flux (sediment - water interface) and organic nitrogen remineralization rate in *Rhizophora mucronata* and *Ceriops tagal* sediments of Gazi bay would imply active involvement of benthic bacterial biomass. Recent studies in mangrove sediments of tropical Australia have documented very high bacterial densities and productivities in these sediments with bacterial productions sometimes being 10 times higher than those reported for other marine sediments (Alongi, 1989; Alongi, 1994). The marine POM therefore possibly acts as a source of the labile organic nitrogen pool available for bacterial utilization supporting the high bacterial productivities observed in sediments. Upon death, these bacterial cells are then remineralized becoming the main source of the produced ammonium in mangrove sediments.

Regeneration and assimilation experiments for the Rm and Ct sediments indicated that about 7.35 and 20.3 mmol N m^{-2} d^{-1}, respectively are made available for either tree uptake or the nitrification process (figs. 7.11 and 7.12).

Potential nitrification rates (PNR) are found to be relatively higher in Rm (ca. 1.07 mmol N m^{-2} d^{-1}) than in Ct (0.23 mmol N m^{-2} d^{-1}) sediments. This low PNR rate in Ct sediments could imply low numbers of nitrifying bacteria due to relatively higher salinity and temperatures (Carlucci and Strickland, 1985; Watson and Waterburg, 1971; Billen, 1975; Chen et al., 1976) observed in this study field. However, it was observed that during rainy season, both salinity and temperature in Ct sediments had a significant drop but this was not accompanied by an increase in PNR. This would then imply the presence of another variable which either on its own, or in combination with the high salinities observed in Ct sediments, results in low numbers (or activity) of nitrifying bacteria. Middelburg et al. (in press) observed relatively low pH values in Ct (ca. 3.5 - 6.0) as compared to Rm (ca. 7 - 8) sediments. Since the limiting pH range of nitrifying bacteria is 6 to 9.5 (Focht and Verstraete, 1977), the low values (3.5 - 6) found in the Ct sediments, combined with the relatively high salinity and temperatures observed in these sediments - especially during neap tide in the absence of water, could explain the relatively low nitrification activity in these Ct sediments.

While the ammonification rate for the 0 - 1 cm depth of Rm sediment indicates net production of 1.74 mmol N m^{-2} d^{-1} (table 5.31), PNR for the same depth (1.07 mmol N m^{-2} d^{-1}: table 6.28) indicates that almost 70 % of the produced ammonium can be oxidized into nitrate. However, the actual nitrification rate (ANR) of the same sediments indicates

relatively lower nitrification activity. Only about 25 % (ca. 0.43 mmol N m^{-2} d^{-1}) of the produced ammonium is nitrified at the upper 1 cm depth while below 1 cm depth, hardly any actual nitrification process is detected. We should however note that the actual nitrification determination technique which involves incubation of sediment cores, normally precludes supply of O_2 which would continuously have been made available by roots. For Ct sediments, ANR (0.18 ± 0.11mmol N m^{-2} d^{-1}) for the upper 1 cm depth was not significantly (ANOVA: $p > 0.05$) different from PNR (0.23 11mmol N m^{-2} d^{-1}). Henriksen et al., (1993) observed that most marine sediments had nitrification rates ranging between 0.7 and 1.8 mmol N m^{-2} d^{-1}. Though our maximal possible nitrification rate in Rm sediments is found to be the same order of magnitude (ca. 0.55 mmol N m^{-2} d^{-1}) as the values mentioned by Henriksen et al. (1993), our values are much lower since our range is essentially 0 - 0.55 mmol N m^{-2} d^{-1} when we also consider the experiments which had undetectable nitrification rates. Since determination of PNR indicated an active nitrification process upto about 4 cm depth, the low ANR observed in Rm sediment is most likely due to either relatively low NH_4^+ stock or low oxygen availability. Organic matter content found in Rm sediment is very high compared to that found in most mangrove sediments. The LOI organic matter content at the sediment surface were found to be about 21 % (D.W.), while POC and PON were found to be about 9 % and 0.4 % respectively. In comparison, LOI organic matter content found in a south-east Asian mangrove swamp was only about 8 % while the POC and PON were ca. 2 % and 0.09 % respectively (Kristensen et al., 1988). In a mangrove swamp of Indus delta, Pakistan, Kristensen et al. (1992) found LOI organic matter content of ca. 5 % (D.W.). Kristensen et al. (1988) demonstrated that up to about 73 % of the available oxygen in mangrove sediments, could be used to support decay of algal cells in a mangrove swamp. The low nitrification process in Rm sediment could thus be due to high use of oxygen to support decomposition of the observed high stock of organic matter hence lowering the concentration of diffused oxygen available for nitrification.

Though Rm sediments were found to have a relatively higher nitrification rate as compared to the Ct sediments, the relatively more oxidizing environment noticed for Ct sediments discourages denitrification process. Woitchik et al. (1995) observed relatively lower denitrification rates in Ct sediments (0.055 mmol N m^{-2} d^{-1}) as compared to the Rm sediments (0.11 mmol N m^{-2} d^{-1}). However, in both cases the denitrification process represented ≤ 30 % of the observed actual nitrification process.

It was also observed that concentration levels of NO_3^- + NO_2^- were significantly lower (ANOVA: $p < 0.05$) and hardly went above 4 % of the observed NH_4^+ concentrations.

Total ammonium concentrations for the upper 12 cm depth for Rm sediments were found to lie between 100 and 200 μM while for Ct sediments, they were between 100 and 300 μM. However, about 52 % of the total NH_4^+ in Rm sediments were adsorbed on to sediment particles leaving only about 48 % as free NH_4^+ while for Ct sediments, only about 15 % of the total NH_4^+ was adsorbed. The low adsorption capacity of the Ct sediments have been attributed to the more acidic conditions found in Ct sediments (Middelburg et al., in press) since as indicated earlier (Schlesinger, 1991), cations in sediments are held and displace one another in the sequence;

$$\mathbf{Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+}$$

Though slight differences were noticed on concentrations of these dissolved inorganic nitrogen (DIN) pools for the two sediment types (Rm and Ct), these concentrations are generally low as it is in other tropical marine sediments (Boto and Wellington, 1984; Shaiful et al., 1986; Blackburn et al., 1987; Kristensen et al., 1988; Alongi et al., 1992). The concentrations were found to be typically within the μM range and composed mostly of ammonia with lesser amounts of nitrate and nitrite. Several reasons have been advocated for these low nutrient values in mangrove ecosystems. Boto and Wellington (1984) demonstrated that the rate of NH_4^+ uptake by mangrove may exceed net NH_4^+ production rate during rapid plant growth. In anaerobic soils, ammonium becomes the main inorganic nitrogen source since oxidation of organic nitrogen during the mineralization process stops at ammonium due to lack of oxygen to oxidize it further to nitrate (Ponnamperuma, 1972; Clough, 1992).

Due to the relatively higher sedimentary stocks of NH_4^+ as compared to $NO_3^- + NO_2^-$, relatively higher fluxes (sediment - water) were observed for NH_4^+ in both sediment types. For Rm sediments, the NH_4^+ flux had the highest frequency occurrence at about 0.4 mmol N m^{-2} d^{-1} while the $NO_3^- + NO_2^-$ flux was mostly between 0.02 to 0.06 mmol N m^{-2} d^{-1}. For Ct sediments, about 0.50 and 0.05 mmol N m^{-2} d^{-1} of NH_4^+ and $NO_3^- + NO_2^-$ respectively, were fluxed out into the overlying water column. The total dissolved inorganic nitrogen pools, $\sum$ N ($\sum$ N = $NH_4^+ + NO_3^- + NO_2^-$) fluxed out from Rm and Ct sediments were therefore averagely 0.46 and 0.55 mmol N m^{-2} d^{-1} respectively. Since the Rm and Ct mangrove species form more than 70 % of the mangrove vegetation in Gazi bay, the average flux rate of the two vegetations (0.51 mmol N m^{-2} d^{-1}) could be assumed to reflect the average flux rate of the entire vegetation.

As indicated earlier (chapter 3), the median elevation levels of the common mangrove species in Gazi bay are;

Sonneratia ≈ **creek-type** ***Avicennia*** < ***Rhizophora*** ≈ ***Bruguierra*** < ***Ceriops*** ≤ **basin shrub-type** ***Avicennia***

The low lying *Rhizophora* stands (Rm plot) were found to have an average water height of about 2 meters during spring high tides while the *Ceriops* plot, at a slightly elevated level, had a water height of about 1 meter decreasing progressively as one moves to higher elevations. Kitheka, et al., 1995 observed high exchange rates (60 to 90 %) between the offshore and inshore waters with short residence time (3 to 4 hrs). If for argument sake, we assume 1 meter to be the average height of water column covering the entire mangrove vegetation during this residence time, we shall have an estimated volume of about 1000 liters standing above the 1 m^2 area of the study plots. At the above indicated average $\sum$ N flux rate of 0.51 mmol N m^{-2} d^{-1}, this would increase the DIN concentration in the water column at the rate of 0.02 μmol N h^{-1}. These increases are so low and fall below our detection limits (NH_4^+ : 0.05 and NO_3^- : 0.1 μM) which could be why no significant fluctuation of dissolved inorganic nitrogen pool is observed in the mangrove creeks during tidal cycle observations in dry seasons. However, despite these low fluxes observed, average gross primary productivity in the mangrove creeks in dry seasons is found to be ca. 400 mg C m^{-3} d^{-1} (Kitheka et al., 1995). At a Redfield C/N ratio of 6.6, this gross primary productivity, would imply a total DIN ($\sum$ N = NH_4^+ + NO_3^- + NO_2^-) utilization rate of about 0.20 μmol per hour. This required nitrogen is 10 times that made available by the sediment - water benthic fluxes, implying that there must be another source of DIN which should supply an additional 0.18 μmol of $\sum$ N per hour to meet the observed primary productivity requirement within the water column of Gazi bay. In the absence of riverine contribution during dry season, two possibilities exist for this extra supply; (1) either through seepage or (2) by leaching and resuspension of surface sediment nutrients during flood and ebb tidal flows (Boto, 1982). Though seapage effects have been noticed in a number of spots in Gazi bay (Ruwa, pers. comm.), detailed information about seapage in the bay is still lacking and therefore its relative importance as a significant nutrient source in the bay is difficult to quantify. However, the second possibility (leaching and resuspension of surface sediment nutrients) could be of significance as a source of the extra required DIN in the water column. It is observed that the rate of carbon fixation per unit chlorophyl-a

biomass (obtained by dividing the average observed gross primary productivity by the chlorophyl-a biomass in fig. 4.70) at the mangrove creek (ca. 1200 g C per unit gram chlorophyl-a) is different from that found at a station close to the open sea (270 g C per unit gram chlorophyl-a) (Kitheka, et al., 1995). Considering the high exchange rates and short residence time of the water in the bay, this difference may imply a different assemblage of primary producers in the two stations. The assemblage found at the open sea station could represent primary producers typical of the open waters while due to the shallowness of the creeks, the assemblage within the mangrove creeks could also include surface benthic primary producers brought into the water column by tidal resuspension during flood and ebb flushings. It is also observed that the C/N molar ratio of senescent leaves of the main mangrove species in Gazi bay is mostly above 100 (Rao et al., 1993). Since this is expected to be the main supply of particulate organic material (POM) in the mangrove bay, we would expect a relatively high C/N molar ratio for the seston observed in the mangrove creeks. However, the recorded C/N molar ratio of the suspended POM in the mangrove creeks of Gazi bay was mainly between 11 and 14 (tables 5.10A and B) during low tide.

The C/N molar ratio of the upper 1 cm sediment depth of Rm and Ct sediments was found to be about 23 and 19 respectively, increasing progressively with depth. Calculation of sedimentary organic matter composition at the Rm and Ct sediments using the C/N molar ratios and $\partial^{13}C$ isotope signature of mangroves and marine POM, indicates that between 20 and 30 % of the organic matter found in mangrove sediments could possibly be of marine origin. Since marine POM would enter the system from the surface, the upper few millimeters of the sediment would then have relatively higher marine POM composition than the deeper sections resulting in even lower C/N molar ratio for the upper few millimeters relative to the overall C/N molar ratio observed for the upper 1 cm sediment. This again supports the theory that the observed relatively low C/N molar ratio of seston within the water column of the mangrove creek could be mainly from resuspended surface sediments and that this same process may lead to supply of the DIN required for primary production in mangrove creeks. Taking Rm sediment as an example, surface NH_4^+ (total) and $NO_3^- + NO_2^-$ concentrations were found to be averagely 130 and 5 μM, respectively for the upper 1 cm depth. If these values are integrated over 1 mm depth intervals, it is observed that periodic resuspension of the upper 1 to 1.5 mm would add between 0.1 and 0.2 mmol N m^{-2} into the water column. This may account for the extra needed DIN to support the observed primary productivity within the mangrove creeks. Leaching and resuspension of the surface sediments, may therefore be playing a more important role in the supply of DIN into the water column than sediment - water epibenthic fluxes.

7.2 General conclusions

In order to understand and assess the role of mangrove sediments in the overall nitrogen budget of a tropical mangrove ecosystem, the following was investigated: (1) granulometry and pore-water chemistry; (2) main nitrogen transformational processes - organic nitrogen mineralization (regeneration and assimilation rates), nitrification (both potential and actual) and (3) sediment - water column nutrient fluxes, for sediments underlying stands of the two most predominant species of mangrove vegetation (i.e. *Rhizophora mucronata* and *Ceriops tagal*) in Gazi bay. These processes were investigated and related to concentrations of dissolved inorganic nitrogenous compounds found in the overlying water column.

Ammonification rates in sediments generally depend on the quantity (stock) and quality (C/N) of the sedimentary organic material (Aller, 1980; Middelburg, 1989). The organic nitrogen stock of *Rhizophora mucronata* (Rm) and *Ceriops tagal* (Ct) sediments intergrated over the upper 6 cm depth was found to be ca. 9300 and 4000 mmol N m^{-2} respectively. Though Rm sediments were found to have relatively higher organic stock than the Ct sediments, both sediments are not expected to register any net production of NH_4^+ since their organic matter quality (C/N $\geq$ 20) is poor. Blackburn (1986), demonstrated that organic matter whose C/N is $\geq$ 20 should favour immobilization with no significant net production of NH_4^+. Though Rm and Ct sediments have C/N $\geq$ 20 (averagely 26 for the upper 6 cm depth), significant net production of NH_4^+ similar to that observed in other mangrove sediments (Shaiful et al., 1986; Blackburn, 1987; Nedwell et al., 1994) was observed in these mangrove sediments. Regeneration rates (release of ammonium from organic matter respiration) in the upper 6 cm depth of the sediment column were found to range between 18.51 $\pm$ 3.60 mmol N m^{-2} d^{-1} (Rm sediments) to 35.97 $\pm$ 9.75 mmol N m^{-2} d^{-1} (Ct sediments) and, when compared with the total nitrogen inventory (Rm: 9300 and Ct: 4000 mmol N m^{-2}), indicate a turnover rate of between 0.3 (Ct) and 1.4 (Rm) years. However, based on the observed sedimentary C/N ratios (between 19 and 39 for the upper 12 cm depth) calculated CO_2 production associated with the sedimentary respiration process exceeds significantly the CO_2 emission rates measured in the field (Middelburg et al., in press). Taking the measured CO_2 fluxes as the reference, the C/N molar ratio of the organic matter being respired by heterotrophic activity is found to be between 3.3 (Rm sediment) and 8.1 (Ct sediment), which is within the C/N values associated with bacterial biomass. While stable carbon isotope composition indicates both mangrove leaf litter and seagrass

detritus (Hemminga, et al., 1994) as possible main organic matter sources to the sediments, the tremendous reduction of the C/N ratio in mangrove sediments in comparison to the mangrove leaf litter (approx. 200: Rao et al., 1993), indicates a high possibility of another (perhaps more important) external supply of organic nitrogen into the sediments. Though this could come from nitrogen fixation, the maximum possible nitrogen addition into both Rm and Ct sediments through N_2 fixation hardly exceeds 0.40 mmol N m^{-2} d^{-1} (Woitchik et al., 1995; Kazungu, et al., 1995) representing less than 2 % of the observed regeneration rate. Generally, maximum possible additions of nitrogen through both nitrogen fixation and mangrove litterfall (Rm: 0.5 and Ct: 0.2 mmol N m^{-2} d^{-1}; Slim et al., 1995) is relatively low when compared to the remineralization rates implying that without an external constant supply of organic nitrogen, the system would not be self-sustaining. Using a simple conservative mass balance model, this study has demontrated the likelyhood of organic material in mangrove sediments to be composed of two main parts; (1) a pool of highly refractory organic material from mangrove vegetation which is very poor in organic nitrogen and; (2) a pool of labile organic nitrogen, most likely of marine POM. However, since marine POM is expected to have a C/N molar ratio of averagely 6.6, bacterial biomass whose C/N molar ratio is usually between 3 and 7 is seen to be actively involved as a souce of the regenerated NH_4^+ in mangrove sediments when comparing actual fluxed CO_2 (Middelburg et al., in press) and the observed nitrogen remineralization rates. The marine PON therefore possibly acts as the easily available source of the labile organic nitrogen pool for bacterial utilization supporting the high bacterial productivities observed in most mangrove sediments (Alongi, 1994). Upon death, these bacterial cells are then remineralized becoming the main source of the produced ammonium in mangrove sediments.

It is furthermore observed that between 44 % and 60 % of the ammonium mineralized is again taken up during bacterial growth. The remaining fraction of ammonium produced is then available for (1) nitrification; (2) outflux to the overlaying water column and (3) uptake by roots. When excluding the effect of O_2 supplied by roots (incubation technique for the actual nitrification process precludes the possible addition of O_2 by the mangrove roots), nitrification appears essentially limited to the first cm of the sediment column and represents only between 25 % (Rm sediment) and 3 % (Ct sediment) of the net ammonification rate found at the upper 1 cm of the sediment (figs. 7.12 and 7.13). These low nitrification rates are ascribed to low oxygen availability (Rm plot) and toxic conditions found in Ct sediments due to relatively high temperatures and salinities (Carlucci and Strickland, 1985; Watson and Waterburg, 1971; Billen, 1975; Chen, et al.,

1976) coupled with extreme acidic conditions (pH; 3.5 - 6: Middelburg et al., in press) lowering the pH of the pore water out of the limiting range (6.0 - 9.5) of most nitrifying bacteria (Focht and Verstraete, 1977).

Denitrification rates (Woitchik, et al., 1995; Kazungu et al., 1995) for the upper 10 cm of the sediments were observed to range between 0.06 (Ct sediments) and 0.10 mmol N m^{-2} d^{-1} (Rm sediments), representing about 33 % and 23 %, respectively, of the nitrification rate measured for the upper 1 cm depth.

The relatively lower denitrification rates observed in Ct sediments as compared to the Rm sediments are attributed to the slightly higher oxidizing environment found in the Ct sediments as deduced from the redox potential profiles. From these results, bacterial ammonium production and uptake appear to be the main processes affecting the organic nitrogen pool while nitrification, denitrification and nitrogen fixation represent relatively minor processes. Between 35 % (Rm) and 55 % (Ct) of the regenerated ammonium is found to be taken up by the trees themselves (figs. 7.11 and 7.12).

The possible strength of the mangrove sediments as a source of dissolved inorganic nitrogen to the overlying water column was also investigated, both by measuring field epibenthic fluxes and by calculating fluxes based on measured concentration gradients across the sediment - water column interface. Observed and calculated ammonium fluxes were found to give rates within the same order of magnitude.

While the observed sediment - water column NH_4^+ and $NO_3^- + NO_2^-$ flux rates were found to vary between -1.0 to +1.4 and - 0.06 to + 0.75 mmol N m^{-2} d^{-1} respectively, for the Rm sediments, highest frequency for the fluxes were found to fall at about +0.4 (for NH_4^+) and 0.06 (for $NO_3^- + NO_2^-$) mmol N m^{-2} d^{-1}. For Ct sediments, the highest frequencies were seen to be +5 and +0.05 mmol N m^{-2} d^{-1} for the NH_4^+ and $NO_3^- + NO_2^-$ fluxes, respectively.

As observed, nitrate (+ nitrite) fluxes were generally much lower and amounted only to about 10 to 15 % of the observed ammonium outflux. Ammonium outflux represents at most 1.1 % (Ct sediments) and 0.7 % (Rm sediments) of the ammonium regenerated stressing the minor role of epibenthic fluxes in the sedimentary nitrogen budget of these mangrove ecosystems. It is estimated that such outfluxes of ammonium to the overlaying water column of Gazi mangrove forest would change the ammonium content by approximately 0.02 μmol l^{-1} h^{-1}. Considering the relatively short inundation period of the sediments (residence time of water within the bay: 3 - 4 hrs: Kitheka et al., 1995) such concentration increases are barely measurable and could be the reason why no significant

fluctuations of DIN are observed in the water column during dry season. It is furthermore observed that the nitrogen thus made available through these epibenthic fluxes is not sufficient to sustain phytoplankton nitrogen requirements deduced from primary production measurements (Kitheka et al., 1995). It is estimated that periodic tidal resuspension of the upper 1.5 mm of sediment is necessary in order to add the required extra $\sum$ N ($NH_4^+ + NO_3^- + NO_2^-$) necessary to support the observed primary productivity in Gazi mangrove creeks. This resuspension will not only introduce the DIN to support the observed primary production requirement but also explain the relatively low C/N molar ratio (11 to 14) of the seston observed in the mangrove creek waters during low tides due to a possible mixture of the POM from the surface sediments (C/N: 19 - 23) and the marine POM of phytoplanktonic origin (C/N: ca. 7).

It thus appears that nitrogen introduced into the mangrove sedimentary compartment is mainly left for (I) recycling through an active bacterial production system; (II) uptake by the mangrove root system and (III) accumulation as refractory nitrogen. These different observations indicate that mangrove ecosystems, at least those similar to the system present in Gazi bay, are probably not important exporters of organic nitrogen and dissolved inorganic nutrients to the coastal ecosystem. Instead, they function as rather efficient traps and appear to efficiently recycle nitrogen in order to primarily satisfy nitrogen requirements of the mangrove trees themselves. Figures 7.11 and 7.12 below give the schematic summary of some of the nitrogen transformational processes described above for the *Rhizophora mucronata* and *Ceriops tagal* sediments.

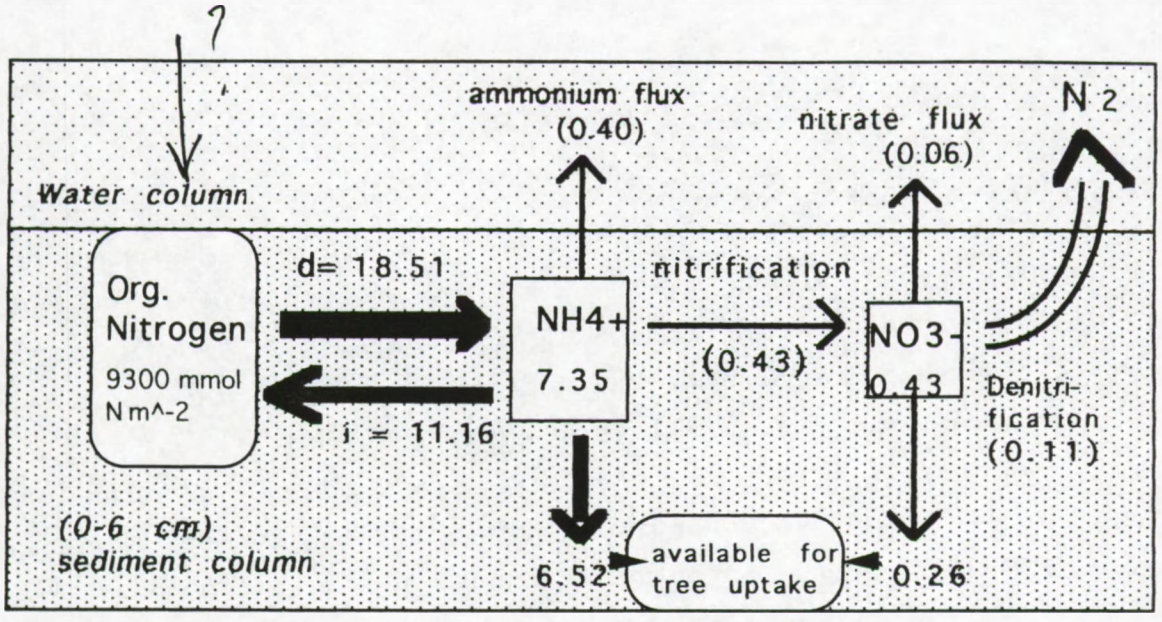


Fig. 7.11: Schematic representation of nitrogen transformational processes in *Rhizophora mucronata* sediments (0 - 6 cm depth) of Gazi bay. All rates are in mmol N m^{-2} d^{-1} while **d** and **i** represent regeneration and assimilation rates.

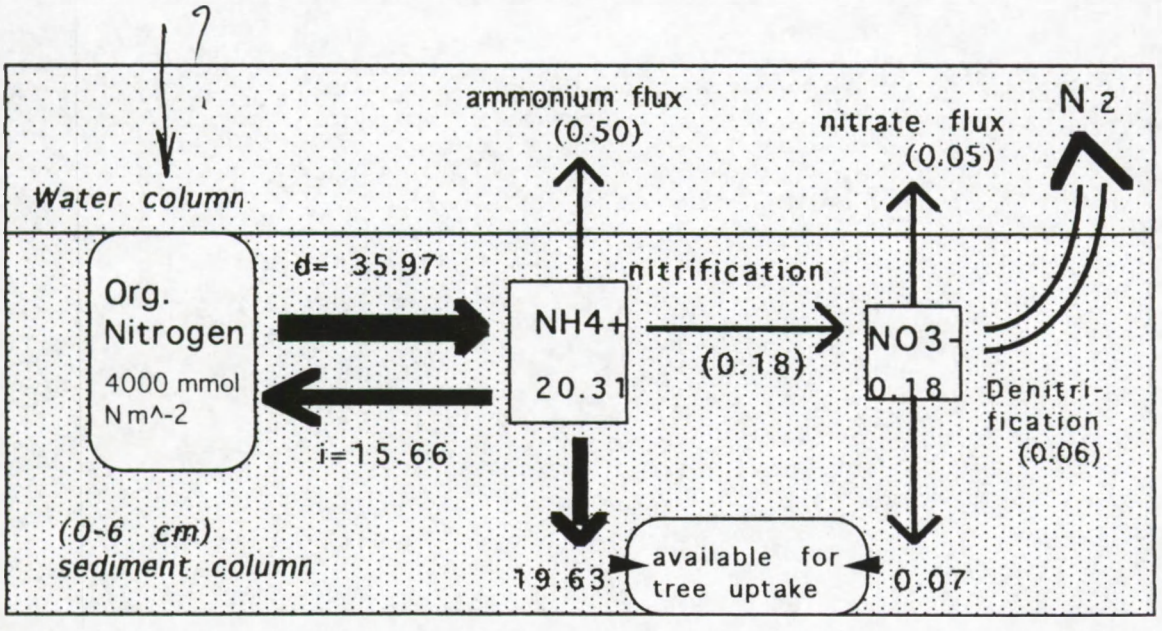


Fig. 7.12: Schematic representation of nitrogen transformational processes in *Ceriops tagal* sediments (0 - 6 cm depth) of Gazi bay. All rates are in mmol N m^{-2} d^{-1} while **d** and **i** represent regeneration and assimilation rates.

RECOMMENDATIONS

1. While adsorption capacities of most marine sediments have been determined using potassium chloride as the extractant, calculations using results obtained from the ^{15}N isotope dilution technique indicate that not all adsorbed NH_4^+ is extracted by the KCl solution. This problem is compounded by the fact that presence of amines in sediment's pore water hinders colour development during NH_4^+ determination. This led us to introduce correction factors in our regeneration and assimilation calculations. However, in order to determine accurately the total ammonium concentrations in mangrove sediments, there is a strong need to examine in detail concentration levels of amines in these sediments and assess their exact contributions in the underestimation of correct NH_4^+ concentrations.

2. From the results obtained during this study, it has also become very apparent that more detailed studies on benthic primary producers in mangrove ecosystems need to be undertaken to assess their exact nitrogen contributions within the ecosystem. Though the nitrogen enrichment observed in mangrove sediments has been attributed to marine particulate organic material, it is still not clear how much of this is imported into the system and how much is actually produced through benthic primary production.

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APPENDICES

APPENDIX 1A

Extraction of total ammonium for *Rhizophora mucronata* sediments in dry season (Jan.1992) using different volumes of 1 N KCl solution.

KCl (0 ml)	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Average (± S.D.)
0	83.8	71.9	77.3	73.9	91.5	87.0	74.2	79.9 ± 7.5
10	127.9	95.3	100.4	116.5	111.2	93.7	138.6	111.9 ± 16.9
20	115.9	157.6	130.9	110.4	143.3	167.9	135.5	140.9 ± 20.4
30	160.0	145.3	154.8	136.0	168.8	150.2	153.9	152.5 ± 9.0
40	138.6	173.2	152.7	153.4	159.5	159.4	155.0	156.0 ± 10.0
50	148.9	160.3	170.8	138.7	143.5	170.4	149.0	154.5 ± 12.8
80	143.3	159.9	153.1	147.7	186.3	158.9	123.9	153.3 ± 18.9
100	160.3	168.5	153.4	129.3	167.9	148.8	172.4	157.3 ± 15.0

APPENDIX 1B

Extraction of total ammonium for *Rhizophora mucronata* sediments in rainy season (May, 1992) using different volumes of 1 N KCl solution.

KCl (ml)	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Average (± S.D.)
0	79.0	60.4	65.7	69.5	65.9	68.1 ± 6.9
10	104.2	117.3	132.9	106.4	139.5	120.1 ± 15.7
20	140.7	138.5	146.2	120.7	167.4	142.7 ± 16.8
30	149.4	137.7	145.3	165.8	153.9	150.4 ± 10.5
40	143.9	148.7	149.8	139.4	170.1	150.4 ± 11.8
50	137.8	153.6	144.7	157.2	148.9	148.5 ± 7.6
80	160.8	149.8	142.7	169.9	140.0	152.6 ± 12.6
100	151.6	190.2	120.3	144.0	145.6	150.3 ± 25.3

APPENDIX 1C

Extraction of total ammonium for *Ceriops tagal* sediments in dry season (Jan. 1992) using different volumes of 1 N KCl solution.

KCl (0 ml)	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Average (± S.D.)
0	249.4	284.7	219.9	233.4	249.7	257.7	290.3	255.0 ± 31.5
5	256.7	301.6	259.5	261.3	286.7	287.8	311.3	280.6 ± 21.8
10	311.8	307.4	263.7	259.7	297.8	314.7	309.3	294.9 ± 23.3
20	299.8	269.7	271.6	297.6	317.9	279.6	303.7	291.4 ± 18.1
30	298.3	342.7	277.8	259.7	297.3	259.7	319.4	293.6 ± 30.7
40	310.1	319.6	263.7	269.7	304.7	268.6	287.6	289.2 ± 22.6
80	329.7	298.3	269.3	258.8	290.0	279.3	327.6	293.3 ± 27.4
100	309.5	299.6	279.4	251.1	319.2	248.7	351.7	294.2 ± 37.3

APPENDIX 1D

Extraction of total ammonium for *Ceriops tagal* sediments in rainy season (May, 1992) using different volumes of 1 N KCl solution.

KCl (ml)	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Average (± S.D.)
0	227.6	243.3	199.7	254.6	249.3	235.9 ± 22.7
5	243.7	267.3	227.8	261.7	287.3	257.6 ± 22.8
10	258.6	246.9	253.2	309.8	286.4	271.0 ± 26.4
20	281.3	276.8	237.4	318.8	249.3	272.7 ± 31.6
30	240.0	269.8	243.8	287.7	294.2	267.1 ± 24.7
40	237.91	278.3	286.9	309.6	267.8	267.8 ± 26.3
80	258.6	269.7	254.8	286.7	266.2	266.2 ± 12.7
100	263.4	271.3	252.4	299.7	270.8	270.8 ± 17.6

APPENDIX 2A

Ammonium and nitrate (+ nitrite) flux rates (sediment - water interface) at the *Rhizophora mucronata* plot between 1992 and 1994.

Date	No. of cores	Incubation time (hrs.)	Mean flux rate NH_4^+ (mmol N m^{-2} d^{-1})	Mean flux rate $NO_3^- + NO_2^-$ (mmol N m^{-2} d^{-1})
13. 02. 92	5	4	+0.366 ± 0.100	+0.017 ± 0.043
27. 02. 92	5	4	+0.294 ± 0.258	+0.031 ± 0.051
31. 02. 92	5	4	+0.394 ± 0.152	+0.092 ± 0.145
15. 04. 92	6	5	+0.305 ± 0.231	+0.067 ± 0.062
26. 04. 92	4	4	+0.153 ± 0.135	+0.025 ± 0.034
11. 05. 92	5	4	+0.166 ± 0.156	+0.126 ± 0.190
28. 05. 92	5	5	+0.241 ± 0.214	+0.048 ± 0.091
07. 07. 92	5	4	+0.181 ± 0.123	+0.138 ± 0.170
26. 08. 92	5	4	+0.231 ± 0.142	+0.013 ± 0.060
11. 01. 93	5	4	+0.212 ± 0.118	+0.162 ± 0.209
01. 02. 93	5	4	+0.456 ± 0.158	+0.048 ± 0.053
26. 02. 93	5	5	+0.545 ± 0.480	+0.070 ± 0.100
22. 05. 93	5	4	+0.323 ± 0.149	+0.009 ± 0.005
07. 06. 93	4	5	+0.349 ± 0.167	+0.190 ± 0.370
08. 04. 93	5	4	+0.453 ± 0.272	+0.061 ± 0.131
21. 04. 93	5	4	+0.489 ± 0.464	-0.003 ± 0.041
01. 05. 93	5	3.5	+0.653 ± 0.350	+0.089 ± 0.069

APPENDIX 2B

Ammonium and nitrate (+ nitrite) flux rates (sediment - water interface) at the *Ceriops tagal* plot between 1992 and 1994.

Date	No. of cores	Incubation time (hrs.)	Mean flux rate NH_4^+ (mmol N m^{-2} d^{-1})	Mean flux rate $NO_3^- + NO_2^-$ (mmol N m^{-2} d^{-1})
13. 02. 92	5	4	+0.504 ± 0.323	+0.054 ± 0.051
27. 02. 92	5	4	+0.604 ± 0.315	+0.053 ± 0.045
31. 02. 92	5	4	+0.368 ± 0.302	+0.059 ± 0.060
15. 04. 92	6	5	+0.499 ± 0.328	+0.015 ± 0.061
26. 04. 92	4	4	+0.909 ± 0.970	+0.009 ± 0.040
11. 05. 92	5	4	+0.399 ± 0.302	
28. 05. 92	5	5	+0.545 ± 0.206	-0.093 ± 0.083
07. 07. 92	5	4	+0.548 ± 0.190	+0.052 ± 0.114
26. 08. 92	5	4	+0.416 ± 0.247	+0.121 ± 0.153
11. 01. 93	5	4	-	-
01. 02. 93	5	4	+0.507 ± 0.206	+0.042 ± 0.050
26. 02. 93	5	5	+0.333 ± 0.362	+0.044 ± 0.017
22. 05. 93	5	4	+0.544 ± 0.320	+0.010 ± 0.049
07. 06. 93	4	5	+0.464 ± 0.252	-0.084 ± 0.082
08. 04. 93	5	4	+0.727 ± 0.293	+0.232 ± 0.140
21. 04. 93	5	4	+0.404 ± 0.263	+0.031 ± 0.043
01. 05. 93	5	3.5	+0.585 ± 0.379	+0.051 ± 0.088

APPENDIX 3A

Daily ammonium and nitrate (+ nitrite) concentrations in *Rhizophora mucronata* and *Ceriops tagal* sediments during dry season of 1993 (January 11th to February 9th, 1993).

Date	Rhizophora mucronata sediments		Ceriops tagal sediments		Tides
	NH_4^+ (μM)	$NO_3^- + NO_2^-$ (μM)	NH_4^+ (μM)	$NO_3^- + NO_2^-$ (μM)	
11.01.93	74.5 ± 21.8	1.3 ± 1.1	192.7 ± 23.6	13.3 ± 5.7	spring
13.01.93	66.1 ± 12.6	4.2 ± 2.7	232.8 ± 33.6	17.5 ± 3.9	
15.01.93	86.5 ± 17.3	3.2 ± 2.8	167.9 ± 21.6	13.6 ± 5.1	
17.01.93	58.6 ± 14.2	2.9 ± 1.9	262.3 ± 32.1	24.4 ± 8.9	
19.01.93	62.3 ± 9.8	2.9 ± 2.1	261.5 ± 17.8	29.3 ± 8.4	neap
21.01.93	66.2 ±15.0	3.9 ± 1.6	331.3 ± 24.7	23.6 ± 5.6	
22.01.93	75.6 ± 22.4	3.3 ± 2.2	293.6 ± 33.7	30.6 ± 9.1	
24.01.93	69.5 ± 17.9	3.1 ± 2.6	203.3 ± 37.4	28.2 ± 3.5	
26.01.93	76.1 ± 15.3	0.9 ± 1.3	223.1 ± 16.8	16.4 ± 7.2	spring
28.01.93	56.3 ± 14.6	2.7 ± 2.1	184.4 ± 17.8	21.6 ± 4.9	
30.01.93	94.5 ± 30.2	5.1 ± 2.4	204.9 ± 28.4	19.6 ± 7.3	
01.02.93	62.7 ± 17.7	3.1 ± 0.7	263.2 ± 36.3	16.8 ± 4.3	
03.02.93	68.9 ± 5.0	3.3 ± 1.9	239.7 ± 24.9	23.6 ± 6.8	neap
05.02.93	61.8 ± 12.0	6.1 ± 2.9	299.1 ± 29.7	22.2 ± 5.6	
07.02.93	82.4 ± 18.5	2.6 ± 1.4	254.6 ± 31.5	19.2 ± 6.2	
09.02.93	67.8 ± 19.0	2.6 ± 1.8	217.4 ± 22.3	19.3 ± 5.8	

APPENDIX 3B

Daily ammonium and nitrate (+nitrite) concentrations in *Rhizophora mucronata* and *Ceriops tagal* sediments during rainy season of 1993 (May 7th to June 7th, 1993).

Date	Rhizophora mucronata sediments		Ceriops tagal sediments		Tides
	NH_4^+ (μM)	$NO_3^- + NO_2^-$ (μM)	NH_4^+ (μM)	$NO_3^- + NO_2^-$ (μM)	
07.05.93	64.2 ± 13.5	3.7 ± 2.3	243.6 ± 33.1	9.4 ± 5.7	spring
09.05.93	61.1 ± 5.9	2.9 ± 2.4	198.7 ± 33.6	6.9 ± 4.7	
11.05.93	70.3 ± 12.5	2.5 ± 0.9	199.4 ± 21.4	18.9 ± 5.3	
13.05.93	73.5 ± 10.5	3.3 ± 1.0	247.9 ± 38.7	13.7 ± 6.7	
15.05.93	71.3 ± 2.2	3.7 ± 2.8	289.3 ± 35.9	21.3 ± 9.2	neap
17.05.93	51.1 ± 7.1	1.9 ± 1.5	201.9 ± 33.3	20.9 ± 7.3	
19.05.93	69.9 ± 4.0	4.3 ± 2.9	247.8 ± 21.7	18.7 ± 3.8	
21.05.93	70.0 ± 9.7	3.2 ± 1.9	289.5 ± 39.3	19.9 ± 5.9	
22.05.93	70.5 ± 6.1	3.7 ± 2.3	231.5 ± 16.6	27.4 ± 8.3	spring
24.05.93	59.1 ± 9.4	2.3 ± 1.9	181.1 ± 27.3	16.7 ± 5.8	
26.05.93	73.1 ± 3.2	2.7 ± 0.9	223.7 ± 31.9	16.8 ± 7.1	
28.05.93	63.0 ± 11.6	4.8 ± 1.7	136.7 ± 19.7	23.4 ± 6.8	
30.05.93	63.3 ± 2.9	2.3 ± 1.9	211.4 ± 29.7	19.23 ± 6.9	neap
01.06.93	70.3 ± 7.6	0.8 ± 0.8	244.4 ± 33.8	13.5 ± 7.4	
03.06.93	77.7 ± 6.5	3.7 ± 2.1	233.7 ± 20.5	17.5 ± 3.9	
05.06.93	51.7 ± 11.8	2.6 ± 1.1	252.6 ± 32.9	25.7 ± 8.4	
07.06.93	62.3 ± 17.3	3.1 ± 2.1	231.9 ± 17.3	21.1 ± 3.9	

APPENDIX 4A

Results of the ammonium pools and their corresponding ^{15}N abundances observed during regeneration and assimilation experiments on *Ceriops tagal* sediments in dry season between 1992 and 1993.

Spike*: 0.1 ml 400 μM $^{15}NH_4Cl$

Date	Depth (cm)	P_o μM	P_i μM	P_r μM	A_i % ^{15}N	A_f % ^{15}N	Water content (%)
6/2/92	0 - 1	115.3 ± 18.1	139.9 ± 20.4	1635 ± 89	9.118 ± 0.219	0.720 ± 0.063	22.6
t = 26 h	1 - 6	130.6 ± 18.3	195.5 ± 29.7	929 ± 72	5.283 ± 0.114	0.939 ± 0.144	32.0
spike*							
20/2/92	0 -1	130.6 ± 18.3	157.4 ± 23.1	1816 ± 103	8.182 ± 0.093	0.678 ± 0.112	24.1
t = 24 h	1 - 6	135.8 ± 15.7	144.7 ±12.9	803 ± 35	5.513 ± 0.154	0.971 ± 0.073	32.9
spike *							
17/3/92	0 -1	98.0 ± 11.8	103.3 ± 16.9	1252 ± 115	11.18 ± 0.315	0.662 ± 0.172	23.0
t = 24	1 - 6	115.7 ±20.1	123.7 ± 22.1	539 ± 50	5.702 ± 0.174	1.173 ± 0.114	34.6
spike*							
08/2/93	0 -1	103.5 ± 15,3	105.5 ± 8.3	1738 ± 87	7.744 ±0.253	0.777 ±0.083	22.5
t = 24	1 - 6	174.3 ± 20.1	218.2 ± 13.2	740 ± 60	3.993 ± 0.089	1.018 ± 0.177	30.6
spike*							
27/2/93	0 - 1	135.8 ± 16.0	144.9 ± 27.3	1627 ± 125	7.504 ± 0.561	0.708 ± 0.115	23.3
t = 24	1 - 6	239.6 ± 18.3	247.3 ± 20.2	665 ± 59	4.425 ± 0.217	0.764 ±0.107	31.9
spike*							
11/3/93	0 - 1	101.4 ± 8.8	103.8 ± 16.1	944 ± 72	9.544 ± 0.321	0.907 ± 0.089	24.6
t = 24 h	1 - 6	153.6 ±19.4	169.3 ± 22.2	484 ± 15	5.929 ± 0.114	1.249 ± 0.107	30.2
spike*							
27/3/93	0 - 1	120.6 ± 14.3	133.7 ±11.6	1693 ± 51	10.70 ± 0.693	0.559 ±0.066	24.7
t = 24 h	1 - 6	194.6 ± 20.3	203.8 ± 29.4	648 ± 70	4.467 ±0.211	1.098 ± 0.183	32.4
spike*							

APPENDIX 4B

Results of the ammonium pools and their corresponding ^{15}N abundances observed during regeneration and assimilation experiments on *Ceriops tagal* sediments in rainy season between 1992 and 1993.

Spike*: 0.1 ml 400 μM $^{15}NH_4Cl$

Date	Depth (cm)	P_o μM	P_i μM	P_f μM	A_i % ^{15}N	A_f % ^{15}N	V c
2/5/92	0 - 1	159.3 ± 20.9	172.6 ± 19	1237 ± 53	6.924 ± 0.319	0.755 ± 0.179	
t = 24 h	1 - 6	215.3 ± 28.9	237.8 ± 15.3	797 ± 58	4.092 ± 0.219	0.891 ±0.101	
spike*							
06/5/92	0 -1	126.9 ± 15.3	130.9 ± 18.4	1032 ± 94	10.48 ± 0.217	0.822 ± 0.018	
t = 24 h	1 - 6	155.1 ± 5.4	168.7 ± 8.3	495 ± 29	6.138 ± 0362	1.437 ± 0.112	
spike *							
21/5/93	0 -1	110.7 ± 14.4	129.4 ± 17.1	1952 ± 89	9.854 ± 0.193	0477 ± 0.078	
t = 27	1 - 6	185.4 ± 5.8	205.6 ± 13.7	872 ± 29	5.691 ± 0.216	1.281 ± 0.159	
spike*							
05/6/93	0 -1	153.8 ± 10.9	161.3 ± 12.3	1549 ± 68	7.885 ± 0.227	0.780 ± 0.118	
t = 24	1 - 6	189.4± 16.1	215.4 ± 23.1	764 ± 61	4.131 ± 0.314	0.851 ± 0.072	
spike*							
16/6/93	0 - 1	93.8 ± 2.3	103.9 ± 7.0	1351 ± 117	9.719 ± 0.337	0.552 ± 0.209	
t = 24	1 - 6	169.4 ± 25.2	193.8 ± 27.3	719 ± 52	4.501 ± 0.179	1.136 ± 0.111	
spike*							

APPENDIX 4C

correction of observed ammonium pools for calculations of regeneration (r) and assimilation (i) rates for *Ceriops tagal* sediments (1992 - 1993).

Date	Depth (cm)	A_i % ^{15}N (observed)	Observed NH_4^+ pool (μM)		Corrected NH_4^+ pool (μM)	
			P_i	P_r	P_i	P_r
06.02.92	0 - 1	9.118	139.9	1635	200.2	1696
	1 - 6	5.283	195.5	929	251.4	985
20.02.92	0 - 1	8.182	157.4	1816	209.5	1869
	1 - 6	5.513	144.7	803	233.1	891
17.03.92	0 - 1	11.179	103.3	1252	158.7	1308
	1 - 6	5.702	123.7	539	214.3	630
02.05.92	0 - 1	6.924	172.6	1237	243.7	1309
	1 - 6	4.092	237.8	797	317.9	877
09.06.92	0 - 1	10.476	130.9	1032	177.9	1079
	1 - 6	6.138	168.7	495	221.7	548
08.02.93	0 - 1	7.744	105.5	1738	238.7	1876
	1 - 6	3.993	218.2	740	356.0	878
27.02.93	0 - 1	7.504	144.9	1627	237.5	1720
	1 - 6	4.425	247.3	665	304.7	722
11.03.93	0 - 1	9.544	103.8	944	174.6	1015
	1 - 6	5.929	169.3	484	234.7	549
27.03.93	0 - 1	10.698	133.7	1693	154.7	1714
	1 - 6	4.467	203.8	648	297.6	742
21.05.93	0 - 1	9.854	129.4	1952	191.3	2014
	1 - 6	5.690	205.6	872	247.7	914
05.06.93	0 - 1	7.885	161.3	1549	229	1617
	1 - 6	4.131	215.4	764	330	879
16.06.93	0 - 1	9.719	103.9	1350	169.74	1416
	1 - 6	4.501	193.8	719	288.11	814

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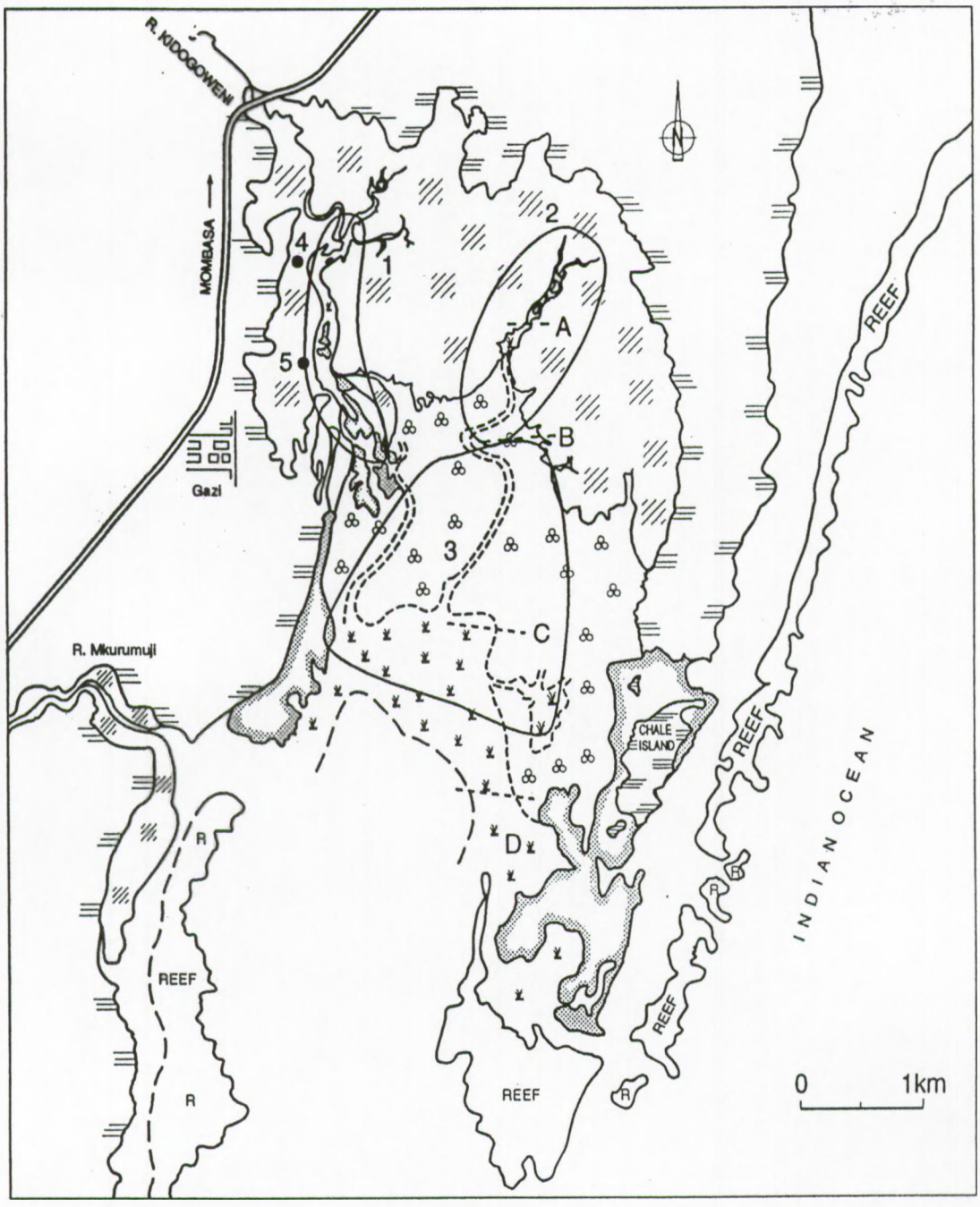

Mangrove
Mainland
Intertidal flat with seagrass (<30%)
Subtidal seagrass (30 - 100%)
Intertidal flat

AQ OEC vd VELDE INDIAN OCEAN A-A TEK J.P FL 10

FIG. (1)