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Sediment biogeochemistry in an East African mangrove forest (Gazi Bay, Kenya)

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Abstract. The biogeochemistry of mangrove sediments was investigated in several mangrove forest communities in Gazi Bay, a coastal lagoon in Kenya, Africa. Carbon dioxide fluxes, sediment median grain sizes, sedimentary organic carbon, nitrogen and phosphorus contents and pore-water characteristics (ammonium, nitrate, sulfate and chloride) could be related to forest type. Mangrove sediments have pH values that range from 3.5 to 8.3 due to the limited buffer capacity of these sediments and intense acidifying processes such as aerobic degradation of organic matter, oxidation of reduced components, ammonium uptake by roots and root respiration. The mangrove sediments are nitrogen-rich compared to mangrove litter, as a result of microbial nitrogen retention, uptake and fixation, and import of nitrogen-rich material. It appears that mangrove sediments in Gazi Bay act as a nutrient and carbon sink rather than as a source for adjacent seagrass and reef ecosystems.

Introduction

The high primary productivity of mangroves implies a high demand for nutrients essential to plant growth. This high nutrient requirement appears to be met by highly efficient systems of nutrient trapping, uptake and recycling (e.g. Dye 1983; Alongi 1989, 1994a, b; Woodroffe 1992; Lugo & Snedaker 1974; Boto & Wellington 1984; Twilley et al. 1986; Kristensen et al. 1988, 1991, 1992, 1994; Alongi et al. 1992, 1993; Robertson et al. 1992; Hemminga et al. 1994; Nedwell et al. 1994; Morell & Corredor 1993). Nevertheless, several studies have indicated that mangroves may be nutrient limited at the whole-forest scale (e.g., Boto & Wellington 1983; Feller 1995). Organic detritus produced by mangroves may either be exported to adjacent ecosystems such as seagrass meadows or coastal waters, or be buried or degraded and recycled in the sediments. Although considerable attention has been given to the export of mangrove-derived material to adjacent systems (e.g., Lugo & Snedaker 1974; Twilley et al. 1986; Robertson et al. 1992; Hemminga et al. 1994), there are comparatively few data on carbon and nutrient pools, transformations and

fluxes within mangrove forests and on the import of particulate carbon and nutrients from adjacent systems (e.g., Robertson et al. 1992; Alongi et al. 1992, 1993). The carbon and nutrient cycles in mangroves are temporally and spatially highly variable since they are regulated by a variety of factors such as soil type and texture, tidal range and elevation, redox state, bioturbation intensity, forest type, temperature and rainfall (Lugo & Snedaker 1974; Alongi et al. 1992). Due to the limited data available on carbon and nutrient cycling, and the great variability within and between mangroves, there is still confusion about whether mangroves generally represent a net carbon source (export) or sink (import). On the one hand, biologists focus on mangroves as highly productive systems that export organic matter, on the other hand geologists are interested in the role of mangroves as traps for sediment and its associated organic matter (Woodroffe 1992).

Our current knowledge on elemental cycling in mangroves is mainly based on studies from North America, Australia and Southeast Asia. In this study we will report our results on the sediment characteristics and pore-water chemistry of mangrove sediments in Gazi Bay, a coastal lagoon in Kenya, Africa. We have also determined carbon dioxide fluxes from the sediment to the atmosphere. The objectives of this study are: (1) to establish the magnitude and variability of carbon dioxide fluxes from mangrove sediments, (2) to determine whether there are relationships between forest type, nutrient status and sediment characteristics of mangrove sediments, and (3) to trace the processes involved in cycling of carbon and nitrogen within mangrove forests.

Methods

Study area

From 19 June to 7 July 1992, a field campaign was carried out in the mangrove forests in Gazi Bay, about 50 km south of Mombasa on the Kenyan Coast (4°25′ S, 39°30′ E). Gazi Bay is a coastal lagoon with a fringing coral reef at the seaward side, a 6.6 km^2 mangrove forest in the intertidal zone on the landward side and seagrasses in between (Van Speybroeck 1992; Hemminga et al. 1994; Rao et al. 1994). There are two major tidal creeks, the western one being the mouth of the river Kidogoweni, a seasonal river (Figure 1). There is seepage of fresh water at various sites within the bay. Gazi Bay has a semi-diurnal tidal regime with an amplitude varying between 290 cm at spring tide and 70 cm at neap tide (Hemminga et al. 1994). Salt pans occur at elevated areas with a very low inundation frequency. The area is influenced by two monsoonal regimes: the North-East monsoon from November to March and the South-West monsoon from May to September.

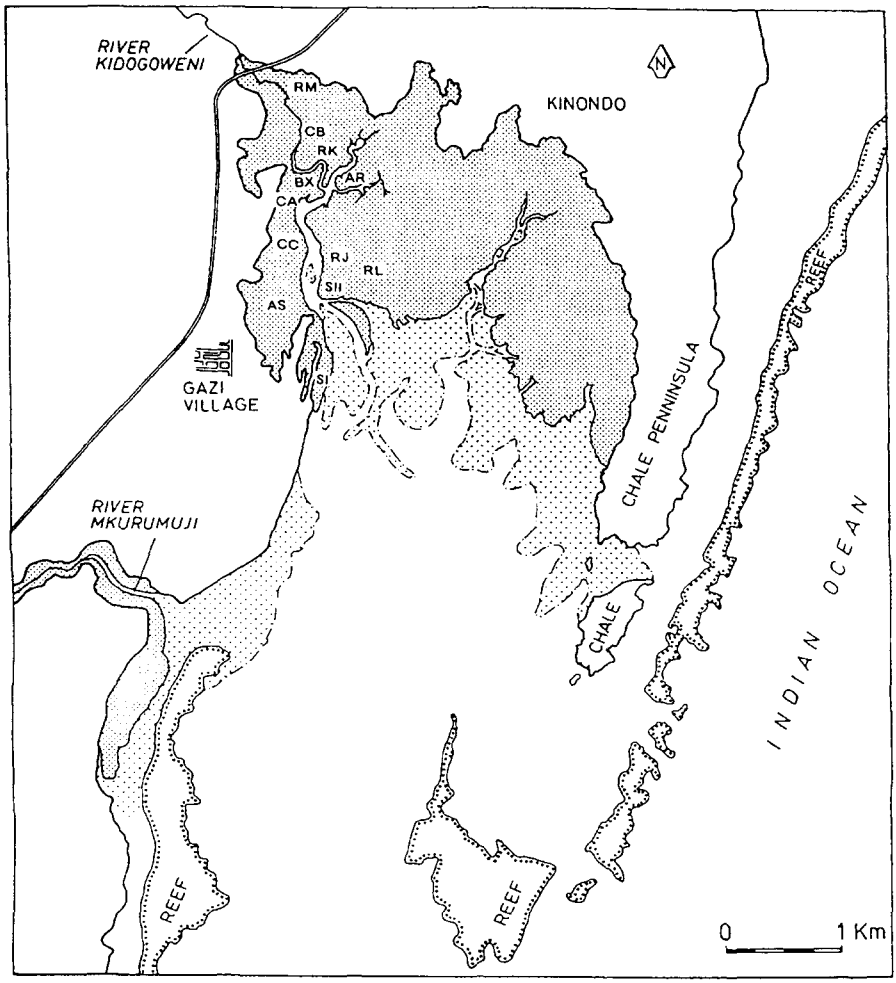

Figure 1. Map of Gazi Bay and mangroves along the river Kidogoweni. Stations are indicated: AS = *Avicennia* saline basin-type; AR = *Avicennia* river-fringing; BX = *Bruguiera*, station X, CA = *Ceriops* station A; CB = *Ceriops* station B; CC = *Ceriops* station C; RJ = *Rhizophora* station J; RK = *Rhizophora* station K; RL = *Rhizophora* station L; RM = *Rhizophora* station M; SI = *Sonneratia* station I; SII = *Sonneratia* station II. Fine dotted and dotted areas relate to mangroves and seagrasses, respectively.

This study focusses on five of the eight mangroves species occurring in Gazi Bay, namely *Sonneratia alba, Rhizophora mucronata, Bruguiera gymnorrhiza, Ceriops tagal* and *Avicennia marina.* Criteria for site selection included the monospecificity of the stands, the position along the river Kidogoweni (i.e. expected salinity), the tidal elevation, the accessibility and the feasibility of flux measurements (Figure 1). The mangrove species occur in

clear zonation patterns, which can be easily recognized in the field. In general, *Sonneratia alba* forms the outermost zone towards the open water, followed by pure stands of *Rhizophora mucronata*, or mixed stands of *Rhizophora mucronata* and *Bruguiera gymnorrhiza*, and in turn these are followed by pure or mixed stands of *Ceriops tagal* and *Avicennia marina*. Along the River Kidogoweni and other creeks, *Avicennia marina* usually replaces *Sonneratia alba*. Creek and river fringing *Avicennia marina* stands are much higher (12–18 m) than those on elevated areas (about 2–3 m; scrub-type) and are therefore treated as different types in the statistical analysis.

Flux measurements

Replicate measurements of carbon dioxide fluxes were made at twelve stations (Figure 1). At low tide the release of these gases was measured by monitoring accumulation of the gas beneath chambers placed over the sediment surface. The chambers have a 0.11 m^2 base, a volume of 45 l and are made of non-transparent polypropylene to exclude any phototrophic activity. Carbon dioxide concentrations were measured by circulating chamber air through Teflon tubes between the chamber and the gas monitor. The measurement principle of the multi-gas monitor used, a Brüel & Kjaer type 1302, is based on the photoacoustic infra-red detection method. Briefly, after thorough flushing of the Teflon tubes and analysis cell, the air sample is hermetically sealed in the analysis cell. The light emitted by a pulsating infra-red light source and purified by a narrow-band optical filter is selectively adsorbed. The temperature of the gas increases and decreases in response to the pulsating light transmitter, and this causes an equivalent increase and decrease of the pressure of the gas in the closed cell. Two ultrasensitive microphones mounted in the cell are used to measure this pressure wave, which is directly proportional to the concentration of the gas. Various gases can be measured in the same sample using different filters. The response time for a sequential measurement of carbon dioxide, methane and nitrous oxide is about 90 sec. The detection limits for carbon dioxide is 3 ppmv, its response is linear up to several thousands of ppmv for carbon dioxide and the reproducibility at ambient levels is about 1%. Fluxes are calculated by regression analysis from the recorded change in concentration over time. Fluxes significant at $p < 0.01$ are normally obtained as low as 1.5 mol CO_2 m^{-2} yr^{-1}, within 30 minutes.

Sediment characteristics and pore-water composition

At each station, pore-water samples from intertidal muds were obtained by pressure filtration of sediments following the collection of cores by hand at low tide. Equivalent depth sections of three replicate cores were combined to

reduce spatial heterogeneity and treated as one sample. No special precautions were taken to control temperature and oxygen levels during squeezing. The recovered pore-water samples were used first for the analyses of ammonium according to the phenol-hypochlorite method (Helder & de Vries 1979) and subsequently stored at −20 °C for transport to our home laboratory. The stored pore-water samples were analyzed for nitrate, nitrite, phosphate and sulfate concentrations using standard colorimetric methods on a Skalar autoanalyzer. The chlorinity was determined by potentiometric titration.

Sediment samples were taken at depth intervals of 0–5, 5–20 and 20–40 cm and were analyzed for grain size distribution, particulate organic carbon, total nitrogen and phosphorus, $CaCO_3$, salinity and pH. Grain-size distribution was assessed with a laser diffraction technique (Malvern Particle Sizer type 3600 Ec). The organic carbon and nitrogen contents of the sediments were determined using a Carlo-Erba CN-analyzer following a recently developed in situ HCl acidification procedure (Nieuwenhuize et al. 1994). Total phosphorus was analysed using a standard colorimetric determination of phosphate (Chen 1956) following digestion by strong oxidizing acid reagents (hydrochloric acid + nitric acid; Nieuwenhuize et al. 1991). The inorganic carbon content was determined by gas-volumetry (Scheibler-method), the pH was determined in a KCl suspension and the salinity was estimated from measured chlorinities and is expressed in practical salinity units (psu ≈ ‰).

Two stations, Rhizophora L (RL) and Ceriops C (CC), were selected for detailed investigation of the depth distribution of organic carbon and total nitrogen. Sediment samples were taken with a depth resolution of 1 cm and also an attempt was made to separate living (root) from non-living organic matter.

Data analysis

Analysis of variance with a nested design was used to evaluate differences among different mangrove types and stations within a given mangrove type. ANOVA was followed by a Tukey-Kramer honestly significant difference method to test for pairwise difference between mangrove types. Six mangrove types are distinguished, namely large creek-fringing *Avicennia marina*, small basin *Avicennia marina* and the four other species. Data were log-transformed if appropriate. SYSTAT (Wilkinson 1990) was used for statistical calculations. The data on which this study is based are listed in full detail in Middelburg et al. (1995).

Table 1. Carbon dioxide fluxes (mol C m^{-2} yr^{-1}) from mangrove sediments.

Type	Location	Mean	Minimum	Maximum
Avicennia	R	136	121	152
Avicennia	S	120	92	141
Bruguiera	X	30	4	56
Ceriops	A	82	21	138
Ceriops	B	55	7	165
Ceriops	C	74	15	133
Rhizophora	J	20	5	29
Rhizophora	K	59	29	115
Rhizophora	L	22	11	41
Rhizophora	M	34	22	47
Sonneratia	I	73	60	96
Sonneratia	II	78	40	129

Results

Flux measurements

Carbon dioxide fluxes were determined at 12 stations covering 66 sites in total and range from about 4 to 165 mol C m^{-2} yr^{-1} (Table 1). Statistical analysis through nested ANOVA indicates that carbon dioxide fluxes differ significantly among the stations ($p = 0.0001$) and among type of mangroves ($p = 0.037$; Table 2).

Sediment characteristics

Sediment characteristics such as the median grain size, salinity, pH, the calcium carbonate, organic carbon, nitrogen and phosphorus contents were measured at 16 sites at 3 depth levels (Table 3). The median grain size ranges from 20 μm at the creek-fringing *Avicennia* to 320 μm at bay-fringing *Sonneratia*. The pH and inorganic carbonate content range from 3.5 to 8.3 and 0.0 to 1.4 wt%, respectively. The salinity of the mangrove sediments ranges from 16 to 68 psu, though the majority of the data cluster between 30 and 35 psu. The organic carbon and nitrogen contents exhibit a wide range, namely from 0.3 to 18 wt% and 0.01 to 3.5 wt% C and N, respectively, with no systematic trend with depth. The organic carbon and nitrogen contents are closely correlated ($r^2 = 0.89$) with a slope corresponding to a molar C/N ratio of 25.3 $\pm$ 1.3 (Figure 2). Sediments from creek-fringing *Avicennia* are strongly enriched in nitrogen (Table 3; Figure 2). Sedimentary phosphorus concentrations range from 35 to 740 ppm and show a moderate correlation

Table 2. Analysis of variance.

	F value type	F value station{type}	Number	Pairwise significant difference ($p < 0.01$; $\underline{\mathbf{p < 0.001}}$)
Carbon dioxide flux	2.564*	4.577***	66	**AS-B**,AS-C,**AS-R**,AR-B,AR-C,**AR-R**,R-S
pH	1.701	1.998	48	
Median	8.981****	2.760*	48	AS-AR,AS-S,**AR-B**,**AR-C**,**AR-S**,**C-R**,**R-S**
Organic Carbon	5.916****	2.616*	48	**AS-AR**,AS-C,**AS-R**,**AR-S**,C-S,**R-S**
Nitrogen	14.271****	1.415	48	**AS-AR**,AR-B,**AR-C**,AR-R,**AR-S**,B-S,C-S,**R-S**
Phosphorus	11.824****	1.794	48	**AS-AR**,AS-R,**AR-C**,**AR-S**,**C-R**,**R-S**
NH_4	2.895*	16.271****	116	**AS-B**,**AS-C**,AS-S,**AR-B**,**AR-C**,AR-S,**B-R**,**B-S**,**C-R**,**C-S**,R-S
NO_3	8.031****	2.833*	116	AS-AR,AS-B,**AS-R**,**AS-S**,**C-R**,**C-S**
SO_4	5.934****	8.460****	116	**AS-AR**,**AS-B**,**AS-C**,**AS-R**,**AS-S**
Cl	4.919****	7.736****	111	**AS-AR**,**AS-B**,**AS-C**,**AS-R**,**AS-S**

Analysis of variance (ANOVA) of the influence of mangrove type and station nested under mangrove type on sediment characteristics, pore water composition and carbon dioxide fluxes.
Significance of F values: ****: $P < 0.001$; ***: $P < 0.005$; **: $P < 0.01$; *: $P < 0.05$.
Degrees of freedom: Type = 5; Station{Type} = 6. Data were log-transformed if appropriate.
A posteriori, pairwise significant differences were calculated with Tukey-Kramer honestly significant difference method: AS = basin *Avicennia*; AR = river/creek-fringing *Avicennia*; B = *Bruguiera*; C = *Ceriops*; R = *Rhizophora*; S = *Sonneratia*.
Only pairwise differences that are significant at $p < 0.01$ are shown, and those better than 0.001 are underlined and bold.

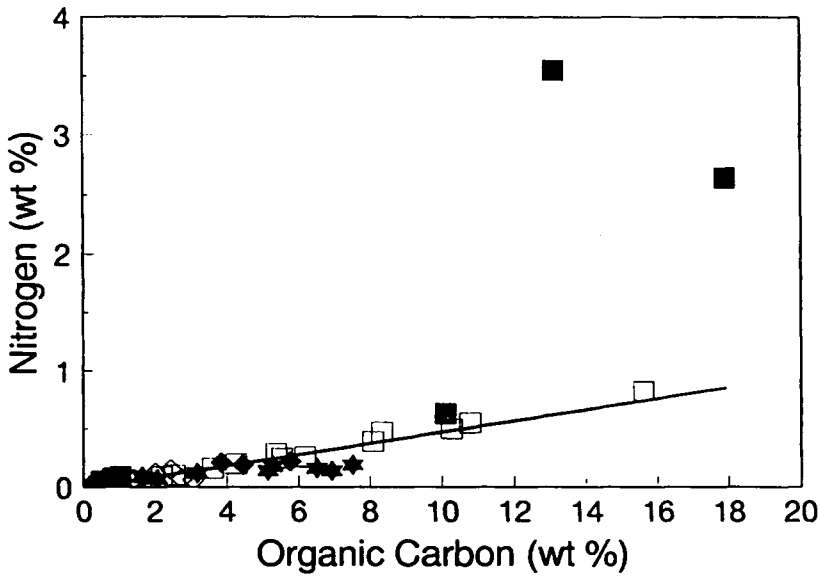

Figure 2. Relation between the organic carbon (wt%) and nitrogen contents (wt%) of Gazi Bay sediments. Filled squares: *Avicennia*; Filled rhombs: *Bruguiera*; Stars: *Ceriops*; Open squares: *Rhizophora*; Open rhombs: *Sonneratia*. The line represents a least-square fit ($r^2 = 0.89$) with a slope corresponding with a molar C/N ratio of 25.3 ± 1.3.

with organic carbon ($r^2 = 0.56$; molar C/P ratio 749 ± 97), but a strong correlation with median grain size ($r^2 = 0.75$). Nested ANOVA analyses indicate that the median grain size and the organic carbon, nitrogen and phosphorus contents differ significantly among the mangrove species (Table 2).

At two stations, Ceriops C and Rhizophora L, the depth distribution of organic carbon and nitrogen was examined in detail (Figure 3). At station Ceriops C, organic carbon and nitrogen concentrations in the top 16 cm are about 2 and 0.1 wt% respectively, they subsequently increase up to about 5 wt% C and 0.24 wt% N. At station Rhizophora L, organic carbon concentrations range from 3 to 8 wt% without any trend with depth, whereas nitrogen contents show a drastic decrease at depths more than 40 cm.

At the same two stations, root material was carefully separated from the bulk sediments and both fractions, as well as the untreated sample, were analysed for organic carbon, nitrogen and phosphorus. The resulting molar C/N and C/P ratios are presented in Table 4. The C/N ratio of root material is significantly higher than that of bulk sediment ($F = 46.016$; $df = 2$; $P = 0.000$) and depends on the type of mangrove ($F = 9.518$; $df = 1$; $P = 0.006$). Application of a post-hoc Tukey-Kramer pairwise comparison test indicated no significant difference between the bulk sediment C/N ratios before and after

Table 3. Sediment characteristics.

Type	Location	Depth (cm)	pH	$CaCO_3$ (wt%)	Salinity (psu)	Median grain size (μm)	Corg (wt%)	Ntot (wt%)	P (ppm)
Avicennia	R	0–5	7.61	1.40	34.91	29	10.10	0.63	712
Avicennia	R	5–20	6.88	0.00	33.34	20	17.91	2.64	589
Avicennia	R	20–40	6.22	0.00	31.43	26	13.11	3.55	458
Avicennia	S	0–5	6.90	0.00	44.76	216	1.04	0.09	91
Avicennia	S	5–20	7.90	0.10	52.15	148	0.82	0.08	124
Avicennia	S	20–40	8.10	0.03	68.57	119	0.51	0.05	148
Bruguiera	X	0–5	7.67	0.00	35.81	179	3.85	0.21	236
Bruguiera	X	5–20	6.36	0.00	30.20	227	4.45	0.19	175
Bruguiera	X	20–40	4.63	0.00	30.20	205	5.77	0.22	148
Ceriops	A	0–5	6.14	0.03	35.14	259	3.17	0.12	83
Ceriops	A	5–20	6.01	0.06	30.87	189	5.28	0.18	118
Ceriops	A	20–40	3.56	0.06	38.06	138	7.52	0.19	70
Ceriops	B	0–5	7.09	0.12	16.62	274	1.68	0.08	188
Ceriops	B	5–20	5.79	0.09	31.88	292	2.06	0.07	87
Ceriops	B	20–40	3.71	0.06	33.01	190	6.51	0.16	127
Ceriops	C	0–5	6.86	0.03	37.95	256	1.64	0.09	61
Ceriops	C	5–20	4.37	0.06	37.38	234	5.14	0.14	74
Ceriops	C	20–40	3.50	0.00	60.17	205	6.93	0.14	52
Rhizophora	J	0–5	6.69	0.06	30.65	101	2.19	0.09	319
Rhizophora	J	5–20	6.73	0.03	29.86	173	2.55	0.10	253
Rhizophora	J	20–40	6.55	0.00	31.32	139	5.38	0.29	218
Rhizophora	K	0–5	7.18	0.02	32.00	38	4.26	0.20	642
Rhizophora	K	5–20	6.32	0.00	29.64	33	6.18	0.26	581
Rhizophora	K	20–40	5.46	0.03	31.21	56	10.79	0.55	341
Rhizophora	L	0–5	7.00	0.00	33.12	51	15.61	0.83	742
Rhizophora	L	5–20	6.60	0.00	32.56	112	10.27	0.50	375
Rhizophora	L	20–40	6.34	0.00	26.72	216	8.10	0.39	341
Rhizophora	M	0–5	6.95	0.00	32.44	62	8.34	0.47	537
Rhizophora	M	5–20	5.97	0.00	31.66	195	3.60	0.16	157
Rhizophora	M	20–40	5.54	0.00	30.09	221	5.54	0.25	218
Sonneratia	I	0–5	7.02	0.03	37.61	281	0.25	0.02	44
Sonneratia	I	5–20	6.85	0.00	28.29	327	0.21	0.02	39
Sonneratia	I	20–40	5.45	0.03	32.56	257	0.58	0.04	57
Sonneratia	II	0–5	6.75	0.06	34.69	285	0.45	0.02	35
Sonneratia	II	5–20	6.17	0.03	32.11	292	0.62	0.03	44
Sonneratia	II	20–40	5.65	0.00	32.00	264	0.86	0.05	48
Sonneratia	III	0–5	8.15	0.12	37.72	248	0.43	0.02	61
Sonneratia	III	5–20	6.20	0.08	26.94	281	0.30	0.01	35
Sonneratia	III	20–40	8.18	0.14	39.07	252	0.40	0.02	83
Sonneratia	IV	0–5	8.20	1.29	30.65	234	2.01	0.12	96

Table 3. Continued.

Type	Location	Depth (cm)	pH	$CaCO_3$ (wt%)	Salinity (psu)	Median grain size (μm)	Corg (wt%)	Ntot (wt%)	P (ppm)
Sonneratia	IV	5–20	8.05	0.15	36.82	263	0.39	0.02	52
Sonneratia	IV	20–40	8.29	0.84	16.28	286	0.74	0.02	83
Sonneratia	V	0–5	7.95	0.99	35.03	227	2.44	0.15	258
Sonneratia	V	5–20	7.75	0.21	29.97	262	1.41	0.07	127
Sonneratia	V	20–40	8.26	0.90	35.48	267	1.38	0.06	144
Sonneratia	VI	0–5	3.44	0.00	25.26	286	2.74	0.07	70
Sonneratia	VI	5–20	5.55	0.09	30.76	259	0.81	0.02	96
Sonneratia	VI	20–40	5.87	0.00	26.61	238	3.06	0.06	118

Table 4. Molar C/N and C/P ratios of root and soil material at stations *Ceriops* C and *Rhizophora* L.

	C/N			C/P		
	Mean	St.Dev.	N	Mean	r St.Dev.	N
Ceriops C						
Root	82.4	21.6	4	3668	1035	3
Bulk	26.8	5.9	4	3090	1244	4
Total	24.8	1.2	3	1987	362	3
Rhizophora L						
Root	55.8	7.5	4	1453	444	4
Bulk	18.1	4.2	4	1104	105	4
Total	18.5	1.7	3	845	82	3

removal of root material. The C/P ratio of root material is also significantly higher than that of bulk sediment ($F = 3.955$; $df = 2$; $P = 0.039$). The C/P ratio depends mainly on the type of mangrove ($F = 33.690$; $df = 1$; $P = 0.000$), consistent with the results presented in Tables 2 and 3, and observations by Boto and Wellington (1983). The very high C/P ratios of living root material from *Ceriops* (3668 $\pm$ 1035) and *Rhizophora mucronata* (1453 $\pm$ 444) are consistent with the C/P ratio of dead root material from *Rhizophora apiculata* (2508) in a Northern Australian forest reported by Alongi et al. (1993).

Pore-water chemistry

The pore-water of Gazi Bay sediments has been analyzed for sulfate, chloride, ammonium, nitrate (Figure 4), nitrite and phosphate. In general, nutrient concentrations are very low for coastal sediments; ammonium ranges from 3

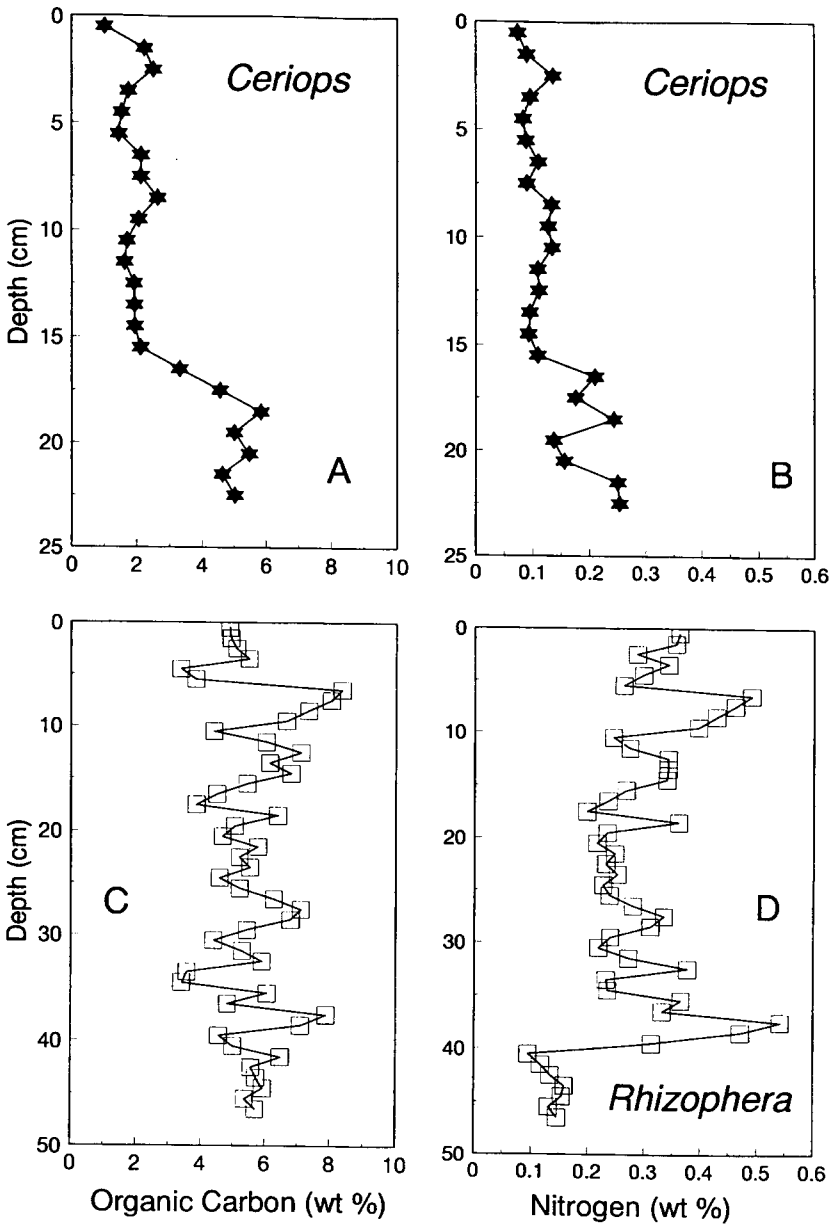

Figure 3. Concentration versus depth profiles; a) Organic carbon (wt%) at station Ceriops C; b) Nitrogen (wt%) at station Ceriops C; c) Organic carbon (wt%) at station Rhizophora L and d) Nitrogen (wt%) at station Rhizophora L.

to 390 μM, nitrate from 1 to 50 μM, nitrite from <0.1 to 2.3 μM, and phosphate from <0.05 to 1 μM. The major components sulfate and chloride show considerable variability related to salinity fluctuations; they range from 12 to 68 mM and 210 to 1125 mM. All pore-water constituents show significant differences among mangrove-types and locations (Table 2).

Discussion

Nested ANOVA analyses have shown that carbon dioxide fluxes, sediment grain sizes, sedimentary organic carbon, nitrogen and phosphorus contents, and pore-water characteristics depend on mangrove forest type. Differences between stations are primarily due to differences in forest type. Site variability, not related to forest type, is significant for carbon dioxide fluxes and pore-water ammonium, sulfate and chloride (Table 2).

These differences in mangrove sediment biogeochemistry could be due to species-specific processes, to differences in elevation at which these mangrove types occur or to interaction between both. Differences in elevation relate directly to differences in tidal inundation frequencies, aerial exposure, litter exchange rates, and depositional conditions. Van Speybroeck (1992) recently summarized differences in elevation between various mangroves in Gazi Bay. Median elevation values (in cm) for the mangroves are: *Sonneratia* (160), *Rhizophora* (212), *Bruguiera* (212), *Ceriops* (245) and basin scrub-type *Avicennia* (258). Van Speybroeck (1992) did not report a median elevation value for creek-fringing *Avicennia*, but this type of mangrove can probably be found between 160 and 212 cm. Accordingly, the relative altitude sequence at which the mangrove types occur is: *Sonneratia* $\approx$ creek-type *Avicennia* $<$ *Rhizophora* $\approx$ *Bruguiera* $<$ *Ceriops* $\leq$ basin scrub-type *Avicennia*. Because of these differences in tidal elevation, it is impossible for us to use field correlations to distinguish between tidal elevation and forest type as factors determining nutrient status of mangrove sediments. On the basis of microbial-nutrient relationships of three different mangrove forest types at roughly the same tidal elevation, Alongi et al. (1993) concluded that forest type does not regulate the biogeochemistry of mangrove sediments in the Fly Delta, Papua New Guinea. Moreover, correlations between mangrove forest type and sediment characteristics in the field, cannot demonstrate cause and effect relationships.

Pore-water composition

Nitrate, ammonium and phosphate concentrations in the overlying tidal water are consistently below 1 μM, irrespective of the site or the phase of the tidal

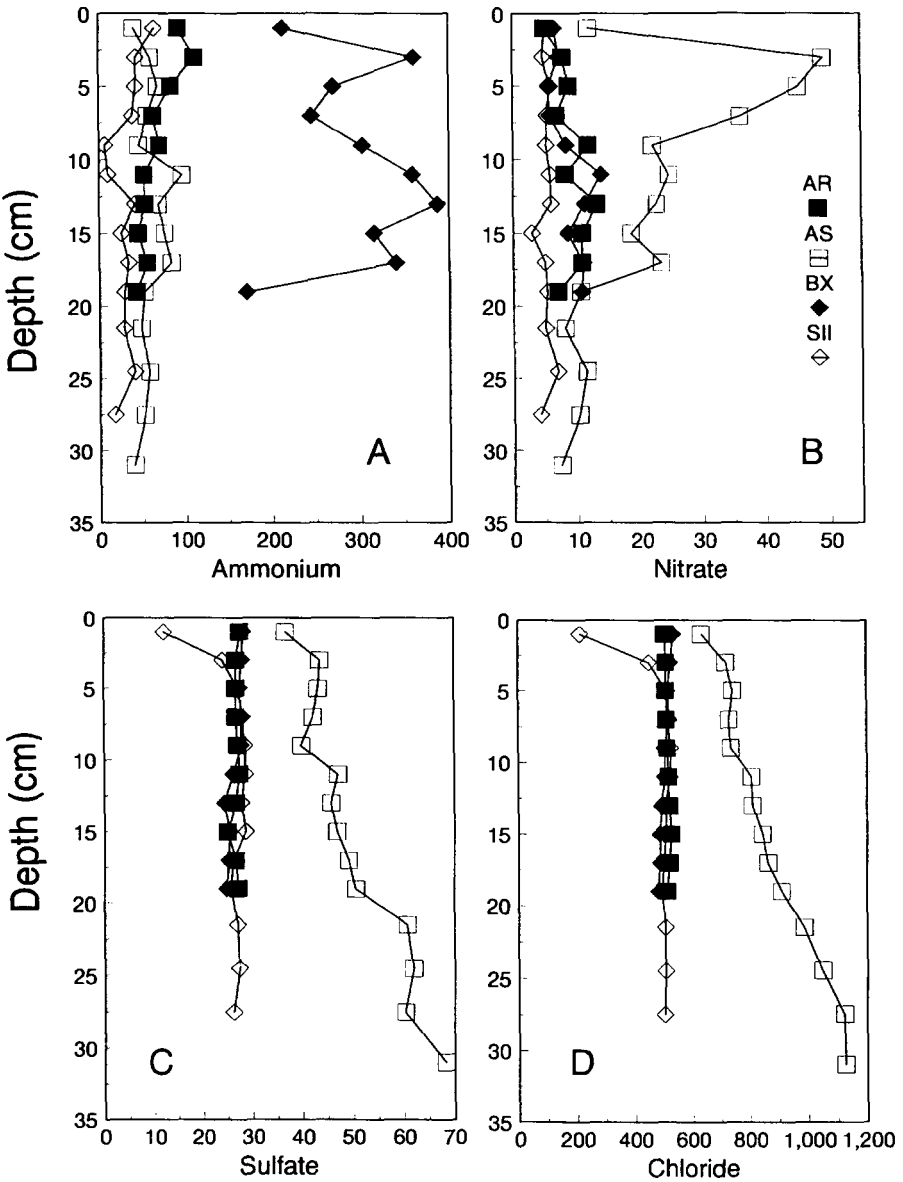

Figure 4. Pore-water concentrations versus depth profiles for ammonium (μM), nitrate (μM), sulfate (mM) and chloride (mM). a,b,c,d: stations *Avicennia* saline (AS), *Avicennia* river-fringing (AR), *Bruguiera* (BX) and *Sonneratia* (SII); e,f,g,h: *Ceriops* stations CA, CB and CC; i,j,k,l *Rhizophora* stations RJ, RK, RL and RM.

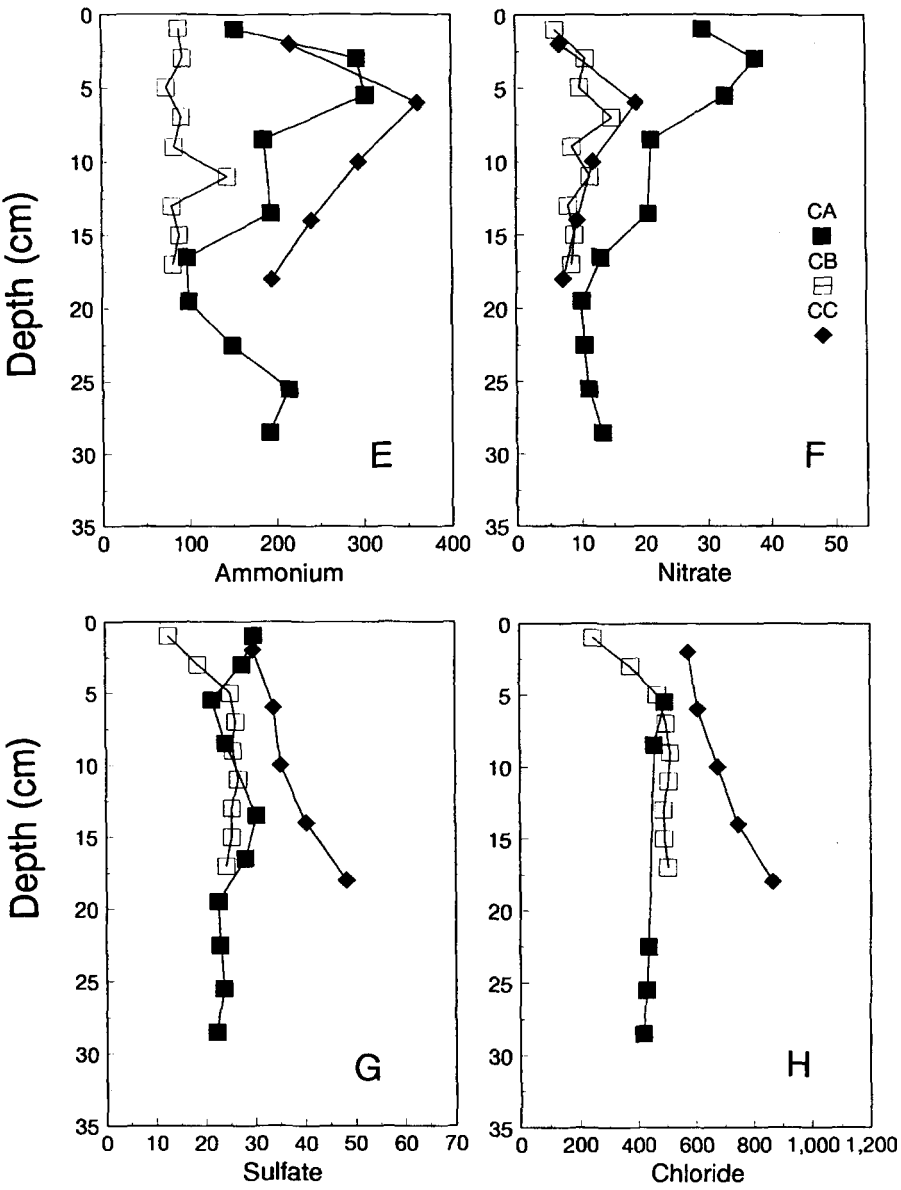

Figure 4. Continued.

cycle (Hemminga et al. 1995). Pore-water concentrations of ammonium, nitrate and phosphate in mangrove sediments from Gazi Bay are very low compared to those usually found in temperate intertidal sediments (e.g., Rutgers van der Loeff 1981), but consistent with observations made in tropical

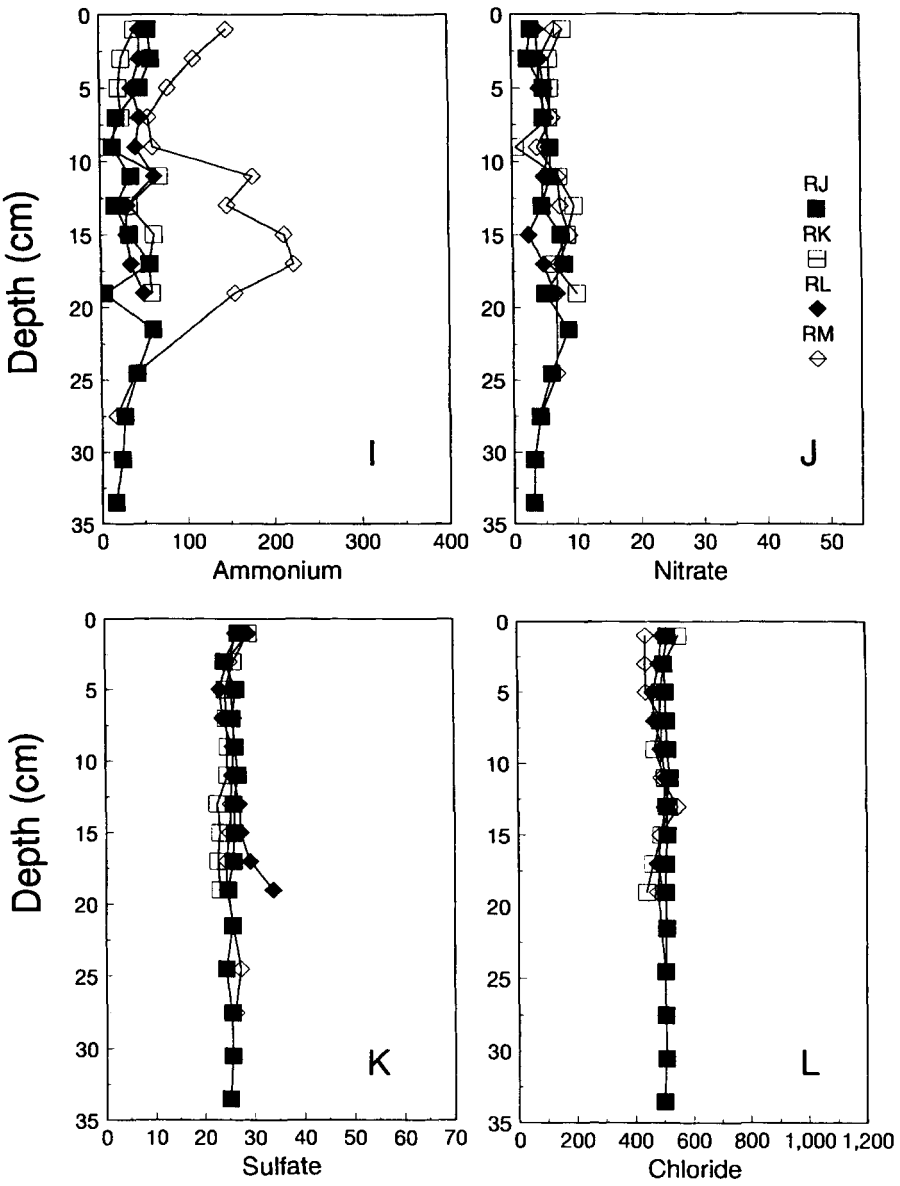

Figure 4. Continued.

intertidal sediments (Alongi 1991; Alongi et al. 1993), tropical seagrass beds (Erftemeyer & Middelburg 1993) and other mangrove sediments (Alongi et al. 1992, 1993; Kristensen et al. 1988; Morell & Corredor 1993). These very low pore-water concentrations probably reflect nutrient uptake by mangrove

roots and microbes and limit the efflux of nutrients from mangrove sediments. Moreover, actual flux measurements made in other mangrove forests usually indicate sediment nutrient uptake rather than release (Corredor & Morell 1989; Kristensen et al. 1988, 1992; Boto et al. 1989; Alongi et al. 1992, 1993).

Pore-water concentrations of nitrate at elevated sites (*Ceriops* stations CA, CB and CC and *Avicennia* station AS) are significantly higher than those observed at sites lower in the intertidal zone (*Rhizophora* stations RJ, RK, RL and RM, and *Sonneratia* station SII; Figure 4; Table 2). Similar observations have been made for nitrate (Alongi et al. 1993) in the Fly Delta, Papua New Guinea, and dissolved organic carbon in Missionary Bay, Australia (Boto et al. 1989). Enhanced pore-water concentrations of nitrate at elevated stations may be due to lower plant uptake rates, evaporative concentrations effects (see below) or limited exchange possibilities. Lower plant uptake rates may be expected with increasing elevation because mangrove biomass and number of roots per unit surface decrease with elevation. Intertidal sediments can exchange non-gaseous components only during inundation and infrequent tidal flushing may consequently cause the build up of dissolved components in pore water.

Interstitial water profiles of sulfate and chloride show minor depletion in the surface layer at *Sonneratia* station SII and *Ceriops* station CB and significant enrichments with depth at the elevated *Avicennia* station AS and *Ceriops* station CC (Figure 4). Pore-water profiles at stations SII and CB are the only two that were obtained on rainy days and the observed depletions in chloride and sulfate at shallow depth are probably caused by dilution with rain. The increases in pore-water concentrations of sulfate and chloride with depth at stations AS and CC indicate the presence of saline pore water deep in the sediment. These elevated stations are flooded during spring tide only (Hemminga et al. 1994) and in between evapotranspiration causes a salinity increase of the remaining water up to about 70 psu. It should perhaps be mentioned that a large salt pan area is located between these two sites. At station AS, sulfate is concentrated with respect to chloride, indicating that mechanisms other than evaporation are involved. One such a mechanism could be selective exclusion of sulfate at the root surface by *Avicennia* (Carlson et al. 1983; Carlson & Yarbrook 1987).

Carbonate dissolution and pH control

For several decades it has been recognized that reclaimed mangrove sediments may develop into acid soils upon drainage and oxidation (e.g. Hart 1959; Hesse 1961). Soil acidification is thought to result from the oxidation of reduced sulfur compounds present in mangrove sediments. The results from

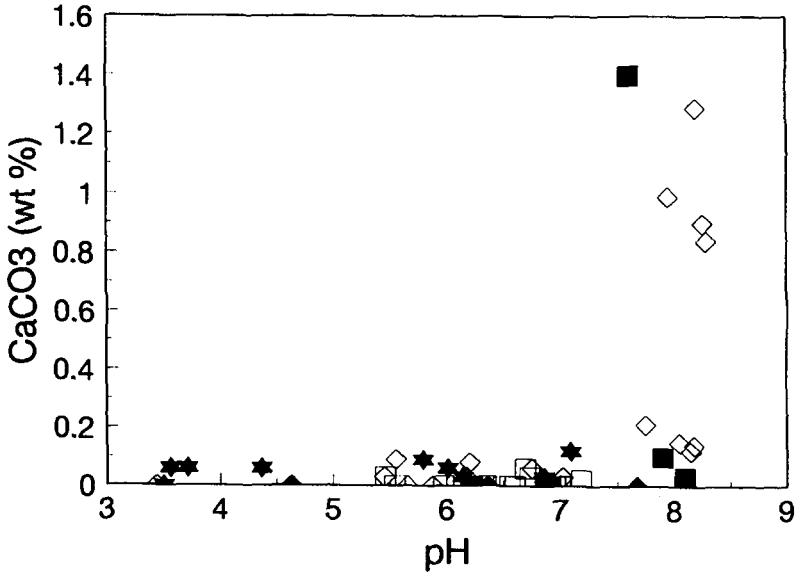

Figure 5. The relation between soil pH and the calcium carbonate content (wt%). Filled squares: *Avicennia*; Filled rhombs: *Bruguiera*; Stars: *Ceriops*; Open squares: *Rhizophora*; Open rhombs: *Sonneratia*.

this study show that acid conditions are not restricted to reclaimed mangrove sediments, but also occur in mangrove sediments that are regularly flooded (Table 3; Figure 5).

Mangroves can affect the acid-base balance of their sediments in a variety of ways. Firstly, through oxygen translocation from their leaves to their roots and subsequent release or leakage of this oxygen to the sediments, they may alter the redox conditions in the sediments. Oxygen release by mangrove roots has been inferred from enhanced Eh levels by Boto & Wellington (1984) and indeed measured using microelectrodes by Andersen & Kristensen (1988). The net effect of oxygen release will be an enhancement of aerobic degradation of organic matter according to:

$$CH_2O + O_2 \rightarrow H_2CO_3, \qquad (1)$$

and oxidation of reduced components such as:

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

sulfide : $H_2S + 2O_2 \rightarrow H_2SO_4$, (2b; sulfide-oxidation)

ironsulfide : $FeS_2 + 3.75\ O_2 + 2.5\ H_2O \rightarrow FeOOH + 2\ H_2SO_4$. (2c; sulfide-oxidation)

The acids generated (H_2CO_3, H_2SO_4, HNO_3) will consume alkalinity and lower the pH and the saturation state with respect to calcium carbonate (lime). If the acid production exceeds the buffer capacity of the pore-water, this will cause dissolution of solid-phase calcium carbonate according to:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2\,HCO_3^- . \quad (3)$$

Secondly, ammonium uptake by mangrove roots will lead to a release of H^+. Thirdly, any carbon dioxide respired by mangrove roots will also lower the pH. It should be realized that carbon dioxide uptake and fixation by roots will enhance the alkalinity and pH. Kristensen et al. (1988) clearly showed that *Rhizophora apiculata* roots lowered the pH and alkalinity of mangrove sediments, indicating that mangrove root activities induce acidification.

In Gazi Bay sediments with calcium carbonate contents above 0.2 wt% the pH is effectively buffered at values around 8 (Figure 5). In calcium carbonate depleted sediments, the buffering capacity of the sediments is limited and pH values decrease down to 3.5. Carbonate dissolution in mangrove sediments from Gazi Bay may be a quantitatively important process considering that calcium carbonate contents of adjacent intertidal flat sediments and subtidal seagrass sediments vary from 55 to 60 and 39 to 80 wt%, respectively (Hemminga et al. 1994). If carbonate dissolution in mangrove sediments is demonstrated to be a general process, it may have implications for coastal and global carbon cycles.

Benthic nitrogen excess

The molar Carbon/Nitrogen ratio of fresh mangrove leaves in Gazi Bay are about 27 to 32 for basin scrub-type *Avicennia marina*, 28 for creek-fringing *Avicennia marina*, 25 to 34 for *Sonneratia alba*, 59 to 69 for *Ceriops tagal*, 45 to 70 for *Bruguiera gymnorrhiza*, and 43 to 78 for *Rhizophora mucronata* (Rao et al. 1994; Hemminga et al. 1994). Part of the variability in reported C/N ratios may be related to the physiological conditions of the leaves sampled and analysed. During senescence of the leaves, i.e. before litterfall, about 64% of the nitrogen is resorbed by the mangroves (Rao et al. 1994). Consequently, the sediments receive mangrove material that is depleted in nitrogen. In contrast, our data indicate that sedimentary carbon/nitrogen ratios are rather low compared to mangrove material and rather independent of mangrove type (Figure 2). In other words, there is a nitrogen excess with respect to carbon in the sedimentary material relative to mangrove material. This might indicate that there are either strong losses of carbon relative to nitrogen, or vice versa that there are benthic nitrogen inputs.

In order to put some limits on the first possibility we have performed some simple conservative mass-balance calculations for two stations, namely

Ceriops C and *Rhizophora* L (Table 5). The calculations are based on the following assumptions: (1) Long-term nitrogen gain rates can be calculated by dividing the carbon mineralization rates with the C/N ratio of the leaf material entering the sediment and being decomposed. In Gazi Bay, carbon dioxide fluxes can be used as an approximate measure for organic carbon mineralization rates because effluxes of methane can be neglected (< 0.1 mol C m^{-2} yr^{-1}; Middelburg et al. 1995). Since an unknown part of the carbon dioxide flux from mangrove sediments might be related to root respiration rather than due to organic carbon mineralization, we will overestimate nitrogen gain rates; (2) All nitrogen is retained in the sediments, whereas all carbon is lost; (3) The sediment layers with abundant living roots are about 16 and 40 cm thick for the *Ceriops* and *Rhizophora* stations respectively (Figure 3). Nitrogen-gain rates at stations CC and RL vary from about 0.3 to 0.7 and 0.4 to 1.1 mmol N m^{-2} d^{-1} respectively, depending on C/N ratio of decomposing organic matter (i.e. fresh or senescent leaves). These calculated N-gain rates are much lower than N-mineralization rates measured elsewhere by ^{15}N-techniques: 3.3 to 21.8 mmol N m^{-2} d^{-1} in Oyster Bay, Jamaica (Nedwell et al. 1994) and 4.3 to 18.0 mmol N m^{-2} d^{-1} at Phuket Island (Blackburn et al. 1987). In a series of papers, Alongi (1994b for a recent summary) has stressed the important role of bacteria in nutrient recycling and conservation in tropical mangrove sediments. He proposed that most bacteria are recycled via natural mortality, with the next generation of cells living from mineralization of bacterial biomass. Rates of ammonium turnover determined with ^{15}N-techniques might therefore refer to the rate of bacterial N-turnover. If benthic bacteria with a C/N ratio of about 4 account for the bulk of the organic carbon and nitrogen turnover in Gazi Bay sediments, we estimate nitrogen turn-over rates of 11 and 15 mmol N m^{-2} d^{-1} for the Ceriops and Rhizophera stations, respectively, consistent with observations by Blackburn et al. (1987) and Nedwell et al. (1994). Accordingly, the calculated N-gain rates based on leaf C/N ratios should be considered as estimates for the long-term net rate of nitrogen addition to the system rather than measures of actual ammonium turnover rates.

The inventories of excess particulate nitrogen relative to fresh-leave input amount to about 12 and 73 mol m^{-2} at the Ceriops and Rhizophera stations (Table 5). Based on these very conservative calculations we estimate that at least between 45 and 114 years at the Ceriops station, and 189 and 548 years at the Rhizophera station, are required to cause the excess nitrogen by mineralizing carbon, while retaining all the nitrogen. Residence times due to burial are 53 and 153 yr at the *Ceriops* and *Rhizophora* stations if sediments accumulate at 3 mm yr^{-1}, the present-day rate of sea-level rise. Thus, even with a 100% retention of the mineralized nitrogen in the sediments due to

Table 5. Mass balance constraints on nitrogen excess.

	Ceriops	Rhizophora	Unit
Organic C	1.9	5.6	wt%
N	0.1	0.3	wt%
C/N	21.6	21.4	mol/mol
Depth	16	40	cm
$C/N_{leavesNew}$	60.5	57.1	mol/mol
$C/N_{leavesOld}$	152.5	165.7	mol/mol
Miner.C	43.5	60.5	mmol $m^{-2}d^{-1}$
Miner. N leav.New	0.72	1.1	mmol $m^{-2}d^{-1}$
Miner. N leav.Old	0.29	0.37	mmol $m^{-2}d^{-1}$
$N_{excessFreshLeaves}$	11.9	73.1	mol m^{-2}
$N_{excessOldLeaves}$	15.8	100.9	mol m^{-2}
$Time_{FreshLeaves}$	45–114	189–548	year
$Time_{OldLeaves}$	60–152	261–757	year

immobilization of nitrogen in microbial biomass and no nitrogen uptake by mangrove roots, we obtain nitrogen enrichments times that are too long relative to the burial rate of the sediments. Hence, there must be addition of nitrogen to mangrove sediments.

There are a few possibilities for nitrogen addition. Firstly, there could be belowground input of nitrogen-rich mangrove material. Although we do not know the annual belowground input of carbon and nitrogen, this nitrogen input pathway cannot explain the nitrogen excess because the C/N ratio of root material is significantly higher than that of the sediment (Table 4). Secondly, nitrogen-fixing bacteria may enrich the sedimentary material. Nitrogen fixation activities have been reported in mangrove sediments (Goto and Taylor 1976; Alongi et al. 1992), and likely account for part of the nitrogen excess found in mangrove sediments of Gazi Bay (Woitchik et al. 1996). Thirdly, benthic bacteria may take up dissolved nitrogen compounds from the overlying water during high tide (Kristensen et al. 1988, 1992; Alongi, 1994b; Alongi et al. 1992, 1993). Fourthly, there might be import and mineralisation of material with C/N ratios much lower than the sedimentary ratio. Import of allochtonous organic matter is consistent with the relative high concentrations of organic carbon in mangrove sediments in Gazi Bay and the $\delta^{13}C$ values of sedimentary organic matter. Average organic carbon concentrations in sediments from Gazi Bay (3.4 to 11.3 wt%) are much higher than those reported for sediments in other mangrove forests (0.4 to 2.2 wt%; Alongi et al. 1993; Kristensen et al. 1988, 1991, 1992, 1994; Blackburn et al. 1987). The $\delta^{13}C$ values of *Ceriops tagal* (−24.12‰) and *Rhizophora mucronata* (−28.25‰)

leaves are close to, but depleted, with respect to values of sedimentary organic material (−22.69 and −25.31‰, respectively; Hemminga et al. 1994). This enrichment in $\delta^{13}C$ values of sedimentary material relative to mangrove material could be related to the import of seagrass or algal material. Import and degradation of algal (C/N ≈ 7), seagrass (C/N ≈ 19), or suspended material (C/N: 6.5 to 10: Hemminga et al. 1994) would provide a mechanism to explain the nitrogen enrichment of the sediments and the relatively high concentrations of organic matter. Creek-fringing *Avicennia* sediments are in particular rich in organic carbon and nitrogen (Table 3; Figure 2), probably because their geographic location and root system (abundant pneumatophores) favour trapping of allochthonous material. To conclude, mangrove sediments in Gazi Bay act as a sink for nitrogen and organic carbon, part of which may have been imported from adjacent ecosystems.

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References

Alongi DM (1989) The role of soft-bottom benthic communities in tropical mangrove and coral reef ecosystems. Rev. Aq. Sci. 1: 243–280

Alongi DM (1991) The role of intertidal mudbanks in the diagenesis and export of dissolved and particulate materials from the Fly Delta, Papua New Guinea. J. Exp. Mar. Biol. Ecol. 149: 81–107

Alongi DM (1994a) Zonation and seasonality of benthic primary production and community respiration in tropical mangrove forests. Oecologia 98: 320–327

Alongi DM (1994b) The role of bacteria in nutrient recycling in tropical mangrove and other coastal benthic ecosystems. Hydrobiology 285: 19–32

Alongi DM, Boto KG & Robertson AI (1992) Nitrogen and phosphorus cycles. In: Robertson AI & Alongi DM (Eds) Tropical Mangrove Ecosystems (pp 251–292). AGU, Washington, DC

Alongi DM, Christoffersen P & Tirendi F (1993) The influence of forest type on microbial-nutrient relationships in tropical mangrove sediments. J. Exp. Mar. Biol. Ecol. 171: 201–223

Andersen FØ & Kristensen E (1988) Oxygen microgradients in the rhizosphere of the mangrove *Avicennia marina*. Mar. Ecol. Prog. Ser. 44: 201–204

Blackburn TH, Christensen D, Fanger AM, Henriksen K, Iizumi H, Iversen N & Limpsaichol P (1987) Mineralization processes in mangrove and seagrass sediments. In: Hylleberg J (Ed) Ao Yon – A Mangrove in the Andaman Sea. Institute of Ecology and Genetics (pp 22–32). University of Aarhus, Aarhus

Boto KG & Wellington JT (1983) Phosphorus and nitrogen nutritional status of a northern Australian mangrove forest. Mar. Ecol. Prog. Ser. 11: 63–69

Boto KG & Wellington JT (1984) Soil characteristics and nutrient status in a northern Australian mangrove forest. Estuaries 7: 61–69

Boto KG, Alongi DM & Nott ALJ (1989) Dissolved organic-carbon bacteria interactions at sediment-water interface in a tropical mangrove system. Mar. Ecol. Prog. Ser. 51: 243–251

Carlson PR & Yarbro LA (1985) Physical and biological controls of mangrove pore water chemistry. In: Hook et al. (Eds) The Ecology and Management of Wetlands (pp 112–132). Croom Helm, London & Sydney

Carlson PR, Yarbro LA, Zimmerman CF & Montgomery JR (1983) Pore water chemistry of an overwash mangrove island. Florida Sci. 46: 239–249

Chen PS (1956) Microdetermination of phosphorus. Analyt. Chem. 28: 1756–1758

Corredor JE & Morell JM (1989) Assessment of inorganic nitrogen flux across the sediment-water interface in a tropical lagoon. Est. Coast. Shelf Sc. 28: 339–345

Dye AH (1983) Oxygen consumption by sediments in a Southern Africa mangrove swamp. Est. Coast. Shelf Sci. 17: 473–478

Erftemeijer PLA & Middelburg JJ (1993) Sediment-nutrient interactions in tropical seagrass beds: a comparison between a terrigenous and a carbonate sedimentary environment in South Sulawesi (Indonesia). Mar. Ecol. Prog. Ser. 102: 187–198

Feller IC (1995) Effects of nutrient enrichment on growth and herbivory of dward red mangrove (*Rhizophera mangle*). Ecol. Monogr. 65: 477–505

Goto JW & Taylor BF (1976) N_2 fixation associated with decaying leaves of the red mangrove (*Rhizophera mangle*) Appl. Envir. Microb. 31: 781–783

Hart MGR (1959). Sulfur oxidation in tidal mangrove soils of Sierra Leone. Plant Soil 11: 215–236

Helder W & de Vries RTP (1979) An automated phenol-hypochlorite method for the determination of ammonia in sea- and brackish waters. Neth. J. Sea Res. 13: 154–160

Hemminga MA, Slim FJ, Kazungu J, Ganssen GM, Nieuwenhuize J & Kruyt NM (1994) Carbon outwelling from a mangrove forest with adjacent seagrass beds and coral reefs (Gazi Bay, Kenya). Mar. Ecol. Prog. Ser. 106: 291–301

Hemminga MA, Gwada P, Slim FJ, de Koeyer P & Kazungu J (1995) Leaf production and nutrient contents of the seagrass *Thalassodendron ciliatum* in the proximity of a mangrove forest (Gazi Bay, Kenya). Aquatic Bot. 50: 159–170

Hesse PR (1961) Some differences between the soils of *Rhizophora* and *Avicennia* mangrove swamps in Sierra Leone. Plant Soil 14: 335–346

Kristensen E, Andersen FØ & Kofoed LH (1988) Preliminary assessment of benthic community metabolism in a south-east Asian mangrove swamp. Mar. Ecol. Prog. Ser. 48: 137–145

Kristensen E, Holmer M & Bussarawit N (1991) Benthic metabolism and sulfate reduction in a south-east Asian mangrove swamp. Mar. Ecol. Prog. Ser. 73: 93–103

Kristensen E, Devol AH, Ahmed SI & Saleem M (1992) Preliminary study of benthic metabolism and sulfate reduction in a mangrove swamp of the Indus Delta, Pakistan. Mar. Ecol. Prog. Ser. 90: 287–297

Kristensen E, King GM, Holmer M, Banta GT, Jensen MH, Hansen K & Bussarawit N (1994) Sulfate reduction, acetate turnover and carbon metabolism in sediments of Ao Nam Bor mangrove, Phuket, Thailand. Mar. Ecol. Prog. Ser. 109: 245–255

Lugo AE & Snedaker SC (1974) The ecology of mangroves. An. Rev. Ecol. Syst. 5: 39–64

Middelburg JJ, Nieuwenhuize J, Markusse R & Ohowa B (1995) Some preliminary results on the biogeochemistry of mangrove sediments from Gazi Bay. In: Heip CHR & Hemminga

MA (Eds) Monsoons and Coastal Ecosystems in Kenya (pp 51–66). Netherlands Indian Ocean Programme, Cruise Reports

Morell JM & Corredor JE (1993) Sediment nitrogen trapping in a mangrove lagoon. Est. Coast. Shelf Sc. 37: 203–212

Nedwell DB, Blackburn TH & Wiebe WJ (1994) Dynamic nature of the turnover of organic carbon, nitrogen and sulphur in the sediments of a Jamaican mangrove forest. Mar. Ecol. Prog. Ser. 110: 223–231

Nieuwenhuize J, Maas YEM & Middelburg JJ (1994) Rapid analysis of organic carbon and nitrogen in particulate materials. Mar. Chem. 45: 217–224

Nieuwenhuize J, Poley-Vos CH, van de Akker AH & van Delft W (1991) A microwave dissolution method for sediment and soil compared with the conventional reflux extraction method for the determination of metals by atomic spectroscopy. Analyst 116: 347–354

Rao RG, Woitchik AF, Goeyens L, van Riet A, Kazungu J & Dehairs F (1994) Carbon, nitrogen contents and stable carbon isotope abundance in mangrove leaves from an east African coastal lagoon (Kenya). Aquatic Bot. 47: 175–183

Robertson AI, Alongi DM & Boto KG (1992) Food chains and carbon fluxes In: Robertson AI & Alongi DM (Eds) Tropical Mangrove Ecosystems (pp 293–326). AGU, Washington, DC

Rutgers van der Loeff MM, Es FB, Helder W & de Vries RTP (1981) Sediment water exchanges of nutrients and oxygen in tidal flats in the Ems-Dollard Estuary. Neth. J. Sea Res. 15: 113–129

Twilley RR, Lugo AE & Patterson-Zucca C (1986) Litter production and turnover in basin mangrove forests in southwest Florida. Ecology 67: 670–683

Van Speybroeck D (1992) Regeneration strategy of mangroves along the Kenya coast: A first approach. Hydrobiology 247: 243–251

Wilkinson L (1990) SYSTAT: The System for Statistics. Systat Inc., Evanston, IL

Woodroffe C (1992) Mangrove sediments and geomorphology. In: Robertson AI & Alongi DM (Eds) Tropical Mangrove Ecosystems (pp 7–41). AGU, Washington, DC

Woitchik AF, Ohowa B, Rao RG, Goeyens L & Dehairs F (1996) Nitrogen enrichment during decomposition of mangrove leaf litter in an East African coastal lagoon (Kenya): Relative importance of biological nitrogen fixation. Biogeochemistry (submitted)