Benthic metabolism and sulfate reduction in a southeast Asian mangrove swamp

Erik Kristensen¹, Marianne Holmer¹, Nipavan Bussarawit²

¹ Institute of Biology, Odense University, DK-5230 Odense M, Denmark
² Phuket Marine Biological Center, PO Box 60, Phuket, 83000 Thailand

ABSTRACT: Sediment metabolism (surface O₂ uptake and CO₂ production) and ³⁵S-SO₄²⁻ reduction (0 to 10 cm) were measured during January 1990 (dry season) at 3 stations in the Ao Nam Bor mangrove, Phuket, Thailand. Sulfate reduction as measured by the chromium reduction technique was highest at 6 to 10 cm depth at all stations (600 to 800 nmol S cm⁻³ d⁻¹), indicating that significant activity may have occurred below 10 cm. Vertical translocation of metabolizable organic substrates, either due to subsurface root growth or due to downward transport of newly deposited organic matter by bioturbation appeared responsible for the high subsurface activity. The major reduced sulfur compound at all stations was FeS₂, both as recovered ³⁵S-label in the sulfate reduction assay (82 to 97 %) and in the total sediment sulfur pool (86 to 100 %). Very low amounts of reduced sulfur were found as HS⁻, FeS and SO₄⁻. The general absence of HS⁻ was caused by precipitation reactions controlled by a large sedimentary iron pool. The estimated areal based rates of sulfate reduction (0 to 10 cm, 28 to 50 nmol m⁻² d⁻¹) could support around 100 % (65 to 142 %) of the measured CO₂ flux across the sediment-water interface. This implies a deficient or non-steady state CO₂ flux since the sulfate reduction estimate ignored any activity occurring below 10 cm depth. Possible causes for this deficit may include CO₂ assimilation by roots, advective loss of pore water CO₂, and excessive CO₂ gas loss during air exposure. In general, the mechanisms underlying carbon and sulfur cycling in this mangrove swamp appears remarkably similar to those operating in salt marshes.

INTRODUCTION

Mangrove swamps occupy a considerable part of tropical and subtropical coastlines, reaching their greatest extent in southeast Asia. They are, along with salt marshes, one of the most productive ecosystems in the world and support highly developed detritus-based food webs (Odum & Heald 1975, Robertson 1986). Organic detritus produced in mangrove swamps will either be degraded and recycled in the sediments or exported to adjacent areas (Woodroffe 1985, Robertson 1986, Twilley et al. 1986, Kristensen et al. 1988). Although the abundant mangrove crab fauna is believed to consume significant amounts of leaf litter as a major portion of their diet (Robertson 1986, Neilson & Richards 1989), decomposition of mangrove detritus is essentially a microbially mediated process (Alongi 1989). Several reports have dealt with aspects of degradation of mangrove detritus such as litter bag studies (Boonruang 1978, Cundell et al. 1979, Rice & Tenore 1981), dissolved organic matter/bacteria interactions (Benner et al. 1986, Gonzalez-Farias & Mee 1988, Boto et al. 1989), microbial distribution, and standing stocks and community structure (Alongi 1989). However, no studies have directly measured rates of the important anaerobic mineralization process, sulfate reduction, in tropical mangrove sediments. This, and the fact that the few published studies on mangrove energy and element cycling have been performed in North America and Australia, emphasize the need for further investigations especially in the mangroves of southeast Asia.

In salt marshes, the ecological equivalent of mangroves in temperate areas, sulfate reduction is known to be the major mineralization process (Howarth & Teal 1979, Howarth & Hobbie 1982, Howarth 1984, King et al. 1985, Mackin & Swider 1989). The large inputs of organic matter support high rates of heterotrophic metabolism. Since oxygen is usually depleted below a few mm depth, even where the sediment surface is exposed to air, anaerobic metabolism predominates with decomposition mediated primarily by fermentative and sulfate-reducing bacteria (Howarth & Teal 1979, Jørgensen 1983, King 1988).
Sulfide formed as the product of bacterial sulfate reduction usually undergoes rapid diagenetic transformations in coastal sediments. Hydrogen sulfide may readily precipitate with Fe$^{2+}$ to form iron sulfides. The exact oxidation/reduction transformations involving various reduced sulfur pools in sediments are not yet fully understood. Most sedimentary sulfide is usually recovered as acid volatile sulfur (AVS = H$_2$S + FeS) and chromium reducible sulfur (CRS = S$^0$ + FeS$_2$) pools (Fossing & Jørgensen 1989, Thode-Andersen & Jørgensen 1989).

The purpose of the present study was to quantify bacterial sulfate reduction in 3 sediments of the southeast Asian mangrove swamp, Ao Nam Bor, by the use of a recently developed $^{35}$S radiotracer technique (Fossing & Jørgensen 1989). The partitioning of reduced inorganic sulfur compounds into various reduced pools was assessed, both as recovered $^{35}$S-label and in the total sediment pool. Estimated depth-integrated rates of sulfate reduction and measured fluxes of O$_2$ and CO$_2$ across the sediment water interface were evaluated and discussed in relation to physical disturbances and transport processes in the sediment.

**MATERIALS AND METHODS**

**Study site.** The study was conducted during January 1990 (dry season) in the Ao Nam Bor mangrove about 5 km north of Phuket Marine Biological Center on the southeast coast of Phuket Island, Thailand (Fig. 1). The mangrove swamp is about 300 m wide from inland to the seaward edge at the study site. The landward fringe is separated from newly established shrimp ponds by a 1.5 m high dike. Tidal creeks that feed all the way through this *Rhizophora apiculata* dominated mangrove forest drain into a wide (0.5 to 1 km) vegetation-free sand- and mudflat. The mangrove is almost completely tidally dominated with freshwater input occurring only during heavy rain periods. Tidal range in the area is ca 2 m, but the inner mudflat is usually not covered by more than 1 m during high tide. During spring tides the landward fringe is inundated for only about 2 h (max. water depth ca 0.3 m), while the mudflat is flooded for about 6 h per tidal cycle. Salinity and water temperature during January are 33 to 35‰, S and 28 to 33°C, respectively. A detailed description of the study site is given by Frith et al. (1976) and Limpsaichol (1978).

Three stations were established in the Ao Nam Bor area: Stn 1, close to the landward fringe on a non-vegetated bank adjacent to a small ca 1 m wide creek (Zone 2 of Frith et al. 1976); Stn 2, within the mangrove forest between prop' roots of *Rhizophora apiculata* ca 30 m from the seaward fringe and ca 15 m from a 4 m wide creek (Subzone 3b of Frith et al. 1976, SUN Stn of Kristensen et al. 1988); and Stn 3 on the mudflat ca 100 m outside the forest (Zone 6 of Frith et al. 1976).

**Sampling procedures.** Sediment cores for solid phase analysis, pore water extractions and redox (Eh) measurements were sampled with 5.2 cm i.d. acrylic core tubes. Cores for flux incubations as well as those for determination of macrofaunal density were taken with 8.0 cm i.d. tubes while 2.6 cm i.d. tubes were used for the measurement of sulfate reduction, inorganic sulfur pools and pH. Cores were sampled by hand at low tide during daytime. All laboratory treatments were initiated within 2 h after sampling. Sediment for solid phase, pore water and sulfate reduction analysis were sectioned into 0–1, 1–2, 2–3, 3–4, 4–6, 6–8, 8–10 cm depth intervals. Most attempts to sample deeper cores failed due to the presence of large roots and stones below 15 to 20 cm. The density of major faunal species were estimated from the number of animals collected after sieving 5 to 10 cores (64 cm$^2$ each) per station through a 1.5 mm mesh.

**Sediment characteristics.** Porosity was calculated from water loss of a known sediment volume after drying at 100°C for 12 h. Organic content was measured on dried and ground sediment samples as loss-on-ignition (LOI) at 520°C for 6 h and as particulate organic carbon (POC) and nitrogen (PON) as described by Kristensen & Andersen (1987). POC and PON were analysed on a Hewlett-Packard 185B CHN Analyzer.

**Pore water.** Pore water was obtained from 3 replicate cores by centrifuging 1 to 2 cm sediment sections for 5 to 10 min at 2000 rpm. Samples for SO$_4^{2-}$ analysis were immediately acidified with concentrated HCl to ca pH 2 and kept refrigerated (4°C) until analysis with a Kontron Ion Liquid Chromatograph. Samples for measurement of free sulfide were fixed in 20% ZnAc immediately after centrifugation and analysed by the methylene blue technique of Cline (1969). Some sulfide may have been lost by evaporation and oxidation during centrifugation, but due to the very low level of free...
sulfide in these sediments (no or only weak sulfide smell) this loss is assumed to be insignificant for the overall sulfur budget.

**Sulfate reduction and inorganic sulfur pools.** Sulfate reduction was measured by the core injection technique (Jorgensen 1978). A volume of 4 μl carrier-free $^{35}$S-SO$_4^{2-}$ (120 kBq) was injected at 1 cm intervals to a depth of 10 cm in 3 undisturbed cores from each station. The cores were incubated without overlying water for 20 h in darkness at 29°C before being cut into segments and transferred to 20% ZnAc (vol:1:1) and frozen to terminate incubation and fix sulfides. The fraction of $^{35}$S-SO$_4^{2-}$ reduced during the incubation was determined as the sum of $^{35}$S in the acid volatile (AVS, defined as FeS and free sulfide) and the chromium reducible (CRS, defined as FeS$_2$ and S$^-$) sulfide pools.

The 2-step distillation procedure of Fossing & Jørgensen (1989) was used to recover AVS and CRS from the sediment. Briefly, sediment samples were mixed and washed 5 times to remove $^{35}$S-SO$_4^{2-}$. About 1 g of each sediment pellet was transferred to a reaction flask with 10 ml 50% ethanol. After degassing and acidification (8 ml 12 M HCl), AVS was liberated as H$_2$S at room temperature under continuous stirring for 40 min using N$_2$ as a carrier gas and trapped as ZnS in 10 ml 5% ZnAc. CRS was determined in the sediment slurry remaining from the AVS distillation. A new ZnAc trap was inserted and 16 ml Cr$_2$O$_7^{2-}$ in 0.5 M HCl was added before distillation was resumed by 45 min of boiling. All traps were later analysed for sulfide to recover the total reduced sulfur pools. Radioactivity of $^{35}$S in the traps were determined on subsamples using a Packard 2200 CA TRI-CARB Scintillation Analyzer.

Elemental sulfur was separated by the CS$_2$ extraction method of Howarth & Jørgensen (1984). Subsamples of 2 to 3 g sediment were extracted with 5 ml CS$_2$ in glass-stoppered test tubes for 12 h on a shaker at room temperature. After centrifugation the supernatant was analyzed spectrophotometrically for S$^0$ (Troelsen & Jorgensen 1982) and counted for $^{35}$S radioactivity.

FeS was determined as the distillated AVS by subtraction of free sulfide and FeS$_2$ as the distilled CRS after subtraction of the measured S$^0$ content.

**Solid phase iron.** Total Fe content in the particulate phase was determined on 100°C dried and ground sediment samples. About 0.1 g of dry sediment was digested with 5 ml of hot 10 M HNO$_3$ for 20 h. After digestion the solution was evaporated to near dryness. The residue was then dissolved in concentrated HCl, diluted with distilled water to give about 1 M HCl and centrifuged at 3000 rpm for 10 min. The resulting digest was analyzed for Fe by atomic absorption spectrometry (Perkin-Elmer 2380 AAS).

**Redox, pH and alkalinity.** Vertical redox profiles were determined with a Pt-electrode inserted into the sediment in steps of 1 cm down to 10 cm. The Eh signal was allowed to stabilize for 3 min at each depth before the reading was noted. Six replicate profiles were measured at each station.

Profiles of pH in the sediment were measured in intervals of 2 mm (0 to 1 cm) or 1 cm (1 to 10 cm). After core sectioning, the segments were immediately transferred to 5 ml scintillation vials and a Knick U 456-KN 2 pH electrode with a 5 mm wide tip was inserted directly into the sediment. The pH reading was noted after 5 to 10 min of stabilization. Four profiles were determined at each of the stations.

Pore water alkalinity was determined in 3 replicates at each station by titration with 0.01 M HCl. Unfortunately, all alkalinity samples had to be diluted with distilled water before titration due to the small amounts of pore water available. However, subsequent dilution tests showed no significant errors due to this method.

On one occasion, pH and alkalinity changes in the tidal water passing the creek adjacent to Stn 2 was followed during one tidal cycle. Water samples from the creek were taken by syringe at 1 h intervals from 8.00 to 19.00 h and filtered through GF/C filter in the field. The samples were analysed the same day.

**Oxygen and carbon dioxide exchange.** Total metabolic rate of the sediment was determined as oxygen uptake and carbon dioxide production on cores kept in darkness. Four cores (15 cm sediment and 10 cm water phase) from each of the stations were supplied with an overlying water phase of fresh sea water immediately after arrival to the laboratory. The cores were equilibrated in darkness with continuous aeration for about 20 h before initiation of flux measurements. The water phase was replaced twice during this dark acclimation period to avoid accumulation of metabolites. Temperature was 29°C during both acclimation and incubation. During incubations all cores were equipped with stirrer motors which maintained a continuous water circulation at a rate less than the resuspension limit. Flux rates were determined from the concentration difference between initial and final samples during incubation periods of 2 to 4 h. Oxygen was analysed by the standard Winkler technique (Parsons et al. 1984). Total carbon dioxide (TCO$_2$) was quantified by potentiometric Gran titration (Talling 1973).

**RESULTS**

**Sediment characteristics**

Stn 1 was heavily bioturbated by burrowing ocypodid and grapsid crabs (1550 burrow openings m$^{-2}$). Very slow tidal currents at this station allowed for the deposition of a thick silt layer. The sediment was com-
posed of grey-brown silt and clay deposits down to a depth of 10 to 12 cm, followed by a narrow (5 to 7 cm) sandy zone which overlay a compact zone of unknown depth dominated by coarse gravel and pebbles. Organic contents were constant with depth in the upper 10 cm: 4 to 6 % LOI; 700 to 900 µmol C g dw⁻¹; 30 to 50 µmol N g dw⁻¹ (molar C:N ratio = 18 to 21). Although the infrequent inundations (10 to 15 tides per month) gave the impression of a rather dry sediment surface, water contents and porosity (0.5 to 0.6) were similar to those found at the other 2 stations. The numerous burrows, which usually reached to 15 to 20 cm depth, were responsible for a 5 to 10 cm thick, continuous light brown oxidized upper zone. Deeper down, the oxidized zone was restricted to a 0.5 mm radial layer around burrows. The bulk reduced sediment was never black and sulfidic.

Stn 2 was less affected by burrowing fauna. The major infaunal species were sipunculid worms (500 m⁻²) and grapsid crabs (10 m⁻²). The sediment consisted of a 4 to 5 cm thick grey-brown silt-zone overlying a grey-black peat-like root zone down to at least 15 cm depth. This 2-layered structure is probably the combined result of salt sedimentation at the surface during high tide and continuous root growth at 4 to 5 cm depth by Rhizophora apiculata. Organic content in the silt zone was 5 to 6 % LOI; 900 to 1200 µmol C g dw⁻¹; 40 to 50 µmol N g dw⁻¹ (C:N = 22 to 27), whereas the richer root zone gave values of 7 to 8; 1400 to 1500; 50 to 60, respectively (C:N = 25 to 27). The silt zone, which had an upper 0.5 to 1 cm thick light brown oxidized zone, was never black and sulfidic. The root zone, on the other hand, had scattered spots of black sulfidic sediment, particularly around dead roots.

The Stn 3 sediment appeared more sandy than at the other 2 stations. Wave action and strong tidal currents probably resuspend and remove the fine particulate fraction at the surface frequently. The dominating burrowing benthic fauna, ocypodid crabs (10 m⁻²), mudskippers (Gobioidae) (5 m⁻²) and small polychaetes (200 m⁻²), was outnumbered by epibenthic cerithiid snails (520 m⁻²). The sediment consisted of silty sand down to a depth of 9 to 12 cm followed by a zone of coarse coral sand. Organic content in the upper 2 cm was low with values around 4 % LOI; 500 µmol C g dw⁻¹; 18 µmol N g dw⁻¹ (C:N = 28), whereas values of 5 to 6: 900 to 1300; 30 to 40, respectively (C:N ≈ 30 to 35) were obtained deeper down. The presence of coral sand was evident as high particulate inorganic carbon (PIC) values in the deeper layers. The 8 to 10 cm depth interval exhibited a PIC content of 2330 µmol C g dw⁻¹ which was about twice the measured POC content. At the other stations PIC was generally below 10 µmol C g dw⁻¹. The upper zone of the Stn 3 sediment had a 0.5 to 1 cm oxidized surface layer overlying a grey-black reduced zone. The sediment was non-sulfidic in the depth interval examined.

### Sediment metabolism

**Oxygen uptake and carbon dioxide production**

Surface O₂ uptake (Jₒ₂) and CO₂ production (J_co₂) were highest at Stn 1, attaining values 37 and 23 % higher than at Stn 2 where the rates were lowest (Table 1). The differences between the 3 stations appeared to be significant only for J_co₂. The community respiratory quotient (CRQ) was close to 1.5 for all stations.

**Table 1. Rates of O₂ uptake (Jₒ₂); CO₂ production (J_co₂), and depth-integrated (0 to 10 cm) SO₄²⁻ reduction (ΣSRR) for the 3 stations in the Ao Nam Bor mangrove. Values (± SD for Jₒ₂ and J_co₂) are in mmol m⁻² d⁻¹ The community respiration quotient (CRQ = J_co₂/Jₒ₂) is presented. Estimated CO₂ production from SO₄²⁻ reduction (2 × ΣSRR) is given as percentage of J_co₂ (% of J_co₂).**

<table>
<thead>
<tr>
<th>Stn</th>
<th>Jₒ₂</th>
<th>J_co₂</th>
<th>CRQ</th>
<th>ΣSRR</th>
<th>% of J_co₂</th>
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<tr>
<td>1</td>
<td>61.1 ± 18.8</td>
<td>86.1 ± 26.7</td>
<td>1.41</td>
<td>27.8</td>
<td>64.6</td>
</tr>
<tr>
<td>2</td>
<td>44.7 ± 3.1</td>
<td>69.9 ± 16.5</td>
<td>1.56</td>
<td>49.7</td>
<td>142.2</td>
</tr>
<tr>
<td>3</td>
<td>50.0 ± 2.4</td>
<td>77.2 ± 5.4</td>
<td>1.54</td>
<td>43.4</td>
<td>112.4</td>
</tr>
</tbody>
</table>

**Sulfate reduction**

Although sulfate reduction generally increased with depth at all stations, the depth profiles of sulfate reduction rate (SRR) reflected the sediment composition at each station (Fig. 2). Thus, an inverse relationship was evident between SRR and Eh (Fig. 3). SRR at Stn 1 was lowest in the bioturbated and relatively oxidized upper 8 cm. Below this zone the rate almost doubled to a value of ca 600 mmol S cm⁻³ d⁻¹ (Fig. 2). At Stn 2 the depressed SRR at 4 to 6 cm depth coincided with the zone of active roots. The steep increase in SRR to ca 800 mmol S cm⁻³ d⁻¹ below the active root zone was associated with a significant drop in Eh. In the reduced coral sand zone (8 to 10 cm) of Stn 3, however, SRR (250 mmol S cm⁻³ d⁻¹) was only 1/3 of the peak rate just above (6 to 8 cm). The integrated SRR in the depth interval from 0 to 10 cm was almost similar at Stns 2 and 3 with a rate twice as high as that found at Stn 1 (Table 1).

FeS₂ was generally the most important end-product during the sulfate reduction assays. However, within and between the 3 stations some variation occurred. At Stn 1, 53 to 80 % of the label was recovered in the FeS₂ pool with the highest values found at intermediate depths. The remainder was almost entirely recovered as FeS since S⁰ only accounted for 0.2 to 1.4 %. The recovery of label
Fig. 2. Depth distribution of sulfate reduction rate and redox at the 3 stations. The sulfate reduction bars indicate the relative recoveries of $^{35}$S in the 3 examined pools of reduced inorganic sulfur as FeS$_2$ at Stn 2 increased with depth from ca 80% at the surface to 95% at 10 cm depth with a corresponding decrease of labelled FeS and S$^0$ (18 to 4.5% and 2 to 0.4%, respectively). The label recovered as FeS at Stn 3 increased dramatically with depth, from 15 to 57%. The remaining label was found in the FeS$_2$ pool, except for the upper 2 cm where S$^0$ accounted for 3 to 5%.

**Pore water and sediment chemistry**

**Inorganic sulfur pools**

The pool of reduced inorganic sulfur almost doubled with depth from the surface to 10 cm depth in all 3 mangrove sediments (from about 50 to 115 $\mu$mol cm$^{-3}$ at Stns 1 and 3, and from about 100 to 190 $\mu$mol cm$^{-3}$ at
Stn 2; Fig. 4). FeS$_2$ was the most important reduced inorganic sulfur species. About 86 to almost 100% of the total pool was recovered as FeS$_2$, whereas FeS only exceeded 1% in the deeper layers of Stns 1 and 3 reaching 13% at 10 cm depth. At Stn 2 the FeS content decreased from 0.6% to 0.1% with depth from the silt-zone to the root-zone. Elemental sulfur generally accounted for less than 0.1% of the total pool. Free sulfide was only measurable at Stn 2 and in very low concentrations, 5 to 10 nmol cm$^{-3}$. Accordingly, no sulfide smell was noticed at any time from freshly collected sediment cores from Stns 1 and 3.

Only limited SO$_4^{2-}$ depletion was evident at any of the 3 stations (Fig. 4). The SO$_4^{2-}$ concentration decreased from between 16 and 17 nmol cm$^{-3}$ in the uppermost cm to between 13 and 16 nmol cm$^{-3}$ at 10 cm depth.

**Iron**

The HNO$_3$ extractable total iron (tFe) content in the 3 mangrove sediments ranged from 350 to 660 nmol cm$^{-3}$ (Fig. 5). The tFe content was lowest in the 2 to 10 cm depth interval of Stn 1 and the upper 4 cm of Stn 2. In the root zone of Stn 2 (4 to 10 cm) and in the upper 6 cm at Stn 3, tFe content appeared about 50% higher. In the coral sand zone of Stn 3 the tFe content was about 20% lower than in the zone above.

Pyritization, $P$, is defined here as the fraction of the HNO$_3$ extractable iron pool which was bound in pyrite: $P = \frac{Fe_{py}}{tFe}$, where $Fe_{py}$ is the pyrite-bound iron pool. This definition is similar to that of Berner (1970) only if $tFe = Fe_{py} + Fe_{HCl}$ ($Fe_{HCl}$ is iron extracted in boiling 12 M HCl for 1 min). $P$ increased with depth in the 2 non-rooted sediments (Stns 1 and 3) from 5 and 3% in the uppermost layers to 18 and 16% at 8 to 10 cm depth, respectively (Fig. 5). The silt-zone of Stn 2 sediment showed an increase from 12 to 23%, but $P$ declined again in the root-zone attaining constant values around 15% down to at least 10 cm depth.

**pH and alkalinity**

The 3 sediments showed very different pH and alkalinity profiles (Fig. 6). In the highly bioturbated Stn 1 a constant pH around 7 was observed for the entire depth interval examined. Stn 2, on the other hand, appeared rather acidic with pH decreasing from 7 at the surface to around 6.4 in the 1 to 5 cm depth interval of the silt zone. In the root zone pH increased slightly to around 6.7. The mudflat sediment (Stn 3) had a pH profile typical of marine sediments with a distinct minimum at 0.5 cm depth ($pH = 6.9$) followed by a gradual increase to 7.4 at 10 cm depth.

Alkalinity was generally low in all 3 mangrove sediments (Fig. 6). At Stns 1 and 2 alkalinity decreased from 2.3 and 2.8 meq. l$^{-1}$, respectively, at the surface to 1.3 and 2.0 meq. l$^{-1}$ at 2 to 3 cm depth. At Stn 1 alkalinity remained constantly low down to a depth of 8 to 10 cm, whereas at Stn 2 there was a gradual increase in the deeper part of the root zone, reaching 3.8 meq. l$^{-1}$ at 8 to 10 cm depth. At Stn 3 alkalinity remained constant around 2.9 meq. l$^{-1}$ for the depth interval examined. The 3 stations apparently represented an alkalinity gradient with a trend for deeper subsurface minimum towards the more dry inland stations. On one occasion where alkalinity was measured down to 20 cm depth at Stn 1 (data not shown) a pattern similar to that at Stn 2, but more extended, was observed with a
Fig. 6. Depth profiles of bulk sediment pH and titration alkalinity at the 3 examined stations. Error bars indicate ± SE.

Fig. 7 Temporal pattern of pH and alkalinity in creek water adjacent to Stn 2 during one tidal cycle. Arrows indicate when Stns 1, 2 and 3, respectively, are inundated during flood and exposed to air during ebb.

gradual increase from 1.1 meq. l⁻¹ at 8 to 10 cm to 2.3 meq. l⁻¹ at 18 to 20 cm.

Temporal changes in creek water pH and alkalinity during one tidal period are shown in Fig. 7. Values typical for oceanic water (pH ≈ 8.2 and alkalinity ≈ 2.1 meq. l⁻¹) were rapidly attained at high tide. During ebb, however, pH gradually dropped to ≈ 7.3 whereas alkalinity increased abruptly to ≈ 4 meq. l⁻¹.

DISCUSSION

Sulfate reduction and distribution of sulfur pools

The depth-integrated rates of sulfate reduction in sediments of the tropical mangrove, Ao Nam Bor, (28 to 50 mmol m⁻² d⁻¹; Table 1) are within the range found in nearshore subtidal sediments but are low compared to most salt marshes (e.g. Skyring 1987). Sulfate reduction rates at the 3 stations generally appear to be associated with low redox potentials; high rates are found only where Eh is below −40 to −50 mV (Figs. 2 & 3). This threshold is in accordance with the results of Balzer et al. (1983). The distinct subsurface maximum in sulfate reduction observed around 6 to 10 cm depth at all stations (Fig. 2) indicates a vertical translocation of metabolizable organic substrates within the sediment (Howarth & Teal 1979), either due to subsurface root growth or due to downward transport of newly deposited organic matter from the surface by bioturbation. In subtidal coastal sediments, where most of the freshly deposited organic matter remains at or near the surface, a sharp peak of sulfate reduction close to the sediment surface is normally followed by a rapidly decreasing rate with depth and more than 80% of the total activity is usually concentrated in the upper 10 cm (Goldhaber et al. 1977, Jørgensen 1982, Berner & Westrich 1985, Swider & Mackin 1989). The areal rates presented here for the upper 10 cm are likely to underestimate the true depth-integrated rates for the entire sediment system since substantial sulfate reduction may occur below 10 cm depth. Significant rates are expected to occur down to the gravel zone at Stn 1 (ca 17 cm depth) and even deeper down at Stn 2. At Stn 3, however, the low rates observed at 8 to 10 cm depth suggest that sulfate reduction is relatively low in the coral sand below. The depth-integrated rates should thus be considered minimum estimates, especially for Stns 1 and 2. It is vital, therefore, that future studies on sulfate reduction in mangrove sediments include deeper layers (>10 cm) to clarify the exact depth distribution of this important process.
The very high recovery of reduced $^{35}$S-label found as FeS$_2$ (82 to 97%) in Stn 2 sediment demonstrates the necessity to include the CRS fraction when sulfate reduction is measured in rooted sediments rich in peat. This is a phenomenon frequently observed in tidally dominated Spartina marshes (Howarth & Giblin 1983, Howarth & Merkel 1984, Swider & Mackin 1989). The only available data on sulfate reduction in southeast Asian mangrove swamps is from the study of Blackburn et al. (1987). Unfortunately, their results were only based on the $^{35}$S-label trapped in the AVS pool, which probably underestimates the true rates more than 10-fold. However, the depth-integrated (AVS based) sulfate reduction of Blackburn et al. (1987) in the upper 10 cm of the sediment from a Rhizophora apiculata mangrove (Ao Yon, Phuket Island), 5.4 mmol m$^{-2}$ d$^{-1}$, is close to the AVS based sulfate reduction found at the R. apiculata site (Stn 2) in the present study. 3.7 mmol m$^{-2}$ d$^{-1}$ The oxidizing activity of roots and relatively low pH in this type of sediment may favour a rapid formation of FeS$_2$ either through direct precipitation of Fe$^{2+}$ with polysulfides or via FeS oxidation with $\mathrm{S}^0$ and polysulfides (Berner 1964, Howarth 1979, Giblin & Howarth 1984, Giblin 1988). The non-rooted and more sandy Stns 1 and 3, where only 43 to 80% of the $^{35}$S-label was found in the CRS fraction, have pH levels (7.0 to 7.5) similar to subtidal, coastal sediments. In these types of sediment the AVS fraction usually is the most important end-product (Howarth & Jørgensen 1984, Thode-Andersen & Jørgensen 1989). In other coastal sediments the net formation of $\mathrm{S}^0$ during short-term sulfate reduction assays is usually more important than found here (King 1988, Thode-Andersen & Jørgensen 1989). Due to the potential role of isotopic exchange reactions between $\mathrm{S}^0$ and other reduced sulfur pools and to the fact that AVS is an operationally defined fraction, however, the distribution of sulfate reduction into FeS, $\mathrm{S}^0$ and FeS$_2$ is only indicative of the tracer distribution and not of the differential formation rates of these compounds (Thode-Andersen & Jørgensen 1989).

Almost all (86 to 100%) reduced sulfur at the 3 stations is found as FeS$_2$ (Fig.4). In most subtidal sediments FeS$_2$ usually accounts for 30 to 50% of the reduced sulfur pool (Thode-Andersen & Jørgensen 1989), whereas this compound generally is the major particulate sulfur component (50 to 90%) in salt marsh sediments (Howarth & Teal 1979, Luther et al. 1982, Howarth & Giblin 1983). The $\mathrm{S}^0$ content close to the detection limit, on the other hand, is low compared to most coastal sediments where this compound usually accounts for 2 to 10% of the total reduced sulfur pool in the upper 10 cm (King et al. 1985, Thode-Andersen & Jørgensen 1989).

The total iron content of these sediments is 2 to 3 times the values previously found in salt marshes (Giblin 1988) and coastal sediments (Sorensen & Jørgensen 1987, Jørgensen et al. 1990). The long-term HNO$_3$ extraction procedure used here, however, may overestimate the pool of reactive iron by extracting a part of the large pool which is bound in silicate minerals (Canfield 1989). Pyritization, $P$, which is defined slightly different here than in previous studies, was generally low in the mangrove sediments, but close to the values found by others (Berner 1970, Jørgensen et al. 1990). The high tFe content and low $P$ may indicate that FeS and FeS$_2$ formation in the present sediments are not limited by the availability of reactive iron. This is substantiated by the general absence of free HS$^-$ in the sediment despite the relatively high rates of sulfate reduction. Thus, Canfield (1989) demonstrated that in marine sediments supporting sulfate reduction, the presence or absence of HS$^-$ is a sensitive indicator as to the presence of reactive iron oxides. Continued reoxidation of iron sulfide minerals by action of roots, crabs and other physical processes may replenish iron oxides constantly at all depth strata in the sediment. Without this renewal the present mangrove sediments would be considerably more reduced.

The low pyritization observed in the upper 4 to 6 cm of the sediment at Stns 1 and 3 probably reflects active removal of FeS$_2$ as opposed to the less disturbed FeS$_2$-rich Stn 2. Burrowing activity by the numerous crabs at Stn 1 transports sediment from deeper strata to the surface where FeS$_2$ is oxidized or removed. Gardner et al. (1988) found that fiddler crab burrowing could remove 17.5% of the FeS$_2$ produced by sulfate reduction each year in a South Carolina (USA) salt marsh. Removal or oxidation of FeS$_2$ in the upper layers of the sediment at Stn 3, on the other hand, is in addition to bioturbation probably coupled with the frequent incidences of sediment resuspension at this shallow, wave-exposed station.

**Benthic metabolism**

Rates of benthic metabolism measured as $\Gamma_{O_2}$ and $\Gamma_{CO_2}$ (Table 1) are in the lower range of reported rates from coastal sediments and salt marshes in colder climates (Howarth & Teal 1979, Hargrave & Phillips 1981, Howarth & Hobbie 1982, Howes et al. 1984, King et al. 1985, Mackin & Swider 1989). In a previous study from the Ao Nam Bor mangrove, however, Kristensen et al. (1988) obtained $\Gamma_{O_2}$ values even lower (ca 50%) than those presented here. They acclimated cores in the dark for only about 0.5 h before starting incubation compared to 20 h in the present study. A very short dark-acclimation period may have resulted in non-
steady state oxygen gradients and seriously underestimated \( J_\text{O}_2 \) due to the previous light induced oxygen production by benthic microalgae at the sediment surface (Kristensen unpubl.).

Oxygen respiration and sulfate reduction are generally considered the most important respiration processes in coastal marine sediments (Jørgensen 1983, Howarth 1984, Mackin & Swider 1989). In the present study, the depth-integrated sulfate reduction converted to \( CO_2 \) production (SRR) is comparable to or slightly higher than the measured \( J_\text{CO}_2 \) across the sediment-water interface (Table 1). This indicates that sulfate reduction in the 0 to 10 cm layer may be responsible for 65 to 142% of the total microbial respiration in these sediments. Since significant microbial activity probably occurs below 10 cm depth, especially at Stns 1 and 2, the actual \( CO_2 \) production by sulfate reduction is expected to exceed the measured \( J_\text{CO}_2 \), considerably at these stations. The presence of oxygen 1 to 2 mm into the sediment surface and walls of crab burrows (Andersen & Kristensen 1988, Kristensen et al. 1988) indicates that oxygen respiration also contributes significantly to \( CO_2 \) production. Similar discrepancies between measured \( CO_2 \) flux and \( CO_2 \) production estimated from sulfate reduction have previously been reported (Howarth & Giblin 1983, Howarth & Merkel 1984, Howes et al. 1984, King et al. 1985, Mackin & Swider 1989). The mechanisms responsible for an apparent \( CO_2 \) deficit in mangrove sediments may include: (1) \( CO_2 \) assimilation by \( Rhizophora \) apiculata roots (Stn 2) and/or sulfate oxidizing chemosynthetic bacteria (Stns 1 and 2); (2) movements of \( CO_2 \)-rich pore water during low tide by evapotranspiration and seepage into tidal creeks (Stns 1 and 2); (3) wave-induced advective \( CO_2 \) flux during high tide (Stn 3); and (4) excessive gas exchange during air exposure (Stns 1, 2 and 3).

The effect of \( Rhizophora \) apiculata roots on sediment chemistry at Stn 2 is clearly evident from the redox, \( pH \) and alkalinity profiles (Figs. 2 & 6). The redox depth pattern is closely related to the distribution of living and dead \( R. \) apiculata roots. The oxidizing activity of living roots is evident as a secondary rise in \( Eh \) (-10 mV) and a depression of sulfate reduction in the 4 to 6 cm depth interval. Such elevated \( Eh \) in active root zones has previously been reported for salt marshes (Howes et al. 1981) and mangrove swamps (Boto & Wellington 1984). Andersen & Kristensen (1988) actually observed a narrow oxic zone around roots of the mangrove tree \( Avicennia \) marina. The low alkalinity in the 2 to 6 cm depth interval suggests significant uptake and fixation of \( CO_2 \) by the roots. Howarth & Merkel (1984) argued that \( CO_2 \) assimilation by marsh grasses could obscure measurements of \( CO_2 \) across the sedi-ment-water interface. The low \( pH \) (6.5) coinciding with the alkalinity minimum in Stn 2 sediment furthermore indicates that sulfide oxidizing chemoautotrophs are present around roots. Assimilation of \( CO_2 \) by sulfide oxidizers, however, is probably of limited quantitative importance here due to a low growth yield of these bacteria (Howarth 1984). It is also unlikely that chemosynthetic \( CO_2 \) fixation in the oxidized wall of the numerous crab burrows at Stn 1 is responsible for the very low alkalinity while bulk sediment \( pH \) remains constant around 7. Salinity (not shown) and sulfate profiles at this station indicate that no freshwater intrusion occurs from land. Bulk sediment \( pH \) measurements, however, do not disclose the presence of acid microzones (e.g. burrow walls) of rapid sulfide oxidation and thereby extensive \( CO_2 \) liberation. Any evolved \( CO_2 \) gas may escape easily from the sediment by diffusion into the numerous burrows.

Movement of pore water at Stns 1 and 2 by evapotranspiration and seepage into the tidal creek may result in significant loss of solutes. Such pore water drainage has previously been found to be important for the sediment chemistry in many salt marshes (Howarth & Teal 1979, Gardner et al. 1988). Although no direct evidence of evapotranspiration was found in the present study, seepage of water at low tide was clearly visible along the creek banks, especially from crevices and infaunal burrows. Samples of the water seeping from these burrows showed high concentrations of both alkalinity (ca 4.5 meq. l\(^{-1}\)) and free sulfide (ca 50 \( \mu M \)), which confirms the deep origin of this drained pore water. Water seepage clearly affects the water chemistry in the tidal creek; low tide alkalinity in the creek water is almost doubled (ca 4 meq. l\(^{-1}\)) and \( pH \) is reduced by 1 unit compared to the incoming seawater at high tide (Fig. 7). Accordingly, the advective transport of pore water may be responsible for a considerable loss of metabolically produced \( CO_2 \) from the sediment column. No seepage occurs at Stn 3 but the wave-induced resuspension of surface sediment may periodically remove significant amounts of pore water solutes, such as \( CO_2 \), from the upper centimetres of the sediment.

The above mentioned mechanisms may contribute to the discrepancies between measured fluxes and \( CO_2 \) production estimated from sulfate reduction rates. The \( CO_2 \) deficit is apparently most serious at Stn 2, where the potential for \( CO_2 \) removal by processes other than upward diffusive flux is largest. The incubation technique used in this study has drawbacks which may affect the measured fluxes. Laboratory core incubations may suppress the influence of roots, pore water drainage, and resuspension on fluxes. However, this is usually considered insignificant during short-term measurements when compared to situ results (Howes et al. 1984). Incubation of tidal sediments with an overlying water phase alone may not be representative for
the gaseous exchange that occurs during air exposure at low tide. Thus, oxygen fluxes are found to be underestimated from 2 to 10 times when incubations are performed with water above the sediment as compared to gas phase measurements (Dye 1983, Howes et al. 1984, Kristensen unpubl.). This may very well be important in the present study since the sediment is exposed to air for up to 20 h per day.

Acknowledgements. We are grateful to the staff of PMBC for hospitality and invaluable assistance during this study. We thank G. M. King and M. H. Jensen for reviewing the manuscript, and H. Brandt for technical assistance. This work was supported by grant No. 89-0307/60 from the Carlsberg Foundation.

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Manuscript received: December 3, 1990
Revised version accepted: March 28, 1991

This article was submitted to the editor