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Decay of plant detritus in organic-poor marine sediment: Production rates and stoichiometry of dissolved C and N compounds

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ABSTRACT

Initial rates (30–60 days) and C:N stoichiometry of decomposition were examined in an organic-poor sediment (0.5% LOI) amended with fresh and dried yeast (Y) and *Ruppia maritima* (R) detritus by the use of "open system" core incubations and "closed system" jar incubations. High organic additions (0.5% dw) inhibited anaerobic carbon mineralization (i.e. sulfate reduction) and stimulated DOC production and nitrogen mineralization 3(R) to 15(Y) times (i.e. hydrolysis and fermentation). This indicated that carbon and nitrogen mineralization in the highly amended anaerobic sediments were uncoupled. Low organic additions (0.08% dw), on the other hand, stimulated both carbon and nitrogen mineralization by 1–2(R) and 3(Y) times. The comparison of reaction rates involving CO_2, SO_4^{2-} and NH_4^+ estimated from (1) modeling of porewater profiles ("open system"), (2) temporal changes in jars ("closed system") and (3) sediment-water fluxes, documented equal applicability of these techniques in non-bioturbated sediment (except for NH_4^+ in (3) where nitrification interfered). The modeling approach (1) also suggested that the TCO_2 deficiency observed in the uppermost oxidized zone of the sediment can be explained by rapid CO_2 fixation by e.g. sulfide oxidizing chemoautotrophs. Although the C:N stoichiometry of inorganic decomposition products based on estimate (1) and (2) generally agreed well, it was found crucial to include dissolved organic pools (i.e. DOC) in estimates from highly amended anaerobic sediments due to the uncoupling of carbon and nitrogen mineralization. The stoichiometry of inorganic mineralization products can only be used to describe particulate organic matter decay in sediments where the concentration of DOC is negligible. C:N ratios obtained in the present study indicated that the major compounds being degraded in unamended (with an indigenous diatom pool) and yeast amended sediment were proteins (C:N = 4–5), whereas in *Ruppia* amended sediment carbohydrates were more important (C:N = 6–9).

1. Introduction

Organic input to most intertidal and shallow coastal sediments is dominated by autochthonously produced detritus from dynamic communities of benthic micro- and macrophytes (e.g. Haddad and Martens, 1987; Harrison, 1987; Kristensen, 1993). The dominance may alternate rapidly between mats of benthic microalgae (e.g. diatoms), layers of attached and drifting seaweeds, and dense growth of macrophytes

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(e.g. seagrasses and marsh grasses) driven by climatic and other environmental factors (Reise, 1983; Harrison, 1987; Sundbäck *et al.,* 1990; Fong *et al.,* 1993). Accordingly, no simple generalization can be established to describe the specific chemical composition of deposited detritus in coastal environments. It may vary unpredictably from highly labile and nitrogen-rich material originating from microalgae to decay resistant lignified vascular plant detritus.

Initial decay of deposited phyto-detritus in most subtidal sediments is considered to occur by aerobic respiration at the sediment surface. Later, when the partly degraded material is buried by continued sedimentation, gradually slower decay by anaerobic communities with terminal electron acceptors other than oxygen (e.g. SO_4^{2-}) takes over (e.g. Emerson and Hedges, 1988; Canfield, 1993). The rates of decay in different depth zones of the sediment seem to be more dependent on the availability of degradable carbon (electron donors) than the actual electron acceptor being used (Kristensen and Blackburn, 1987; Burdige, 1991). The reactivity of organic matter is therefore considered the controlling factor for fermentation and remineralization processes in most anaerobic marine sediments. Both the chemical structure of deposited organic matter and factors, such as the particle size of the organic material, variation in the microbial consortia mediating degradation and physical-chemical associations with the surrounding sediment matrix, may determine the reactivity of organic matter (Keil *et al.,* 1994).

However, the classic concept, where the lability of organic matter to microbial decay is inversely related to burial depth, is too simplified to explain decay patterns in heterogeneous intertidal and shallow coastal ecosystems. Initial decay in these environments may occur anaerobically when freshly-deposited plant detritus is buried rapidly by the action of e.g. waves and bioturbating infauna (Sundbäck *et al.,* 1990; van Duyl *et al.,* 1992; Webb and Montagna, 1993). Studies have shown that burial of fresh detritus in sediments may either stimulate or hamper the anaerobic microbial community (Andersen and Hargrave, 1984; van Duyl *et al.,* 1992; Holmer and Kristensen, 1994). The actual response of the anaerobic bacteria may, besides the quantity and quality (or reactivity) of buried detritus, depend on e.g. the composition and nutritional status of the microbial community and thus the size and chemical structure of the indigenous organic pool in the sediment (Aller and Yingst, 1980; Hackney, 1987; Parkes *et al.,* 1993). When the community is poorly adapted to the specific type of organic matter being buried, inhibitory effects, time-lags and accumulation of dissolved organic intermediates not usually observed in sediments may occur (Rudnick and Oviatt, 1986; Holmer and Kristensen, 1994).

Rates of organic matter decay in anaerobic marine sediments have generally been studied by two major approaches. Processes such as fermentation, sulfate reduction, and ammonium production have been quantified either directly by various incubation techniques both with and without addition of radiotracers (e.g. Jørgensen, 1978; Westrich and Berner, 1984; Henrichs and Doyle, 1986; Aller and Mackin, 1989;

Burdige, 1991; Sun *et al.,* 1993) or estimated using diagenetic models applied to both porewater and solid phase sedimentary profiles (e.g. Aller, 1978; Berner, 1980; Boudreau *et al.,* 1992). While there generally is good agreement for carbon and nitrogen diagenesis, only a few (if any) studies have attempted to compare carbon and nitrogen stoichiometry determined by the two mentioned approaches. Usually, the stoichiometry of carbon and nitrogen mineralization in marine sediments has either been derived from diagenetic models (Berner, 1977; Aller and Yingst, 1978; Klump and Martens, 1987) or simply by applying the standard Redfield ratio for average marine plankton, 6.6 (Redfield *et al.,* 1963). Although the true carbon and nitrogen stoichiometry may be close to the Redfield ratio in anoxic sediments with a sufficient supply of phytoplankton detritus (Klump and Martens, 1987), serious deviations can be expected in shallow coastal environments where sources of organic matter vary from benthic diatoms to vascular plant detritus (Kristensen, 1993).

The aim of this experimental study was to evaluate the initial rates and stoichiometry of microbial decay when two different doses of fresh yeast and seagrass detritus were mixed homogeneously into organic-poor, sandy sediment. Production rates of dissolved carbon and nitrogen compounds resulting from anaerobic decay processes were determined by the use of both "open system" and "closed system" incubation approaches, combined with diagenetic modelling of porewater profiles. The techniques used agreed well and provided specific and valuable information on the coupling between anaerobic fermenting and respiring microorganisms and the stoichiometry of dissolved products after addition of various types and quantities of organic matter to a sediment.

2. Materials and methods

a. Sediment collection and handling. Organic-poor, sandy sediment was collected in June and September 1992 from the shallow (0.2–0.6 m) marine lagoon, Fællesstrand, on the northeast coast of Fyn, Denmark. The sediment was homogeneous and consisted of well sorted quartz sand (>99%) with medium particle size of 0.2 mm mixed with small amounts of silt + clay (0.5%). Most of the organic matter in the sediment (ca. 0.5% Loss-On-Ignition) originated from benthic diatoms, as these are the dominating primary producers in the lagoon. The macrophyte vegetation is poor and consists almost entirely of the seagrass *Ruppia maritima.* For further details consult Kristensen (1993).

The uppermost 5–10 cm of the sediment was dredged and sieved through a 1.5-mm mesh on location to remove macrofauna and larger particles. After return to the laboratory, the sediment was homogenized and split into three portions: (1) *Y*-sediment—added dried (105°C) and ground yeast (commercially available bakers yeast) as a substitute for microalgae, (2) *R*-sediment—added dried (105°C) and blended (<500 μm) fresh *Ruppia maritima* detritus (whole plants were collected, washed and dried on the days of sediment sampling), and (3) *C*-sediment—

maintained as an unamended control. The added materials were mixed homogeneously into the sediment and allowed to compact for a few hours in tanks. Aerating the sediment during homogenization, which may temporarily inhibit obligate anaerobic bacteria, is not considered to affect the comparative aspect of this long term laboratory experiment (Sun *et al.,* 1991).

b. Core experiments (corexp). Two "open system" core experiments, corexp1 and corexp2, were conducted. *Y*- and *R*-sediments in corexp1 (*Y*1 and *R*1) were amended with 4 g dw of yeast and *R. maritima* material per kg wet sediment (equivalent to ca. 0.5% dw) and in corexp2 (*Y*2 and *R*2) with 0.6 g dw per kg wet sediment (equivalent to ca. 0.08% dw). Three sediment cores of each type were taken from the compaction tanks with acrylic core liners (30 cm long and 5.2 cm i.d.) to a depth of about 15 cm. Cores were kept at 15°C in darkness using an incubator with circulating seawater (Kristensen, 1993). Salinity was 14 ‰ in corexp1 and 22‰ in corexp2. Porewaters in the latter experiment were enriched with Na_2SO_4 to obtain an initial SO_4^{2-} concentration of 35 mM in order to avoid SO_4^{2-} depletion. Corexp1 was not enriched with SO_4^{2-} (initial porewater concentration: 12 mM).

Cores were maintained in the seawater incubator with open tops for 29–35 days only interrupted by 2 incubations (corexp1: day 24 and 30; corexp2: day 16 and 23) for determination of O_2, total CO_2 ($TCO_2 = H_2CO_3 + HCO_3^- + CO_3^{2-}$) and NH_4^+ flux across the sediment-water interface. Two randomly chosen cores of each type were sealed with a magnetic stirrer motor as the lid during flux incubations. Stirring was kept below the resuspension level. Water samples for O_2, TCO_2 and NH_4^+ were taken at the start (before inserting the motors) and at the end (after removing the motors). Incubation time was 2–4 h depending on treatment. Concentration changes during incubations are assumed linear, since O_2 rarely decreased below 60% of air saturation. Samples for O_2 and TCO_2 were analyzed within 12 h of sampling. Those for NH_4^+ were frozen immediately and analyzed as soon as possible. No TCO_2 and NH_4^+ flux was obtained in corexp1 on day 24 due to lost samples.

All cores were sectioned at the end, i.e. day 29–32 (corexp1) and day 33–35 (corexp2), by slicing into 1 cm intervals to 12 cm depth in corexp1 and 1 cm intervals down to 6 cm followed by 2 cm intervals to 10 cm depth in corexp2. Subsamples of the sediment slices and the initial sediment mixtures were examined for wet density (weight of a known volume), water content (weight loss after drying at 130°C for 6 h), and particulate organic carbon (POC) and nitrogen (PON). The dimensionless linear adsorption coefficient (K) for NH_4^+ was determined by extracting samples of 2–3 g sediment in 5 ml 2 M KCl for 30 min at 5°C (Mackin and Aller, 1984). After centrifugation at 3000 rpm for 10 min the supernatant was frozen for later NH_4^+ analysis. Filtered porewater for TCO_2, dissolved NH_4^+, SO_4^{2-} and dissolved organic carbon (DOC) analysis was isolated by centrifuging the remaining sediment at 1800 rpm for 5 min in double centrifuge tubes containing GF/C filters. Samples for TCO_2

were analyzed within 12 h, those for NH_4^+ and DOC were stored frozen for later analysis, and those for SO_4^{2-} were acidified with 0.5 M HCl to pH ca. 2 and stored at 5°C until analysis. DOC sampling from porewaters by core sectioning and centrifugation is problematic, since physical stress may cause cells to break and release DOC. Artifacts due to sediment handling are generally large in rooted sediments (root breakage) and in sediments with much lower DOC concentrations than found in the present study (Howes *et al.*, 1985).

c. Jar experiment (jarexp). Samples of the sediment mixtures used in corexp2 were transferred to 50-ml polyethylene centrifuge tubes (jars). A number of 30 jars were used for each sediment type (*Y2j*, *R2j*, *C2j*). The sediment-filled jars were sealed (no headspace) with screwcaps, taped, and held submerged in anaerobic, sandy sediment to avoid oxygen contamination. The temporal pattern and rates of anaerobic decomposition processes in the "closed system" jars were followed for 59 days at 15°C. Two jars of each type were sacrificed at regular intervals (frequency decreasing from once a day initially to once a week at the end) for the determination of solid phase parameters and porewater solutes as described above. In addition, porewater was occasionally analyzed for methane (day 37) and acetate (day 1, 8, 32 and 59).

d. Chemical analysis. POC and PON content of 130°C pre-dried sediment subsamples were analyzed on a Carlo Erba EA1108 CHN Elemental Analyzer according to the difference on ignition procedure of Kristensen and Andersen (1987). TCO_2 was determined by the flow injection/diffusion cell technique of Hall and Aller (1992) using a Kontron Ion Chromatograph. Interfering sulfides were precipitated before analysis by adding $ZnCl_2$. The standard Winkler technique was used for O_2 analysis. NH_4^+ was determined by the standard autoanalyzer technique of Solorzano (1969). SO_4^{2-} was analyzed on a Kontron Ion Chromatograph with 2.5 mM potassium hydrogen phthalate (pH = 4.5) as eluent. DOC was determined on 0.45 μm filtered samples by a Shimadzu TOC-5000 Total Organic Carbon Analyzer after acidification with 2 M HCl (pH <2) to remove dissolved inorganic carbon. Methane was analyzed on a Hewlett-Packard 5830A Gas Chromatograph using a flame ionization detector (FID) at 230°C after separation in a Porapak Q column (80/100) with N_2 as carrier gas. Acetate was measured by the HPLC-technique of Bøtte and Jørgensen (1992) using ion-exclusion with 1 mM H_2SO_4 as eluent followed by an Anion MicroMembrane Supressor (AMMS-ICE, Dionex Corp.) with 5 mM TBaOH as regenerant. The precision of the various analytical techniques were 5% or better.

3. Results

a. Sediment description. The visual appearance of the sediment in core experiments varied according to the treatments. Control cores (*C1* and *C2*) had a well defined upper oxidized brown zone of 0.5–0.7 cm thickness. Deeper in these cores the

Table 1. Initial and final sediment organic content measured as POC and PON (μmol cm^{-3}) and C:N ratios in corexp1 (day 30), corexp2 (day 35) and jarexp (day 44). S.D. of 3 replicates for corexp and range of 2 replicates for jarexp are shown. Final values significantly different (*t*-test, $p < 0.05$) from initial values are indicated by *.

treatment:	*C*1	*C*2	*Y*1	*Y*2	*R*1	*R*2
POC						
initial:	200 ± 5	208 ± 8	475 ± 6	249 ± 8	340 ± 5	229 ± 8
corexp final:						
0–1 cm	209 ± 3	230 ± 14	391 ± 25*	258 ± 10	284 ± 32	238 ± 17
>2 cm	175 ± 13	194 ± 7	419 ± 5*	208 ± 7*	283 ± 9*	200 ± 4*
jarexp final:	—	194 ± 2	—	204 ± 9*	—	188 ± 11
PON						
initial:	21.5 ± 0.5	21.6 ± 0.8	58.3 ± 0.7	27.6 ± 0.9	26.4 ± 0.4	22.8 ± 0.7
corexp final:						
0–1 cm	na	22.9 ± 1.4	na	28.1 ± 1.1	na	23.2 ± 1.7
>2 cm	na	18.2 ± 1.8	na	22.2 ± 1.3*	na	19.5 ± 0.5*
jarexp final:	—	15.5 ± 0.2*	—	25.0 ± 1.1	—	13.8 ± 0.8*
C:N						
initial:	10.8	9.6	8.1	9.0	12.9	10.0
corexp final:						
0–1 cm	—	10.0	—	9.2	—	10.3
>2 cm	—	10.7	—	9.4	—	10.3
jarexp final:	—	12.5	—	8.2	—	13.6

na = not analyzed.

sediment gradually changed color to grey and greyish-black. A distinct sulfide odor was only noticed below 3 cm depth. No oxidized zone was evident at any time in yeast (*Y*1) and *Ruppia* (*R*1) cores of corexp1. The sediment in these cores was black with a strong sulfide smell from the surface and down. They all developed a *Beggiatoa*-like, white bacterial film on the sediment surface within the first 15 days. Yeast (*Y*2) cores of corexp2 had an oxidized sediment surface of 0.2–0.3 cm thickness with scattered white *Beggiatoa*-like spots. The deeper anoxic sediment was always black and sulfide smell was noticed below 1 cm depth. *Ruppia* (*R*2) cores all had an oxidized zone of 0.4–0.5 cm overlying a black anoxic sediment (sulfide smell below 2 cm depth). Porosity in all cores varied from 0.45–0.50 in the top cm to 0.25–0.30 at 10 cm depth.

Initially, the basic sediment contained 200–208 μmol POC cm^{-3} and 18.5–21.6 μmol PON cm^{-3}, providing a C:N ratio of 9.6–10.8 (Table 1). Organic matter additions in the highly enriched corexp1 increased the carbon and nitrogen content by 138 and 215%, respectively, in the yeast treatment (bulk C:N = 8.1), and 70 and 43%, respectively, in the *Ruppia* treatment (bulk C:N = 12.9). In the less enriched corexp2 and jarexp the carbon and nitrogen content increased 20 and 28%, respectively in the yeast treatment (bulk C:N = 9.0), and 10 and 6% in the *Ruppia*

treatment (bulk C:N = 10.0). The added yeast and *Ruppia* detritus had a C:N ratio of 6.9 and 17.7, respectively.

When the cores were sectioned after 30–35 days, POC and PON showed a consistent, but individually nonsignificant, increase in the 0–1 cm section of all corexp2 sediments (Table 1). In the same interval of corexp1 cores, POC only showed an increasing trend in *C*1-, whereas *Y*1- and *R*1-cores lost about 17% of the initial POC in this interval ($p \leq 0.05$). Below 2 cm depth, all sediments lost 7–17% and 15–20% of the initial POC and PON content, respectively—although not statistically significant in *C*1- and *C*2-cores. The losses of POC and PON in the "closed system" jar experiment appeared similar to those found below 2 cm in the "open system" corexp2, but only statistically significant for PON in *C2j*- and *R2j*-jars. It must be recognized here that the measured values of POC and PON actually include unknown quantities of non-volatile DOC and DON remaining after drying the sediment at 130°C. Carbon and nitrogen budgets based on dissolved and particulate pools can therefore not be balanced because dissolved porewater C and N constituents are included in both pools. Changes in POC and PON should merely be considered a qualitative information on the spatial distribution of gains and losses.

b. Porewater solutes in cores. Accumulation of mineralization products, TCO_2 and NH_4^+, and consumption of the most important electron acceptor for anaerobic respiration, SO_4^{2-}, in sediment porewaters were highly dependent on organic additions (Fig. 1). Porewater TCO_2 in *C*1- and *C*2-cores increased smoothly to 17–20 mM at 10 cm depth (Figs. 1A,D), except for a deflection in the uppermost cm where TCO_2 was lower than the overlying water level ($p < 0.05$). TCO_2 in cores highly amended with yeast (*Y*1) was only significantly higher ($p < 0.01$) than the overlying water concentration in the 0–1 cm interval (6.5 mM, Fig. 1A). The same pattern was observed in cores highly amended with *Ruppia* detritus (*R*1), but with significantly higher ($p < 0.05$) concentrations (up to 10 mM) to 6 cm depth. The total dissolved carbon, TDC (=TCO_2 + DOC), concentration in *Y*1- and *R*1-cores, however, increased to 400 and 150 mM, respectively, at 10 cm depth (Fig. 2A). In *Y*2- and *R*2-cores of corexp2, where the organic addition was lower, TCO_2 increased steeply with depth, reaching 54 and 38 mM, respectively, at 10 cm (Fig. 1D). The deflection of TCO_2 profiles in the uppermost cm of these cores was not as dramatic as in control cores. No porewater DOC was evident in *R*2, but concentrations up to 16 mM in *Y*2 provided a total dissolved carbon (TDC) pool in these cores of about 70 mM at 10 cm depth (Fig. 2B). While the maximum TDC concentration in *C*1 and *C*2 cores only was equivalent to 3–4% of the initial POC pool, the excess TDC accumulation in *Y*-cores (*Y*1 and *Y*2) and *R*-cores (*R*1 and *R*2) was equivalent to 45–48% and 33–35%, respectively, of the added POC pool.

The depth patterns of SO_4^{2-} were almost the exact mirror image of TCO_2 profiles

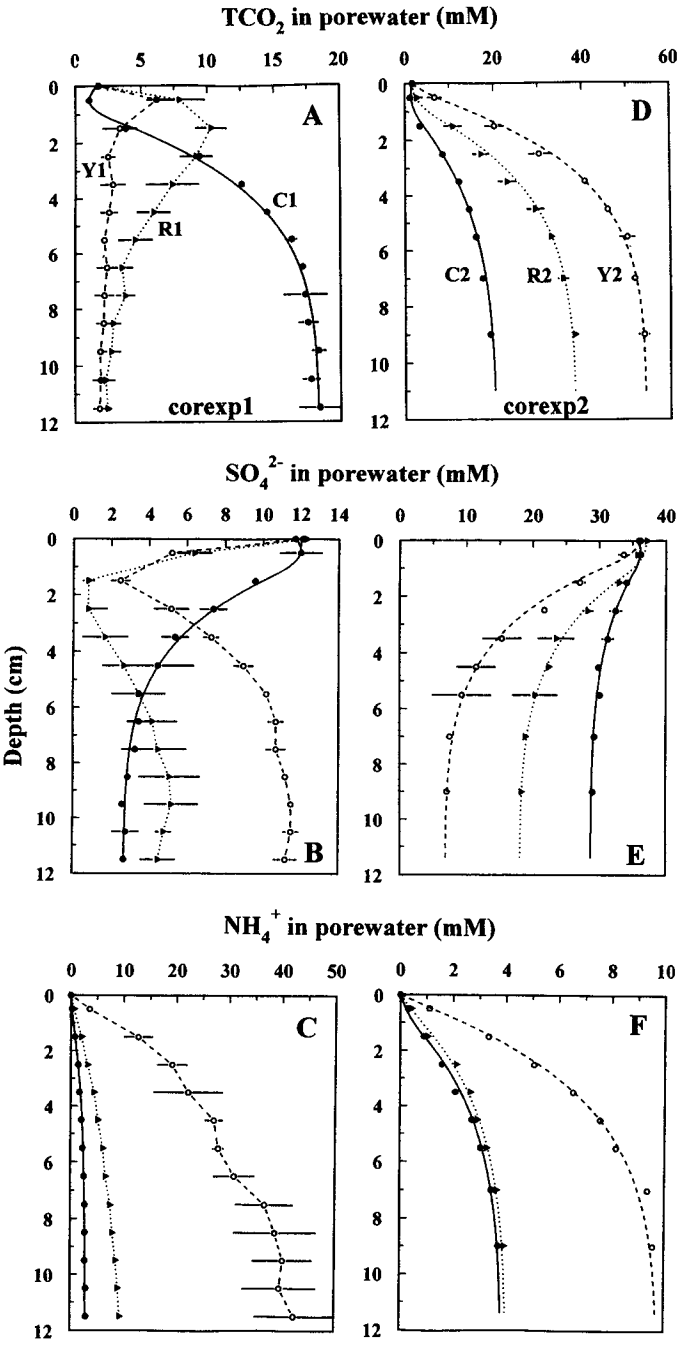

Figure 1. 'Corexp'. Depth profiles of (A) TCO_2 in *C*1-, *Y*1- and *R*1-cores; (B) SO_4^{2-} in *C*1-, *Y*1- and *R*1-cores; (C) NH_4^+ in *C*1-, *Y*1- and *R*1-cores; (D) TCO_2 in *C*2-, *Y*2- and *R*2-cores; (E) SO_4^{2-} in *C*2-, *Y*2- and *R*2-cores; (F) NH_4^+ in *C*2-, *Y*2- and *R*2-cores. Concentrations are given as mean ± SE of 3 cores. Smooth curves drawn for *C*1, *C*2, *Y*2, *R*2 are fitted according to the numerical solution of the two-layer diagenetic model (Eq. (1)) with the parameters shown in Table 5 (see text).

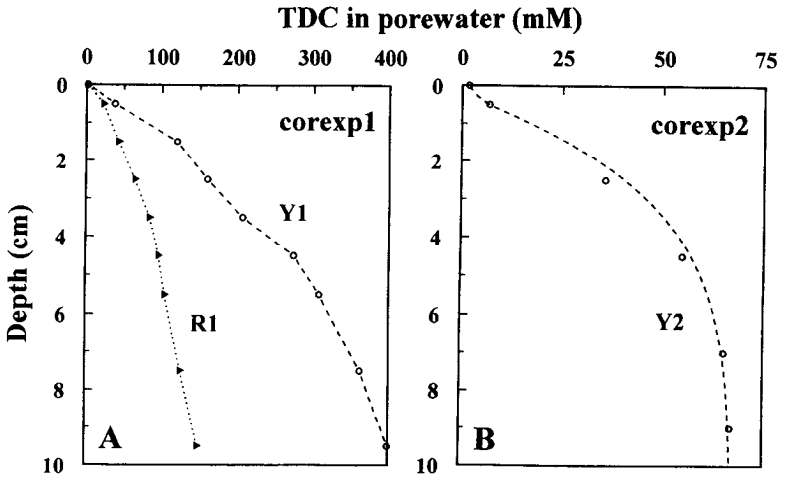

Figure 2. 'Corexp'. Depth profiles of TDC (total dissolved carbon); (A) in *Y*1- and *R*1-cores; (B) in *Y*2-cores. Symbols represent single determinations. Smooth curve drawn for *Y*2 is fitted according to the numerical solution of a two-layer diagenetic equation (Eq. (1)) with the parameters shown in Table 5 (see text).

(Figs. 1B,E), indicating a close coupling of the processes involving these two compounds. The C:S stoichiometry (1.8 ± 0.1 for all except *Y*1 and *R*1) was identical to the theoretical ratio for sulfate reduction when corrected for diffusion ($2 \times D_{SO4}/D_{HCO3}$).

Porewater profiles of NH_4^+ and TCO_2 were of similar shape when no DOC was detected (in *C*1, *C*2, and *R*2), except that NH_4^+ generally was less deflected in the uppermost cm (Figs. 1C,F). In *Y*1-, *R*1- and *Y*2-cores, on the other hand, NH_4^+ increased much steeper and more regularly than TCO_2, reaching concentrations of 42, 10 and 10 mM, respectively, around 10 cm depth. *C*1-, *C*2- and *R*2-cores only attained porewater concentrations of 3–4 mM at this depth. The nondimensional adsorption coefficient (K) of NH_4^+ was 0.21 in *C*-sediment, 0.11 in *Y*-sediment and 0.15 in *R*-sediment, indicating that 80–90% of all NH_4^+ was in dissolved form.

c. Core fluxes. Although rates of O_2 and TCO_2 flux generally were 2–3 times higher in corexp1 than in corexp2 ($p < 0.05$), the overall pattern remained the same in both experimental series (Table 2). Organic matter additions stimulated fluxes relative to control cores (*C*1 and *C*2) by 3.8–4.0 ($p < 0.001$) and 2.5–3.7 ($p < 0.01$) times for yeast *Y*1- and *Y*2-cores, and 2.0–2.2 ($p < 0.01$) and 1.6–2.0 ($p < 0.01$) times for *Ruppia* *R*1- and *R*2-cores. The flux of NH_4^+ in control cores behaved inconsistently with uptake in *C*1 and release in *C*2 of similar magnitude. The remaining cores all showed a release of NH_4^+ from the sediment. The 6 times higher organic matter addition in *Y*1 was evident as a 4.4 times higher NH_4^+ release than in *Y*2 ($p < 0.01$). No such impact of organic matter addition was evident in *R*1 and *R*2. The NH_4^+ flux

Table 2. Flux of O_2, TCO_2, and NH_4^+ across the sediment-water interface in *C*-, *Y*-, and *R*-cores. Values represent the average ± S.D. (n = 4). Positive values indicate flux from the sediment.

	C	*Y*	*R*
O_2-FLUX		mmol $m^{-2}d^{-1}$	
corexp1			
day 24	−41 ± 12	−160 ± 5	−84 ± 4
day 30	−40 ± 2	−153 ± 16	−88 ± 8
corexp2			
day 16	−18 ± 1	−66 ± 3	−36 ± 4
day 23	−20 ± 1	−63 ± 10	−33 ± 1
TCO_2-FLUX			
corexp1			
day 24	—	—	—
day 30	35 ± 6	137 ± 6	72 ± 3
corexp2			
day 16	25 ± 1	71 ± 6	39 ± 0
day 23	23 ± 3	57 ± 3	38 ± 2
NH_4^+-FLUX			
corexp1			
day 24	—	—	—
day 30	−1.2 ± 0.1	28.4 ± 1.7	1.7 ± 0.3
corexp2			
day 16	1.5 ± 0.2	6.6 ± 0.2	1.9 ± 0.2
day 23	0.8 ± 0.1	6.4 ± 0.1	1.8 ± 0.0

in these two treatments was not significantly higher than in *C2*. The within incubation date variation was generally equal to or even lower than the between incubation date variation.

d. Porewater solutes in jars. TCO_2 evolution in *C2j*-jars showed 2 linear phases during the 59 day period; an initial phase with a TCO_2 production of 240 nmol cm^{-3} d^{-1} (first 18 days) followed by a significantly slower phase ($p < 0.01$) with a rate of 52 nmol TCO_2 cm^{-3} d^{-1} until the end (Fig. 3A). After 14 days with rates similar to *C2j*-jars, carbon mineralization in *Y2j*- and *R2j*-jars increased rapidly (exponentially!), reaching maximum rates of 1455 nmol cm^{-3} d^{-1} at day 24–28 and 828 nmol cm^{-3} d^{-1} at day 18–24, respectively. Subsequently, rates decreased dramatically to 41 nmol cm^{-3} d^{-1} in *Y2j*-jars and 129 nmol cm^{-3} d^{-1} in *R2j*-jars.

Since DOC only was detected in *C2j*-jars within the first 8 days (2–3 mM), all produced DOC must have been mineralized to CO_2 after this time (Fig. 4A). In *Y2j*- and *R2j*-jars, however, a large accumulation of DOC occurred within the first 14–18 days (45 and 28 mM, respectively), coinciding with the initial period of relatively low carbon mineralization. Subsequently, DOC decreased rapidly to 3.5 mM from day 18

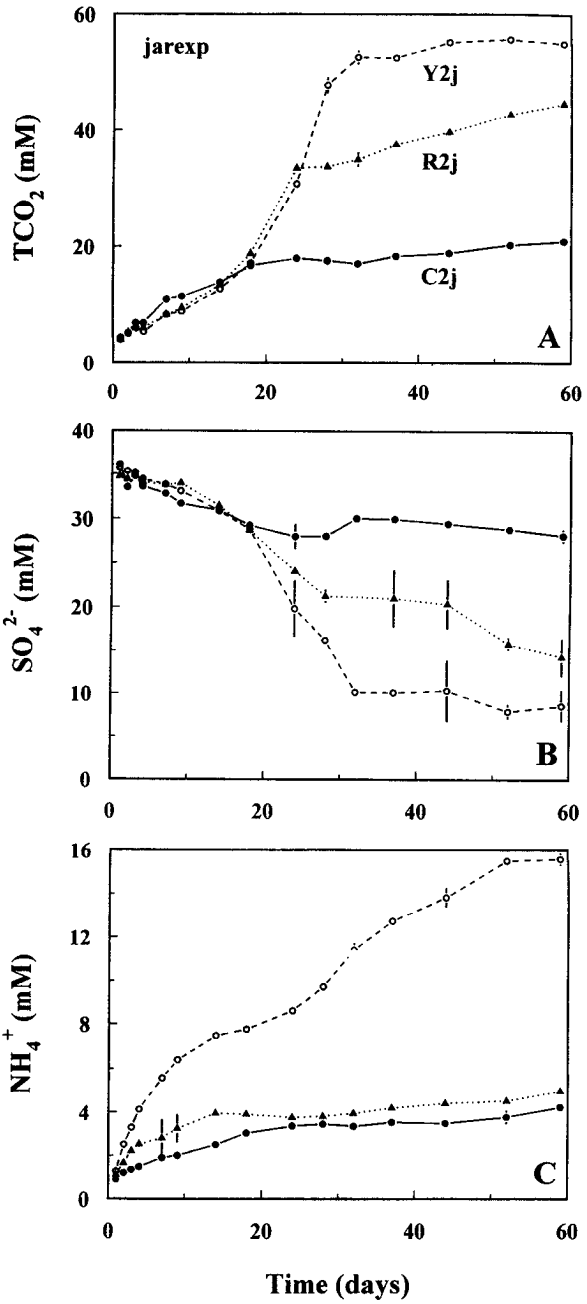

Figure 3. 'Jarexp'. Temporal pattern of (A) TCO_2; (B) SO_4^{2-}; and (C) NH_4^+ in *C2j*-, *Y2j*- and *R2j*-jars over 59 days. Concentrations are given as mean ± range of duplicates.

to 28. As the concomitant increase in TCO_2 only was 31 and 20 mM, total dissolved carbon (TDC = DOC + TCO_2) was lost from solution (Fig. 4B). After day 30 when carbon mineralization was low in *Y2j*-jars, DOC increased linearly to 37 mM at day 52. In *R2j*-jars, however, only a small and gradually decreasing DOC pool around 2–3 mM was found after day 28. Acetate generally accounted for about half of the measured DOC, except during the initial leaching phase in *Y2j*- and *R2j*-jars (28 and 26%) and during the steady phase after day 28 in *R2j*-jars (3–11%, Table 3). No CH_4 was detected at any time in the jars. About 3% of the initial POC pool was recovered as CO_2 in *C2j*-jars during the 59 day incubation period. In *Y2j*- and *R2j*-jars, however, 28 and 39% of the added POC pool were recovered as CO_2 at the end, whereas 60 and 39%, respectively, were recovered as TDC.

The temporal pattern of SO_4^{2-} in jars was, as in the core experiments, an almost exact mirror image of TCO_2 with a C:S stoichiometry (2.0 ± 0.1) similar to the expected ratio of 2 for sulfate reduction (Fig. 3B). It must be noted that the reduced carbon mineralization in *Y2j*-jars after day 28 was not caused by SO_4^{2-} depletion since 8–10 mM remained after this date.

The initial accumulation of NH_4^+ was rapid in all treatments (Fig. 3C). Nitrogen mineralization in *C2j*-jars, where DOC was low, showed the same 2 phase pattern as observed for TCO_2. When corrected for adsorption, the initial rate during the first 18 days was 39 nmol cm^{-3} d^{-1} followed by a significantly lower ($p < 0.01$) final rate of 8 nmol cm^{-3} d^{-1}. In *Y2j*- and *R2j*-jars the rate of NH_4^+ accumulation was almost linear after day 14 (69 and 8 nmol cm^{-3} d^{-1}), except for a depression from day 18 to 28 which coincided with the period of rapid TCO_2 production. A preferential mineralization of nitrogen occurred in *C2j*- and *Y2j*-jars as 5 and 62% of the initial and added PON pools were recovered as dissolved + adsorbed NH_4^+ after 59 days. In *R2j*-jars, on the other hand, nitrogen mineralization was slower than that of carbon as only 15% of the added PON pool was found as NH_4^+ at the end.

4. Discussion

a. Decomposition processes. Although the present study compares biogeochemical responses and reaction kinetics after addition of two different organic sources to sediment systems, it does not attempt to determine *in situ* decomposition rates. The experimental set-up was designed to remove the natural variability caused by factors, such as bioturbating macrofauna and roots of vascular plants. Mixing and homogenization may temporarily destroy the natural chemical, physical and biological structure of sediments, but it has been shown (Aller and Mackin, 1989; Sun *et al.,* 1991) that effects of such manipulations are short-term (days) relative to an incubation time of 1–2 months.

Generalized examples of the most important reactions involving carbon and nitrogen in the present sediment systems are listed in Table 4. The anaerobic processes, fermentation and sulfate reduction, dominated all systems as indicated by

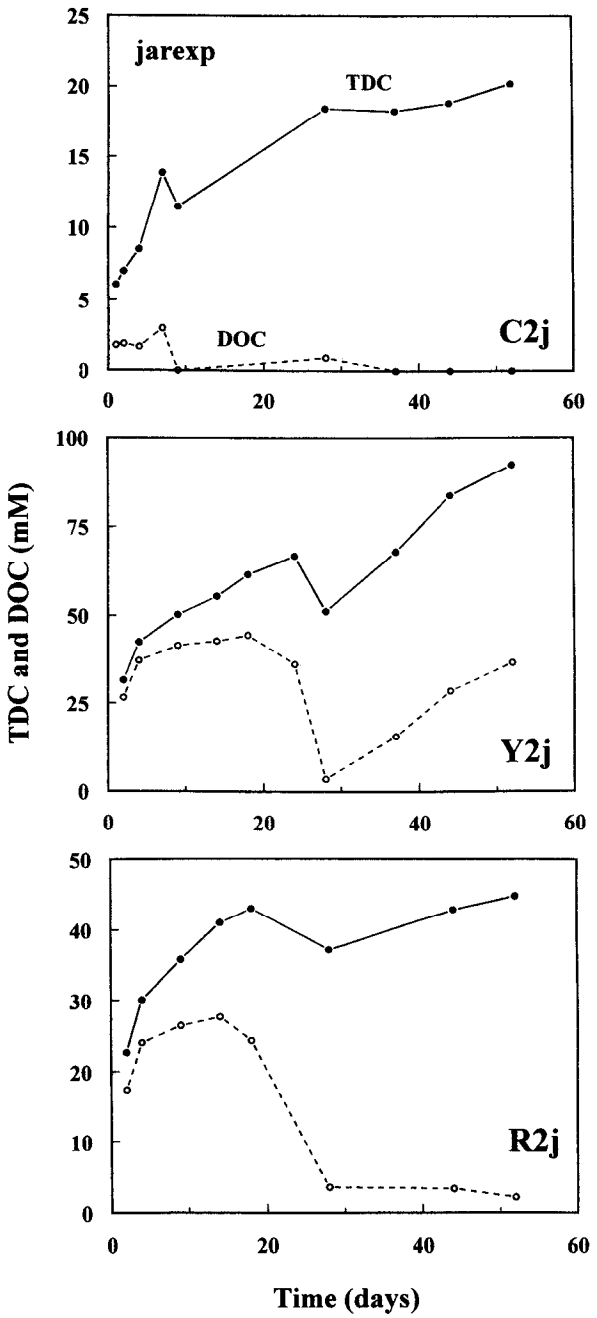

Figure 4. 'Jarexp'. Temporal pattern of DOC and TDC (=DOC + TCO_2) in *C2j-* (upper), *Y2j-* (mid) and *R2j-* (lower) jars over 59 days. Note difference in concentration scale.

Table 3. DOC and acetate concentration (mM C) at selected dates in jarexp. The fraction of DOC that is acetate is presented (%).

	C2j			*Y2j*			*R2j*		
	DOC	Acetate	%	DOC	Acetate	%	DOC	Acetate	%
day 1	1.8	0.8	43	21.3	5.9	28	14.1	3.6	26
day 8	ud	na	—	41.5	19.0	46	26.5	14.1	53
day 14	ud	ud	—	42.8	na	—	27.6	na	—
day 24	ud	na	—	36.2	na	—	3.5	0.4	11
day 32	ud	ud	—	15.5	8.3	54	ud	na	—
day 59	ud	ud	—	36.6	8.2	50	2.1	0.1	3

ud = under detection limit.
na = not analyzed.

the observed DOC concentration patterns and C:S stoichiometries. Other anaerobic respiration processes (e.g. denitrification and Fe^{3+} reduction) are generally assumed to be of minor importance in sedimentary carbon and nitrogen mineralization (Canfield, 1993) and were therefore ignored here. Aerobic processes (respiration, nitrification and sulfide oxidation) were only present the oxic upper zone of cores in corexp1 and corexp2. While the oxic zone probably reached a few millimetres into the surface sediment of control (*C*1 and *C*2) cores, this zone was extremely narrow in amended (*Y* and *R*) cores where *Beggiatoa* occasionally was visible on the surface. Aerobic respiration is assumed to account for only a few percent of the total carbon

Table 4. Generalized stoichiometric relationships of governing aerobic and anaerobic processes involving carbon and nitrogen in sediment (after Fenchel and Blackburn, 1979). The subscripts x and y in Eqs. (A) and (D) vary depending on the origin and age of substrates, and the ratio x:y is equivalent to the C:N ratio of the organic matter actually being decomposed.

A. Aerobic respiration:

$$(CH_2O)_x(NH_3)_y + x\,O_2 \rightarrow x\,CO_2 + x\,H_2O + y\,NH_3$$

B. Nitrification:

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

C. Sulfide oxidation:

$$HS^- + 2\,O_2 \rightarrow SO_4^{2-} + H^+$$

D. Fermentation:

$$(CH_2O)_x(NH_3)_y \rightarrow \frac{1}{2}x\,CH_3COO^- + y\,NH_4+$$

E. Sulfate reduction:

$$CH_3COO^- + SO_4^{2-} \rightarrow 2\,HCO_3^- + HS^-$$

metabolism in the present cores due to the limited oxygen penetration and even distribution of reactive organic carbon with depth in the sediment. The deflection of TCO_2 profiles in the uppermost cm of control (*C*1 and *C*2), *Y*2 and *R*2 cores, (Fig. 1A, D) however, indicated that CO_2 fixation must have occurred below the oxic zone, probably driven by e.g. chemoautotrophic sulfide oxidation with other electron acceptors than oxygen (e.g. nitrate). Aller and Yingst (1985) and McNichol *et al.* (1988) ascribed a similar subsurface minimum in CO_2 to carbon fixation associated with rapid sulfide, ammonium and metal oxidation near the sediment surface. Most O_2 consumed by coastal sediments is either directly or indirectly (via NO_3^-, Fe^{3+} or Mn^{4+}) involved in chemoautotrophic sulfide oxidation (Mackin and Swider, 1989; Aller and Rude, 1988).

The accumulation of TDC observed with depth and time in amended sediments (Figs. 2, 4) indicated that the primary microbial attack by hydrolyzers and fermenters in the anaerobic sediment could manage a rapid initial decay of even a large input of labile particulate organic matter. After 30–35 days, 30–50% of the added organic carbon in the 8–10 cm layer of both core experiments were recovered as TDC, of which up to 50% was acetate (Figs. 1, 2, Table 3). The anaerobic respirers (i.e. sulfate reducers), on the other hand, were inhibited by the presence of labile organic substrates in excess. An increase of POC by 140% (*Y*1) and 70% (*R*1) gradually hampered sulfate reduction with increasing depth and DOC concentration in the sediment, whereas addition of 20% (*Y*2) and 10% (*R*2) stimulated this process and thus carbon mineralization by a factor of 2–3. Holmer and Kristensen (1994) found similar responses in highly reactive, organic-rich fish-farm sediment with different amounts of fish food pellets added. The actual mechanisms responsible for the inhibition of sulfate reduction in highly amended sediments are not fully understood. Since hydrolysis and fermentation, which are mostly driven by exoenzymes (Somville and Billen, 1983), appeared unaffected, the actual site of inhibition may be located within the cells of the anaerobic respirers, e.g. membrane transport and electron transport system. Studies have shown that sulfate reducers can be inhibited by high levels of acetate (20–80 mM) combined with low pH (McCartney and Olezkiewicz, 1991; Reis *et al.,* 1992). The inhibition is strengthened by accumulation of hydrogen sulfide (2–3 mM), which is known as a respiratory poison (Holmer and Kristensen, 1994; Postgate, 1984).

Rates of anaerobic carbon mineralization (measured as changes in CO_2 and SO_4^{2-}) in the jar experiment with low-amended sediment varied up to two orders of magnitude within the first 30 days after organic additions (Figs. 3A,B). The initial rate of CO_2 production, which was similar in all treatments irrespective of DOC concentrations (Figs. 3,4), may represent the maximum initial capacity for DOC oxidation by the indigenous population of sulfate reducers. The subsequent steep increase of carbon mineralization in amended *Y* and *R* sediment, associated with a decrease in SO_4^{2-} and DOC, suggested that sulfate reducers after a 2 week lag phase

reached maximum activity within the third and fourth week. Westrich and Berner (1984) found a similar lag phase (5–10 days) of sulfate reduction after addition of planktonic organic matter to anoxic sediment. Carbon and nitrogen assimilation and incorporation due to rapid bacterial growth during the active phase in *Y2j*- and *R2j*-jars were evident from the net consumption of TDC and cessation of NH_4^+ production (Figs. 3,4). The higher efficiency of carbon incorporation (i.e. gross growth efficiency estimated as the difference between DOC consumption and CO_2 production) by sulfate reducers in *Y2j* (41%) than in *R2j*-jars (24%) suggested that the nitrogen-rich yeast substrate either provided the best growth conditions or supported the most efficient populations of sulfate reducers (Linley and Newell, 1984; Goldman *et al.,* 1987; Parkes *et al.,* 1993).

The relatively high initial rates of carbon mineralization (until day 18) and concentrations of DOC (until day 8) in *C2j*-jars were probably short term handling artifacts; mixing and enclosing the sediment may have released labile DOC (e.g. acetate) from the organic matrix and from dead organisms (e.g. meiofauna) keeping the anaerobic respirers at their maximum capacity (Kristensen and Blackburn, 1987). The lower rates of carbon mineralization found in *C2j* and *R2j* during the last 20–30 days, on the other hand, were controlled by the primary hydrolytic and fermentative attack on detritus particles as indicated by low DOC pools. The almost complete cessation of carbon mineralization in *Y2j*-jars after 30 days, however, must be caused by metabolite inhibition (e.g. by mM concentrations of free sulfide; not shown) as both sulfate and an increasingly surplus of DOC substrates were present.

A striking pattern from the present experiments is the uncoupling of terminal anaerobic carbon and nitrogen mineralization in the enriched *Y* and *R* treatments (Figs. 1B,C and 3A,C). The jar experiment showed that accumulation of DOC was associated with low carbon and high nitrogen mineralization in *Y2j* and *R2j*. This indicated that the added organic carbon was primarily hydrolyzed and fermented to small organic molecules (fatty acids, e.g. acetate), while organic nitrogen was mineralized to NH_4^+. Much of the NH_4^+ was probably produced by deamination of amino acids via urea during the fermentative decay of proteins (Lund and Blackburn, 1989). Although significant NH_4^+ production by sulfate reducers has been observed (Burdige, 1989; Hansen *et al.,* 1993), uncoupling between carbon and nitrogen mineralization in marine sediments has generally been implied (Jacobsen *et al.,* 1987; Burdige, 1991). The similar patterns of carbon and nitrogen mineralization (i.e. CO_2 and NH_4^+ production) observed in unamended sediments (Figs. 1,2) may be due to an indirect coupling: carbon respiration by e.g. sulfate reducers could keep pace of DOC and thus NH_4^+ production by fermenters. The limited increase in net NH_4^+ production in the low-amended *R*1 sediment compared with the controls (*C*1 and *C*2), was caused by low nitrogen availability (C:N of the added material was ca. 17);

nitrogen being recycled rapidly within the microbial community with no apparent net mineralization (Lancelot and Billen, 1985).

b. Reaction rates. Microbial reaction rates involving dissolved carbon and nitrogen in the present experimental systems were estimated by 3 approaches: (1) diagenetic modeling of porewater profiles in corexp1 and corexp2 ("open system"), (2) temporal changes in jars ("closed system"), (3) measured fluxes in corexp1 and corexp2.

(1) Diagenetic modeling. Reaction rates of DOC, CO_2, SO_4^{2-} and NH_4^+ in the "open system" core experiments were estimated from measured porewater profiles. When profiles are assumed to be the result of transport and reaction processes (i.e. no net sedimentation and compaction), the concentration of any solute, $C(x,t)$, in the porewater can be described by the one dimensional diffusion-reaction equation (Berner, 1980):

$$\frac{dC}{dt} = \frac{D_s}{(1+K)}\frac{d^2C}{dx^2} + \frac{R}{(1+K)} \tag{1}$$

where:

t = time
x = depth in the sediment
K = adsorption coefficient of solute
D_s = molecular diffusion coefficient in sediment
R = production or consumption rate of solute

Because the sediment in the present study was homogenized initially, reactivity of the organic matter basically should be constant with depth. However, chemoautotrophic sulfide oxidation caused reactions in the upper 1–2 cm to be different both in rates and direction from those in the deeper more reduced sediment as indicated by deflections of especially TCO_2 and SO_4^{2-} profiles (Fig. 1). The diffusion-reaction model can depict a two-layered case by separating the sediment column into an upper surface (Zone 1: $0 < x < L_1$) and a lower subsurface zone (Zone 2: $L_1 < x < L_2$), each with a specific reaction rate (R_1, R_2 assumed constant within each zone) and diffusion coefficient (D_1, D_2 assumed constant within each zone).

Steady state with respect to reaction and transport could not be assumed here, since the distance significantly influenced by diffusion in cores after 30–35 days only was 6–8 cm (Fig. 1) as indicated by the vertical shape of profiles below this depth (Aller and Mackin, 1989). Instead, transient state solute profiles were calculated from Eq. (1) using common numerical techniques (Hornbeck, 1975; Christensen *et al.,* 1984). By expressing Eq. (1) in terms of a centered-difference form for n vertical depth increments and arranging into a tridiagonal matrix, the time dependent profiles were obtained. Given the depths L_1 and L_2 of the two zones, the molecular diffusion coefficients, D_1 and D_2, the initial porewater concentration, C_{init}, the

overlying water concentration, C_T, the time, T, and the reactions rates, R_1 and R_2, the n finite difference equations were solved for concentration profiles using Gauss-Jordan elimination. The appropriate initial and boundary conditions are:

1. $t = 0, C = C_{\text{init}}, 0 < x < L_2$
2. $t > 0, C = C_T, x = 0$
3. $dC/dx = 0, x = L_2$

The depth L_2 was fixed at 15 cm (core depth), D_1 and D_2 were estimated from porosities according to Ullman and Aller (1982) and Li and Gregory (1974), C_{init} and C_T were measured values, and T is 30 (corexp1) and 35 (corexp2) days. Reaction rates (R_1 and R_2) and depth L_1 (Table 5) in the sediment were then approximated as the values that provide the best fit to the measured porewater profiles of all dissolved species (smooth curves in Figs. 1, 2). Unfortunately, no curve fittings and reaction rate estimates were possible for any compound in *Y*1- and *R*1-cores due to gradually inhibited sulfate reduction and thus variable reaction rates with depth in the sediment.

The estimated reaction rates in zone 1 were generally of opposite direction and up to 5 times higher than those in zone 2 (Table 5). Highest rates of CO_2 uptake in zone 1 and production in zone 2 occurred in *Y*2-; 2–3 times the rates in *R*2-, *C*1- and *C*2-cores. The rates of SO_4^{2-} generation in zone 1 were about 3 times higher in *Y*2- than in *C*1- and *C*2-cores. The consumption of SO_4^{2-} in zone 2 was related to CO_2 production with a C:S stoichiometry (1.9 ± 0.2) close to the theoretical ratio of 2 for sulfate reduction. Production estimates of TDC was hampered by the lack of a well defined diffusion coefficient. However, a good fit obtained for TDC in *Y*2 (smooth curve in Fig. 2B) based on an estimated D_{TDC} of 0.2–0.3 $\text{cm}^2\ \text{d}^{-1}$ (see below) provided a production estimate which, as expected, was higher (15%) than the estimated CO_2 production (Table 5). Net NH_4^+ consumption rate in zone 1 of control cores was twice the net production rates in zone 2, whereas the rates in zone 1 of amended cores were considerably lower than those in zone 2. NH_4^+ production in zone 2 was highest in *Y*2- with 2–3 times higher rate than in *C*1-, *C*2- and *R*2-cores.

(2) Jar estimates. Reaction rates of DOC, CO_2, SO_4^{2-} and NH_4^+ in the "closed system" jar experiment were estimated from the time-dependent change in concentrations (NH_4^+ was corrected for adsorption) and separated into the period before and the period after day 35. Although this verge was 17(*C2j*), 7(*Y2j*) and 11(*R2 j*) days after the visible transition between rapid and slow rates, it corresponded to the time when cores were sectioned and thus facilitates the comparison of the various estimates of reaction rates. Mean rates of CO_2 production, SO_4^{2-} consumption and NH_4^+ production in control (*C2j*) and *Ruppia* amended (*R2j*) jars before day 35 were consistently 2–4 times higher than during the period after (Table 5). Although DOC production was similar before and after day 35 in the yeast amended (*Y2j*) jars, the

Table 5. Depth of zone 1 (L_1), estimated sediment diffusion coefficients in zone 1 and 2 (D_{s1}, D_{s2}), initial concentration at time 0 (C_{init}), overlying water concentrations (C_T) and estimated reaction rates (R_1, R_2) of CO_2, SO_4^{2-}, NH_4^+ and TDC obtained from the diagenetic two-layer model (Eq. (1), only *C1, C2, Y2, R2*). Equivalent rates of CO_2 and NH_4^+ production, estimated from flux data is given as the average of the 15 cm sediment column (R_{flux}). Production of CO_2, NH_4^+ and TDC from 'jar' data is presented as both the average for the first 35 days ($R_{<35}$) and for the last 24 days ($R_{>35}$). Positive rates (R) indicate production of the various compounds.

	L_1 cm	D_{s1} cm^2d^{-1}	D_{s2} cm^2d^{-1}	C_{init} mM	C_T mM	R_1	R_2	R_{flux}	$R_{<35}$	$R_{>35}$
						nmol cm^{-3} d^{-1}				
CO_2										
C1	1.2	0.296	0.266	3.60	1.78	−855	173	233	na	na
C2	1.2	0.295	0.266	3.42	1.72	−748	158	160	155	52
Y2	0.6	0.348	0.259	3.04	1.68	−1880	508	427	558	41
R2	1.0	0.296	0.273	2.91	1.74	−1056	370	257	350	129
SO_4^{2-}										
C1	1.2	0.269	0.242	12.0	11.7	405	−107	na	na	na
C2	1.2	0.268	0.242	36.5	35.9	374	−74	na	−95	−25
Y2	0.6	0.275	0.235	37.1	36.2	1175	−298	na	−248	−27
R2	1.0	0.269	0.248	37.3	37.1	528	−198	na	−167	−84
NH_4^+										
C1	1.2	0.498	0.448	0.51	0.01	−63	34	na	na	na
C2	1.2	0.498	0.448	0.49	0.00	−81	41	8	35	15
Y2	0.6	0.510	0.435	0.55	0.00	−52	102	43	128	62
R2	1.0	0.498	0.460	0.50	0.00	−13	43	13	39	16
TDC										
Y2	0.6	0.28	0.23	8.1	1.68	−2975	585	340*	503	596

na = not available.
* = only TCO_2.

inhibition of sulfate reduction after day 35 resulted in a 9–14 times lower CO_2 production and SO_4^{2-} consumption than the period before day 35. Mean NH_4^+ production in *Y2j*-jars, on the other hand, was only 2 times faster before day 35 than after.

(3) Flux estimates. The per volume estimated rates of carbon and nitrogen mineralization from flux data of CO_2 and NH_4^+ presented in Table 5. (R_{flux}) were based on the assumption that measured fluxes (J) across the sediment-water interface were the integrated result of mineralization processes occurring in the entire 15 cm (L) sediment column and that reaction rates (R) were constant with depth: $J = -LR$. This is probably true in the reduced parts of most well mixed and homogeneous sediments. However, in the highly amended *Y1*- and *R1*-cores of corexp1, where reaction rates of especially CO_2 varied greatly with depth (Fig. 1), no reliable estimates were obtained.

The 3 approaches used here to estimate reaction rates in the sediment agree well and are within the range of rates reported from coastal sediments (Aller and Mackin, 1989; Mackin and Swider, 1989). The only serious discrepancy was the low NH_4^+ flux in cores. When NH_4^+ produced in the sediment diffuses upward across the oxic surface layer nitrification and subsequently denitrification significantly reduces the NH_4^+ efflux across the sediment-water interface (Lancelot and Billen, 1985). Fluxes of NH_4^+ are therefore not reliable measures of the depth-integrated nitrogen mineralization in sediments beneath an oxic water column. Both the "open system," diagenetic modeling technique and the "closed system" jar technique provided reliable estimates of reaction rates in non-bioturbated sediment. However, in coastal sediments, where benthic animals may cause solute transport processes to vary unpredictably (Kristensen, 1988; Aller and Mackin, 1989), the modeling approach may be less reliable. Here, the "closed system" approach is recommended.

In contrast to the measured efflux of CO_2, the profiles in the uppermost cm (especially control cores) indicated a flux into the sediment due to chemoautotrophy (Figs. 1A,D). Reaction rates obtained in zone 1 by the diagenetic model did in fact propose large CO_2 fixation rates in the upper 0.5–1.5 cm (Table 5). These estimates may even be underestimated as $CaCO_3$ dissolution was likely to occur due to undersaturation in the upper cm of most cores (data not shown). The POC enrichment found in the uppermost cm of most cores (Table 1) substantiated the presence of rapid chemoautotrophic CO_2 fixation. The low depth resolution of the measured CO_2 profiles (1 cm intervals), however, may have masked the true profiles and thus the exact depth distribution of various processes. If CO_2 was consumed in the upper cm and the sediment system at the same time released CO_2, steep changes in gradients must have occurred within this upper layer (Wei-Jun and Reimers, 1993). There may have been a shunt that transferred organic carbon (e.g. bacterial carbon) fixed by sulfide oxidizing chemoautotrophs in the lower oxic and suboxic zones to the sediment-water interface where a rapid mineralization occurred. The very rapid consumption of DOC in the upper 0.6 cm of *Y*2-cores substantiates this notion (Table 5). The CO_2 gradient needed to drive the flux of CO_2 could then be established close to the surface without any overall accumulation in the uppermost cm. However, further work is needed to fully elucidate the dynamics of CO_2 at high resolution close to the sediment-water interface.

c. Stoichiometry of decay. Berner (1977) has shown that if simple stoichiometric decomposition following first-order kinetics occurs, the C:N ratio of the mineralized organic matter may be ascertained from vertical porewater profiles of SO_4^{2-} and NH_4^+ using one dimensional diffusion-reaction models (Eq. (1)). In the present study, regeneration of carbon and nitrogen can be expressed directly from TCO_2 (TDC) and NH_4^+ profiles by a modification of the Berner (1977) approach. Since the solute profiles in the present non-steady state system clearly were controlled by

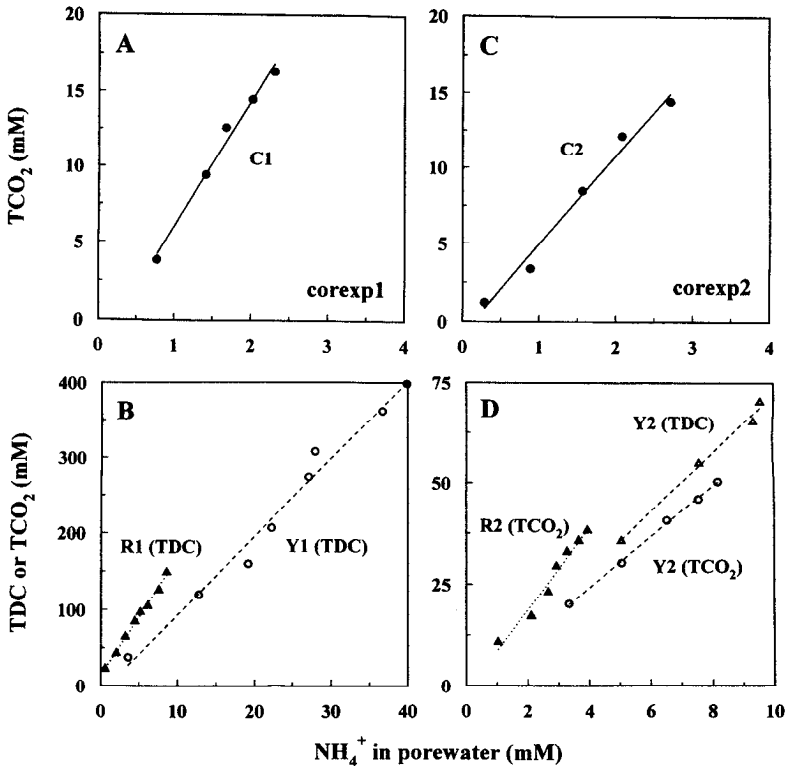

Figure 5. 'Corexp.' Relationship between profiles of TCO_2 or TDC and NH_4^+ in porewaters of (A) *C*1-cores; (B) *Y*1- and *R*1-cores; (C) C2-cores; (D) *Y*2- and *R*2-cores. Only data from the upper "open system" sediment section (0–6 cm) is presented with regression lines according to Eq. (2).

diffusion down to 6–8 cm depth, the upper part of the sediment can be considered an open, diffusion dominated zone. As no sedimentation and compaction occurred, and reaction rates are assumed constant with depth below ca. 1 cm, the reaction stoichiometry in the diffusion dominated zone can be described by:

open
$$\frac{R_c}{R_n} = \frac{D_{sc}}{D_{sn}} \frac{dC_c}{dC_n} \tag{2}$$

where subscripts c and n denote TCO_2 (or TDC) and NH_4^+, respectively; R is the reaction rate; dC_c/dC_n is the slope of a dissolved TCO_2 (or TDC) vs. NH_4^+ plot (Fig. 5); and D_s is sediment diffusion coefficient. The ratio of TCO_2 and NH_4^+ production rate (C:N ratio of organic matter being mineralized) is then approximately equal to the slope of the relationship between vertical porewater profiles of TCO_2 and NH_4^+ multiplied by the ratio (r) between sediment diffusion coefficients of the major ions, $r = D_{HCO3-}/D_{NH4+} = 0.6$.

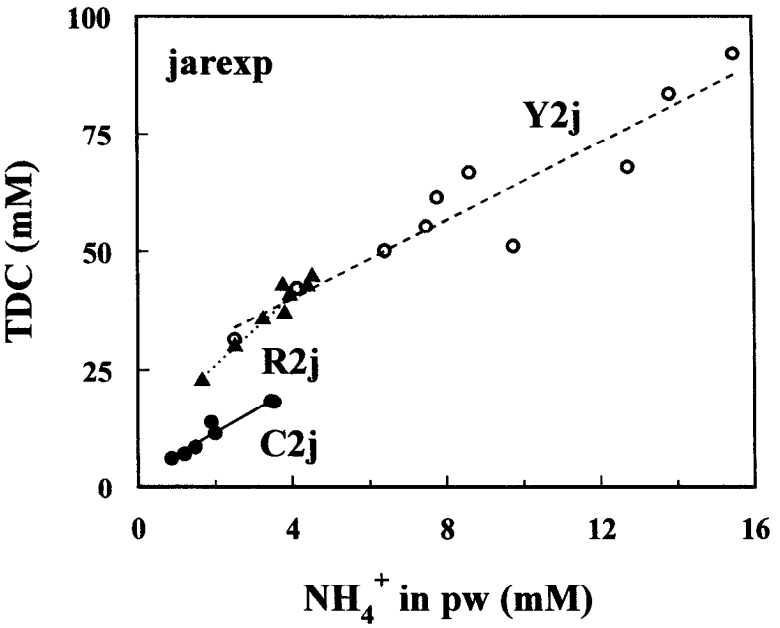

Figure 6. 'Jarexp'. Relationship between TDC and NH_4^+ concentration in *C2j*-, *Y2j*- and *R2j*-jars over 59 days.

In the jar experiment the sediment behaved like a closed system, with the following reaction stoichiometry:

closed
$$\frac{R_c}{R_n} = \frac{dC_c}{dC_n\,(1 + K_n)} \tag{3}$$

where K_n is adsorption coefficient of NH_4^+. In this case dC_c/dC_n is the slope of a relationship between time dependent accumulation of TDC and NH_4^+ in jars (Fig. 6).

Dissolved porewater TCO_2 (TDC) and NH_4^+ from the diffusion dominated "open system" zone in all cores and treatments showed an excellent linear relationship (Fig. 5). By including the diffusion correction (r), the C:N stoichiometry of organic matter decay was 3.5–5.0 in control cores (*C*1 and *C*2) (Table 6). These values were similar to the C:N ratios of reaction rates obtained directly from the curve fitting model (Eq. (1)) and the "closed system" jar experiment (Fig. 6), but generally much lower than estimates based on measured fluxes of CO_2 and NH_4^+.

Linear relationships between alkalinity or SO_4^{2-} and NH_4^+ have been obtained in a variety of anoxic marine sediments (e.g. Berner, 1977; Klump and Martens, 1987; Kristensen, 1993). These studies substantiate that although anaerobic carbon and nitrogen mineralization are not directly coupled, both processes occur simultaneously and appear to be indirectly coupled in most natural sediments. In sediments

Table 6. Carbon and nitrogen stoichiometry of organic matter decomposition (C:N ratios) determined as 1. the ratio of measured TCO_2 and NH_4^+ efflux from the sediment in 'corexp1 and 2' (Flux), 2. the ratio between reaction rate estimates of TCO_2 and NH_4^+ based on the diagenetic porewater model (Eq. (1)) in 'corexp1' and 'corexp2' (Model), 3. the slope of the porewater TCO_2 (TDC) and NH_4^+ relationship in 'corexp1 and 2', in the upper "open system" zone (Eq. (2)) corrected for differential diffusion (Plot) and 4. the ratio between TDC and adsorption corrected NH_4^+ accumulation through time in the 'jar' experiment (Jar). Data marked with * indicate that dissolved organic carbon is present and included in the data.

	C:N ratios		
	*C*1	*Y*1	*R*1
1. Flux	−29.7	4.8	42.4
2. Model	5.1	—	—
3. Plot	5.0	3.4*	5.5*
	*C*2	*Y*2	*R*2
1. Flux	20.9	9.8	20.8
2. Model	3.9	5.0 (5.7*)	8.6
3. Plot	3.5	3.7	6.0
	*C*2*j*	*Y*2*j*	*R*2*j*
4. Jar	3.9	3.7*	6.6*

enriched with reactive organic substrates, where sulfate reduction either is inhibited (e.g. *Y*1 and *R*1 cores) or not capable of consuming all produced DOC, the TCO_2 versus NH_4^+ relationship may not represent the stoichiometry of particulate organic matter decay. It is therefore important to gain knowledge on porewater DOC in sediments before any stoichiometric relationship of particulate organic matter decay is derived from inorganic mineralization products. Unfortunately, dissolved organic nitrogen (DON), which may be important in sedimentary nitrogen cycling (Lund and Blackburn, 1989), was not measured here.

The C:N stoichiometry of anaerobic fermentation processes in sediments with high DOC content can only be derived from vertical porewater profiles (*Y* and *R* cores in Fig. 5) when an estimate of the diffusion correction ($r = D_{TDC}/D_{NH4+}$) and thus the average diffusion coefficient of the TDC mixture is available. Such estimate, although crude, can be obtained here from *Y*2 sediment by the use of Eq. (2) when NH_4^+ in both jars and cores is assumed to be derived solely from fermentation processes, and the C:N stoichiometry of TDC and NH_4^+ production in *Y*2*j*-jars and *Y*2-cores is similar irrespective of the actual DOC contribution to TDC. The R_{TDC}:R_{NH4+} stoichiometry in *Y*2*j*-jars (when corrected for NH_4^+ adsorption) was 3.7 (Table 6), whereas the slope of TDC vs. NH_4^+ in *Y*2-cores was 7.1 (Fig. 5), which implies that the diffusion correction in cores should be $r = 3.7/7.1 = 0.52$. Accordingly, the diffusion coefficient of the TDC mixture in *Y*2-cores was: $D_{TDC} = D_{NH4+} \times$

0.52 = 0.23 $cm^2\ d^{-1}$. When D_{TDC} is assumed the average diffusion coefficient of the individual components in the TDC mixture, D_{DOC} can be estimated roughly by knowing D_{HCO3-} (0.259 $cm^2\ d^{-1}$) and the contribution of DOC to TDC (25 ± 4% in Y2-cores): $D_{DOC} = (D_{TDC} - D_{HCO3-} \times 0.75)/0.25 = 0.14\ cm^2\ d^{-1}$. This is equivalent to a fatty acid with 15–20 carbon units (molecular weight (MW) of 500) according to the empirical relationship between D_{DOC} and MW presented by Burdige *et al.* (1992). Since MW of DOC in porewaters of unamended sediments usually is between 1000 and 10000 (Burdige *et al.,* 1992), the high proportion of acetate and other short chain fatty acids produced from the added fresh plant materials must be responsible for the low average porewater MW found for DOC here. In *Y*1- and *R*1-cores, where almost all TDC is DOC, a C:N stoichiometry of 3.4 and 5.5, respectively (Table 6), is achieved using a diffusion correction (r) of 0.30–0.35 based on the D_{DOC} estimated above.

A source of error in C:N stoichiometry estimates based on porewater profiles of TCO_2 and NH_4^+, is carbonate dissolution/precipitation processes (Boudreau *et al.,* 1992). Although $CaCO_3$ dissolution and precipitation may have occurred in the present study (data not shown) several lines of evidence suggest that these processes were of minor importance: (1) The excellent linearity of TCO_2 versus NH_4^+; (2) The agreement between the theoretical and measured C:S ratios of TCO_2 and SO_4^{2-} changes; (3) The generally good agreement between the various stoichiometry estimates.

The C:N ratios of 4–5 estimated from both porewater and reaction rates in control cores indicate that nitrogen was mineralized preferentially to carbon since the C:N ratio of the bulk particulate organic pool in the sediment was around 10. A similar pattern has been observed in many coastal sediments (Klump and Martens, 1987; Boudreau *et al.,* 1992; Kristensen, 1993). The low porewater C:N ratios found in control sediment may reflect the occurrence of a small, but labile and nitrogen-rich detritus pool in the sediment. The production and concentration of benthic diatoms at Fællesstrand, where the sediment was sampled, is generally high (Kristensen, 1993). When surface sediment was homogenized for use in the unamended trials, decay of protein-rich diatoms dominated for some time. The stoichiometry estimates indicated that proteins with a C:N of ca. 4 were degraded preferentially during the first 60 days. Since there was similarity in the C:N ratio of degraded organic matter between control and yeast amended cores, proteins were also the likely substrate for degradation in the yeast amended sediment. The almost two times higher C:N ratio of decomposition products in *R*-cores is in accordance with the high C:N ratio (17) of the *Ruppia maritima* detritus. Accordingly, Kristensen (1994) found that the ratio of carbon and nitrogen lost from decaying *Ruppia maritima* in sediment-free slurries is 19. The organic compounds being degraded in *R*-cores during the first 60 days is probably a mixture of proteins and structural carbohydrates, like cellulose.

5. Conclusions

By the use of "open system" and "closed system" sediment incubations, the present study has demonstrated that:

1. Primary microbial attack by hydrolyzing and fermentative bacteria in anaerobic sediment can manage a rapid initial decay of even a large input of labile organic matter. Anaerobic respirers, like sulfate reducers, are inhibited by the presence of labile organic substrates in excess.

2. Carbon and nitrogen mineralization in anaerobic sediments are uncoupled; carbon is mineralized by respiring heterotrophs (e.g. sulfate reducers) and nitrogen by the fermenting microbial community. This may result in accumulation of DOC associated with low carbon and high nitrogen mineralization in organic-rich sediments.

3. Rapid CO_2 fixation (by e.g. sulfide oxidizing chemoautotrophs) in the uppermost oxidized zone of sediments can explain a commonly observed TCO_2 deficiency in the upper few cm of marine sediments.

4. Both "open system" and "closed system" sediment incubations provide reliable and comparable estimates of reaction rates and C:N stoichiometry in non-bioturbated sediment.

5. C:N stoichiometry of organic matter decomposition can be deduced from inorganic mineralization products when no DOC is present in the porewater. If present, however, DOC must be included to obtain the true stoichiometry of particulate organic matter decay.

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