Vol. 141: 217–228, 1996 | MARINE ECOLOGY PROGRESS SERIES Mar Ecol Prog Ser | Published October 3

Composition and fate of dissolved organic carbon derived from phytoplankton detritus in coastal marine sediments

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ABSTRACT: The influence of fresh phytoplankton detritus on carbon mineralization was studied by burying phytoplankton detritus (40 g C m^{-2}) in the surface layer (0 to 2 cm) of sediment cores collected at an intertidal location in Odense Fjord, Denmark. The enriched sediment showed increased carbon mineralization during the first 20 d of incubation at 15°C compared to control cores. The depth integrated sulfate reduction rates (5.9 ± 1.6 mmol m^{-2} d^{-1}) were not significantly different from the control sediments (4.0 ± 1.4 mmol m^{-2} d^{-1}), and were responsible for less than 26% of the total sediment metabolism (44.9 to 95.4 mmol m^{-2} d^{-1}). About 10% of the added detritus was mineralized during the 1 mo incubation. A parallel anaerobic incubation of the sediment with a similar amendment showed rapid carbon mineralization and high accumulation of dissolved organic compounds (DOC) and short-chain fatty acids. About 19% of the added phytoplankton detritus was mineralized within 1 mo in this incubation. The effect of sediment depth and temperature on carbon mineralization was studied by incubation of amended and unamended surface sediment (0 to 2 cm) and deep sediment (8 to 10 cm) at a winter (5°C) and a summer temperature (15°C). Sulfate reduction was the main terminal mineralization process accounting for 71 to 100% of the CO_2 production, and attained its highest rates in the surface sediment at 15°C. Acetate was an important component of the DOC pool, especially in the deep layer, where up to 100% of the DOC pool consisted of acetate. The net particulate organic carbon decomposition (DOC and total CO_2 production) was similar in all amended sediments, whereas the terminal mineralization (sulfate reduction) was related to sediment depth and temperature. This indicates that the initial hydrolysis and fermentation processes are dependent on the organic matter source rather than temperature.

KEY WORDS: DOC · Sulfate reduction · Detritus Decomposition pathways

INTRODUCTION

Eutrophication of coastal zones has caused higher sedimentation rates of organic matter during the past several decades (Jonsson & Carmen 1994). However, it is not fully understood whether increased input of organic matter to sediments will lead to increased preservation or instead induce higher mineralization and thus regeneration of nutrients back to the water column. Sedimentation of organic matter to oxic sediment layers often leads to a rapid mineralization (Hansen & Blackburn 1991, 1992), and the presence of benthic organisms may stimulate this mineralization (Andersen & Kristensen 1991, Kristensen et al. 1992, Aller 1994). Transformation of organic matter in anaerobic sediments occurs exclusively through microbial processes with sulfate as the most important electron acceptor for terminal mineralization (Canfield 1994, Moeslund et al. 1994). Numerous factors affect the degradation of organic matter under anaerobic conditions, such as temperature, the composition of organic matter (e.g. lignins and aromatic compounds only degrade slowly), physical and chemical properties of the sediments (e.g. particle surface area), and the pool size of dissolved organic compounds (DOC) (Henrichs & Doyle 1986, Haddad et al. 1992, Keil et al. 1994, Mayer 1994, Henrichs 1995, Kristensen et al. 1995).

One of the major sources of organic matter in coastal sediments is detritus derived from phytoplankton. The decomposition of plankton detritus is relatively fast, as

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the content of labile proteinaceous structural compounds is high (Henrichs & Doyle 1986). Most studies of organic matter degradation in sediments have concentrated on the terminal mineralization processes with associated regeneration of nutrients, while only a few have examined the intermediate pathways in the degradation process (Alperin et al. 1994, Holmer & Kristensen 1994a, b). Alperin et al. (1994) observed large seasonal variation in the production and composition of DOC caused by fluctuations in the hydrolysis and fermentation processes. As the terminal mineralization is limited by the supply of low-molecular-weight organic electron donors, changes in hydrolysis and fermentation activities may regulate the overall decomposition.

The purpose of the present study was to examine the decomposition of phytoplankton detritus in a low organic coastal sediment with focus on the carbon cycling. Phytoplankton detritus, corresponding to a normal spring bloom sedimentation, was mixed to a depth of 2 cm in sediment cores. Decomposition was followed by measuring total sediment metabolism [fluxes of O_2 and and total CO_2 (TCO_2)], flux of DOC across the sediment-water interface, anaerobic microbial activity (sulfate reduction), pools of particulate organic matter (carbon, nitrogen and acid-digestible carbon) and pools of dissolved carbon compounds [DOC, short chain fatty acids (SCFA), TCO_2] over a period of 1 mo. A parallel anaerobic decomposition experiment with the phytoplankton detritus was performed in 2 sediment layers, 1 at the same depth as the amended layer in the sediment cores (0 to 2 cm) and 1 at a greater depth (8 to 10 cm). The latter incubation allowed an examination of the time-dependent changes in the anaerobic decomposition processes. The temperature effect was evaluated by incubations at a winter (5°C) and a summer temperature (15°C).

MATERIALS AND METHODS

Sampling site and sediment collection. Sediment was collected with acrylic core liners (80 mm i.d., 30 cm length) in February 1995 from the shallow (0.5 to 1.5 m) southeastern part of Odense Fjord on the island of Fyn, Denmark. The sediment was composed of silty sand with an organic content of 0.68‰ dry wt particulate organic carbon (POC) and 0.06% dry wt particulate organic nitrogen (PON). The average C:N ratio was 14.7. The phytoplankton primary production in the area is on average 50 to 200 g C m^{-2} yr^{-1} (Fyns Amt 1995). The benthic primary production has not been measured at the location, and was considered low at the time of sampling. The benthic fauna is dominated by *Nereis diversicolor* (1576 ind. m^{-2}; B. Christensen pers. comm.). During sampling the water temperature was 4°C and the salinity 5‰.

Sediment core experiments. Fifteen cores were collected with a 20 cm sediment depth and 10 cm overlying water. The cores were then defaunated in the laboratory by bubbling the water column with N_2 and leaving the cores anoxic overnight. On the following day all visible animals present on the sediment surface were removed. After re-aeration, the cores were kept open with continuous stirring for 6 d in an incubation system (250 l reservoir) at a salinity of 13.5‰ [the median (1976 to 1993) salinity at the location in summer, Fyns Amt (1995)] and a constant temperature of 15°C (the mean summer temperature). One day before the experiment was started, the top sediment layer (0 to 2 cm) was removed from 12 of the cores. To 6 of the top layers, 188 µg C g sed wet wt^{-1} and 29 µg N g sed wet wt^{-1} (= 40.0 g C m^{-2} and 6.2 g N m^{-2}) of fresh phytoplankton detritus (see below) were added, and 6 cores were unamended. Subsequently, the sediment (unamended and amended) was transferred back into the cores. Three cores were sectioned for examination of initial parameters (see below). On the following day the first flux incubations were made as follows. From the reservoir, 3 replicate samples were taken for initial measurement of O_2, TCO_2 and DOC (filtered through pre-combusted GF/F filters) concentrations. Tests showed no significant difference between the concentration of O_2, TCO_2 and DOC in the reservoir and in the cores ($p < 0.005$, $n = 9$). The cores were closed with lids and incubated for 3 to 4 h and final samples were taken from the overlying water in each core. Samples for O_2 and TCO_2 were analysed within 12 h, and DOC was kept frozen in pre-combusted glass vials until analysis. Flux measurements were repeated 12 times during the experimental period of 34 d.

Sulfate reduction, pore water and sediment characteristics. Sulfate reduction was measured by carefully sub-coring (i.d. 26 mm) the experimental cores (i.d. 80 mm). These smaller cores were injected with 2 µl $^{35}S\text{-}SO_4^{2-}$ through silicone-stoppered holes at 1 cm intervals down to 12 cm and incubated for 6 h at 15°C. The incubation was terminated by sectioning the cores at 1 cm intervals from 0 to 6 cm and 2 cm intervals down to 10 cm depth into 1 M zinc acetate. The sediment of the large core was sectioned for pore water extraction (SO_4^{2-}, TCO_2, DOC, SCFA) and sediment characteristics (density, water content, organic content). Pore water was obtained by centrifugation (1500 rpm, 1250 × *g*; 10 min) through pre-combusted GF/F filters. Samples for TCO_2 were analysed within 12 h, and those for SO_4^{2-}, DOC and SCFA were kept frozen until analysis. Cores were handled and sectioned initially (INI), after 14 d (MID) and at the end of the experiment (FIN) (34 d).

Sediment jar incubations (SEDINC). A number of cores were collected to obtain surface (SURF, 0 to 2 cm) and deep (DEEP, 8 to 10 cm) sediment for jar incubations. Sediment from each layer was homogenised in N_2 atmosphere in a glove bag. To half of the sediment was added 112 µg C phytoplankton detritus (see below) per gram wet sediment and half was kept unamended. Approximately 40 g sediment (both amended and unamended) was transferred into each of forty 20 ml glass vials. The vials were filled completely, closed with screw cap lids, sealed with tape and kept anoxic (buried in anoxic sediment) during the incubation (53 to 56 d) at 5 and 15°C. Pore water was obtained from 2 replicate jars twice a week by centrifugation (1500 rpm, 1250 × *g*; 10 min) through pre-combusted GF/F filters. Pore water was sampled for TCO_2 (1 ml sample fixed with 10 µl of 125 mM Hg Cl_2 to precipitate sulfides), SO_4^{2-} (400 µl sample fixed with 50 µl of 0.1 M HCl to liberate sulfides), DOC and SCFA (1 ml sample of each fixed with 50 µl of 0.1 M HCl to prevent precipitation during freezing). Samples for TCO_2 were analysed within 12 h, and SO_4^{2-}, DOC and SCFA were kept frozen until analysis. Sediment characteristics were determined (density, water content, organic content) at the start and end of the experiment.

Phytoplankton detritus. Phytoplankton detritus was obtained from a continuous culture of the flagellate *Rhodomonas* sp. The culture had 5 million cells l^{-1}, which were harvested, centrifuged (3000 rpm, 2500 × *g*; 10 min) and frozen. The algae had a POC content of 23.6% dry wt and PON content of 3.6% dry wt, with a C:N ratio of 7.6. The algal material (1 l of culture) was resuspended into artificial sea water (13.5‰), and 50 ml of this suspension was added per 1000 g sediment.

Analysis. Oxygen was measured by the standard Winkler technique, and TCO_2 was measured by the flow injection analysis of Hall & Aller (1992). SO_4^{2-} was measured by ion-chromatography with a Dionex autosuppressed anion-system (IonPac AS4A-SC column and ASRS suppressor). DOC was measured with a total organic carbon analyzer (Shimadzu TOC-5000) on acidified samples. SCFA were measured using a Dionex IonPac-Exclusion column (ICE-A56) and 0.4 mM hydrochloric acid as eluent followed by an Anion Micromembrane Suppressor (AMMS-ICE, Donex Corp.) with 5.00 mM tetrabutylammonium hydroxide as regenerant (Bøtte & Jørgensen 1992, Holmer & Kristensen 1994b).

Sediment density was obtained by measuring the weight of a known sediment volume, and water content was measured as the weight difference after drying overnight at 105°C. Wet sediment was hydrolyzed in 6 M HCl for 24 h at 110°C to obtain the total amount of hydrolyzable organic carbon (THOC) The hydrolyzates were analyzed as DOC (see 'Sediment jar incubations (SEDINC)'). POC and PON were determined in pre-dried (105°C) sediment, and inorganic carbon and nitrogen were measured in ignited (520°C) sediment according to Kristensen & Andersen (1987) using a Carlo Erba 1100EA elemental analyzer

RESULTS

Flux in sediment cores

The O_2 and TCO_2 fluxes in control and detritus-amended cores decreased gradually from high initial fluxes (O_2: 126.1 ± 26.3 and 153.0 ± 21.9 mmol m^{-2} d^{-1}, respectively; TCO_2: 149.6 ± 38.4 and 191.6 ± 24.5 mmol m^{-2} d^{-1}, respectively) towards a constant level after 22 d of incubation (O_2: 28.4 ± 4.0 and 31.6 ± 2.5 mmol m^{-2} d^{-1}; TCO_2: 50.5 ± 3.2 and 60.0 ± 4.6 mmol m^{-2} d^{-1}) (Fig. 1). The fluxes were 14 to 35% higher for O_2 and

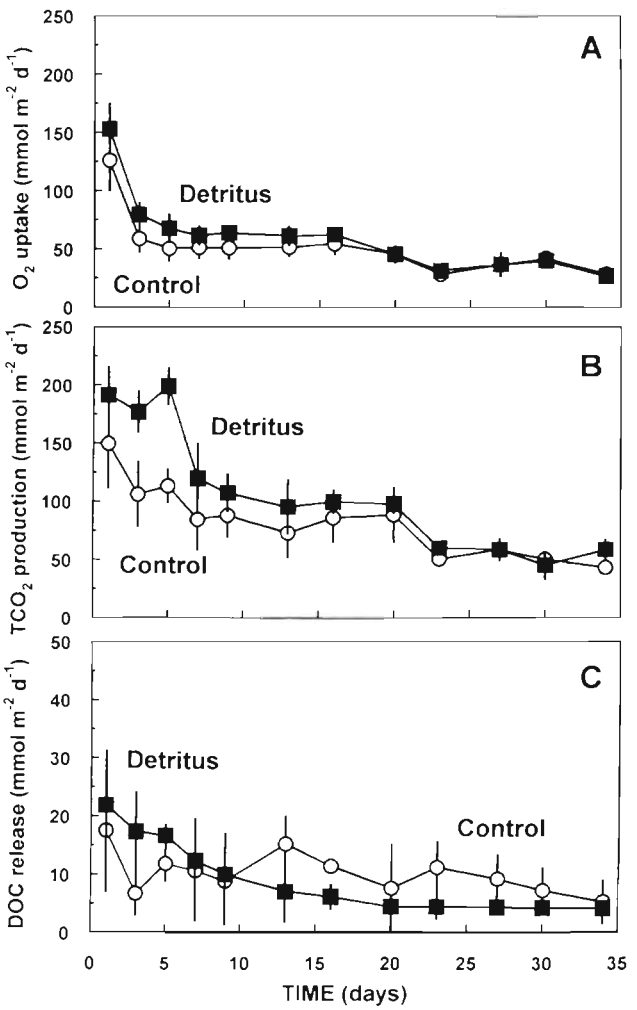

Fig. 1 Time dependent changes in benthic fluxes. (A) Oxygen uptake, (B) TCO_2 production and (C) DOC efflux. All flux values are reported as mean ± SE of 3 replicate cores

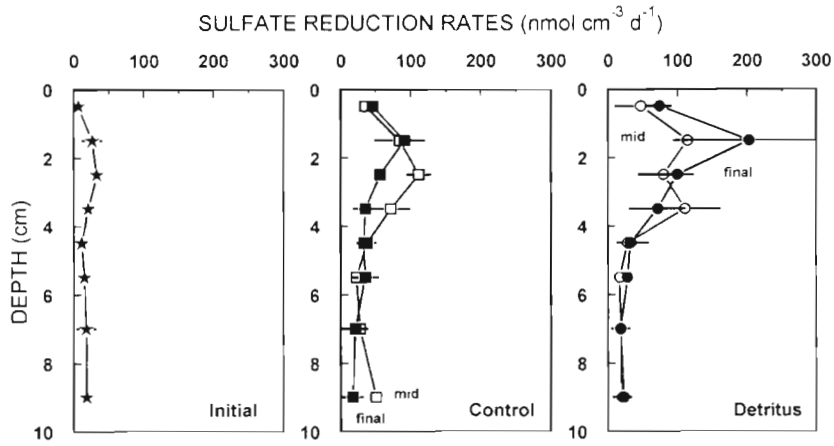

Fig. 2. Depth profiles of sulfate reduction rates from the initial (left panel), mid and final sampling in the control (middle) and detritus-amended (right) sediment. Each value represents the mean ± SE of 3 replicate cores

16 to 75% higher for TCO_2 in the amended cores relative to the control cores during the first 20 d of incubation, whereas no difference was evident during the rest of the experiment. The flux of DOC showed large variability (11 to 85% variance among replicates), and in the control cores the temporal pattern was erratic with rates between 6.7 and 18.7 mmol m^{-2} d^{-1} (Fig. 1). In the amended cores, DOC release rates were high initially (21.9 mmol m^{-2} d^{-1}) and decreased to a constant level of ~4.5 mmol m^{-2} d^{-1} after 20 d of incubation.

Anaerobic activity in sediment cores

The sulfate reduction rates increased in all the cores throughout the incubation (Fig. 2). Initially, sulfate reduction rates showed a maximum at 2 to 3 cm depth (32.7 ± 9.0 nmol cm^{-3} d^{-1}) with low rates (6.3 ± 2.9 nmol cm^{-3} d^{-1}) in the surface layer and almost constant rates (11.2 to 18.1 nmol cm^{-3} d^{-1}) below this depth. The control cores maintained similar depth profiles during MID measurement, but the maximum rates increased to 111.6 ± 17.6 nmol cm^{-3} d^{-1}. At the end, however, the maximum was displaced upwards to the 1 to 2 cm layer with rates of 91.2 ± 8.0 nmol cm^{-3} d^{-1}. Sulfate reduction rates (SRR) in the amended cores also showed a 1 cm upward displacement of the maximum with time. The rates in amended sediment above 4 cm (max. 202.8 ± 96.1 nmol cm^{-3} d^{-1}) were generally twice those obtained in the control cores. Rates in the amended cores at the MID sampling were not significantly different than at the end at any depth ($n = 6$, $p > 0.1$).

The depth integrated SRR was initially low (1.8 ± 0.4 mmol m^{-2} d^{-1}) and increased with time in all the cores to between 4.0 and 5.9 mmol m^{-2} d^{-1} (Table 1), although no significant effect of detritus addition ($F = 0.817$, $p = 0.392$) and time (MID and FIN) ($F = 0.442$, $p = 0.525$) was evident (tested with a 2-way ANOVA).

Table 1 Depth integrated sulfate reduction rates (ISRR) in control and detritus-amended sediment cores during the incubation. Rates are given as mean of 3 cores (±SE)

	ISRR (mmol m^{-2} d^{-1})	
	Control	Detritus
Initial	1.83 ± 0.36	–
Mid	5.69 ± 1.06	5.52 ± 2.35
Final	4.02 ± 1.35	5.92 ± 1.62

Organic carbon sources in the sediment cores

The average particulate organic matter content in control sediment was: POC, 568 ± 100 µmol g dry wt^{-1}, and PON, 39 ± 9 µmol g dry wt^{-1}; there was no obvious trend with depth (Fig. 3). The C:N ratio increased with depth from 12.5 to 17.3. THOC (average 223 ± 53 µmol g dry wt^{-1}) showed similar scatter with depth as did POC and PON accounting for 31 to 50% of the POC (Fig. 3). There was no apparent difference in POC and PON between the surface layer of control cores and amended cores at MID and FIN sampling (Table 2). Only THOC was consistently higher in the 0 to 2 cm layer of the amended cores (314 to 462 µmol C g dry wt^{-1}), compared to the control cores (180 to 206 µmol C g dry wt^{-1}). In phytoplankton detritus almost all POC (>99%) was found as THOC (Table 2). Analysis of particulate organic compounds was only done in single cores so it is not possible to statistically test if there were significant changes with incubation time and treatment.

Pore water pools in sediment cores

The TCO_2 profiles (Fig. 4) showed concentrations increasing from the surface values (2.0 mM) to 3.3 mM

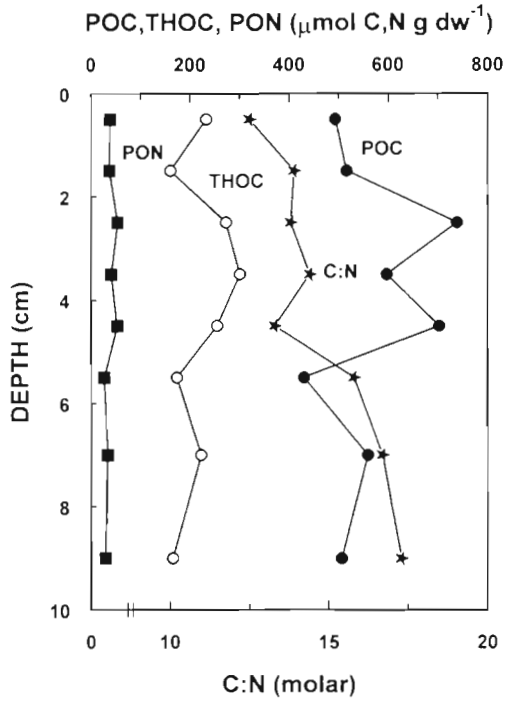

Fig. 3. Depth profiles of initial particulate organic carbon (POC) and nitrogen (PON), total hydrolyzable carbon (THOC) and C:N ratios (molar). POC and THOC are given in µmol C g dry wt^{-1} and PON in µmol N g dry wt^{-1}. Each value represents 1 core

in the initial cores, 3.3 to 4.0 mM in the control and 3.9 to 4.9 mM in the amended cores at 10 cm depth. No differences were evident between MID and FIN samplings. The DOC concentration was approximately 0.8 mM in the surface water, and in the initial cores increased with depth to a maximum of 2.1 mM. In the control cores a similar depth profile was obtained at the MID and FIN sectioning although some scatter was evident. In the amended cores the MID sampling showed higher values throughout the core (1.6 to 2.6 mM), but these pools were lower at the FIN sampling (<2.0 mM). Pools of SCFA were below the detection limit (<5 µM) in all cores during the entire experiment.

Respiration rates in SEDINC

The anaerobic microbial activity and TCO_2 production in the jar incubations were calculated (Table 3) using least-squares linear regression analysis on the time dependent changes in sulfate and TCO_2 concentrations (Figs. 5 & 6). However, the changes in sulfate were variable in the control sediments (Fig. 5), leading to weak correlations (R^2 = 0.55 to 0.92). The estimated SRR were similar (86 and 50 nmol cm^{-3} d^{-1}) to the rates measured by the ^{35}S technique in intact sediment cores

Table 2. Sediment organic content given as particulate organic carbon (POC) and nitrogen (PON), and extracted by acid digestion (THOC), in the upper sediment layers at the INI (initial), MID (after 14 d) and FIN (after 34 d) sectioning of the sediment cores, and initially in the sediment jars (as only loss-on-ignition was measured at the end) and in the phytoplankton detritus (*Rhodomonas* sp. concentrated culture)

	POC (µmol C g dry wt^{-1})	PON (µmol N g dry wt^{-1})	C:N (molar)	THOC (µmol C g dry wt^{-1})
Control INI				
0–1 cm	493	39	12.5	233
1–2 cm	516	37	13.9	167
2–3 cm	739	54	13.8	273
Control MID				
0–1 cm	513	41	12.5	222
1–2 cm	531	41	13.0	180
2–3 cm	651	52	12.5	256
Control FIN				
0–1 cm	572	49	11.8	214
1–2 cm	598	45	13.3	206
2–3 cm	604	50	12.1	267
Detritus MID				
0–1 cm	527	43	12.3	239
1–2 cm	611	55	11.1	462
2–3 cm	475	41	11.5	260
Detritus FIN				
0–1 cm	512	38	13.5	247
1–2 cm	566	40	14.2	314
2–3 cm	563	50	11.3	207
Sediment jars				
Surface				
Control	505	38	13.3	244
Detritus	543	43	12.6	282
Deep				
Control	506	29	17.3	166
Detritus	544	34	16.0	204
Phytodetritus	19638	2579	7.6	19518

at the same depth intervals (35 and 51 nmol cm^{-3} d^{-1}). The TCO_2 production was close to 2 times higher than the SRR (1.6 to 2.6 times), except in SURF control sediment at 5°C (7.8) and in DEEP control sediment at 15°C (1.0). When sulfate reduction is the main mineralization pathway, a 2:1 relationship of TCO_2 production to sulfate reduction is expected. The deviations from this expected ratio may either be due to poor estimates of SRR or TCO_2 production, or to other processes producing or consuming TCO_2 during the incubation. The TCO_2 production rates were about 4 times higher in the SURF layer compared to the DEEP section, and these rates doubled with the 10°C increase in temperature. The SRR were equal in SURF and DEEP sediment at 5°C, and these rates increased by 6 and 3 times in SURF and DEEP layers, respectively, with the 10°C increase in temperature.

Table 3. Sulfate reduction rates (SRR) and TCO_2 production rates in the sediment jar incubations, estimated from least-squares linear regression analysis of the time dependent changes in sulfate and TCO_2 concentration. The day of sulfate depletion is estimated from the linear least-squares analysis (*x*-axis intersection)

	SRR (nmol cm^{-3} d^{-1})	R^2	Day of sulfate depletion	TCO_2 (nmol cm^{-3} d^{-1})	R^2
5°C					
Surface					
Control	14	0.84	–	110	0.96
Detritus	321	0.92	33	576	0.89
Detritus after sulfate depletion				0	
Deep					
Control	16	0.55	–	26	0.72
Detritus	130	0.92	–	223	0.95
15°C					
Surface					
Control	86	0.92	–	221	0.96
Detritus	482	0.97	19	932	0.91
Detritus after sulfate depletion				81	0.93
Deep					
Control	50	0.63	–	50	0.97
Detritus	338	0.97	30	662	0.98
Detritus after sulfate depletion				9	0.03

The amendment enhanced the sulfate reduction and TCO_2 production by 5.6 to 23.0 and 4.2 to 13.2 times, respectively, compared to the control sediment. Sulfate was respired rapidly in the surface sediment, leading to sulfate depletion after 32 and 20 d at 5 and 15°C, respectively. In DEEP sediment, SRR were 30 and 60% of the SURF rates, and sulfate was only depleted at 15°C after 30 d of incubation. The TCO_2 production rate decreased about 90% after sulfate was depleted in SURF sediment.

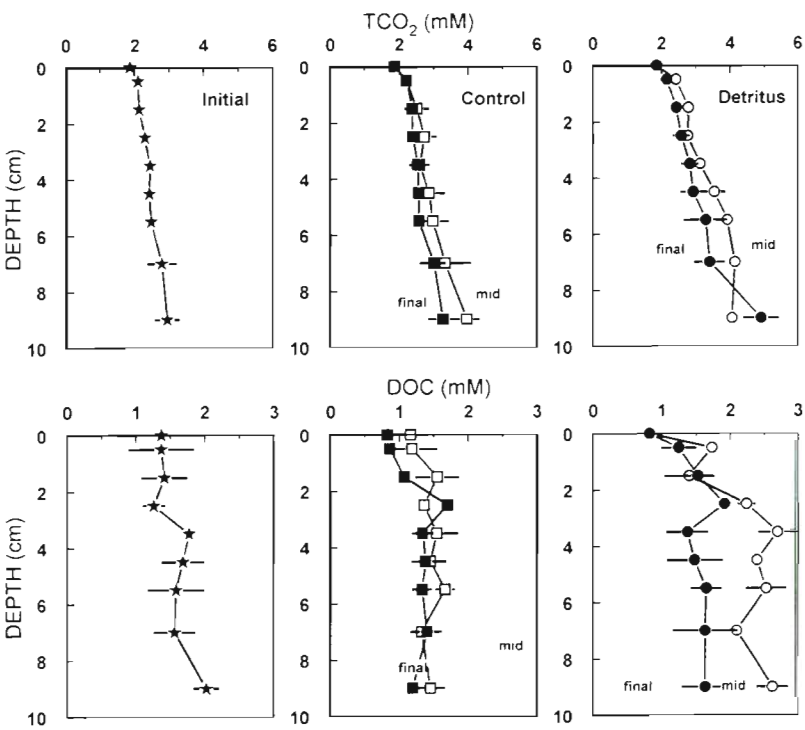

Fig. 4. Depth profiles of pore water carbon compounds at the initial sampling (left), and for the control (middle) and detritus-amended (right) sediment for the mid and final sampling. Upper panels: TCO_2 concentration; lower panels: DOC concentration. Each value represents the mean ± SE of 3 replicate cores

Organic carbon sources in SEDINC

The amendment was on the same order of magnitude as in the sediment cores, and the total amount of POC was increased by 7.5% in both SURF and DEEP sediment, PON by 13 and 17% and THOC by 16 and 23% in SURF and DEEP sediment, respectively (Table 2). The C:N ratio was lower in both SURF and DEEP sediment in the amended jars (12.6 and 16.0) compared to the control (13.3 and 17.3).

Dissolved organic pools in SEDINC

The initial DOC concentration in the homogenized SEDINC sediment differed from the depth profiles of the undisturbed sediment cores, possibly

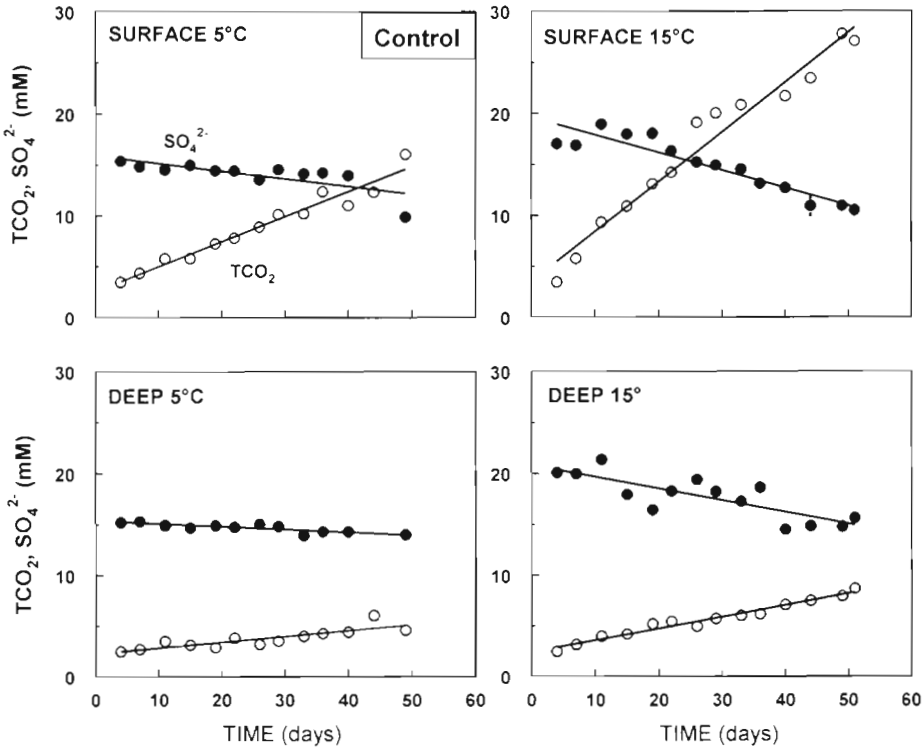

Fig. 5. Time dependent changes in sulfate (SO_4^{2-}) and TCO_2 concentration in jar incubations with control sediment taken from surface (SURFACE) layers (0 to 2 cm) and deeper (DEEP) layers (8 to 10 cm) and incubated at 5 and 15°C. Each value represents the mean ± SE of 2 replicate jars. Solid lines indicate the best fit with least-squares linear regression of the time dependent changes

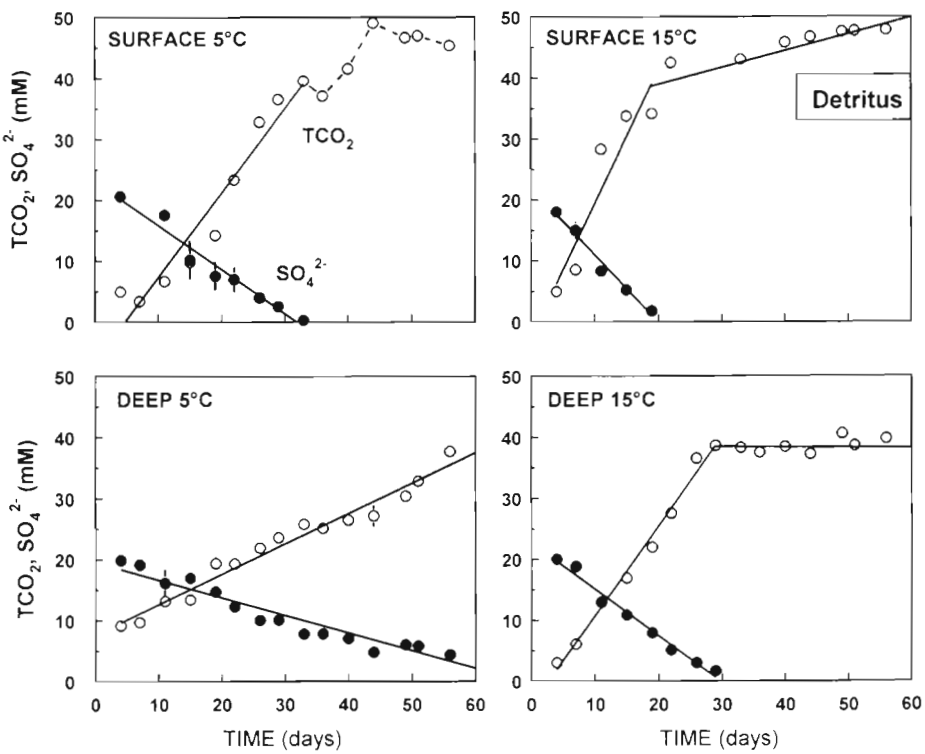

Fig. 6 Time dependent changes in sulfate (SO_4^{2-}) and TCO_2 concentration in jar incubations with detritus-amended sediment taken from surface layers (0 to 2 cm) and deeper layers (8 to 10 cm) and incubated at 5 and 15°C. Each value represents the mean ± SE of 2 replicate jars. Solid line indicates the best fit with least-squares linear regression of the time dependent changes. In incubations where sulfate was depleted, 2 lines were fit for the TCO_2 concentration, i.e. 1 before and 1 after sulfate depletion. It was not possible to fit a line for the surface layer at 5°C after sulfate depletion (dashed line)

due to spatial heterogeneity at the sampling location and handling of sediment in the laboratory. In controls, the initial concentration was higher in SURF sediment (1.5 to 2.0 mM) and lower in DEEP sediment (0.6 to 1.0 mM) compared to cores (Fig. 7). In SURF control sediments at 5°C, DOC increased initially to 3.2 mM after which it remained constant for the next 30 d. At 15°C DOC showed irregular changes with time at a level

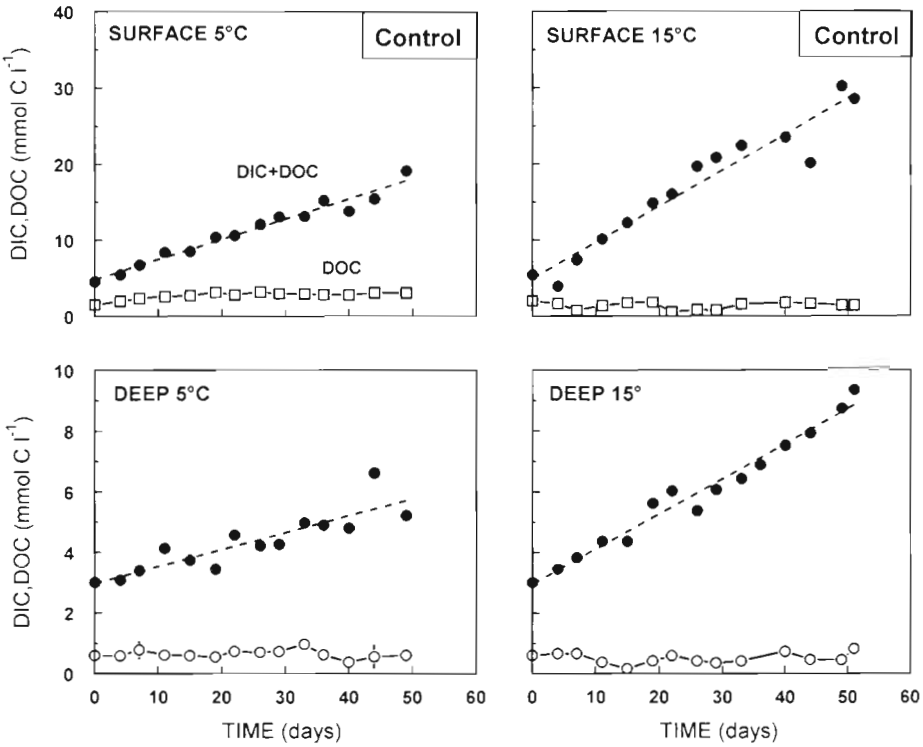

Fig. 7 Time dependent changes in DOC and total organic and inorganic carbon (DIC+DOC) concentrations in the jar incubations with control sediment taken from surface layers (0 to 2 cm) and deeper layers (8 to 10 cm) and incubated at 5 and 15°C. Each value represents the mean ± SE of 2 replicate jars. Total organic and inorganic carbon is calculated by adding DOC and TCO_2 (in Fig. 5) concentration. Dashed line indicates the best fit with least-squares linear regression of the time dependent DIC+DOC accumulation. Notice the different scales for SURFACE and DEEP

30 to 50% lower than at 5°C. In DEEP control sediments at 5°C, a slight increase in DOC was evident during the first 35 d of incubation, after which the concentration decreased. Total net POC decomposition after 53 d of incubation in the controls was estimated from the time dependent changes in the total pool of dissolved carbon ($DOC+TCO_2$) and was 3.8 and 8.8 µmol C g dry wt^{-1} at 5 and 15°C in SURF sediment and 1.3 and 2.7 µmol C g dry wt^{-1} in DEEP sediment, respectively.

The amendment with detritus increased the DOC pool several fold, resulting in initial concentrations of 8.4 to 9.1 mM in both SURF and DEEP sediment (Fig. 8). The time dependent changes in DOC at 5°C was most significant in DEEP amended sediments, where an increase was observed until Day 33 (26.3 mM) followed by a stable period of 15 d and another increase during the last 8 d (38.5 mM). In SURF amended sediment at 5°C the DOC concentrations increased slightly with time reaching 14.2 mM by the end of the experiment, and no changes were associated with sulfate depletion at Day 30. At 15°C, a maximum appeared in the DEEP sediment after 15 d of incubation (22.4 mM). The maximum was followed by a decrease over the next 15 d to a constant level (5.7 to 9.5 mM), which was much lower than at 5°C. In the amended SURF sediment at 15°C, DOC concentrations remained initially constant (8.9 to 10.1 mM) while sulfate was present. After sulfate depletion at Day 20, DOC increased to 25.3 mM until Day 45, after which there was a rapid decrease to 6.2 mM at Day 56.

In the control sediments the concentration of SCFA remained below the detection limit (<5 µM) throughout the incubation period (data not shown). In the amended sediment, however, acetate was the most important (>99%) component of the measured SCFA (Fig 8). Acetate pools were initially generally low (<100 µM) in all sediments. In SURF sediments at 5°C, acetate concentrations increased to 71% of the total DOC pool at the end. At 15°C acetate showed the same temporal trend as DOC and generally accounted for 22 to 60% of the total DOC pool. In DEEP sediments at 5°C acetate was the primary component (>72%) of the DOC pool from Day 15 to 45, but the importance of acetate decreased towards the end of the experiment. Acetate contribution to the total DOC pool at 15°C was high from Day 7 to 27, and acetate concentrations and contribution to the DOC pool were generally higher in DEEP sediment than SURF sediment (2 to 6 times), except at the end of the 15°C experiments. Acetate concentrations may have been overestimated due to the use of an acidic eluent which may cause liberation of organically complexed SCFA. The DOC, however, may have been underestimated due to recalcitrant DOC resistant against high temperature catalytic combustion (Alperin & Martens 1993).

Total net POC decomposition in amended sediment after 53 d of incubation, estimated from the accumula-

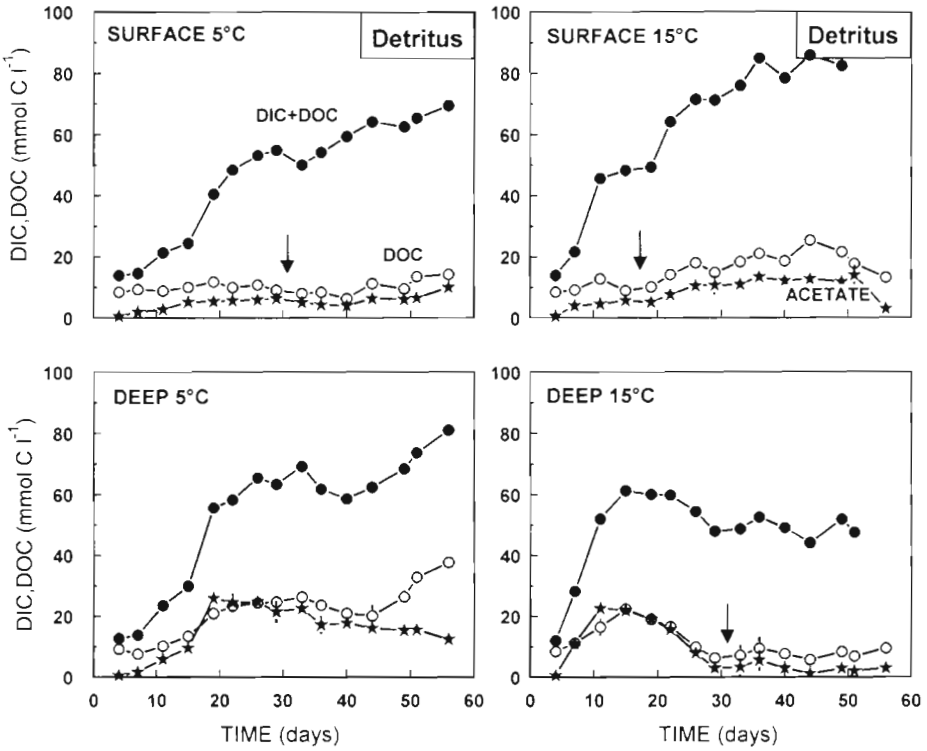

Fig. 8. Time dependent changes in concentrations of acetate, DOC and total inorganic and organic carbon (DIC+DOC) in the jar incubations with detritus-amended sediment taken from surface layers (0 to 2 cm) and deeper layers (8 to 10 cm) and incubated at 5 and 15°C. Results are given in carbon equivalents (mmol C l^{-1}) and each value represents the mean ± SE of 2 replicate jars. Total organic and inorganic carbon is calculated by adding DOC and TCO_2 concentration. Arrows indicate the time of sulfate depletion

tion of dissolved carbon (DOC+TCO_2), was 20.5 and 24.9 µmol C g dry wt^{-1} in SURF sediment, and 24.1 and 17.6 µmol C g dry wt^{-1} (calculated after 22 d as DOC+TCO_2 decreased during the rest of the incubation) in DEEP sediment at 5 and 15°C, respectively.

DISCUSSION

Addition of fresh phytoplankton detritus enhanced the O_2 and CO_2 fluxes during the first 3 wk of incubation, indicating a rapid initial decomposition of microalgae (Hansen & Blackburn 1991, 1992, Andersen & Kristensen 1992). Although total CO_2 production was 30.8% higher when the sediments were treated with phytoplankton detritus, the efflux of DOC (9 to 22% of TCO_2 production) and the pools of dissolved organic carbon in the pore waters were similar irrespective of the treatment. The turnover of DOC was rapid in the pore waters in both treatments, as the pools of DOC remained low (the pool from the SRR was estimated to turn over at a rate of 1 d^{-1}) and the SCFA concentrations were below the detection limit during the experiment. A similar lack of DOC enrichment has previously been found after addition of microalgae to surface sediments (Andersen & Kristensen 1992). Microbial DOC uptake and DOC adsorption to particles have been suggested as the major factors removing DOC in sediments (Andersen & Kristensen 1992). High efflux of DOC in both control and amended cores suggests that loss across the sediment-water interface can be an important sink of DOC in sediments. A similar flux pattern has been found in estuarine sediments (Burdige & Homstead 1994).

The depth integrated SSR were not significantly enhanced by the addition of phytoplankton detritus, although rates increased through time in amended sediment. Experimental studies have shown a time lag of 1 to 2 wk before sulfate reducing bacteria have adjusted to new conditions (Westrich & Berner 1984, Holmer & Kristensen 1994a, Kristensen & Hansen 1995). Sulfate reduction was, however, an important process in organic matter decomposition in this sediment, as sulfate reduction accounted for 15 to 26% of the CO_2 production in all treatments. SSR were low compared to those found for other coastal sediments (Thode-Andersen & Jørgensen 1989, Moeslund et al. 1994), and sulfate reduction is usually considered to account for more than 50% of the CO_2 production (Mackin & Swider 1989). The sediment remained visibly oxidized to 1 cm depth despite the addition of phytoplankton detritus, suggesting that other electron acceptors (O_2, NO_3^-, Fe^{3+} and Mn^{4+}) were important in the POC decomposition at this location (E. Kristensen pers. comm.). Field studies of spring bloom sedimentation (Moeslund et al. 1994) and sedimentation of fish farm waste products (Holmer & Kristensen 1992, 1996) have shown highly stimulated SSR. In these studies the fresh organic matter was present at the sediment-water interface, causing a high microbial activity close

to the sediment surface, and associated depletion of electron acceptors such as oxygen, nitrate and iron (Hansen & Blackburn 1991, 1992, Moeslund et al. 1994).

POC decomposition under anaerobic conditions

Sulfate reduction was the main terminal carbon mineralization process in amended jars. The rates were stimulated by the addition of phytoplankton detritus and attained 69 to 141% higher levels than in amended layers in sediment cores. The terminal mineralization was reduced considerably upon sulfate depletion, as the accumulation of CO_2 nearly stopped. Accumulation of methane was not measured during this study, but others have found methanogenesis after sulfate depletion under similar experimental conditions in organically rich sediments (Alperin et al. 1994, Holmer & Kristensen 1994a).

The low pools of DOC relative to the high production of CO_2 in control jars indicate a rapid turnover of DOC (4 to 11% d^{-1}). The acid-digestion of the sediment showed that 32 to 48% of POC was hydrolyzable. However, only between 0.8 and 3.6% of this THOC pool was utilized during the incubation, with the least in the DEEP sediment layer at low temperature and the highest in the SURF sediment at high temperature. The stimulation of decomposition rates by addition of fresh phytoplankton detritus indicates that the terminal mineralization was limited by the supply of electron donors (i.e. organic matter). Limitation of carbon mineralization by availability of organic matter has been observed previously (Canfield 1994, Kristensen et al. 1995). Sediment was collected at the end of the winter when the mineralization as well as the input of fresh detritus had been low for several months. Alperin et al. (1994) observed a winter net accumulation of organic matter which was available as soon as the temperature increased. This also seems to be the case in the surface of control sediments at the present location. The mineralization was 4 times higher in the SURF sediment than in the DEEP sediment although the THOC was only 32% higher. The organic matter present in DEEP sediment was probably less degradable, as indicated by the high C:N ratio of 17.3 compared to 13.3 in SURF sediment (Henrichs & Doyle 1986, Burdige 1991, Kristensen et al. 1995).

DOC accounted for a high proportion of the organic carbon at the beginning of the amended jar incubations because of leaching from phytoplankton cells after freezing Despite similar initial concentrations, the time dependent changes in DOC differed in the examined depth intervals at the 2 temperatures. The main process for the terminal mineralization in the incubations, sulfate reduction, was an important sink of DOC. Due to high sulfate reduction in the amended SURF sediment, the concentration of DOC was low and remained at a constant level until sulfate was depleted. In the DEEP sediment, changes in the DOC pools were more dynamic, with distinct maxima at higher levels than found in the SURF sediment. This suggests that DOC was utilized as fast as it was produced in the SURF sediment, whereas the initial production was higher than consumption in the DEEP sediment. Subsequently, DOC was depleted at a rate similar to sulfate reduction and CO_2 production rates, indicating that the production of new DOC was reduced.

The temperature dependence of terminal mineralization by sulfate reduction (Q_{10} = 1.5 to 2.6) was less than previously found in coastal sediments (Q_{10} = 2.5 to 3) (Moeslund et al. 1994). The pattern of DOC accumulation, however, was similar at the 2 temperatures with constant concentrations in the SURF sediment, and a concentration maximum in the DEEP sediment, although the maximum was reached earlier at 15°C. This is evidence that the spatial accumulation pattern of DOC is controlled by sulfate reduction.

The gradually increasing proportion of acetate in the DOC pool initially suggests that high-molecular-weight components of DOC were degraded to smaller compounds like acetate, while at the same time new DOC was continuously being produced as sulfate reducers removed acetate. The conversion of DOC to acetate was almost complete in the DEEP layer, where acetate accounted for 100% of the DOC pool within the first 8 and 19 d at 15 and 5°C, respectively. As only changes in pool sizes have been measured the exact rates of acetate production and consumption cannot be evaluated. The high proportion of acetate in the DEEP sediment indicates that production due to rapid hydrolysis and/or fermentation initially dominates. Later in the incubation, acetate was rapidly depleted at a rate corresponding to the SSR, indicating a shift in the production-consumption balance. The terminal mineralization of DOC was strongly dependent on sulfate reduction, as the CO_2 production immediately ceased when the sulfate was depleted.

The total net POC decomposition was almost the same in all the incubations, except for a lower decomposition in the DEEP layer at 15°C. The main difference among treatments was the accumulation of DOC, which was higher at 5°C indicating that the POC decomposition was less complete. The hydrolysis and/or fermentation of fresh organic matter seems to be less sensitive to temperature changes than the terminal mineralization (sulfate reduction). Alperin et al. (1994) also found a low temperature dependence for hydrolysis and fermentation processes.

Comparison of phytoplankton detritus decomposition in sediment cores and anaerobic jars

The decomposition of phytoplankton detritus is rapid in intact cores of this organically poor sandy sediment. The mineralization within 1 mo after addition of phytoplankton to the surface layer corresponds to 2 to 8% of the annual phytoplankton primary production at the location. Although the phytoplankton detritus was mixed into the upper 2 cm layer, there was only a minor stimulation of the SSR compared to unamended cores. There was a high efflux of DOC across the sediment-water interface, and no enhancement of DOC pools in the sediments compared to unamended cores.

In the anaerobic jar experiment the mineralization of phytoplankton detritus through sulfate reduction was stimulated apparently without any delay and the accumulation of dissolved organic pools was higher than in the sediment cores. Noticeable differences between the 2 incubation methods are the diffusion conditions and the availability of electron acceptors. In the jar experiment, DOC was not lost through diffusion across the sediment-water interface and sulfate reduction was favored due to depletion of other electron acceptors. Also, the unamended sediments showed higher accumulation of DOC and lower turnover rates in jars. There was a major difference between surface and deeper sediments, where the mineralization was most rapid in the surface layer, probably due to the presence of a reactive organic pool accumulated during the winter period at the location. Increasing the temperature by 10°C had a significant effect on the terminal mineralization, whereas the net POC decomposition was almost the same in all the amended incubations, indicating that the hydrolysis and fermentation processes were less dependent on temperature but correlated with the presence of a reactive organic pool. The overall net POC decomposition after 1 mo incubation was on the same order of magnitude (19%) as in the sediment cores (10%), whereas the terminal mineralization to TCO_2 was lower and varied among treatments. The composition of DOC was related to the terminal mineralization rates, as the accumulation of SCFA was high in incubations with relatively low SSR and lower in incubations with high SSR.

Acknowledgements. I am thankful to Susanne Boeriths for technical assistance and Hans Ulrik Riisgård and students at the Fjord Laboratorium for providing the *Rhodomonas* sp. culture. I am grateful to Gary Banta for suggestions and correction of the language.

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This article was submitted to the editor

Manuscript first received: February 2, 1996
Revised version accepted: May 13, 1996