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Decomposition of plant materials in marine sediment exposed to different electron acceptors (O_2, NO_3^-, and SO_4^{2-}), with emphasis on substrate origin, degradation kinetics, and the role of bioturbation

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Abstract—Carbon mineralization of fresh and aged diatoms (*Skeletonema costatum*) and barley hay (*Hordeum vulgare*) was followed for 23 to 35 d in sandy and silty sediment. By the use of a thin-layer flow-through technique, it was possible to expose the sediment selectively for oxygen, nitrate or sulfate as electron acceptors in the terminal oxidation of organic carbon. Decomposition took place in two basic stages. Mineralization of the rapidly leachable fraction of the fresh materials occurred rapidly and with the same constant rate regardless of the electron acceptor available, indicating that the dissolved organic carbon released initially was labile and readily available for all heterotrophic respirers. In the case of diatoms, decay of the remaining, more refractory, particulate fraction of fresh and aged diatoms were strikingly similar, although both were degraded 5 to 10 times faster under oxic than anoxic conditions. Most of the particulate remains of diatoms after leaching apparently belong to one fraction, which maintains the same degradability even after prolonged aging. With respect to hay, the late divergence in rates of aerobic and anaerobic decay (a factor of 4 to 5 for aged hay only after 20 d) indicated that the larger hay particles (<500 μm) became exhausted in labile organic matter much slower through time than fine-particulate diatoms (~ 20 μm). Anaerobic carbon mineralization rates of diatoms and hay particulates with sulfate and nitrate as electron acceptors were similar or up to two times faster with sulfate. The generally low levels of dissolved organic carbon in all incubations after the initial leaching phase suggest that the limiting step of decomposition under both aerobic and anaerobic decay is the initial hydrolytic attack on the complex particulate remains. Based on a volumetric model, we show that the exposure of anoxic subsurface sediment containing partly degraded organic material to oxygen via irrigated worm burrows or by reworking may significantly enhance total sediment carbon oxidation. The enhancement in the irrigation case increases linearly with density (up to 80%) and is higher than the density-independent enhancement (10%) in the reworking case when abundance is above a lower limit of $\sim$400 individuals/m^2. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

A large fraction of organic matter deposited on sediment surfaces is degraded and remineralized by early diagenetic processes near the sediment-water interface (Henrichs, 1992; Canuel and Martens, 1996). The degradation is mediated by an array of aerobic and anaerobic microbial processes in the dynamic interface with a concurrent release of inorganic nutrients (Mackin and Swider, 1989; Canfield et al., 1993). Several factors are believed to control reaction rates in surficial sediments, including organic matter quality (i.e., the chemical composition), age (i.e., decomposition stage), particle associations (i.e., sorption to mineral surfaces, organic matrices, clay lattice structures and micropores), bioturbation (i.e., physical disturbance and macrofaunal consumption) and environmental conditions (i.e., temperature and the concentration of O_2 and other electron acceptors) (Mayer, 1994; Keil et al., 1994; Aller, 1994; Fenchel et al., 1998).

Planktonic material and macrophyte detritus are usually deposited in a relatively fresh and labile form at the oxic sediment-water interface of coastal marine sediments (Suess, 1980). Almost all aerobic microorganisms have the enzymatic capacity to perform a total mineralization of complex organic substrates. Organic matter may therefore be completely metabolized by a single organism to H_2O, CO_2, and inorganic nutrients using oxygen as an electron acceptor. A unique feature of aerobic decomposition is the formation and consumption of reactive oxygen-containing radicals such as superoxide anion ($\cdot O_2^-$), hydrogen peroxide (H_2O_2), and hydroxyl radicals ($\cdot$OH). These radicals are capable of breaking bonds and depolymerize relatively refractory organic compounds like lignin (Canfield, 1994).

As the oxic zone in coastal sediments usually is limited to a thin uppermost layer, a large fraction of the organic matter is buried in a more or less decomposed form into anoxic layers. Mutualistic consortia of bacteria accomplish anaerobic decomposition because no single type of anaerobic bacterium seems capable of complete mineralization (Fenchel et al., 1998). The large and normally complex polymeric organic molecules are first split into smaller and water soluble moieties (organic acids like formate, acetate, propionate etc.) and inorganic nutrients by hydrolysis and fermentation (Kristensen and Hansen, 1995; Holmer, 1999). The small organic acids are then oxidized completely to H_2O and CO_2 by a number of respiring microorganisms using a variety of inorganic compounds as electron acceptors (e.g., NO_3^- and SO_4^{2-}). The usually observed decreasing degradation rate with depth in sediments is not necessarily caused by less efficient electron acceptors in the deeper anoxic layers, but rather by the decreasing quality of organic

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Table 1. The combination of factors in the four decomposition experiments made in this study. Letter in brackets denote the abbreviations used in the text for the various treatments.

	Exp 1	Exp 2	Exp 3	Exp 4
Sediment	Silt	Sand	Sand	Sand
Plant material	Diatom (D)	Diatom (D)	Hay (H)	Diatom (D) Hay (H)
Decomposition stage	Fresh (F) Aged (A)	Fresh (F) Aged (A)	Fresh (F) Aged (A)	Fresh (F) Aged (A)
Electron acceptor	O_2 (O) SO_4^{2-} (S)	O_2 (O) SO_4^{2-} (S)	O_2 (O) NO_3^-(N)[a] SO_4^{2-} (S)	NO_3^- (N) SO_4^{2-} (S)

[a] Only with fresh hay.

matter (lability or degradability) and metabolite exchange with depth (Canfield, 1994; Aller and Aller, 1998).

The concept of unidirectional redox succession with depth in sediments is often emphasized as a universal biogeochemical phenomenon. This concept may be valid in marginal environments, such as areas defaunated by frequent bottom water anoxia or with very high sedimentation rates, but has little association to reality for bioturbated sediments. Oscillations between oxic and anoxic conditions and corresponding metabolic pathways on timescales of minutes to hours typically occur deep in bioturbated sediments (Jumars et al., 1990; Forster and Graf, 1992). Active irrigation and particle reworking by the macroinfauna inject oxygen and other electron acceptors via burrows to anoxic layers and displace particles rapidly between oxic and anoxic layers (Aller, 1994). The resulting mosaic of oxic microzones in the otherwise anoxic sediment clearly promotes oxic and suboxic sediment metabolism.

Which electron acceptor supports the fastest decay of sediment detritus? Much work has been devoted to determine rates of organic matter decomposition under oxic and anoxic conditions (e.g., Canfield, 1994). It has been suggested that the rate of decay under different redox conditions depends primarily on the composition, stage of decomposition and origin of the organic matter (Westrich and Berner, 1984; Kristensen et al., 1995; Hulthe et al., 1998). Thus, the terminal oxidation rate of dissolved organic carbon (DOC) originating from the initial leaching and early hydrolysis of fresh plant detritus should be similar with both O_2 and SO_4^{2-} as electron acceptor. When structural components become a dominant fraction of particulate remains in sediments, anaerobic processes are gradually hampered by the inefficient and slow bacterial hydrolysis of the structurally complex macromolecules. However, no studies have yet examined the relative rates of terminal mineralization in sediments with NO_3^- and SO_4^{2-} as electron acceptors, but according to the suggestion of Kristensen et al. (1995) there should be no difference.

Kristensen et al. (1995) based their conclusions on a thin-layer study using fresh barley hay and aged diatom detritus. A comparison between two so widely different substrates may not be valid. In the present study we were able to confirm the conclusions of Kristensen et al. (1995) by the use of fresh and aged barley hay, and fresh and aged diatoms in an identical experimental set-up. Furthermore, we found that the electron acceptors NO_3^- and SO_4^{2-} support organic matter oxidation equally fast, although rates occasionally appeared to be fastest with SO_4^{2-}.

2. MATERIALS AND METHODS

Four separate decomposition experiments (Exps. 1 to 4) were made by combinations of the following factors: two sediments types, two plant materials, two decomposition stages of plant material, and three electron acceptors. An overview of experiments is given in Table 1.

2.1. Sediment and Labeled Plant Materials

Organic-rich, silty sediment (silt) was sampled in October 1996 (Exp. 1) from the northern Lillebælt (southern Kattegat), Denmark at 19- to 20-m water depth using a 13.5-cm inner diameter HAPS corer. Water content of the sediment was 68% to 76%. Surface sediment was oxidized and had a brownish color down to 1.5 to 2.0 cm depth, whereas subsurface sediment appeared uniformly black. There was no smell of free hydrogen sulfide.

Organic-poor, sandy sediment (sand) was sampled in November 1996 (Exp. 2), May 1997 (Exp. 3), and June 1997 (Exp. 4) by hand in Kertinge Nor (Island of Fyn), Denmark at ½- to 1-m water depth using 8-cm inner diameter Plexiglas core liners. Sediment water content was 20% to 27%. The oxidized surface layer varied in thickness from 1 cm in June to 3 cm in November. Subsurface sediment appeared grey to black with sulfide smell only in June. The range of water temperature and salinity during samplings at both locations was 7°C to 20°C and 18‰ to 20‰, respectively.

Homogeneously ^{14}C-labeled *Skeletonema costatum* cells (diameter 20 μm) were harvested by flow centrifugation from $H^{14}CO_3^-$ enriched cultures. After rinsing to remove excess $H^{14}CO_3^-$, the retained portion of labeled diatoms was mixed (1:8) with an unlabeled batch from a continuous culture grown under comparable conditions. Subsequently, the mixture was split into halves. One portion (fresh diatom) with a specific activity of 25 kBq/mmol C (Table 2) was immediately frozen for later use. The other portion was predecomposed aerobically at room temperature in 20‰ seawater for 40 d to half of the original radiochemical activity (aged diatom). After centrifugation, the aged diatoms with a specific activity of 36 kBq/mmol C (Table 2) were kept frozen until the start of experiments

Homogeneously ^{14}C-labeled barley (*Hordeum vulgare)* seedlings were grown at the Risø Nuclear Power Test Plant, Denmark in a $^{14}CO_2$ atmosphere for ~1 month, before being harvested and dried to constant weight at 60°C (water content, 73 ± 1%). The dried material was ground, and the size fraction smaller than 500 μm with a specific activity of 33 kBq/mmol C (Table 2) was used (dried fresh hay). Grinding was only possible on the dried material. The mild drying procedure will not alter the composition of the biochemical constituents and is therefore not expected to compromise the degradation results. A portion of 4 g dry weight was suspended in 1.5 L of 20 ‰ seawater and decomposed aerobically for 50 d to 33% of the original radiochemical activity (aged hay). The slurry was centrifuged at 2500 rpm for 5 min and rinsed once in seawater. The residue with a specific activity of 37 kBq/mmol C (Table 2) was frozen until the start of experiments.

Table 2. Elemental composition (C and N) content, and specific activity of the ^{14}C-labeled materials and sediment used in the decomposition experiments.

Material	Carbon content (mmol/g dw)	Nitrogen content (mmol/g dw)	Molar C:N	Specific activity (kBq/mmol C)
Diatom:				
Fresh (DF)	11.5 ± 0.1	1.27 ± 0.31	9.0 ± 1.2	25 ± 2
Aged (DA)	12.4 ± 0.1	0.86 ± 0.22	14.4 ± 0.8	36 ± 3
Hay:				
Fresh (HF)	38.7 ± 4.6	3.37 ± 1.41	11.5 ± 1.1	33 ± 4
Aged (HA)	20.0 ± 1.7	2.07 ± 0.85	9.7 ± 0.9	37 ± 3
Sediment:				
Silt	3.2 ± 0.3	0.33 ± 0.02	9.7 ± 0.2	—
Sand	0.3 ± 0.0	0.03 ± 0.00	8.8 ± 0.3	—

Carbon and nitrogen content are given as mean ± SD (n = 3).

2.2. Experimental Procedures

In order not to favor depth related processes, fresh surface (0 to 1 cm) and subsurface (9 to 10 cm) sediment were mixed (1:1) immediately before the start of each experiment. The mixture was split into three (Exps. 1 to 3) or four (Exp. 4) portions of 50 mL (one of 80 mL in Exp. 3) and treated as follows: Exps. 1 and 2, to one portion was added 5.0 g wet wt. fresh ^{14}C-diatom (DF), to one portion was added 5.0 g wet wt. aged ^{14}C-diatom (DA), and one portion was kept as an unamended control; Exp. 3, to the 80-mL portion was added 0.56 g dry wt. (wet wt./dry wt. ratio = 3.7) fresh ^{14}C-hay (HF), to one 50-mL portion was added 4.0 g wet wt. aged ^{14}C-hay (HA) and one 50-mL portion was kept as an unamended control; Exp. 4, there was no control and to the four portions were added 5.1 g wet wt. DF, 5.2 g wet wt. DA, 0.35 g dw HF, and 4.1 g wet wt. HA, respectively. After thorough hand mixing under air, 7 mL subportions of each sediment type were transferred to each of 4 (6 for HF in Exp. 3) incubation chambers (250-mL straight-sided Plexiglas jars, 8-cm inner diameter). The added sediment was spread to a 1.4-mm thin-bottom layer (the thin-layer approach of Sun et al., 1993; Kristensen et al., 1995; Fig. 1.) After the chambers were filled with NO_3^--poor (<5 μM) and SO_4^{2-}-rich (15 mM) 20‰ seawater, they were sealed with rubber stoppers leaving no gas phase (enclosing ~200 mL of water) and, in series of two, connected with 2-L seawater reservoirs via 2-mm inner diameter nylon tubing. A total of six to eight reservoirs were employed during each experiment.

Flow of water between each chamber and the reservoir was maintained with a peristaltic pump at a rate of ~3 mL/min (chamber turnover time: 70 min). Rotating magnetic bars activated by an externally rotating central magnet (60 rpm) stirred all chambers. In Exps. 1 to 3, four of the eight reservoirs were continuously aerated with moist air to maintain 100% oxygen saturation (promoting aerobic respiration), whereas the other four received moist N_2 to remove oxygen (promoting sulfate respiration). In Exp. 4, all reservoirs were maintained anoxic throughout the experiment. The gases were moistened (and N_2 equilibrated with CO_2) by bubbling through a frequently replaced 40-cm (2 L) column of seawater. TCO_2 and pH in the anoxic reservoirs were never significantly different from the oxic reservoirs. NO_3^- was added to a concentration of ~2 mM (promoting nitrate respiration) in one of the anoxic reservoirs with HF in Exp. 3 and half of the reservoirs in Exp. 4. Studies have shown that most nitrate respirers in both cultures and natural sediments exhibit zeroth-order kinetics with respect to NO_3^- at concentrations from 100 to 200 μM to several mM (Murray et al., 1989; Joye et al., 1996).

Gases leaving both the oxic and anoxic reservoirs were stripped of all CO_2 in a series of two NaOH traps (200 mL, 0.5 mol/L, Fig. 1).

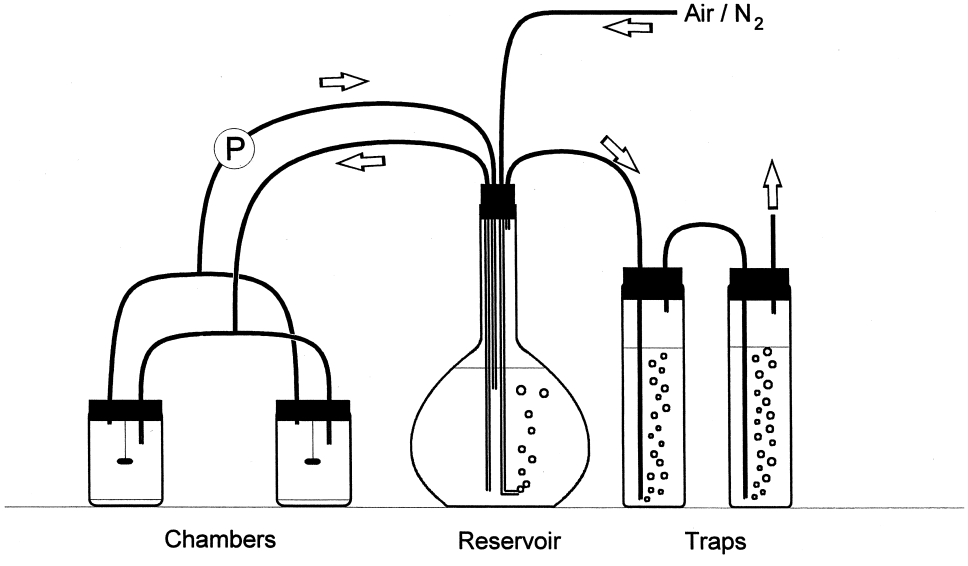


Fig. 1. Schematic presentation of the incubation system used in the experiment. Water flow (indicated by arrows) between incubation 'chambers' and the seawater 'reservoir' is driven by a peristaltic pump (indicated by 'P'). Flow of moistened atmospheric 'air' (oxic incubation) and 'N_2' (anoxic incubation) is bubbled through the reservoir and subsequently through the two NaOH 'traps' (direction indicated by arrows).

Tests have shown that more than 95% of the $^{14}CO_2$ entering each trap was retained (Kristensen et al., 1995), so the combined efficiency of the two traps was more than 99%. Reservoirs and traps were renewed every third day. The entire set up was kept in darkness at 15°C throughout the 23-d (Exps. 1 and 2), 35-d (Exp. 3), and 23-d (Exp. 4) experiments.

2.3. Sampling and Chemical Analysis

The release of ^{14}C-labeled solutes ($^{14}CO_2$ and [^{14}C]DOC) from the sediments was determined on a 3-d basis, with samples taken from the reservoirs and traps after every renewal. To 5-mL GF/F filtered samples from the reservoirs were added 125 μL of 1 mol/L NaOH and mixed with 15 mL of scintillation cocktail in 20-mL scintillation vials. These samples were counted for total dissolved labeled carbon ([^{14}C]TDC) in a Packard 2200 CA Tricarb liquid scintillation analyzer with internal quench correction. Then, 250 μL of 0.5 mol/L HCl was added to another 5 mL from the reservoirs and purged with N_2 for 2 h to release $^{14}CO_2$ before scintillation cocktail was added and the sample was counted for [^{14}C]DOC. Trap samples were treated like the [^{14}C]TDC samples from the reservoirs, except that no NaOH was added. The total release of $^{14}CO_2$ from the chambers was calculated as the sum of $^{14}CO_2$ activity in reservoirs (i.e., the difference, [^{14}C]TDC − [^{14}C]DOC) and traps. The flux rates obtained in each system represent the accumulated amount of dissolved ^{14}C released from two chambers.

The exchange of O_2 and unlabeled CO_2 in Exps. 1, 2, and 3 were determined at 3-d intervals (out of phase with reservoir and trap renewal) from Day 3. The pump was stopped and 10 mL of start water samples were taken from the chambers by syringes via a valve in the chamber lids (replacement water was passively pulled from the reservoirs). Final samples were taken similarly after a 5-h incubation period. Subsamples of 5 mL were analyzed for O_2 by the standard Winkler technique (Parsons et al., 1984), and subsamples of 2 mL were analyzed for total CO_2 (TCO_2) by the flow injection/diffusion cell technique of Hall and Aller (1992). The precision of O_2 and CO_2 analysis was within 1%.

Samples of 10 mL were taken at 3-d intervals from the reservoirs in Exp. 4 for monitoring DOC and NO_3^- concentrations. DOC was determined on a Shimadzu TOC-5000 total carbon analyzer (Shimadzu Scientific Instruments, Columbia, MD, USA; precision better than 5%). NO_3^- was analyzed by a standard flow injection technique (Tecator FIAstar 5010 Tecator, Höganäs) by using the method of Armstrong et al. (1967) with a precision better than 2%.

Samples of diatom, hay, and sediment materials for determination of initial particulate organic carbon (POC) and nitrogen (PON) content were freeze dried. POC and PON content were analyzed by a Carlo Erba EA 1108 elemental analyzer (Carlo Erba, Milano) according to the difference on ignition technique of Kristensen and Andersen (1987). ^{14}C-labeled POC from the initial and final sediment mixtures, and diatom and hay materials was recovered by trapping the evolved $^{14}CO_2$ from the effluent gas after combustion in the CHN analyzer, using two 5-mL NaOH (0.5 mol/L) traps, and counted as described above. Tests showed no cross contamination between samples. Precision of elemental analysis was better than 5%.

3. RESULTS

3.1. Particulate Organic Pools

The amount of organic matter added to the sediments was equivalent to an increase in POC and PON of ~10% in Exp. 1 and 70% in Exps. 2 to 4. The molar C:N ratios of the diatom (9–14) and hay (10–12) materials were within the range of the sediment organic matter (9–10, Table 2). POC contents of fresh (DF) and aged (DA) diatoms were roughly similar, whereas PON was 30% lower in the latter. The apparent isotope fractionation (i.e., 44% increase in specific radioactivity) during aging of the diatom mixture was probably caused by a preferential degradation of organic carbon in the unlabeled batch. The continuous culture of unlabeled *S. costatum* was harvested in the exponential growth phase, whereas the labeled batch culture was harvested at a later growth stage with a higher fraction of aged and thus less degradable cells. Fresh hay (HF) contained 3.3 times more POC and 2.7 times more PON than DF. Predecomposition reduced POC and PON in the hay material by ~50 and 40%, but the levels were still 60 and 140% higher than for DF. The isotope fractionation (i.e., 12% increase in specific radioactivity) occurring during hay aging was within the variation among replicates, and is thus not statistically significant.

3.2. Evolution Pattern of Dissolved ^{14}C Compounds

There was no apparent difference between silty and sandy sediments with respect to the magnitude and time course of $^{14}CO_2$ evolution from both DF and DA (Fig. 2, Exps. 1 and 2). DF showed a rapid and exponential decrease in $^{14}CO_2$ production within the first 5 to 6 d by both aerobic ($DF1_O$ and $DF2_O$), nitrate respiration ($DF4_N$) and sulfate respiration ($DF1_S$, $DF2_S$, and $DF4_S$) and remained more or less constant throughout the rest of the experiments. In the DA treatments $^{14}CO_2$ evolution was equivalent to the final rates in the DF treatments. The relatively high rates of $^{14}CO_2$ evolution observed in DA during the first 5 d may be caused by the release of a small leachable pool generated during freezing and handling of the detritus before experiments.

The evolution of $DO^{14}C$ was low (<10 Bq/cm^3/d) in all diatom treatments, except at the initial sampling date for the DF systems (data not shown). The $DO^{14}C$ release at this date was 649 and 638 Bq/cm^3/d in $DF1_S$ and $DF2_S$ (equivalent to the initial $^{14}CO_2$ release) and 462 and 274 Bq/cm^3/d in $DF1_O$ and $DF2_O$ (equivalent to 50% and 20% of the initial $^{14}CO_2$ release). The higher $DO^{14}C$ evolution in $DF1_S$ and $DF2_S$ almost balanced the higher initial rates of $^{14}CO_2$ evolution found in $DF1_O$ and $DF2_O$.

The temporal pattern of $^{14}CO_2$ evolution in the HF treatment with aerobic ($HF3_O$) and sulfate respiration ($HF3_S$) also showed a rapid exponential decrease initially (Fig. 3, Exp. 3). $^{14}CO_2$ evolution due to sulfate ($HF4_S$) and nitrate ($HF4_N$) respiration followed the same general pattern as in Exp. 3, but with a secondary maximum around Day 8 (Fig. 3, Exp. 4). A crucial pump failure from Day 7 to 11 in Exp. 3 may have obscured a similar peak in this experiment. The HA treatments in Exp. 3 ($HA3_O$ and $HA3_S$) behaved inconsistently during the first 15 d, partly caused by the pump failure (Fig. 3, Exp. 3). Subsequently, $^{14}CO_2$ evolution in $HA3_O$ increased rapidly to a constant level after Day 21, whereas the rate in $HA3_S$ remained more or less constantly low. Sulfate ($HA4_S$) and nitrate ($HA4_N$) respiration in the HA treatment were constant throughout the experimental period, except for somewhat elevated rates at the first sampling day (Fig. 3, Exp. 4).

$DO^{14}C$ evolution in the HF treatments was high at the initial sampling, with rates of 335 and 402 Bq/cm^3/d in $HF3_O$ and $HF3_S$ (equivalent to 110% and 60% of the initial $^{14}CO_2$ release), and rates of 669 and 595 Bq/cm^3/d in $HF4_S$ and $HF4_N$ (equivalent to the initial $^{14}CO_2$ release). Subsequently, the $DO^{14}C$ evolution decreased below 10 Bq/cm^3/d in $HF3_O$ and $HF3_S$ (except for rates up to 150 Bq/cm^3/d during the period with pump failure) and below 20 Bq/cm^3/d in $HF4_S$ and $HF4_N$. $DO^{14}C$ evolution in the HA treatments was constantly below 10 Bq/cm^3/d in $HA3_O$ and $HA3_S$ and below 5 Bq/cm^3/d in $HA4_S$ and $HA4_O$ throughout the experimental periods.

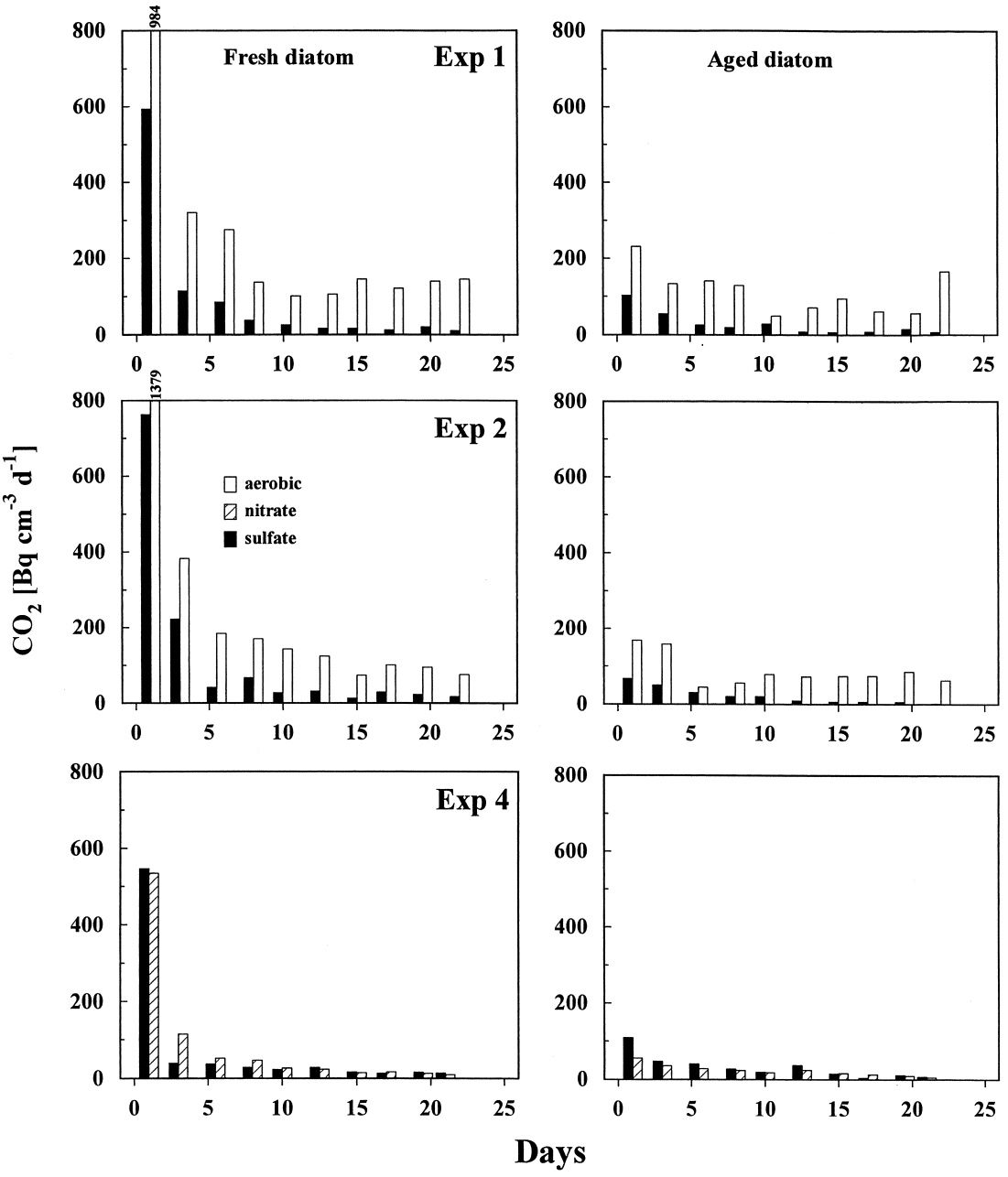


Fig. 2. Volume-specific rates of $^{14}CO_2$ release from sediment amended with fresh and aged *Skeletonema costatum* detritus in aerobic and anaerobic chambers during a 23-d incubation period. Sulfate was the only electron acceptor available (~15 mM) in anaerobic treatments of Exps. 1 and 2, whereas excess nitrate (~2 mM) was available in one of the treatments in Exp. 4.

The budgets of ^{14}C which included all trapped label in the POC, CO_2, and DOC pools and fluxes revealed a high (77–121%) recovery in all four experiments (Table 3). The recovery of added label, however, generally appeared to be higher for fresh than aged materials in sandy sediment.

3.3. Decomposition Kinetics

The comparison of decomposition rates in absolute terms is dependent on the quantity of substrate available for the decomposers. In the present case the amount of added ^{14}C-labeled materials varied more than fourfold among experiments (Table 3). The absolute rates obtained are, therefore, only comparable within each experimental batch, but not between experiments. For comparative purposes it is more appropriate to present decomposition in relative terms. Accordingly, the $PO^{14}C$ loss can be calculated as the initial amount of added $PO^{14}C$ minus the cumulative release of dissolved ^{14}C compounds (i.e., $^{14}CO_2$ and $DO^{14}C$) and expressed as the percentage of the initial

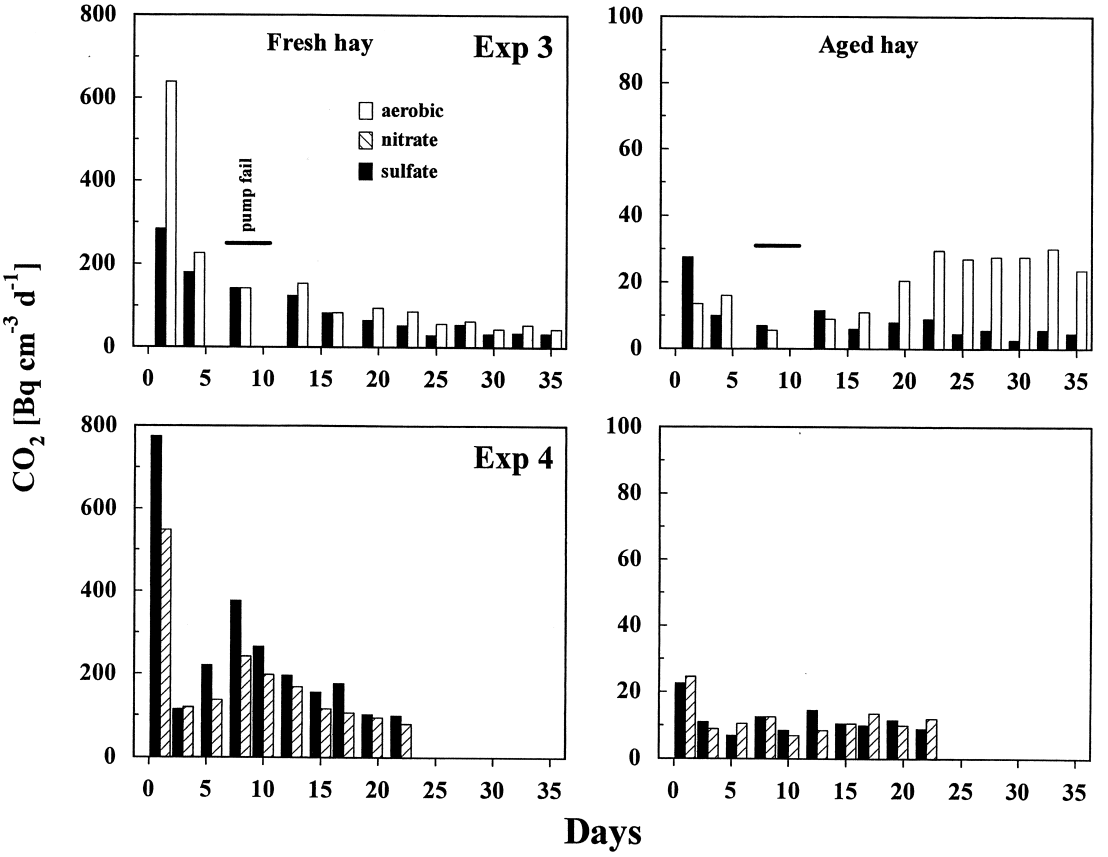


Fig. 3. Volume-specific rates of $^{14}CO_2$ release from sediment amended with fresh and aged barley hay detritus in aerobic and anaerobic chambers during a 35-d (Exp. 3) or 23-d (Exp. 4) incubation period. Sulfate was the only electron acceptor available (~15 mM) in the anaerobic treatment of Exp. 3, whereas excess nitrate (~2 mM) was available in one of the treatments in Exp. 4.

amount of PO^{14}C (Figs. 4 and 5). The apparent two-phase decrease with time in ^{14}C loss of particularly the fresh materials suggests a double-exponential decay pattern according to the two-G model of Westrich and Berner (1984): $G(t) = G_1 \exp(-k_1 t) + G_2 \exp(-k_2 t)$, where $G(t)$ is the label remaining in the POC pool at time t (days), G_1 and G_2 are the initial pool of the rapidly and slowly degrading fractions, k_1 and k_2 are the corresponding first-order decay constants. The decay pattern in Exp. 3 was irregular during the first 12 d due to the pump failure and induced some uncertainty into the curve fitting. In a few cases (aged hay under oxic conditions in Exp. 3 and all hay treatments in Exp. 4) there was no clear double exponential pattern (Fig. 5). Instead, a single exponential model [$G(t) = G_2 \exp(-k_2 t)$] was applied to simulate degradation of the G_2 fraction only. We have chosen exponential decay models without a residual term, because the relatively short duration of the incubations provided no evidence for a nonreactive fraction as a significant ^{14}C loss of the G_2 fraction remained to the end in all treatments. However, knowledge on the size of the G_2 fraction is critical for the interpretation of actual decay constants, and the apparent value of this fraction may be a function of the oxidant present; i.e., larger reactive fraction under oxic than anoxic conditions (Sun et al., 1993). Because studies on plant and microalgal decomposition have reported a wide range of values for the nonreactive fraction (e.g., 4–87% for microal-

Table 3. Budget of ^{14}C (kBq/cm^3) in the various treatments over the entire length of the four experiments.

Treatment	Added POC	ΣCO_2	ΣDOC	Final POC	% Recovery
$DF1_O$	14.0	5.5	1.0	7.3	99
$DF1_S$	14.0	2.0	1.3	10.3	97
$DA1_O$	4.9	2.5	0.1	3.0	114
$DA1_S$	4.9	0.7	0.1	4.2	102
$DF2_O$	11.4	5.9	0.7	6.5	115
$DF2_S$	11.4	2.6	1.4	8.5	110
$DA2_O$	4.7	2.0	0.1	2.4	96
$DA2_S$	4.7	0.5	0.1	3.7	91
$DF4_S$	8.5	1.6	0.5	6.4	100
$DF4_N$	8.5	1.8	0.6	6.9	109
$DA4_S$	5.3	0.7	0.1	4.4	98
$DA4_N$	5.3	0.5	0.1	4.0	87
$HF3_O$	7.9	5.0	2.0	2.4	119
$HF3_S$	7.9	3.3	2.7	2.6	109
$HA3_O$	3.9	0.6	0.2	2.8	92
$HA3_S$	3.9	0.3	0.2	3.3	97
$HF4_S$	9.3	5.5	1.8	4.0	122
$HF4_N$	9.3	4.0	1.5	3.5	97
$HA4_S$	3.2	0.3	0.1	2.1	78
$HA4_N$	3.2	0.3	0.1	2.4	88

Aerobic respiration is denoted by subscript O, sulfate reduction by subscript S and nitrate respiration by subscript N.

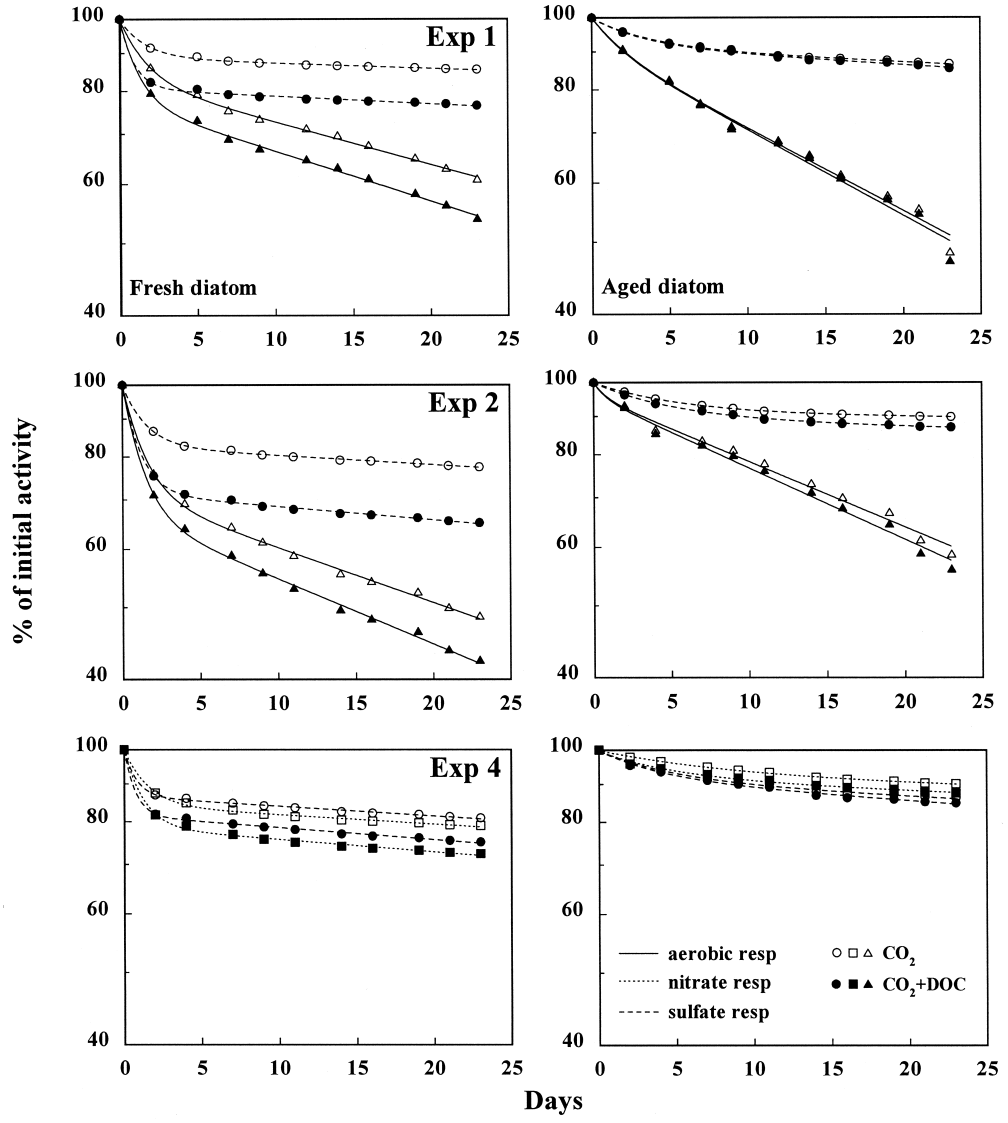


Fig. 4. Decay pattern of fresh and aged *Skeletonema costatum* detritus with oxygen and sulfate (Exps. 1 and 2) or nitrate and sulfate (Exp. 4) as electron acceptors. The $PO^{14}C$ loss is presented as the percentage of initial activity and estimated by subtracting the cumulative release of dissolved ^{14}C compounds ($^{14}CO_2$ and $DO^{14}C$) from the initial amount of added $PO^{14}C$. Open symbols represent decay due to carbon mineralization ($^{14}CO_2$ release) and closed symbols represent total decay, including hydrolysis/fermentation ($^{14}CO_2$ + $DO^{14}C$ release). Full lines indicate aerobic respiration, broken lines decay under sulfate reducing conditions and dotted lines decay under nitrate reducing conditions. The lines are drawn according to the best fit to two-G decay models (see text and Table 4 for further information).

gae, Jewell and McCarty, 1971; Westrich and Berner, 1984; Harvey et al., 1995), we have decided to ignore this in our kinetic calculations of the G_2 fraction. Instead, we focus on bulk rates of decomposition for fractions $> G_1$, where the decay constants provide evidence for the degradability of the total amount of substrate left after the rapid loss of the G_1 fraction, rather than the specific decay rate of an unknown amount of G_2.

Decay (k_1) for the fast degrading organic fraction (G_1) of fresh materials was rapid (200–500/yr, Table 4) and not very different between the various treatments (DF vs. HF, and aerobic vs. anaerobic respiration, Table 5). However, the apparent decay of the G_1 fraction based on total dissolved carbon (TDC) was 1.1 to 1.8 times faster than the CO_2 based decay due to net DOC release by leaching from the fresh materials (Table 4). The G_1 fraction in the fresh materials accounted for 11% to 30% (DF) and 40 to 50% (HF) of the total added pool with 1.2 to 1.7 times higher values when based on TDC (Table 6). No leaching was apparent from the aged materials as the TDC and CO_2 based initial decay (k_1) as well as the size of the G_1 fraction were similar, but generally much lower than those for the fresh materials. The G_1 fraction of the aged materials was degraded 1.6 to 6.8 times faster by aerobic respiration than sulfate reduction, whereas anaerobic decay with sulfate as electron acceptor was twice as high as under nitrate-reducing conditions (Table 5).

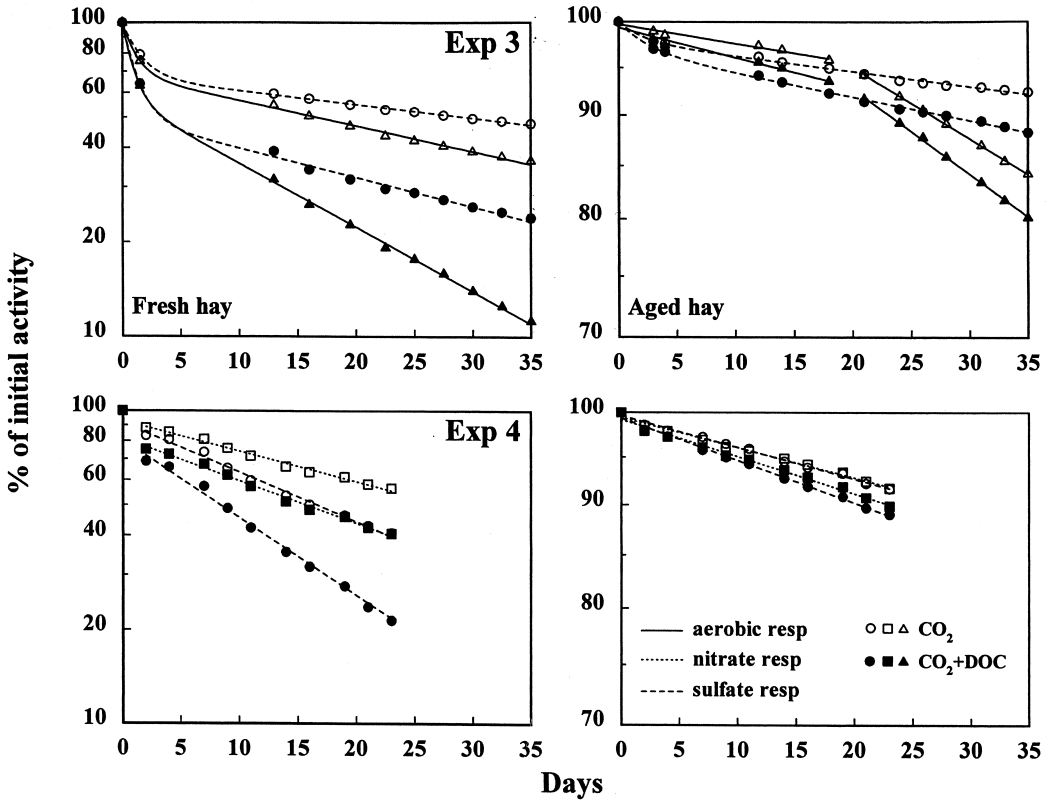


Fig. 5. Decay pattern of fresh and aged barley hay detritus with oxygen and sulfate (Exp. 3) or nitrate and sulfate (Exp. 4) as electron acceptors. The $PO^{14}C$ loss is presented as the percentage of initial activity and estimated by subtracting the cumulative release of dissolved ^{14}C compounds ($^{14}CO_2$ and $DO^{14}C$) from the initial amount of added $PO^{14}C$. Open symbols represent decay due to carbon mineralization ($^{14}CO_2$ release) and closed symbols represent total decay, including hydrolysis/fermentation ($^{14}CO_2$ + $DO^{14}C$ release). Full lines indicate aerobic respiration, broken lines decay under sulfate reducing conditions and dotted lines decay under nitrate reducing conditions. The lines are drawn according to the best fit to one- and two-G decay models (see text and Table 4 for further information).

Decay constants (k_2) of the slowly degrading (G_2) fraction were generally 1 to 2 orders of magnitude lower than those of the fast fraction (k_1) for both diatoms and hay (Table 4). The G_2 decay of DF and DA was similar, but generally with 5 to 10 times higher rate constants under oxic than anoxic (both with sulfate and nitrate) conditions (Table 5) and only the very slow decay rates in the $DA2_s$ treatment appeared biased. The similarity of TDC and CO_2 based G_2 decay in all diatom treatments substantiated the limited net DOC release from the slow fraction (Table 4). The decay of the slow HF fraction was 1 to 2 (CO_2) and 2 to 3 (TDC) times higher than for DF under oxic conditions and 4 to 6 (CO_2) and 5 to 9 (TDC) times higher under anoxic conditions. Thus, decay of the slow HF fraction in Exp. 3 was only ~2 times faster under oxic than anoxic conditions, whereas decay constants of HF in Exp. 4 was about twice as high in the presence of sulfate than nitrate (Table 5). A continued release of DOC contributed to increase the TDC-k_2 by a factor of 2 compared with CO_2-k_2 in most HF treatments (Table 4). The decay of HA under oxic conditions was relatively slow initially with rates similar to those under sulfate reducing conditions. However, after Day 18 the rate increased abruptly by a factor of 3 to 4, but only to a ⅓ of the rate found for DA. While there was about a factor of 2 higher decay of DA in the presence of sulfate than nitrate, the opposite pattern with 1.2 to 1.4 times higher rates in the presence of nitrate was evident for HA. As for DA, there was only a limited impact of DOC in the decay of HA.

3.4. Exchange of O_2 and total CO_2

The similarity in O_2 consumption by sediments with added fresh and aged materials in Exps. 1, 2, and 3 indicated that sediment metabolism was independent of organic matter age (Table 7). A general stimulatory impact of added diatom materials on the aerobic microbial community was evident from the almost twice as high O_2 uptake in amended chambers as in the unamended controls of Exps. 1 and 2. No such dramatic effect was apparent for the oxic chambers with hay additions (Exp. 3). Furthermore, sand (Exps. 2 and 3) showed somewhat higher O_2 uptake than silt (Exp. 1), most conspicuous for the unamended sediments.

Total CO_2 production in the oxic systems showed the same general pattern as O_2 consumption in all three experiments (Table 7). The respiratory quotients (RQ = CO_2 production/O_2 consumption) were close to 1 for the sandy sediment and slightly above unity (1.2 to 1.4) for the silty sediment. Total CO_2 production in anoxic systems (both with sulfate and nitrate

Table 4. Decay constants k_1 and k_2 (yr^{-1}) for the fast and the slowly degrading organic fractions in the diatom and hay materials added to the experimental chambers.

	k_1		k_2	
Treatment	CO_2	TDC	CO_2	TDC
$DF1_O$	214 ± 24	298 ± 34	4.78 ± 0.19	5.58 ± 0.22
$DF1_S$	224 ± 19	408 ± 41	0.62 ± 0.08	0.87 ± 0.10
$DA1_O$	162 ± 124	179 ± 154	9.27 ± 0.77	9.60 ± 0.77
$DA1_S$	97 ± 14	109 ± 17	0.84 ± 0.15	1.10 ± 0.15
$DF2_O$	256 ± 21	285 ± 23	6.24 ± 0.26	7.41 ± 0.29
$DF2_S$	249 ± 12	331 ± 16	1.02 ± 0.04	1.50 ± 0.10
$DA2_O$	438 ± 949	443 ± 972	7.41 ± 0.44	8.07 ± 0.44
$DA2_S$	64 ± 4	70 ± 8	0.15 ± 0.07	0.44 ± 0.18
$DF4_S$	471 ± 68	527 ± 70	1.10 ± 0.07	1.35 ± 0.08
$DF4_N$	245 ± 21	308 ± 27	1.06 ± 0.11	1.39 ± 0.14
$DA4_S$	76 ± 23	89 ± 25	0.91 ± 0.37	1.28 ± 0.29
$DA4_N$	40 ± 15	71 ± 9	0.47 ± 0.44	0.73 ± 0.00
$HF3_O$	300 ± 32	358 ± 24	6.83 ± 0.32	17.23 ± 0.41
$HF3_S$	224 ± 11	278 ± 20	3.65 ± 0.14	7.88 ± 0.51
$HA3_O$	—	—	0.77 ± 0.07	1.20 ± 0.11[a]
			2.92 ± 0.04	3.54 ± 0.05[b]
$HA3_S$	162 ± 50	130 ± 23	0.62 ± 0.03	0.99 ± 0.03
$HF4_S$	—	—	13.14 ± 0.47	20.81 ± 0.80
$HF4_N$	—	—	8.03 ± 0.29	11.32 ± 0.37
$HA4_S$	—	—	1.31 ± 0.04	1.28 ± 0.04
$HA4_N$	—	—	1.75 ± 0.04	1.53 ± 0.07

The decay constants were derived by fiting a two-G exponential decay model to the time-dependent cumulative loss of $^{14}CO_2$ and total dissolved ^{14}C (TDC = CO_2 + DOC). Aerobic respiration is denoted by subscript O, sulfate reduction by subscript S, and nitrate respiration by subscript N. k_1 constants for some HF treatments are unavailable because of an apparent single exponential decay pattern.

[a] Initial 18 days before the break in decay rate.

[b] Final 14 days after the break in decay rate.

Table 6. Size of the fast (G_1) and the slowly (G_2) degrading organic fractions in the diatom and hay materials (% of total) added to the experimental chambers.

	G_1		G_2	
Treatment	CO_2	TDC	CO_2	TDC
$DF1_O$	17.2 ± 0.8	22.6 ± 0.9	82.8 ± 0.7	77.4 ± 0.7
$DF1_S$	11.3 ± 0.4	19.4 ± 0.5	88.7 ± 0.3	80.6 ± 0.3
$DA1_O$	8.5 ± 3.2	8.1 ± 3.4	91.5 ± 3.1	91.9 ± 3.1
$DA1_S$	8.6 ± 0.7	8.3 ± 0.7	91.3 ± 0.7	91.7 ± 0.7
$DF2_O$	28.5 ± 0.9	32.9 ± 1.0	71.5 ± 0.8	67.0 ± 0.8
$DF2_S$	17.4 ± 0.3	28.6 ± 0.4	82.6 ± 0.3	71.4 ± 0.3
$DA2_O$	4.2 ± 2.1	4.3 ± 2.2	95.9 ± 1.6	95.7 ± 1.6
$DA2_S$	9.5 ± 0.5	10.7 ± 0.9	90.5 ± 0.5	89.2 ± 0.9
$DF4_S$	13.5 ± 0.4	18.5 ± 0.4	86.5 ± 0.3	81.5 ± 0.3
$DF4_N$	15.8 ± 0.5	21.3 ± 0.6	84.1 ± 0.4	78.6 ± 0.5
$DA4_S$	8.6 ± 1.9	8.2 ± 1.4	91.1 ± 1.9	91.6 ± 1.5
$DA4_N$	7.8 ± 3.2	7.8 ± 0.4	92.0 ± 3.2	91.7 ± 0.3
$HF3_O$	31.6 ± 1.6	42.7 ± 1.4	68.4 ± 1.4	57.3 ± 1.4
$HF3_S$	32.8 ± 0.7	50.4 ± 1.6	67.2 ± 0.6	49.6 ± 1.6
$HA3_O$	—	—	99.7 ± 0.2	99.4 ± 0.3
$HA3_S$	2.1 ± 0.3	3.1 ± 0.3	97.9 ± 0.2	96.9 ± 0.2
$HF4_S$	—	—	91.5 ± 1.4	80.6 ± 1.7
$HF4_N$	—	—	92.9 ± 0.9	81.5 ± 1.0
$HA4_S$	—	—	99.6 ± 0.1	99.4 ± 0.2
$HA4_N$	—	—	99.3 ± 0.2	99.2 ± 0.2

The pool sizes were derived by fitting a two-G exponential decay model to the time dependent cumulative loss of $^{14}CO_2$ and total dissolved ^{14}C (TDC = CO_2 + DOC). Aerobic respiration is denoted by subscript O, sulfate reduction by subscript S, and nitrate respiration by subscript N. G_1 values for some HF treatments are unavilable because of an apparent single exponential decay pattern.

respiration) was only 40% to 60% of the rates found in oxic systems irrespective of treatment.

Excess fluxes caused by the added detritus (estimated as flux in systems added detritus minus flux in controls) were almost similar for O_2 and CO_2, providing RQ's around 1 for diatoms and 1.5 to 2 for hay. The total CO_2 production of the added radioactive materials (estimated as $^{14}CO_2$ evolution divided by the specific activity of the initial materials) was remarkably similar to the corresponding excess fluxes (Table 7). Even when a certain degree of isotope fractionation is allowed in the fresh diatom mixture, the agreement remains good. This indicates a limited priming effect on the decay of the indigenous organic pools by addition of diatoms and hay to the sediment.

Table 5. Ratios between decay constant (k_1, k_2, see Table 4) obtained by aerobic respiration (subscript O), sulfate reduction (subscript S), and nitrate respiration (subscript N).

	k_1		k_2	
Treatment	CO_2	TDC	CO_2	TDC
$DF1_O/DF1_S$	1.0	0.7	7.7	6.4
$DA1_O/DA1_S$	1.7	1.6	11.0	8.7
$DF2_O/DF2_S$	1.0	0.9	6.1	4.9
$DA2_O/DA2_S$	6.8	6.3	49.4	18.3
$DF4_N/DF4_S$	0.5	0.6	1.0	1.0
$DA4_N/DA4_S$	0.5	0.8	0.5	0.6
$HF3_O/HF3_S$	1.3	1.3	1.9	2.2
$HA3_O/HA3_S$	—	—	1.2	1.2[a]
			4.7	3.6[b]
$HF4_N/HF4_S$	—	—	0.6	0.5
$HA4_N/HA4_S$	—	—	1.3	1.2

[a] Initial 18 days before the break in decay rate.

[b] Final 14 days after the break in decay rate.

4. DISCUSSION

4.1. Experimental Concerns

The experimental approach used here is identical to the open thin-layer technique presented by Sun et al. (1993) and Kristensen et al. (1995). The limited diffusive scale obtained by such procedure assures that all organic matter in the sediment is in immediate contact with the prevailing electron acceptor (O_2, NO_3^- or SO_4^{2-}) for the terminal mineralization of organic carbon. Based on the relationship between oxygen penetration depth, benthic oxygen flux and bottom water oxygen concentration derived by Cai and Sayles (1996) for continental margin sediments, the potential O_2 penetration depth in our sediments is estimated to 5 to 10 mm for silt and 1.5 to 2.5 mm for sand, indicating that O_2 reached all sediment (1.4-mm layer) in the

Table 7. Exchange of O_2 and unlabelled CO_2 between sediment and overlying water in Exp. 1, 2, and 3.

Treatment	O_2	*n*	CO_2	*n*	ΔO_2	ΔCO_2	$*\Delta CO_2$
$DF1_O$	-6.5 ± 2.7	4	8.2 ± 2.7	4	2.6	2.8	6.7
$DF1_S$	—		4.9 ± 1.5	5	—	1.6	1.6
$DA1_O$	-7.3 ± 3.6	6	8.3 ± 3.4	5	3.4	2.9	2.7
$DA1_S$	—		5.0 ± 1.3	5	—	1.7	0.6
$C1_O$	-3.9 ± 1.6		5.4 ± 1.7	5			
$C1_S$	—		3.3 ± 1.1	5			
$DF2_O$	-10.9 ± 0.9	6	10.8 ± 1.7	6	4.8	5.4	5.9
$DF2_S$	—		4.2 ± 1.2	6	—	1.2	2.0
$DA2_O$	-10.4 ± 1.6	6	10.1 ± 1.5	6	4.3	4.7	2.1
$DA2_S$	—		5.4 ± 2.0	6	—	2.4	0.4
$C2_O$	-6.1 ± 1.0	6	5.4 ± 1.9	6			
$C2_S$	—		3.0 ± 0.6	5			
$HF3_O$	-9.3 ± 2.9	6	10.6 ± 1.4	3	1.2	2.3	2.7
$HF3_S$	—		4.8 ± 2.1	6	—	1.4	2.2
$HF3_N$	—		5.3 ± 2.0	5	—	1.9	2.3
$HA3_O$	-9.4 ± 2.5	5	10.3 ± 1.0	3	1.3	2.0	0.4
$HA3_S$	—		3.5 ± 1.2	5	—	0.1	0.2
$C3_O$	-8.1 ± 2.6	7	8.3 ± 4.3	3			
$C3_S$	—		3.4 ± 1.2	5			

* Values are averaged ($\pm$ SD) from Day 3 to the end of the experimental period. ΔO_2 and ΔCO_2 represent the excess flux derived form the added detritus (i.e., flux in the treatments with detritus added minus flux in controls). for comparison, ΔCO_2 represents the total CO_2 flux derived form added detritus, estimated from $^{14}CO_2$ flux, and specific radioactivity of the added material. Aerobic respiration is denoted by subscript O, sulfate reduction by subscript S, and nitrate respiration by subscript N. Positive values indicate release from the sediment. Rates are given as μmol/cm^3/d.

oxic chambers. Thus, upward diffusion and reoxidation of reduced inorganic metabolites (e.g., H_2S), which is responsible for a significant part of total sediment O_2 demand in most deep sediment columns (Jørgensen, 1983; Canfield, 1989; Mackin and Swider, 1989; Boudreau, 1991), will not occur. When O_2 is absent and NO_3^- is present in surplus, all respiration will be mediated with NO_3^- as electron acceptor, and SO_4^{2-} respiration occurs when both O_2 and NO_3^- is absent (Fenchel et al., 1998).

The volume-specific unlabeled CO_2 exchange rates obtained in the open 1.4-mm sediment layer under both oxic and anoxic conditions are more than 10 times higher than previously found for the same sediment type in closed incubations and in deep cores (Kristensen and Hansen, 1995). Aller and Aller (1998) also observed a dramatic increase in sediment mineralization rates with decreasing diffusion scale (sediment thickness) and increasing efficiency of solute exchange with overlying water. They proposed that simultaneous decreases in solute uptake into microbial biomass, abiogenic precipitation, and enhanced removal of inhibiting metabolites are responsible for higher microbial mineralization when the diffusion scale decreases. Our continuous flow system not only allows the introduction of selected electron acceptors, but also dilution of potential inhibitory metabolites. Any product inhibition in the later stages of decomposition is avoided and the rate is controlled by the lability of organic substrates and the kinetics of hydrolytic enzymes. Thus, Harvey et al. (1995) argued that open flow-through systems, in contrast to closed static systems, usually show only a limited refractory fraction of degrading microalgae.

The fresh diatoms (*Skeletonema costatum*) were low in carbon (~14% dry wt.) and nitrogen (1–2% dry wt.) content compared with published values of 20% to 30% C and 3 to 6% N for various diatom species (Parsons et al., 1961). Freezing and subsequent thawing and rinsing of the fresh algal material may have led to leaching and thus a loss of dissolved organic matter (e.g., proteins and carbohydrates) due to disruption of cell walls (Andersen, 1996). The aged diatoms, which were similar to fresh diatoms in organic content (Table 2), were first frozen after predecomposition. Furthermore, the generally low organic content of both fresh and aged diatoms indicates that most of the dry weight consists of inorganic material (e.g., silicate frustules). The carbon content of fresh barley hay (24–48% dry wt.), on the other hand, was similar to values previously observed for this type of material (Kristensen, 1990). While much of the hay carbon is fixed in structural carbohydrates (e.g., cellulose), most nitrogen is of cytoplasmic origin (e.g., proteins, amino sugars, and nucleic acids). The sap-rich barley seedlings therefore contained ~10 times more nitrogen (3–5% dry wt.) than usually found in postharvest hay (Kristensen, 1990). Based on the similarity of decay patterns of HF and DF in Exps. 2 and 3, and on the similarity of the final release of $^{14}CO_2$ in the fresh hay treatment with the initial release in the aged treatment of Exp. 3, there appeared to be no effect of using dried hay in the fresh treatments. The different particle size of materials used in the HF (<500 μm) and the DF (~20 μm) treatments may have resulted in a slower aerobic decomposition of the hay material. This was certainly not the case in the anaerobic treatments, where hay was degraded faster than diatoms. We therefore believe that the decomposition behavior of the two substrates is not controlled by size alone, but rather by their structural and chemical composition. It is important, however, to notice that we are dealing with decomposition patterns of low-organic and nitrogen-poor diatoms and high-organic and nitrogen-rich hay.

4.2. Decomposition Kinetics

The fast degrading (G_1) fractions of the fresh diatom and hay materials were rapidly leached and hydrolyzed as DOC and partly mineralized during the initial 5 d. These compounds were most likely short-chain carbohydrates, proteins, and fatty acids (Dunstan et al., 1992; Harvey et al., 1995; Herbreteau et al., 1997). The fresh hay treatments in Exps. 3 and 4 indicated that the initial releases for hay were of similar magnitude, but of shorter duration than for diatoms, whereas the total leachable and easily hydrolyzable organic compounds accounted for less of the initial carbon content in fresh diatoms (20–30%) than in fresh hay (40–50%). The secondary peak in carbon mineralization after ~8 d in the anoxic treatments with fresh hay (Fig. 3, Exp. 4) was probably caused by a microbial lag period, during which the populations adapted to the new and for marine bacteria unknown fresh hay substrate. A similar lag phase in TCO_2 production after addition of exotic organic substrates to anoxic sediments has previously been reported (Boyer, 1994; Kristensen and Hansen, 1995; Andersen, 1996). It is not possible here to evaluate the behavior of aerobic bacteria to the addition of fresh hay in Exp. 3 due to the unfortunate pump failure during the critically period from Day 7 to 11, when a secondary peak in carbon mineralization might have occurred.

However, Kristensen et al. (1995) found an almost instant response of aerobic respirers with no secondary peaks, but a 5- to 10-d lag phase for anaerobic respirers to the addition of fresh barley hay.

The CO_2-based decay constants (CO_2-k_1) of the fast degrading fraction of fresh diatoms were almost similar in the presence of oxygen, nitrate, and sulfate reduction, indicating that the DOC released initially was labile and readily available for all heterotrophic respirers. Our estimated decay constants were generally 2 to 4 times higher than commonly found for phytoplankton constituents (50–100/yr) (e.g., Emerson and Hedges, 1988; Sun et al., 1993; Andersen, 1996), but values of 200 to 4000/yr has been reported for free amino acids (Henrichs and Doyle, 1986). The fast initial rates are probably related to an instant mineralization of the leachable fraction remaining after freezing and released during thawing and mixing of fresh diatoms with sediment (Andersen, 1996). The relatively higher TDC (CO_2 + DOC)-based decay constants (TDC-k_1) by anaerobic than aerobic respirers could be explained by considerably lower carbon incorporation efficiency of anaerobic (e.g., ~0.2) than of aerobic (e.g., ~0.5) bacteria (Payne and Wiebe, 1978; Fenchel et al., 1998). In agreement with the present data, a number of studies have reported that the labile leachable fractions from fresh organic substrates are degraded at similar rates under oxic and anoxic conditions (Henrichs and Reeburgh, 1987; Lee, 1992; Andersen, 1996; Sun et al., 1997), whereas others have found that aerobic decay was fastest initially (Lee, 1992; Sun et al., 1993; 1997; Harvey et al., 1995). The outcome must depend strongly on the origin and chemical composition of the released DOC. Thus, it appears that the relatively small G_1 fraction of aged diatoms must have a chemical composition less susceptible to anaerobic decay than the fraction released by fresh diatoms as suggested by the apparent 2 to 7 times faster decay under oxic conditions.

The decay constants (k_2) of the slow (G_2) fraction of fresh and aged diatoms are strikingly similar (i.e., generally within a factor of 2, Table 4), but both were degraded 5 to 10 times faster under oxic than anoxic conditions. It appears that most of the fresh diatoms remaining after the initial rapid leaching and decay belongs to one fraction which maintains the same degradability even after prolonged aging. Also the oxygen and unlabeled CO_2 fluxes (after Day 3) appeared unaffected by the age of added diatom detritus (Table 7). The hay material becomes exhausted in labile organic matter much slower through time than diatoms as indicated by the faster decay of fresh hay than aged hay or fresh diatoms after the initial rapid leaching phase. Leaching may be slower and extended in time providing decay constants of the G_2 fraction of fresh hay, which only differed by a factor of 2 under oxic and anoxic conditions. The faster TDC than CO_2 based decay supports this contention. The slow loss of labile compounds from hay detritus is also confirmed by the late divergence in rates of aerobic and anaerobic decay (a factor of 4–5 for aged hay only after 20 d). The chemical composition and physical structure of the two different plant materials may control the time of divergence between aerobic and anaerobic rates of mineralization. Differences in reactivity of marine versus terrestrial organic matter are generally related to structural components, which make labile algal constituents more available for degradation than the higher molecular weight materials of terrestrial origin (Haddad et al., 1992; Canuel and Martens, 1996). However, the generally larger particle size of hay (<500 μm) than diatoms (~20 μm) used here may have extended the leaching phase of the former. The decay constants and impact of changing redox conditions found here for the G_2 fraction of both diatoms and hay are similar in magnitude to values found previously for compounds in marine sediments (Westrich and Berner, 1984; Henrichs and Doyle, 1986; Sun et al., 1993; Andersen, 1996). However, many studies have appointed this fraction G_1 and in addition reported a G_2 fraction with an order of magnitude lower decay constant. We found no evidence of fractions with decay constants lower than our G_2 fraction, but the relatively short duration of the present experiments may have masked any later change in reactivity.

It has been hypothesized that the introduction of fresh organic matter to sediments may stimulate the decomposition of otherwise stable residual organic matter (Schink, 1988; Graf, 1992; Canfield and Van Cappelen, 1992). However, no such "priming" of the indigenous sediment detritus was evident after addition of fresh diatom and hay detritus to our sediments. In fact, the excess unlabeled CO_2 determined from flux measurements in sediments with diatom and hay additions was roughly similar to the contribution estimated from $^{14}CO_2$ rates and the initial specific activity (Table 7). The limited difference between aerobic and anaerobic decay of the indigenous organic pool (around a factor of 2), on the other hand, suggests that the fraction being degraded was of a relatively fresh and labile nature. Thus, more than 10% of the organic matter in the upper 3 cm of surface sediment at shallow sandy locations can be derived from live microphytobenthos (e.g., diatoms) (Kristensen, 1993).

The generally low levels of DOC found in all systems after the initial leaching phase suggest, in accordance with Kristensen et al. (1995), that the limiting step of decomposition under both aerobic and anaerobic decay is the initial hydrolytic attack on the complex particulate remains of both diatoms and hay. The several-fold faster decay of aged materials under oxic than anoxic conditions indicates that the initial cleavage of macromolecules by hydrolytic enzymes from aerobic heterotrophs occurs more aggressively than by enzymes of anaerobic hydrolytic bacteria. Other studies have shown that refractory substances irrespective of origin, such as petroleum hydrocarbons (Atlas, 1981), lignin (Benner et al., 1984), and pollen (Keil et al., 1994) are degraded significantly faster in the presence than absence of oxygen.

NO_3^- is generally recognized as a more potent electron acceptor providing more energy per oxidized carbon molecule than SO_4^{2-} (Fenchel et al., 1998). However, anaerobic carbon mineralization of diatoms and hay appeared similar with the two electron acceptors or up to two times higher with SO_4^{2-} (Table 5). Fetzner (1998) reported a similar pattern for bacterial degradation of *N*-heteroaromatic compounds. Despite the occasional differences between rates of NO_3^- and SO_4^{2-} respiration, it must be concluded that both these anaerobic processes rely on the release rate of low-molecular organic substrates by hydrolysis and fermentation.

4.3. Implications for Decomposition in Bioturbated Sediments

It is known that macrobenthic activity usually results in more rapid and complete decomposition relative to sediments without bioturbation (Andersen and Kristensen, 1992; Aller, 1994; Banta et al., 1999). Studies have shown enhancements, measured as O_2 uptake or CO_2 production, between 25% and 300% (Kristensen, 2000). A number of factors are commonly thought responsible for the faunal-induced stimulation of organic matter degradation in sediments. Of these, changes in the transport regime during particle reworking, burrow formation and irrigation are of primary importance (Kristensen, 1988a; Aller and Aller, 1998). Experimental evidence indicates that redox oscillations may be one of the most important factors and that periodic re-exposure to oxygen results in more rapid decomposition of the partly degraded sediment detritus than under constant conditions (Aller, 1994; Hulthe et al., 1998).

No studies have yet provided a quantitative estimate of the enhanced decomposition caused by injection of oxygen into actively irrigated burrows or by oxygen exposure due to particle reworking. By the use of simple volumetric models, we will here present rough estimates of the stimulated carbon reaction rate in sandy coastal sediment shortly after the introduction of macrobiotic activity in the form of either irrigated burrows of e.g., the polychaete *Nereis diversicolor* or reworked by e.g., the head-down conveyor-belt feeding polychaete, *Heteromastus filiformis*. The two species are of comparable size and are commonly found in similar abundances (in the order of 500-4000 ind./m^2) in sandy coastal sediments (Cadee, 1979; Kristensen, 1988b). *N. diversicolor* is a facultative surface deposit feeder/suspension feeder, which irrigate its 10- to 20-cm long U-shaped burrow vigorously (up to 10^4 L/m^2/d; Vedel and Riisgård, 1993). *H. filiformis* derives all its food from sediment ingested in the reduced layer 10 to 30 cm below the surface and deposits faecal pellets at the surface. This sluggish irrigator and active reworker handle large amounts of sediment (100–2500/cm^3/m^2/d; Cadee, 1979).

In both cases our calculations are based on the following common assumptions: 1) all diagenetic processes occur in the upper L cm of the sediment column; 2) the oxic surface zone is L_{ox} cm thick; 3) the rate of deposition (e.g., phytoplankton) to or production (e.g., benthic diatoms) at the sediment surface of labile organic matter is similar irrespective of the species present; 4) the fresh and labile detritus is mineralized A_1 times faster (both in the presence and absence of oxygen) than the old and partly degraded detritus in the anoxic zone ($R_{1ox} = R_{1an} = R_1 = A_1\ R_{2an}$); 5) mineralization of old and partly degraded organic matter from anoxic zones is enhanced by a factor of A_2 when exposed to oxygen at the surface during reworking or along irrigated burrow walls ($R_{2ox} = A_2\ R_{2an}$); 6) no depth dependent change in degradability of sediment detritus occur in oxic and anoxic zones ($dR/dx = 0$), and anoxic mineralization rate is independent of electron acceptors.

In the *N. diversicolor* irrigation model (Fig. 6a) the following specific conditions are assumed: I) all fresh and labile detritus deposited at the surface is located in the oxic surface layer; II) the *N. diversicolor* abundance is d ind./m^2; III) burrows are U-shaped with two openings at the surface and a total length of L_b cm and a radius of r cm; IV) irrigation is continuous and the oxic zone around burrows is permanently B_{ox} cm thick. By relating volumes with reaction rates in the various zones, total sediment carbon oxidation per m^2 in the presence and absence of irrigated burrows with oxic walls can be estimated according to:

(1) Irrigated:

$$C_{iox} = R_{2an}\,[V - (V_{ox} + V_{ban} + V_{wox})] + R_1\,(V_{ox} - V_{box}) + R_{2ox} \cdot V_{wox}$$

(2) Defaunated:

$$C_{dox} = R_{2an}\,(V - V_{ox}) + R_1 \cdot V_{ox}$$

where:

$V = L \cdot 10^4$ − total sediment volume (cm^3/m^2) to depth L

$V_{ox} = L_{ox} \cdot 10^4$ − volume oxic surface sediment without burrows

$V_{ban} = \pi \cdot r^2 \cdot (L_b - 2\ L_{ox}) \cdot d$ − subsurface burrow lumen volume

$V_{box} = \pi \cdot r^2 \cdot 2\ L_{ox} \cdot d$ − surface burrow lumen volume

$V_{wox} = \pi \cdot (B_{ox}{}^2 + 2\ r \cdot B_{ox}) \cdot (L_b - 2\ L_{ox}) \cdot d$ − oxic subsurface burrow wall volume

The initial enhancement of carbon oxidation caused by the presence of irrigated burrows with oxic walls are then, $E_i = C_{iox}/C_{dox}$. Aller (1988) used a similar oxic/anoxic zone approach in a diagenetic model to describe the role of irrigated burrows and their abundance on nitrification and denitrification in sediments.

In the reworking case with *H. filiformis* (Fig. 6b) the following specific conditions are assumed: i) reworking is continuous and subsurface sediment is distributed in an even layer on top of the sediment with a steady-state thickness at least similar to the depth of the oxic surface layer (L_{ox}); ii) labile surface sediment with a thickness similar to that in the defaunated situation ($L_l = L_{ox}$) is continuously pushed downward into the anoxic zone (Fig. 7); and iii) the *H. filiformis* abundance is d ind./m^2; iv) because burrows are vertical and narrow with no or only limited oxic walls, the burrow lumen is ignored in calculations. From sediment volumes and reaction rates in the various zones, total sediment carbon oxidation per m^2 in the presence and absence of sediment reworking can be estimated according to:

(3) Reworked:

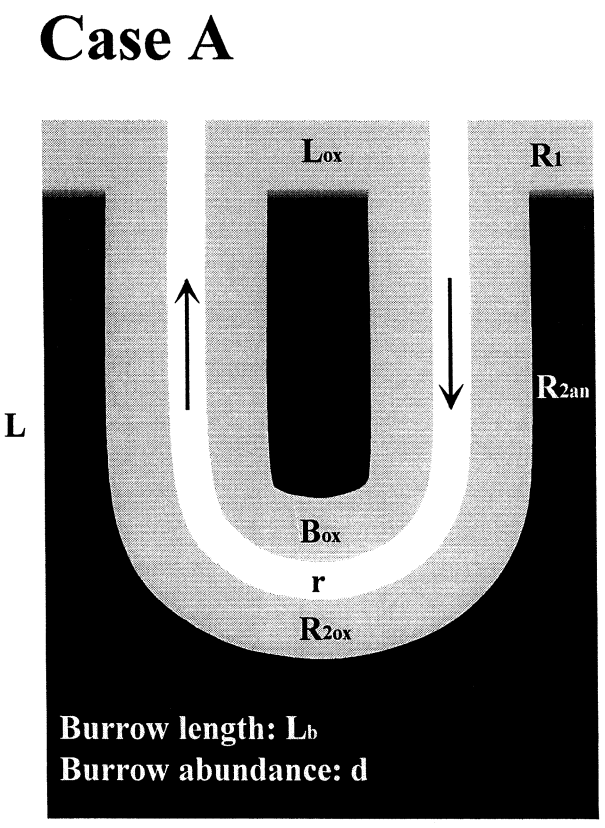
$$C_{rox} = R_{2an}\,[V - (V_l + V_{rox})] + R_1\ V_l \cdot R_{2ox}\ \cdot V_{rox}$$

(4) Defaunated:

$$C_{dox} = R_{2an}\,(V - V_{ox}) + R_1 \cdot V_{ox}$$

where the volume reduced subsurface sediment deposited at the oxic surface ($V_{rox} = L_{ox} \cdot 10^4$ cm^3/m^2) is similar to the volume of buried sediment containing labile detritus ($V_l = L_l \cdot 10^4$ cm^3/m^2). However, due to the simultaneous input of labile detritus and deposition by reworking a dilution of the labile material into a larger sediment volume obviously occur. Nevertheless, based on the assumption above the volumetric reaction rate should remain unaffected. The initial enhancement of carbon oxidation caused by sediment reworking are then, $E_r = C_{rox}/C_{dox} = [L + (A_1 + A_2 - 2)\ L_{ox}]/[L + (A_1 - 1)\ L_{ox}]$.

In the irrigation model, the variables L, L_b, L_{ox}, r, B_{ox}, A_1, and A_2 may all change depending on factors like season, sediment



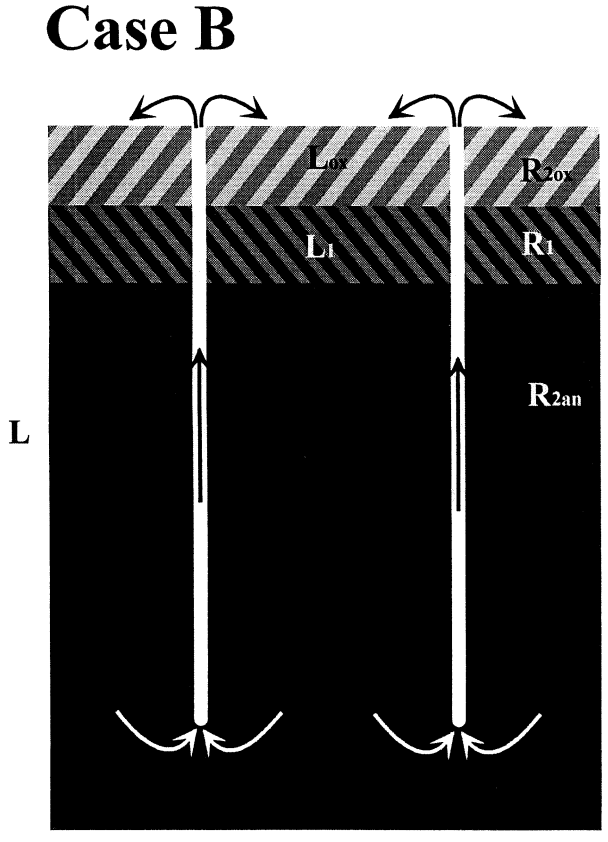


Fig. 6. A schematic presentation of the volumetric model used for quantification of carbon reaction rates in sandy coastal sediment with a depth of L cm: Case A. with irrigated burrows of the polychaete *Nereis diversicolor*. The grey zones indicate oxic surface sediment (thickness, L_{ox} cm) and oxic burrow walls (thickness, B_{ox} cm). All burrows have a radius of r cm and a length of L_b cm; Case B. with reworking by the head-down conveyor-belt feeding polychaete, *Heteromastus filiformis.* The lightly hatched zone indicates oxic surface sediment (thickness, L_{ox} cm) consisting of recently reworked subsurface material and the dark hatched zone (thickness $L_l = L_{ox}$ cm) indicates surface related labile material displaced into anoxic sediment. In both cases, the carbon oxidation rate (R_1) of the labile detritus under both oxic and anoxic conditions is A_1 times faster than the carbon oxidation rate (R_{2an}) of the partly degraded detritus in the anoxic black sediment ($R_l = A_1\ R_{2an}$). When deep subsurface sediment is exposed to oxygen in irrigated burrows or by reworking the reaction rate is enhanced A_2 fold ($R_{2ox} = A_2\ R_{2an}$).

type, and worm size. However, for simplicity we have chosen to keep them all constant: $L = 20$ cm; $L_b = 20$ cm; $L_{ox} = 0.3$ cm; $r = 0.3$ cm; $B_{ox} = 0.2$ cm; $A_1 = 20$; $A_2 = 10$. These fixed values are chosen based on past and present experience on nereid polychaetes (Kristensen, 1984; Kristensen, 1988a) and sediment biogeochemistry in shallow sandy areas (Kristensen, 1993). By varying d, our model predicts that the degree of stimulation is directly proportional to worm abundance, when the oxic zone around burrows is assumed independent of the distance between burrows. Accordingly, the enhancement of total sediment carbon oxidation due to 2000 irrigated burrows of *N. diversicolor* per m^2 is estimated to $E_i = 1.61$. This is within the previously mentioned range of published enhancements of benthic metabolism caused by a similar abundance of these animals (Kristensen, 2000). However, as the worm abundance increases above a certain level, the anoxic to oxic volume of subsurface sediment and thus the production and reoxidation of reduced metabolites decreases. The oxic zone around burrows may therefore expand, resulting in a proportionally larger oxic volume at high abundances, and thus larger impact of irrigated burrows on sediment decomposition. This is not included in our model.

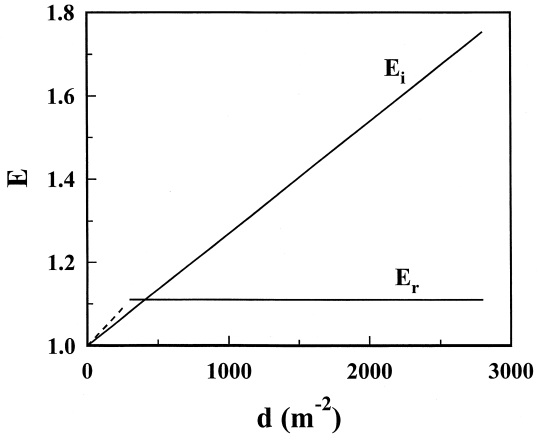


Fig. 7. Enhancement of total sediment carbon oxidation due to increased microbial degradation in the presence of irrigated burrows ($E_i = C_{iox}/C_{dox}$) and reworking ($E_r = C_{rox}/C_{dox}$) as a function of abundance (d). Other variables are fixed: $L = 20$ cm; $L_b = 20$ cm, $L_{ox} = 0.3$ cm; $r = 0.3$ cm, $B_{ox} = 0.2$ cm; $A_1 = 20$ and $A_2 = 10$. See text for further details.

The reworking model predicts that carbon oxidation in the presence of *H. filiformis* is enhanced by $E_r = 1.11$, when the variables L, L_{ox}, A_1, and A_2 are similar to those used in the irrigation model, and that the enhancement is independent of worm abundance, d. This prediction is only valid when reworked subsurface sediment containing reactive organic material covers the sediment surface to a depth similar to the oxic zone and that reaction rates are not so fast as to eliminate entirely the organic material exposed in a single transit. This means that below a certain threshold the enhancement must be proportional to abundance. As one average sized individual deposits 4×10^{-5} cm/d sediment at the surface (Cadee, 1979), a population size of 300/m^2 is needed to deposit a 0.3-cm layer (equivalent to L_{ox}) every 25 d. The actual threshold of abundance is probably lower than this limit, because there were no signs of changes in reactivity of aged materials exposed to oxygen for ~25 d.

It is important to note that these model calculations are only valid for the initial conditions after introduction of macrobenthic activity. For a fixed influx of material, the steady-state mass of reactive organic material in a sediment deposit where decomposition rates are enhanced by faunal activities must be lower than for a defaunated situation. In reality, the ratio of reactive organic pools in defaunated and faunated sediments is inversely related to the ratio of reaction rates in the two environments (Kristensen, 2000).

Nevertheless, our model examples illustrates that above an abundance of ~400 ind./m^2, decomposition of partly degraded organic matter along oxic walls of irrigated infaunal burrows is enhanced progressively more than by exposure of subsurface sediment to oxygen during reworking (Fig. 7). Although both mechanisms should be considered significant contributors to the increased capacity for decomposition in bioturbated sediments, it must be noted that injection of oxygen into burrows and exposure of subsurface sediment to oxygen during reworking is only two of several factors believed to increase rates of microbial processes in bioturbated sediments (Aller, 1994; Aller and Aller, 1998).

5. CONCLUSIONS

The present study supports the conclusions of Kristensen et al. (1995) that the decomposition of fresh and labile organic materials in sediments is independent of redox conditions, whereas partly degraded materials are degraded faster when exposed to oxygen. A major drawback in their study was the comparison of fresh hay with aged diatoms, in reality not a comparable pair. Here we have shown that the initial decay of both fresh diatoms and hay occurs at almost the same rate in both oxic and anoxic sediment. After aging, however, both materials are degraded 5 to 10 times faster under oxic than anoxic conditions. The aging process and divergence in aerobic and anaerobic decay rates occur much faster for diatom than hay materials. Among anaerobic processes, sulfate respiration mediates similar or slightly higher carbon mineralization than nitrate respiration.

Volumetric model considerations show that exposure of anoxic sediment to oxygen in irrigated burrows and by sediment reworking enhances total carbon oxidation. The enhancement in the irrigation case increases linearly with density. Above a lower threshold of abundance (i.e., 400/m^2) the irrigation enhancement becomes progressively higher than the density independent enhancement in the reworking case. The oxygen effect is an important factor for the commonly observed stimulation of benthic metabolism by bioturbating infauna in marine environments.

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