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Effects of oxygen and redox oscillation on degradation of cell-associated lipids in surficial marine sediments

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Abstract—Degradation patterns of sedimentary algal lipids were tracked with time under variable redox treatments designed to mimic conditions in organic-rich, bioturbated deposits. Uniformly ^{13}C-labeled algae were mixed with Long Island Sound surface muddy sediments and exposed to different redox regimes, including continuously oxic and anoxic, and oscillated oxic: anoxic conditions. Concentrations of several ^{13}C-labeled algal fatty acids (16:1, 16:0 and 18:1), phytol and an alkene were measured serially. Results showed a large difference (~10×) in first-order degradation rate constants of cell-associated lipids between continuously oxic and anoxic conditions. Exposure to oxic conditions increased the degradation of cell-associated lipids, and degradation rate constants were positive functions (linear or nonlinear) of the fraction of time sediments were oxic. Production of two new ^{13}C-labeled compounds (*iso*-15:0 fatty acid and hexadecanol) further indicated that redox conditions and oxic: anoxic oscillations strongly affect microbial degradation of algal lipids and net synthesis of bacterial biomass. Production of ^{13}C-labeled *iso*-15:0 fatty acid (a bacterial biomarker) was inversely proportional to the fraction of time sediments were oxic, rapidly decreasing after 10 days of incubation under oxic and frequently oscillated conditions. Turnover of bacterial biomass was faster under continuously or occasionally oxic conditions than under continuously anoxic conditions. ^{13}C-labeled hexadecanol, an intermediate degradation product, accumulated under anoxic conditions but not under oxic or periodically oxic conditions. The frequency of oxic: anoxic oscillation clearly alters both the rate and pathways of lipid degradation in surficial sediments. Terminal degradation efficiency and lipid products from degradation of algal material depend on specific patterns of redox fluctuations. *Copyright © 2002 Elsevier Science Inc.*

1. INTRODUCTION

The efficiency of aerobic versus anaerobic degradation processes and the role of these processes in sedimentary carbon preservation have been widely debated (Emerson and Hedges, 1988; Pedersen and Calvert, 1990; Lee, 1992; Canfield, 1994). The effects of redox environment on organic matter degradation in particular are usually considered from the standpoint of either completely oxic or anoxic conditions. It was recently proposed that organic matter preservation is likely dependent on the diagenetic "oxygen exposure time" when sinking particulate organic matter passes through the oxic zone in marine sediments (Hartnett et al., 1998; Hedges et al., 1999). In coastal areas, redox properties in surface sediments can change seasonally due to variation of dissolved oxygen content in bottom waters [e.g., occurrence of hypoxia in Chesapeake Bay or Long Island Sound (Beristain and Arnold, 1991; Parker and O'Reilly, 1991; Mackin et al., 1991)]. In addition, sediments in bioturbated deposits experience oscillations between oxic and anoxic states over a broad spectrum of timescales during irrigation and feeding activities. Oscillating redox conditions in surface bioturbated sediments may represent a functional environmental state, distinct from end-member oxic or anoxic conditions, potentially promoting degradation and minimizing burial of organic matter (Aller, 1994).

Lipids account for 5 to 20% of carbon in phytoplankton, which is the initial local source of particulate organic matter to the seafloor (Parsons et al., 1961). Sedimentary diagenetic processes further alter lipid composition and distribution (Cranwell, 1982; Volkman et al., 1983). Lipids degrade at different rates in various depositional sites with distinct redox conditions (McCaffery et al., 1991; Sun and Wakeham, 1994; Canuel and Martens 1996; Sun et al., 1997). During the consumption of organic matter, benthic microbes synthesize a range of new compounds, including specific lipid compounds which have been widely used to characterize the microbial community (Dowling et al., 1986; Vestal and White, 1989; Findlay et al., 1989).

The present study was designed to specifically test the effect of redox oscillation frequency on the degradation of planktonic lipids in sedimentary deposits. Uniformly ^{13}C-labeled algae were used to mimic the input of fresh planktonic detritus to surface sediments. ^{13}C-labeled lipids contained in the algae were tracked to distinguish them from other lipid sources in bulk sediments. Six sets of incubations were conducted with different redox regimes: continuously oxic and anoxic, oscillating oxic: anoxic conditions in diffusively open systems with metabolite exchange, and continuously anoxic conditions under closed conditions where metabolite build up occurred. Degradation rates and apparent rate constants in these different regimes were determined by following the changes in concentration in a subset of ^{13}C-labeled lipids as a function of time. In addition, two ^{13}C-labeled degradation products were identified and their production was linked to microbial processes.

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2. METHODS

2.1. Incubation Set Up

Sediment samples were taken from surface (top 1 cm) deposits collected by grab from central Long Island Sound (41°16.00'N and 72°57.92'W, October 1996). Sediment was passed through a 1-mm sieve (no water added) and mixed with uniformly labeled ($^{13}C > 98\%$) algal cells. The ^{13}C-labeled algae (*Chlorella*) were obtained from Cambridge Isotope Laboratories. About 1 g of labeled algae (lyophilized cells) was ground finely and then mixed with ~200 g wet sediment by hand stirring for 30 min. Addition of algae resulted in an approximately 0.7% increase in total organic carbon, similar to that from a pulse input during plankton blooms in LIS (Sun et al., 1994; Gerino et al., 1998). The mixed sediments were made into thin plugs (1.5 mm thick, 8 cm I.D.), held by a plastic ring on a PVC plate. These thin plugs of sediment were used in diffusively "open" incubations, as described in previous papers (Aller and Mackin, 1989; Sun et al., 1993a).

Briefly, in "open" incubation systems, sets of sediment plugs sit on the bottom of large water reservoirs (usually ~10 L; 0.2 μ filtered). The upper surfaces of the plugs were exposed to well-stirred reservoirs, allowing for diffusive exchange of solutes between sediment and overlying water. Depending on treatment, oxic or anoxic conditions were maintained by continual purging of the water reservoirs with either air or with a N_2/CO_2 mixture (the ratio of N_2 and CO_2 was chosen to maintain a particular fixed pH, 8.05 ± 0.03). Traces of O_2 in the N_2/CO_2 stream were stripped using an Alltech indicating O_2 trap. Then the stream was hydrated by bubbling through a gas-washing bottle filled with distilled water. Oscillation between oxic and anoxic conditions was carried out by switching purging gas in water reservoirs; ~2 h were needed for complete conversion between redox states. Five sets of "open" incubations were conducted according to the following redox regimes (Fig. 1): I (continuously oxic); II (continuously anoxic); III (1d oxic: 1d anoxic); IV (1d oxic: 3d anoxic); V (1d oxic: 7d anoxic). Incubations were carried out in the dark at room temperature (19 ± 2°C) for three weeks. Portions of the experimental sediment were inserted into small (4 mL) screw cap jars (without headspace) and buried in bulk sediment for "closed" anoxic incubations (VI).

2.2. Sampling and Analysis

At six time points, a sediment plug was taken from each incubation chamber and split into several parts, one of which was taken for lipid analysis and the remainder retained for additional analyses not discussed here. Samples for lipid analysis were stored frozen (−20°C) for later extraction. Extraction and analysis procedures are described elsewhere (Sun et al., 1997). Briefly, the thawed sediments were extracted first with methanol, then methylene chloride: methanol. Extracts were saponified with 0.5 N KOH solution, and neutral and acidic lipids were separated by extraction under different pH conditions. Fatty acids from acidic extraction were methylated with BF_3/MeOH to form fatty acid methyl esters (FAME). Neutral lipids from basic extraction were treated with BSTFA in acetonitrile to convert phytol and other alcohols into TMS-ethers. FAMEs and alcohol-TMS ethers were analyzed by gas chromatography. ^{13}C-labeled lipids were separated and identified using a Shimadzu QP-5000 GC/MS system with a 30 m × 0.25 mm I.D. XTI-5 column (Sun, 2000).

3. RESULTS

We chose to follow the dynamics of five ^{13}C-labeled lipid compounds initially present in the ^{13}C-labeled algae: 16:1(ω7), 16:0 and 18:1(ω9) fatty acids, phytol and 17:1 alkene. In addition, we followed production of two newly produced ^{13}C-labeled: *iso*-15:0 fatty acid and hexadecanol. The net formation patterns of these two compounds during different redox regimes were documented. Based on triplicate measurements for initial mixed samples (t = 0), relative standard deviations of various lipid analyses (total concentration and ^{13}C-labeled concentration) were in the range of 1 to 6%.

3.1. Oxic and Anoxic End-Member Incubations

Open oxic (I) and anoxic (open, II; closed, VI) incubations of sediments (Fig. 2) showed obvious differences between oxic and anoxic degradation of the five ^{13}C-labeled target compounds initially present in the algae. These compounds degraded much faster under continuously oxic conditions than under continuously anoxic conditions. Within three weeks, the ^{13}C-labeled lipids initially present either degraded completely or were nearly eliminated from incubated sediments under oxic conditions. In contrast, a large fraction of these compounds remained in incubated sediments under anoxic conditions.

3.2. Oxic: Anoxic Oscillated Incubations

The five target compounds degraded at different rates depending on oscillation frequency (Fig. 3). Lipid degradation rates during oscillated incubations lay between those of continuously oxic and anoxic conditions. The more frequent the oscillation, the faster planktonic lipids degraded. Compared with continuously oxic conditions over a 3-week period, a significant fraction of initially-added planktonic lipids remained in sediments after redox oscillated conditions. The experiments were not long enough to determine whether lipids would reach a defined residual level.

3.3. First Order Rate Constants

Assuming first-order degradation kinetics, reaction rate constants can be estimated from the lipid degradation rates for specific compounds and redox treatments. The general kinetic function is given by:

$$dC_i/dt = -kC_i \quad (1)$$

Where C_i is the concentration of compound i in the sediment solid, t is time, and k is the pseudofirst order rate constant. In the oxic case, residual compound concentrations are negligible so that entire compound pools can be considered reactive in Eqn. 1. For the present calculations we assume the same is true in all redox treatments (see Middelburg, 1989), although the effective reactive pool of a specific compound may in fact depend on redox conditions (Sun et al., 1993a; Ingalls et al., 2000). Rate constants calculated in this way vary regularly with redox treatment (Table 1), and are positive functions of the fraction of oxic exposure time during incubation (Fig. 4). Phytol and 17:1 alkene rate constants are nearly linear functions of percentage oxic exposure time, whereas slightly nonlinear or exponential functions of oxic exposure appear to characterize the remaining compounds (16:0, 16:1, 18:1 fatty acids).

3.4. Formation of Newly Produced ^{13}C-Labeled Compounds

Iso-15:0 fatty acid and hexadecanol were both formed and degraded in regular patterns during incubation (Fig. 5). Based on mass spectral analysis, *iso*-15:0 fatty acid was partially

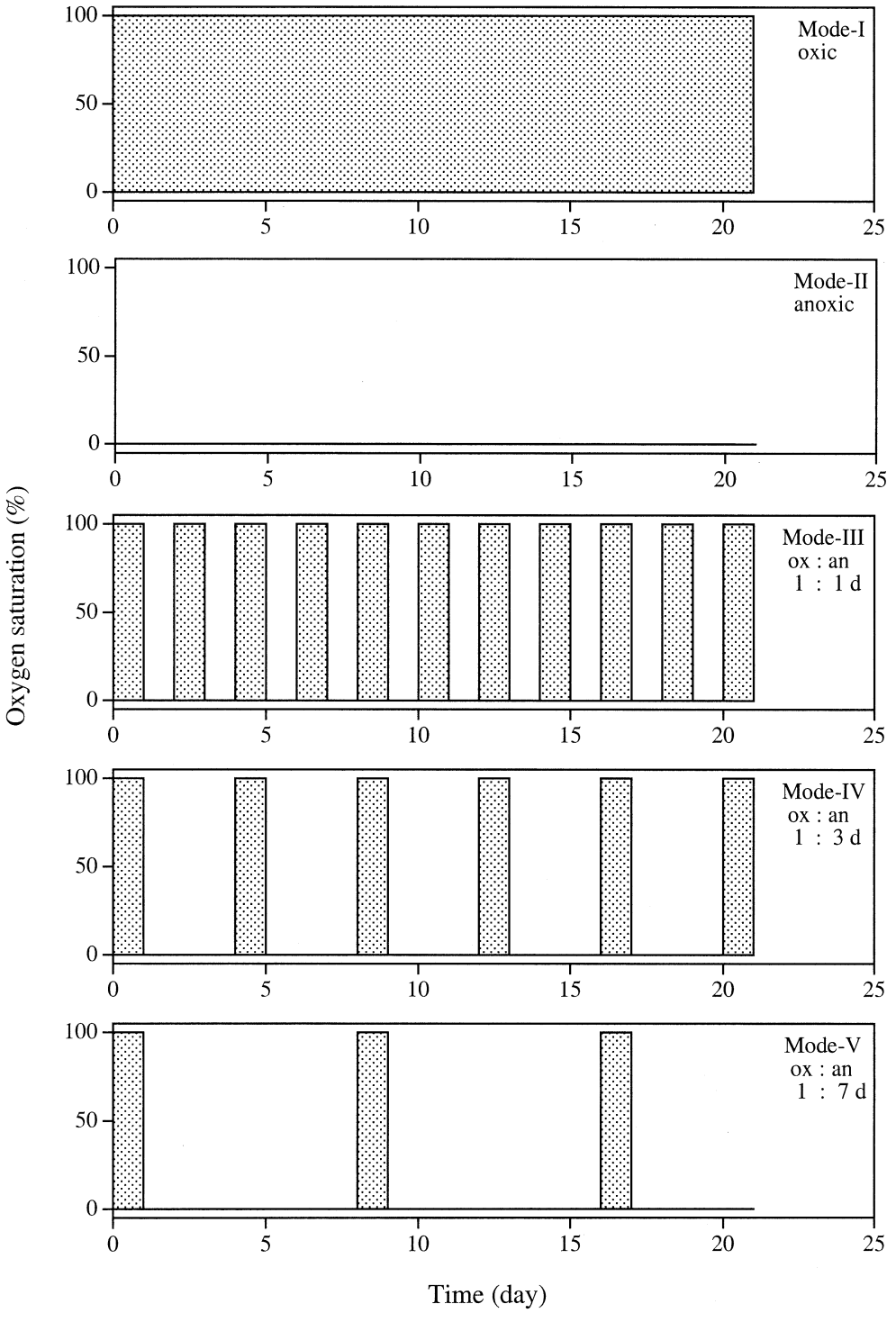

Fig. 1. Modes of oscillation of oxygen: (I) continuously oxic; (II) continuously anoxic; (III) 1d oxic:1d anoxic; (IV) 1d oxic:3d anoxic; and (V) 1d oxic:7d anoxic.

^{13}C-labeled while hexadecanol was uniformly labeled (Sun, 2000). Except for the closed anoxic case, both newly produced ^{13}C-labeled compounds first increased in concentration with time, reaching a maximum or plateau value of varied duration and magnitude depending on redox conditions, and then decreased. No decrease was observed in the closed anoxic incubation. Concentrations of ^{13}C-labeled *iso*-15:0 fatty acid and hexadecanol increased to the largest values under continuously anoxic conditions (II - open and VI - closed). Under continuously oxic conditions (I), the labeled *iso*-15:0 initially increased as in the anoxic case, but dropped dramatically after 10 d when most labeled lipid compounds were also entirely consumed.

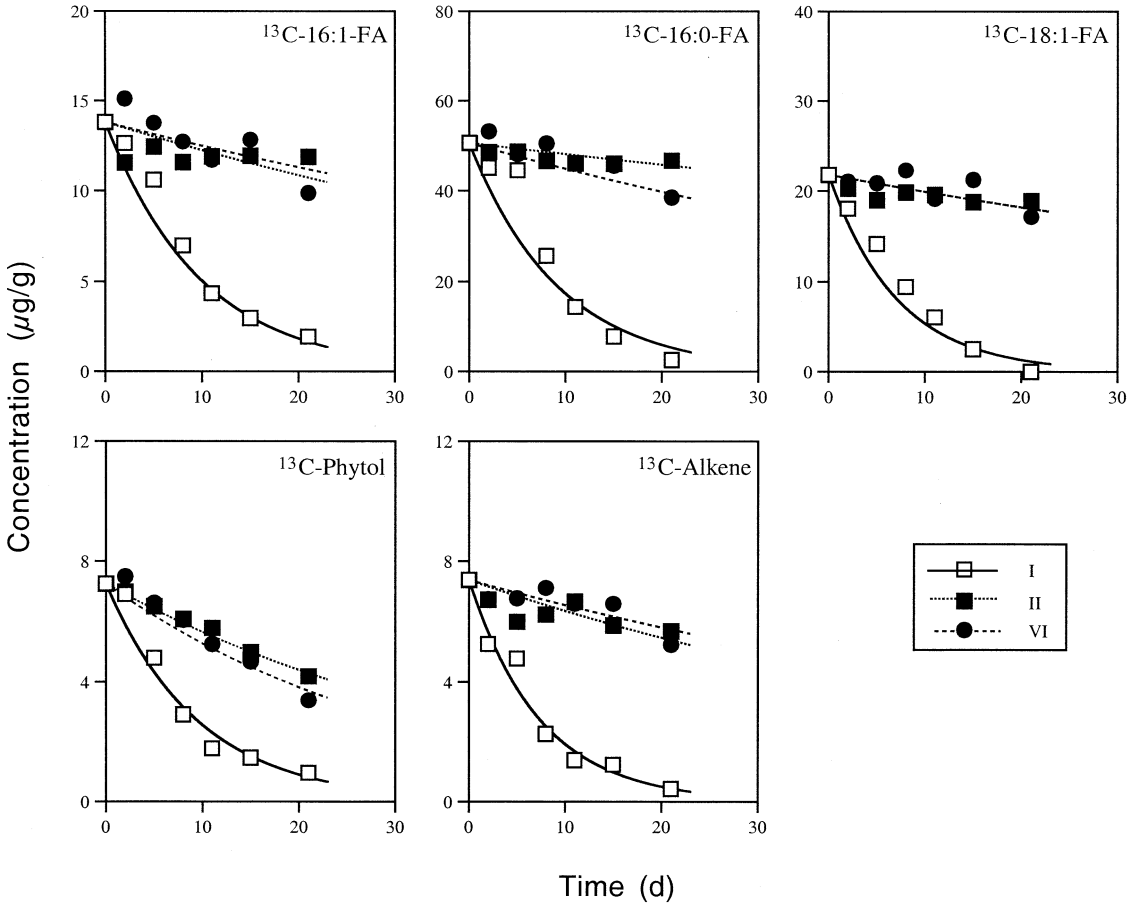

Fig. 2. Concentration variations of five cell-associated ^{13}C-labeled compounds during oxic (I: open) and anoxic (II: open and VI: closed) incubations. The lines are curves fit to a first-order degradation model of the concentration data.

Concentrations of labeled hexadecanol steadily increased under anoxic conditions (II and VI), but there was little accumulation of labeled hexadecanol during oxic incubation (I). Both the peak and average concentrations obtained for *iso*-15:0 and hexadecanol during incubation are inversely related to the fraction of oxic exposure (Fig. 6). The relations appear to be approximately linear for *iso*-15:0 and decidedly nonlinear (exponential) in the case of hexadecanol (open treatments). Closed anoxic conditions result in an increase of *iso* −15:0 fatty acid and a decrease of hexadecanol relative to diffusively open sediment.

4. DISCUSSION

4.1. Reactivity of Planktonic Lipids Under Oxic and Anoxic Conditions

Recent considerations (e.g., Hedges and Keil, 1995; Kristensen et al., 1995; Harvey et al., 1995; Hulthe et al., 1998) suggest that the effect of oxygen on degradation of sedimentary organic matter is dependent in part on the lability, chemical composition, and age of the organic matter undergoing degradation. For example, aerobic and anaerobic remineralization rates are similar for soluble organic matter originating from the initial leaching and early hydrolysis of fresh plant detritus (Kristensen et al., 1995), or for isolated compounds (Lee, 1992). However, when structural components (e.g., lipid complexes) are dominant in aged plant detritus, anaerobic degradation rates are apparently slower than aerobic degradation rates (Kristensen et al., 1995). Even for fresh plant materials, different compound classes, including pigments and lipids, can degrade at different rates under oxic and anoxic conditions, and substrate reactivity may shift between oxic and anoxic conditions (Leavitt and Carpenter, 1990; Bianchi and Findlay, 1991; Lee, 1992; Harvey et al., 1995; Harvey and Macko, 1997; Bianchi et al., 2000).

In the present experiments, estimates of planktonic lipid degradation rate constants (Table 1; Fig. 4) showed consistent and regular trends as a function of redox regime. Such dependencies might differ if compounds were present in mixtures of associations and forms (mineral, molecular) more complicated than present in the relatively simple starting material (e.g., plankton) used here. Due to multiple sources of lipids in sediments, degradation of the planktonic lipid component is very difficult to specifically follow using sedimentary distributions. In the present experiments, addition of ^{13}C-labeled algae allowed individual planktonic lipids (initially cell-associated) to be distinguished from other sedimentary lipids based on mass spectral analysis. The estimates of oxic and anoxic degradation rate constants represent those of fresh planktonic lipids in sediments. Many previous degradation experiments for sedi-

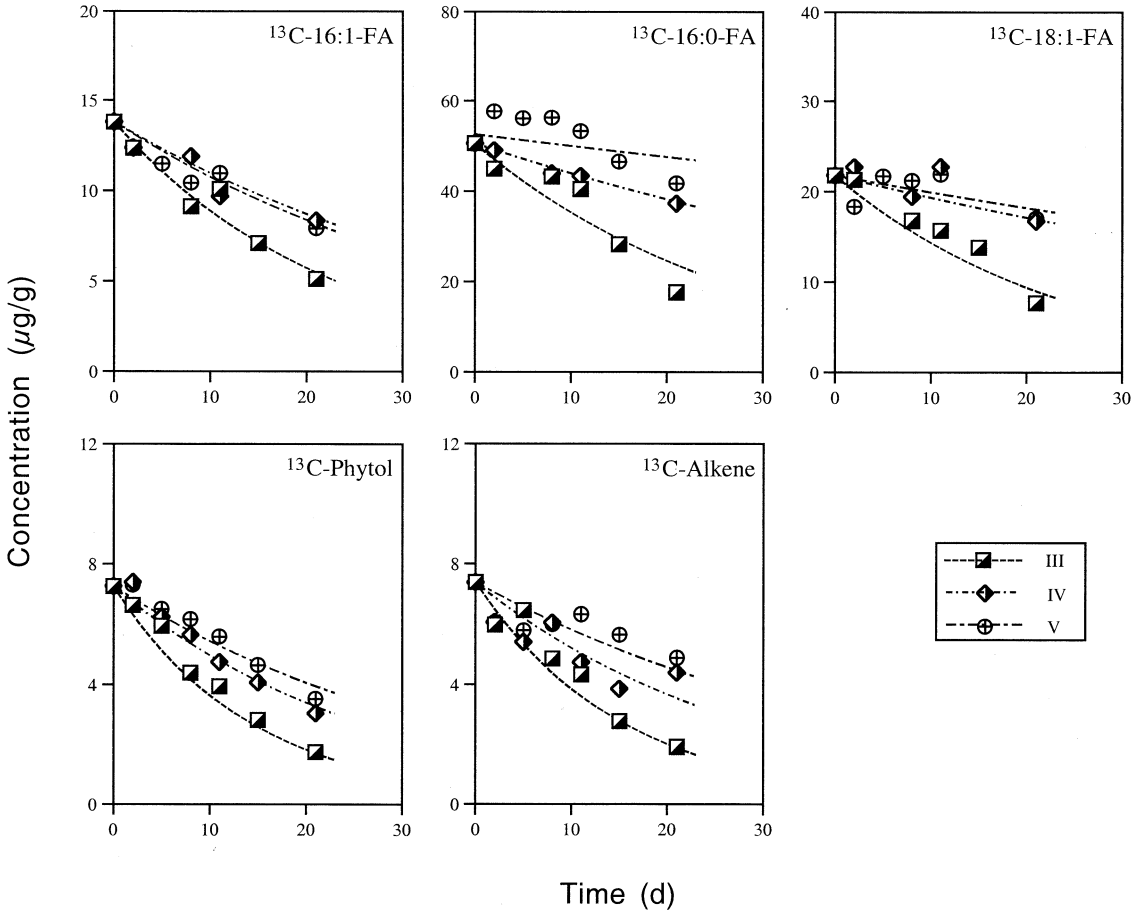

Fig. 3. Concentration variations of five cell-associated ^{13}C-labeled compounds during various oscillated incubations (III - V). The lines are curves fit to a first-order degradation model of the concentration data.

mentary organic compounds have used individual ^{14}C-labeled molecules (Henrichs and Doyle, 1986; Lee, 1992; Sun et al., 1997), largely precluding possible effects of molecular association on degradation. When ^{14}C-labeled free fatty acids were incubated in oxic and anoxic sediments under similar conditions (Sun et al., 1997), the degradation rate constants were 2 to 7× higher than those of planktonic lipids derived from the present study, indicating free molecules have much higher overall reactivity than combined forms. Higher ratios of oxic to anoxic degradation rate constants from the present study also imply that the difference between oxic and anoxic degradation of cell-associated lipid molecules is greater for free lipids.

We found similar behavior in measurements of chlorophyll-*a* degradation in previous studies (Sun et al., 1993b). Free ^{14}C-labeled chlorophyll-*a* molecules degraded similarly in oxic and anoxic sediments, but algal-cell-associated chlorophyll-*a* exhibited large differences in reactive pools under oxic and anoxic conditions. One reason may relate to the presence of various pigment-protein complexes which have different reactivities to degrading enzymes due to differences in size, solubility, association and molecular arrangement (Larkum and Barrett, 1983; Downs, 1989).

4.2. Effect of Oscillation Frequency between Oxic and Anoxic Conditions

In bioturbated sediments with high carbon content, organic matter typically degrades under oscillating redox conditions in

Table 1. Degradation Rate Constants (Day^{-1}) and Correlation Coefficients of ^{13}C-Lipids During Various Incubations.

Incubation	16:1 fatty acid	16:0 fatty acid	18:1 fatty acid	Phytol	17:1 alkene
I-oxic	0.101 (0.98)	0.107 (0.96)	0.14 (0.97)	0.104 (0.96)	0.134 (0.97)
II-anoxic	0.012 (0.21)	0.005 (0.63)	0.009 (0.57)	0.025 (0.99)	0.015 (0.62)
III-oxic:anoxic (1:1)	0.044 (0.94)	0.036 (0.87)	0.042 (0.91)	0.069 (0.99)	0.065 (0.96)
IV-oxic:anoxic (1:3)	0.023 (0.93)	0.014 (0.99)	0.012 (0.62)	0.038 (0.99)	0.035 (0.74)
V-oxic:anoxic (1:7)	0.018 (0.63)	0.005 (0.61)	0.011 (0.29)	0.029 (0.97)	0.024 (0.67)
VI-anoxic (close)	0.010 (0.78)	0.010 (0.83)	0.009 (0.54)	0.032 (0.97)	0.012 (0.70)

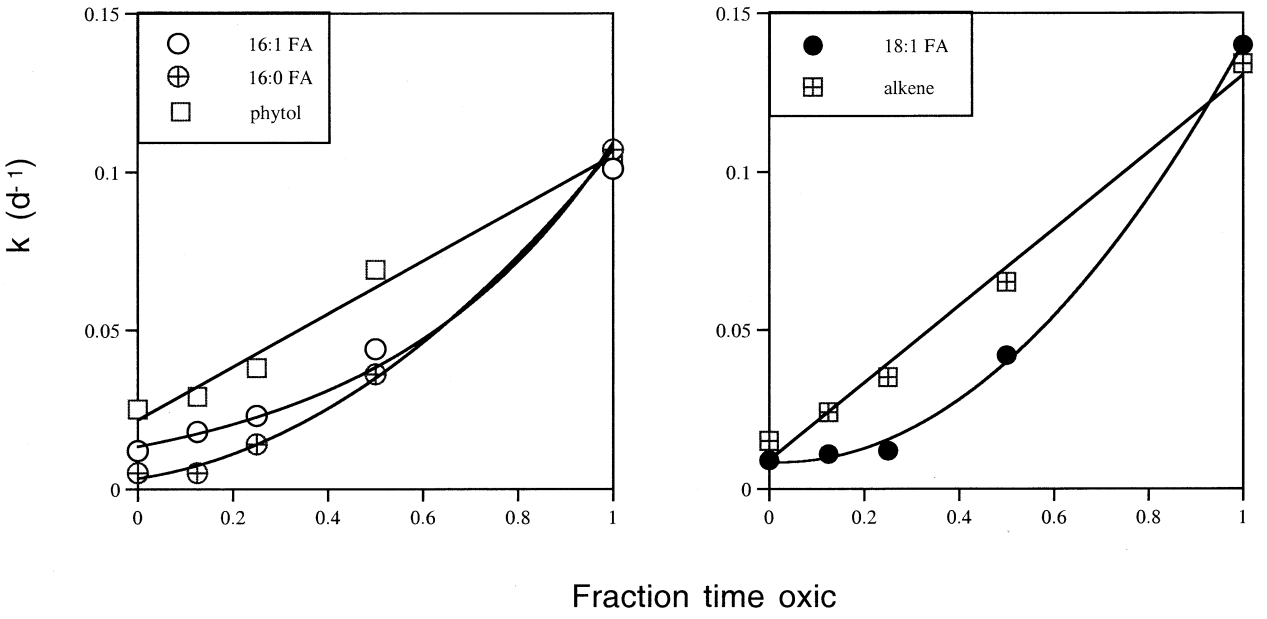

Fig. 4. Relations between degradation constants of five cell-associated ^{13}C-labeled compounds and fraction of time exposure to oxic conditions. Two neutral compounds (phytol and alkene) showed a positive liner relation and three fatty acids (16:1, 16:0, and 18:1) showed a positive exponential relation.

complex, heterogeneous geometries (Aller, 1994). Residence times for freshly-input organic particles are expected to be <1 to 30 d in the oxic zone (top 2 to 3 mm in sediments), and 10 to 100× longer in the mixed anoxic regions (~4 to >20 cm in thickness) of typical estuarine and shelf sediments. Frequency and duration of oscillation may exert an important influence on the degradation of organic matter, particularly on specific compounds and pathways of degradation. The degradation rate constants estimated from our redox oscillation experiments (Table 1; Fig. 4) unambiguously indicated that planktonic lipids degrade faster when oscillation is more frequent and exposure to oxygen is longer in duration. In several cases (phytol, 17:1 alkene) the degradation rate constant is apparently a simple linear function of percentage oxic exposure time, whereas in others (16:1, 16:0, and 18:1 fatty acids), rate constants appear to increase exponentially as percentage exposure to oxygen increases. These patterns suggest that variable oscillation frequencies and combinations of linear and nonlinear relative rate dependence in the bioturbated zone could produce complex product mixtures reflecting particular redox histories.

Harvey et al. (1995) proposed two mechanisms which might be responsible for slower degradation of lipids under anoxic conditions. The first mechanism involves incorporation of free sulfide into highly functionalized lipids, as supported by field observations (Kohnen et al., 1990, 1992). The second mechanism is that inherent structural characteristics of lipids (fewer functionalized oxygen atoms than other cellular components) limit the ability of microbial enzymes to degrade lipids anaerobically. Our results do not directly support either of the above mechanisms. The first mechanism seems unlikely to be dominant in our diffusively open treatments given the combination of abundant sedimentary Fe and the potential diffusive loss of free sulfide (both of which decrease H_2S concentration). If the second mechanism were important, it is also unclear why periodic exposure to oxic conditions does not appear in any instance to result in a functional dependence of reaction rate constant on oxic exposure time which has a negative second derivative (e.g., an asymptotic hyperbolic function; Fig. 4). Introduction of reactive molecular sites during brief exposure to oxygen, followed by periods of anaerobic metabolism which could utilize those activated sites, might be expected to produce enhanced anaerobic degradation (Schink, 1988).

Hulthe et al. (1998) observed that sediment removed from the surface and artificially buried to 20 cm (15 yr) in the anoxic zone was more extensively degraded than surficial sediment held under continuously oxic conditions, despite relatively lower rates of anoxic degradation. They concluded based on those observations and manipulative laboratory experiments, that long-term degradation of bulk sedimentary organic material is less complete under either oxic or anoxic conditions alone than under repeated oxic and anoxic conditions. Aller (1994) also demonstrated that redox oscillation and brief exposure to O_2 stimulated complete remineralization of organic carbon and nutrient release. The causes in the case of older sedimentary material can be explained by a synthesis of the surface area control theory of Mayer (1994a, 1994b), the adsorptive preservation-oxic degradation balance hypothesis of Hedges and Keil (1995) and the experimental findings of Kristensen et al. (1995). The key process is that when buried refractory organic matter, which had been adsorbed within mesopores of mineral surface not available to anaerobic bacteria, was exposed to oxic conditions, aerobic microorganisms could enhance the degradation through production of H_2O_2, which is small enough to diffuse into the mesopores and produce smaller, soluble products. In the present study, target compounds came from fresh labeled algae and adsorption of particulate lipids into mesopores can presumably be ignored. Oscillation of redox might, however, change the lability of

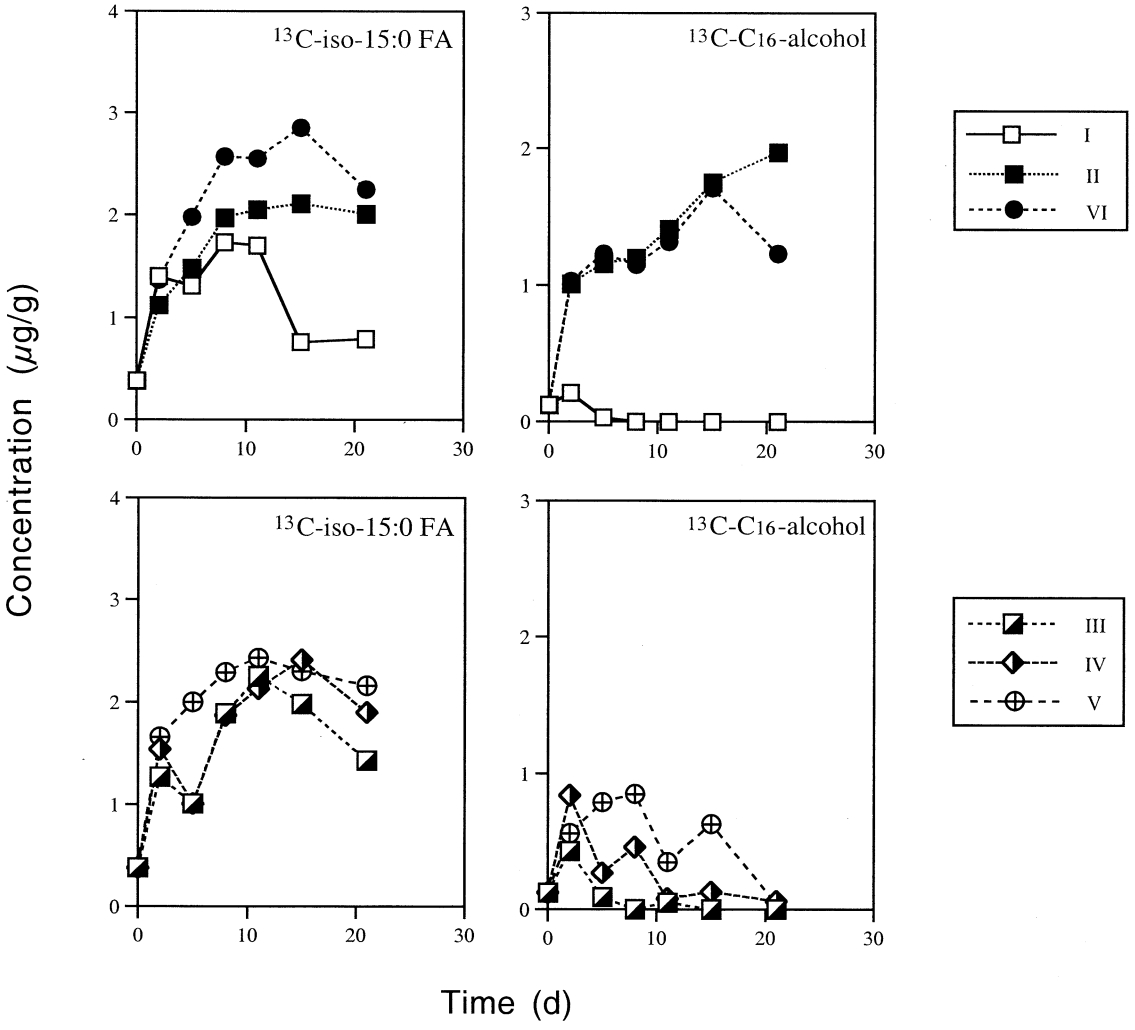

Fig. 5. Concentration variations of two newly-produced ^{13}C-labeled compounds during oxic (I), anoxic (II and VI), and various oscillated (III - V) incubations.

structural complexes of lipids in a similar fashion. Additionally, the spectrum of enzyme activities and facultative metabolic capacities associated with microorganisms attacking organic matter may be enhanced by repeated redox changes (Lovley, 1991; Nealson and Myers, 1992).

4.3. Microbial Processes and Degradation Pathways

The presence of newly-produced ^{13}C-labeled lipids clearly demonstrates similarities and differences in microbial community dynamics that are closely related to redox regime. When bacteria grow, they generate specific compounds including *iso*-15:0 fatty acid in their biomass (Volkman et al., 1980; Parker and Taylor, 1983). During the first few days of incubation, rapid increases of ^{13}C-labeled *iso*-15:0 fatty acid in all treatments (oxic, anoxic, oscillated) indicated immediate response of bacteria to ^{13}C-labeled substrate, including uptake and net incorporation of the added algal substrate into biomass. Because the spiked algae were uniformly labeled (^{13}C >98%), but mass spectral analysis showed that newly-produced *iso*-15:0 fatty acid was partially labeled (Sun 2000), the resynthesis of this compound within bacterial biomass clearly used metabolites from both labeled algae and other sedimentary or cellular organic matter. It has been observed that, following addition of new organic substrate into sediments, transient build-ups of intermediate metabolic products in the DOC pool can occur before complete remineralization to TCO_2 (Westrich and Berner, 1984; Kristensen and Hansen, 1995). Nonsteady build-ups of metabolites following substrate input are influenced by adaptations of the microbial community to the added substrate, and such adaptation may be dependent on sediment type or previous substrate exposure history (Hansen and Kristensen, 1998). In contrast to measures of net remineralization which may show time lags and nonsteady variation in intermediate metabolite concentrations, our experimental results suggest that within the sampling resolution there was essentially immediate synthesis of biomass from added substrate (Fig. 5).

Although initial rates of *iso*-15:0 net synthesis were similar in all treatments, large differences in labeled *iso*-15:0 concentrations emerged after several days of incubation under different redox conditions. The concentration of labeled *iso*-15:0

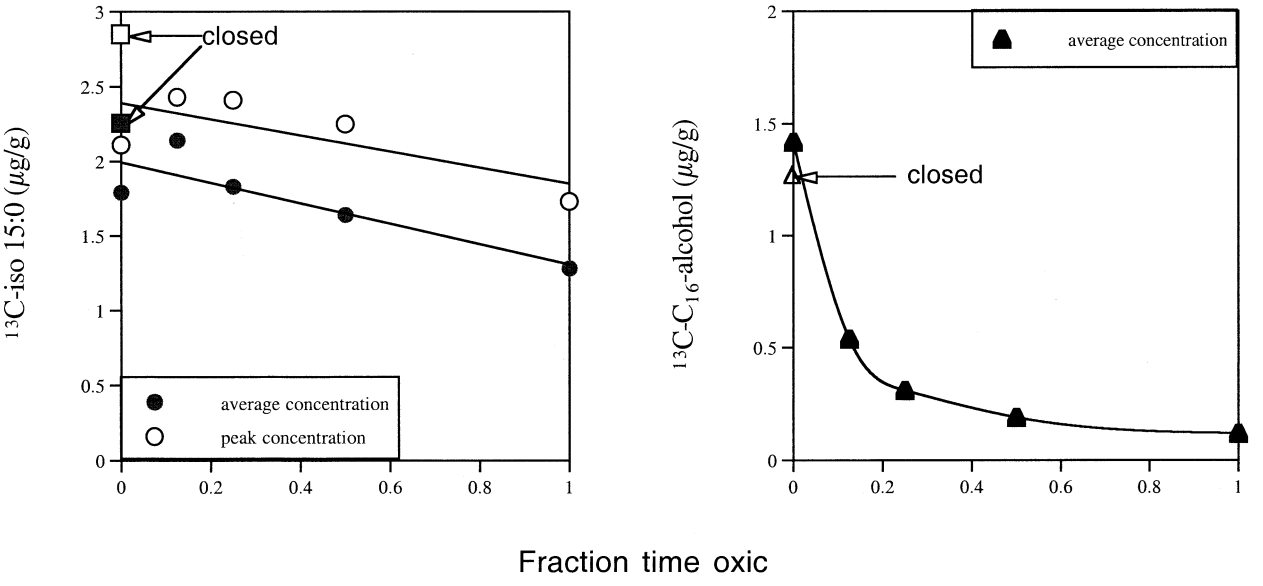

Fig. 6. Relations between concentrations of two newly-produced ^{13}C-labeled compounds (*iso*- 15:0 fatty acid and hexadecanol) and fraction of time exposure to oxic conditions. *Iso*-15:0 fatty acid concentrations (average of peak) are inversely proportional (nearly linear) to the fraction time oxic while hexadecanol concentration exponentially decreases with fraction time oxic.

fatty acid quickly dropped under continuously oxic or more frequent (1d oxic: 1d anoxic) redox oscillation, while it remained almost unchanged after 10 d under continuously anoxic or less frequent redox oscillation. Bacterial biomass may be quickly turned over by faunal grazing in the presence of oxygen, and lead to a loss of this bacterial lipid. An important difference between oxic and anoxic sediments is the presence or abundance of benthic organisms which are major grazers of bacteria and which metabolize aerobically. In our experimental sediments, although macrofauna (>1 mm in size) were removed by sieving before incubation, meiofauna and protozoans might still be present. Our previous experiments (Sun et al., 1993a) showed that several species of meiofauna existed in 0.5 mm sieved sediments under oxic conditions. Under oxic or frequently-oscillated redox conditions, these organisms may rapidly graze bacteria whose biomass contains labeled *iso*-15:0. Grazers are usually absent or less common under anoxic or less frequently-oscillated conditions. On the other hand, production of labeled *iso*-15:0 fatty acid also depends on supply of ^{13}C-labeled algae or, more likely, its metabolites since it appears that the labeled *iso*-15:0 is synthesized de novo from labeled algal carbon. When ^{13}C-labeled metabolites that would be available for bacterial uptake are no longer being produced, they may become limited; this would result in a decrease in labeled *iso*-15:0 fatty acid in bacterial biomass as it degrades under oxic or more frequently-oscillated redox conditions. In other words, destruction of bacterial biomass by grazing may exceed the production of new labeled *iso*-15:0 fatty acid by the bacteria. Under anoxic or less frequently-oscillated redox conditions, however, labeled *iso*-15:0 remained almost constant, implying that turnover of bacterial biomass may not be significant on the time scale of this experiment.

Grazing of bacteria by benthic organisms (fauna and protozoans) is thought to enhance the rate of organic matter degradation (Lee, 1980; Kemp, 1990; Lee, 1992) since grazing can stimulate continuous rapid growth of microbial populations (Plante et al., 1990). Changes in labeled *iso*-15:0 fatty acid concentrations under different redox conditions indirectly confirm this. In our experiments, the rapid degradation of planktonic lipids under oxic or more frequently-oscillated redox conditions appears to correlate with lower bacterial biomass, as implied by reduced amounts of *iso*-15:0 fatty acid shown in Figure 6.

Production of labeled hexadecanol (Figs. 5, 6) during our incubation experiments appears to relate to bacterial metabolic capacity. Uniformly-labeled hexadecanol is derived exclusively from labeled algal substrate based on mass spectral analysis (Sun, 2000). In the present experiment, labeled hexadecanol was produced steadily under anoxic conditions but little was produced under oxic conditions. We do not know what the precursor of hexadecanol is and which transformation pathway is involved. It is possible that uniformly-labeled hexadecanol could be derived from reduction of labeled 16:0 fatty acid (the most abundant lipid component in labeled algae) under anoxic conditions. Newly-produced hexadecanol remains stable under anoxic conditions, implying that anaerobic bacteria can not further degrade this new compound. Similar reductions are well known to occur during sedimentary diagensis, e.g., the anaerobic reduction of unsaturated steroidal alcohols (stenols) to saturated analogs (stanols) (Gagosian et al., 1980; Mermoud et al., 1984; Wakeham, 1989). Teece et al. (1999) demonstrated by measuring molecular isotopic fractionation that aerobic and anaerobic bacteria use distinctly different assimilation pathways when they grow on a sole carbon source.

Under oscillating redox conditions, more hexadecanol was produced under less frequent redox oscillation, the relation being a roughly exponential decrease with oxygen exposure (Fig. 6). Decreases in labeled hexadecanol concentration ap-

pear to occur immediately after exposure to oxic conditions in the oscillating treatments (Fig. 5). Short exposure (one day) to O_2 may cause hexadecanol (intermediates of bacteria metabolism) to degrade. Redox oscillation can promote degradation of organic matter in two alternative ways: either brief exposure to O_2 accelerates subsequent anaerobic degradation of otherwise refractory compounds, or exposure to anaerobic conditions allows anaerobes to rapidly decompose otherwise aerobically stable compounds. The example of the former pathway is aliphatic compounds that are stable against anaerobic degradation but can be destroyed after exposure to O_2 due to formation of a single terminal double bond in the structure (Schink, 1988). Examples of the latter pathway are methoxychlor (Fogel et al., 1982) and polychlorinated biphenyls (Sokol et al., 1994), which are stable in oxic environments but degrade by reductive dechlorination in anoxic environments. Therefore, changes in redox conditions directly affect bacterial metabolism and lead to different transformation pathways for specific organic compounds. The fact that the build-up pattern can be a nonlinear function of oxic exposure time (Fig. 6) implies, as in the case of lipid degradation (Fig. 4), that residual sedimentary product mixtures may be complex functions of redox dynamics experienced during various stages of diagenesis.

Our results are consistent with many other studies showing the importance of oxygen on organic matter degradation (e.g., Lee, 1992; Harvey et al., 1995; Sun et al., 1997; Hulthe et al., 1998) and further emphasize the effects of oscillating sedimentary redox conditions (Aller, 1994). In recognition of the relationship between oxygen and organic matter degradation (and consequently its preservation), the concept of "oxygen exposure time" (OET) has been proposed (Hartnett et al., 1998; Hedges et al., 1999). This concept assumes that organic matter degradation is strongly determined by the average time that the organic compounds are exposed to porewater oxygen. Oxygen can penetrate into the sediments by diffusion from overlying bottom waters and by bioturbation. Aerobic degradation in organic-rich coastal sediments will rapidly consume oxygen delivered by diffusion, leading to anoxia and low rates of degradation. However, if a mobile, bioturbating organism enters the picture, then a much more dramatic introduction of oxygen can occur, even if only transient, and degradation rates may rise quickly. As the organism moves away or becomes inactive, anoxic conditions will return. The result of chronic slow degradation under normally anoxic or suboxic conditions coupled with pulses of intense oxygen exposure and aerobic degradation is an increase in net degradation rate. Our experiments have suggested that these dynamic redox oscillations greatly influence net overall rates of organic matter degradation and product formation in sediments.

5. CONCLUSIONS

Incubation of algal lipids under variable redox conditions in the laboratory demonstrated that the degradation of cell-associated lipid compounds was least under continuously anoxic conditions and increased either linearly or nonlinearly with time of exposure to oxygen. Changes in redox condition significantly affect lability of specific organic compounds. Under continuously oxic conditions, bacteria are turned over quickly, presumably due to grazing by meiofauna and protozoans, thus stimulating rapid degradation. Under continuously anoxic conditions, bacteria do not as efficiently remineralize lipid compounds, and reaction intermediates may accumulate. Oscillation of redox conditions regulates microbial activity and lipid degradation, minimizes the accumulation of intermediates, and produces complex product mixtures dependent on specific redox dynamics.

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