RECYCLING OF ORGANIC CARBON NEAR THE SEDIMENT-WATER INTERFACE IN COASTAL ENVIRONMENTS

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ABSTRACT

Labile detrital organic matter is rapidly recycled near the sediment-water interface in both deep-sea and nearshore environments. Detailed studies of benthic organic carbon recycling at a single non-bioturbated coastal site, including direct seasonal rate determinations and sediment-water dissolved carbon flux measurements, serve to test the usefulness of a simple kinetic model for degradation based strictly on sedimentary organic carbon distribution. The model is extremely sensitive to the choice of an upper boundary concentration and becomes useful only when tuned with either the direct rate or flux data.

Studies of the vertical depth distribution and sedimentation of specific classes of organic compounds in the deep sea clearly reveal the reactive nature of labile components associated with organic detritus. For example, Wakeham et al. (1980) have demonstrated that significant alteration of particulate organic compounds produced by phytoplankton and zooplankton takes place in the upper few hundred meters in the equatorial Atlantic Ocean. Transformations of labile components in the water column are also important in coastal areas. For example, Lee and Taylor (1983) have shown that greater than 80% of the particulate amino acids produced during photosynthesis in surface waters are remineralized before reaching the bottom in the Peru upwelling area.

However, as reviewed by the above authors, numerous recent sediment trap and in situ pump studies have illustrated the importance of rapidly sinking, large particles as a source of labile organic materials to the sea floor. Benthic transformation and remineralization processes associated with this rain of organic detritus are therefore of great importance in the deep sea and should become increasingly important as one moves toward highly productive coastal waters, especially in view of the direct proportionality generally observed between rates of primary productivity in the euphotic zone and downward organic detritus fluxes (Suess, 1980). Radiochronometric tracers, particularly the pairs ^{228}Th-^{228}Ra (Broecker et al., 1973; Li et al., 1981) and ^{234}Th-^{238}U (Bhat et al., 1969; Aller et al., 1980), have proven to be useful quantitative tools for describing the removal of particles including organic-rich detritus from the water column in both oceanic and nearshore environments. Results from the use of these radioisotopes indicate that particle residence times shrink from months in oceanic surface waters (Broecker et al., 1973) to less than several days in shallow coastal waters (Aller et al., 1980). Comparisons of the organic C:N:P ratios of sinking particles caught by sediment trap arrays in productive coastal waters versus the open ocean water column (Knauer et al., 1979) indicate a substantially higher nutritive content for the former as might be expected as a result of their shorter residence times prior to sedimentation.

The demonstration of potential linkages between benthic nutrient remineralization and water column primary productivity in shallow coastal systems provides some index of just how important benthic recycling processes can be. Microbially-mediated degradation of organic materials in coastal sediments frequently can

provide greater than 50% of the N and/or P requirements of primary producers in overlying waters (Rowe et al., 1975; Davies, 1975; Nixon et al., 1976).

In this paper the results of recent studies of organic carbon degradation and resultant chemical fluxes in the rapidly accumulating sediments of a small coastal basin are reviewed with the intent of demonstrating how recycling rates near the sediment-water interface can be quantified. Emphasis is placed on an analysis of simple kinetic models for organic carbon frequently utilized to model rates from solid phase organic carbon depth-concentration profiles. In deep sea environments where surface water productivity and organic detritus fluxes are low, much of the labile organic matter deposited is degraded immediately at the sediment-water interface (Emerson and Bender, 1981). In contrast, rapid degradation processes in organic-rich coastal environments frequently take place over tens of cm in the sediment column, directly leading to the well known series of microbially-mediated respiration and fermentation processes in which a series of oxidants including dissolved O_2, dissolved nitrate, solid phase manganese and iron oxides, and dissolved sulfate are sequentially depleted, followed by methanogenesis (Sorensen et al., 1979; Froelich et al., 1979; Crill and Martens, 1983). Nevertheless, it is well established that degradation rates in nearshore sediments are most rapid near the sediment-water interface in response to recent inputs of labile organic detritus (Berner, 1980; Westrich and Berner, 1983).

A number of methods have been utilized to quantify sedimentary organic carbon degradation rates in coastal sediments. In addition to kinetic models for organic carbon these methods include direct measurements of degradation rates via production of end products such as ΣCO_2 or utilization of oxidants such as SO_4^{2-} and measurements of fluxes of degradation end-products such as ΣCO_2 and CH_4 across the sediment-water interface.

The results of using all three of these methods at a single location are utilized here to direct attention at potential difficulties associated with the use of kinetic models based strictly on measurements of organic carbon distributions in the sediment column. Detailed descriptions of the research site, Cape Lookout Bight, located on the Outer Banks of North Carolina, can be found in Martens and Klump (1980) and Chanton et al. (1983). Organic carbon degradation processes occurring in its fine grained sediments, the upper meter of which are accumulating at a rate of approximately 10 $cm \cdot yr^{-1}$, are dominated by sulfate reduction and methanogenesis (Martens and Klump, 1984). Figure 1 schematically illustrates the rates of organic carbon cycling processes known from the work of Martens and Klump (1980; 1984), Chanton et al. (1983) and Crill and Martens (1983). The objective will be to compare what can be learned from kinetic models based on organic carbon concentration distributions with these measured degradation rates and sediment-water fluxes.

KINETIC MODEL FOR ORGANIC CARBON REMINERALIZATION

Jørgensen (1982) has recently demonstrated the overall importance of organic carbon oxidation via sulfate reduction in nearshore environments. In coastal sediments sulfate reducers can oxidize as much organic matter to CO_2 as all aerobes combined. The oxidation of sedimentary organic matter during sulfate reduction has been simplistically modeled using stoichiometric equations derived from the original of Richards (1965) such as:
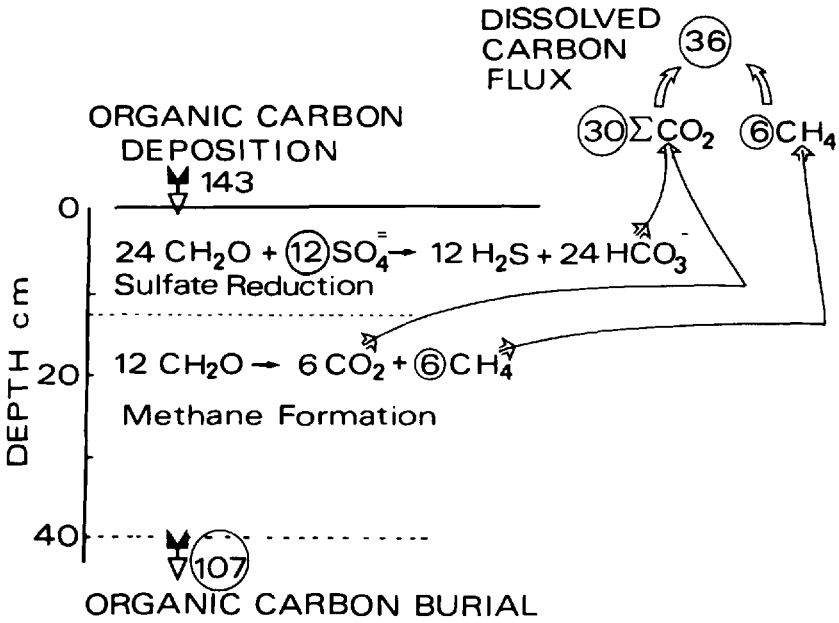
$$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + \tfrac{1}{2}xSO_4^{2-}$$
$$\rightarrow xHCO_3^- + \tfrac{1}{2}xH_2S + yNH_3 + zH_3PO_4 \qquad (1)$$
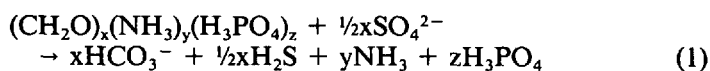
Figure 1. Rates of organic carbon input, degradation to ΣCO_2 and CH_4, burial below the zone of rapid methanogenesis, and resulting sediment-water ΣCO_2 and CH_4 fluxes in Cape Lookout Bight sediments. Directly measured rates are circled; other numbers are based on calculations as discussed in the text.

The stoichiometric relationship between carbon and sulfur reduces to:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad (2)$$
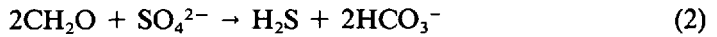
where CH_2O represents the particulate organic matter undergoing oxidation. The overall decomposition rate has been assumed to be first order with respect to metabolizable organic matter concentration (Berner, 1974; 1980), an assumption reviewed extensively by Skopentsev (1981) and recently verified by Westrich and Berner (1983) for nearshore sediments. In terms of metabolizable organic carbon (G_m):

$$\frac{dG_m}{dt} = -kG_m \qquad (3)$$

where k is a first order rate constant.

The remineralization of metabolizable organic carbon in marine sediments thus has been studied by applying a steady state diagenetic equation to concentration data such as that seen in Figure 2 which employs first order decomposition (Berner, 1974):

$$-w\frac{\partial G_m}{\partial z} - kG_m = 0 \qquad (4)$$

Solution for the boundary conditions:

$$z = 0; \quad G_m = G_m{}^0$$
$$z \rightarrow \infty; \quad G_m \rightarrow 0$$

yields

$$G_m = G_m{}^0 \exp\left(-\frac{k}{w}z\right) \qquad (5)$$

where w is the sediment accumulation rate.

A constant w, no sediment compaction, and no sediment mixing are assumed in this simplified model. In addition to avoiding these assumptions, more sophisticated models divide G_m into groups of compounds with differing reactivities, and hence, different first order decomposition rate constants (Jørgensen, 1979; Westrich and Berner, 1983). Such models predict the successive dominance of each group with depth prior to its depletion; however, the present study is restricted to modeling the disappearance of total metabolizable organic carbon with a single first order rate constant, k.

An integrated value of the total metabolizable organic carbon remineralized in the sediment column can be obtained by substitution of equation 5 into equation 3 above followed by integration:

$$\frac{dG_m}{dt} = -kG_m{}^0 \int_0^{z^*} \exp\left(-\frac{k}{w}z\right) dz \qquad (6)$$

$$= G_m{}^0\left[1 - \exp\left(-\frac{k}{w}z\right)\right] \qquad (7)$$

where z* is the depth interval over which organic carbon mineralization occurs.

In order to utilize equation 7, a value for k/w was obtained by an error minimization computer curve fit to the Figure 2 data using an equation of the form:

$$G_z = (G_0 - G_\infty)\exp - \alpha z + G_\infty \qquad (8)$$

where $G_m{}^0 = G_0 - G_\infty$), the difference between *total* organic carbon concentration at the sediment-water interface and at depth where a constant concentration is reached, and the attenuation constant, α, equals the ratio k/w. Using chosen values of G_0, the computer program best fit α and G_∞ values by summed error minimization. Because the percent organic carbon (G) analyses were made on a dry weight basis and our preceding ^{210}Pb sediment accumulation rate was corrected for depth dependent porosity variations to a dry weight basis (Chanton et al., 1983), the organic carbon data was also fit on a dry weight basis by replacing measured depth (z) with mass depth, ΣM_z whose units are total dry mass accumulation in the sediment column above depth z per unit area of whole wet sediment (g·cm^{-2}). This was accomplished by fitting the distribution of calculated solid phase mass concentration ($m_z = [1 - \phi_z]\rho_{\text{solids}}$) using the equation:

$$\sum M_z = \frac{1}{\beta}(m_\infty - m_0)(e^{-\beta z} - 1) + m_\infty z \qquad (9)$$

where m_0 and m_∞ are dry mass concentrations at the interface and at depth where porosity becomes constant respectively, and β (cm^{-1}) is the attenuation constant for porosity obtained by a curve fit to the data of Klump (1980). Values of m_0 and m_∞ were 0.185 and 0.365 g·cm^{-3} respectively for a measured dry sediment density of 2.5 g·cm^{-3}, $\phi_0 = 0.926$, and β value for porosity of 0.127 cm^{-1} as determined by Klump (1980). It should be pointed out that the lack of significant bioturbation at the site allows us to avoid corrections of the model for mixing.
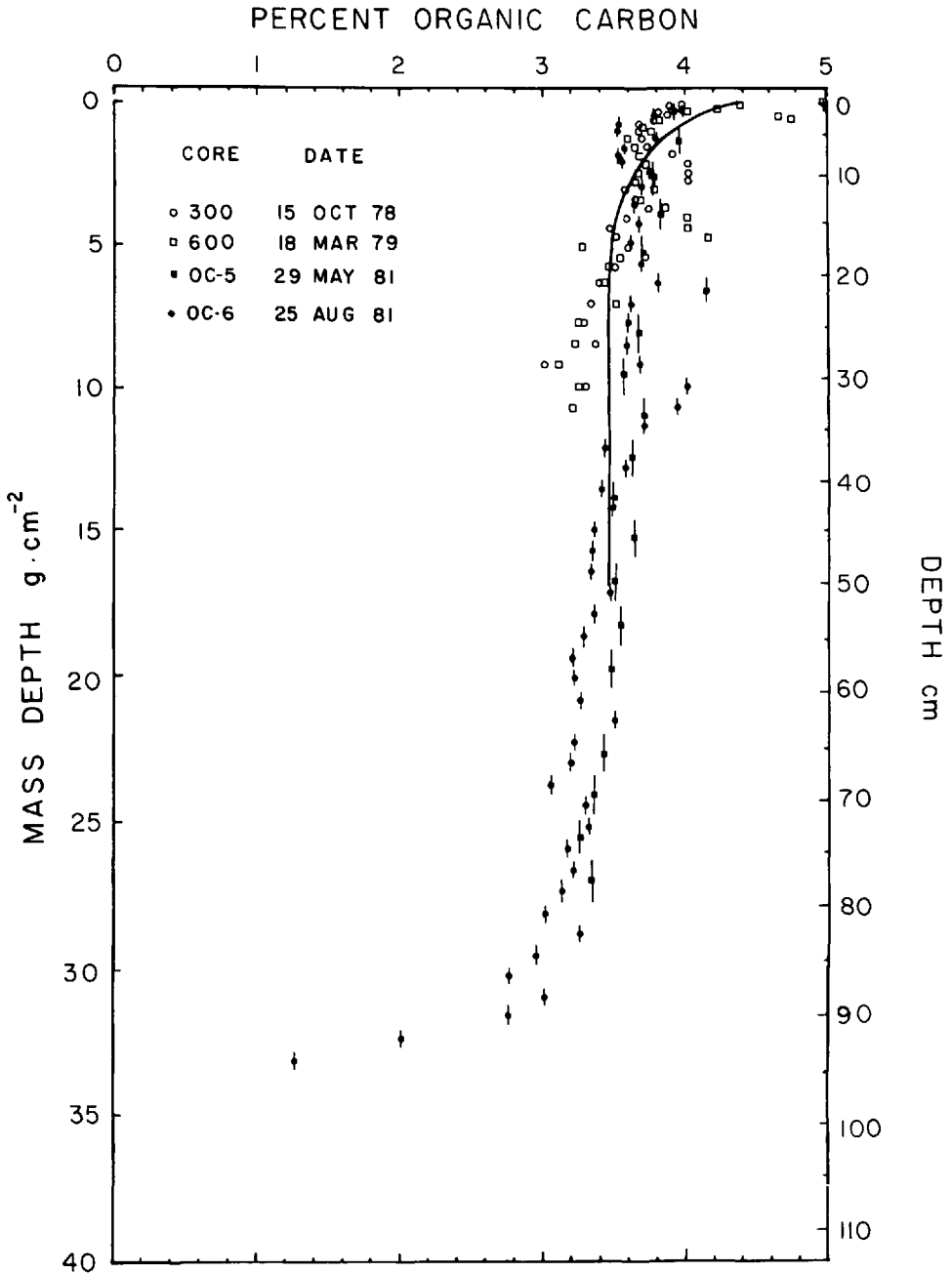
Figure 2. Sedimentary organic carbon concentrations observed in Cape Lookout Bight sediments (Martens and Klump, 1984). The solid lines represent fits of equation 5 to the data with G_0 value of 4.4%.

Table 1 summarizes the best fit attenuation constants, α, values of k, and depth-integrated organic carbon remineralization rates obtained from equation 7. Total depth intervals over which integrated remineralization is calculated are reported as the more familiar measured depth in cm; however, the attenuation constant,

Table 1. Organic carbon remineralization rates, α and k values calculated using G_0 values ranging from 4.0 to 5.0% (The remineralization rates corresponding to each G_0 value represent depth-integrated values from the sediment-water interface down to the depth listed above each column)

					Depth cm						
					5	10	15	20	30	40	50
G_0 %	G_∞ %	G_m^0 %	α cm^2·g^{-1}	k yr^{-1}				Rate: mole·m^{-2}·yr^{-1}			
4.00	3.30	0.70	0.163	0.67	4.1	8.3	11.9	14.9	18.9	21.2	22.4
4.20	3.37	0.83	0.302	1.25	8.4	15.6	20.7	23.8	26.9	28.0	28.3
4.40	3.45	0.95	0.620	2.56	16.8	26.4	30.5	32.0	32.7	32.8	32.8
4.60	3.51	1.09	1.44	5.93	30.4	36.6	37.4	37.5	37.5	37.5	37.5
4.80	3.53	1.27	2.09	8.64	35.9	43.6	43.8	43.8	43.8	43.8	43.8
5.00	3.54	1.46	2.72	11.2	48.2	50.3	50.4	50.4	50.4	50.4	50.4

α, has units of cm^2·g^{-1} rather than the usual cm^{-1}. Values of k (yr^{-1}) were obtained by multiplying these α values by w_d, the dry sediment accumulation rate which is 4.13 ± 0.67 g·cm^{-2}·yr^{-1} (Chanton et al., 1983). This sedimentation rate, which is based on a steady state model of the excess lead-210 distribution at the site, has been verified by direct measurements of yearly sediment accumulations of approximately 10 cm·yr^{-1} of whole wet sediment above a 1971 sand layer deposited during a hurricane.

Calculated remineralization rates integrated over the upper 0–50 cm range from 22.4–50.4 mole·m^{-2}·yr^{-1} for choices of G_0 values ranging from 4.0–5.0. It should be emphasized that the correct factor to emphasize is the initial concentration of metabolizable organic carbon G_m^0. The G_0 values correspond to G_m^0 values ranging from 0.70–1.46%. It is clear that overall rates are extremely sensitive to the choice of a G_0, or actually G_m^0 value. The parameter α whose value is largely fixed by the choice of G_0, actually drives the rate calculation. The depth distribution of remineralization (or ΣCO_2 production via equation 2) in the upper 10 cm where much of the total degradation occurs (Fig. 2) shows a dramatic dependency with modeled rates ranging from 8.3 to 50.3 mole·m^{-2}·yr^{-1} for G_0 values of 4.0 to 5.0%.

Rates of Sulfate Reduction and ΣCO_2 and Methane Production. — Representative peak summertime rates of sulfate reduction and ΣCO_2 and CH_4 production are illustrated in Figure 3 in order to demonstrate the depth dependency of these processes. Annually averaged rates of sulfate reduction at the site (Martens and Klump, 1984) are summarized in Table 2. These values represent total depth

Table 2. Annual sulfate reduction, ΣCO_2 production and methane production rates in Cape Lookout Bight sediments

	Mole·m^{-2}·yr^{-1}
Sulfate Reduction Rates*	
Kinetic model	13
Gradient-predicted	12
ΣCO_2 Production Rates	
Sulfate zone	20–32
Methane zone	5–6
Methane Production Rate†	
Seasonal average	5–6

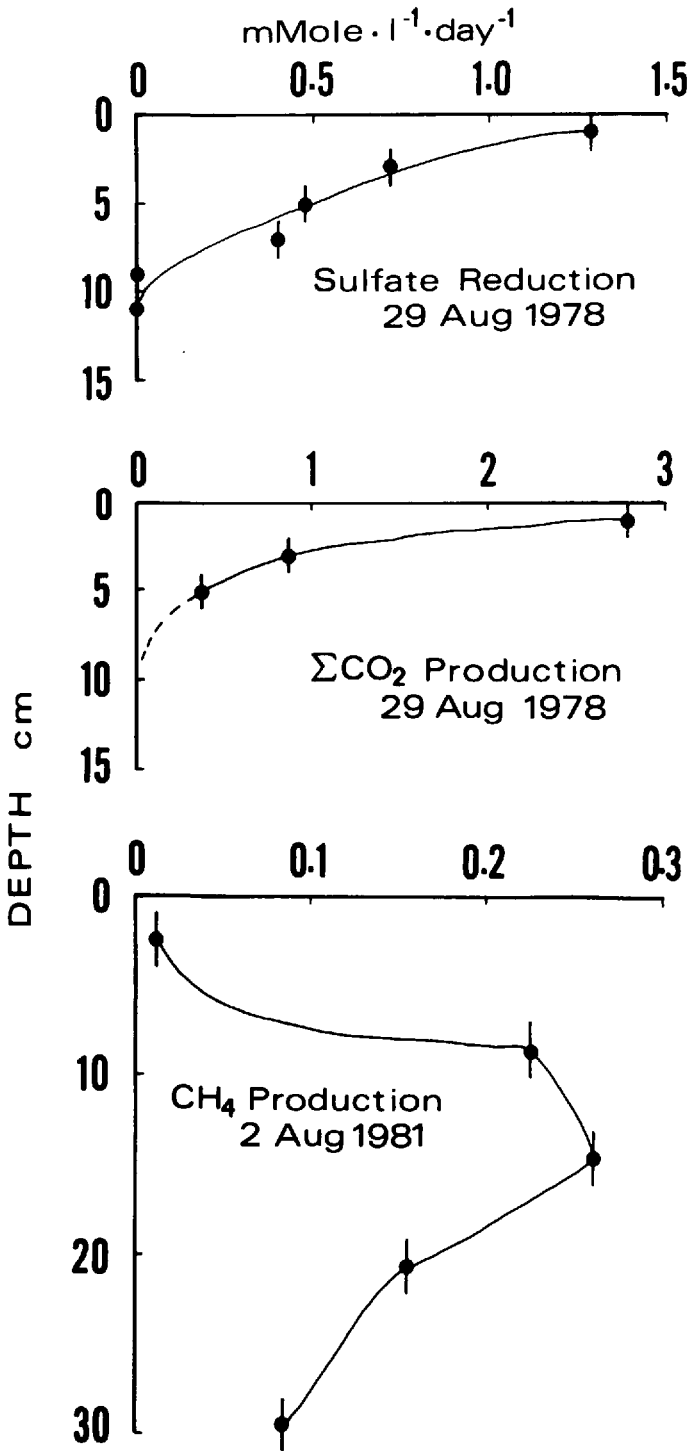* Martens and Klump (1984); † Crill and Martens (1983).

Figure 3. Representative sulfate reduction, ΣCO_2 production (Klump, 1980) and methane production rates (Crill and Martens, 1983) observed in Cape Lookout Bight sediments during warm summer months.

Table 3.   Observed sediment-water ΣCO_2 and methane fluxes from Cape Lookout Bight sediments

Sediment-water flux	Mole·m^{-2}·yr^{-1}
ΣCO_2 diffusive	29.8 ± 4.5
CO_2 gas bubbles	0.06 ± 0.03
CH_4 diffusive	0.85 ± 0.29
CH_4 gas bubbles	4.85 ± 2.57
Total dissolved carbon	35.6 ± 5.2

integrated rates typically spanning a sulfate reduction zone of 8–10 cm during warm summer months (Fig. 3) and 25–30 cm depth during winter months (Martens and Klump, 1984). Application of equation (2) above suggests that depth-integrated ΣCO_2 production rates supported by sulfate reduction (multiply by 2) should sum to approximately 20–32 mole·m^{-2}·yr^{-1}.

The annual methane production rate calculated from the 1979–1981 rate data of Crill and Martens (1983) is 5–6 mole·m^{-2}·yr^{-1}. Assuming that approximately equal amounts of CO_2 are produced during methanogenesis, a reasonable assumption based on studies by Tarvin and Buswell (1934) and others, an additional 5–6 mole·m^{-2}·yr^{-1} of ΣCO_2 should thus be produced in the methane production zone. Annual rates of ΣCO_2 production thus calculated for both the sulfate reduction and methane production zone as well as the methane production rate are summarized in Table 2. The total ΣCO_2 plus CH_4 production rate is 25–44 mole·m^{-2}·yr^{-1}. Average rates appear in Figure 1.

Sediment-water ΣCO_2 Plus Methane Fluxes.—Under quasi steady-state conditions and in the absence of significant unidentified removal processes in the sediment column or at the interface, ΣCO_2 and methane production rates (Table 2) should equal the measured sediment-water fluxes reported by Martens and Klump (1984). These fluxes are summarized in Table 3. The agreement between values predicted from rate measurements as discussed above and observed fluxes is quite good. We can now proceed to "tune" the organic carbon kinetic model in order to bring it into agreement with these constraining latter results.

"Tuning" the Organic Carbon Kinetic Model

The total organic carbon remineralization rates independently indicated by production and sediment-water fluxes of ΣCO_2 and methane are approximately 36 mole·m^{-2}·yr^{-1}. This ignores what appears to be an insignificant rate of dissolved organic carbon loss from these sediments (Martens and Klump, 1984).

These results force the choice of G_0 values to range from approximately 4.3–4.5%. Such a choice is not at all obvious from organic carbon concentrations in the upper few cm of profiles. In fact, choosing a G_0 value of 0.2% higher or lower than a mean value of 4.40% results in predicted rates which are a factor of approximately two higher or lower (Table 1) than those predicted from the Table 2 and 3 data. Choice of a value of approximately 4.0% where surficial values appear to cluster results in calculated organic matter remineralization rates clearly in disagreement with the depth distributions of remineralization as well. Depth integrated mean annual sulfate reduction rates of approximately 12 mole·m^{-2}·yr^{-1}, supported largely by rapid rates in warmer months in the upper 10–15 cm require the 24 mole·m^{-2}·yr^{-1} of ΣCO_2 production attributable to sulfate reduction to occur within that same depth interval. Values for G_0 on the order of 4.4% are required.

In conclusion, the critical dependence of the simple kinetic model for organic carbon on an upper boundary G_0 value or in reality, $G_m{}^0$ argues that independent information on the depth distribution of degradation rates must be available in order to accurately assess recycling rates near the sediment-water interface. Such independent rate information may be obtained from direct rate determinations and/or from systematic sediment-water flux measurements. Kinetic models of the pore water distributions of oxidants such as oxygen and sulfate or end products such as ΣCO_2 and ammonium may also serve this purpose, however, these models also require key assumptions involving the actual degradation mechanisms.

The application of kinetic models to organic carbon distributions in nearshore sediments in the future must also take into account other factors such as the non-steady state nature of organic matter inputs resulting from episodic organic matter production and/or supply via normal or storm-induced transport phenomena. Short-lived radiochronometric tracers such as ^{7}Be ($t^{1/2} = 54$ days) and ^{234}Th (24.1 days) should see increasing usage by biogeochemists seeking to directly monitor recent sediment accumulation and/or resuspension events (Krishnawami et al., 1980). Furthermore, we still know very little about the dynamics of microbial processes occurring near the sediment-water interface even in relatively easily studied coastal environments. Clearly information concerning the quantitative importance of autotrophic versus heterotrophic processes is necessary in order to utilize models so sensitively attuned to choices of boundary conditions. Questions concerning the roles of organisms as well studied as *Beggiatoa* sp. must still be resolved before their influence on near-interface organic carbon distributions can be ascertained (Nelson and Castenholz, 1981). We must also determine the relative importance of potentially rapid "geopolymerization" processes which may serve to render inert the formerly labile components of incoming organic detritus.

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