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THE VARIABILITY OF BENTHIC FLUXES AND SEDIMENTARY REMINERALIZATION RATES IN RESPONSE TO SEASONALLY VARIABLE ORGANIC CARBON RAIN RATES IN THE DEEP SEA: A MODELING STUDY.

W. R. MARTIN* AND M. L. BENDER
Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island 02881

ABSTRACT. While studies of sediment community oxygen consumption indicate that benthic organic carbon remineralization varies seasonally, other studies of the reactivity of sedimentary organic carbon indicate that its half life with respect to degradation is too long to allow seasonal variability. We have conducted modeling studies to examine the conditions under which these observations can be reconciled. While observed seasonal variability in benthic O_2 fluxes is consistent with observed variability in organic carbon rain rates, the amplitude of the seasonal benthic flux signal is strongly damped by the presence of organic matter which degrades too slowly to produce seasonal signals. For most pelagic sediments, bioturbation is not rapid enough to bury the most labile fraction of the organic carbon rain significantly before it is degraded; thus, seasonal variability in pore water O_2 and nutrient profiles is unlikely.

INTRODUCTION

Recent studies of sediment community oxygen demand have shown that the benthic dissolved oxygen flux may vary seasonally by as much as a factor of four (Smith and Baldwin, 1984). This result implies that organic carbon is degraded within months of its arrival at the sea floor. Direct studies of the reactivity of sedimentary organic carbon reach a contrasting conclusion: they indicate a mean life for sedimentary organic carbon of about 50 yrs (Emerson, Fischer, and others, 1985; Emerson, Stump, and others, 1985). Reconciling these lines of evidence is important, as the lifetime of organic carbon on the sea floor has a large influence on sedimentary redox conditions (Froelich and others, 1979) and on the preservation of calcium carbonate on the sea floor (Emerson and Bender, 1981).

The first requirement for the existence of seasonal variability in benthic fluxes in the deep sea is a seasonally variable rain rate of organic carbon. Such variability has been detected by deep sediment traps in the North Atlantic southeast of Bermuda (Deuser and Ross, 1980; Deuser, 1984) and in the North Pacific at Ocean Station Papa (Honjo, 1984); it has also been documented using benthic cameras in the temperate North Atlantic (Billet and others, 1983; Lampitt, 1985). During his two-year study, Honjo observed maximum fluxes approximately ten times larger than the minimum fluxes and a quasi-annual periodicity

*Present address: Chemistry Department, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

with large maxima in August/September and smaller maxima in May/June. Deuser (1984), in his six year study, also observed considerable variability in fluxes; upon averaging his data, he found a quasi-sinusoidal pattern in organic carbon fluxes, with a one-year period. The maximum in the averaged flux cycle, occurring in April, was approximately three times the minimum, occurring in November.

A second requirement for seasonally variable benthic fluxes is that the raining organic carbon must react rapidly enough to make its mean lifetime in the sediments shorter than the seasonal cycle. Fresh planktonic carbon has the requisite reactivity (Westrich and Berner, 1984), but the organic carbon whose reactivity is measured via sediment organic carbon and pore water nutrient profiles in the deep sea does not; its mean lifetime in the sediments ranges from 15 to 100 yrs (Emerson, Fischer, and others, 1985). Emerson and coworkers (Emerson, Fischer, and others, 1985; Emerson and Dymond, 1984) inferred, from the rough agreement between benthic fluxes calculated from pore water profiles and average organic carbon rain rates from sediment trap measurements at MANOP sites, that this pool of organic carbon must make up at least 50 percent of the organic carbon rain. Evidence for the existence of a labile component of the organic carbon rain comes from the benthic oxygen flux measurements of Smith and Baldwin (1984). They detected seasonal variability in benthic fluxes at two sites in the Pacific: at a site in the oligotrophic central North Pacific, the maximum flux was four times the minimum; at a southern California borderlands site, the maximum was twice the minimum.

The purpose of this paper is to examine the consistency of the sets of observations just presented: the existence of large seasonal variability in rain rates of organic carbon to the pelagic ocean floor; and, despite the fact that a substantial fraction of the organic carbon rain reacts too slowly to produce a seasonal signals, the existence of marked seasonal variations in the flux of oxygen across the sediment-water interface.

To examine the relationships between seasonally variable rain rates, benthic fluxes, and pore water profiles, we use two models. They are based on the proposal that the organic carbon rain is made up of a "labile" fraction, degrading rapidly enough to produce seasonal signals, and a "refractory" fraction, with a degradation rate constant of 0.02 yr^{-1}. This first model describes sedimentary organic carbon inventories in the presence of sinusoidally varying rain rates. After assuming that pore water oxygen concentrations are in steady state with respect to the current organic carbon profile, we use this model to predict the effects of seasonally varying rain rates on benthic fluxes. We examine the effects of varying the rate constant for degradation of the "labile" fraction and the relative sizes of the "labile" and "refractory" fluxes. We use a second model to examine the effects of seasonally variable rain rates on pore water dissolved oxygen profiles. This model is an extension of that presented by Emerson, Fischer, and others (1985). We assume that the degradation of organic carbon is first order with respect

to the sedimentary organic carbon concentration; that O_2 is the only oxidant; that bioturbation is analogous to Fickian diffusion and constant in the oxic zone; and that the effects of burial advection are unimportant relative to those of bioturbation and pore water solute diffusion. Our model differs from that of Emerson, Fischer, and others, in that we allow the flux of organic carbon to the sediments to vary sinusoidally with time, with a period of one year; and we allow two types of organic carbon, "refractory" and "labile."

THE MODELS

Organic carbon inventories depend on the form of the rate law for organic carbon degradation and on the magnitude of the rate constant. Organic carbon degradation in pelagic sediments is adequately explained using a first order rate law (Berner, 1980; Jahnke and others, 1982; Emerson, Fischer, and others, 1985). We assume that this rate law applies both to a "labile" fraction of the organic carbon rain, degrading with rate constant k_L, and a "refractory" fraction, with rate constant k_R · k_L is greater than 1 yr^{-1}, while k_R is fixed at 0.02 yr^{-1}. Both k_L and k_R are independent of time and of depth in the sediment column. The rain rates of labile (F_L) and refractory (F_R) carbon are given by

$$F_L(t) = f_0 + f_1 \sin(2\pi t/T)\ \mu mol/cm^2.yr \qquad (1A)$$

$$F_R = f_0\ \mu mol/cm^2.yr \qquad (1B)$$

f_0 is the average annual rain rate of labile organic carbon, assumed, arbitrarily, to be equal to the rain rate of refractory carbon (we relax this assumption later; see fig. 3); f_1 is the amplitude of the seasonal vaiability; T is the period of the seasonal cycle, taken to be 1 yr. For our calculations, we use f_0 = 10 and f_1 = 6.5 $\mu mol/cm^2.yr$. The maximum labile organic carbon rain rate is then 16.5, and the minimum is 3.5.

The rate of change of the inventory (that is, the concentration integrated over all depths in the sediment column) depends on the organic carbon rain rate and its degradation rate,

$$\frac{dI_i}{dt} = F_i(t) - k_i I_i \qquad (2)$$

I = the inventory of labile or refractory carbon ($\mu mol/cm^2.yr$)
i = L (labile fraction) or R (refractory fraction)

F_R and F_L are as given in eq (1A) and (1B). Solving (2) with $I(0) = I_0$ and considering the solution for long times, so that calculated inventories are independent of initial values,

$$I_R = F_R/k_R$$

$$I_L = \frac{f_0}{k_L} + \frac{f_1}{k_L^2 + (2\pi/T)^2}\left[k_L \sin(2\pi t/T) - (2\pi/T)\cos(2\pi t/T)\right] \qquad (3)$$

We have calculated model benthic O_2 fluxes from model organic carbon data by assuming that pore water $[O_2]$ responds quickly enough to changes in the labile organic carbon distribution to be approximately in a steady state determined by the current distribution of sedimentary C_{org}. This assumption is satisfactory because particle mixing is slower than O_2 diffusion in pore water; therefore the sedimentary organic carbon inventory is nearly constant during the length of time required for the pore water $[O_2]$ profile to approach a steady state. We assume further that the stoichiometric relationship between carbon oxidized and oxygen consumed is the same for the labile and refractory carbon pools. Then, in the absence of advection, the benthic O_2 flux is given by

$$F_{O2} = \gamma (k_R I_R + k_L I_L),$$

where γ is the stoichiometric coefficient relating moles of oxygen consumed to moles of carbon oxidized (assumed to be 138/106).

The calculation of model organic carbon profiles requires assumptions about the nature and rate of particle mixing in addition to assumptions about the rate law governing organic carbon degradation. We assume that sediments are mixed by bioturbation at a constant rate throughout the oxygen consumption zone. The mixing parameter, D_B, is a Fickian diffusion coefficient. We neglect sedimentation. We ignore the effect of oxidants other than O_2 on the organic carbon profile. Assuming constant porosity and solid phase density, the distribution of labile organic carbon (C_L, μmol/cm^3 of bulk sediment) is described by

$$\frac{\partial C_L}{\partial t} = D_B \frac{\partial^2 C_L}{\partial x^2} - k_L C_L \qquad x > 0,\ t > 0 \qquad (4)$$

$$-D_B \left.\frac{\partial C_L}{\partial x}\right|_{x=0} = F_L(t) \qquad t > 0 \qquad (4A)$$

$$C_L(x \to \infty, t) = 0 \qquad t > 0 \qquad (4B)$$

$$C_L(x, t = 0) = 0 \qquad x > 0 \qquad (4C)$$

The seasonal C_L flux (F_L) is given by eq (1A). The initial condition, (4C), is arbitrary; because we only consider solutions at long times, our results are independent of the particular value chosen. The solution to eq (4), in integral form, is

$$C_L(x, t) = (\pi D_B)^{-1/2} \int_0^\tau A(\tau) F(t - \tau)\, d\tau$$
$$A(\tau) = \exp\{-k_L\tau - x^2/(4D_B\tau)\}\tau^{-1/2}$$
$$F(t - \tau) = f_0 + f_1 \sin\{2\pi(t - \tau)/T\} \qquad (4D)$$

We have evaluated the integral numerically using Simpson's rule (Hornbeck, 1975). The integrand has a maximum at a small value of τ, when x

is small, and its value at the maximum becomes very large as x approaches zero. To calculate the integral accurately, it is necessary to include this maximum within the limits of integration. Thus, to calculate $C_L(x, t)$ for $x > 0.001$ cm, we use $\tau = 10^{-7}$ as the lower limit of integration. Agreement between C_L inventories calculated using profiles derived from eq (4D) and using eq (3) indicates that calculation of C_L closer to the interface than 0.001 cm is unnecessary for our purposes.

It is important to note that our model does not include reaction at $x = 0$ (eq 4A). In effect, we define the sediment-water interface as an infinitesimally thin plane immediately overlying the sediment column. Organic carbon degradation begins an infinitesimal distance below this plane. Thus, in the context of our model, reactions "very near" the interface have the important characteristic that they leave no detectable signal in pore waters, and an operational distinction can be made between these reactions and those that occur "within" the sediment column.

The refractory organic carbon fraction (concentration C_R μmol/cm^3 of bulk sediment) is described by the steady state form of eq (4). Boundary condition (4A) is applied with a constant flux, F_R. We have examined two cases: a "low flux" case, in which $C_R \rightarrow 0$ at depth, and a "high flux" case, in which the sediments become anoxic at depth x* and $(dC_R/dx) \rightarrow 0$ as $x \rightarrow x^*$ (this condition is valid in our model, because we have assumed that O_2 is the sole oxidant). The solution for C_R in the latter case is derived in Emerson, Fischer, and others (1985); in the former case,

$$C_R(x) = \frac{F_R}{(k_R D_B)^{1/2}} \exp\{-(k_R/D_B)^{1/2} x\}$$

We have used these solutions to examine the seasonal variability in sediment properties when

$$F_L = \theta(10 + 6.5 \sin(2\pi t)) \ \mu\text{mol/cm}^2 \cdot \text{yr}, \tag{5A}$$

and

$$F_R = \theta(10) \ \mu\text{mol/cm}^2 \cdot \text{yr}. \tag{5B}$$

For the "high flux" case, we take $\theta = 1$; for the "low flux" case, $\theta = 0.25$. The ratio of the maximum F_L to the minimum F_L is 4.7; averaged over the year, the labile and refractory fluxes are equal.

Assuming that pore water dissolved O_2 at any time is in a steady state determined by the contemporaneous organic carbon profile and neglecting porosity variation and advection, $[O_2]$ in the sediments is described by

$$D_s \frac{d^2O_2}{dx^2} - \gamma(k_R C_R + k_L C_L) = 0 \tag{6}$$

D_s = sediment diffusion coefficient for O_2.

Following Emerson, Fischer, and others (1985), we use

$$D_s = 6 \times 10^{-6}\ cm^2/sec.$$

At the sediment-water interface, the O_2 concentration approaches the bottom water O_2 concentration (which we assume to be 200 μmol/l). At depth in the sediment,

$$\text{A. low flux case: } dO_2/dx \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$\text{B. high flux case: } O_2 \rightarrow 0 \text{ as } x \rightarrow x^*$$

Because of our use of the condition, $C_L(x \rightarrow \infty, t) \rightarrow 0$ (eq 4B), we restrict our calculations to cases in which $C_L \rightarrow 0$ above depth x^*. We have calculated O_2 as a function of x from numerical solutions to eq (6). The numerical approximation procedure has been described elsewhere (Martin and Sayles, 1987). For the high flux case, choice of the correct x^* is essential to obtaining accurate O_2 profiles; the procedure used here is to vary x^* until the benthic O_2 flux calculated from the pore water O_2 profile equals the flux calculated from the organic carbon inventory.

RESULTS AND DISCUSSION

In figures 1 to 3, we consider the response of the sediments to a sinusoidally varying labile organic carbon rain rate. The sedimentary quantities examined are the inventory of labile organic carbon and the flux of dissolved oxygen to the sediments. To calculate the O_2 flux, we assume that pore water O_2 is in a steady state determined by the current organic carbon profile, and we assume Redfield stoichiometry for organic matter oxidation.

Figure 1 shows the relationship between the labile organic carbon inventory (I_L) in the sediments and its rain rate (F_L). Clearly, first order rate constants (k_L) in excess of 1 yr^{-1} are necessary to produce seasonal inventory fluctuations. As the rate constant increases, the amplitude of the seasonal signal increases, and the phase lag of the sedimentary labile C_{org} inventory relative to its rain rate decreases. In the limit as $k_L \rightarrow \infty$, $F_L = k_L I_L$.

In figure 2, we compare the amplitude of the seasonal benthic O_2 flux variation, as a function of k_L, for two cases: one in which all the organic carbon rain is labile, and one in which 50 percent is labile. The seasonal signal increases as k_L increases, reaching an asymptotic value when $k_L \rightarrow \infty$. Reducing the fraction of the organic carbon rain that is labile has a dramatic effect on the seasonal signal, as the constant flux due to oxidation of the relatively refractory component damps out the variability. For the case examined in figure 2, the magnitude of seasonality is decreased by a factor of 2.4 when the labile fraction is decreased from 100 to 50 percent of the C_{org} rain. This relationship is generalized (for the case in which $F_L(max) = 4.7\ F_L(min)$) in figure 3, which shows the variation in the maximum amplitude of the seasonal signal (that is, the amplitude when $k_L \rightarrow \infty$) as the fraction of the rain that is labile varies.

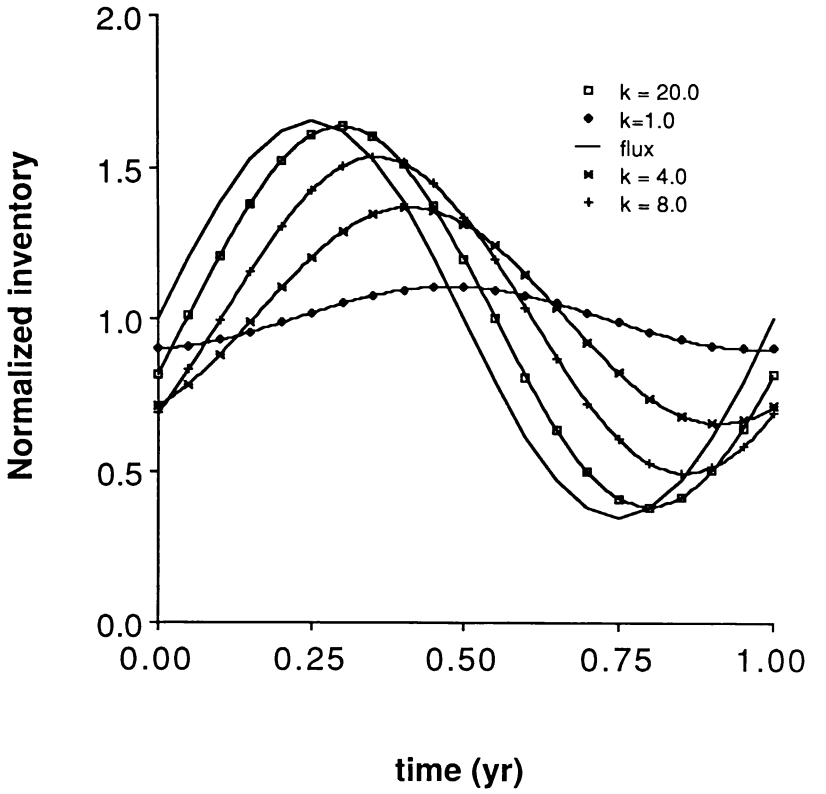

Fig. 1. Seasonal variability in organic carbon inventories in response to a seasonally variable organic carbon rain rate. The rain rate (the "flux" line) and the inventories are normalized in each case by dividing by the average annual rain rate or inventory. The time axis shows the fraction of the seasonal cycle that has elapsed. Each curve represents a different k_L: the range of values is from 1 yr^{-1} to 20 yr^{-1}.

The asymptotic ratio of the maximum to the minimum benthic O_2 fluxes is

$$\frac{F_{max}}{F_{min}} = \frac{F_L(max) + F_R}{F_L(min) + F_R} \tag{7}$$

The seasonal signal is only about 60 percent of that in the 100 percent labile case when three-fourths of the rain is labile and drops to 33 percent of the maximum signal when a third is labile.

These results clearly show that key parameters in determining seasonality in benthic processes are (1) the amplitude of the seasonal variability in rain rates, (2) the fraction of the rain that reacts rapidly enough to produce seasonal signals, and (3) the relative values of the

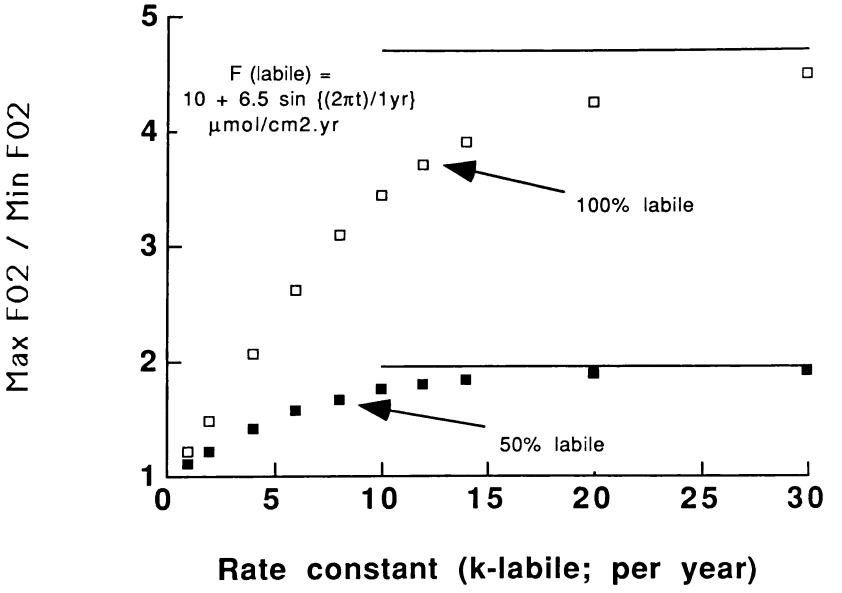

Fig. 2. The ratio of the maximum benthic O_2 flux to the minimum benthic O_2 flux as a function of the labile organic carbon degradation rates (k_L). Two cases are shown: one in which 100 percent of the organic carbon rain is "labile" (open squares), and one in which half is labile, while half degrades with a rate constant of 0.02 yr^{-1} (filled squares). In each case, a horizontal line is drawn at the asymptotic ratio of the maximum to the minimum flux (that is, the ratio when $k_L \rightarrow \infty$).

period of the rain rate cycle and the mean lifetime of the labile organic carbon in the sediments ($1/k_L$). As an example, the maximum variability in rain rates detected in deep sediment traps by Deuser and Honjo in their long-term studies is about a factor of ten. From eq (7), if, as suggested by Emerson, Fischer, and others, (1985), not more than 50 percent of the raining organic carbon is "labile," then the maximum variation in the benthic O_2 flux is about a factor of 2.4. This signal is further damped as k_L is decreased: to about a factor of two if k_L is 10 yr^{-1} and to 1.6 times if k_L is 4 yr^{-1}. A maximum allowable value for k_L has not been determined for deep ocean conditions. At temperatures of about 20°C and atmospheric pressure, various workers have estimated k_L to range from 3 to 33 yr^{-1} during oxic remineralization (Westrich and Berner, 1984). Westrich and Berner found that these rate constants were applicable for 70 days after degradation of fresh planktonic material began.

If the variability in organic carbon rain rates observed by Deuser (1984) and Honjo (1984) is applicable to other regions, it appears that resulting signals in benthic fluxes should be quite small (less than factor

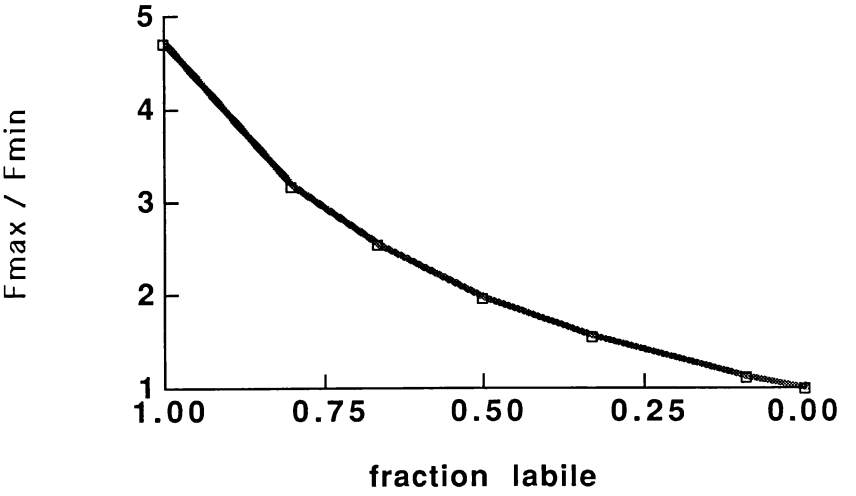

Fig. 3. The asymptotic ratio of the maximum to the minimum benthic O_2 flux as a function of the fraction of the organic carbon rain that is "labile." The "refractory" fraction is assumed to degrade with a rate constant of 0.02 yr^{-1}; the "labile" fraction degrades instantaneously. To derive this curve, the maximum labile organic carbon rain rate was assumed to be 4.7 times the minimun rate.

of two variability in benthic fluxes). To produce the factor of four variability observed by Smith and Baldwin (1984) in the north Pacific, a dramatic event would be required: for instance, a plankton bloom causing large, short-term variability in the flux of labile organic carbon. Alternatively, greater variability than our model predicts could result if k_L itself varies seasonally. A mechanism for such events is the spring bloom occurring in temperate waters. At the Panulirus station in the Sargasso Sea, for instance, a period of high productivity occurs when surface water is mixed down to the level of the permanent thermocline (Menzel and Ryther, 1960). The largest particle fluxes to the deep sea at this site are observed at this time of year (Deuser, 1984). It is likely that a large fraction of the seasonal flux is composed of labile organic carbon. Zooplankton grazing is insufficient to recycle phytoplankton carbon during bloom conditions (Roman, 1986); benthic cameras have recorded an influx of phytoplankton aggregates at the sea floor coincident with the spring bloom in the temperate north Atlantic (Billet and others, 1983; Lampitt, 1985). This undigested phytoplankton material may be more rapidly decomposed than the more extensively metabolized material arriving at other times of year. Thus, a mechanism exists for producing significant variability in benthic fluxes at middle and high latitudes. Honjo (1982) has also observed dramatic variability in particle fluxes at a site in the Panama Basin, where regional upwelling produces

an annual peak in primary productivity. In 1980, Honjo observed that his site received 80 percent of its annual particle flux in less than a two month period (Honjo, 1984).

We have also investigated the degree to which pore water O_2 profiles can be expected to reflect seasonality in organic carbon rain rates. Our results are based on numerical solutions of eq (6), using labile organic carbon profiles determined from eq (4). We have determined $[O_2]$ versus depth profiles for two cases: one in which the total flux of organic carbon is 5 μmol C/cm^2 · yr (the "low flux" case), and one in which it is 20 μmol C/cm^2 · yr (the "high flux" case). For comparison, Emerson, Fischer, and others (1985) reported seasonally averaged fluxes from sediment trap measurements at MANOP sites of 2 to 15 μmol C/cm^2 · yr, and Deuser (1984) measured an average flux of about 5 μmol C/cm^2 · yr in the Sargasso Sea. In each case, we have assumed that 50 percent of the organic carbon degrades with $k_L = 4$ yr^{-1}, while 50 percent degrades with $k_R = 0.02$ yr^{-1}. Because of the short lifetime of the labile fraction of organic carbon in the sediments (90 days for $k_L = 4$ yr^{-1}), seasonality in pore water profiles requires a rapid particle mixing rate. We have calculated $[O_2]$ versus depth profiles using D_B ranging from 0.06 to 1.57 cm^2/yr. Our largest D_B exceeds the values reported for a wide range of pelagic sediments (for example, DeMaster and Cochran, 1982; Cochran, 1985) but is smaller than the largest values reported for the deep sea (Aller and DeMaster, 1984).

The $[O_2]$-depth profiles resulting from these calculations are smooth, not showing the fluctuations with depth present in C_{org}-depth distributions. This result is in agreement with earlier work of Lasaga and Holland (1976) showing that solute diffusion damped oscillations in solid phase distributions effectively except when very high deposition rates caused the fluctuations to be large.

In the "low flux" case, we found little change in pore water $[O_2]$-depth profiles during the course of the seasonal cycle. With $k = 4$ yr^{-1} and $D_B = 1.57$ cm^2/yr, for instance, $[O_2]$ varies by only 3 percent at a depth of 1 cm below the sediment-water interface (from 171 μM at the time of minimum C_L inventory to 166 μM at the time of maximum inventory; we have assumed bottom water $[O_2] = 200$ μM). Results from the "high flux" calculations are shown in figures 4 to 6. Only when $D_B = 1.57$ cm^2/yr does the seasonal variability in pore water $[O_2]$ at a given depth exceed 10 μmol/l. While this is a significant change, it would be difficult to detect given the steepness of the O_2 gradient, sampling uncertainties, and the likelihood of spatial variability in sediment properties. Rapid degradation rates are required for sediment chemistry to vary in response to seasonal flux variations. Therefore, taking into account the moderate bioturbation rates observed in pelagic sediments, we conclude that seasonality, as reflected in time-dependent benthic fluxes, should be more prominent in processes occurring in the sediments immediately below the sediment-water interface than within the sediment column.

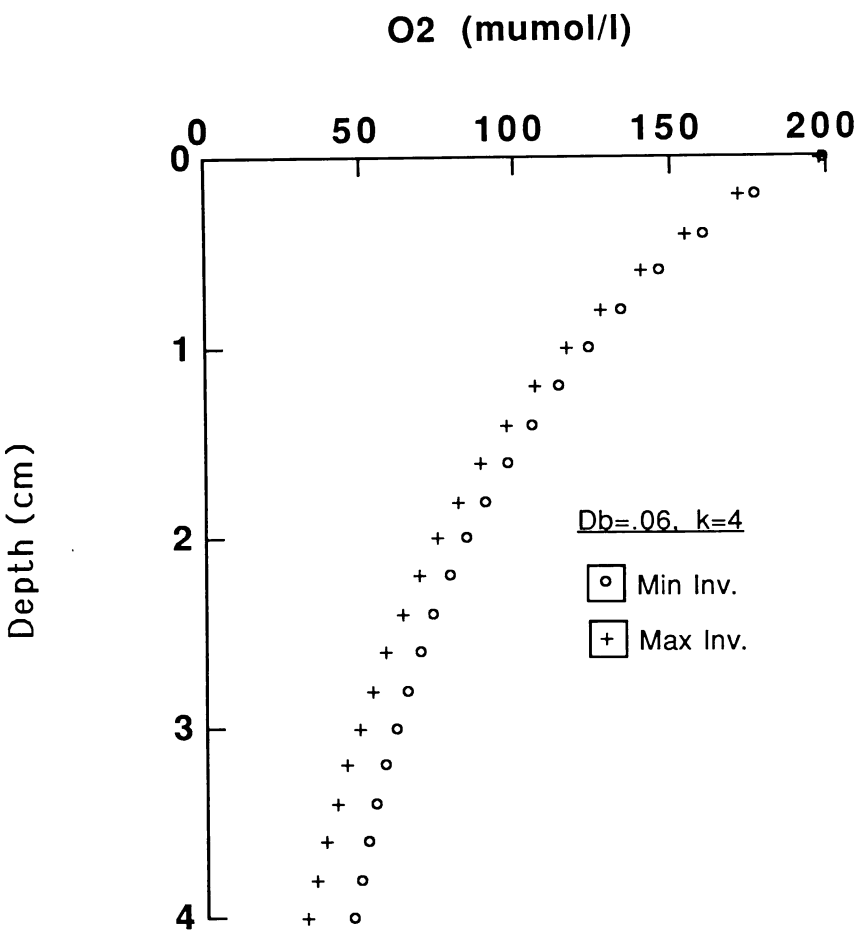

Fig. 4. Pore water dissolved oxygen profiles determined from model organic carbon profiles in the "high flux" case. Profiles at two times of year are shown for a chosen value of the bioturbation mixing coefficient (D_B = 0.06 cm^2/yr). The circles denote the profile at the time when the labile organic carbon profile is at its annual minimum, and the crosses denote the profile when the labile C_{org} inventory is at its annual maximum.

CONCLUSIONS

Observed variability in organic carbon rain rates to the pelagic sea floor may lead to measurable variability in benthic fluxes. For observable variability in fluxes to occur, organic carbon degradation constants in excess of about 4 yr^{-1} are required. While rate constants in excess of this value have been documented for oxic degradation of fresh planktonic organic matter at 20°C and atmospheric pressure, their applicability to deep-sea benthic processes is unknown. The most important

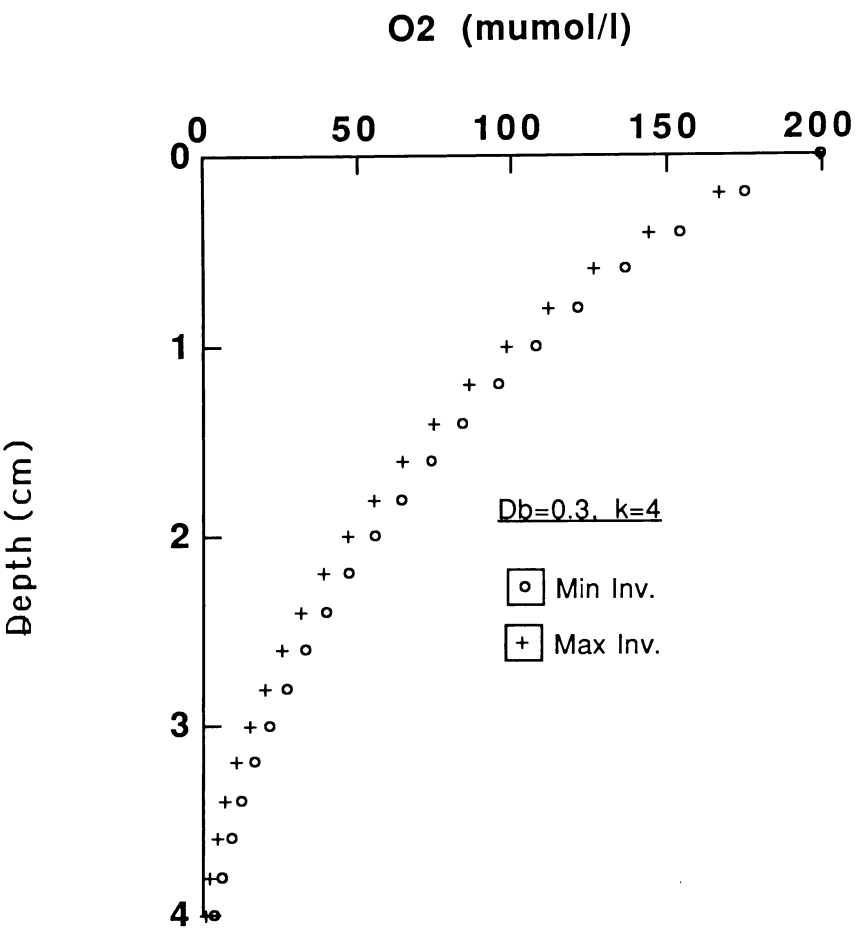

Fig. 5. Pore water dissolved oxygen profiles determined from model organic carbon profiles in the "high flux" case. Profiles and symbols are as for figure 4. $D_B = 0.3$ cm^2/yr.

limitation on seasonality of benthic fluxes in response to seasonal rain rates is a requirement that, on average, at least 50 percent of the raining organic carbon degrade with a mean life of 5 to 150 yrs. The presence of this relatively refractory carbon greatly diminishes seasonal variability in benthic fluxes. Variations greater than about a factor of two probably require large departures from average rain rates or a covariance of degradation rate constants with rain rates. Surface water conditions capable of producing such variations may exist in middle and high latitudes and regionally at lower latitudes. For most pelagic sediments, bioturbation rates do not bury the labile fraction of the organic carbon rain rapidly enough to produce measurable variability in pore water O_2

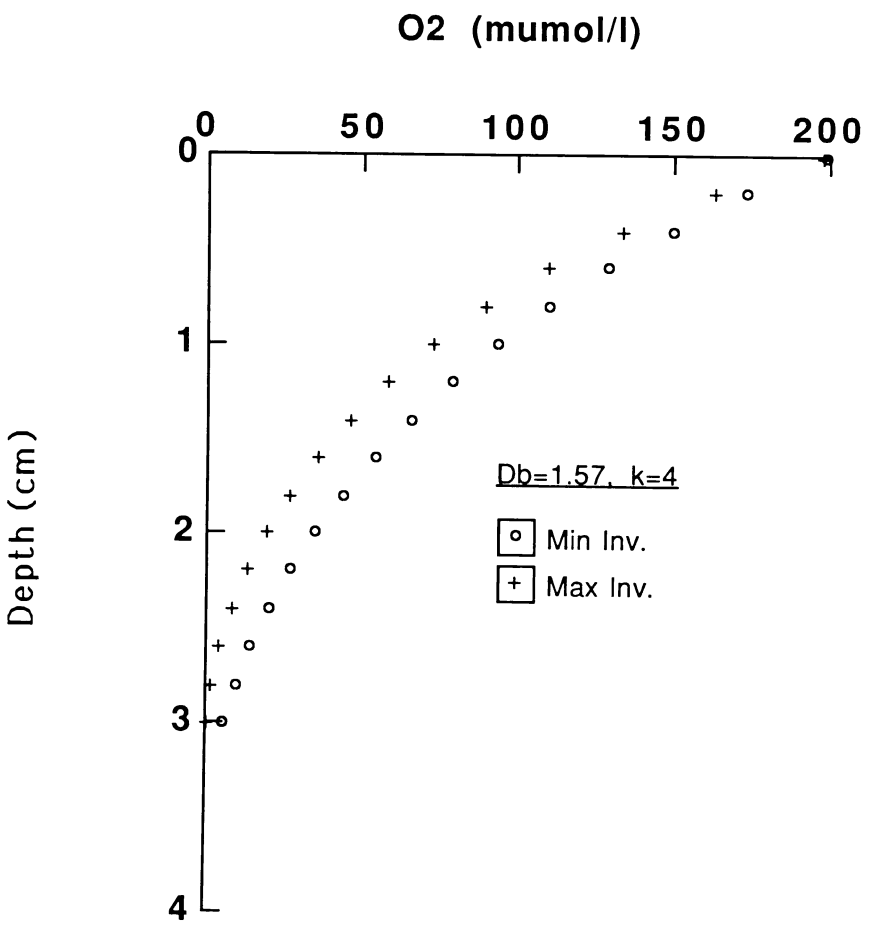

Fig. 6. Pore water dissolved oxygen profiles determined from model organic carbon profiles in the "high flux" case. Profiles and symbols are as for figure 4. D_B = 1.57 cm^2/yr.

and nutrient profiles. To a first approximation, seasonal variability in benthic fluxes reflects variability in organic matter remineralization rates in the sediments immediately below the sediment-water interface. Remineralization within the sediment column is predominantly a steady-state process.

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