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Journal

Geochimica et Cosmochimica Acta, 52(6)

ISSN

0016-7037

Authors

McNichol, Ann P
Lee, Cindy
Druffel, Ellen RM

Publication Date

1988-06-01

DOI

10.1016/0016-7037(88)90223-2

Peer reviewed

Carbon cycling in coastal sediments: 1. A quantitative estimate of the remineralization of organic carbon in the sediments of Buzzards Bay, MA*

ANN P. McNICHOL[1],[†], CINDY LEE[2] and ELLEN R. M. DRUFFEL[1]

[1]Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A.
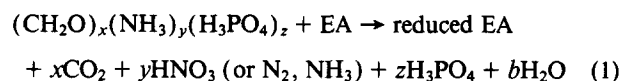[2]Marine Sciences Research Center, SUNY at Stony Brook, Stony Brook, NY 11794, U.S.A.

Abstract—Seasonal remineralization rates of organic carbon are calculated in the top 20–30 cm of biologically irrigated, organic-rich sediments of Buzzards Bay, MA. Six cores were collected over a period of two years, and the pore water concentrations of the following species were measured: dissolved inorganic carbon (ΣCO_2), PO_4^{3-}, ΣH_2S, Alk, and Ca^{2+}. Overall, these constituents showed large gradients with depth, which are larger in summer than in winter.

Remineralization rates in the sediments were estimated by applying a non-local exchange, vertical molecular diffusion, reaction model to the ΣCO_2 depth profiles. The major processes affecting the pore water concentration of ΣCO_2 described in the model are diffusion, irrigation, and the oxidation of organic carbon. The calculated remineralization rates varied seasonally with the high of 7.5×10^{-9} mol/L-sec observed in August 84 and the low (0.6×10^{-9}) in December 1983. The remineralization rates were dependent on the amount of irrigation in the sediments. It was possible to calculate remineralization rates between 0 and 20 cm because the amount of irrigation was well-characterized at this site. We calculated that 69 gC/m^2 are oxidized annually and 5–33 gC/m^2-yr are buried. It appears that there is a highly reactive portion of organic matter which is oxidized at the sediment water interface. Examination of the Alk and dissolved Ca^{2+} profiles indicates that there was significant production of acid which dissolved $CaCO_3$ in the spring and early summer.

INTRODUCTION

THE CARBON CYCLE plays a dominant role in controlling many biological and chemical processes in the marine environment. Many reactions and processes in the water column and sediments are related to the fixation of CO_2 to organic carbon and the subsequent degradation of this organic matter. Thus, it is important to quantify the rates of carbon fixation and remineralization. In this study, we investigate the seasonality of the remineralization of organic carbon in coastal sediments.

The concentration of dissolved inorganic carbon (ΣCO_2) in marine sediment interstitial solutions reflects the remineralization of organic carbon to CO_2 in marine sediments. In coastal environments where there is relatively little $CaCO_3$, seasonal ΣCO_2 depth profiles and a knowledge of irrigation rates can be used to calculate the amount of carbon oxidized to CO_2. The overall oxidation of sedimentary organic carbon is summarized in the following equation:

$$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + EA \rightarrow reduced\ EA$$

$$+ xCO_2 + yHNO_3\ (or\ N_2,\ NH_3) + zH_3PO_4 + bH_2O \quad (1)$$

The electron acceptors (EA) and the order in which they are used are: O_2, NO_3^- and MnO_2, Fe_2O_3, SO_4^{2-}, and CO_2 and low molecular weight organic compounds (FROELICH *et al.*, 1979).

The remineralization of organic carbon has been studied in a variety of coastal environments (*e.g.* ALLER, 1980a,b; MARTENS and KLUMP, 1984; JØRGENSEN, 1977a,b). In most nearshore marine sediments, oxygen and sulfate appear to

be the quantitatively important electron acceptors. In sediments at water depths of 20 m or less, sulfate can account for 50 to 70% of the total sediment respiration (HOWARTH, 1984). Oxygen reduction is limited by its ability to diffuse into the sediments across the sediment water interface or through burrow walls in the sediments (JØRGENSEN and REVSBECH, 1985). Nitrate is available, although its concentration is so low relative to other oxidants that it is not quantitatively important in a carbon budget. The importance of iron and manganese as oxidants in nearshore environments is uncertain. Solid-phase and pore water analyses indicate that both iron and manganese are available and are used to oxidize organic matter, either directly or indirectly (REEBURGH, 1983; MARTIN, 1985; ALLER and RUDE, 1986). However, the amount of organic matter remineralized by these oxidants is difficult to assess because of their solid-phase chemistry. Both iron and manganese are present as reactants and products in numerous solids, *e.g.* iron is present as iron oxides, pyrite, and iron monosulfides.

In previous studies, the determination of oxidation rates and the construction of carbon budgets were made using benthic flux measurements (MARTENS and KLUMP, 1984; BALZER, 1984; ANDERSON *et al.*, 1986), pore water constituents (GOLDHABER *et al.*, 1977), and measured oxidation rates (JØRGENSEN, 1977a; WESTRICH, 1983; MARTENS and KLUMP, 1984). The modelling of pore water profiles or benthic fluxes of electron acceptors, such as SO_4^{2-}, or degradation products, such as NH_4^+, requires the use of a stoichiometric assumption that defines the ratio of carbon produced to sulfate oxidized or the ratio of carbon to nitrogen in the oxidized material and may be complicated by other reactions, such as adsorption in the case of NH_4^+. Stoichiometric models have been applied to alkalinity (Alk), ΣCO_2, and dissolved Ca^{2+} data from deep-sea sediments (EMERSON *et al.*, 1980; SAYLES, 1981). These models assume that organic

matter with Redfield stoichiometry (C:N:P = 106:16:1) is oxidized to CO_2 according to Eqn. (1). Changes in Alk and ΣCO_2 with depth are predicted considering equilibrium with $CaCO_3$, the stoichiometry of oxidation, the diffusion of solutes through pore water, and assumed rates of oxidation of organic carbon. This approach has been useful in understanding processes in deep sea sediments; however, its application to nearshore systems is more uncertain. Abyssal sediments are deposited in a relatively quiescent environment where solute transport is assumed to be described by molecular diffusion. In contrast, the active benthic community in nearshore sediments enhances solute transport through mixing and irrigation. Increased productivity and a shorter water column provide a greater supply of highly labile organic matter to the sediment water interface. The full suite of electron acceptors from O_2 to SO_4^{2-} can be reduced over a distance as small as 0.5 cm (REEBURGH, 1983).

In this paper, seasonal ΣCO_2 depth profiles are used to construct a carbon budget for the sediments of Buzzards Bay, MA. The use of the concentration of ΣCO_2 provides a direct measure of the amount of organic carbon oxidized to CO_2 and requires no stoichiometric assumption in modelling. It also reflects the remineralization by a variety of electron acceptors, from O_2 to SO_4^{2-}. This paper demonstrates that, in an environment where the effects of irrigation on pore water are well-defined, depth profiles of the concentration of ΣCO_2 are described accurately by a model accounting for diffusion, irrigation, and the remineralization of organic carbon. This study shows that the most important contribution of ΣCO_2 to pore water comes from the oxidation of organic carbon. Another source of inorganic carbon to pore water, bottom water carbonate ion, is discussed in MCNICHOL (1986).

STUDY SITE

The research reported here was conducted at Site M in Buzzards Bay, MA (41°31.25'N, 70°45.7'W), shown in Fig. 1. The sediments in Buzzards Bay range from coarse sands to silty clays; the coarsest sediments are closest to the edges of the bay. Site M has been used for a variety of biogeochemical studies. It is the same location used by MARTIN and SAYLES (1987) for their study of transport rates in sediments and by BROWNAWELL (1986) as part of his study of PCB-colloidal organic matter interactions in pore water. Site M is the same as station 49 of Moore's bottom sediment study (MOORE, 1963), lies between stations K and L of Sanders' benthic community study (SANDERS, 1958), and is near station 31 of a 1982-83 hydrographic study (ROSENFELD et al., 1984). The sampling site is in 15 m of water and has predominantly silty-clay sediments (17% silt and 93% silt/clay; SANDERS, 1958; MOORE, 1963). The faunal assemblage at this site is a community of Nephthys incisa and Nucula proxima, deposit feeders that find their food on or in the sediment (SANDERS, 1958, 1960). The sediments contain approximately 20 mg/gdw organic carbon and are primarily sulfate-reducing. However, the SO_4^{2-} concentration in the top 30 cm of the sediments at this site is never more depleted than 10-15% below bottom water values (MARTIN, 1985). The overlying water is oxic throughout the year.

Particle and solute transport parameters are well-characterized at this site. A laboratory study of artificially laminated sediments from Buzzards Bay indicated that extensive biogenic reworking of the sediments occurred to depths of 2-3 cm (RHOADS, 1967). This observation was substantiated at Site M by [234]Th studies which showed that the maximum depth of penetration of [234]Th was 3.0 cm (MARTIN and SAYLES, 1987). Transport studies of the solution-phase using [222]Rn indicated that biological irrigation of the sediments in warm months affected the [222]Rn profile to depths of 10 to at least 20 cm (MARTIN and SAYLES, 1987).
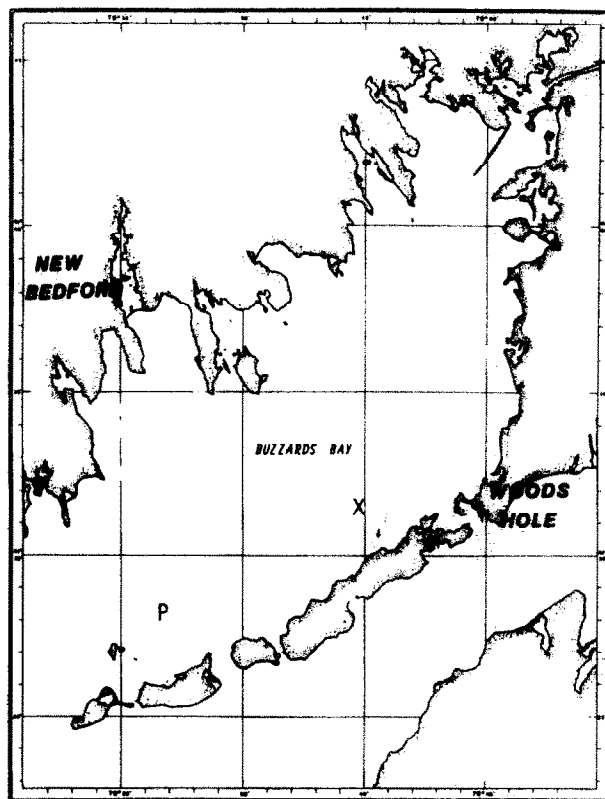

FIG. 1. The study site in Buzzards Bay, MA. Station M is marked with an 'x'. Station P is marked with a 'P'.

METHODS

Sampling strategies

The pore water chemistry of six cores was analyzed in this study. The dates of collection and bottom water temperature at time of collection are listed in Table 1. The results from a seventh core collected in September 1983 as part of another study at this site are used also (MARTIN, 1985). All cores were collected by SCUBA divers. In October 1983, an 8 cm diameter PVC core liner was used to collect the core; all the other cores were collected with a 20 cm diameter PVC core liner. The tops of the core liners were sealed under water and the bottoms were sealed tightly on deck after retrieval. The cores were transported to the laboratory within three hours of collection. In a N_2-filled glove bag, the cores were sectioned in consecutive 0.5 cm intervals to 3 or 4 cm depth in the core and at selected 1 cm intervals below this depth in all months except October 1983. In this month, the core was sectioned in consecutive 1 cm intervals to 4 cm and in consecutive 2 cm intervals to 30 cm. Sectioning was always completed within 12-15 hours of core collection.

In the glove bag, mud was transferred to 50 ml centrifuge tubes, sealed, removed from the glove bag, and centrifuged at 3000-3500 rpm for 15-20 min to isolate the pore water. No attempt was made to maintain the in situ temperature during either sectioning or centrifugation. The laboratory temperature was essentially the same as the in situ temperature in the summer and fall; however, there was up to a 16°C difference between laboratory and in situ temperatures in the cold months. After spinning down, the centrifuge tubes were returned to the glove bag, opened, and pore water was drawn into 10 ml syringes. All pore water was passed through a 0.45 μm Nuclepore polycarbonate filter. The first 1-2 ml of pore water were discarded and the next aliquot was filtered directly into a 1 ml syringe and analyzed within the hour for ΣCO_2. In October 1983, instead of measuring ΣCO_2, pH was measured on the first aliquot of pore water collected. The pH electrode was inside the glove bag and pH was measured immediately after collecting the sample. For the March

Table 1. The dates on which cores were collected for this study. Also listed are the measured bottom water temperatures at the time of collection and the calculated sediment diffusion coefficients for ΣCO_2 and Ca. The Rn sediment diffusion coefficients are those reported in Martin and Sayles (1987).

Core date	Bottom Water Temp., °C	$D_s \times 10^6$, cm²/sec		
		D_{c1}	D_{ca}	D_{Rn}
Sept. 7, 83*	16	6.5	4.2	6.9
Oct. 17, 83	15	6.4	4.1	6.7
Dec. 16, 83	7	5.3	3.4	5.4
June 20, 84	16	6.5	4.2	6.9
Aug. 30, 84	21	7.1	4.6	7.7
March 26, 85	4	5.0	3.2	4.9
Oct. 30, 85	14	6.2	4.0	6.5

* Data from this core are reported in Martin (1985).

1985 core, a different method of collecting the sample for ΣCO_2 analysis was used. A 1-ml aliquot of the filtered sample was stored in a poisoned ($HgCl_2$) 2-ml septum vial. The samples were analyzed within 10 hours of collection. After sampling for ΣCO_2, subsequent samples were collected for analysis of $\partial^{13}C-\Sigma CO_2$ (2 ml), sulfide (1 ml), phosphate (1 ml), alkalinity (1 ml), DOC (1-2 ml), calcium (1.5-3 ml), and sulfate (0.5-1 ml). Methods and results for the analyses of $\partial^{13}C-\Sigma CO_2$ and DOC are discussed in McNICHOL (1986). Mud for solid phase analyses was transferred to clean glass jars, frozen at -40°C, and stored at this temperature until freeze-drying.

A gravity core was taken near the study site for the analysis of natural levels of radiocarbon in Buzzards Bay sediments. A 1-meter long core was collected in a 10-cm diameter PVC core liner. The core was stored at 4°C overnight, sectioned at 5-6 cm intervals and stored frozen in glass jars until analysis. The radiocarbon core was taken at a site within one-half kilometer of the array of buoys which defined the sampling site.

Chemical analyses

Standard analytical methods were used for the analyses of ΣCO_2, Alk, dissolved H_2S, dissolved PO_4^{3-}, and dissolved Ca^{2+}. ΣCO_2 samples were acidified with 2 N H_3PO_4, stripped with helium, and measured by gas chromatography. This analysis was made immediately after sample collection; the precision of the analyses was ±3%. In March 1985, a headspace technique was used to measure ΣCO_2. Exactly one ml of sample was drawn into a syringe and acidified with sulfuric acid. CO_2-free air was added to bring the volume of headspace and sample to 10 ml. The sample was agitated to force most of the CO_2 into the gas phase, and the headspace was analyzed for CO_2 by gas chromatography. The precision of the analyses was ±10%. Alkalinity was measured by Gran titration; the precision of the analyses was ±1%. Sulfide was measured by the method of GILBOA-GARBER (1971) against a methylene-blue solution which was calibrated against sulfide standards according to FONSELIUS (1976). Phosphate was measured colorimetrically as described in STRICKLAND and PARSONS (1972). These analyses were made within 1-3 days of sample collection.

A high precision EGTA [ethyleneglycol-bis(2-aminoethylether)-N,N,N',N'-tetra-acetic acid] titration described by SHILLER and GIESKES (1980) was used to measure calcium. The precision of the Ca^{2+} titration was ±0.2%; this precision was obtained only when the sample was pre-titrated to >99% with EGTA. The EGTA solution was standardized each day against IAPSO seawater, and Ca^{2+} concentrations were calculated assuming a Ca/Cl ratio of 0.02109 g Ca/‰ Cl for the IAPSO seawater.

For CHN analyses, portions of freeze-dried sediments were placed in petri dishes, treated with 1 N HCl, and allowed to air-dry overnight in a hood. Drying was completed by placing the petri dishes in an oven for 1 hour at 60°C. The samples were analyzed on a Perkin-Elmer 240A CHN analyser using a combustion temperature of 975–

1000°C. Duplicate analyses run on 15 samples from December 1983 indicate that the precision of the analyses is ±4%. Sediment samples from March 1985 were not analyzed for CHN content.

Radiocarbon levels were measured in organic carbon samples according to procedures outlined in GRIFFIN and DRUFFEL (1985). Sediment samples were acidified, rinsed with distilled water, and dried prior to burning. The combustion is performed at 600°C in a large Vycor tube (packed with CuO at the end) with a flow of oxygen for a period of 2 hours. The samples were counted as CO_2 in a 200 cm³ copper gas proportional beta counter. The radiocarbon age is reported as years before present using the Libby half-life of 5568 years. An error of ±90 years was obtained for these samples based on counting statistics.

RESULTS

Profiles of solid-phase organic carbon concentration *vs.* depth are shown in Fig. 2. In general, the concentration of organic carbon is about 20–24 mg C/gdw in the surface sediments and decreases to a value of about 15–16 mg C/gdw by 30 cm. The top 4 cm of the December 1983 core were approximately 10 mg C/gdw higher in organic carbon concentration than in any other core. The ^{14}C age measured in the sediment is shown in Fig. 3; it increases from 1330 yr (0 to 6 cm) to 2970 yr (102 to 106 cm).

Depth profiles of ΣCO_2, Alk, Ca^{2+}, H_2S, and PO_4^{3-} for each month are shown in Fig. 4. The concentration of ΣCO_2, Alk, H_2S, and PO_4^{3-} in bottom water collected at the same time as the cores remained essentially constant throughout the year (ΣCO_2, 2.0 mM; Alk, 2.1 meq/L; H_2S, not detectable; PO_4^{3-}, not detectable; McNICHOL, 1986; MARTIN, 1985). The bottom water Ca^{2+} concentration was measured in December 1983, June 1984, and March 1985 and varied from 9.04 in June 1984 to 9.47 mM in March 1985 (average = 9.22 ± 0.22). It is likely that some of the variation is related
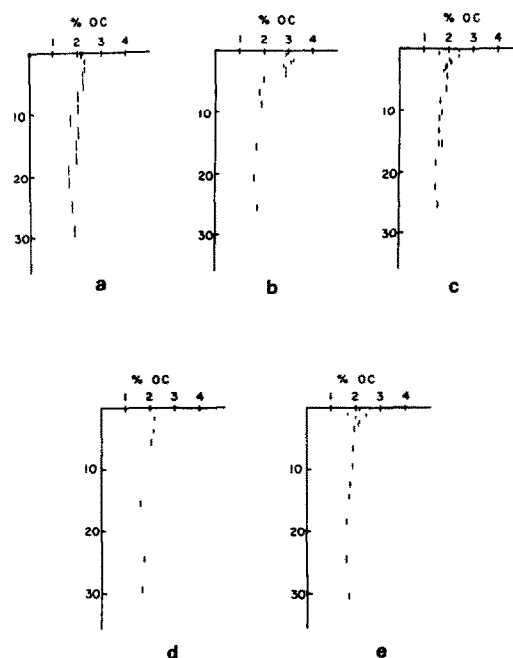

FIG. 2. Profiles of solid-phase organic carbon with depth at Site M; a) October 1983, b) December 1983, c) June 1984, d) August 1984, e) October 1985.
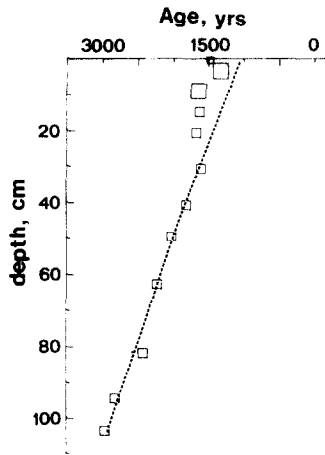
FIG. 3. Profile of ^{14}C-calculated age with depth in the sediments at Site M. The dotted line is the best-fit line through the data below 25 cm and corresponds to a sedimentation rate of 0.05 cm/yr. The height of the symbol indicates the depth interval sampled and the width of the symbols below 20 cm indicates the error in the age determination.

to observed seasonal salinity fluctuations in Buzzards Bay. In a hydrographic study of a station near Site M, the bottom water salinity ranged from a high of 31.876‰ in October 1982 to a low of 31.236‰ in May 1983 (ROSENFELD et al., 1984); this could account for approximately one-half of the observed change in Ca^{2+} concentration.

The concentration of ΣCO_2 measured in the pore water is always greater than that in bottom water. The highest concentration measured in the pore waters is 6.09 mM between 3.5 and 4 cm in June 1984. In general, the concentrations measured in warm months are greater than those measured in cold months. The data from October 85 are an exception and will be discussed later. In most months, the ΣCO_2 concentration increases rapidly in the upper 2–4 cm, reaches a maximum value between 4 and 10 cm, and is followed by a region of either decreasing concentration or of no change. Below 20 cm, the concentration begins to increase again.

In all months, the Alk profiles below 4 cm are qualitatively similar to the ΣCO_2 profiles, i.e. in the zones where ΣCO_2 increases, Alk also increases. The highest concentration measured is 5.74 meq/L between 3.5 and 4 cm in June 1984, and, again the concentrations measured in the warm months are greater than those measured in cold months. The Alk data from June 1984 and March 1985 exhibit minima in the profiles between 0 and 4 cm. In June 1984, the concentration of Alk measured between 0 and 0.5 cm (1.90 meq/L) is less than that in bottom water (2.20 meq/L); and, in March 1985, a minimum is observed between 2.5 and 3 cm. Similar features may be evident between 1 and 1.5 cm in August 1984 and October 1985. In December 1983, the pore water concentration of Alk is greater than bottom water in all samples. The concentration remains fairly constant between 0 and 4 cm; below this, it increases. In October 1983, there were not enough samples in the surface sediments to observe a minimum.

Dissolved Ca^{2+} concentrations were measured in all months except October 1985. The measured concentration

of dissolved Ca^{2+} in the pore water is greater than the average bottom water value in every core except for one sample in December 1983. In June 1984 and March 1985, there is a maximum in the Ca^{2+} profile above 10 cm. There may be a similar feature in October 1983, but there were not enough samples taken to show this feature conclusively. Below 10 cm, the Ca^{2+} concentration reaches a constant value of 9.34 ± 0.07 mM.

Dissolved sulfide and phosphate were measured in order to correct total Alk to carbonate Alk. Dissolved sulfide is absent or only present at background levels in the top 4 cm of all the cores in which it was measured. Below this depth, sulfide increases to values as great as 1 mM (August 1984). Dissolved phosphate profiles usually exhibit a maximum in the top 4 cm. Below this depth, the concentration approaches a constant value at depth except in December 1983.

DISCUSSION

The data collected in this study were used to calculate seasonal rates of remineralization of organic carbon to CO_2. In general, the concentration of degradation products such as ΣCO_2 and H_2S reach their highest concentrations in the warmest months. Exceptions to this trend do exist and are discussed later in the text. The rate of oxidation of organic matter was determined by modelling the seasonal profiles of ΣCO_2 at Site M.

Organic carbon oxidation model

The concentration of ΣCO_2 in pore waters is affected mainly by the oxidation of organic carbon, the dissolution or precipitation of $CaCO_3$, and mixing with bottom water through irrigation. In this section, a model is developed to describe quantitatively the profiles of ΣCO_2; the model is shown schematically in Fig. 5.

The oxidation of organic carbon is described as a CO_2-production rate, $R_c(z)$, which is controlled by the quality of the organic matter in the sediment column, the location and size of the microbial population, and the temperature. $R_c(z)$ is assumed to decrease exponentially with depth; in this model, $R_c(z)$ may be described by two exponential functions. WESTRICH and BERNER (1984) have shown that the remains of phytoplankton from Long Island Sound consist of 2 "metabolizable" fractions, of very different reactivities, and a non-degradable fraction. The two reactive fractions decompose at different rates that decrease exponentially over time. Thus, the functions describing $R_c(z)$ are:

$$R_c = R_0 \exp(-\beta_1 z) \qquad \text{from 0 to } z_b$$
$$R_c = R_{zb} \exp[-\beta_2(z - z_b)] \qquad \text{from } z_b \text{ to } \infty$$

where z_b is the length at which the rapidly degradable material is exhausted and $R_{zb} = R_0 \exp(-\beta_1 z_b)$.

There is no assumption in this model concerning the electron acceptor used to produce CO_2. As defined, R_c can describe the oxidation of organic carbon in these sediments by a variety of electron acceptors. The absence of dissolved sulfide in the surface sediments suggests that sulfate is not the only oxidant available in these sediments. It is likely that the absence of dissolved sulfides is the result of oxidation to sulfate
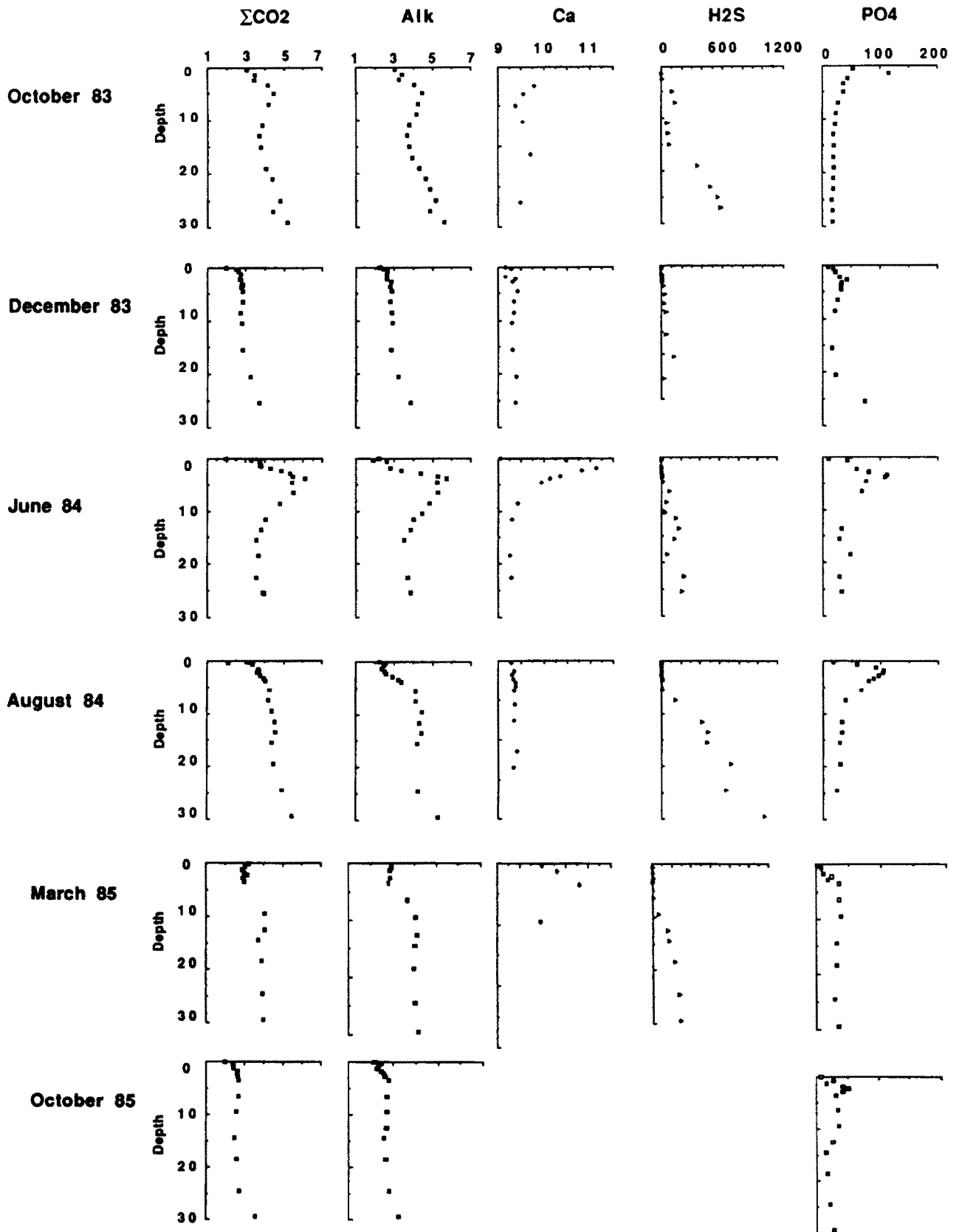
FIG. 4. Pore water profiles collected at Site M. ΣCO_2 is reported in mmol/L, Alk in meq/L, Ca in mmol/L, H_2S in μmol/L, and PO_4^{3-} in μmol/L.
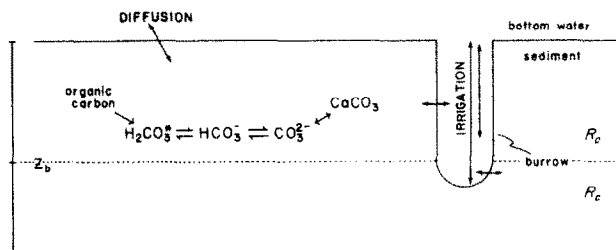
FIG. 5. Model used to describe the ΣCO_2 profiles in the warm months. The model is described in the text.

by oxygen or precipitation as iron sulfides. The sediments at this site are overlain by a fully oxygenated water column and at certain times of the year there is significant irrigation of the surface sediments. Oxygen and nitrate can diffuse across the sediment water interface and across burrow walls. The presence of microenvironments in sediments (JØRGENSEN, 1977b) may make it possible for oxygen and sulfate reduction to occur in the same sediment layer even though sulfate reducers are obligate anaerobes. Nitrate was present in pore water from Station P in Buzzards Bay in a winter core, and absent in a summer core (HENRICHS, 1980). Dissolved iron and manganese profiles indicate that organic matter is oxidized by MnO_2 and Fe_2O_3 in the sediments between 0 and 1.5 cm (MARTIN, 1985). The depth to which these oxidants are important varies seasonally, with the shallowest depths occurring in warmer months. Thus, R_c most likely reflects the oxidation of organic carbon by a variety of electron acceptors in the surface sediments and primarily by sulfate in the deeper sediments.

As defined, R_c is a combination of two processes—the net production of inorganic carbon from the oxidation of organic carbon and from the dissolution or precipitation of $CaCO_3$, i.e.

$$R_c = R_{org} + R_{CaCO_3}.$$

The importance of R_{CaCO_3} is discussed later.

Enhanced transport of ΣCO_2 due to biological irrigation can be described using the non-local source model of EMERSON et al. (1984). The irrigation parameter, $\alpha(z)$, was estimated from $\alpha_{Rn}(z)$, the irrigation parameter calculated at this site by MARTIN and SAYLES (1987) using $^{222}Rn/^{226}Ra$ disequilibrium. The value of $\alpha(z)$ used in the ΣCO_2 model has been calculated from $\alpha_{Rn}(z)$ assuming that transport across burrow walls is by molecular diffusion, and that there are no chemical reactions in the burrow walls and linings that impede ΣCO_2 transport. Thus, it is assumed here that the irrigational transport of ^{222}Rn and ΣCO_2 differ only because of the difference in their molecular diffusion coefficients, i.e. $\alpha = \alpha_{Rn}(D_{Ct}/D_{Rn})$, where D_{Ct} and D_{Rn} are the sediment diffusion coefficients for ΣCO_2 and Rn, respectively.

The sediment diffusion coefficient (D_s) was assumed to be constant with depth. Sediment diffusion coefficients were corrected for tortuosity and porosity at this site (MARTIN and SAYLES, 1987). Values of D_s calculated for each month are listed in Table 1. These values were calculated using the molecular diffusion coefficients for HCO_3^- and Ca^{2+} in seawater reported by LI and GREGORY (1974) corrected to observed temperatures. The molecular diffusion coefficients for

Rn are those reported by MARTIN and SAYLES (1987). The dissolved Ca^{2+} profile in sediments may also be affected by adsorption to clay surfaces; under certain conditions, consideration of this process may significantly change the effective diffusion coefficient (see Carbon budget). The sediments are assumed to have a constant porosity. Values actually vary in the upper 4 cm (MARTIN and SAYLES, 1987), but neglecting this change will not affect the results of the model.

Given the above assumptions, the equation defining the change of ΣCO_2 with time is:

$$\partial C/\partial t = D_{Ct}(\partial^2 C/\partial z^2) - \alpha(z)(C - C_0) + R_c(z). \quad (2)$$

To solve Eqn. (2), the observed ΣCO_2 profile was assumed to be in steady state, i.e. $\partial C/\partial t = 0$. Since seasonal changes are seen in the ΣCO_2 profiles, the validity of this assumption must be examined. In his study of sediment diagenesis in Long Island Sound, ALLER (1980b) used a radial diffusion model to interpret his pore water data. He found that the short diffusion distance from sediment to burrow channel in the radial diffusion model coupled with the rapid reaction rates observed in nearshore sediments led to the rapid re-establishment of steady-state. The description of irrigation in the non-local source model of EMERSON et al. (1984) is analogous to the radial diffusion model (BOUDREAU, 1984). Thus, the above argument is valid for the model presented here, too. Finally, McNICHOL (1986) solved Eqn. (2) without assuming steady-state using a depth averaged value of $\alpha(z)$ and a single exponential function for $R_c(z)$ appropriate for Site M. Reaction rates are rapid enough in warmer months for pore water to achieve steady state on shorter time scales than those of seasonal values in parameter values. This will be demonstrated further by comparing model-calculated rates to independently estimated rates.

Using the steady-state assumption and a centered-difference approximation for $\partial^2 C/\partial z^2$, a numerical approximation of Eqn. (2) is:

$$C_{i+1} + A_i C_i + C_{i-1} = B_i(\Delta z)^2 \quad (3)$$

where

$A_i = -[2 + (\Delta z)^2 \alpha_i/D]$
$B_i = -(\alpha_i C_0 + R_i)/D$
$R_i = R_c(z)$ at $z = z_i$
$\alpha_i = \alpha(z)$ at $z = z_i$
$C_0 = $ bottom water concentration.

To apply the model to the observed data the following boundary conditions were used:

1) $i = 0, z = 0, C = C_0$

2) $i = n + 1, z = z_m, C = C_m$

where the subscript 'm' refers to the maximum depth sampled. The model was fit to data from the warm months with $\Delta z = 0.05$ cm, using the values for $\alpha(z)$ and $R_c(z)$ discussed below. The model fits to the data are shown in Fig. 6. The parameters used to fit the data are listed in Table 2. The data from October 1985 were not fit with the steady-state model and will be discussed later.

The second boundary condition ($z = z_m, C = C_m$) forces the calculated profile through the deepest observed data point.
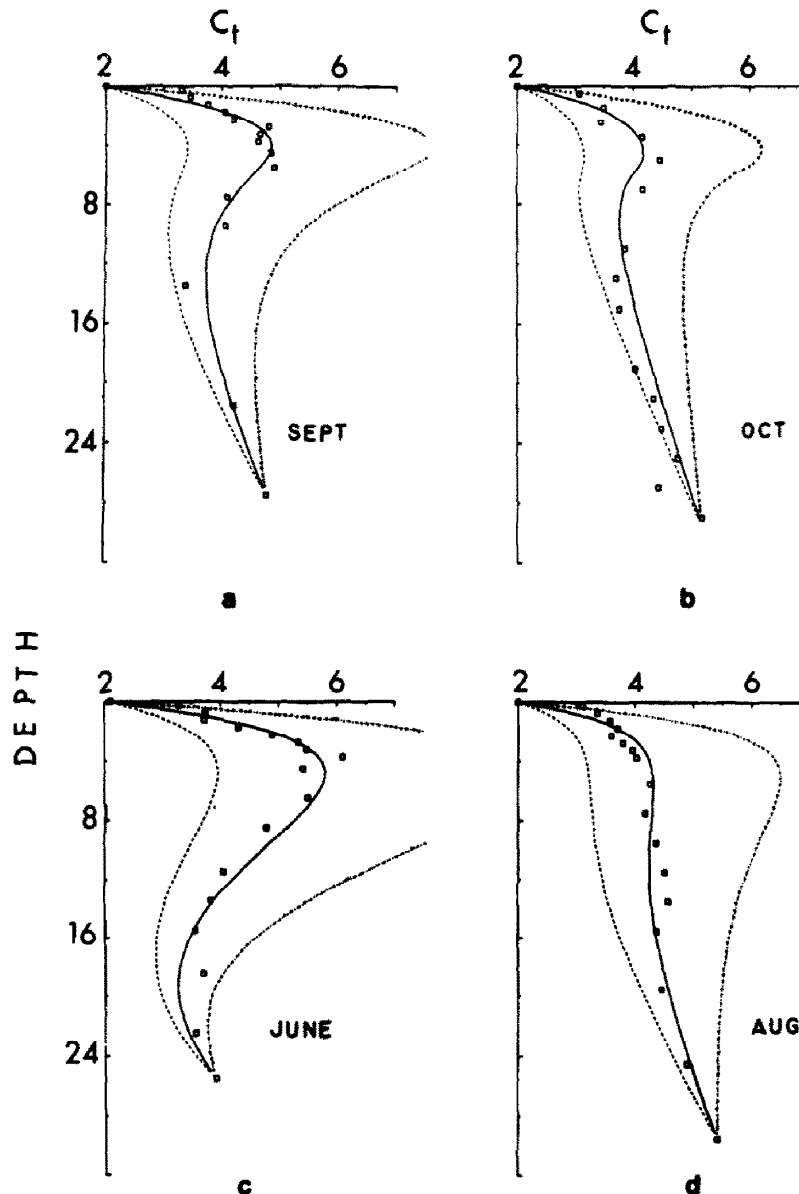
FIG. 6. Model fits to ΣCO_2 data; a) September 1983, b) October 1983, c) June 1984, d) August 1984; the parameters used to fit the data are listed in Table 2. ΣCO_2 axis is labelled C_t and is reported in mmol/L, and depth in cm. The best-fit is represented with a solid line. The dotted line shows the values calculated using a value of R_0 twice the best-fit value and the dashed line a value one-half the best-fit R_0.

However, in most months, the CO_2 production term is very small at this depth ($<1\%$ of R_c at the surface of the sediments for all the months modelled) and cannot account for the increase observed in the ΣCO_2 profile below 20 cm. The increase must be due to production deeper in the sediment column. Based on the observed flux of ΣCO_2 at 25–30 cm, we calculate that 1.6 gC/m^2-yr are oxidized below this depth. As will be shown later, this is a very small part of the annual carbon budget for the sediments. Comparison of the observed gradients in ΣCO_2 and SO_4 (this study; MARTIN, 1985) at 30 cm suggests that SO_4 is not depleted entirely until a depth of approximately 5 m in the sediment column. Assuming that sediment has been accumulating in Buzzards Bay since the last glacial period at 0.05 cm/yr (calculated later in the

paper using ^{14}C data), we calculate that the sediment column in Buzzards Bay is approximately 5 m, also. Thus, the observed increase in ΣCO_2 below 30 cm is most likely due to continued sulfate reduction in these sediments. It is unlikely that methanogenesis is important at this site because sulfate is still present.

Application of the model

To use this model to calculate $R_c(z)$, the irrigation parameter, $\alpha(z)$, must be known independently. The results of the MARTIN and SAYLES (1987) study of $^{222}Rn/^{226}Ra$ disequilibria at Site M were used to define $\alpha(z)$. They found that irrigation was an important transport mechanism for dis-

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Table 2. Parameters used to fit the observed ΣCO_2 data. The model fits are shown in Figure 6. The sub-headings under $\alpha(z)$ refer to the depth interval for which the listed function is valid. $R_c(z)$ refers to the function $R_0 \exp(-\beta_1 z)$ used to describe the CO_2-production rate; if two exponential functions are used, the second is $R_2 \exp[-\beta_2(z - z_b)]$ where $R_2 = R_0 \exp(-\beta_1 z_b)$.

| | R_u (x10⁹) | $R_c(z)$ | | | $\alpha_{Rn}(z)$ | | |
		β_1	β_2	z_b	$0-\infty$	$0-20$	$20-\infty$
Sept. 83	5.4	0.07	0.67	4.0	$1.8\times10^{-6}e^{-a}$		
Oct. 83	5.8	0.19	4.80	5.4	$3.5\times10^{-6}e^{-b}$		
Dec. 83	0.6	-	-	-		-	-
June 84	5.1	0.14	0.20	3.30	-	3.7×10^{-7}	$5.6\times10^{-5}e^{-c}$
Aug. 84	7.5	0.30	0.32	0.30	$1.8\times10^{-6}e^{-a}$		

where a = z/4.34, b = z/2.63, and c = z/4.

solved species in warm months up to depths of at least 20 cm, their maximum sampling depth. In the warmer months, they used an exponentially decreasing function to describe the observed ^{222}Rn profiles in October 1982, June 1983 and September 1983 and a constant function for $\alpha_{Rn}(z)$ in June 1984. In colder months (December through March), their ^{222}Rn profiles were adequately described by considering molecular diffusion as the only transport process. MARTIN (pers. commun.) has estimated that the calculated values of $\alpha(z)$ are known to ±20%.

We modelled the ΣCO_2 data from September 1983, October 1983, June 1984, and August 1984 using $\alpha_{Rn}(z)$ reported in MARTIN and SAYLES (1987) for the months of September 1983, October 1982, June 1984, and September 1983, respectively. The data were fit by correcting $\alpha_{Rn}(z)$ to $\alpha(z)$ and by subsequently varying $R_c(z)$ to optimize the fit to the data using a grid-search method (BEVINGTON, 1969) and four adjustable parameters, R_0, β_1, β_2, and z_b. A grid-spacing (Δz) of 0.05 was used to obtain the fits. The fits obtained for September 1983, October 1983, June 1984, and August 1984 are shown in Fig. 6; the parameters used to fit the data are listed in Table 2. The model-calculated values of R_0, the CO_2-production rate at the sediment water interface, range from a low of 5.1×10^{-9} mol/L-sec in June 1984 to a high of 7.5×10^{-9} mol/L-sec in August 1984. The variation of $R_c(z)$ with depth for each month is shown in Fig. 7. The calculated values of $R_c(z)$ are known as well as the values of $\alpha(z)$; thus, R_c is known to ±20%.

In general, the data are well-fit using this model. However, in every month, the measured ΣCO_2 concentrations between 0 and 1 cm are greater than that predicted by the model. If the data are real they suggest that there is an extremely active zone of remineralization near the sediment water interface and that the CO_2-production rate near the sediment water interface is much greater than that calculated for the remainder of the sediment column. WESTRICH and BERNER (1984) identified two reactive portions of coastal phytoplanktonic organic matter, whose reactivity differs by about an order of magnitude. Their study of SO_4^{2-} reduction in sediments suggested that very little of the highly reactive portion of the organic matter reaches depths of 2-6 cm in the coastal sediment column. The ΣCO_2 data collected here suggest that if a highly reactive portion of organic matter does reach the sediments, most of it is oxidized at the sediment water interface. It is also possible that the data observed be-

tween 0 and 1 cm are an artifact of the sampling procedure. The production of CO_2 between 0 and 0.5-1 cm may be rapid enough for the ΣCO_2 concentration to increase from the time sampled to the time analyzed. Based on the highest calculated R_c at the sediment surface (7.5×10^{-9} mol/L-sec), it would take approximately 18 hours for the ΣCO_2 to increase 0.5 mM. All ΣCO_2 analyses were complete within less than 18 hours of sampling. However, sample handling may artificially increase the CO_2-production rate by an uncertain amount. Thus, it is not possible to distinguish unequivocally whether the elevated ΣCO_2 concentrations at the sediment surface are real without further study.

The values of R_0, β_1, β_2, and z_b used to fit the data for each month are listed in Table 2. In all months except August 1984, $R_c(z)$ is described best using two exponential functions. The exponential factors β_1 and β_2 are not significantly different in August 1984. The calculated functions indicate that there is a more reactive form of organic matter present in the sediments between 0 and 3-5 cm. This is somewhat deeper than the surface sediment mixing depth of 2.5-3 cm predicted based on ^{234}Th measurements made in warm months at Site M (MARTIN and SAYLES, 1987).

The depth dependence of $R_c(z)$ is shown in Fig. 7a. In general, the profiles indicate that, based on the ΣCO_2 profiles, the production of CO_2 is most rapid at the sediment water interface and decreases rapidly to very low values by ap-
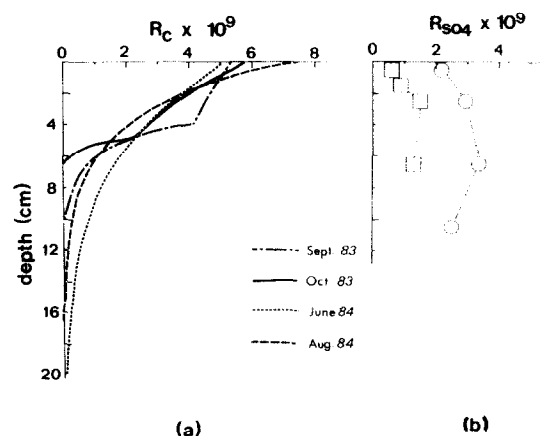

FIG. 7. a) Profiles of R_c with depth. b) Profiles of R_{SO_4} for December 1983 (squares) and June 1984 (circles) with depth.

proximately 10 cm. The values of R_c below 10 cm suggest that CO_2 production is insignificant at this depth. In October 1983, R_c is essentially zero at 8 cm. This is most likely because irrigation was more important at depth in this core than it was in October 1982, the month for which $\alpha_{Rn}(z)$ was defined. If the irrigation term used to model the October 1983 data does not account for the actual amount of irrigation at depth in the sediments, R_c is forced to be very small in order for the model to describe the observed concentrations of ΣCO_2 at depth. It is likely that in October 1983, the profile observed at depth in the sediments is less representative of the average Site M sediment profile than the other profiles. A much smaller diameter core liner (8 vs. 20 cm) was used in this month and the burrow of a very large organism was present between 8 and 26 cm. Similar burrows were observed in other cores sampled in warm months, although usually only one per core was observed (this study; MARTIN, 1985). Thus, in October 1983, the effects of irrigation at depth are maximized because a small area which contained a large burrow was sampled.

Two cores were sampled in low temperature months, December 1983 and March 1985. Using Eqn. (3), MCNICHOL (1986) showed that a steady-state assumption was not valid for the conditions typical of the low temperature months. However, the ΣCO_2 data from December 1983 could be used to calculate a value of R_c for the low temperature months because $^{222}Rn/^{226}Ra$ disequilibrium measurements set time limitations on the observed concentration of ΣCO_2. Transport parameters were not measured for March 1985, but $^{222}Rn/^{226}Ra$ measurements in December 1983 could be explained without invoking irrigation (MARTIN and SAYLES, 1987). However, the concentrations of ΣCO_2 in December 1983 were very low compared to values observed at this site in nine other months (this study; MARTIN, 1985); the data from October 1985 are the only ones that are similarly low. The December 1983 core was sampled a few days after several large storms had passed through Buzzards Bay, and the October 1985 core was sampled one month after Hurricane Gloria and one week after a stormy period. Both these cores appear to have had pore water constituents washed out by a storm-related mechanism and had not had time to re-establish steady-state concentrations. In order for the $^{222}Rn/^{226}Ra$ system to have re-established equilibrium in December 1983, the irrigating event discussed above must have occurred at least two weeks prior to sampling. If it is assumed that the pore water ΣCO_2 between 0 to 20 cm was diluted to the bottom water ΣCO_2 concentration and that it took two weeks to establish a constant final concentration of 2.75 mM, an estimate of the maximum R_c can be calculated from:

$$R_c = \Delta C / \Delta t.$$

The rate calculated for December 1983 is 0.6×10^{-9} mol/ L-sec and is listed in Table 3 along with the surface values of R_c calculated from model fits for September 1983, October 1983, June 1984, and August 1984.

In December 1983 and June 1984, $^{35}SO_4^{2-}$-sulfate reduction rates were measured at Site M in conjunction with the pore water sampling (R. W. HOWARTH, pers. commun.). The measured sulfate reduction rates can be converted to CO_2 production rates by assuming that two moles of CO_2

Table 3. Calculated values of R_c and R_{SO_4} and the associated error at the sediment surface and calculated values of ΣC_{ox}. R_{SO_4} refers to the CO_2-production rate that is calculated from the measured sulfate-reduction rate. The units of the rate are mol/l-sec; ΣC_{ox} is expressed in gC/m^2-yr.

Month	$R_c \times 10^9$	$R_{SO_4} \times 10^9$	ΣC_{ox}
Sept. 83	5.4 ± 1.1		94
Oct. 83	5.8 ± 1.2	--	76
Dec. 83*	.6 ± .1	1.0 ± .2	19
June 84	5.1 ± 1.0	2.7 ± .7**	107
Aug. 84	7.5 ± 1.5	--	89
annual average			69

*Values reported for December 83 are depth-averaged over the surface 10 cm, not surface values.

**No replicates reported; error assumed to be the same relative magnitude as December 83.

are produced for each mole of SO_4^{2-} reduced (WESTRICH, 1983). The depth profiles of the CO_2-production rates calculated from the sulfate reduction rates (R_{SO_4}) are shown in Fig. 7b. In December 1983, the depth-averaged value of R_{SO_4} is $1.0 \pm 0.25 \times 10^{-9}$ mol/L-sec which is similar to, but slightly greater than, R_c ($0.6 \pm .12 \times 10^{-9}$). In June 1984, the depth-averaged value of R_c ($2.5 \pm .5 \times 10^{-9}$ mol/L-sec) is the same as the depth-averaged value of R_{SO_4} ($2.5 \pm .7 \times 10^{-9}$), but the shapes of the depth profiles are completely different. The value of R_c at the surface of the sediments in June 1984 may be higher than R_{SO_4} at the surface because O_2, as well as SO_4^{2-}, may be an important electron acceptor in the surface sediments. JØRGENSEN (1977a) has estimated that as much as 50% of the CO_2 produced at the surface of reducing sediments overlain by an oxic water column may be from O_2 reduction. If the Mn profile from June 1984 (MARTIN, 1985) is used to define an O_2 zero depth of 0.25 cm, it can be shown that approximately 10% of the total organic carbon oxidized may be oxidized by O_2. This is a minimum estimate because a linear gradient was assumed for the O_2 profile, and irrigation as a source of O_2 was ignored. The value of R_{SO_4} ($2.5 \pm .7 \times 10^{-9}$) at 10 cm is higher than the value of R_c ($0.75 \pm .1 \times 10^{-9}$) at this depth. It is likely that the calculated value of R_c is closer to the correct value, because it is based on calculations made from observed pore water concentrations, rather than incubations of sediment. Finally, in general, some of the discrepancy between R_c and R_{SO_4} observed in December 1983 and June 1984 may be due to spatial heterogeneity. Because the values of R_c calculated in this study represent an average over a larger area of sediment than the R_{SO_4}, R_c is a better indicator of the average remineralization occurring at a given site.

$CaCO_3$ in the sediments

As stated earlier, the calculated value of R_c measured the net production of ΣCO_2 from the oxidation of organic carbon

and from the dissolution or precipitation of $CaCO_3$. Dissolution of $CaCO_3$ appears to be controlled by seasonal processes and was of importance in only one of the months modelled here; precipitation of $CaCO_3$ does not appear to be important in these sediments. Figure 8 shows the calculated values of the ion concentration product (ICP) of $[Ca][CO_3^{2-}]$ with depth as well as the equilibrium ICP values for calcite and aragonite. It is evident that the surface sediments are undersaturated with respect to $CaCO_3$ at least two months of the year. Undersaturation with respect to $CaCO_3$ in the surface sediments at Site M has been shown for other months (MARTIN, 1985). Below 4 cm, it appears that the pore waters are in equilibrium with some phase of $CaCO_3$. Disequilibrium in the surface sediments is not necessarily evidence that dissolution occurs; it indicates only that conditions are favorable for dissolution. However, there is visual evidence for the dissolution of $CaCO_3$ in the sediments. Small clam shells taken from cores are obviously pitted and microscopic examination of the surface sediments reveals some severely eroded foraminifera shells. In addition, dissolved Ca^{2+} concentrations provide direct evidence that dissolution of $CaCO_3$ occurs in these sediments. It is assumed that the dissolution of $CaCO_3$ is the major source of dissolved Ca^{2+} to the pore water at Site M. The concentrations of Ca^{2+} in the pore waters of the surface sediments are always greater than those in the bottom water; these data indicate that there is dissolution of $CaCO_3$ at or near the sediment water interface.

In June 1984 and March 1985, a large maximum was observed in the dissolved Ca^{2+} profile, indicating the dissolution of $CaCO_3$ within the sediment column. In March 1985, there is a minimum observed in the Alk profile in the upper 4 cm, and in June 1984, the Alk measured in the surface interval was less than bottom water Alk. In both these cores there appears to be significant dissolution of $CaCO_3$ at the same time that there is net consumption of Alk. This is surprising because the dissolution of $CaCO_3$ is a source of Alk. It is most likely that these cores were sampled at a time when benthic activity was just beginning to increase as temperatures increased in the spring. Animals would start turning the sediment over much more quickly and bringing solid-phase sul-

fides (e.g. FeS) from depth in the sediment to the surface where they could be oxidized with O_2. This process can produce a large amount of acid which can dissolve $CaCO_3$. Based on the Alk and Ca^{2+} profiles, it appears that, in June 1984, the oxidation of sulfides is important very close to the sediment water interface, while the data from March 1985 indicate that the oxidation occurs deeper in the sediments— between 2 and 4 cm. This means that O_2 must be introduced to the sediments to a depth of 4 cm, presumably through irrigation. Further evidence for oxidation of sulfides is shown by the dissolved iron measured in June 1984 (MARTIN, 1985). The maximum Fe concentration of 600 μM is observed at 0.25 cm and is the highest measured at this site. The oxidation of solid-phase sulfides has been proposed as one mechanism for the removal of reduced sulfur from coastal sediments (ALLER, 1982; HOWARTH, 1984). The data from March 1985 and June 1984 are consistent with this mechanism.

The Ca^{2+} data from June 1984 and March 1985 (Fig. 2) indicate that there was a loss of dissolved Ca^{2+} at depth in the sediments. While some of this loss is to bottom water through biological irrigation, it appears that either the sediment system is not at steady-state with respect to dissolved Ca^{2+} or that there is precipitation of some Ca mineral. It is possible that the system is not at steady-state and that the observed maxima are transient spikes due to seasonal dissolution of $CaCO_3$. However, if the system is at steady-state, then there must be precipitation of a Ca mineral in the sediments. In June 1984, based on the curvature of the Ca^{2+} profile, the zone of Ca^{2+} consumption is between 2 and 4 cm. As this is a region that is undersaturated with respect to $CaCO_3$, $CaCO_3$ could not be precipitating. Instead, a calcium phosphate phase may be forming as the zone of Ca^{2+} consumption is coincident with a zone of PO_4^{3-} consumption. This would be consistent with the suggestion by JAHNKE et al. (1983) that apatite is formed by the precipitation of amorphous calcium phosphate under reducing conditions in recent sediments of the Mexican continental margin.

Carbon budget

The calculated rates of remineralization can be used with the other data collected in this study to construct a carbon budget for the sediments at Site M. To do this, it is necessary to know the amount of carbon in the sediments and its rate of burial, as well as the rate at which it is oxidized. The amount of carbon oxidized in the sediments annually can be calculated from $R_c(z)$. The amount of ΣCO_2 produced is:

$$\Sigma C_p = \phi F \int_0^\infty R_c(z)dz \tag{4}$$

where

F = concentration conversion factor and
ϕ = porosity at depth > 30 cm (assumed to be 0.737 based on equation of MARTIN and SAYLES, 1987).

ΣC_p corresponds primarily to carbon produced from the oxidation of organic carbon. Of the months for which the ΣC_p calculation can be made, the dissolution of $CaCO_3$ was important only in the month of June 1984. Its effect was
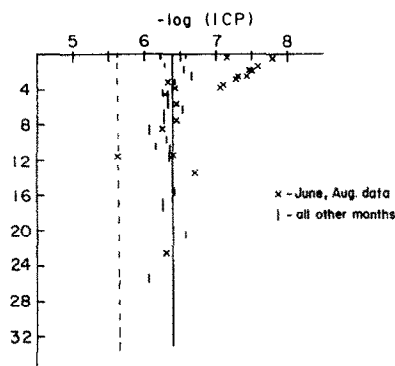

FIG. 8. Calculated values of the ion concentration product (ICP) $[Ca][CO_3^{2-}]$ and equilibrium values for calcite (solid line) and aragonite (dashed line). The value for calcite was calculated using the relationship given in INGLE (1975), and the value for aragonite was assumed to be 1.5 times the calcite value (ALLER, 1982).

removed in the following manner. A curve-fitting routine was used to calculate a polynomial function that describes the concentration of Ca^{2+} with depth. Under a steady-state assumption, the net amount of CO_3^{2-} added due to dissolution can be calculated from:

$$\Sigma C_{Ca} = \int_{z1}^{z2} R_{Ca}$$

$$= \int_{z1}^{z2} [D'_{Ca} d^2 Ca/dz^2 - \alpha(Ca - Ca_0)] \quad (5)$$

where D' is the adsorption-corrected sediment diffusion coefficient. Under a steady-state assumption, the sediment diffusion coefficient for Ca^{2+} needs to be corrected for adsorption only if the solid-phase mixing coefficient is of the same order as the adsorption corrected sediment diffusion coefficient (BERNER, 1980). In June 1984, this is the case in the top 2–3 cm. The corrected diffusion coefficient is:

$$D'_{Ca} = (1 + \phi K_j)D_1 + D_s = 5.4 \times 10^{-6} \text{ cm}^2/\text{sec} \quad (6)$$

where D_1 is the solid-phase mixing coefficient in the surface sediments, 52×10^{-8} cm^2/sec (MARTIN and SAYLES, 1987) and K_j is the distribution coefficient for red clays, 1.7, from LI and GREGORY (1974). The amount of carbon oxidized in the sediments is thus:

$$\Sigma C_{ox} = \Sigma C_p - \Sigma C_{Ca}.$$

The amount of carbon oxidized has been calculated on an annual basis and is listed in Table 3. In June, the dissolution of $CaCO_3$ accounts for only 2% of the ΣCO_2 produced.

Assuming that remineralization in September 1984 returns to a rate similar to that in September 1983, the area under the curve of ΣC_{ox} vs. time represents an annual average of the carbon oxidized in the sediments. The amount of carbon oxidized to CO_2 in one year in the sediments is thus 69 gC/m^2. This is similar to the amount of organic carbon oxidized by sulfate at NWC in Long Island Sound and less than that at Cape Lookout Bight in North Carolina. WESTRICH (1983) calculated that sulfate reduction in the sediments oxidized 100 gC/m^2-yr at NWC, a site similar to Site M. MARTENS and KLUMP (1984) calculated that 360 gC/m^2-yr of organic carbon are oxidized to CO_2 in Cape Lookout Bight sediments, an area of unusually high organic carbon input. However, the value of 69 gC/m^2-yr is significantly greater than the value of 14 gC/m^2-yr calculated by HENRICHS and FARRINGTON (1987) at another site in Buzzards Bay. While it is possible that the difference is due to spatial heterogeneity in the rates of remineralization and supply of organic carbon to the sediments in Buzzards Bay, the calculations made here may be more appropriate for measuring the amount of carbon remineralized in coastal sediments. The calculation by HENRICHS and FARRINGTON (1987) was made by modelling the profiles of solid-phase organic carbon. They assumed the profiles were at steady-state concentrations and that mixing had a negligible effect on the observed profiles. Data on the concentration of solid-phase organic carbon collected as part of this study show that the largest gradient in organic carbon is in the surface 2 to 4 cm (Fig. 2). This is the region shown by MARTIN and SAYLES (1987) to be mixed rapidly and, by the modelling in this paper, to be the region where most of

the remineralization occurs. Accurate estimates of carbon remineralization from solid-phase profiles must take the solid-phase mixing into account. Also, the uncertainty in sediment mixing rates between 2 and 20 to 30 cm discussed in the next section make it extremely difficult to model solid-phase profiles in coastal sediments well.

Finally, it should be kept in mind that the amount of carbon remineralized annually that is calculated in this study is based on results from 5 cores. The 5 cores provided us with data representative of the winter and summer extremes (December 1983 and August 1984) and the developing and waning summer conditions (June 1984, September 1983, and October 1983). We believe that we have provided a good estimate of the carbon remineralized in one year, but realize that a more accurate estimate could be obtained by sampling more frequently throughout the year. The carbon budget has been presented to demonstrate the utility of the remineralization model developed in this paper. Also, we are aware that interannual variability in remineralization and irrigation rates exist at coastal sites. Thus, a more detailed sampling over a longer period of time would provide the best estimate of carbon remineralization at Site M.

Burial of organic carbon

The amount of organic carbon buried in the sediments (C_b) at site M is calculated from the sedimentation rate (ω) and the concentration of sedimentary organic carbon below the mixed zone ($[OC]_d$) with the following equation:

$$C_b = \omega[OC]_d \rho(1 - \phi) = 5.5 \text{ gC/m}^2\text{-yr} \quad (7)$$

where

ρ = density of solids = 2.62 g/cm^3, and
ϕ = porosity at depth greater than 30 cm = 0.737 (MARTIN and SAYLES, 1987);
$[OC]_d$ = 16.0 mg C/gdw.

To calculate the amount of carbon buried, we assume that the oxidation of organic carbon in the sediments at depths greater than 1 m does not affect the amount of carbon preserved in the sediments. Oxidation rates calculated in this paper confirm this assumption. Additionally, the ΣCO_2 and SO_4^{2-} gradients observed in these sediments (this study; MARTIN, 1985) indicate that, if mixing and irrigation are minimal below 30 cm, there will be negligible changes in the solid-phase organic carbon profile.

The most difficult parameter to define in Eqn. (6) is the sedimentation rate. Determination of coastal sedimentation rates is complicated by the possibility of extensive mixing in the surface sediments. MARTIN and SAYLES (1987) used ^{234}Th profiles to show that sediment at this site is rapidly mixed to depths of 2 to 3 cm. BROWNAWELL (1986) studied mixing and sedimentation at Site M with ^{210}Pb and concluded that rapid mixing was important to 10 cm. Using the data below 10 cm, he calculated a sedimentation rate of 0.3 cm/yr. However, this value was inconsistent with solid-phase PCB penetration and Brownawell suggested that mixing was important to depths greater than 10 cm. Examination of the ^{14}C ages presented in Fig. 3 suggests that mixing is important to a depth of 20 to 30 cm. Thus, the sedimentation rate cal-

culated from ^{210}Pb data is most likely an overestimate. A sedimentation rate can be calculated from the ^{14}C ages calculated from data collected at depths greater than 25 cm. It is assumed that below this depth sediment mixing has a negligible effect on the Δ^{14}C profile and that the input of ^{14}C has remained constant over the time period mentioned. With these assumptions, the calculated sedimentation rate is 0.05 cm/yr and is shown by the dotted line in Fig. 3. This value is similar to that reported for site NWC in Long Island Sound, a site similar to Station M, using ^{14}C data (BENOIT et al., 1979) and sediment accumulation arguments (BOKUNIEWICZ et al., 1976). However, based on this sedimentation rate, the sediment used to calculate the sedimentation rate was deposited more than 500 years ago. It is likely that the sedimentation rate in Buzzards Bay has increased in recent times due to agricultural and industrial activity. Thus, currently, the sedimentation rate at Site M is most likely greater than 0.05 cm/yr and less than 0.3 cm/yr. Using this range of values in Eqn. (6) we calculate C_b to be between 5.5 and 33.1 gC/m^2-yr. This range is less than the 36 gC/m^2-yr buried reported for a different site in Buzzards Bay by HENRICHS and FARRINGTON (1987). The value they report was calculated using a sedimentation rate of 0.3 cm/yr, the same as the upper limit for the sedimentation rate for Site M. When the amount of carbon oxidized at Site M is added to the amount preserved in the sediments, we calculate that a total of 74–102 g C/m^2 reaches the sediments annually.

SUMMARY AND CONCLUSIONS

In this paper, we have shown that profiles of ΣCO_2 can be modelled to calculate the rate of remineralization of organic carbon in coastal sediments. The most important processes affecting the profiles of ΣCO_2 are the remineralization of organic carbon, irrigation of the pore water by benthic organisms, and diffusion to overlying water. Most of the remineralization in coastal sediments similar to Site M occurs in the surface sediments between 0 and 3–5 cm. This is an active, well-mixed region which appears to contain the most labile organic matter.

The values of R_c calculated from the steady-state model in the warm months for the surface sediment range from a low of $5.1 \pm 1.0 \times 10^{-9}$ mol/L-sec in June 1984 to a high of $7.5 \pm 1.5 \times 10^{-9}$ mol/L-sec in August 1984. Values of R_c at 5 and 10 cm are 20–40% and 0–15% of the surface remineralization rates, respectively. The model-calculated values of R_c are dependent on the values chosen for the irrigation parameter, α. This dependence emphasizes the importance of a knowledge of the mechanisms and magnitude of pore water transport in a nearshore environment when modelling pore water profiles. At this study site the enhanced transport of solutes by irrigation was well-characterized using ^{222}Rn (MARTIN and SAYLES, 1987). During colder months, the pore water parameters measured were not at steady-state concentrations and the rate of remineralization was slow. It was possible to calculate a CO_2 production term for only one of these winter months (December 1983). The value of R_c was $0.6 \pm .1 \times 10^{-9}$ mol/L-sec, significantly lower than those calculated in the summer months.

Modelling the ΣCO_2 profile provides an estimate of the

remineralization by all electron acceptors from O_2 to SO_4^{2-}. It may be possible to use models of ΣCO_2 profiles in conjunction with measured oxidation rates to calculate the relative importance of the various electron acceptors used in the oxidation of organic carbon. The role of DOC in the overall remineralization has not been discussed in this paper. It is assumed that solid-phase organic carbon is oxidized to both DOC and CO_2, and that DOC may be an important component of the organic carbon cycle in sediments. Its role needs to be further investigated.

Editorial handling: C. S. Martens

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