

## Variations in sedimentary carbon remineralization rates in the White Oak River estuary, North Carolina

Cheryl A. Kelley, Christopher S. Martens, and Jeffrey P. Chanton<sup>1</sup>

Curriculum in Marine Science, 12-5 Venable Hall CB 3300, University of North Carolina, Chapel Hill 27599-3300

### Abstract

Rates of microbially mediated sedimentary organic carbon remineralization vary along the salinity gradient of the White Oak River estuary, N.C. A direct comparison of two sites, one upriver dominated by methanogenesis and one downriver dominated by sulfate reduction, indicates a more rapid rate of remineralization upriver. Measurements of diffusive  $\Sigma\text{CO}_2$  flux plus  $\text{CH}_4$  diffusive (56%) and bubble (44%) fluxes at the upriver, freshwater site from June 1986 to March 1988 yield an average yearly flux of  $1.35 \pm 0.35 \text{ mmol m}^{-2} \text{ h}^{-1}$ . At the downriver midestuarine site, the dominant  $\Sigma\text{CO}_2$  flux for the same period is  $0.46 \pm 0.02 \text{ mmol m}^{-2} \text{ h}^{-1}$ . The uncertainties in these yearly fluxes are calculated from observed ranges in duplicate flux measurements. About 43% of the incoming organic C is remineralized at both sites. The greater remineralization upriver, of which 47% can be attributed to methanogenesis, appears to be supported by rapid decomposition of detritus derived from freshwater, emergent and submersed macrophytes, including *Pontederia*, *Ceratophyllum*, and *Najas* in surficial sediments. The high organic C content of these upriver sediments may, however, result from the long-term storage of slower degrading plants, such as *Typha* and *Taxodium*.

The role of sulfate reduction and methanogenesis in the degradation and remineralization of sedimentary organic matter in both marine- and freshwater-wetland environments has been the subject of numerous investigations (Yavitt et al. 1987; Strayer and Tiejde 1978; Kelly and Chynoweth 1981; Martens and Klump 1984). Studies of the rates of these processes in marine sediments have been reviewed by Reeburgh (1983). King and Wiebe (1978) and Bartlett et al. (1985) have demonstrated the importance of methanogenesis in carbon cycling from soils and sediments of freshwater wetlands and salt marshes.

<sup>1</sup> Current address: Department of Oceanography, Florida State University, Tallahassee 32306-3048

### Acknowledgments

We thank Fanghua Wang, Liz Canuel, Paul Renaud, Frank Wilson, and the rest of team CHAOS for field and laboratory assistance. Thanks also to the faculty and staff of our field lab, the Institute of Marine Science at Morehead City, N.C., with special thanks to Hans Paerl for use of his equipment. Isotopic analyses were performed by Randy Culp. Reviews by Val Klump, Bill Reeburgh, and an anonymous reviewer significantly improved this paper.

This work was supported by a National Science Foundation Graduate Fellowship to C.A.K. and by NASA grants NAGW-593, NAGW-1455, and NAGW-834 from the Biospherics Research and Interdisciplinary Research programs.

There is little quantitative information, however, concerning the rates of these processes along a salinity gradient in the sediments of river-estuarine systems (e.g. Bartlett et al. 1987). Little is known about the relative rates of methanogenesis and sulfate reduction in upstream sediments dominated by terrestrial inputs vs. downstream environments influenced by marine biogeochemical processes. Martens and Goldhaber (1978), however, demonstrated that methanogenesis is relatively more important upstream. Presented here are the results of a study of the rates of sedimentary organic C remineralization in the White Oak River estuary, N.C. The work focuses on a comparison of the rates of organic matter decomposition and C cycling, as measured by total dissolved inorganic C ( $\Sigma\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) evolution, between a predominantly freshwater site dominated by methanogenesis and a midestuarine site dominated by  $\text{SO}_4^{2-}$  reduction.

The nature of organic matter accumulating as sediment, as well as the primary mode of microbially mediated degradation and remineralization of the sedimented organic matter, differs along the salinity gradient. Based on isotopic composition, Martens and Goldhaber (1978; unpubl. data) found increasing plankton-derived components of

sedimentary organic matter downstream in the White Oak River estuary. Shifts in the mode of organic C degradation result from changes in the availability of specific oxidants, particularly dissolved oxygen and sulfate. Wherever significant sedimentary organic matter accumulates, such as in low-energy environments near bends in a river or in oxbows or old river channels, dissolved oxygen in sediment pore water is totally consumed, typically within a centimeter of the sediment-water interface (Revsbech et al. 1980a,b). This situation results in the dominance of anaerobic degradation, particularly  $\text{SO}_4^{2-}$  reduction and, when dissolved  $\text{SO}_4^{2-}$  is exhausted, methanogenesis. The availability of dissolved  $\text{SO}_4^{2-}$  and competition between  $\text{SO}_4^{2-}$  reducers and methanogens determines the primary mechanism by which sedimentary organic C degradation occurs.

Biogeochemical zonation models, as described by Claypool and Kaplan (1974), Martens and Berner (1974), Froelich et al. (1979), and others, can be used to predict the distribution of these degradative processes along the estuarine gradient. These zonation models are usually one dimensional with the oxidants being consumed in a well-defined order of depth below the sediment-water interface. In a river-estuarine system, this zonation also occurs horizontally. Because of the salt wedge intrusion into an estuary, dissolved sulfate concentrations are higher downstream; there the process of  $\text{SO}_4^{2-}$  reduction dominates. Upstream, in the freshwater environment,  $\text{SO}_4^{2-}$  concentrations are 2–3 orders of magnitude lower than in a marine system (Drever 1982) and so methanogenesis dominates. A comparison of the rates of these processes along the salinity gradient allows quantitative comparison of sedimentary organic carbon remineralization rates within an estuarine system.

During our investigation, such rates were measured from June 1986 to March 1988 at an upstream site dominated by methanogenesis and a downstream site dominated by sulfate reduction. The central objective of the work was to determine the in situ rates at which the end products of organic C degradation,  $2\text{CO}_2$  and  $\text{CH}_4$ , were

produced in order to deduce differences, if any, in the rates of sedimentary organic matter remineralization in upstream freshwater vs. downstream estuarine sediments.

### Study site

The White Oak River estuary is a small coastal river-estuary in eastern North Carolina (Fig. 1). The river system, located entirely within the coastal plain of North Carolina, is just under 50 km long, with the lower 30 km tidally affected (Cleneay 1974). The river is characterized by a fairly narrow channel until ~10 km north of Swansboro, where it opens to form the estuary.

Station Hadnot Creek (H), described by Gruebel (1981), is located midestuary, just north of the Hadnot Creek junction. At this point the estuary is ~1.5 km wide with a tidal range of ~1 m. The surface water salinities from this study ranged from 5‰ on 9 September 1987 to 20‰ on both 8 October 1986 and 11 July 1987. There is no macroscopic benthic vegetation at this site; the nearby marsh community consists primarily of the rush, *Juncus*.

Station Goldhaber's Island (GI) is ~25 km upstream from station H and 5 km upstream from the freshwater end-member (station F) described by Martens and Goldhaber (1978). This environment is tidal freshwater as classified by Odum et al. (1984), with a tidal range of about 70 cm (Chanton and Martens 1988). The upriver area is primarily a cypress swamp cut by tidal creeks and old river channels. The abundant marshes are composed of *Typha* (cattails), *Pontederia* (pickerelweed), and other species. Aquatic benthic vegetation at the upriver site is also plentiful. The submerged vegetation blanketing station GI is entirely composed of the vascular plants, *Ceratophyllum demersum* (hornwort), a rootless species, and *Najas guadalupensis* (water nymph), a species that has very small, threadlike roots. Both plants are common in sluggish streams or quiet waters on the outer coastal plain of North Carolina (Beal 1977).

Most of the work was concentrated at the above two sites. Some measurements were made at two other tidal freshwater sites near station GI, stations Upper Fork (UF) and

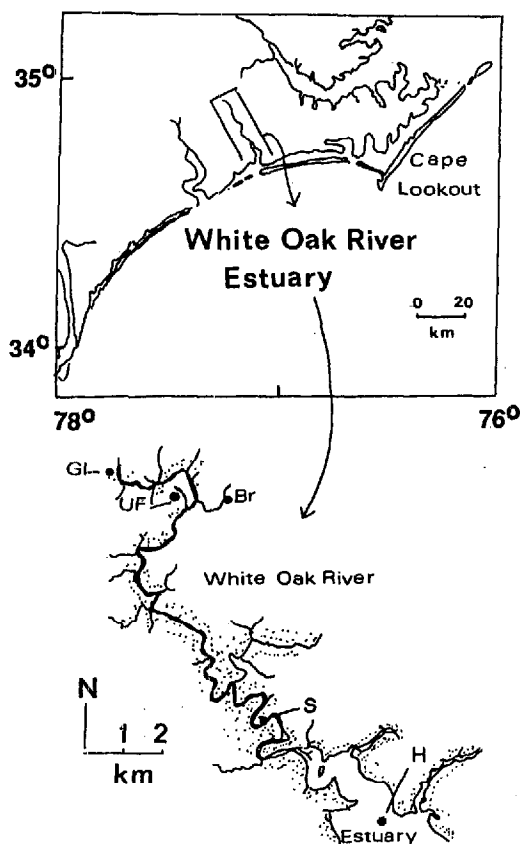


Fig. 1. Map of the study sites. Stations GI, Br, and UF are freshwater sites, station H is a midestuarine site, and station S is an intermediate site.

Branch (Br), as well as station Stella (S), an intermediate site between GI and H. The two freshwater sites are within 5 km of and very similar in appearance to station GI. Station UF is nearest to Martens and Goldhaber's (1978) station F. The intermediate site, station S, is near the town of Stella, ~6 km upstream from station H. At this point the river is still fairly narrow, ~0.1 km wide, and the surrounding marsh vegetation consists predominantly of the big cordgrass, *Spartina cynosuroides*, with *Spartina alterniflora* growing adjacent to the river channel. Pore-water salinities vary with distance from station H (Table 1).

#### Methods and materials

**Total dissolved inorganic carbon ( $\Sigma\text{CO}_2$ )**—Beginning in June 1986, 8-cm-diameter sediment cores were obtained from the study

Table 1. Pore-water salinities (surface 6 cm) for each site measured from squeezed samples. Distance from station H, the most saline site, is also given.

Sta.	Distance from H (km)	Pore-water salinity (‰)
GI	25	$0.2 \pm 0.1$
Br	21	$0.2 \pm 0.1$
UF	20	$0.2 \pm 0.1$
S	6	$4.1 \pm 3.0$
H	0	$18.9 \pm 7.0$

sites. These cores were extruded in either 1- or 2-cm intervals, and Reeburgh squeezers (Reeburgh 1967) were used to express the pore water from each interval within 6–8 h of collection. Measurements of  $\Sigma\text{CO}_2$  concentration were made with a Carle gas chromatograph with a thermal conductivity detector and He as the carrier gas. Attached to the Carle GC was a dissolved-gas stripping rig that allowed the pore-water samples to mix with 0.2 ml of 30% phosphoric acid in a liquid stripping tube in line with the carrier flow (Weiss and Craig 1973).

From September 1986, benthic chambers as described by Klump and Martens (1981) were used to obtain direct flux measurements. The chambers, deployed in groups of either two or four, were carefully placed on the sediment to prevent disturbance of the surficial flocculent layers. Initial samples were taken with plastic syringes. The chambers were then left in place for either 2 or 3 d to ensure at least a 10–25% rise in  $\Sigma\text{CO}_2$  levels. After this time the water within the chambers was circulated with a 12-V bilge pump attached to rubber tubing at the top of the chamber. Once mixing was complete, usually 3–5 min, final samples were taken. The  $\Sigma\text{CO}_2$  sediment–water flux was calculated from the change in  $\Sigma\text{CO}_2$  concentration between the final and initial samples, assuming a constant rate. Cores were taken at either the beginning or end of the chamber experiments as a second method of determining flux rates. We used 11–13 sampling dates at the two sites occurring roughly every 6 weeks during winter and more often during the warmer months (see Table 2).

At the freshwater station, GI, we observed a high abundance of submersed macrophytes. The effect of photosynthesis and

respiration by these plants on the measured flux of  $\Sigma\text{CO}_2$  was determined by darkening two of the four chambers deployed with aluminum foil to prevent photosynthesis. The light-dark chamber method was also used downstream at station H for comparison.

**Methane ( $\text{CH}_4$ )**—Dissolved  $\text{CH}_4$  profiles were obtained with pore-water equilibrators ("peepers," Hesslein 1976) with 3- $\mu\text{m}$ -thick Teflon membranes. After equilibration (usually 2 weeks), the ports were sampled in the field with gastight glass syringes. The  $\text{CH}_4$  concentrations in the pore-water samples were then analyzed via the headspace phase equilibration method (McAuliffe 1971) with a gas chromatograph equipped with a flame ionization detector.

**Organic C**—Cores for solid-phase organic C analysis were frozen after they had been sectioned and squeezed. A portion of each frozen mud patty (50–100 mg) was freeze-dried, and 2 ml of 10% high purity HCl was added to each sample to remove any carbonate-C. The samples sat in acid overnight. The next day they were quickly frozen with liquid nitrogen and freeze-dried to remove the acid. The samples were weighed before and after acid addition and freeze-drying to correct for any weight gain due to salt formation during the acid treatment. Carbonate-free samples were then analyzed with a Carlo Erba CNS analyzer (model 1500). Samples of benthic macrophytes were also freeze-dried and analyzed for their organic C contents. The  $\text{CO}_2$  gas produced during the organic C analysis for each sample was collected cryogenically, and a subset of the samples were analyzed for  $\delta^{13}\text{C}$  at the Center for Applied and Isotopic Studies, University of Georgia.

**Calculations**—Sedimentary organic C remineralization rates, via any process, can be determined from the production rates of  $\Sigma\text{CO}_2$  and  $\text{CH}_4$ . In the case of  $\text{SO}_4^{2-}$  reduction, the remineralization rate of organic C equals the production rate of  $\Sigma\text{CO}_2$  alone. For methanogenesis, the remineralization rate equals the sum of the rates of  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  evolution. If steady state can be assumed for the system over the period of interest, then these production rates can be equated with the  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  sediment-water fluxes.

Two methods for determining chemical fluxes across the sediment-water interface were used: flux calculations from concentration-depth gradients and direct flux measurements with benthic chambers. For  $\Sigma\text{CO}_2$  both methods were used. Because  $\text{CH}_4$  is transported out of the sediments by two mechanisms, bubble ebullition and molecular diffusion across the sediment-water interface, both types of fluxes had to be quantified. The bubble flux of  $\text{CH}_4$  for this freshwater site had been determined by Chanton and Martens (1988). The diffusive sediment-water flux of dissolved  $\text{CH}_4$  was determined only through gradient calculations, because naturally occurring  $\text{CH}_4$  ebullition at low tide at the upriver sites caused bubbles to collect in the chambers. The partial dissolution of  $\text{CH}_4$  from these bubbles allowed abnormally high concentrations of dissolved  $\text{CH}_4$  to occur within the chambers. Thus, the dissolved  $\text{CH}_4$  sediment-water flux could not be accurately measured with the benthic chambers over the period needed to measure changes in  $\Sigma\text{CO}_2$  concentration.

To determine if the gradient calculations from pore-water profiles accurately reflected the dissolved  $\text{CH}_4$  sediment-water flux, we conducted a short-term chamber experiment at station GI at high tide when no bubbling occurs. This experiment showed that the dissolved  $\text{CH}_4$  flux calculated from the concentration gradient across the sediment-water interface agreed with the chamber flux,  $0.35$  and  $0.32 \pm 0.18 \text{ mmol m}^{-2} \text{ h}^{-1}$  ( $\pm 1 \text{ SD}$ ,  $n = 4$  chambers), respectively.

Gradient flux calculations were based on Fick's first law modified for sediments (Li and Gregory 1974; Ullman and Aller 1982):

$$J = -\phi D_s (\delta C / \delta z) \approx -\phi^3 D_o (\delta C / \delta z) \quad (1)$$

where  $J$  is the flux of the dissolved species ( $\text{mmol m}^{-2} \text{ h}^{-1}$ ),  $\phi$  the porosity of the sediment ( $\text{cm}^3_{\text{pore water}} / \text{cm}^3_{\text{whole wet sediment}}$ ),  $D_s$  the whole-sediment diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $D_o$  the free-solution diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ), and  $(\delta C / \delta z)$  the concentration gradient in the  $z$  (vertical) direction at the sediment-water interface ( $\text{mM cm}^{-1}$ ). The measured sediment surface porosity values were 0.86 and 0.95 for stations H and GI. The other two freshwater sites were

assumed to have the same porosity as station GI and station S the same as station H. The free-solution diffusion coefficients, corrected for temperature effects, were obtained from Li and Gregory (1974) for  $\text{HCO}_3^-$  and from Klump and Martens (1981) for  $\text{CH}_4$ .

The  $\text{HCO}_3^-$  ion diffusivity was used to represent the  $\Sigma\text{CO}_2$  pool, since the mean pore-water pH values were 7.2 for station H (J. P. Chanton unpubl. data; C. S. Martens and M. B. Goldhaber unpubl. data) and 6.9 for station GI. At these pH values, precipitation of  $\text{CO}_3^{2-}$  species (in the form of  $\text{CaCO}_3$ ) should not occur until  $\Sigma\text{CO}_2$  concentrations become  $\geq 24$  mM. The highest  $\Sigma\text{CO}_2$  concentration measured at either site was 14 mM, so precipitation reactions were not considered in this study.

Concentration gradients of  $\Sigma\text{CO}_2$  at the sediment-water interface were calculated from fits of the pore-water data to the equation (Berner 1971, 1980)

$$C = (C_o - C_\infty)\exp(-\alpha z) + C_\infty \quad (2)$$

where  $C$  is the concentration at any depth (mM),  $C_o$  the concentration at the sediment-water interface (mM),  $C_\infty$  the asymptotic concentration at depth (mM),  $\alpha$  the curve-fitting parameter equal to  $k/\omega$  ( $\text{cm}^{-1}$ ) [ $k$  is the rate constant ( $\text{s}^{-1}$ ) and  $\omega$  the sediment accumulation rate ( $\text{cm s}^{-1}$ )], and  $z$  the depth from the sediment-water interface measured positively downward (cm). The Simplex curve-fitting program (Caceci and Cacheris 1984) allowed  $C_o$  to be fixed (assumed to be equal to the water-column concentration), while both  $\alpha$  and  $C_\infty$  were varied to fit the data.

Once the fluxes had been determined, monthly means for both  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  were calculated. These monthly means were weighted by day to determine seasonal and yearly averages. Uncertainties in  $\Sigma\text{CO}_2$  fluxes were calculated from the ranges of the chamber fluxes or from the ranges of the calculated gradient fluxes extrapolated to monthly, seasonal, and yearly error estimates. Monthly uncertainties of  $\text{CH}_4$  fluxes were determined to be  $\pm 20\%$  for diffusive  $\text{CH}_4$  based on fluxes obtained on the same date in successive years and  $\pm 50\%$  for bubble fluxes (Chanton and Martens 1988). All

other uncertainties quoted, except when noted, are combined uncertainties with the square root of the sum-of-squares technique for propagation of errors (Shoemaker et al. 1981).

## Results

Representative  $\Sigma\text{CO}_2$  pore-water profiles at station H show little variation (Fig. 2A). The profiles of  $\Sigma\text{CO}_2$  for station GI show some seasonal variability with a buildup of  $\Sigma\text{CO}_2$  near the sediment surface as summer progresses (Fig. 2B). The  $\Sigma\text{CO}_2$  profiles at the other freshwater sites (UF and Br) are similar to station GI, whereas station S, the intermediate site, appears most like station H (Kelley 1988).

At station H the flux calculated from the pore-water gradient agrees well with the flux as determined by the chambers (Fig. 3A). This agreement between the two methods of determining the  $\Sigma\text{CO}_2$  flux is not surprising, since there is neither visible vegetation nor are there conduits in the sediment due to either macrofaunal bioturbation (e.g. Aller 1982) or methane gas ebullition (Martens and Klump 1980) that might influence the chemical gradients and sediment-water exchange mechanisms. For station GI, the  $\Sigma\text{CO}_2$  fluxes measured by the light chambers are less than those obtained from the dark chambers on each sampling date with the calculated gradient flux generally falling somewhere between the two (Fig. 3B, Table 2).

Because the chamber work at station H was done predominantly during summer months, only a summer chamber flux is shown for the midestuarine site (Fig. 4). The calculated gradient flux exhibits a summer high  $\Sigma\text{CO}_2$  flux of  $0.71 \pm 0.06 \text{ mmol m}^{-2} \text{ h}^{-1}$  and a winter low of  $0.29 \pm 0.02$ , with a yearly mean flux of  $0.46 \pm 0.02$ . The summer chamber flux at station H,  $0.83 \pm 0.06 \text{ mmol m}^{-2} \text{ h}^{-1}$ , is somewhat higher than the calculated gradient flux. Seasonally, station GI also shows a high summer and a low winter  $\Sigma\text{CO}_2$  flux, with the chamber fluxes reported as the midpoint between the light and dark chambers (Fig. 4). The chamber fluxes are  $1.87 \pm 0.62$  and  $0.35 \pm 0.25 \text{ mmol m}^{-2} \text{ h}^{-1}$  for summer and winter, giving a yearly mean flux of  $1.03 \pm 0.35$ . The calculated gradient

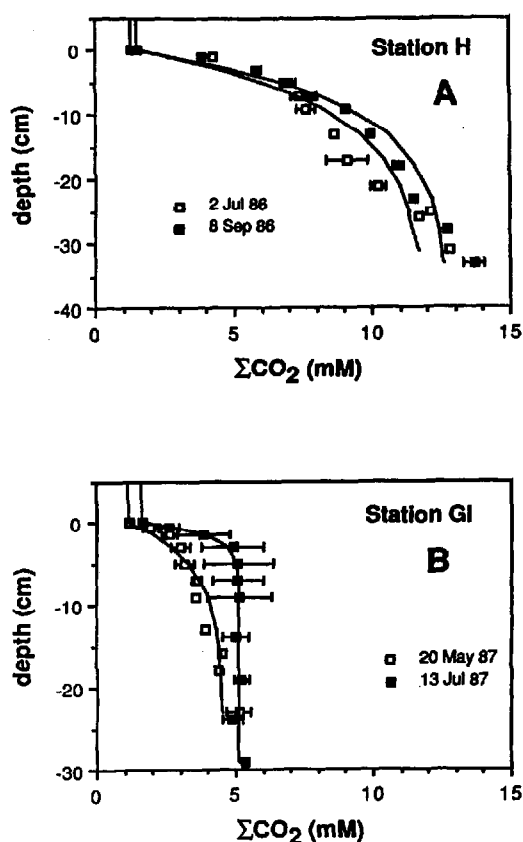


Fig. 2. Typical  $\Sigma\text{CO}_2$  pore-water profiles for stations H and GI. Error bars represent the range in concentration of two cores.

fluxes are  $1.83 \pm 0.41$  and  $0.32 \pm 0.04$   $\text{mmol m}^{-2} \text{h}^{-1}$  for summer and winter, with a yearly mean flux of  $0.82 \pm 0.13$ .

Water-column  $\text{CH}_4$  concentrations at both sites are quite low, generally  $<1$   $\mu\text{M}$  (Fig. 5). For the summer sampling dates at station H,  $\text{CH}_4$  concentrations in the pore water remain low above a depth of  $\sim 60$  cm (Fig. 5). At this depth, presumably the base of the  $\text{SO}_4^{2-}$ -reducing zone (Chanton unpubl. data),  $\text{CH}_4$  concentrations increase dramatically. During winter,  $\text{CH}_4$  concentrations increase linearly from the sediment-water interface down to  $\sim 45$  cm (Fig. 5). In both cases the sediment-water  $\text{CH}_4$  flux is negligible ( $<0.01$   $\text{mmol m}^{-2} \text{h}^{-1}$ ) at station H.

At station GI the dissolved  $\text{CH}_4$  concentrations in the pore water reach saturation by a depth of 2–3 cm in the sediment (Fig. 5), and  $\text{CH}_4$ -rich (70–80%) bubbles (Chan-

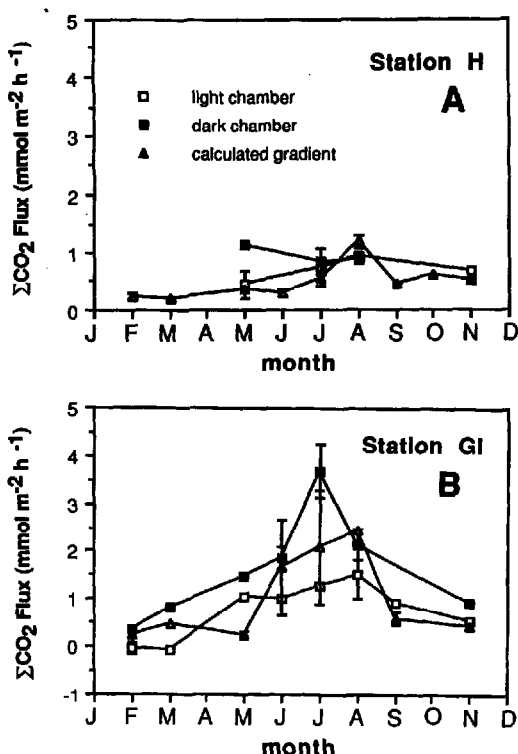


Fig. 3. Mean monthly  $\Sigma\text{CO}_2$  fluxes showing both light and dark chamber fluxes, as well as the calculated gradient flux for stations H and GI.

ton et al. 1989) are transported from the sediment via ebullition. These bubbles are released during summer months at low tide when the hydrostatic pressure is lessened (Martens and Klump 1980; Chanton et al. 1989) and during times of sediment disturbance. As discussed above, the sediment-water flux of  $\text{CH}_4$  at the upriver sites has two components: diffusion and ebullition.  $\text{CH}_4$  fluxes via both transport modes are about equal on a yearly time scale ( $56 \pm 4\%$  diffusive,  $44 \pm 13\%$  bubble), showing both mechanisms are important and need to be considered (Fig. 6, Table 3).

At the midestuarine site (H), the sedimentary organic C content and the  $\delta^{13}\text{C}$  values vs. depth are fairly constant at about 5% and  $-25$  to  $-26\text{‰}$  (Fig. 7). The profiles at station GI are slightly more variable with an organic C content of about 20% at the sediment-water interface decreasing slightly with depth to about 18% and a  $\delta^{13}\text{C}$  signature varying between  $-29$  and  $-31\text{‰}$

Table 2.  $\Sigma\text{CO}_2$  flux data ( $\text{mmol m}^{-2} \text{h}^{-1}$ ) for stations GI and H on each sampling date. Fluxes from both light and dark chambers, as well as the calculated gradient flux from sediment cores, are listed. Temperatures are of the water column. Values listed are midpoints and ranges ( $n = 2$ ). Where no errors are listed, only one sample was taken. (Not sampled—ns.)

		Chambers		
	Temp (°C)	Light	Dark	Calculated gradient flux
Station GI				
2 Jun 86	28.0	ns	ns	1.58±0.04
19 Jun 86	26.0	ns	ns	2.73±0.98
21 Jul 86	31.0	ns	ns	3.31±0.62
10 Sep 86	21.5	0.87±0.29	ns	0.74±0.10
20 Sep 86	21.0	1.00±0.07	ns	0.46±0.02
20 May 87	23.0	1.07	1.46	0.24±0.06
3 Jun 87	31.0	1.02	1.85±0.23	0.72±0.42
11 Jul 87	29.0	1.24±0.36	ns	ns
13 Jul 87	27.5	1.32	3.70±0.56	0.91±0.60
22 Aug 87	27.0	1.52±0.52	2.15±0.34	2.46
17 Nov 87	13.0	0.56±0.01	0.94±0.04	0.43±0.01
7 Feb 88	3.5	-0.02±0.12	0.36±0.01	0.22±0.14
24 Mar 88	14.0	-0.07	0.83	0.48±0.01
Station H				
2 Jun 86	30.0	ns	ns	0.29±0.08
2 Jul 86	31.0	ns	ns	0.42±0.06
8 Sep 86	31.0	ns	ns	0.46±0.02
10 Oct 86	23.0	ns	ns	0.62
31 May 87	28.5	0.44±0.24	1.12±0.01	0.36
5 Jul 87	30.0	0.62	0.63±0.10	0.68±0.16
8 Jul 87	33.5	0.88±0.16	1.06	ns
16 Aug 87	29.5	0.95	0.86	1.18±0.12
12 Nov 87	10.0	0.68	ns	0.52±0.04
11 Feb 88	9.0	ns	ns	0.24±0.04
24 Mar 88	16.0	ns	ns	0.20±0.04

throughout the core (Fig. 7). The  $\delta^{13}\text{C}$  signature of the submersed plants at station GI is within 2‰ of the sedimentary organic C,  $-30.7\text{‰}$  for *Najas* and  $-31.3\text{‰}$  for *Ceratophyllum*.

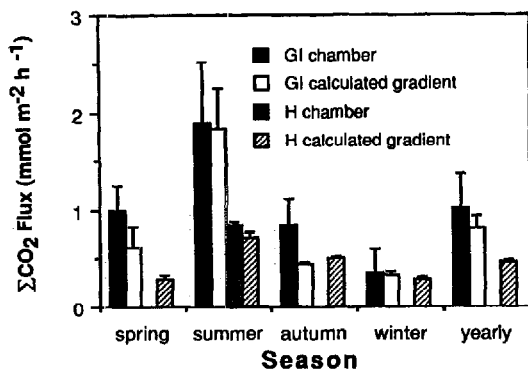


Fig. 4. Seasonal  $\Sigma\text{CO}_2$  fluxes for stations GI and H.

## Discussion

The three major trends seen in this work include higher fluxes of sediment-water  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  upstream, higher organic C content in upstream sediments, and heavier  $\delta^{13}\text{C}$  values of the sedimentary organic C downstream.

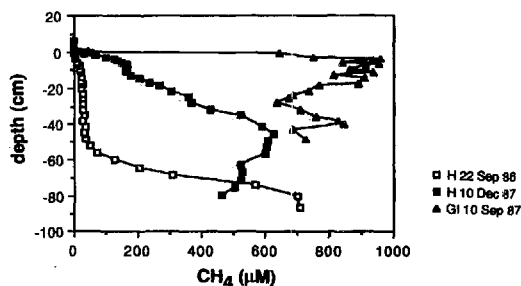


Fig. 5. Typical  $\text{CH}_4$  pore-water profiles for stations H and GI.

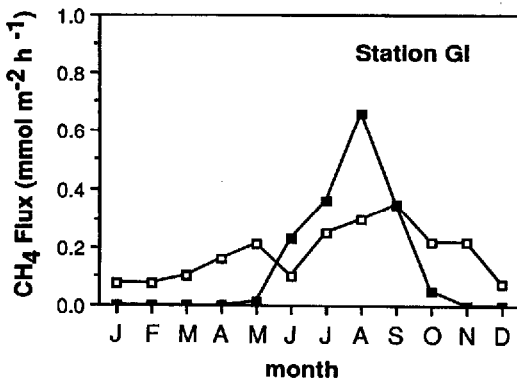


Fig. 6. Mean monthly  $\text{CH}_4$  diffusive ( $\square$ ) and bubble ( $\blacksquare$ ) fluxes at station GI. These data were collected in this study and by Chanton and Martens (1988) and Chanton et al. (1989).

*Measured fluxes at stations H and GI*—Downstream, due to seawater input,  $\text{SO}_4^{2-}$  is abundant with water-column  $\text{SO}_4^{2-}$  concentrations at station H ranging from 3 to 16 mM. The major mode of anoxic organic matter degradation is microbially mediated  $\text{SO}_4^{2-}$  reduction. This process of  $\text{SO}_4^{2-}$  reduction is seen both directly by the experimental reduction of  $^{35}\text{SO}_4^{2-}$  to  $^{35}\text{S}^{2-}$  and indirectly by the exponential decrease of  $\text{SO}_4^{2-}$  concentration in the pore water with depth in these midestuarine sediments (Kelley 1988). The seasonal production rates of  $\Sigma\text{CO}_2$  at station H seem to be fairly constant with a summer high of  $0.71 \pm 0.06 \text{ mmol m}^{-2} \text{ h}^{-1}$  and a yearly rate of  $0.46 \pm 0.02$  (Fig. 4; Table 3).

The sediment–water dissolved  $\text{CH}_4$  flux at station H is negligible, being  $<0.01 \text{ mmol m}^{-2} \text{ h}^{-1}$ . The concavity of the summer  $\text{CH}_4$  profiles (Fig. 5) suggests that  $\text{CH}_4$  consumption is occurring and contributing to the  $\Sigma\text{CO}_2$  pool. If  $\text{CH}_4$  consumption is assumed to follow first-order kinetics (Martens and Berner 1977), we calculate  $\text{CH}_4$

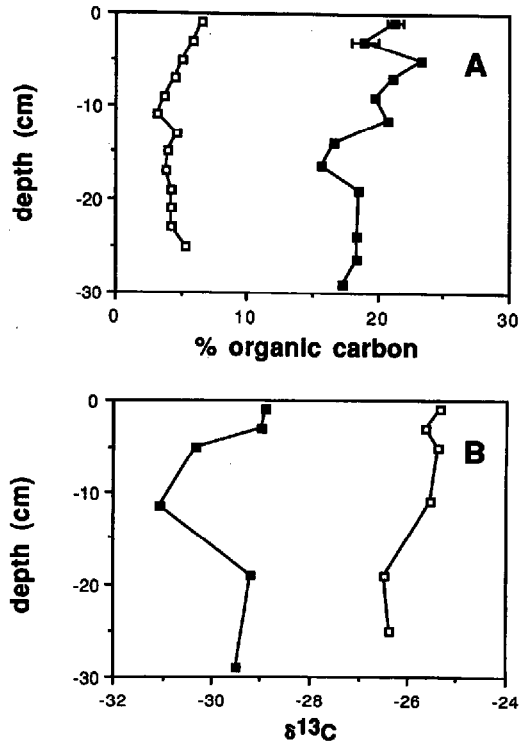


Fig. 7. Organic C content of the sediment and the  $\delta^{13}\text{C}$  signature of the organic carbon at stations H ( $\square$ ) and GI ( $\blacksquare$ ).

consumption rates of  $0.01$ – $0.02 \text{ mmol m}^{-2} \text{ h}^{-1}$  for station H during warm summer months, which accounts for  $<3\%$  of the rate of summer  $\Sigma\text{CO}_2$  production. The linear  $\text{CH}_4$  profile measured at station H in December 1987 suggests that methane consumption is very temperature-dependent—virtually shutting off during winter.

Due to very low  $\text{SO}_4^{2-}$  concentrations in the freshwater reaches of the estuary, methanogenesis is the major pathway for organic matter remineralization in the anoxic sediments. During methanogenesis, both  $\Sigma\text{CO}_2$

Table 3. Summer and yearly mean sediment–water fluxes ( $\text{mmol m}^{-2} \text{ h}^{-1}$ ) of  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  for stations GI and H.

Species	Station GI		Station H	
	Summer	Yearly	Summer	Yearly
$\Sigma\text{CO}_2$	$1.87 \pm 0.62$	$1.03 \pm 0.35$	$0.71 \pm 0.06$	$0.46 \pm 0.02$
$\text{CH}_4$ (diff)	$0.27 \pm 0.05$	$0.18 \pm 0.01$	$<0.01$	$<0.01$
$\text{CH}_4$ (bubble)	$0.44 \pm 0.13$	$0.15 \pm 0.04$	—	—
Total	$2.58 \pm 0.64$	$1.36 \pm 0.35$	$0.71 \pm 0.06$	$0.46 \pm 0.02$



and  $\text{CH}_4$  are produced and need to be considered when determining remineralization rates. Complicating the sediment-water fluxes of these two chemical species is the benthic vegetation blanketing the sediment surface at the upriver sites.

By invoking photosynthesis and respiration, we can explain the chamber  $\Sigma\text{CO}_2$  fluxes. In the light chambers, net photosynthesis occurs, depleting the chamber of  $\Sigma\text{CO}_2$ ; the actual sediment-water flux is greater than what was measured. In the dark chambers, net respiration by the plants releases  $\Sigma\text{CO}_2$ ; the dark chambers thus measure a  $\Sigma\text{CO}_2$  flux greater than the actual sediment-water flux. The actual sediment-water  $\Sigma\text{CO}_2$  flux lies somewhere between these measured fluxes. For this reason the chamber fluxes are reported as the midpoints between the light and dark chambers. The calculated gradient fluxes generally lie within this range (Fig. 3B). This range is greatest when the plants are most abundant and least during times of senescence. The increase in the uncertainty of the  $\Sigma\text{CO}_2$  chamber flux from spring to summer,  $1.00 \pm 0.26$  to  $1.87 \pm 0.62$   $\text{mmol m}^{-2} \text{h}^{-1}$  (Fig. 4), reflects the widening of this range during the period of plant growth (Fig. 3B).

The submersed macrophytes at station GI appear not to affect the sediment-water flux of  $\text{CH}_4$ , although increased  $\text{CH}_4$  flux due to aquatic plant ventilation has been described (e.g. Dacey 1981). In an experiment at station GI described earlier, a short-term  $\text{CH}_4$  chamber flux was compared to the flux calculated from a  $\text{CH}_4$  profile yielding similar results. If the plants affected the  $\text{CH}_4$  flux, the flux measured within the chambers would be different from the flux calculated from the concentration profile with Fick's first law (Eq. 1) based on diffusivities. Molecular diffusion has previously been found to be the major transport mode for the dissolved gas, radon, in similar sediments at nearby station F (Martens et al. 1980). At these upriver sites, the nonbullitive  $\text{CH}_4$  flux is controlled by molecular diffusion with the benthic plants having little or no effect.

If methanogenesis were the only process occurring at station GI, then the total production rate of  $\text{CH}_4$ , consisting of both dissolved and bubble fluxes, should approxi-

mate the rate of  $\Sigma\text{CO}_2$  production, assuming that the organic matter has a carbohydrate-like composition. Variations in the organic matter composition could shift the ratio of  $\text{CH}_4$  to  $\Sigma\text{CO}_2$  (Tarvin and Buswell 1934). The total  $\text{CH}_4$  flux at station GI is about a third of the  $\Sigma\text{CO}_2$  flux on both summer and yearly time scales (Table 3). Even though methanogenesis dominates organic matter remineralization in these upriver sediments, it appears that other processes significantly contribute to the observed  $\Sigma\text{CO}_2$  flux.

*Remineralization rates: Upriver vs. downriver*—Stations H and GI have fairly similar  $\Sigma\text{CO}_2$  fluxes throughout most of the year (Fig. 4). It is only during spring and summer months, with the growth of vegetation upriver, that the  $\Sigma\text{CO}_2$  flux at station GI greatly exceeds that of station H. The remineralization rate at station H is about a third of the rate of the upriver site (GI) on both summer and yearly time scales (Table 3).

In view of these very different remineralization rates, it needs to be established that these sites are representative of the environments they depict. Although station GI has a somewhat higher summer  $\Sigma\text{CO}_2$  flux ( $1.83 \pm 0.41$   $\text{mmol m}^{-2} \text{h}^{-1}$ ) than the other two freshwater sites (Br,  $1.16 \pm 0.17$   $\text{mmol m}^{-2} \text{h}^{-1}$ ; UF,  $1.04 \pm 0.18$   $\text{mmol m}^{-2} \text{h}^{-1}$ ), all three have larger fluxes than either the intermediate site (S,  $0.59 \pm 0.07$   $\text{mmol m}^{-2} \text{h}^{-1}$ ) or the midestuarine site (H,  $0.71 \pm 0.06$   $\text{mmol m}^{-2} \text{h}^{-1}$ ), which have about equal, but lower, rates. Therefore, it seems that stations GI and H are representative of the upriver and downriver environments.

As mentioned earlier, the upriver sites are highly vegetated, and the organic matter at station GI may be derived from submersed macrophytes as well as nearby emergent plants. From plant biomass measurements taken in July and August 1987, the submersed plants degrade quite rapidly, with almost two-thirds of their wet weight lost in the 6 weeks between sampling (Kelley 1988). The  $\delta^{13}\text{C}$  value for these plants ( $-31\text{‰}$ ) is within 2‰ of the sedimentary organic C value (Fig. 7), suggesting that they are not merely washed away, but contribute

significantly to the sedimentary organic C pool. *Ceratophyllum* is rootless and *Najas* has small, threadlike roots, so most of the biomass of these plants must be deposited at the sediment surface instead of being injected directly into the sediment column.

The nearby emergent marsh vegetation may be another source of organic matter at station GI. Identified species include *Pontederia* and *Sagittaria*, which can lose up to 90% of their ash-free dry weight in 50 d (Odum et al. 1984), and *Taxodium* (cypress trees) and *Typha*. These latter plants are slow degraders, with *Typha* losing only 30% of its weight in 50 d (Odum et al. 1984). The fast-degrading plants of the marsh, along with the rapidly degrading submersed macrophytes, may account for the high rate of organic matter remineralization at station GI, whereas the slow degraders may explain the high percentage of organic C preserved in the sediment (Fig. 7).

A buildup of the  $\Sigma\text{CO}_2$  profile at station GI over the course of summer occurs near the sediment-water interface with the slope of the profile near the interface being much steeper at station GI than downriver at station H (Fig. 2). The upriver site does not, however, show high  $\Sigma\text{CO}_2$  concentrations at depth. These results argue that the rapid remineralization occurring at station GI must be at, or very near, the sediment surface where the organic matter from both emergent and submersed vegetation is deposited.

**Sedimentary organic C**—The  $\delta^{13}\text{C}$  signature of the sedimentary organic C at station H is enriched in  $^{13}\text{C}$  by about 5‰ relative to station GI (Fig. 7). If  $-20$ ‰ is assumed to be the  $\delta^{13}\text{C}$  signature for marine plankton (Deines 1980) and if the  $-29$  to  $-31$ ‰ value seen at station GI is taken to be the terrestrial, freshwater end-member, then by a simple dilution-mixing model, the organic C accumulating at station H may be as much as 50% plankton derived. Plankton is easily degraded (Westrich and Berner 1984), in part because it does not contain lignin—a structural component found in higher vascular plants (Deines 1980). The lower rates of organic C remineralization at station H are not consistent with a large input of plankton-derived organic matter.

The nearby marsh vegetation, *Juncus*, has a  $\delta^{13}\text{C}$  signature of about  $-26$ ‰ (N. Blair pers. comm.)—a value very similar to the sedimentary organic carbon at station H. It is possible that the low rate of remineralization at this site, as indicated by  $\Sigma\text{CO}_2$  fluxes (Table 2), results from the slow decomposition of *Juncus*.

**Carbon budgets**—Determination of C budgets at the two sites requires knowledge of rates of sediment accumulation. At the upstream stations,  $^{137}\text{Cs}$  profiles with subsurface maxima are observed (Kelley 1988) that can be related to the 1963 peak in global fallout due to atmospheric bomb testing (HASL 1977). The accumulation rate upriver with the 1963 peak is  $0.6 \text{ cm yr}^{-1}$ . Similarly, with  $^{210}\text{Pb}$  as a radiochronometric tracer, Benninger and Martens (1983) estimated an accumulation rate of  $0.5 \text{ cm yr}^{-1}$  for the upstream sediments at nearby station F.

Under the more saline conditions present at station H, the concentration and activity of Cs in the sediment is smaller due to competition for available binding sites on particle surfaces with ions such as  $\text{K}^+$  and  $\text{NH}_4^+$  (Evans et al. 1983). Because of this smaller activity,  $^{137}\text{Cs}$  is not an adequate radiochronometric tracer for the sediment at this site. Earlier work (Chanton unpubl. data; Benninger and Martens 1983) with  $^{210}\text{Pb}$  as the tracer has shown that the sediment accumulation rate at station H is  $0.3 \text{ cm yr}^{-1}$ .

Organic C burial rates at both sites (Fig. 8) are determined from

$$J_{\text{buried}} = C_{\text{org}} \omega \rho_{\text{sed}} (1 - \phi) \quad (3)$$

where  $J_{\text{buried}}$  is the organic C burial rate ( $\text{mmol m}^{-2} \text{ h}^{-1}$ ),  $C_{\text{org}}$  the fraction of organic C in sediment (%/100), and  $\rho_{\text{sed}}$  the sediment density ( $\text{g cm}^{-3}$ ). Mean sediment densities are  $2.11 \pm 0.14$  and  $1.66 \pm 0.15 \text{ g cm}^{-3}$  ( $\pm 1 \text{ SD}$ ) and mean porosities are  $0.78 \pm 0.04$  and  $0.90 \pm 0.02$  ( $\pm 1 \text{ SD}$ ) for stations H and GI, respectively. From these burial rates and the measured remineralization rates, the rate of organic C coming into each of these systems,  $J_{\text{in}}$ , can be calculated from

$$J_{\text{in}} = J_{\text{out}} + J_{\text{buried}} \quad (4)$$

where  $J_{\text{out}}$  is the remineralization rate ( $\text{mmol m}^{-2} \text{ h}^{-1}$ ).

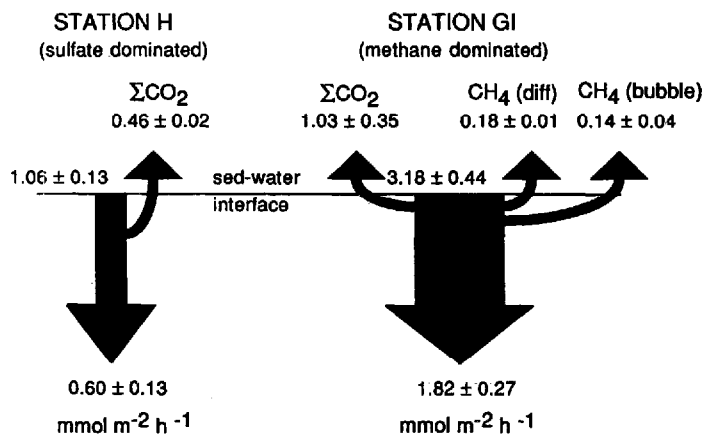


Fig. 8. A carbon budget for stations H and GI.

At station H, the downriver sulfate-dominated site,  $\sim 43 \pm 6\%$  of the incoming organic C is being remineralized primarily by microbially mediated  $\text{SO}_4^{2-}$  reduction. At station GI,  $42 \pm 12\%$  of the incoming organic C is also being remineralized. Because much more organic C enters the system, both turnover and burial rates are higher upstream. Of the organic C being remineralized,  $47 \pm 14\%$  can be attributed to methanogenesis, assuming a 1:1 ratio between  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  produced. The remainder must be remineralized through other pathways.

It appears that the remineralization rates at these sites may be controlled more by the source and reactivity of the organic matter deposited than by the mode of degradation. Upriver inputs of highly reactive organic matter into the system result in high remineralization rates, whereas lower remineralization rates downriver have been hypothesized to result from more slowly decaying organic matter. More work is needed, however, to determine the relative control on rates resulting from changes in sources of organic matter vs. pathways of remineralization.

## References

- ALLER, R. C. 1982. The effects of macrobenthos on chemical properties of marine sediment and overlying water, p. 53–102. *In* P. L. McCall and M. J. S. Tevesz [eds.], *Animal-sediment relations*. Plenum.
- BARTLETT, K. B., D. S. BARTLETT, R. C. HARRIS, AND D. I. SEBACHER. 1987. Methane emissions along a salt marsh salinity gradient. *Biogeochemistry* 4: 183–202.
- , R. C. HARRIS, AND D. I. SEBACHER. 1985. Methane flux from coastal salt marshes. *J. Geophys. Res.* 90: 5710–5720.
- BEAL, E. O. 1977. A manual of marsh and aquatic vascular plants of North Carolina with habitat data. N.C. Agric. Exp. Sta. Tech. Bull. 247.
- BENNINGER, L. K., AND C. S. MARTENS. 1983. Sources and fates of sedimentary organic matter in the White Oak and Neuse River estuaries. Univ. N. Carolina Water Resour. Res. Inst.
- BERNER, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill.
- . 1980. Early diagenesis: A theoretical approach. Princeton.
- CACECI, M. S., AND W. P. CACHERIS. 1984. Fitting curves to data: The Simplex algorithm is the answer. *Byte* 9(5): 340–362.
- CHANTON, J. P., AND C. S. MARTENS. 1988. Seasonal variations in ebullitive flux and isotopic composition of methane in a tidal freshwater estuary. *Global Biogeochem. Cycles* 2: 289–298.
- , ———, AND C. A. KELLEY. 1989. Gas transport from methane-saturated, tidal freshwater and wetland sediments. *Limnol. Oceanogr.* 34: 807–819.
- CLAYPOOL, G. E., AND I. R. KAPLAN. 1974. The origin and distribution of methane in marine sediments, p. 99–139. *In* I. R. Kaplan [ed.], *Natural gases in marine sediments*. Plenum.
- CLENEAY, C. A. 1974. Modern sediments and sedimentary structures of the Bogue Inlet-White Oak estuary area, North Carolina. M.S. thesis, Bowling Green State Univ. 87 p.
- DACEY, J. W. H. 1981. How aquatic plants ventilate. *Oceanus* 24: 43–51.
- DEINES, P. 1980. The isotopic composition of reduced organic compounds, p. 329–406. *In* P. Fritz and J. C. Fontes [eds.], *Handbook of environmental isotope geochemistry*. V. 1. Elsevier.
- DREVER, J. I. 1982. The geochemistry of natural waters. Prentice-Hall.

- EVANS, D. W., J. J. ALBERTS, AND R. A. CLARK III. 1983. Reversible ion-exchange fixation of cesium-137 leading to mobilization from reservoir sediments. *Geochim. Cosmochim. Acta* **47**: 1041-1049.
- FROELICH, P. N., AND OTHERS. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**: 1075-1090.
- GRUEBEL, K. A. 1981. Radon sediment-water exchange in the White Oak River estuary, North Carolina. M.S. thesis, Univ. North Carolina, Chapel Hill. 72 p.
- HASL 1977. Health and Safety Laboratory Environmental Quarterly: Final tabulation of monthly  $^{90}\text{Sr}$  fallout data: 1954-1976, Health and Safety Laboratory. U.S. ERDA.
- HESSLEIN, R. H. 1976. An in situ sampler for close interval pore water studies. *Limnol. Oceanogr.* **21**: 912-914.
- KELLEY, C. A. 1988. Sedimentary organic carbon remineralization rates along the salinity gradient of the White Oak River estuary, North Carolina. M.S. thesis, Univ. N. Carolina, Chapel Hill. 110 p.
- KELLY, C. A., AND D. P. CHYNOWETH. 1981. The contribution of temperature and of the input of organic matter in controlling rates of sediment methanogenesis. *Limnol. Oceanogr.* **26**: 891-897.
- KING, G. M., AND W. J. WIEBE. 1978. Methane release from soils of a Georgia salt marsh. *Geochim. Cosmochim. Acta* **42**: 343-348.
- KLUMP, J. V., AND C. S. MARTENS. 1981. Biogeochemical cycling in an organic-rich coastal marine basin. 2. Nutrient sediment-water exchange processes. *Geochim. Cosmochim. Acta* **45**: 101-121.
- LI, Y., AND S. GREGORY. 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* **38**: 703-714.
- MCAULIFFE, C. 1971. Gas chromatographic determination of solutes by multiple phase equilibrium. *Chem. Technol.* **1**: 46-51.
- MARTENS, C. S., AND R. A. BERNER. 1974. Methane production in the interstitial waters of sulfate-depleted marine sediments. *Science* **185**: 1167-1169.
- , AND ———. 1977. Interstitial water chemistry of anoxic Long Island Sound sediments. 1. Dissolved gases. *Limnol. Oceanogr.* **22**: 10-25.
- , AND M. B. GOLDBABER. 1978. Early diagenesis in transitional sedimentary environments of the White Oak River estuary, N.C. *Limnol. Oceanogr.* **23**: 428-441.
- , G. W. KIPPHUT, AND J. V. KLUMP. 1980. Sediment-water chemical exchange in the coastal zone traced by in situ radon-222 flux measurements. *Science* **208**: 285-288.
- , AND J. V. KLUMP. 1980, 1984. Biogeochemical cycling in an organic-rich coastal marine basin. 1. Methane sediment-water exchange processes. 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. *Geochim. Cosmochim. Acta* **44**: 471-490; **48**: 1987-2004.
- ODUM, W. E., T. J. SMITH III, J. K. HOOVER, AND C. C. McIVER. 1984. The ecology of tidal freshwater marshes of the United States east coast: A community profile. U.S. Fish Wildl. Serv. FWS/OBS-83/17.
- REEBURGH, W. S. 1967. An improved interstitial water sampler. *Limnol. Oceanogr.* **12**: 163-165.
- . 1983. Rates of biogeochemical processes in anoxic sediments. *Annu. Rev. Earth Planet. Sci.* **11**: 269-298.
- REVSBECH, N. P., B. B. JØRGENSEN, AND T. H. BLACKBURN. 1980a. Oxygen in the sea bottom measured with a microelectrode. *Science* **207**: 1355-1356.
- , J. SØRENSEN, T. H. BLACKBURN, AND J. P. LOMHOLT. 1980b. Distribution of oxygen in marine sediments measured with a microelectrode. *Limnol. Oceanogr.* **25**: 403-411.
- SHOEMAKER, D. P., C. W. GARLAND, J. I. STEINFELD, AND J. W. NIBLER. 1981. Experiments in physical chemistry. McGraw-Hill.
- STRAYER, R. F., AND J. M. TIEDJE. 1978. In situ methane production in a small, hypercutrophic, hard-water lake: Loss of methane from sediments by vertical diffusion and ebullition. *Limnol. Oceanogr.* **23**: 1201-1206.
- TARVIN, D., AND A. M. BUSWELL. 1934. The methane fermentation of organic acids and carbohydrates. *J. Am. Chem. Soc.* **56**: 1751-1755.
- ULLMAN, W. J., AND R. C. ALLER. 1982. Diffusion coefficients in nearshore marine sediments. *Limnol. Oceanogr.* **27**: 552-556.
- WEISS, R. F., AND H. CRAIG. 1973. Precise shipboard determination of dissolved nitrogen, oxygen, argon and total inorganic carbon by gas chromatography. *Deep-Sea Res.* **20**: 291-303.
- WESTRICH, J. T., AND R. A. BERNER. 1984. The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. *Limnol. Oceanogr.* **29**: 236-249.
- YAVITT, J. B., G. E. LANG, AND R. K. WIEDER. 1987. Control of carbon mineralization to  $\text{CH}_4$  and  $\text{CO}_2$  in anaerobic, *Sphagnum*-derived peat from Big Run Bog, West Virginia. *Biogeochemistry* **4**: 141-157.

Submitted: 6 February 1989

Accepted: 12 June 1989

Revised: 5 December 1989