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Fluxes of dissolved organic carbon from Chesapeake Bay sediments

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Abstract—Benthic fluxes of dissolved organic carbon (DOC) were measured over an annual cycle at two contrasting sites in Chesapeake Bay. At an organic-rich, sulfidic site in the mesohaline portion of the Bay (site M) DOC fluxes from the sediments ranged from 1.4 to 2.9 mmol/m^2/d. Measured benthic DOC fluxes at site M corresponded to ~3–13% of the depth-integrated benthic C remineralization rates (ΣOCR), and agreed well with calculated diffusive DOC fluxes based on porewater DOC profiles. This agreement suggests that DOC fluxes from site M sediments were likely controlled by molecular diffusion. The second site that was studied is a heavily bioturbated site in the southern Bay (site S). The activity of macrobenthos did not appear to enhance DOC fluxes from these sediments, since measured benthic DOC fluxes (<0.5 mmol/m^2/d) were lower than those at site M. The ratios of benthic DOC fluxes to ΣOCR values at site S were also slightly smaller than those observed at site M.

Benthic DOC fluxes from Chesapeake Bay sediments do not appear to significantly affect the transport of DOC through this estuary, although uncertainties in the reactivity of DOC in estuaries makes this conclusion somewhat tentative at this time. However, when these results are used to make a lower limit estimate of the globally integrated benthic DOC flux from marine sediments, a value similar to that previously calculated by BURDIGE et al. (1992) is obtained. This observation further supports suggestions in this paper about the importance of benthic DOC fluxes in the oceanic C cycle.

INTRODUCTION

IN THE POREWATERS of many surficial sediments, concentrations of dissolved organic carbon (DOC) can be up to an order of magnitude higher than those in the overlying waters (STARIKOVA, 1970; NISSENBAUM et al., 1971; KROM and SHOLKOVITZ, 1977; LYONS et al., 1979; KROM and WESTRICH, 1981; SUESS and MUELLER, 1981; EMERSON and DYMOND, 1984; HEGGIE et al., 1987; ALPERIN et al., 1992; BURDIGE et al., 1992; CHEN et al., 1993; MARTIN and MCCORKLE, 1994). This observation suggests the possibility of DOC fluxes from sediments to the overlying waters. Numerous authors have discussed the possible importance of benthic DOC fluxes in sedimentary and oceanic C cycling (WILLIAMS et al., 1980; EMERSON and DYMOND, 1984; HEGGIE et al., 1987; WILLIAMS and DRUFFEL, 1987; BENDER et al., 1989; MCNICHOL et al., 1991; MOPPER et al., 1991a; ALPERIN et al., 1992; BURDIGE et al., 1992; HEDGES, 1992; MARTIN and MCCORKLE, 1994). However, the role of sediments as a source of DOC to the oceans, as well as the production of DOC in sediments are both still poorly understood. For example, it has been suggested that sediment porewaters (and benthic DOC fluxes) may represent an important source of DOC to the deep ocean (WILLIAMS and DRUFFEL, 1987; MOPPER et al., 1991a; HEDGES, 1992), and that such benthic DOC fluxes might provide a possible explanation for the apparent discrepancy between the chemical properties of deep-water DOC and the average mixing time of the ocean (see the references cited above and BURDIGE et al., 1992, for further details). Similarly, the occurrence of benthic DOC fluxes may play a role in explaining discrepancies in the stable carbon isotope budget of surficial marine sediments (ALPERIN, 1989; MCNICHOL et al., 1991; MARTIN and MCCORKLE, 1994).

In spite of the potential importance of benthic DOC fluxes in the oceanic C cycle, there have been few quantitative studies of these processes. We recently carried out such a study (BURDIGE et al., 1992), using porewater DOC data to calculate diffusive DOC fluxes from several marine sediments. These results were then used to make the first estimate of the globally integrated benthic DOC flux from marine sediments. Although this calculated value (0.1–0.9 × 10^{14} g C/y) is likely a lower limit, it is comparable in magnitude to processes such as riverine inputs of DOC and POC to the oceans (2 and 2.3 × 10^{14} g C/y, respectively; MEYBECK, 1982; ITTEKKOT, 1988), remineralization of organic C in surficial sediments (0.2–5 × 10^{14} g C/y; EMERSON and HEDGES, 1988), and burial (with depth) of sedimentary organic C (0.6–1.4 × 10^{14} g C/y; BERNER, 1982; ROMANKEVICH, 1984; SMITH and MACKENZIE, 1987). Similar conclusions about the importance of benthic DOC fluxes in the oceanic carbon cycle were also reached by CHEN et al. (1993), who used porewater DOC fluorescence data to estimate benthic DOC fluxes.

While these observations presented the first quantitative evidence for the importance of benthic DOC fluxes in oceanic and sedimentary C cycling, there are potential problems with estimating benthic DOC fluxes (or benthic fluxes of any other dissolved constituent) using porewater gradients (see discussions in BERELSON et al., 1987; DEVOL, 1987; BENDER et al., 1989; BURDIGE et al., 1992). In an attempt to overcome these difficulties, several recent studies have directly measured benthic DOC fluxes. BURDIGE et al. (1992) presented the results of benthic DOC flux studies (using core incubation techniques) from two anoxic, near-coastal sediments (Cape Lookout Bight, NC and the mesohaline portion of Chesapeake Bay), while preliminary benthic DOC flux measurements have also been made in continental margin sediments using benthic landers (MOPPER et al., 1991b; BURDIGE et al., 1993). These observations provide additional evidence for the importance of marine sediments as a source of DOC to the oceans.

In this paper, we present the results of a more detailed study of benthic DOC fluxes from two contrasting sites in the Chesapeake Bay. These results are used to examine several aspects of the role of benthic DOC fluxes in sedimentary C cycling at these sites, as well as the role of sediments as a source of DOC to the oceans.

METHODS

Study Sites

Studies were primarily carried out at two sites in Chesapeake Bay, corresponding to two of the three primary sites studied by the benthic biogeochemistry component of the University of Maryland LMER/PROTEUS program (Fig. 1). Site M is in the mesohaline portion of the Bay (bottom water salinities of ~10–20 psu) where seasonal anoxia (or low oxygen) generally occurs during the summer months (Officer et al., 1984a; Smith et al., 1992). Low oxygen conditions were observed at this site in the summer of 1991, although they were not seen at the time of our summer 1992 sampling. Site S is in the southern Bay (bottom water salinities of ~20–30 psu), where the bottom waters are well oxygenated year-round. The water depth at site M is approximately 12 m, and approximately 10 m at site S.

The sediments at site M are fine-grained, highly porous (ϕ values range from ~0.95–0.85 in the upper 20 cm) and organic-rich (>3% organic C). The sedimentation rates at this site is ~0.7 cm/y (based on a mass flux of 0.178 g/cm^2/y and an average sediment porosity of 0.9; J. Cornwell, unpubl. data). ^{210}Pb profiles at this site also suggest that the upper ~5–10 cm of these sediments are mixed, with a particle mixing constant (D_B) that appears to range from 10–25 cm^2/y (Officer et al., 1984b; D. Rice, unpubl. data as cited in Roden and Tuttle, 1994; J. Cornwell, unpubl. data). The causes of this sediment mixing are not well understood. Sulfate reduction dominates C metabolism at this site (Roden and Tuttle, 1994; Marvin and Capone, 1992).

Site S, the southern Bay site, is heavily bioturbated, primarily by tube-dwelling organisms (Schaffner, 1990). The site has integrated annual rates of sulfate reduction that are half those of the mid-Bay region (Marvin and Capone, 1992). The sediments at site S are coarser grained and less porous (ϕ values range from 0.5–0.6 in the upper 20 cm) than those at site M. Reported sedimentation rates in this portion of the Bay range from 0.04–0.6 cm/y (Officer et al., 1984b; Nixon, 1987; G. Wong, unpubl. data), although specific information on the sedimentation rate at site S is not available.

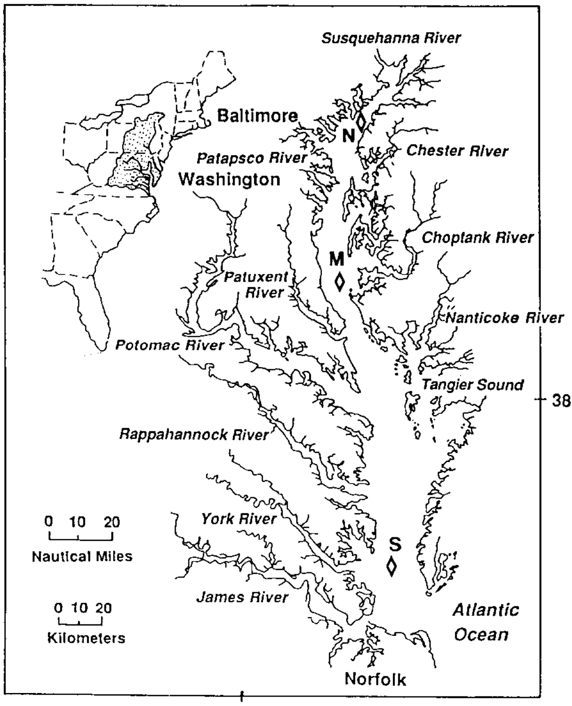


Fig. 1. A map of Chesapeake Bay showing the study sites.

Sample Collection

Sediment cores were collected by box core and sub-cored for sediment porewater and benthic flux studies. Subcores collected in 2.25 in. (i.d.) Plexiglass core tubes were sectioned and porewaters extracted using sediment squeezers (Reeburgh, 1967) operated at low pressures (20–40 psi = ~1.5–3 atm). Sediment "squeezer cakes" were saved (frozen at −20°C) for later elemental analysis. Subcores were also collected in 3.5 in. (i.d.) Plexiglass core tubes which were designed to be used as pressurized core barrels for porewater extraction (Jahnke, 1988). These pressurized core barrels were modified slightly from those originally described by Jahnke (1988) as follows: 0.5 in. pieces of 0.125 in. (o.d.) porous polypropylene rod were used in the fittings of each sampling port, in place of paper filters; the core barrel was pressurized with N_2 (maximum pressure of 60 psi = ~4 atm) rather than mechanically. All subcores used for porewater sampling were stored at in situ temperatures until processed (within 12 h of collection).

Porewaters collected in either fashion were processed onboard ship as follows. Samples for dissolved sulfate and ammonium analyses were filtered through 0.45 μm Nucleopore filters into cleaned plastic vials, acidified to pH 2 with HCl, and refrigerated (4°C) until analyzed. Samples for ΣCO_2 (total dissolved inorganic C) analyses were filtered into 3 mL plastic syringes sealed with luer-lock three-way stopcocks, and stored at 4°C (with no headspace in the syringe) until analyzed. We have observed no loss of dissolved inorganic C from samples stored in this fashion.

In the majority of our studies, porewater samples for DOC analyses were filtered through 0.45 μm polycarbonate Nucleopore filters into cleaned glass ampoules and acidified to pH 2 with 6 N HCl (glassware cleaning procedures are described below). Ampoules were sealed with a propane torch, quick-frozen, and stored at −20°C until analyzed. We observed no loss of DOC from samples stored in this fashion, which agrees with recent results of other workers (Hansell, 1993; Williams et al., 1993). Beginning in July, 1992, filtered DOC samples (both porewater and benthic flux experiment samples) were stored in cleaned, 8 mL Wheaton glass vials sealed with Teflon-lined silicone septa (similar to those used in the JGOFS Equatorial Pacific cruises for archiving DOC samples; Sharp et al., 1994). Again, these samples were acidified, quick-frozen, and stored frozen until analyzed.

Subcores for benthic flux studies were collected in 3.25 in. (i.d.) glass core tubes (18 in. length). These cores were initially sealed at the top and bottom with rubber stoppers and placed in a darkened water bath at the in situ bottom water temperature. To avoid oxygen depletion and metabolite buildup in the waters overlying the core, this water was flushed with ~2 L of fresh bottom water every day until flux experiments were begun (<3 days). Bottom water used to flush the cores was collected with either Nisken or GO-Flo bottles and stored in cleaned glass carboys in the dark.

Benthic Flux Measurements

In shallow water environments it has been shown that shipboard or laboratory based incubations of cores at in situ temperatures yields inorganic fluxes that are comparable to those measured in situ using benthic flux chambers (Nixon et al., 1980; Klump and Martens, 1981; Chanton et al., 1987; Roden et al., 1994). As such, the laboratory incubation procedures described below were used in our flux studies. In our studies we also found that replicate flux measurements could be made using the same core. At the conclusion of one flux determination the water over the core was flushed with fresh bottom water, and the measurement was then repeated. Within experimental uncertainties, this approach yielded reproducible DOC, sulfate, and ΣCO_2 fluxes from the same core, and provided a greater degree of confidence in our measured benthic fluxes.

Sediment cores used in our benthic flux studies were collected as discussed above. To start a flux experiment, the water over the subcore was first flushed with ~2 L of bottom water, and adjusted to a height of 9–13 cm. A cover plate was then placed on top of the core (Fig. 2) in such a way as to leave a slight "headspace" between the top of the water column and this plate. This eliminated the need for air and water tight seals, which could potentially lead to flux chamber blanks associated with the gasket materials used to make these seals.

The cover plate is equipped with a sampling port, and a 12 V electric motor is attached to the plate and used to slowly rotate a glass "T" stirring rod. The stirring rod is connected to the drive shaft of the motor using a small piece of tygon tubing as a coupler, and is passed through a small hole in the cover plate. A glass tube also extends through the cover plate into the water overlying the core, and in most cases filtered (0.2 μm) and humidified lab air was bubbled through this tube at a rate of 1 bubble every 4–5 s. This procedure maintained oxygen concentrations in the water over the cores at near-constant values similar to those in the bottom waters at the time of collection. Control experiments (data not shown) indicated that this bubbling rate was sufficiently slow that we lost only negligible amounts of ΣCO_2 from the water over the cores, and that this loss accounted for <1% of measured benthic ΣCO_2 fluxes. In our initial flux studies (August, 1992; also see Fig. 3 in BURDIGE et al., 1992) this bubbling tube was placed in the headspace of the cores and used to pass N_2 (at a much higher flow rate) across the water overlying the core. This approach was taken because the bottom waters at site M contained no dissolved oxygen at this time.

Samples of the water overlying the core were taken as a function of time for the determination of benthic fluxes of DOC, sulfate, and ΣCO_2. For each time point, a 10 mL aliquot was removed through the sampling port with a cleaned glass pipette, and then replaced with an equal volume of ambient bottom water. This "recharge" water was stored in the dark in a clean glass bottle at in situ bottom water temperatures during the course of an experiment (for anoxic experiments the bottle was also placed in a N_2-filled anaerobic jar). Samples of recharge water were also collected as a function of time during flux determinations, as a control experiment accounting for any in situ consumption or production of DOC in the water overlying the core. All benthic flux and recharge water samples were filtered, acidified (DOC and sulfate only), and stored until analyzed as described below. Dissolved oxygen was also periodically determined on unfiltered samples by electrodes (Microelectrodes, Inc., model MI-730), as in our previous flux studies in the southern Chesapeake Bay (BURDIGE, 1989).

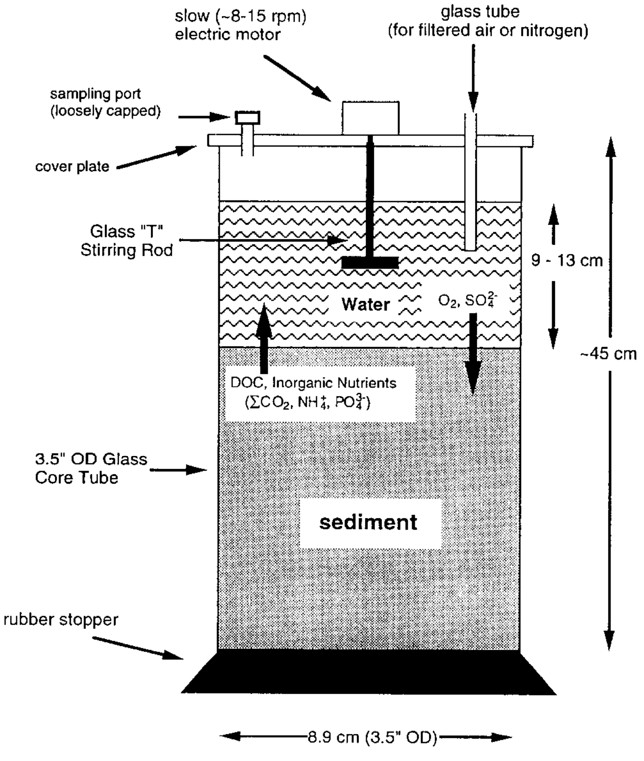


FIG. 2. A schematic representation of the flux chamber used in these studies.

Dissolved and Solid Phase Analyses

Sulfate was analyzed by ion chromatography, while ammonium was analyzed by a modified version of the phenol-hypochlorite method (GIESKES et al., 1991). ΣCO_2 was determined using a Shimadzu TOC-5000 total carbon analyzer. Particulate nutrient analyses (C, N, and S) were performed by high temperature combustion using a Carlo Erba NCS elemental analyzer (VERARDO et al., 1990).

Analysis of Dissolved Organic Carbon

DOC analyses were carried out by a high temperature catalytic oxidation (HTCO) technique, using a Shimadzu TOC-5000 total C analyzer. This technique was initially chosen based on the results of studies which suggested that wet oxidation techniques (i.e., UV and persulfate-based oxidation) underestimated DOC concentrations in marine water samples (see WILLIAMS, 1992, for a more detailed discussion of this problem). While recent results have not unequivocally borne out these earlier observations (WILLIAMS, 1992; HANSELL et al., 1993; SHARP et al., 1994), the HTCO technique yields results that are certainly comparable to the more "traditional" wet chemical oxidation techniques.

The Shimadzu TOC-5000 total C analyzer is a commercially available instrument based on that described by SUZUKI et al. (1992). Samples are injected into a 680°C quartz combustion tube containing a Pt (on alumina) catalyst, and the resulting CO_2 produced by the catalytic oxidation of the DOC in the water sample is swept by ultra-pure air (after some cleanup) into a nondispersive IR detector. Additional details on the operation of this instrument are presented in BENNER and STROM (1993).

Samples for DOC analyses were first thawed and bubbled with ultra-pure air to remove all dissolved inorganic C, and then analyzed for DOC. All samples were analyzed at minimum in triplicate. Standards for instrument calibration were prepared with K phthalate in distilled, deionized water. Calibration consisted of running four standards (over an appropriate concentration range for porewater or bottom water, i.e., benthic flux, samples) and a laboratory blank (distilled, deionized water), and fitting all the data (five data points total) by least-squares linear regression. The slope of this best-fit line was taken as the response factor of the instrument, and along with the instrument blank (see below), used to calculate concentrations in samples. We observed no significant difference between slopes determined with standards prepared in distilled water and slopes obtained in standard addition experiments with low DOC seawater.

In recent papers on the determination of DOC in natural waters, several authors have discussed problems associated with quantifying the blank associated with the HTCO measurement of DOC (WILLIAMS, 1992; BENNER and STROM, 1993; HEDGES et al., 1993; SHARP et al., 1993). Our experiences with this problem were similar to those reported by BENNER and STROM (1993). We have also observed that new catalyst material shows a very high blank, and that repeated injections of "C-free" water decreases the blank to a value of ~10–20 μM (a value that is generally less than 10% of the measured DOC concentrations in our samples). Furthermore, once a catalyst is thus "conditioned", this blank changed only very slowly with time. To verify that this observation is not a function of decreasing efficiency of the catalyst, we keep a daily log of the distilled water plus instrument blank, and the instrument response factor. In addition, the ability of our system to quantitatively recover antipyrine (a relatively refractory C compound) was also examined periodically. Over the time period of this study this recovery efficiency averaged 103.2 ± 2.3% (*n*

= sixty-two daily sets of triplicate analyses), and was not a function of the age of the catalyst bed. The results of the study by BENNER and STROM (1993) also suggested that the vast majority of this blank was from the instrument itself (e.g., C bleed from the catalyst), rather than from the water used to prepare standards. Our examination of this problem concurred with their observation, and our data was therefore corrected accordingly.

Glassware Cleaning

All glassware used for DOC determinations was cleaned by washing in an Alconox solution, rinsing with tap water, soaking in 10% HCl, and finally rinsing with distilled, deionized water. Glassware was then dried at 110°C in a conventional lab oven and finally, baked clean of any residual organic matter in a muffle furnace (550°C) overnight. Plasticware and Teflon-backed silicone septa were also cleaned as discussed above, with the exception that they were dried in a conventional oven at 40°C.

RESULTS

Porewater and Solid Phase Sediment Profiles

Inorganic porewater profiles at site M (Fig. 3) were similar to those observed in other anoxic sediments such as Cape Lookout Bight (MARTENS and KLUMP, 1984), and other portions of the meso-haline Chesapeake Bay (MATISOFF et al., 1975; BURDIGE, 1991a). These profiles provided further evidence for the dominance of sulfate reduction in organic matter remineralization, since plots of porewater sulfate vs. ΣCO_2 for four individual cores yield a ratio of 0.58 ± 0.08 for the number of moles of sulfate reduced per mole of ΣCO_2 produced. Assuming that sedimentary organic C has an average oxidation state of ~0 (e.g., "CH_2O") the theoretical value of this ratio should be 0.5 (BERNER, 1980).

The sediments at site M are organic-rich (Fig. 4), and contain relatively high levels of total S (8–12 mg S/gdw), primarily in the form of iron monosulfides (AVS) and pyrite (J. CORNWELL, unpubl. data). Total C (TC) depth profiles at this site also showed a large amount of variability. In the three cores analyzed, significant variations were seen in the surface sediment TC concentrations (~37–77 mg C/gdw), although all three cores reached similar C levels at depth (~30 mg C/gdw). Core IVM25D (March, 1992) showed the largest concentration change with depth, and the most pronounced exponential-like decrease. Core VM12C (July, 1992) showed much smaller TC concentration changes and curvature with depth, while core IIIM18B (October, 1991) showed virtually no curvature and downcore variations in TC concentrations. Organic C appeared to constitute the vast majority of the total C in these sediments, since analyses of acidified and unacidified sediment samples indicated that carbonate C accounted for only ~0.2 mg C/gdw. Carbonate C also showed no apparent trend with depth.

Site S sediments showed virtually no sulfate and ΣCO_2 porewater gradients (Fig. 3), and ammonium gradients that were almost an order of magnitude smaller than those seen in site M sediments (Burdige et al., 1994). This lack of discernable porewater gradients at site S does not appear to be the result of substantially lower rates of biogeochemical processes in these sediments, based on a comparison of integrated annual sulfate reduction rates (MARVIN and CAPONE, 1992), benthic C remineralization rates (see below), and measured ΣCO_2 production rates (LUSTWERK and BURDIGE, 1993) in these sediments and those at site M. Rather, it appears that the observed porewater profiles at site S result from the bioturbation (bioirrigation and/or sediment mixing) of these sediments by benthic fauna. SCHAFFNER (1990) has observed that the sediments in this region of the Bay contain a variety of tube-dwelling and burrowing organisms, and our own visible observations of the cores collected at site S qualitatively agree with her observations. The activity of these organisms therefore ventilates or irrigates these sediments to such an extent as to significantly alter the sulfate, ΣCO_2 and ammonium porewater gradients (e.g., BERNER, 1980; ALLER, 1982). Total C concentrations in these sediments were substantially lower than those observed at site M (0.6–0.8 mg C/gdw) and showed virtually no downcore variations over the upper 15 cm of sediment (Fig. 4).

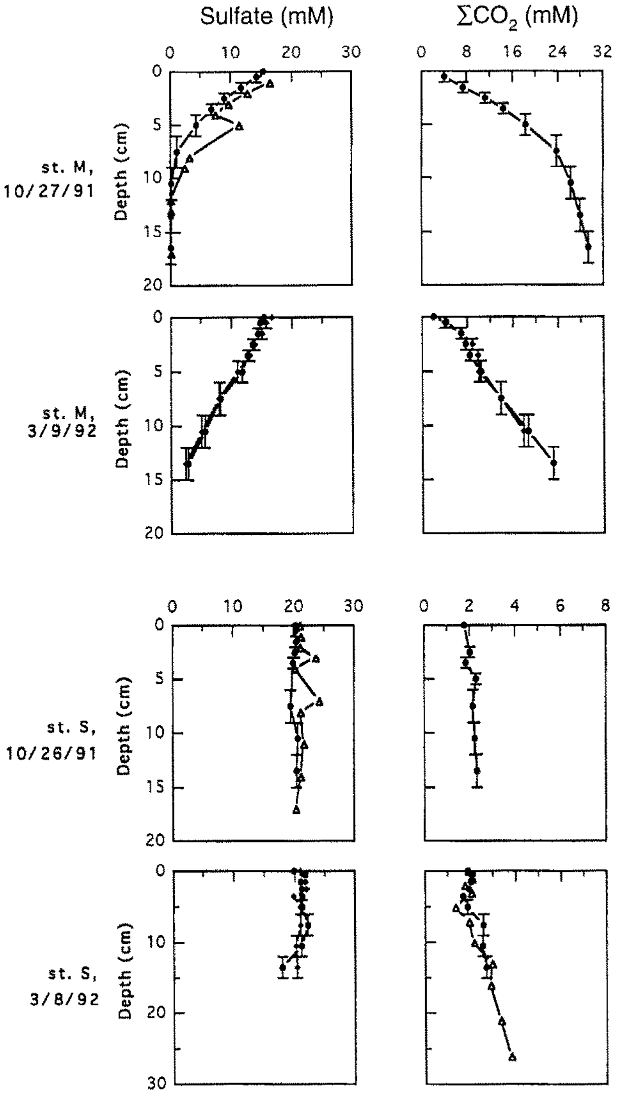


FIG. 3. Selected sulfate and ΣCO_2 porewater profiles in cores collected at sites M and S. Open symbols represent porewaters collected by pressurized core barrel techniques while closed symbols represent porewaters collected by Reeburgh squeezers. Note the differences in the concentration axes for the site S ΣCO_2 profiles, and the differences in the depth axes for the March 8, 1992 site S profiles.

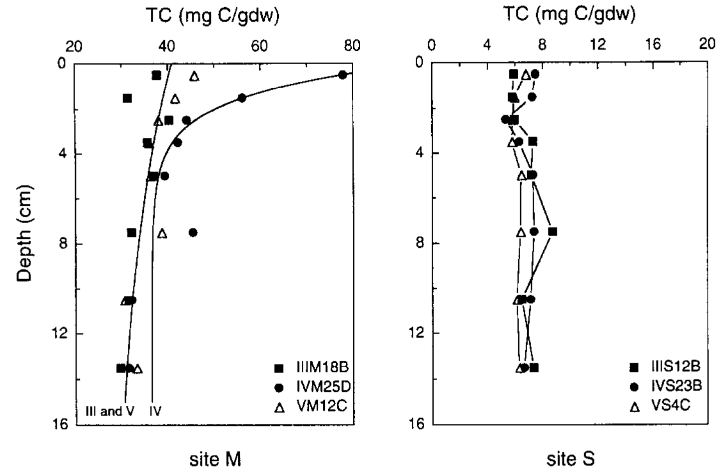


FIG. 4. Profiles of total C vs. depth in cores collected at sites M and S. For each core designator the roman numeral indicates on which cruise the core was collected. Also shown here for the site M cores are the best fits to the data using Eqn. 1 (see text for further details). For core IVM25D, the resulting best-fit parameters are: G_m^o = 59.3 ± 10.4 mg C/gdw; G_{nr} = 36.4 ± 2.7 mg C/gdw; α = 0.73 ± 0.22 cm^{-1}. For cores IIIM18D and VM12C, combined curve fitting of the data from these two cores yielded the following best-fit parameters: G_m^o = 13.3 ± 9.9 mg C/gdw; G_{nr} = 27.6 ± 11.3 mg C/gdw; α = 0.10 ± 0.16 cm^{-1}.

Porewater DOC profiles in the sediments of these two sites are shown in Fig. 5. In general, profiles from site M showed a continual, and in many cases, exponential-like increase with depth. In addition to a certain amount of spatial heterogeneity among "replicate" cores at this site, cores collected on March 3, 1992 showed a substantial DOC subsurface maxima in the upper 2 cm of the sediments (~5–15 mM DOC vs. the generally observed maximum concentration of ~2 mM

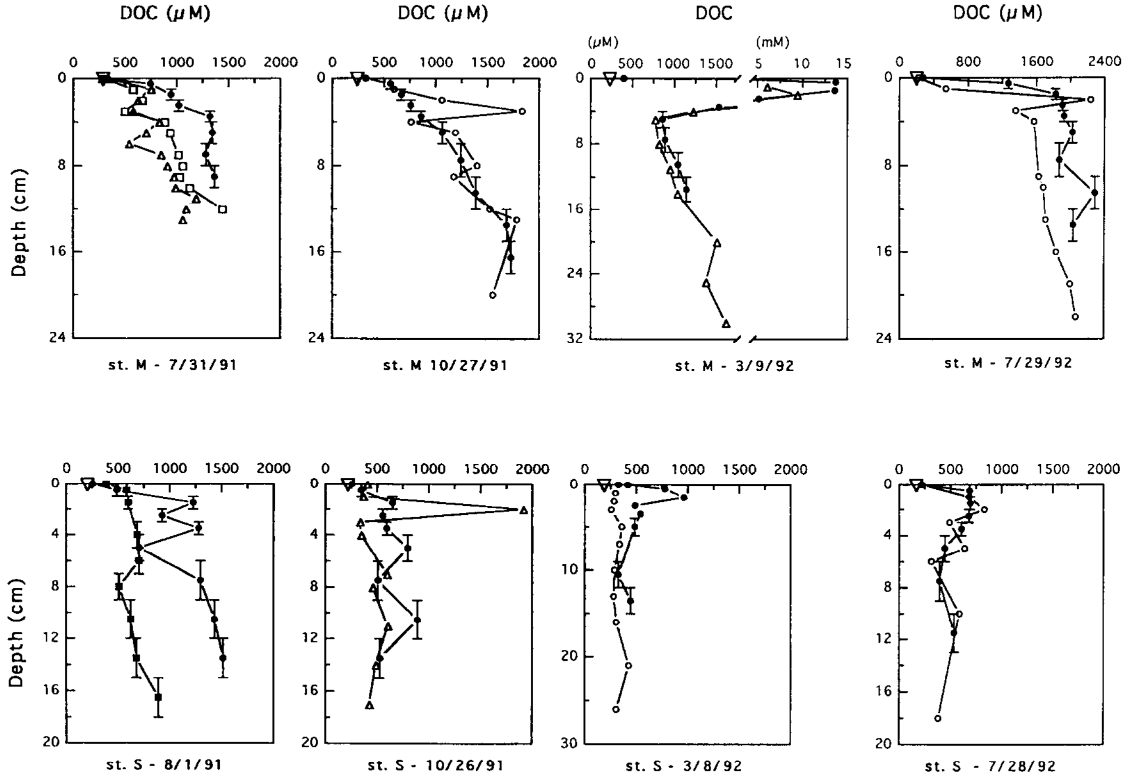
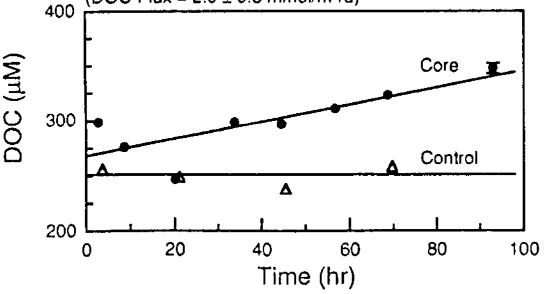
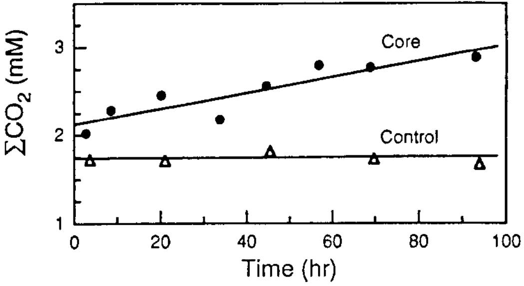
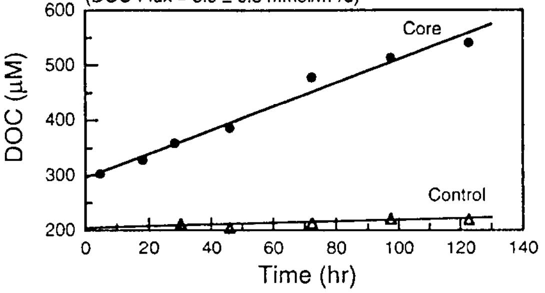
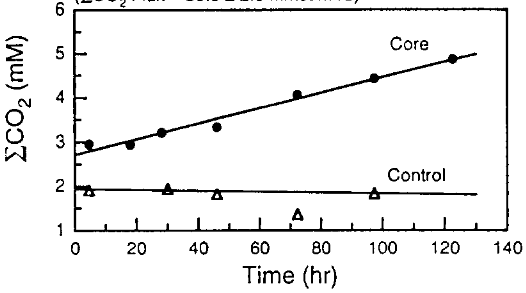


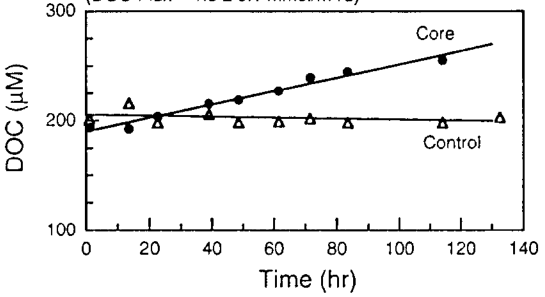
FIG. 5. Porewater DOC profiles in cores collected at sites M and S in Chesapeake Bay. Open symbols represent porewaters collected by pressurized core barrel techniques. Closed symbols represent porewaters collected by Reeburgh squeezers. Triangles on the x-axes are DOC concentrations in bottom water hydrocast samples. Replicate subcores at site M on October 27, 1991 and July 29, 1992, and site S on March 8, 1992 and July 28, 1992 came from the same box core; other replicate subcores on each graph came from different box cores.

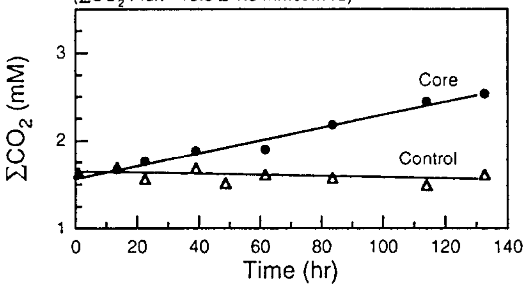

Core IIIM6B (st. M, 10/91) - Flux Expt. #3
(DOC Flux = 2.0 ± 0.8 mmol/m^2/d)

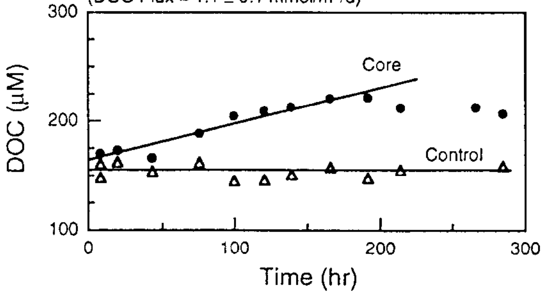

Core IIIM6B (st. M, 10/91) - Flux Expt. #3
(ΣCO_2 Flux = 22.0 ± 4.8 mmol/m^2/d)

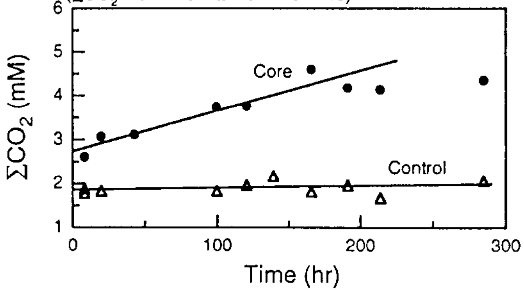

Core IVM7A (st. M, 3/92) - Flux Expt. #3
(DOC Flux = 3.9 ± 0.3 mmol/m^2/d)

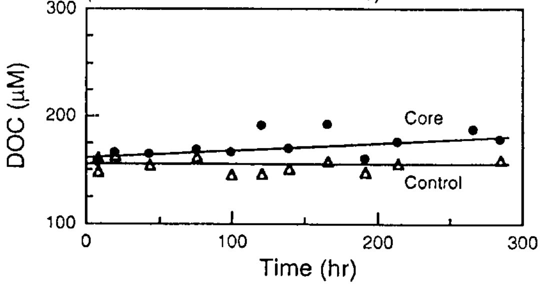

Core IVM7A (st. M, 3/92) - Flux Expt. #3
(ΣCO_2 Flux = 35.9 ± 2.6 mmol/m^2/d)


Core VM9D (st. M, 7/92) - Flux Expt. #1
(DOC Flux = 1.5 ± 0.1 mmol/m^2/d)


Core VM9D (st. M, 7/92) - Flux Expt. #1
(ΣCO_2 Flux =18.0 ± 1.5 mmol/m^2/d)


Core VS2A (st. S, 7/92) - Flux Expt. #2
(DOC Flux = 1.1 ± 0.1 mmol/m^2/d)


(ΣCO_2 Flux = 29.1 ± 4.9 mmol/m^2/d)


Core VS5A (st. S, 7/92) - Flux Expt. #2
(DOC Flux = 0.25 ± 0.08 mmol/m^2/d)

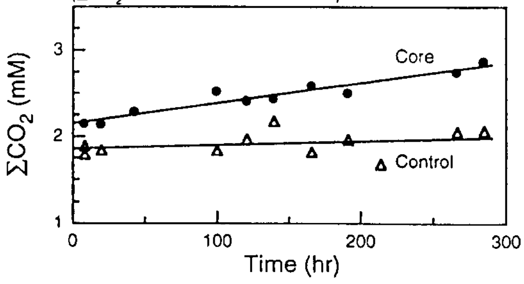

Core VS5A (st. S, 7/92) - Flux Expt. #2
(ΣCO_2 Flux =6.8 ± 2.2 mmol/m^2/d)

Table 1 - A Summary of the Benthic Flux Studies in Chesapeake Bay

	T (°C)[b]	$[O_2]$[c]	---------Measured Benthic Fluxes[a]---------			
			DOC	Sulfate	ΣCO_2	
station M						
CHAMPS II (CII; 8/91)						
M2			1.10±0.39	-18.84±5.05	nd	(n=2)
M3			1.51±0.21	-15.75±1.69	nd	(n=4)
Avg.	26	0[d]	1.31±0.21	-17.29±2.66		
CHAMPS III (CIII; 10/91)						
IIIM6B			2.20±0.73	-5.30±1.43	17.31±0.90	(n=3)
IIIM7A			1.29±0.29	-2.09±1.63	4.45±1.23	(n=3)
Avg.	18	140	1.75±0.45	-3.70±1.61	10.88±6.43	
CHAMPS IV (CIV; 3/92)						
IVM5B			2.77±0.25	-26.11±3.79	20.28±1.31	(n=3)
IVM7A			3.08±0.21	-21.05±3.28	37.22±2.23	(n=3)
Avg.	6	120	2.92±0.15	-23.58±2.53	28.75±8.47	
CHAMPS V (CV; 7/92)						
VM9D			1.65±0.25	-11.92±6.06	20.44±4.60	(n=3)
VM7A			2.21±0.38	-11.86±5.33	25.12±2.49	(n=3)
Avg.	22	170	1.93±0.28	-11.89±4.03	22.78±2.34	
station S						
CHAMPS III (CIII; 10/91)						
IIIS4A			0.22±0.41	-3.23±2.83	6.77±1.13	(n=1)
IIIS4B			0.65±0.40	3.05±3.12	6.46±0.44	(n=1)
Avg.	18	120	0.44±0.29	-0.09±3.14	6.62±0.61	
CHAMPS IV (CIV; 3/92)						
IVS2B			0.01±0.26	1.92±3.21	3.28±1.59	(n=2)
IVS2A			-0.12±0.27	-8.29±2.44	10.45±1.41	(n=2)
Avg.	6	170	-0.06±0.19	-3.18±5.11	6.86±3.59	
CHAMPS V (CV; 7/92)						
VS5A			0.26±0.08	-2.95±5.73	12.02±1.27	(n=2)
VS2A			0.78±0.09	-12.26±3.96	33.79±3.59	(n=2)
Avg.	22	240	0.52±0.26	-7.61±4.66	22.90±10.89	

[a] All fluxes are mmol/m^2/d and nd = not determined. Positive fluxes are out of the sediments, while negative fluxes are into the sediments. The number in parentheses to the right of each set of flux measurements with a given core is the number of replicate flux determinations with that core.

[b] The temperatures at which these benthic fluxes were determined. They are ± 1°C of the measured bottom water temperatures when these cores were collected.

[c] The average oxygen concentration (μM) in the waters overlying the cores during these experiments. These values are within 30 - 40% of the measured bottom water oxygen concentrations at the time these cores were collected.

[d] The bottom waters at this site contained no detectable oxygen at the time these cores were collected, and these flux determinations were carried out under anoxic conditions. Oxygen measurements indicated that there was no detectable oxygen in the waters overlying these cores, and the faint smell of hydrogen sulfide was also noted in water samples collected during these flux measurements.

DOC). At site S, porewater DOC concentrations were generally lower than those at site M, and the downcore concentration gradients were also smaller. It is also interesting to note that, while bioturbation appears to almost completely homogenize any potential sulfate and ΣCO_2 porewater gradients in site S sediments, DOC cycling appeared to be rapid enough to lead to some structure in the porewater DOC profiles.

At both sites, replicate subcores collected on each sampling date showed some differences in measured DOC concentrations (Fig. 5). Similar differences were generally not seen in sulfate and ΣCO_2 profiles (Fig. 3). Small-scale heterogeneity of coastal sediments (see the references discussed below) may lead to these observed differences in DOC profiles, although differences in methods of porewater collection (pressurized core barrels vs. sediment squeezers) may also be responsible. All of these possibilities will be discussed below in greater detail.

FIG. 6. Concentrations of DOC and ΣCO_2 vs. time in selected flux determinations with cores collected at sites M and S (also see Fig. 3 in BURDIGE et al., 1992). Error bars not shown on a data point indicates that the error is smaller than the point itself. The best fit line through the concentration data from water overlying the core (closed circles, line labelled "Core") was used to calculate the DOC or ΣCO_2 flux in each experiment, taking into account the volume of water overlying the core (which is slightly different in each case) and any changes with time in DOC or ΣCO_2 concentrations in the recharge water (open triangles, line labelled "Control"). The results of all of our benthic flux studies are listed in Table 1.

Benthic Flux Studies

The results of our benthic flux studies are listed in Tables 1 and 2 and representative flux experiments are shown in Fig. 6. It should be noted that much of the variability in these results comes from averaging observations between duplicate flux cores, rather than from the individual uncertainties in flux determinations with a single core. Similar levels of variability have been seen in other inorganic and organic benthic flux studies in coastal sediments, and appears to result from small-scale horizontal heterogeneity in such environments (see KLUMP and MARTENS, 1981; BOYNTON and KEMP, 1985; HOPKINSON, 1987; DOLLAR et al., 1991, and discussions therein).

Measured benthic DOC fluxes at site M ranged from 1.36–2.92 mmol/m^2/d (Table 1), and corresponded to ~3–13% of the depth-integrated benthic C remineralization rates (ΣOCR; see Table 2). This ratio of benthic DOC fluxes to ΣOCR varied inversely with ΣOCR (Fig. 7). As discussed in Table 2, ΣOCR values were determined two ways: from measured benthic ΣCO_2 and sulfate fluxes; and from modeling of porewater data (Fig. 3). These two estimates of ΣOCR agree reasonably well, and also are consistent with independent estimates of this quantity based on measured sulfate reduction rates, and data on particulate organic C deposition and burial (Table 3).

ΣOCR values at site M (Fig. 7) showed a seasonal pattern typical of other near coastal sediments (e.g., MARTENS and KLUMP, 1984). Benthic DOC fluxes at this site also appeared to show a slight seasonal variation, although the highest fluxes were observed in the spring (March, 1992) rather than in the summer (Fig. 8). With the exception of the March, 1992 sampling date, measured benthic DOC fluxes at site M were consistent with calculated diffusive DOC fluxes based on porewater DOC profiles from the site (Fig. 8).

At site S, benthic DOC fluxes, C remineralization rates, and the ratio of DOC fluxes to ΣOCR were slightly smaller than those observed at site M (Table 2). While macrofaunal activity likely plays an important role in controlling benthic fluxes from site S sediments, measured DOC fluxes from these sediments also showed good agreement with calculated, "diffusive" fluxes (Fig. 8). Finally, measured benthic fluxes at site S indicate the occurrence of sulfide oxidation in these sediments, presumably as a result of macrofaunal activity either transporting oxygen (e.g., BERNER, 1980; ALLER, 1982) or downwardly mixing solid phase manganese oxides (ALLER and RUDE, 1988) into the sediments. This is suggested by the essentially zero or positive benthic sulfate fluxes observed in some flux determinations (see Table 1, cores IIIS4A and 4B, core IVS2B, and perhaps core VS5A). Zero sulfate fluxes likely result from a balance between sulfide oxidation and sulfate reduction (i.e., sulfide production), while positive sulfate fluxes (i.e., out of the sediment) should occur as a result of the additional oxidation of sulfide minerals "stored" in the sediments (SAMPOU and OVIATT, 1991).

Table 2 - Benthic DOC Fluxes and Carbon Remineralization Rates in Chesapeake Bay Sediments

	Temp. (°C)	DOC Flux	ΣOCR[a]			DOC/ΣOCR[b]
			M	PW	Avg.	
st. M						
C II (8/91)	26	1.31±0.21	34.60±5.40	47.77±17.88	41.18±9.34	3.2±0.9%
C III (10/91)	18	1.75±0.45	14.36±9.65	35.37±5.31	24.87±5.51	7.0±2.4%
C IV (3/92)	6	2.92±0.15	28.75±8.47	15.71±4.67	22.23±6.52	13.1±3.9%
C V (7/92)	22	1.93±0.28	22.78±2.34	59.17±3.90	41.23±17.95	4.7±2.1%
Integrated Annual Average[c]		2.16±0.12 (0.79±0.04)			29.11±4.56 (10.63±1.66)	7.4±1.2%
st. S						
C III (10/91)	18	0.44±0.29	6.62±0.61			6.6±4.4%
C IV (3/92)	6	-0.06±0.19	6.86±3.59			-0.8±2.8%
C V (7/92)	22	0.52±0.26	22.90±10.89			2.7±3.1%
Integrated Annual Average[a]		0.27±0.09 (0.10±0.03)	12.64±2.52 (4.61±0.92)			2.1±0.8%

All values are mmol/m^2/d with the exception of the values in parentheses, which are mol/m^2/yr.

[a] ΣOCR values determined by: M = measured benthic fluxes; PW = pore water modeling; Avg. = average of the M and PW values. In general, the measured ΣCO_2 flux is assumed to be equal to ΣOCR. However in the CIII cores from site M the ratio of the measured ΣCO_2 flux to the sulfate flux exceeded 2 (the value expected if sulfate reduction predominates organic matter remineralization). ΣOCR was therefore calculated by $2|CF| - 2|SF|$, where $|CF|$ is the absolute value of the ΣCO_2 flux and $|SF|$ is the absolute value of the sulfate flux. This takes into account carbon remineralized to CH_4 during methanogenesis (Martens and Klump, 1984). For the C II st. M flux experiments we have taken ΣOCR as two times the sulfate flux (since ΣCO_2 fluxes were not determined in these flux experiments). Depth integrated rates based on pore water modeling (PWM) were determined using the pore water sulfate and ΣCO_2 data (e.g., Fig. 3) and eqns. (14) - (19) in Martens and Klump (1984). These depth-integrated rates were converted to ΣOCR values as discussed above.

[b] For st. M the ΣOCR values used here are the average values.

[c] Integrated annual averages were determined by integrating under the curve of measured benthic DOC fluxes (or ΣOCR) versus time by trapezoidal approximation, and then dividing by the time period of integration.

Table 3 - Independent Estimates of the Depth-Integrated Rate of Total Organic Carbon Remineralization in the Sediments of Site M

Approach	Value (mol C/m^2/yr)
Sum of the integrated annual ΣOCR value, benthic DOC flux plus pore water DOC and ΣCO_2 burial (This study)[a]	11.4±1.9
Yearly depth-integrated sulfate reduction rate, converted to carbon equivalents[b]	
1986 - 1989 (Roden *et al.*, 1994)[c]	13.0
1989 - July, 1992 (Marvin and Capone, unpub. data)	17.9±5.6
The difference between POC deposition to the sediment-water interface and POC burial below the zone of early diagenesis (Roden *et al.*, 1994)[c,d]	15.1
Diagenetic modeling of total carbon profiles (see Fig. 4)	
core IVM25D[e]	8.8±1.6
cores IIIM18B and VM12C[f]	1.2 - 22.8

[a] Integrated annual averages of ΣOCR and the benthic DOC flux were taken from Table 2. Pore water burial of DOC and ΣCO_2 was estimated by multiplying the 'asymptotic' concentrations of DOC and ΣCO_2 by the sedimentation rate (~0.7 cm/yr) and the porosity at depth (0.88; unpub. data). A comparison of these calculated burial fluxes with the ΣOCR and benthic DOC flux values in Table 2 indicates that pore water burial of DOC and ΣCO_2 is less than 1% of the total carbon remineralization.

[b] Yearly depth-integrated sulfate reduction rates were converted to carbon equivalent by assuming a 2:1 stoichiometry for moles of particulate organic carbon oxidized per mole of sulfate reduced. This calculation does not take into account any possible relationship between net DOC production and sulfate reduction (see the text for further details).

[c] Note that the site studied by Roden *et al.* (1994) is very close to, but not "identical" to, site M.

[d] POC deposition to the sediment-water interface was estimate from sediment trap data as discussed in Roden *et al.* (1994). POC burial was estimated from the sedimentation rate and the concentration of 'non'-reactive POC below the zone of early diagenesis.

[e] The data from this core suggested that sediment mixing was likely not a significant process in this core, and this TCR value was calculated as discussed in the text.

[f] As discussed in the text we have assumed here that the entire 15 cm of both cores are mixed with a bioturbation coefficent (D_B) that ranges from 10-25 cm^2/yr. The range in TCR listed here was then determined as discussed in the text.

DISCUSSION

A Comparison of Techniques for the Collection of Porewaters for DOC Analyses

In later sections, we will examine the factors controlling benthic DOC fluxes from these two sites in the Chesapeake Bay. In part, this will involve a comparison of directly measured benthic DOC fluxes with those estimated from porewater profiles. Given recent discussions in the literature regarding potential artifacts associated with different techniques for the collection of porewaters for dissolved organic matter analyses (HOWES et al., 1985; SHAW and MCINTOSH, 1990; BOLLINGER et al., 1992; MARTIN and MCCORKLE, 1994) a brief discussion of the methods used in this study is warranted.

In this study we used two techniques for the collection of porewaters: sediment squeezers (REEBURGH, 1967) and the pressurized core barrel (PCB) technique of JAHNKE (1988). Both were operated at low pressures (~1.5–3 atm). While we are not aware of any published work using PCB to extract porewaters for DOC analyses, sediment squeezers have been "successfully" used in porewater dissolved organic matter studies in a wide range of sediments (HENRICHS and FARRINGTON, 1987; BURDIGE and MARTENS, 1990; ALPERIN et al., 1992). However, a recent study (BOLLINGER et al., 1992) has also shown that sediment squeezing using pressures much higher than we used (50–350 atm) can lead to anomalously high porewater DOC concentrations, possibly as a result of disruption (e.g., lysis) of sedimentary organisms.

As can be seen in Fig. 5, slight differences exist between porewater DOC profiles obtained with these two techniques for porewater extraction. However, much of this variability may result from small-scale heterogeneity at these sites (see the discussions above), since some of the replicate cores shown in each graph were subcores collected from different box cores (st. M - July 31, 1991 and March 9, 1992; st. S - August 1, 1991 and October 26, 1991). Furthermore, replicate subcores collected from the same box cores (st. M - October 27, 1991 and July 29, 1992; st. S - March 8, 1992 and July 28, 1992) also showed similar levels of agreement. These trends appeared to be most pronounced for porewater DOC, since sulfate and ΣCO_2 porewater data from these sites show much better agreement among replicate subcores and different procedures used for porewater extraction (Fig. 3; also data not shown here).

These results appear to be consistent with the results of other workers (HOWES et al., 1985; MARTIN and MCCORKLE, 1994) who also observed that organic porewater constituents are more susceptible to potential porewater sampling "artifacts" than are inorganic constituents. At the present time though, we cannot unequivocally explain the observed variability in our porewater DOC data. However, the levels of variability seen in Fig. 5 appear to be much less than those seen in the other studies discussed above, and may result primarily from the types of sediment heterogeneity previously discussed. Calculated DOC fluxes from replicate cores at these sites (regardless of the method of porewater extraction) also generally showed good agreement among themselves, with most of the uncertainty in the calculated fluxes in Fig. 8 resulting from the range of the diffusion coefficients used in these calculations (see "The Factors Controlling Benthic DOC Fluxes" . . . . section for further details). In addition, calculated DOC fluxes at site M generally agreed well with directly measured fluxes (Fig. 8), although again this agreement results in part from the choice of the DOC diffusion coefficients used in these calculations (see the discussion below). Based on these observations we, therefore, feel that there are no major artifacts associated with the collection of these pore water DOC samples, although more detailed studies will be required to more rigorously verify this suggestion.

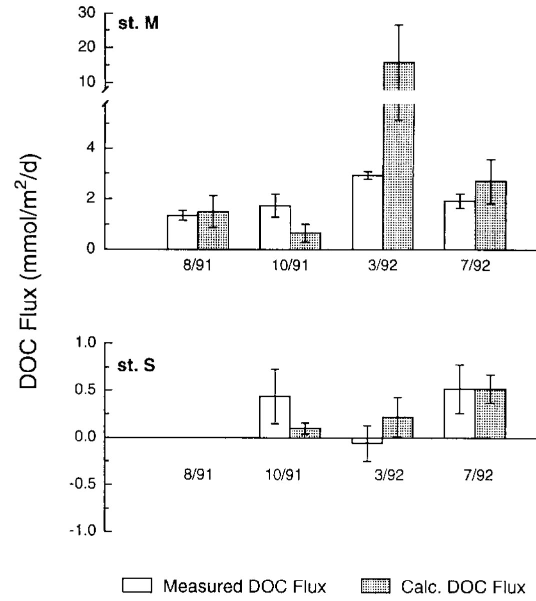


FIG. 8. Measured and calculated benthic DOC fluxes from Chesapeake Bay sediments. Calculated DOC fluxes were determined with a modified form of Fick's First Law as described in BURDIGE et al. (1992). The DOC diffusion coefficients used in these flux calculations were determined as discussed in the text.

Benthic DOC Fluxes in Sediment Carbon Budgets

In coastal sediments that are in steady-state on roughly seasonal timescales, the difference between the deposition of organic C to the sediment-water interface and that which is buried below the zone of early diagenesis should be balanced by the integrated annual benthic fluxes of DOC and ΣCO_2 (and CH_4 in highly reducing sediments), and the burial of these compounds in sediment porewaters (MARTENS and KLUMP, 1984; ALPERIN et al., 1992; MARTENS et al., 1992).* To differentiate this quantity from ΣOCR (which is defined here as the depth-integrated rate of organic C remineralization to ΣCO_2) we will define this as TCR. At site M, we are able to estimate TCR in four independent ways that are discussed below (Table 3). At site S, we are unable to make similar comparisons, in part because the lack of quantitative information on bioturbation and bioirrigation at this site precludes similar comparisons using either our data or the results of studies by other workers.

For a site very close to site M, sediment trap and sediment organic C data can be used to estimate TCR (RODEN et al., 1994). This value (15.1 mol C/m²/y) agrees reasonably well with our calculation of TCR (11.4 ± 1.9 mmol/m²/y) based on benthic flux and porewater data (Table 3). Annual depth-

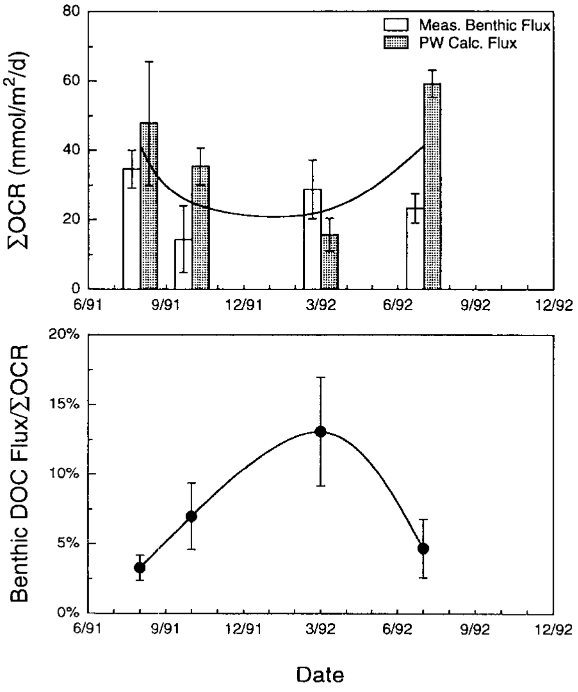


FIG. 7. Depth-integrated benthic carbon remineralization rates (ΣOCR; upper figure) and the ratio of the benthic DOC flux to ΣOCR (lower figure), both vs. time at site M. The two estimates of ΣOCR on each sampling date are taken from Table 2, and were determined as discussed in note (a) of this table.

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* DOC in sediments is a heterogeneous collection of organic compounds, many of which are intermediates in the overall remineralization of sedimentary organic matter (e.g., BURDIGE and MARTENS, 1990; HENRICHS, 1992; LEE, 1992). The reactions (both biological and/or chemical) affecting DOC production and consumption in sediments are complex and not completely understood. Most DOC produced in sediments is remineralized to ΣCO_2 or methane, although a slight imbalance between DOC production and consumption leads to benthic DOC fluxes and burial of porewater DOC. Since it is presumed that the ultimate source of porewater DOC is particulate organic matter deposited in the sediments, these net losses of DOC from surface sediments are included in the calculation of TCR.

integrated sulfate reduction rates can also be used to estimate TCR (MARTENS and KLUMP, 1984), since in sediments such as those at site M sulfate reduction is the dominant process by which organic matter remineralization occurs. TCR values calculated in this manner (13 to ~18 mol C/m^2/y) also agree well with the other estimates of TCR in Table 3. Finally, modeling of total C sediment profiles (see section below) yields estimates of TCR that do not show quite as good agreement, although the reasons for this disagreement are discussed below in greater detail.

In making these calculations there are three assumptions which should be discussed here briefly. The first is the assumption that sulfate reduction dominates organic C remineralization at site M. While plots of porewater sulfate vs. ΣCO_2 support this suggestion, methane profiles in the mid-Bay demonstrate that methanogenesis also occurs in the deeper portions of these sediments (REEBURGH, 1969; D. J. Burdige, unpubl data; M. C. Marvin and D. G. Capone, unpubl. data). However, its importance in C remineralization at site M is, as yet, unquantified. Based on results from other highly reducing sediment such as Cape Lookout Bight (MARTENS and KLUMP, 1984) and Skan Bay (ALPERIN et al., 1992) we estimate that methanogenesis (and benthic methane fluxes) accounts for less than 20% of the C that is remineralized at site M, and as such, its omission here is not likely to significantly affect the comparison in Table 3. Second, we have also used the generally accepted value of two for the stoichiometry of the number of moles of organic carbon oxidized per mole of sulfate reduced (see the discussion in "Porewater and Solid Phase Sediment Profiles" section). And finally, implicit in this calculation is the assumption that all particulate carbon in the sediments is completely oxidized to ΣCO_2, and that there is no net loss of dissolved organic C from the sediments (i.e., that $\Sigma OCR \approx TCR$). This third assumption is actually tied to the second assumption, since the extent to which *net* DOC production (approximately equal to the DOC benthic flux) is coupled to sulfate reduction, and the extent to which this DOC is oxidized relative to the starting sedimentary organic matter, will both affect the stoichiometric ratio of the moles of organic C oxidized to moles of sulfate reduced. However DOC fluxes from these sediments are generally less than 10% of the ΣCO_2 flux (and ΣOCR; see Table 2), so net DOC loss from the sediments does not likely add significant uncertainty to calculated TCR values based on measured sulfate reduction rates. Adequately examining these latter two assumptions are important areas of future research, and will require further studies of the characteristics of porewater DOC, and the processes that produce and consume DOC in sediments (e.g., NISSENBAUM et al., 1971; LYONS et al., 1979; HENRICHS and FARRINGTON, 1987; BURDIGE and MARTENS, 1990).

Based on the results of these studies, benthic DOC fluxes at site M constituted 6.9 ± 1.2% of the total carbon remineralized in these sediments over an annual cycle (=0.79 ± 0.04/11.4 ± 1.9; see Tables 2 and 3). At site S, this value is 2.1 ± 0.8%. These values are similar to recent estimates of this ratio for other anoxic sediments such as Cape Lookout Bight (4.6 ± 3.6%; MARTENS et al., 1992) and Skan Bay (16.8 ± 7.4%; ALPERIN et al., 1992). However in these latter studies the contribution of benthic DOC fluxes to sediment C remineralization was estimated using porewater DOC data to calculate benthic DOC fluxes. Our approach differs in that here we have used directly measured benthic DOC fluxes in these calculations.

Finally, in an attempt to further examine the relationship between benthic C remineralization rates (ΣOCR) and benthic DOC fluxes we have compared our Chesapeake Bay data with studies of benthic DOC fluxes in the coastal sediments of Cape Lookout Bight (BURDIGE et al., 1992) and Monterey Bay (D. J. Burdige et al., unpubl. data). While benthic DOC fluxes and ΣOCR appear to be positively correlated (Fig. 9a), the fact that the slope of this double log plot (or the exponent in the equation shown on Fig. 9a) is less than one indicates that DOC fluxes do not increase linearly with increasing ΣOCR values. As a result, the ratio of benthic DOC fluxes to ΣOCR varies inversely with ΣOCR, with this

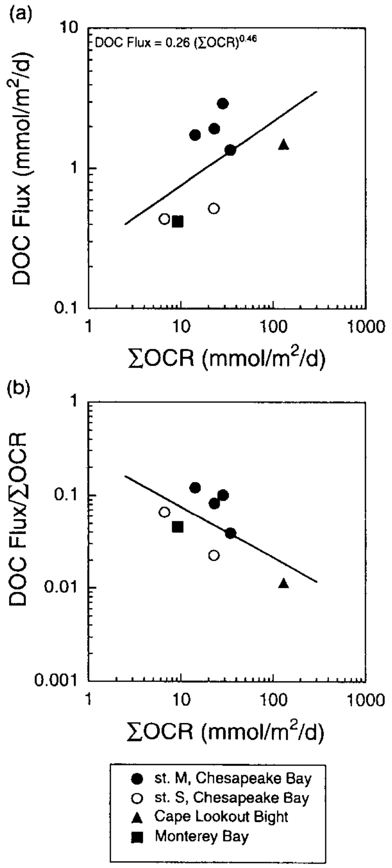

FIG. 9. (a) Benthic DOC fluxes versus ΣOCR for several coastal sediments. The Chesapeake Bay data are from Table 2, the Cape Lookout Bight result is from BURDIGE et al. (1992), and the Monterey Bay result is for a bioturbated site at water depth of 100 m in the Bay (D. J. Burdige et al., unpubl. data). Benthic DOC fluxes and ΣOCR values for Cape Lookout Bight and Monterey Bay sediments were determined with core incubation techniques similar to those used here. (b) The ratio of measured benthic DOC fluxes to ΣOCR vs. ΣOCR for the same sites. As discussed in the text, the results in Fig. 9a indicate that this ratio should decrease as ΣOCR increases, as is shown here. The best fit line through these data is included here to indicate this inverse correlation, and is not meant to imply that there is a known functional relationship (at the present time) between these two quantities.

ratio increasing as ΣOCR decreases (Fig. 9b; also see Fig. 7). The reasons for this observation are unknown at the present time, although if the trends seen in Fig. 9 are shown to be robust, they may provide insights into the factors controlling DOC fluxes from marine sediments. In addition, they may also be useful in more accurately estimating the global importance of benthic DOC fluxes in oceanic C cycling (BURDIGE et al., 1992; also see the discussion below).

Calculation of benthic carbon remineralization rates at site M using sediment carbon profiles

Modeling of particulate organic C profiles represents an additional way in which TCR can be calculated. In general, diagenetic models of sedimentary organic C lead to equations of the form (BERNER, 1980),

$$G = G_{nr} + G^{\circ}_{m}e^{-\alpha x}, \quad (1)$$

where: x = depth (positive downward); G = concentration of total organic C; G_{nr} = concentration of "nonreactive" organic C (i.e., organic matter that appears to be refractory on the timescales of early diagenesis); G°_{m} = concentration of "metabolizable" organic C at the sediment-water interface. The attenuation constant α will differ depending on the type of transport processes affecting particulate material in the sediments (BERNER, 1980; see also WESTRICH and BERNER, 1984, and BURDIGE, 1991b, for discussions of the validity of this model).

While previous results have suggested that the upper ~5–10 cm of sediments at site M are mixed, the shape of the TC profile in core IVM25D, when compared to the other two cores we have analyzed, suggests that sediment mixing processes may not be important in this particular core. Neglecting bioturbation and/or physical mixing, TCR is then given by wG°_{m}, where w is the sedimentation rate (MARTENS and KLUMP, 1984). With a dry sediment accumulation rate of 0.178 ± 0.011 g/cm^2/y (J. CORNWELL, unpubl. data) and the best fit value of G°_{m} of 59.3 ± 10.4 mg C/gdw (Fig. 4), this leads to a TCR value of 8.8 ± 1.6 mol C/m^2/y for this core. This value is in good agreement with other independent estimates of TCR (Table 3).

In contrast, the shapes of the TC profiles in cores IIIM18B and VM12C suggest that sediment mixing processes play important roles in these cores. In the absence of detailed information on sediment mixing in these cores, we have modeled the data from these cores by assuming that the entire zone of early diagenesis in each core is mixed. Under these circumstances, TCR is given by $(D_b\alpha + w)G^{\circ}_{m}$ (see the Appendix for further details). Large uncertainties in the fitting parameters G°_{m} ($= 13.3 \pm 9.9$ mg C/gdw) and α ($= 0.10 \pm 0.16$ cm^{-1}; Fig. 4), coupled with uncertainties in the sediment mixing coefficient (D_b, assumed to range from 10–25 cm^2/y) lead to a large range in the TCR value calculated with these data (1.2–22.8 mole C/m^2/y). However, we also note that the other values of TCR listed in Table 3 fall within this range. While we have no way at the present time to independently verify several of the assumptions made in this calculation, these results suggests that these assumptions are not entirely unreasonable.

The causes of sediment mixing at site M are not well understood, although RODEN and TUTTLE (1994) suggested that it might be caused by the seasonal (spring) colonization of the sediments by small polychaetes and bivalves. Methane bubble ebullition may also mix these sediments (RODEN and TUTTLE, 1994), and the results of REEBURGH (1969) indicate the occurrence of methane bubble ebullition from mid-Bay sediments. However, studies in Cape Lookout Bight sediments (where similar seasonal macrofaunal colonization occurs, and where active methane bubble ebullition occurs in the summer) suggest that it is unlikely that these processes lead to the magnitude of sediment mixing seen in site M sediments (KIPPHUT and MARTENS, 1982; CHANTON et al., 1983; MARTENS and KLUMP, 1984).

Another process which may lead to this observed sediment mixing is physical mixing of the sediments as a result of episodic storm events or sediment resuspension during tidal exchange. Such processes are common in shallow, estuarine environments such as the Chesapeake Bay (e.g., DYER, 1973; WRIGHT et al., 1987), and may contribute to the observed ^{210}Pb and organic C profiles in site M sediments. The occurrence of these processes is not incompatible with the observed porewater gradients seen in site M sediments (Fig. 3), since sediment mixing characterized by the D_b values discussed above (<25 cm^2/y) would not significantly affect porewater gradients (e.g., ALLER, 1982). A better understanding of the factors controlling sediment mixing in these Bay sediments is clearly an important problem which may have implications not only on the coupling of benthic and pelagic processes in the Bay, but also on the role of Bay sediments as sources of dissolved constituents to the overlying waters.

The Factors Controlling Benthic DOC Fluxes from Chesapeake Bay Sediments

Site M

The results in Fig. 8 indicate that, with the exception of the March, 1992 sampling date, there is good agreement at this site between measured benthic DOC fluxes and calculated, diffusive DOC fluxes. These observations suggest that molecular diffusion controls DOC fluxes from these sediments. Sediment-water exchange of inorganic nutrients (e.g., ammonium) from site M sediments also appears to be controlled by diffusional processes (J. Cornwell and W. Boynton, unpubl. data). Furthermore, studies of benthic DOC fluxes from the anoxic sediments of Cape Lookout Bight suggest that molecular diffusion controls DOC fluxes from these sediments as well (BURDIGE et al., 1992).

However, this agreement between measured and calculated benthic DOC fluxes at both site M and Cape Lookout Bight rests strongly on the diffusion coefficient chosen for the complex, and largely uncharacterized, pool of DOC in sediment porewaters. The diffusion coefficients used in these calculations were determined by first assuming that the average molecular weight of porewater DOC is between 1,000 and 10,000 daltons, based on the available data on the molecular weight distribution of porewater DOC (KROM and SHOLKOVITZ, 1977; OREM and GAUDETTE, 1984; CHIN and GSCHWEND, 1991). A range of free solution diffusion coefficients at 25°C (D°) were then calculated with an empirical relationship between D° and the molecular weight of an organic compound (BURDIGE et al., 1992). This relationship was derived with literature values of diffusion coefficients for a wide range of organic compounds, including well characterized compounds such short chain organic acids, individual amino acids and proteins, and more poorly characterized humic substances. Free solution diffusion coefficients at temperatures other than 25°C were determined with the Stokes-Einstein equation (LI and GREGORY, 1974), and were converted to bulk sediment diffusion coefficients (D_s) as discussed in ULLMAN and ALLER (1982).

These assumptions predict that porewater DOC has a diffusion coefficient (at 25°C) that varies from $1.4–3.5 \times 10^{-5}$ cm^2/s. For comparison, the only reported diffusion coefficient for natural porewater DOC is that of MACKIN (1986), whose value of 5.6×10^{-6} cm^2/s suggests (using the equation in BURDIGE et al., 1992) that the average molecular weight of this material is ~300 daltons (as opposed to the 1,000–10,000 dalton range discussed above). This difference may be related to differences between the porewater DOC in the salt marsh sediments studied by Mackin and the porewater DOC examined by these other workers. However MACKIN (1986) also discussed the possibility that his measured diffusion coefficient may be an underestimate, due to adsorption effects associated with the diffusion cell used in his studies. A more careful characterization of the diffusivity of porewater DOC, along with additional studies examining the assumptions in our diffusive flux calculations are clearly important next steps in further understanding the controls on DOC fluxes from these (and other) marine and estuarine sediments.

At site M, very poor agreement was seen between measured and calculated benthic DOC fluxes from cores collected in March, 1992. A comparison of Figs. 5 and 8 suggests that in March, 1992, there is a relatively large pool of porewater DOC near the sediment-water interface which apparently does not escape the sediments as a benthic flux. This "accumulation" of DOC appears to be a transient phenomena, since cores collected before and after March, 1992 show much lower DOC concentrations in the surface sediments, and much better agreement between measured and calculated benthic DOC fluxes.

Similar trends were also seen in a seasonal study of dissolved, free amino acids (DFAAs) in the anoxic sediments of Cape Lookout Bight (BURDIGE and MARTENS, 1990). Here, porewater DFAAs in the surface (upper 2 cm) sediments increased from ~20–60 μM to over 200 μM during the spring (March and April), and it was suggested that this was either a sampling artifact or a real phenomenon associated with the seasonal colonization of these sediments by polychaete worms (BURDIGE and MARTENS, 1990). By analogy with these results from Cape Lookout Bight, the high DOC concentrations at site M in March, 1992 may also be related to the seasonal macrofaunal colonization of site M sediments (KEMP et al., 1990). Another possible explanation for these high, transient DOC concentrations in the surface sediments is that there was a temporary imbalance between the production and consumption of DOC in site M sediments during this time period (see footnote in "Benthic DOC Fluxes . . ." section). This might occur as a result of differences in the temperature responses of these two sets of processes, with the input of fresh (labile) organic matter to the surficial sediments from episodic winter storm events possibly also playing a role in the occurrence of this imbalance (e.g., SANSONE and MARTENS, 1982).

If elevated DOC concentrations at site M in March, 1992 are not artifacts associated with porewater collection (e.g., see the discussion in BURDIGE and MARTENS, 1990), then a comparison of calculated and directly measured benthic DOC fluxes (Fig. 8) suggests that the vast majority of this DOC is somehow temporarily retained in the sediments. Two possible explanations for this observation include adsorption of upwardly diffusing DOC on surficial sediment particles (THENG, 1982; SANSONE et al., 1987), and enhanced biological consumption of this DOC near the sediment-water interface. Both processes would lead to much smaller DOC concentration gradients near the sediment-water interface than those observed here with the ~1 cm resolution of our data and hence, much smaller benthic fluxes.

Finally, it is interesting to note that temporary macrofaunal colonization of site M sediments may lead to substantially elevated DOC concentrations in the porewaters, while more permanent macrofaunal colonization as is seen at site S does not lead to such elevated DOC concentrations. At the present time, we cannot explain these differences, although they may be related to differences in the species composition and/or biogeochemical activity (or "stability") of these two macrobenthic communities, or the extent to which the different macrofauna in these sediments affect sediment redox conditions (see the discussion below for further details).

Site S

The results in Fig. 8 suggest that molecular diffusion controls DOC fluxes from site S sediments. However, given the extent to which bioturbation likely controls sediment-water exchange processes in these sediment, this agreement between measured and calculated benthic DOC fluxes may be fortuitous. Although quantitative information on bioturbation at this site is not available, several lines of evidence suggest that these processes exchange porewater with bottom waters from at least the upper 10–12 cm of the sediments. This is based on the fact that at this site we see minimal to nonexistent sulfate and ΣCO_2 porewater gradients in the upper portion of these sediments (Fig. 3), in spite of measured benthic ΣCO_2 (and occasionally sulfate) fluxes (Table 1), and measured rates of sedimentary sulfate reduction and ΣCO_2 production (MARVIN and CAPONE, 1992; LUSTWERK and BURDIGE, 1993). These observations suggest that the factors controlling benthic DOC fluxes from site S sediments are more complex than those controlling benthic fluxes at site M, although in the absence of quantitative information on bioturbation in site S sediments we are unable to further examine these differences.

It also seems possible that bioturbation (and the presence of benthic macrofauna) affects benthic DOC fluxes at site S in other ways. As discussed above, measured benthic sulfate fluxes at site S indicate that macrofaunal activity may transport oxygen into these sediments. This oxygen transport could then stimulate DOC consumption (oxidation) in the sediments by either macrofauna or heterotrophic bacteria (e.g., see discussions in LEE, 1992). This would then lead to smaller *net* DOC production rates in these sediments, and hence smaller benthic DOC fluxes, in spite of enhanced sediment-water exchange via bioturbation. For comparison, the results of sediment microcosm experiments led HANSEN and BLACKBURN (1991) to suggest that the mineralization (oxidation) of dissolved organic matter was less efficient under anoxic vs. oxic conditions, an observation which is consistent with this suggestion. In addition, HINES et al. (1982) also observed that the onset of active bioturbation in Great Bay (New Hampshire) estuarine sediments led to a decrease in porewater DOC concentrations. Such phenomena would also likely have an impact on the chemical composition of the porewater DOC in these sediments, in addition to the magnitude of the benthic DOC flux. Future comparative studies of the specific organic compounds found in the porewaters of bioturbated and nonbioturbated sediments may therefore prove useful in understanding the possible role of oxygen in preserving different types of sedimentary organic matter (EMERSON and HEDGES, 1988; CANFIELD, 1989; LEE, 1992).

The Role of Benthic DOC fluxes in the Estuarine Geochemistry of DOC in Chesapeake Bay

Annual rates of net primary production in the mid-Bay range from about 300–600 g C/m^2/y (MALONE et al., 1988). However RODEN et al. (1994) noted that about half of this C is deposited in the sediments (with the other half presumably remineralized in the water column), suggesting that ~200–300 g C/m^2/y are remineralized in the water column of the mid-Bay region. When this value is compared to the integrated annual benthic DOC flux from these sediments (2.16 ± 0.12 mmol/m^2/d = 9.46 ± 0.52 g C/m^2/y; see Table 2) it appears that benthic DOC fluxes are probably not a significant source of reduced C for water column respiration, even if all of the DOC transported out of the sediments was labile and remineralized in the mid-Bay water column. Furthermore, since much of the DOC transported out of the sediments may be more refractory in nature, this flux would then be an even less important component of water column respiration than that predicted by this simple comparison.

The results presented here can also be used to make an estimate of the integrated flux of DOC from all Bay sediments (Table 4). When this value (1.2–3.1 × 10^{10} g C/y) is compared to estimates of the riverine input of DOC to the Bay (4.1–4.7 × 10^{11} g C/y; VELINSKY et al., 1986) it appears that benthic DOC fluxes from Bay sediments are less than 10% of this riverine input. This observation suggests that benthic DOC fluxes do not exert a major effect on the transport of DOC through the Chesapeake Bay estuary. However, examining this problem also depends on other factors, such as the reactivity of DOC transported out of sediments and the residence time and reactivity, in general, of DOC in estuaries. In many estuarine systems DOC appears to behave conservatively (SHARP et al., 1982; MANTOURA and WOODWARD, 1983) although individual components such as humic and fulvic acids show strong nonconservative removal (SHOLKOVITZ et al., 1978; SHARP et al., 1982; FOX, 1983). Based on the results in Table 4, benthic DOC fluxes might act to offset (to some extent) the importance of such removal processes during the estuarine transport of DOC. In addition, depending on the chemical nature of the DOC transported out of estuarine sediments, benthic DOC fluxes could also have a significant effect on the characteristics (e.g., C/N ratio, δ^{13}C) of estuarine DOC. As such, the DOC leaving an estuary might be very different chemically from riverine DOC, in spite of the apparent near-conservative behavior of total DOC during estuarine mixing. Further studies of the nature of estuarine DOC, and of all of the processes affecting DOC in estuarine systems will be required to critically examine these suggestions.

The Role of Benthic DOC Fluxes in Oceanic Carbon Cycling

As discussed in the introduction, there have recently been two estimates of the global significance of benthic DOC fluxes

Table 4 - Integrated Bay-wide Benthic DOC Fluxes

	Annual Benthic DOC Flux [a] (mol/m^2/yr)	Sfc. Area [b] (10^9 m^2)	Integrated Flux (10^9 mol C/yr)
Upper Bay	0.089±0.005	0.44 to 0.84	0.04 to 0.08
Mid Bay	0.788±0.044	0.75 to 2.30	0.59 to 1.91
Lower Bay	0.099±0.033	4.02 to 4.30	0.38 to 0.57
Total Bay-wide Benthic DOC Flux			1.0 to 2.6 [= 1.2 to 3.1 x 10^{10} gr C/yr]

[a] Values for the Mid and Lower Bay were taken from the integrated annual averages in Table 2 for stations M and S. The value for the Upper Bay was determined with calculated benthic DOC fluxes from sediment cores collected at site N (Fig. 1). Sediment cores were collected at this site during CHAMPS III, IV and V for pore water studies alone. Pore waters were collected as discussed in the text, and benthic DOC fluxes were calculated as discussed in the text and in Burdige *et al.* (1992). The integrated annual value of the benthic DOC flux from these sediments was then determined by trapezoidal approximations. The sediments at site N are clay dominated and iron-rich, with sediment porosities ranging from 0.75 - 0.85. Organic matter in these sediments appears to be largely refractory and terrestrially-derive (J. Cornwell and D. Capone, pers. comm.).

[b] From Nixon (1987).

(BURDIGE et al., 1992; CHEN et al., 1993), both based on benthic DOC fluxes calculated with porewater data. The results presented here can be used to begin to verify these observations.

BURDIGE et al. (1992) estimated that benthic DOC fluxes from estuarine sediments range from 0.11–0.66 mol C/m^2/y, a range which agrees extremely well with integrated annual benthic DOC fluxes from site M and S sediments (~0.1–0.8 mol C/m^2/y; see Table 2). However, in spite of this agreement, it should be noted that the impact of benthic DOC fluxes from estuarine sediments on the oceanic C cycle depends on the extent to which this material behaves conservatively during estuarine mixing (see discussion above). For these reasons, such estimates of the importance of benthic DOC fluxes from estuarine sediments on the oceanic C cycle may represent upper limits of their true impact.

Nonetheless, the results of these studies can be used in another fashion to reestimate the global significance of benthic DOC fluxes from marine sediments. An examination of the biogeochemical characteristics (e.g., porewater and solid phase profiles, ΣOCR values) of the sediments at sites M and S indicates that they are not unique to estuarine environments, and that these sediments are similar to many other nonestuarine sediments found in the coastal region and on the continental margin. As such, the benthic DOC fluxes observed at sites M and S may be representative of fluxes from similar coastal and margin sediments. Based on this observation, and arguments presented in BURDIGE et al. (1992) and CHEN et al. (1993), one might conservatively suggest that benthic DOC fluxes from ~5% of all marine sediments worldwide could be similar to those seen at either site M or S. Given a total marine sediment area of 360 × 10^{12} m^2 (HENRICHS and REEBURGH, 1987), the integrated DOC flux from these sediments would then range from 1.8–14.4 × 10^{12} mol C/y. This range is similar to the estimate in BURDIGE et al. (1992) of ~1–8 × 10^{12} mol C/y, for the integrated benthic DOC flux from sediments in water depths less than 2,000 m (where most coastal and continental margin sediments are found). This observation, therefore, provides further evidence in support of the arguments presented in this paper for the importance of benthic DOC fluxes in the oceanic C cycle.

CONCLUSIONS

Benthic fluxes of dissolved organic C (DOC) were measured over an annual cycle at two contrasting sites in Chesapeake Bay. At an organic-rich, sulfidic site in the meso-haline portion of the Bay (site M) DOC fluxes from the sediments ranged from 1.4 to 2.9 mmol/m^2/d. These measured DOC fluxes corresponded to ~3–13% of the depth-integrated benthic C remineralization rates (ΣOCR). Measured benthic DOC fluxes at site M also agreed reasonably well with calculated diffusive DOC fluxes, based on porewater DOC profiles. This agreement suggests that DOC fluxes from site M sediments were likely controlled by molecular diffusion.

The second site that was studied is a heavily bioturbated site in the southern Bay (site S). Macrofaunal activity did not appear to enhance DOC fluxes from these sediments, since measured benthic DOC fluxes were <0.5 mmol/m^2/d, considerably lower than those observed at site M. The ratio of DOC fluxes to ΣOCR values at site S was also slightly smaller than that seen at site M (<~6%).

When these results are compared with benthic flux studies carried out in other coastal sediments, it is observed that the ratio of benthic DOC fluxes to ΣOCR appears to increase as ΣOCR decreases. The reasons for this observation are unknown at the present time, although if this trend is shown to be robust, it may provide further insights into the factors controlling benthic DOC fluxes from marine sediments. It may also prove useful in more accurately estimating the global importance of benthic DOC fluxes in oceanic C cycling.

The results of these studies suggest that benthic DOC fluxes from Chesapeake Bay sediments do not likely represent a significant source of reduced C to Bay waters. These fluxes may also not significantly affect the transport of DOC through the Chesapeake Bay estuary, although uncertainties in the reactivity of DOC in estuaries makes this conclusion somewhat tentative at this time. However, when these results are used to make a lower limit estimate of the globally integrated benthic DOC flux from marine sediments, a value similar to that previously calculated by BURDIGE et al. (1992) is obtained. This observation further supports suggestions in this paper regarding the importance of benthic DOC fluxes in the oceanic C cycle.

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APPENDIX

Calculation of TCR in Bioturbated Sediments

If biological and/or physical processes mix sediments, the modeling of organic C profiles can become complicated, depending on the nature of the mixing processes. In the simplest case, this mixing is assumed to be a random process analogous to molecular diffusion (BERNER, 1980; ALLER, 1982). If we also assume that the entire zone of early diagenesis is mixed with a constant D_b value, the flux of organic C to the sediment surface (J_{in}) is given by (BERNER, 1980);

$$J_{in} = -D_b \left.\frac{dG}{dx}\right|_{x=0} + wG_{x=0} = \alpha D_b G^{\circ}_{m} + w(G^{\circ}_{m} + G_{nr}), \quad \text{(A1)}$$

where the right side of this expression is obtained with Eqn. 1. The flux of organic C below the zone of early diagenesis (J_{bur}) is given by

$$J_{bur} = wG_{nr}. \quad \text{(A2)}$$

The difference between J_{in} and J_{bur} is TCR, and is then given by

$$\mathrm{TCR} = (\alpha D_b + w)G^{\circ}_{m}. \quad \text{(A3)}$$