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# Fluxes of dissolved organic carbon from California continental margin sediments

DAVID J. BURDIGE, <sup>1,\*</sup> WILLIAM M. BERELSON, <sup>2</sup> KENNETH H. COALE, <sup>3</sup> JAMES MCMANUS, <sup>4</sup> and KENNETH S. JOHNSON <sup>3</sup>

<sup>1</sup>Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, Norfolk, Virginia 23529, USA 

<sup>2</sup>Department of Earth Sciences, University of Southern California, Los Angeles, California 90089-0740, USA 

<sup>3</sup>Moss Landing Marine Laboratories, P. O. Box 450, Moss Landing, California 95039, USA 

<sup>4</sup>Large Lakes Observatory, University of Minnesota, Duluth, Minnesota 55812, USA

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Abstract—Fluxes of dissolved organic carbon (DOC) from marine sediments represent a poorly constrained component of the oceanic carbon cycle that may affect the concentration and composition of DOC in the ocean. Here we report the first in situ measurements of DOC fluxes from continental margin sediments (water depths ranging from 95 to 3,700 m), and compare these fluxes with measured benthic fluxes from 20 other coastal and continental margin sediments. With this combined data set data we have estimated that benthic DOC fluxes are less than ∼10% of sediment carbon oxidation rates, and that the integrated DOC flux from sediments in water depths less than 2,000 m is ∼180 Tg C/yr. These fluxes are roughly equivalent to the riverine DOC flux, and the organic carbon burial rate in marine sediments. Benthic DOC fluxes therefore represent an important net source of DOC to the oceans. We also note that: (1) benthic DOC fluxes represent a loss of organic carbon from sediments; (2) in many sediments these fluxes appear to be controlled by molecular diffusion (i.e., by pore water concentration gradients); (3) pore water DOC may be an important intermediate in sediment carbon burial and preservation. These observations therefore suggest a linkage between benthic DOC fluxes and sediment carbon preservation that may be mediated by pore water DOC concentrations and cycling. The magnitude and fate of DOC effluxing from marine sediments is thus important to understanding carbon cycles and budgets in the marine environment. *Copyright* © *1999 Elsevier Science Ltd* 

#### 1. INTRODUCTION

Concentrations of dissolved organic carbon (DOC) in sediment pore waters are generally elevated over bottom water values (up to an order of magnitude), increase with depth in most sediments, and often approach "asymptotic" concentrations in the upper centimeters or several meters of sediment (Krom and Westrich, 1981; Heggie et al., 1987; Burdige et al., 1992; Chen et al., 1993; Martin and McCorkle, 1993; Alperin et al., 1994; Burdige and Homstead, 1994; Bauer et al., 1995; Burdige and Gardner, 1998; and others). Simple diffusive calculations therefore predict a flux of DOC from marine sediments. Initial attempts to scale up these calculated fluxes to estimate their global significance indicated that benthic DOC fluxes are a significant net source of DOC to the oceans, as compared to riverine DOC inputs or carbon burial rates in sediments (Burdige et al., 1992; Chen et al., 1993). Benthic DOC fluxes may also be important in other aspects of the oceanic carbon cycle, since these fluxes may affect calcite dissolution in deep-sea sediments, depending on the relationship between sediment O<sub>2</sub> consumption, DOC cycling, and CO<sub>2</sub> production from aerobic respiration (Jahnke et al., 1994).

Other estimates of DOC fluxes from continental margin sediments based on pore water profiles suggested that these fluxes could be >50% to up to 140% of sediment carbon oxidation rates (or dissolved inorganic carbon fluxes; Martin and McCorkle, 1993; Bauer et al., 1995). In contrast, Jahnke (1996) concluded that benthic DOC fluxes from marine sediments in water depths greater than 1,000 m cannot be compa-

rable in magnitude to benthic oxygen fluxes or sediment carbon oxidation rates, since such large benthic DOC fluxes would be inconsistent with  $^{14}\mathrm{C}$  ages of DOC in the water column, sediment trap carbon fluxes, and water column  $^{14}\mathrm{C}\text{-AOU}$  relationships. Measurements of the  $\Delta^{14}\mathrm{C}$  content of surficial pore water DOC from two marine sediments also imply that sediments are not likely a significant source of the "old" DOC in the water column (Bauer et al., 1995). On the other hand, determinations of the  $\Delta^{14}\mathrm{C}$  content of colloidal (>10 kDa) organic matter suggest that sediments could be an important source of DOC to deep waters (Guo et al., 1996, 1998).

Attempts to directly quantify benthic DOC fluxes and their role in sediment carbon cycling, and therefore better constrain the significance of sediments as a source of DOC to the oceans, have produced equivocal results. Studies in estuarine (Chesapeake Bay) sediments show that measured benthic DOC fluxes are only  $\sim 2\%-7\%$  of the sediment carbon oxidation rates (Burdige and Homstead, 1994; Burdige and Zheng, 1998). However the magnitude of these fluxes further supported previous suggestions about their importance in the oceanic carbon cycle. Recent studies of benthic DOC fluxes from Wedell Sea sediments (Hulth et al., 1997) yielded some measured DOC fluxes that are comparable in magnitude to those determined in Chesapeake Bay. However, given the much lower remineralization rates in Wedell Sea sediments as compared to Chesapeake Bay sediments, the relative importance of benthic DOC fluxes in Wedell Sea sediment carbon cycling appeared to increase accordingly (i.e., in these sediments benthic DOC fluxes are  $\sim 3\%-150\%$  of the measured benthic  $\Sigma CO_2$  fluxes).

To further examine these problems we have examined benthic DOC fluxes from contrasting continental margin sedi-

<sup>\*</sup>Author to whom correspondence should be addressed (E-mail: dburdige@odu.edu).

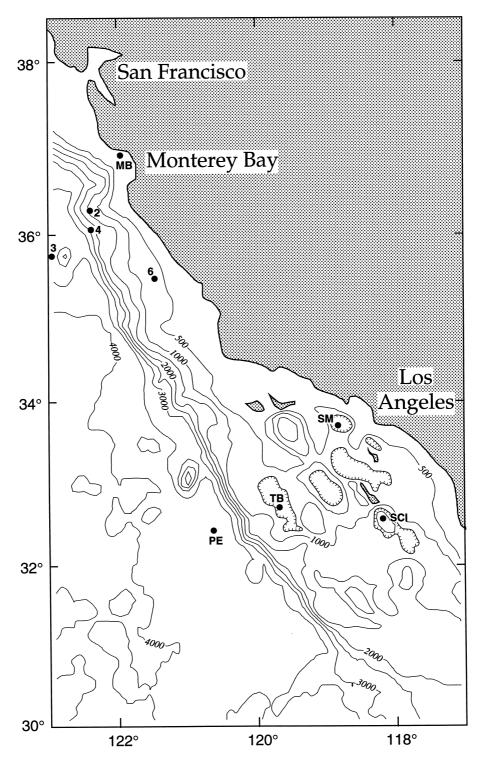
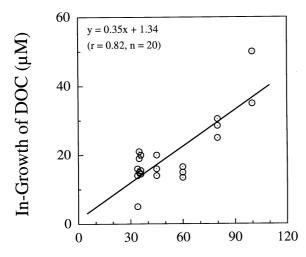


Fig. 1. A map showing the field sites of this study. The Central California margin stations are stations MB, 2, 3, 4 and 6, and the Southern California Borderland stations are stations SM (Santa Monica Basin), Cl (San Clemente Basin), TB (Tanner Basin), and PE (Patton Escarpment). Contour depths are meters.

ments, and compared these results with measured DOC fluxes from a range of other coastal and continental margin sediments. This study was motivated by the issues described above, along with other studies indicating the importance of these environments as the major sites of sediment carbon burial (preservation) and remineralization in the oceans (Berner, 1989; Reimers et al., 1992; Hedges and Kiel, 1995; Berelson et al., 1996; Middelburg et al., 1997).



# Time Between Sample #1 Draw and Processing (hr)

Fig. 2. The concentration of DOC in lander sample draw #1 minus the bottom water DOC concentration (In-growth of DOC) versus the time between this sample draw and its processing. The best-fit line through these data was used to calculate the in-growth correction factor discussed in the text.

#### 2. STUDY SITES AND METHODS

Our studies were carried out in November, 1995 at a series of sites in the southern California Borderland region and the central California continental margin (Fig. 1). Water depths at these sites ranged from 95 m (station MB in Monterey Bay) to 3,700 m (station PE on the Patton Escarpment). Bottom water oxygen values at these sites varied from  $\sim$ 140  $\mu$ M (stations MB and PE) to <6  $\mu$ M at station SM in the semienclosed Santa Monica Basin, and 10–15  $\mu$ M at station 6 in the core of the oxygen minimum zone off central California. Additional details on the biogeochemical characteristics of these sites can be found elsewhere (Berelson et al., 1987, 1996; Jahnke, 1990; Reimers et al., 1992).

Benthic DOC flux measurements were made in situ using the University of Southern California (USC) free-vehicle benthic lander (Berelson et al., 1987, 1996), and were determined from the change in DOC within the water of a lander chamber during the length of an incubation (typically 24-72 h). The USC lander is capable of taking up to six sequential samples from three separate chambers over time during a lander deployment, and it was our intention to use such time courses to calculate benthic DOC fluxes. Chamber samples were therefore analyzed with the expectation that DOC concentrations would increase with successive sample draws. Sample draw #1, taken shortly after the chamber lid was closed, always showed a nutrient concentration very close to that established for bottom water from Niskin casts. In contrast, the DOC concentration in sample draw #1 was always much greater than the bottom water value, and the longer the time of the chamber deployment, the more the DOC concentration in draw #1 was elevated over the bottom water concentration. The data in Fig. 2 show that there was a linear relationship between this concentration difference (i.e., draw #1 DOC concentration-bottom water DOC concentration) and the time that sample #1 spent in the sample bulb prior to filtration (i.e., the time of the lander deployment plus the time for lander ascent and recovery and ultimately, sample processing on-board ship; see the discussion below). We therefore utilized this linear "in-growth" of DOC to correct the draw #6 DOC concentrations (draw #6 is the last sample collected just prior to the end of a lander deployment). The time between draw #6 collection and sample filtration on-board ship was typically 6-11 h. Utilizing the relationship in Fig. 2, an in-growth correction of 5 µM was subtracted from the measured DOC concentrations for sample draw #6 (Table 1).

In calculating benthic fluxes with this data we assumed that the flux of DOC was constant with time, and that the initial chamber water was compositionally similar to ambient bottom water collected with either a Niskin bottle attached to the lander or with bottom water hydrocasts. This latter assumption was based on the above-discussed comparison of bottom water nutrient data and initial (draw #1) nutrient lander samples. A two-point flux determination was then made using these bottom water values as the initial DOC concentration and the corrected, draw #6 DOC concentration as the final value (Table 1). Fluxes were determined as the difference between these final and initial DOC concentrations multiplied by chamber height and divided by the length of the incubation period. We recognize that this two-point flux determination is not ideal, and our correction of draw #6 DOC concentrations is a large determinant in the final calculated benthic DOC flux. However, because we had three working chambers at all but two stations (stations 2 and 3), and good chamber-to-chamber agreement again at all but two stations (stations 4 and TB) we feel confident in these flux determinations.

Pore water DOC profiles were obtained from sediment cores collected with an Ocean Instruments multi-corer. Sediment cores were processed (cut into 0.5-2 cm sections) under an inert ( $N_2$ ) atmosphere at in situ temperatures in a cold van. Pore waters were subsequently collected by centrifugation of these sediment core subsections (see Burdige and Gardner, 1998, and Burdige and Zheng, 1998, for further details on pore water collection and sample processing).

Bottom water samples for DOC analyses were collected from either a Nisken bottle mounted on the benthic lander or from bottom water hydrocasts. An all-polypropylene syringe was placed directly into the nipple of the bottle, and the syringe was rinsed three times with water from the bottle before collecting a water sample. Bottom water samples were then filtered through 0.45  $\mu m$  Gelman Acrodisc filters, placed into cleaned glass vials, acidified to pH  $\sim 2$  with 6 M HCl, quick frozen in an aluminum block placed in a standard freezer, and stored frozen until analyzed (Burdige and Gardner, 1998; Burdige and Zheng, 1998). Lander samples for DOC analyses were similarly processed upon retrieval of the lander.

Concentrations of DOC in lander, pore water, and bottom water samples were determined by high temperature catalytic oxidation using a Shimadzu TOC-5000 (Burdige and Homstead, 1994; Burdige and Gardner, 1998). Sediment carbon oxidation rates were determined with benthic lander measurements as described in Berelson et al. (1996).

### 3. RESULTS

Lander-determined benthic DOC fluxes from these California continental margin sediments ranged from  $\sim\!0.1~\rm mmol/m^2/d$  (station PE) to  $\sim\!2~\rm mmol/m^2/d$  (station MB; see Table 1 and Fig. 3). These fluxes were comparable to those seen in other coastal and continental margin sediments (Fig. 4). The amount of DOC effluxing from California margin sediments was roughly proportional to the amount of organic carbon oxidized ( $C_{\rm ox}$ ) within the sediments ( $\sim\!25\%$ ) over a 20-fold range of  $C_{\rm ox}$  values (Fig. 3), and did not appear to be significantly affected by bottom water oxygen concentrations (e.g., stations with high and low bottom water oxygen concentrations fall roughly along the same trend lines in Fig. 3).

Pore water DOC concentrations at these sites generally increased with depth (Fig. 5), as has been seen in other continental margin sediments (Heggie et al., 1987; Martin and McCorkle, 1993; Bauer et al., 1995). A more detailed discussion of these profiles is presented elsewhere (Burdige et al., in prep; also see Burdige and Gardner, 1998), although for the purposes here we will simply focus on the concentration gradient across the sediment–water interface, and the diffusive benthic DOC flux that it predicts. Benthic DOC fluxes were calculated with these data as done previously (Burdige et al., 1992; Burdige and Homstead, 1994) using Fick's first law of

Table 1. Benthic DOC fluxes from California continental margin sediments

Station ID <sup>a</sup> (depth, m)	Chamber ht. (cm)	Bottom water DOC (μM)	Incubation time (h)	Corrected last draw DOC ( $\mu$ M)	Flux <sup>b</sup> (mmol/m <sup>2</sup> /d)
MB (99)					
В	12.3	53.0	16.5	61.4	$1.50 \pm 1.85$
Y	12.2	53.0	16.5	70.6	$3.12 \pm 2.77$
R	11.9	53.0	16.5	63.0	$1.73 \pm 1.97$
Average					$2.12 \pm 1.29$
Sta 2 (1,400)					
В	9.5	29.0	36.0	48.7	$1.25 \pm 0.85$
Y	9.5	29.0	36.0	67.2	$2.42 \pm 1.34$
Average					$1.83 \pm 0.79$
Sta 3 (3,595)					
Y	12.9	36.2	104	52.5	$0.49 \pm 0.38$
R	13.6	36.2	104	66.9	$0.96 \pm 0.60$
Average					$0.72 \pm 0.36$
Sta 4 (2,144)					
В	10.0	35.5	33.0	35.9	$0.03 \pm 0.13$
Y	11.9	35.5	33.0	35.6	$0.01 \pm 0.08$
R	9.8	35.5	33.0	41.0	$0.39 \pm 0.49$
Average					$0.14 \pm 0.18$
Sta 6 (665)					
В	9.8	36.9	35.5	45.8	$0.59 \pm 0.61$
Y	9.6	36.9	35.5	39.4	$0.16 \pm 0.30$
R	12.9	36.9	35.5	41.7	$\frac{0.42 \pm 0.57}{}$
Average					$0.39 \pm 0.30$
SM (910)					
В	8.3	33.6	34.5	48.1	$0.84 \pm 0.68$
Y R	9.2 8.9	33.6 33.6	34.5 34.5	53.6 46.2	$1.28 \pm 0.91$ $0.78 \pm 0.67$
	0.7	55.0	34.3	40.2	
Average					$0.97 \pm 0.44$
SC1 (2,058)	0.2	22.0	50.0	44.4	0.20 + 0.21
B Y	9.3 9.0	33.8 33.8	59.0 59.0	41.4 39.5	$0.29 \pm 0.31$ $0.21 \pm 0.25$
R	8.7	33.8	59.0	44.1	$0.21 \pm 0.23$ $0.36 \pm 0.34$
Average	0.7	23.0	57.0		$\frac{0.29 \pm 0.17}{0.29 \pm 0.17}$
•					0.27 = 0.17
PE (3,733)	11.7	22.5	91.0	24.6	0.10 ± 0.19
B Y	11.7 13.8	32.5 32.5	81.0 81.0	34.6 35.8	$0.10 \pm 0.18$ $0.13 \pm 0.21$
R	12.3	32.5	81.0	34.3	$0.07 \pm 0.14$
Average					$0.10 \pm 0.10$
ГВ (1,509)					
В (1,309)	8.4	37.7	47.5	42.7	$0.21 \pm 0.29$
Y	9.1	37.7	47.5	63.9	$1.20 \pm 0.81$
R	8.6	37.7	47.5	37.9	$0.01 \pm 0.06$
Average					$0.48 \pm 0.52$

<sup>&</sup>lt;sup>a</sup> B, Y, and R represent the three different chambers on the USC lander. See Fig. 1 for the locations of each station.

diffusion (J =  $-\phi_0 D_s \, dC/dz_0$ ). In this calculation the following assumptions were made:

- (1) The DOC concentration gradient across the sediment—water interface (dC/dz<sub>0</sub>) can be approximated by  $\Delta C/\Delta z$ , where  $\Delta C$  is the difference between the DOC concentra-
- tion in the bottom waters and in the first sediment sample, and  $\Delta z$  is the depth of the midpoint of this sediment sample (i.e., 0.25 cm for a 0-0.5 cm sediment sample);
- (2) The average molecular weight of pore water DOC is between 1 and 10 kDa. This assumption is based in part on literature data cited in Burdige et al. (1992), and recent

<sup>&</sup>lt;sup>b</sup> Two point fluxes were calculated with this data as described in the text. The uncertainty for a given chamber flux measurement includes a 15% uncertainty in the value of the in-growth correction (see text) and uncertainties in the bottom water DOC value (~4%) and chamber height (~15%). Uncertainty for the mean flux at each station is either the standard deviation of the mean of the individual chamber fluxes, or the square root of the sum of the squares of the uncertainty for each chamber flux. The larger of these two uncertainties was reported here.

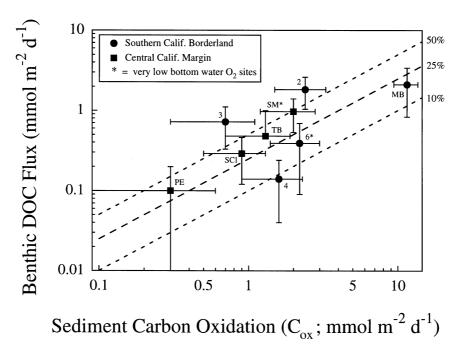


Fig. 3. Measured benthic DOC fluxes versus depth-integrated sediment carbon oxidation rates  $(C_{ox})$  for the California continental margin sediments shown in Fig. 1.

pore water DOC molecular weight studies carried out in a range of estuarine and continental margin sediments, including those in the Santa Monica Basin (Burdige and Gardner, 1998).

With this second assumption, an observed inverse cube root relationship between molecular weight and the free solution diffusion coefficient  $(D^{\circ})$  for an organic compound was then used to calculate the average  $D^{\circ}$  for pore water DOC (Burdige et al., 1992; Alperin et al., 1994). The resulting  $D^{\circ}$  was  $0.107 \pm 0.045$  cm<sup>2</sup>/d, based on the simple average of the 1 kDa and 10 kDa DOC  $D^{\circ}$  values. This value was corrected for sediment tortuosity and converted to a bulk sediment diffusion coefficient  $(D_s)$  as described previously (Burdige and Homstead, 1994).

At five out of the eight California continental margin sites, average lander-measured benthic DOC fluxes (n = 2-3 chambers/site) agreed, to within 1 standard error (s.e.) (or roughly  $\pm \sim 40\%$ ), with average calculated diffusive pore water fluxes (n = 2 cores/site; Fig. 6). This agreement between measured and calculated DOC fluxes is similar to that seen by Burdige and Homstead (1994) in anoxic, nonbioturbated sediments of Chesapeake Bay (also see Burdige and Zheng, 1998). At one California margin site (station 2), the chamber DOC flux was 3–4 times greater than the diffusive flux, although this is a site of known bioirrigation (Townsend, 1998). At two sites (stations 4 and PE), calculated diffusive DOC fluxes were  $\sim$ 4–5 times greater than chamber fluxes. These latter observations may be caused by artifactually high DOC concentrations in our surface sediment pore water samples from these sites, associated with the collection of pore water samples for DOC analyses via centrifugation from bioturbated sediments (see Martin and Mc-Corkle, 1993, Burdige and Gardner, 1998, and Alperin et al., 1999, for further discussions of this possible artifact). Such anomalously high DOC concentrations would then lead to overestimates of the calculated, diffusive DOC flux from these sediments.

# 4. DISCUSSION

Figure 4 shows a comparison of our measured DOC fluxes in California continental margin sediments with previously reported measured DOC fluxes from a range of other coastal and continental margin sediments. Water depths at these sites vary from  $\sim\!10$  to 3,700 m, although of the 29 sites included in this figure only five are in water depths greater than 2,000 m. In attempting to develop a relationship between benthic DOC fluxes and  $C_{\rm ox}$  values, we have fit these data to

$$(DOC flux) = m*(C_{ox})^b$$
 (1)

since equations such as this have been used to examine other geochemical data sets that similarly vary over several orders of magnitude (Jahnke, 1996; Middelburg et al., 1997).

The best fit of these data to the log-log transformation of Eqn 1 is also shown in Fig. 4 (note that a similar nonlinear relationship between benthic DOC fluxes and  $C_{ox}$  was previously observed by Burdige and Homstead, 1994, with a subset of the data shown here). Although there is scatter around this best-fit line and the  $r^2$  value is low (=0.25), the regression appears to be significant based on the F statistic (which determines the probability  $[\alpha]$  that this  $r^2$  value occurs by chance;  $\alpha < 0.001$  for this data set; Sokal and Rohlf, 1981).

The observation here that the best fit value of b is less than 1 implies that benthic DOC fluxes are a nonconstant fraction of  $C_{ox}$  in this larger data set, and that benthic DOC fluxes increase in a nonlinear fashion with  $C_{ox}$  (compare with Fig. 3). Furthermore, as  $C_{ox}$  values decrease, benthic DOC fluxes as a fraction

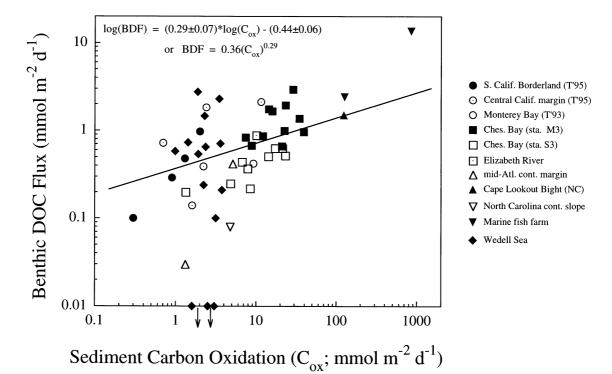


Fig. 4. Measured benthic DOC fluxes versus depth-integrated sediment carbon oxidation rates (Cox) for a wide range of coastal and continental margin sediments, including the California continental margin stations in Fig. 1. With the exception of the results from this study and those for the marine fish farm, all other benthic fluxes were determined by core incubation techniques, either on-board ship or in the lab (see the original references for details on these flux studies and on how the Cox values were determined). The Monterey Bay (T'93) result is from a core incubation study of benthic DOC fluxes (reported in Burdige and Homstead, 1994) carried out at the same Bay site shown in Fig. 1, two years earlier than the lander studies at this site reported here. The Chesapeake Bay results are from two seasonal studies of benthic DOC fluxes from contrasting sites in Chesapeake Bay (time period 8/91-7/92 from Burdige and Homstead, 1994, and time period 3/95-10/96 from Burdige and Zheng, 1998). One site is an organic-rich sediment in the mesohaline portion of the Bay that undergoes seasonal anoxia (station M3), while the other is a bioturbated site in the lower Bay where bottom water oxygen values remain high year-round (station S3). The Elizabeth River (Va.) result is from an organic-rich sediment in this anthropogenically impacted urban estuary (Burdige, unpublished data). The mid-Atlantic continental margin results are from a site (station WC4) on the shelf/slope break, SE of the mouth of Delaware Bay in a water depth of 450 m (Burdige, unpublished data; site described in Burdige and Gardner, 1998). The North Carolina continental slope (NCCS) result is from sites SE of the mouth of Chesapeake Bay in water depths of ~750 m (Alperin et al., 1999). The marine fish farm results are from sediments underlying a marine fish farm in Gullmar Fjord, western Sweden (water depth 18-21 m; Hall et al., 1990). The Wedell Sea results are from sediments in the southern portion of this basin, in water depths ranging from 280 to 2,500 m (Hulth et al., 1997). The best-fit line shown here was calculated using a weighted least squares fit of "regional" averages of these Cox values and benthic DOC fluxes. In this fitting procedure, each pair of values was weighted by the number of individual measurements that were used to obtain the average. This approach was taken in part because of the negative DOC fluxes (sediment uptake of DOC) observed by Hulth et al. (1997) at three of their 14 sites in the Wedell Sea (indicated by the symbols and arrows along the lower x axis). The following regions were used in this calculation [n = number of data]points used to determine each of these averages]: Chesapeake Bay station M3 (integrated annual averages for data from 8/91-7/92 [n=4] and 3/95-4/96 [n=6]); Chesapeake Bay Station S3 (same as Chesapeake Bay Station M3). Cape Lookout Bight [n = 1]; Swedish marine fish farm [n = 2]; Elizabeth River [n = 1]; Atlantic shelf/slope break stations (average of measurements at station WC4 and the NCCS sites [n = 3]); Central California region (average of measurements at stations 2, 3, 4, and 6 [n = 4]; Monterey Bay [n = 2]; Southern California Borderland region (average of measurements at stations SM, SCl, and TB [n = 3]); Patton Escarpment [n = 1]; Wedell Sea [n = 14].

of  $C_{\rm ox}$  increase (see also the last column in Table 2). For example, for a  $C_{\rm ox}$  value of 5 mmol/m²/d benthic DOC fluxes are  $\sim\!10\%$  of  $C_{\rm ox}$ , while at a sediment carbon oxidation rate of 50 mmol/m²/d this percentage decreases to  $\sim\!2\%$  (see Fig. 4 for further details).

With this best-fit equation we can further refine our previous estimate of the global significance of benthic DOC fluxes in oceanic and sedimentary carbon cycling. Our calculations in Table 2 suggest that the integrated DOC flux from coastal and continental margin sediments (0-2,000 m) water depth) is  $\sim 180$ 

Tg C/yr. This quantity is larger than (though of roughly similar magnitude) a previous estimate of benthic DOC fluxes from this same region of the seafloor (~10–90 Tg C/yr; Burdige et al., 1992). However this earlier estimate was determined using calculated, benthic DOC fluxes based on pore water DOC profiles. In contrast, the results presented here uses measured DOC fluxes, including the first in situ measurements of DOC fluxes from continental margin sediments. The estimate here of DOC fluxes from coastal sediments (~90 Tg C/yr) is also similar to a previous estimate of benthic DOC fluxes from this

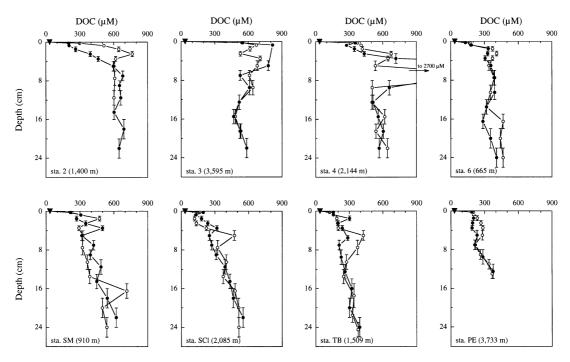


Fig. 5. Pore water DOC concentrations versus depth in replicate sediment cores collected in the central California continental margin (upper panels) and the southern California Borderland region (lower panels). Symbols ( $\blacktriangledown$ ) on the upper x axis represent bottom water values determined by hydrocasts.

same sediment regime ( $\sim$ 20–170 Tg C/yr), based on a subset of the Chesapeake Bay results shown in Fig. 4 (Burdige and Homstead, 1994).

The implications of these results are several-fold. First, we note that the integrated benthic DOC flux estimated here is comparable to estimates of the organic carbon burial rate in all marine sediments (~160 Tg C/yr; Hedges and Kiel, 1995) and the riverine DOC input (200 Tg C/yr; Meybeck, 1982). Thus, as has been noted previously (Burdige et al., 1992; Burdige and

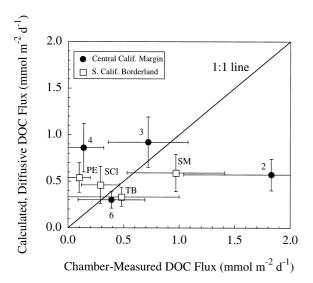


Fig. 6. Calculated, diffusive DOC fluxes versus chamber-measured benthic DOC fluxes.

Homstead, 1994) DOC fluxes from marine sediments are an important net source of DOC to the oceans, and a significant component of the oceanic carbon cycle. Second, we observe that while there is considerable scatter in the data shown in Fig. 4, the best-fit to Eqn 1 with these data and the results in Table 2 demonstrate that DOC fluxes from coastal and margin sediments are less than  $\sim 10\%$  of sediment carbon oxidation rates.

Finally, we note that there may be additional significance to the fact that integrated benthic DOC fluxes and sediment carbon burial rates are of comparable magnitude, since coastal and continental margin sediments represent the major sites of carbon deposition and burial in the oceans (Berner, 1989; Hedges, 1992; Hedges and Kiel, 1995). In many of the California continental margin sediments examined here (Fig. 6), as well as in other nonbioturbated estuarine and coastal sediments (Burdige et al., 1992; Burdige and Homstead, 1994), measured and calculated DOC fluxes appear to agree with one another. To a first order, this observation suggests that the shape of the DOC pore water profile and the DOC pore water concentration gradient at the sediment-water interface both play a major role in determining the magnitude of the benthic DOC flux. At the same time pore water DOC is an important intermediate in several proposed models for sediment carbon preservation, including the geopolymerization model (Tissot and Welte, 1978; Krom and Westrich, 1981), the mesopore protection/ surface area adsorption model (Mayer, 1994a, 1994b; Hedges and Kiel, 1995), and "hybrid" models which propose that geopolymerization reactions are catalyzed by adsorption of organic molecules to mineral surfaces (Mayer, 1994b; Collins et al., 1995). These processes, along with the rates of biological DOC cycling (Alperin et al., 1994; Henrichs, 1995; Burdige

Table 2. Integrated benthic DOC fluxes from coastal and continental margin sediments.\*

	Sediment Carbon Oxidation (Cox)		Benthic DOC Flux		
	Integrated <sup>b</sup> (Tg C/yr) <sup>†</sup>	Average <sup>c</sup> (mmol/m <sup>2</sup> /d)	Average <sup>d</sup> (mmol/m <sup>2</sup> /d)	Integrated <sup>e</sup>	
Sediment regime <sup>a</sup>				(Tg C/yr)	(% of C <sub>ox</sub> ) <sup>f</sup>
"Coastal" sediments (0-200 m; 9%)	1630 (52%)	14.7	0.91	$88 \pm 30$	5.4%
"Margin" sediments (200-2,000 m; 7%)	940 (30%)	6.6	0.65	$89 \pm 25$	9.5%
Coastal plus margin sediments (0-2,000 m)	2570 (82%)			$177 \pm 56$	6.9%

- \* This calculation is limited to sediments in these two regimes because only a relatively small fraction of the sites in Fig. 4 are in water depths >2,000 m. Thus we are not able to confidently extrapolate these results to sediments in deeper water depths.
  - $^{\dagger}$  Note that Tg C/yr =  $10^{12}$  g C/yr.
  - <sup>a</sup> The percentage of all marine sediments found in each sediment regime is listed in parentheses.
- <sup>b</sup> Using an extensive database of published rates of sediment biogeochemical processes, Middelburg et al. (1997) have estimated globally integrated rates of sediment processes in these two regimes (and in a third regime, "ocean basin" sediments, defined as sediments in water depths >2,000 m). Listed in parentheses in this column is the integrated  $C_{ox}$  in each region as a percentage of the integrated  $C_{ox}$  for all marine sediments (=3130 Tg C/yr).
  - <sup>c</sup> Obtained by dividing the integrated C<sub>ox</sub> in each region by the sediment surface area in the region.
  - $^{\rm d}$  Obtained using the average  $C_{\rm ox}$  in each region and the best-fit to Eqn 1 with the data in Fig. 4.
  - Obtained by multiplying the average benthic DOC flux in each region by the sediment surface area in the region.
  - $^{\rm f}$  Values in this column are the average benthic DOC flux as a percentage of the average  $C_{\rm ox}$  in each sediment regime.

and Gardner, 1998), also likely affect the shape of pore water DOC profiles.

These observations, and the fact that benthic DOC fluxes represent a net loss of carbon from sediments, therefore suggest a linkage between benthic DOC fluxes and sediment carbon preservation, "mediated" by pore water DOC concentrations and cycling. Changes in the factors controlling benthic DOC fluxes (and/or the cycling of DOC in sediments) may then affect or control sediment carbon preservation (also see similar discussions in Hedges and Kiel, 1995, and Henrichs, 1995). The exact details of the relationship between benthic DOC fluxes and sediment carbon preservation awaits further studies. However, these results suggest a strong link between the two processes. The magnitude and fate of DOC effluxing from marine sediments is therefore important for understanding carbon cycles and budgets both in sediments and in the water column.

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