Limnol. Oceanogr., 46(7), 2001, 1684–1690

Role of the oxygen-deficient zone in transfer of organic carbon to the deep ocean

Allan H. Devol and Hilairy E. Hartnett[1]
School of Oceanography, University of Washington, Seattle, Washington, 98195-7940

Abstract

Benthic carbon oxidation rates and carbon burial rates have been determined for two contrasting continental margins and their sum has been used as an estimate of carbon rain rate to the sediments. On the Washington State margin, where the water column is oxic, rain rates at 100 m were about 15 to 20 mmoles C m^{-2} d^{-1} and they decreased with increasing water depth to values of near 3 mmoles C m^{-2} d^{-1} at 1,000 m. The rain rate estimates, C_R, were described by a power function, $C_R = C_{R\,100m}\,(z/100)^{-\alpha}$, with an attenuation coefficient, α, of 0.93 ($C_{R\,100m} = 16.2$, $r^2 = 0.89$). This attenuation rate is similar to numerous others previously reported for various oceanic areas. In contrast, off northwest Mexico, where the water column is oxygen deficient between 180 and 700 m, rain rates at 100 m were considerably less, about 7.5 mmoles C m^{-2} d^{-1}, but rain rates at 1,000 m were similar to those off Washington. Thus, the attenuation coefficient for the Mexican margin was significantly lower, $\alpha = 0.36$ ($C_{R\,100m} = 7.4$, $r^2 = 0.77$). Off Mexico, the rain rates estimated from sedimentary parameters were corroborated by values determined directly from sediment-trap deployments. The generally smaller rain rates off Mexico are probably due to the lower primary production, hence lower initial supply. The lower attenuation rate, however, is hypothesized to result from a decreased oxidation rate of the sinking flux within the oxygen-deficient zone relative to a more typical oxic water column.

The transition from the last glacial to the present interglacial was accompanied by an 85 ppm increase in the CO_2 content of the atmosphere. It is currently thought that much of this change was due to movement of CO_2 between the deep ocean and the atmosphere, although the exact mechanism is still under debate (*see* Broecker and Henderson 1998 for discussion). Three important carbon cycle processes that determine CO_2 uptake from the atmosphere and subsequent transfer and storage in the ocean interior are (1) photosynthetic carbon fixation in the euphotic zone, (2) transfer of some fraction of this fixed carbon out of the euphotic zone as export production, and (3) permanent carbon burial in marine sediments. As the export flux falls through the oceans, it is biologically oxidized such that the sinking flux of organic matter decreases progressively with increasing depth leaving only a small fraction available for burial. The manner in which the export flux, or carbon rain rate, decreases with depth is important for two reasons. First, it determines the quantity and time scale at which carbon is sequestered as CO_2 in the deep ocean, i.e., the shallower the regeneration depth the shorter, in general, the sequestration time. Second, greater attenuation rates result in proportionally less of the initial carbon flux reaching the sediments, which has attendant implications for benthic ecology and ultimately for carbon burial. To date nearly all estimates of the flux attenuation rate have been determined from sediment-trap studies in open ocean areas with well-oxygenated water columns. Nearly all of these studies have been empirically fit by power functions with the attenuation coefficients falling in a narrow range (Bishop 1989).

Much less is known about the attenuation rate of the sinking flux through suboxic water columns. However, for a trap deployment through the oxygen-deficient water column off Peru a much lower attenuation coefficient was observed (Martin et al. 1987). Similarly, Haake et al. (1992) observed a diminished attenuation of rain rate through the suboxic zone of the Arabian Sea. Recently it has been suggested that organic matter sinking through an oxygen-deficient zone, where denitrification is dominant, is metabolized differently than similar material falling through oxygenated water columns (Kristensen et al. 1999; Van Mooy et al. in press). If there is, indeed, a difference in relative carbon degradation between particles transiting suboxic and oxic water columns, it has important potential implications for climate models that predict larger oxygen-deficient zones in the past as well as for our understanding of suboxic carbon degradation in general.

Here we use benthic carbon oxidation rates coupled with burial rates to estimate carbon rain rates at different depths for transects across the continental shelves of Washington State (oxygenated water column) and western Mexico (oxygen-deficient water column). Calculated rain rates off Mexico agreed with rain rates estimated from sediment traps. However, the vertical attenuation of rain rate was much less off Mexico than off Washington. The data suggest that the presence of an oxygen-deficient zone greatly increases the amount of carbon transferred to the deep ocean.

Description of study sites

Samples were collected from the Washington State continental margin and the northwest Mexican margin along

[1] Current address: Institute of Marine and Coastal Sciences, Rutgers University, 71 Dudley Road, New Brunswick, New Jersey 08901.

Acknowledgements

We thank Dean Lambourn and Gerard van der Jagt for their invaluable assistance with deployment and recovery of benthic landers, sediment-trap arrays, and coring devices. Jim Murray kindly allowed us to use his sediment traps. We are also indebted to the crews of the R/V *New Horizon* and R/V *Wecoma* for their skillful seamanship during numerous lander and sediment-trap deployments and recoveries. Many undergraduate REU students helped with the various chemical analyses. This work was funded by NSF grants OCE 9116275, OCE 9416626, and DOE DE-FG02-98ER62535.

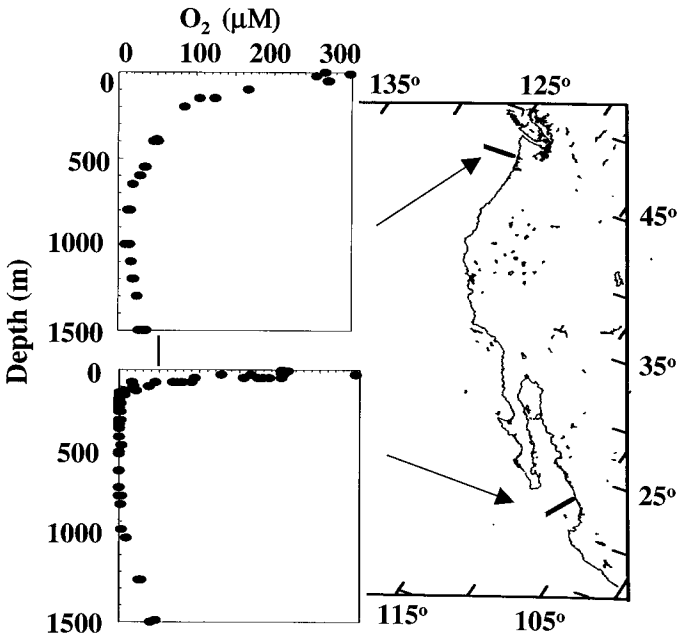

Fig. 1. Locations of the Washington State and Mexican continental margin transects along with the dissolved oxygen profiles from the two areas.

transects roughly perpendicular to the coasts of the two study areas (Fig. 1). The Washington State margin was sampled during cruises in July 1988, June 1991, and June 1994, while the Mexican margin was sampled in April 1990, November–December 1993, and November–December 1996. The Washington State margin is a typical eastern boundary current region where wind-driven coastal upwelling induces relatively high primary production during the summer months. Average annual primary production for the Washington margin is on the order of 450 gC m^{-2} yr^{-1} (Perry et al. 1989). In contrast, the Mexican margin in the region of the mouth of the Gulf of California is much less productive. Maximum pigment concentrations occur during late winter with average annual primary productivities of, at most, 200 gC m^{-2} yr^{-1} (Longhurst et al. 1995). One of the most distinct differences between the two study regions is the dissolved oxygen distribution (Fig. 1). The Mexican margin is characterized by the intense oxygen-deficient zone of the eastern tropical North Pacific, within which oxygen concentrations are undetectable between about 180 and 700 m, resulting in denitrification being the dominant water-column respiratory process (Codispoti and Richards 1976). Although oxygen concentrations off Washington are also low in the main thermocline, values remain above about 20 μM and denitrification is not an important water-column process (Hartnett et al. 1998).

Analytical methods

On each cruise a benthic flux-chamber lander (Devol and Christensen 1993) was used to determine the fluxes of dissolved oxygen, nitrate, and in some instances nitrogen gas between the sediments and the overlying water in the 100- to 1,000-m depth zone. Additionally, on each cruise, sediments were collected with either a Soutar box corer or a multicorer. These cores were then subsampled for determination of sulfate reduction rate by the $^{35}SO_4^=$ radiotracer technique (Kristensen et al. 1999) and for determination of porewater nitrate and ammonium concentration. All subcoring for nutrient analyses was done in a N_2 filled glove box, and pore waters were separated from the bulk sediments by refrigerated centrifugation as described by Devol and Christensen (1993). Denitrification rates were either determined directly from the nitrogen gas flux as measured by the lander incubations or they were calculated from a nitrogen mass balance as described by Devol and Christensen (1993). Subcores were also taken to determine sedimentation rate and bulk organic carbon content. Many of the data presented here are in common with the data used by Hartnett et al. (1998).

To calculate sedimentary carbon oxidation rates, oxygen fluxes and sulfate reduction rates were converted to carbon equivalents using the stoichiometry of Froelich et al. (1979). Denitrification rates were similarly, stoichiometrically converted to carbon equivalents. Finally, a total carbon oxidation rate was calculated by adding the larger of the carbon oxidation rate due to oxygen or sulfate to that due to denitrification. Implicit in this calculation is the maximum amount of reoxidation of reduced species (i.e., Mn^{+2}, Fe^{+2}, and HS^-) by the oxygen flux (Hartnett et al. 1998). For example, if the oxygen flux were only slightly greater than sulfate reduction rate, the implicit assumption would be that most of the oxygen flux was used to reoxidize sulfide (and other reduced species) and only a small amount was used to oxidize carbon. Also, since Fe^{+2} and Mn^{+2} were not included in calculation the implicit assumption is that there was no flux of these metals out of the sediments, i.e., all reduced metals were oxidized. The other extreme would be to sum the carbon oxidation rates due to oxygen, nitrate, and sulfate, with the implicit assumption that little of the reduced material was reoxidized. By using the larger of the oxygen flux or sulfate reduction rate we produce a conservative (minimum) estimate of carbon oxidation rate. The two approaches to calculating carbon oxidation rate differ most when the oxygen flux and the sulfate reduction rate are similar. When one is much larger than the other, such as in the oxygen-deficient zone, the two approaches give nearly the same result.

Sedimentary carbon burial rates were estimated as the product of the weight percent organic carbon at depth in the core and the sedimentation rate. Subcores from each station were sectioned into discrete depth intervals (0.5–1.0 cm thick). Sedimentary organic carbon content was subsequently determined by the method of Hedges and Stern (1984). ^{210}Pb distributions were determined by the method outlined in Nittrouer et al. (1983/1984), from which sedimentation rates were estimated (except for the two deepest stations off Mexico, which were determined from AMS-^{14}C dating; Hedges et al. 1999). ^{210}Pb profiles were visually inspected to determine the depth of the bioturbated mixed layer and sediment accumulation rates were calculated from the exponential decay profile below this layer. If some mixing is present below the surface mixed layer, our ^{210}Pb accumulation rates will overestimate the true accumulation. However,

Table 1. Station locations, depths, carbon oxidation rates, carbon burial rates, and carbon rain rates for the Washington State (WA prefix) and northwest Mexican (MX prefix) continental margins. Carbon oxidation, burial, and rain rates all have units of mmoles C m^{-2} d^{-1}. Errors are given as ±1 standard deviation.

Station	Lat.	Long.	Depth (m)	Carbon oxidation	Carbon burial	Carbon rain rate
WA 03	46°52.9′	124°29.6′	100	14.2 ± 1.96	3.23 ± 0.97	17.4 ± 2.14
WA 204	46°46.6′	124°35.3′	105	7.94 ± 0.78	3.59 ± 1.08	11.5 ± 1.34
WA 101	46°45.7′	124°33.5′	110	16.5 ± 1.68	3.77 ± 1.13	20.2 ± 2.04
WA 01	46°48.6′	124°35.4′	130	9.24 ± 0.91	4.63 ± 1.39	13.9 ± 1.68
WA 18	46°10.0′	124°32.7′	150	9.42 ± 0.93	0.77 ± 0.23	10.2 ± 0.96
WA 211	46°34.5′	124°33.4′	219	8.17 ± 1.04	2.00 ± 0.60	10.1 ± 1.20
WA 07	46°50.3′	124°50.7′	212	6.52 ± 0.84	1.57± 0.47	8.01 ± 0.97
WA 107	46°44.6′	124°50.4′	255	7.62 ± 0.95	0.74 ± 0.31	8.44 ± 0.98
WA 105	46°44.7′	124°51.3′	323	4.07 ± 0.51	0.81 ± 0.42	4.81 ± 0.56
WA 202	46°47.8′	124°54.4′	440	3.39 ± 0.38	1.46 ± 0.44	4.86 ± 0.59
WA 213	46°29.9′	124°43.8′	620	1.48 ± 0.19	0.36 ± 0.11	1.84 ± 0.22
WA 12	46°48.3′	125°03.2′	640	2.62 ± 0.28	0.43 ± 0.14	3.05 ± 0.31
WA 206	46°48.1′	125°12.7′	1025	1.09 ± 0.12	0.35 ± 0.11	1.44 ± 0.16
MX 03	22°43.2′	106°17.4′	100	5.52 ± 0.71	1.72 ± 0.52	7.42 ± 0.88
MX 102	22°44.3′	106°21.5′	145	5.36 ± 0.68	0.85 ± 0.26	6.22 ± 0.73
MX 07	22°43.2′	106°25.1′	190	5.57 ± 0.76	1.61 ± 0.49	7.81 ± 0.91
MX 112	22°40.3′	106°27.0′	310	3.62 ± 0.45	1.32 ± 0.46	4.94 ± 0.66
MX 12	22°41.3′	106°21.7′	322	3.08 ± 0.39	0.89 ± 0.27	3.97 ± 0.48
MX 103	22°37.3′	106°28.6′	500	2.15 ± 0.35	1.69 ± 0.51	3.84 ± 0.62
MX 06	22°36.9′	106°30.9′	620	3.55 ± 0.44	2.02 ± 0.61	5.55 ± 0.76
MX 209	22°21.5′	106°31.1′	800	2.81 ± 0.38	1.34 ± 0.46	4.15 ± 0.56
MX 104	22°31.2′	106°39.1′	1020	1.44 ± 0.19	1.02 ± 0.31	2.46 ± 0.36

Nittrouer et al. (1983/1984) have used ^{234}Th, ^{60}Co, and ^{137}Cs to show that for the Washington coast, ^{210}Pb accumulation rates reasonably estimate the true sedimentation rate. In the oxygen-deficient zone off Mexico bioturbation is minimal.

Finally, carbon rain rates to the sediments were estimated as the sum of the carbon oxidation rate plus the carbon burial rate (Hartnett et al. 1998). Error estimates for the rain rates were also determined. Errors associated with the oxygen consumption and denitrification rates were estimated from the pooled, duplicate chambers on the lander to be ±11% and ±22% (sd), respectively. Errors associated with sulfate reduction rate were estimated at ±15% (Kristensen et al. 1999). Errors associated with sediment carbon content were ±5% (Hedges and Stern 1984) and those associated with sedimentation rate were estimated at ±30%. Propagation of these errors leads to an average overall error on the rain rate estimate of ±12%, which varied between ±9% and ±15% depending on relative magnitude of the various components.

Sediment-trap arrays were deployed at three locations along the Mexican margin sampling transect during two different years (at water depths of 550 and 1,100 m during 1993 and at a water depth of 2,050 m during 1996). The particle interceptor traps (PITs) were based on the VERTEX design used by Martin et al. (1987). Duplicate traps were filled with filtered seawater, and a brine solution (0.2 kg NaCl L^{-1}) was siphoned into the bottom 10 cm of each trap before deployment at each sampling depth. After recovery, trapped material was filtered onto precombusted glass fiber filters (Whatman, GF-F) and macrozooplankton (swimmers) were removed under low-power magnification. Samples were then dried at 65°C and stored frozen or desiccated for later analysis. Multiple traps were deployed at several depths for 3–4 d on a subsurface mooring. Bulk organic carbon content of trap material was determined using a Leeman Laboratories CHN elemental analyzer.

Results and discussion

For both the Washington and Mexican transects, carbon rain rates calculated from carbon oxidation rates and carbon burial rates were highest at the shallowest station and decreased as water depth increased (Table 1, Fig. 2). Off Washington State, shallow values were 15 to 20 mmol m^{-2} d^{-1} and decreased with increasing depth to values approaching 3 mmol m^{-2} d^{-1} at 1,000 m depth. On average 19% of the total rain rate was accounted for by burial, with a maximum value of 33% and a minimum of 10%. Off northwest Mexico shallow water rates were considerably lower, about 7 mmol m^{-2} d^{-1} at 100 m, but they nevertheless decreased to values comparable to those at similar, deeper depths off Washington. However, in contrast to the Washington margin, burial accounted for a much greater portion of the rain rate, on average 30% with values as high as 44%. The higher burial rates off Mexico as compared to Washington have been reported previously (Hartnett et al. 1998)

There are two notable differences between the carbon rain rate profiles observed off Washington State and northwest Mexico. The first major difference is that shallow values were significantly higher off Washington than off Mexico, with the second being that, while values decreased with depth by nearly an order of magnitude off Washington State, they decreased by only a factor of about 2.5 off Mexico. The lower carbon rain rates off Mexico result from lower values of both the carbon oxidation component and the burial component of the rain rate (Fig. 2). These generally lower rates

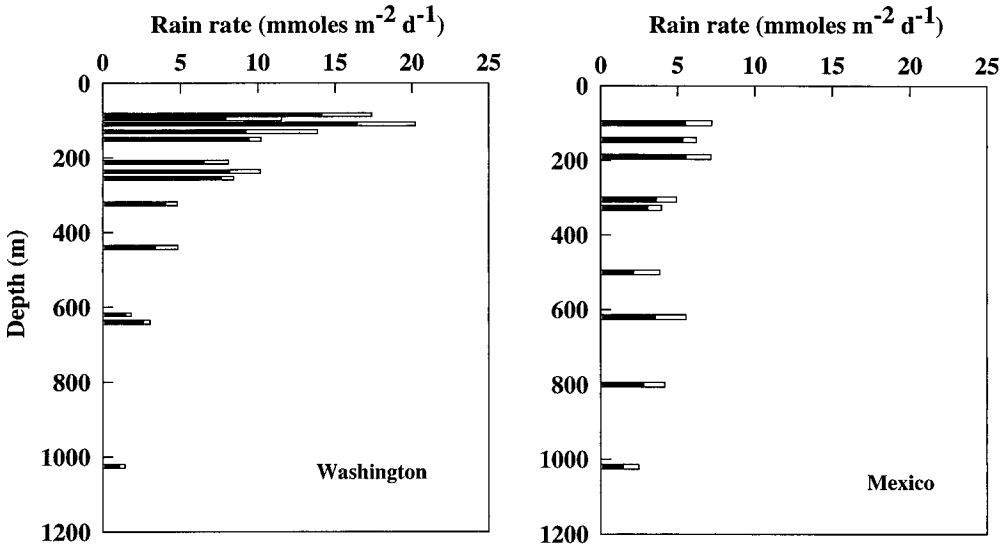

Fig. 2. Carbon rain derived from the sedimentary data for the two Washington and Mexican transects. Rain rates are shown as histograms of the two components with the solid portion representing benthic carbon oxidation rate and the white portion showing the carbon burial component.

likely reflect a smaller initial supply for the sinking flux off Mexico. Primary production rates in the Mexican study area have been estimated to be 100 to 200 g C m^{-2} yr^{-1}, or about 22 to 44 mmol C m^{-2} d^{-1} (Longhurst et al. 1995), while off Washington the primary production has been determined as 300–500 g C m^{-2} yr^{-1}, or 68 to 115 mmol C m^{-2} d^{-1} (Perry et al. 1989). This difference alone could easily explain the differences between the shallow rain rates in the two areas. Given a ratio of export production to total production, or *e*-ratio, of about 0.15 (calculations based on table 4 in Dunne et al. 1997) and productivities in the middle of the ranges given above (33 mmol C m^{-2} d^{-1} for Mexico and 92 mmol C m^{-2} d^{-1} for Washington), one would predict export fluxes of 5.0 and 13.7 mmol C m^{-2} d^{-1} for the Mexican and Washington margins, respectively. These values are in reasonable agreement with the observations (Tables 1 and 2). Thus, the lower carbon rain rates to shallow water Mexican sediments may primarily reflect lower primary productivity of that area.

Table 2. Average sediment trap rain rates derived from duplicate traps at each depth for three deployments off northwest Mexico (mmoles C $m^{-2}d^{-1}$; ± gives the range). The numbers associated with the cruise give the year and the letters a and b distinguish two different trap deployments during the same cruise. Locations and water depths for the deployments were as follows: NH93a, 22°36.07′N, 106°29.19′W, 500 m; NH93b, 22°31.09′N, 106°39.07′W, 1100 m; NH96, 22°25.24′N, 107°02.11′W, 2050 m.

Cruise	Trap depth (m)	Carbon flux
NH93b	150	6.3 ± 1.1
NH93a	200	7.6 ± 0.91
NH96	250	5.9 ± 1.2
NH93b	250	5.4 ± 1.6
NH93b	350	3.5 ± 0.21
NH93a	400	6.1 ± 0.24
NH93b	450	4.4 ± 0.75
NH96	500	4.2 ± 0.22
NH93a	600	5.4 ± 0.11
NH96	800	3.2 ± 0.59
NH93a	900	4.7 ± 0.33
NH96	1100	3.5 ± 0.32

The depth attenuation of the rain rate also appears significantly different between Mexico and Washington, and this difference is more difficult to explain. A general decrease in oceanic carbon rain rate with depth is well documented from many previous sediment-trap studies, and it has been frequently parameterized as a power function of depth:

$$\text{Flux}_z \propto z^{-\alpha}$$

where z is depth and α is an attenuation coefficient. We fit our carbon rain rates as estimated from oxidation plus burial from both the Washington and Mexican margins with a power function of the type proposed by Martin et al. (1987):

$$C_R = C_{R\,100\text{m}}(z/100)^{-\alpha}$$

where the carbon rain rate, C_R, for any given depth is normalized to the rain rate at 100 m (Fig. 3). Data from the Washington margin were fit well with the attenuation coefficient $\alpha = 0.93$ and $C_{R\,100\text{m}} = 16.2$ ($r^2 = 0.89$). In contrast, and as would be expected from Fig. 2, the Mexican data were fit with a much lower attenuation, $\alpha = 0.36$, and a $C_{R\,100\text{m}} = 7.4$ ($r^2 = 0.77$). Because on average 80% of the calculated rain rate was due to the carbon oxidation term, it, primarily, determined the regression characteristics. However, when fit separately, both components of the rain rate had nearly the same power-curve attenuation off Washington, while off Mexico the sedimentation rate was nearly constant with depth.

Sediment-trap fluxes are also an estimate of rain rate and the trap fluxes from the Mexican margin are presented in Table 2 and Fig. 4. Fluxes varied from a high of 7.6 mmol C m^{-2} d^{-1} in the shallow traps to 3.5 mmol C m^{-2} d^{-1} in the deep trap at 1,100 m. The agreement between the traps deployed at the three different locations was, in general,

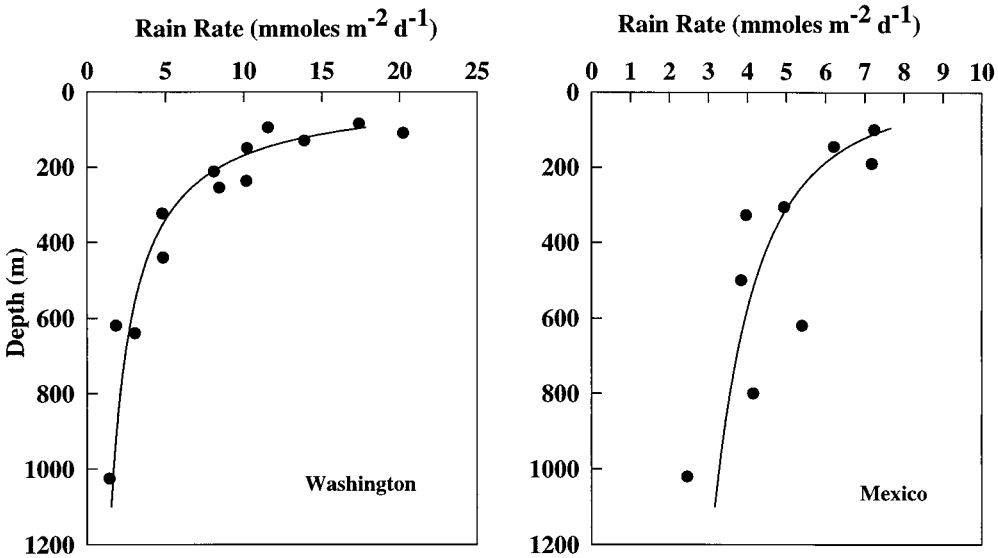

Fig. 3. Power-curve regressions of the sediment-derived carbon rain rates (C_r) for the Washington margin ($C_r = 16.2 \cdot [z/100]^{-0.93}$) and the Mexican margin ($C_r = 7.4 \cdot [z/100]^{-0.36}$). Note that the scale on the *x*-axis is different between the two panels.

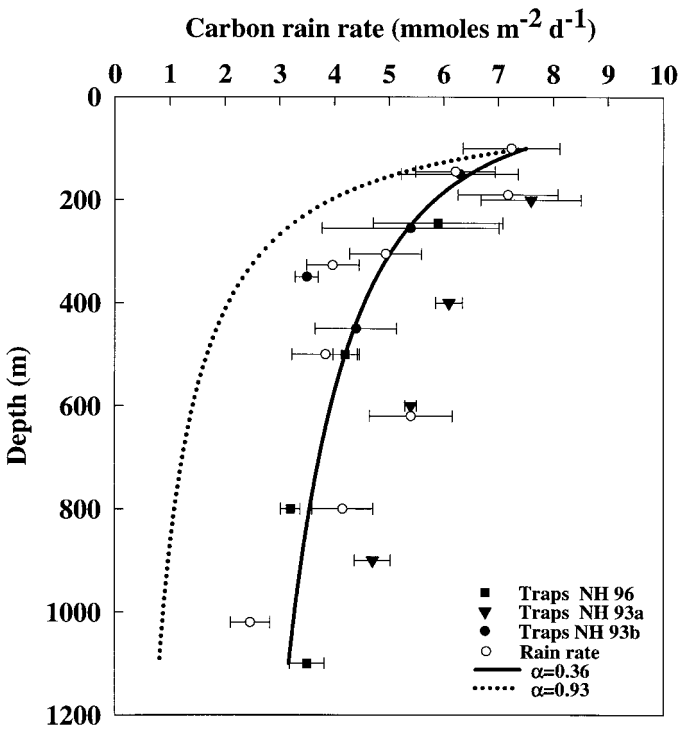

Fig. 4. Sediment-trap–derived rain rates (solid symbols) from three deployments of trap strings and rain rates derived from carbon oxidation and burial (open circles) on the Mexican margin. Also shown are a 100-m rain rate of 7.5 mmoles C m^{-2} d^{-1} attenuated as the Martin et al. (1987) power function with the attenuation coefficient derived from the Mexican data, $\alpha = 0.36$ and the attenuation coefficient derived from the Washington data, $\alpha = 0.93$. Error bars on the trap data show the range of replicate sediment-trap measurements, while error bars on oxidation plus burial derived rain rates are standard deviations.

good. The sediment-trap rain rate estimates at any given depth are also in good agreement with the rain rate estimates for that same depth as calculated from carbon oxidation and burial. Not only are the trap-derived rain rates in good agreement with the ones calculated from the sediment data, both show the same decreased attenuation through the water column. Also shown on Fig. 4 are the regression equations for the attenuation rate functions fit to the sediment-derived rain rates from both margins. Two of the three sediment-trap deployments follow the Mexican margin attenuation regression reasonably well. The third trap deployment had somewhat higher rain rates at all depths, but the attenuation of the rain rate with depth was about the same as for the other trap deployments and the rain rates calculated from the sedimentary data.

The attenuation of the carbon rain rate calculated for the Washington margin data is in excellent agreement with those determined from sediment-traps studies in other, non–oxygen-deficient areas. Published values for the attenuation coefficient from various oceanic areas range between 0.628 and 1.138, with the average being about 0.85 (Karl and Knauer 1984; Martin et al. 1987; Bishop 1989; Bender et al. 1992; and others). The Washington margin sediment-derived attenuation coefficient can also be compared directly with a nearby trap-derived one. Boyd et al. (1999) present data from an array of eight sediment traps deployed between 100 m and 1,000 m at Ocean Station Papa (50°N, 145°W). Their data are also well fit to a Martin et al. (1987) type power function with an attenuation coefficient of $\alpha = 0.87$ ($r^2 = 0.87$). The general agreement between our sediment-derived attenuation rate and the trap-derived one suggests that the sediment-derived attenuation is representative of water-column rain rate in the sub-Arctic North Pacific. The Washington margin attenuation coefficient is also in agreement with the estimate for the depth attenuation of the sedimentary carbon oxidation rate for the California margin, $\alpha \cong 0.85$ (Berelson et al. 1996).

In contrast, the attenuation rate for the Mexican margin data set is one of the smallest reported values. Interestingly, similar diminished carbon rain rate attenuation has been reported for the other two major oxygen-deficient zones. A comparable low value, $\alpha = 0.36$, was derived from sediment traps deployed off the coast of Peru (Martin et al. 1987), where there is a similar oxygen-deficient water column in the same general depth interval as off Mexico. Likewise, Haake et al. (1992) observed carbon fluxes through the oxygen-deficient zone of the Arabian sea that were significantly greater than would be predicted by a Martin et al.-type relationship, i.e., less attenuation.

The lesser decrease in vertical carbon rain rate off Mexico relative to Washington must be due either to an additional source of carbon to these sediments, other than just the vertical flux of particles from the mixed layer, or to inhibited degradation of sinking organic material. Additional sources of carbon might include chemolithotrophic production within the water column of the oxygen-deficient zone (Karl et al. 1984) and possibly off-shelf transport of primary production originating on the shelf (Reimers et al. 1992; Anderson et al. 1994; Hensen et al. 1998). Assuming that the average sediment-trap attenuation rate from the literature represents the ''normal'' oceanic situation, we can calculate the off-shelf transport required to account for the decrease in flux attenuation. The fit to the Mexican margin calculated rain rates yields a 100 m rate of 7.4 mmol C m^{-2} d^{-1}, and depth integration of the rain rate equation results in an average shelf (100–200 m) rain rate of 6.5 mmol C m^{-2} d^{-1} and an average slope (200–1,000 m) rate of 4.1 mmol C m^{-2} d^{-1}. If the same 100-m rate is attenuated with the ''normal'' attenuation of $\alpha = -0.85$, the shelf and slope rates become 5.4 and 1.9 mmol C m^{-2} d^{-1}, respectively. These rates are lower because the higher attenuation results in more of the carbon being oxidized in the water column. Thus, the two attenuation rates predict continental slope rates that differ by about 2.2 mmol C m^{-2} d^{-1}. Could this difference be a result of off-shelf transport? A comparison of the production rates and oxidation rates for the Mexican shelf suggests that this is an unlikely scenario. Given a high primary production estimate of 44 mmol C m^{-2} d^{-1} and an *e*-ratio of 0.15 (Dunne et al. 1997), the flux out of the euphotic zone would be 6.6 mmol C m^{-2} d^{-1}. As the area of the shelf and slope are about equal in the study region, the 6.6 mmol C m^{-2} d^{-1} is barely enough to support the approximate export flux of 7.4 mmol C m^{-2} d^{-1} (i.e., the rain rate at 100 m), let alone leave a surplus for off-shelf transport that is one-third as great as the export production. A similar argument can be made for chemolithotrophic production as the 2.2 mmol C m^{-2} d^{-1} ''excess'' carbon oxidation on the Mexican margin is much greater than the maximum rate of chemolithotrophic production (0.04 mmol C m^{-2} d^{-1}) observed by Karl et al. (1984).

The alternative, decreased carbon oxidation during transit through the water column seems more likely. Denitrification is the major carbon oxidation pathway in the oxygen-deficient water column (Codispoti and Richards 1976). The lack of oxygen, itself, could be responsible for diminished attenuation as bacteria attached to sinking particles may not be able to rapidly switch from oxygen consumption to denitrification or there may be insufficient time for new populations of denitrifying bacteria to become established. Although it remains the subject of considerable controversy, it has been hypothesized that organic matter decomposition under anaerobic conditions is not as rapid and/or complete as oxic decomposition (*see* discussion in Hedges et al. 1999). Indeed, in their comparison of sedimentary carbon diagenesis on the Mexican and Washington margins, Hartnett et al. (1998) found the relative oxidation of carbon in the sediments to be reduced off Mexico as compared to Washington as well. Also, Van Mooy et al. (in press) have shown that sedimenting material trapped just below the euphotic zone of the oxygen-deficient Mexican margin did not degrade as efficiently under suboxic denitrifying conditions as under fully oxic conditions. Thus, the experiments of Van Mooy et al. strongly support the hypothesis that organic matter sinking through the oxygen-deficient water column is not degraded as fully as under oxic conditions. Finally, another possible mechanism for reduced carbon oxidation could result from the diminished populations of zooplankton that have been observed within oxygen-deficient waters (Wishner et al. 1998). Zooplankton are the primary top-down control on particle export from the surface and are important in the reprocessing and repackaging of sinking particles (Wassman 1998) and their absence, or diminished presence, could result in less remineralization of sinking organic material (Wishner et al. 1998).

Regardless of the mechanism, passage of a substantially greater amount of the export production to the deep-sea and sediments when an oxygen-deficient zone is present has significant consequences for marine geochemistry and paleoceanographic models. Currently, the three major oxygen-deficient zones, the eastern tropical North and South Pacific and the Arabian Sea, occupy only about 10% of the world's oceans area. The differences between the Mexican and Washington margin flux equations suggest that per unit of export production, four times more carbon reaches 1,000 m when there is an oxygen-deficient zone present. (Compare solid and dotted line in Fig. 4.) Thus, if the areal extent of oxygen-deficient zones were increased in the past, as is predicted by some paleoclimate models (Sarmiento and Sundquist 1992), a much greater percentage of export production would reach the deep water column and sediments and could further enhance sequestration of carbon in the deep ocean.

References

ANDERSON R. F., G. T. ROWE., P. KEMP, S. TRUMBORE, AND P. E. BISCAYE. 1994. Carbon budget for the mid-slope depocenter of the Middle Atlantic Bight. Deep-Sea Res. II **41:** 669–703.

BENDER M., H. DUCKLOW, J. KIDDON, J. MARRA, AND J. MARTIN. 1992. The carbon balance during the 1989 spring bloom in the North Atlantic Ocean, 47°N, 20°W. Deep-Sea Res. **39:** 1707–1726.

BERELSON, W. M., J. MCMANUS, K. H. COALE, K. S. JOHNSON, T. KILGORE, D. BURDIGE, AND C. PILSKALN. 1996. Biogenic matter diagenesis on the sea floor: A comparison between two continental margin transects. J. Mar. Res. **54:** 731–762.

BISHOP, J. 1989. Regional extremes in particulate matter composition and flux: Effects on the chemistry of the ocean interior.

In W. H. Berger, V. S. Smetacck, and G. Wefer [eds.], Productivity of the ocean: Present and past. Wiley.

BOYD, P. W., AND OTHERS. 1999. Transformations of biogenic particulates from the pelagic to deep ocean realm. Deep-Sea Res. II **46:** 2761–2792.

BROECKER, W. S., AND G. M. HENDERSON. 1998. The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes. Paleoceanography **13:** 352–364.

CODISPOTI, L. A., AND F. A. RICHARDS. 1976. An analysis of the horizontal regime of denitrification in the eastern tropical North Pacific. Limnol. Oceanogr. **21:** 379–388.

DEVOL, A. H., AND J. P. CHRISTENSEN. 1993. Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. J. Mar. Res. **51:** 345–372.

DUNNE, J. P., J. W. MURRAY, J. YOUNG, L. S. BALISTRIERI, AND J. BISHOP. 1997. ^{234}Th and particle cycling in the central equatorial Pacific. Deep-Sea Res. II **44:** 2049–2083.

FROELICH, P. N., AND OTHERS. 1979. Early oxidation of organic matter in pelagic sediments of the equatorial Atlantic: Suboxic diagenesis. Geochim. Cosmochim. Acta **43:** 1075–1090.

HAAKE, B., V. ITTEKKOT, V. RAMASWAMY, R. R. NAIR, AND S. HONJO. 1992. Fluxes of amino acids and hexosamines to the deep Arabian Sea. Mar. Chem. **40:** 291–314.

HARTNETT, H. E., R. G. KEIL, J. I. HEDGES, AND A. H. DEVOL. 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature **391:** 572–574.

HEDGES, J. I., F.-S. HU. A. H. DEVOL, H. E. HARTNETT, E. TSAMAKIS, AND R. G. KEIL. 1999. Sedimentary organic matter preservation: A test for selective degradation under oxic conditions. Am. J. Sci. **299:** 529–555.

———, AND J. H. STERN. 1984. Carbon and nitrogen determinations of carbonate containing solids. Limnol. Oceanogr. **29:** 657–663.

HENSEN, C., H. LANDENBERGER, M. ZABEL, AND H. D. SCHULZ. 1998. Quantification of diffusive benthic fluxes of nitrate, phosphate and silicate in the southern Atlantic Ocean. Glob. Biogeochem. Cycles **12:** 193–210.

KARL, D. M., AND G. A. KNAUER. 1984. Vertical distribution, transport and exchange of carbon in the northeast Pacific Ocean: Evidence for multiple zones of biological activity. Deep-Sea Res. **31:** 245–270.

———, ———, J. H. MARTIN, AND B. B. WARD. 1984. Bacterial chemolithotrophy in the ocean is associated with sinking particles. Nature **309:** 54–56.

KRISTENSEN, E., A. H. DEVOL, AND H. E. HARTNETT. 1999. Organic matter diagenesis in sediments on the continental shelf and slope of the Eastern Tropical and temperate North Pacific. Cont. Shelf Res. **19:** 1331–1351.

LONGHURST, A., S. SATHYENDRANATH, T. PLATT, AND C. CAVERHILL. 1995. An estimate of global primary production in the ocean from satellite radiometer data. J. Plankton Res. **17:** 1245–1271.

MARTIN, J. H., G. A. KNAUER, D. M. KARL, AND W. W. BROENKOW. 1987. VERTEX: Carbon cycling in the northeast Pacific. Deep-Sea Res. **34:** 267–285.

NITTROUER, C. A., D. J. DEMASTER, B. A. MCKEE, N. H. CUTSHALL, AND I. L. LARSEN. 1983/1984. The effect of sediment mixing on ^{210}Pb accumulation rates for the Washington continental shelf. Mar. Geol. **54:** 201–221.

PERRY, M. J., J. C. BOLGER, AND D. C. ENGLISH. 1989. Primary production in Washington coastal waters. *In* M. L. Landry and B. M. Hickey [eds.], Coastal oceanography of Washington and Oregon. Elsevier.

REIMERS, C. E., R. A. JAHNKE., AND D. C. MCCORKLE. 1992. Carbon fluxes and burial rates over the continental slope off California with implications for the global carbon cycle. Glob. Biogeochem. Cycles **6:** 199–224.

SARMIENTO, J. L., AND E. T. SUNDQUIST. 1992. Revised budget for the oceanic uptake of anthropogenic carbon dioxide. Nature **356:** 589–593.

VAN MOOY, B. A. S., R. G. KEIL, AND A. H. DEVOL. In press. Enhanced flux of particulate organic matter in oxygen deficient waters: Impact of suboxia on early degradation. Geochim. Cosmochim. Acta.

WASSMAN, P. 1998. Retention versus export food chains: Processes controlling sinking loss from marine pelagic systems. Hydrobiologia **363:** 29–57.

WISHNER, K. F., M. M. GOWING, AND C. GELFMAN. 1998. Mesozooplankton biomass in the upper 1000 m in the Arabian Sea: Overall seasonal and geographic patterns, and relationship to oxygen gradients. Deep-Sea Res. II **45:** 2405–2432.

Received: 11 December 2000
Accepted: 10 July 2001
Amended: 24 July 2001