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Impact of suboxia on sinking particulate organic carbon: Enhanced carbon flux and preferential degradation of amino acids via denitrification

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Abstract—Fluxes of particulate organic carbon (POC) through the oxygen deficient waters in the eastern tropical North Pacific were found to be relatively less attenuated with depth than elsewhere in the eastern North Pacific. The attenuation coefficient (b) for the flux was found to be 0.40 versus the composite value of 0.86 determined by Martin et al. (1987). To examine this further, sinking POC was collected using sediment traps and allowed to degrade in oxic and suboxic experiments. Using a kinetic model, it was found that degradation proceeded at similar rates (roughly 0.8 day^{-1}) under oxic and suboxic conditions, but a greater fraction of bulk POC was resistant to degradation in the suboxic experiments (61% vs. 23%). Amino acids accounted for 37% of POC collected at 75m, but following degradation the value dropped to 17% and 16% in the oxic and suboxic experiments respectively. POC collected from 500m was 10% amino acids. The non-AA component of POC collected at 75m was not degraded under suboxic conditions, while under oxic conditions it was. These results suggest that microbes degrading OC under suboxic conditions via denitrification preferentially utilize nitrogen-rich amino acids. This preferential degradation of amino acids suggests that 9% more nitrogen may be lost via water column denitrification than is accounted for when a more "Redfieldian" stoichiometry for POC is assumed. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The flux of particulate organic matter through the sea links atmospheric and oceanic processes, fuels the growth of heterotrophic organisms in both water column and sedimentary systems, and provides input to the long-term sedimentary record. The vast majority (>99%) of sinking organic matter is degraded within the upper water column (Wakeham and Lee, 1993; Wakeham et al., 1997). Generally, the attenuation of this flux with depth in the water column has been thought to be fairly uniform throughout the oceans (Martin et al., 1987). However, there are indications that particles sinking through suboxic water columns may escape remineralization more effectively than their counterparts sinking through oxic water columns (Haake et al., 1992; Hartnett, 1998; Devol and Hartnett, 2001).

In suboxic water columns, denitrification is the primary mode of organic matter respiration. Roughly one third of global denitrification occurs in marine suboxic waters, and thus these regions represent a large net loss of nitrogen from the ocean (Codispoti and Christensen, 1985). It is thought that during denitrification, both NO_3^- and the nitrogen in organic matter is converted to N_2 (Codispoti and Christensen, 1985; Gruber and Sarmiento, 1997). However, little is known about how the reactivity and composition of organic matter affects the efficiency of denitrification, and vice-versa. In fact, it is equivocal whether the lability of organic matter is influenced or determined by the electron acceptor used during oxidation (references in Hulthe et al., 1998). While there are numerous articles comparing oxic degradation with sulfate reduction (Lee 1992, Harvey et al., 1995, Hulthe et al., 1998; Dauwe et al., 2001), to our knowledge, there are no studies that specifically compare the degradation of organic matter via oxic respiration and denitrification in marine waters.

Whether there are differences in the rates of oxic and anoxic degradation of organic matter appears to be related to the time scale at which the observations are made. Lee (1992) studied the degradation of simple dissolved organic substrates (e.g., putrescine, acetate) in seawater incubations that lasted a few hours. She concluded that they were degraded at similar rates under oxic and anoxic conditions. However, Dauwe et al. (2001) examined the degradation of sedimentary organic matter over the period of a month, and concluded that only when degradation rates were slow was there a difference between oxic and anoxic degradation. Similarly, Harvey et al. (1995) in an experimental study of phytoplankton decay lasting several months, observed a difference in the degradation rate between oxic and anoxic experiments. Harvey et al. (1995) also noticed that a substantial fraction of the POC remained following degradation under anoxic conditions while under oxic conditions POC was efficiently degraded. Further, the molecular level analyses by Harvey et al. (1995) revealed that proteins were completely degraded under both conditions, but the extent to which carbohydrates, lipids, and uncharacterizable organic matter was degraded was different.

In this study, we evaluated the downward flux of organic matter and its degradation via denitrification in the oxygen deficient zone (ODZ) of the eastern tropical North Pacific (ETNP). The organic matter flux was measured using sediment traps, and trapped material from surface waters was incubated under both oxic and suboxic conditions. In addition to monitoring the flux and degradation of total organic matter, the content and composition of amino acids were analyzed because they represent a significant component of the labile sinking material (Cowie and Hedges, 1992a; Wakeham and Lee, 1993;

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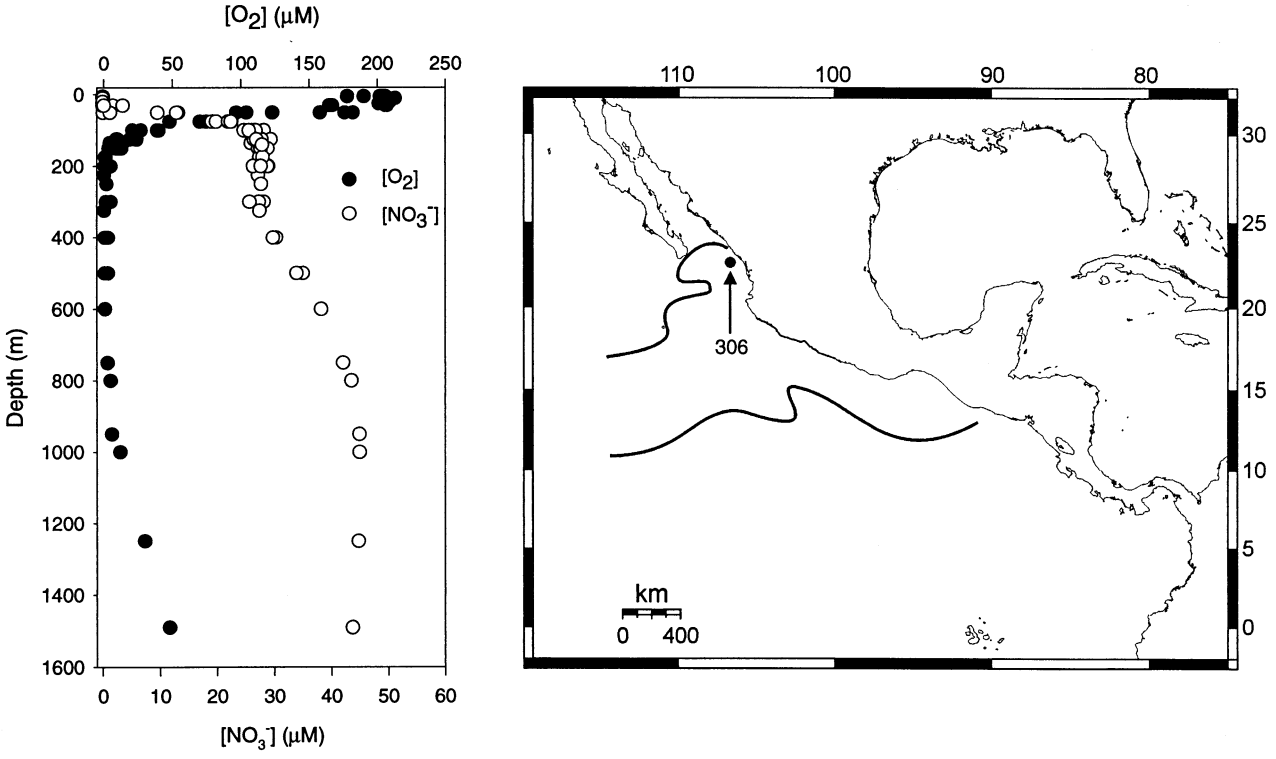

Fig. 1. Left panel: Water column profile of O_2 and NO_3^- concentrations from the suboxic zone of the ETNP. The data were collected at stations that showed a secondary NO_2^- maximum (data not shown), which is indicative of denitrification. Right panel: Map of Central America and the ETNP. The location of Station 306 is shown. The lateral border of the persistent secondary NO_2^- maximum (from Codispoti, 1973) is indicated by the curved lines.

Wakeham et al., 1997). The incubation data were fit to a two component kinetic model (Westrich and Berner, 1984) to determine both changes in degradation rate and the abundance of non-reactive components. Based on our data, it appears that the modes of oxic and suboxic degradation of sinking POC are distinct, and that these differences may impact our current understanding of the coupling between the global cycles of carbon and nitrogen during denitrification.

2. METHODS

Samples were collected and experiments conducted aboard the R/V *New Horizon* in February and March 1999. Data for this study originate from one station located on the continental slope, 50 km southwest of Mazatlan, Mexico, at 22° 24′ N and 106° 18′ W (Fig. 1). The depth of the water was approximately 530 m. Water samples for O_2 and NO_3^- analyses were collected throughout the water column using a CTD equipped with 20 L Niskin bottles and a transmissometer. Dissolved O_2 concentrations were determined by a modified Winkler titration method and NO_3^- concentrations were determined by a colorimetric method (Strickland and Parsons, 1972).

Cylindrical sediment traps, nearly identical in design to those employed by Martin et al. (1987) and described by Knauer et al. (1979) were deployed at 130, 230, 280, 330, 380, and 480 m below the surface. These particular traps had an effective trapping area of 0.0053 m^2 and a height/width ratio of 8.7. The cylinders were partially filled with dense solution of seawater and NaCl (final $\rho = 1.05$ g cm^{-3}) to inhibit mixing and retard in situ degradation (Lee et al., 1992; Hedges et al., 1993). The traps were moored for 2.9 d. Following low-vacuum filtration of the trapped material onto GF/F filters, zooplankton swimmers were meticulously picked off of the filter under a dissecting microscope. The filters were quick-frozen for transport to the laboratory at the University of Washington where they were dried at room temperature in a desiccator until their weight was constant. Carbon and nitrogen were quantified using a Carlo-Erba CHN analyzer as described by Hedges and Stern (1984).

Larger, funnel-shaped sediment traps (0.4072 m^2 trapping area), designed to recover large quantities of particles for organic geochemical analyses, were moored at 75m and 500m below the surface during two separate, successive deployments of 3.9 d. This trap was identical to that described by Peterson et al. (1993), except the lower valve assembly (IRS-valve), designed for time series collection and exclusion of swimmers, was removed and replaced with a single polycarbonate cylinder. Because of this modification, deploying the trap with a dense solution is nearly impossible. Instead, 200g of solid NaCl in a small polypropylene bottle with holes drilled in it was placed in the bottom of the cylinder to create, upon dissolution, a density layer similar to the cylindrical traps. Although, earlier work has suggested that funnel-shaped traps may not trap the exact same material as cylindrical traps (Gardner, 1980a,b; Honjo et al., 1992), we assume that these differences are negligible. Following retrieval of the trap, the contents of the polycarbonate cylinder were centrifuged at $\approx 1000 \times g$ for 15 min. Again, zooplankton swimmers were immediately removed from the particulate matter under low-power magnification while on ice. The resultant particles (nearly 1g) were then resuspended in 100 mL of seawater and quantitatively split into fractions that were either used immediately for degradation experiments or frozen for later analysis.

Incubation experiments were initiated in one-liter glass bottles filled with 500ml of seawater collected either from above the oxygen deficient zone (ODZ) (75m) or within the ODZ (275m) and designated "oxic" or "suboxic" respectively. Five experiments were initiated under each condition. A quantitative fraction of particulate slurry from the large traps (as described above) was introduced within two hours of retrieval. A small, clean magnetic stir bar was placed in each bottle. The bottles were sealed with silicon stoppers and secured with electri-

cal tape. The bottles were then briefly purged with gas (O_2 or N_2) flowing through a needle that was pushed through the stopper until the tip was below the seawater surface in the bottles. A separate needle was also pushed through the stopper to vent the headspace such that the pressure in the sealed bottles did not greatly exceed 1 atm. The O_2 concentrations in the seawater were slightly supersaturated in the oxic experiments and below detection in suboxic experiments. The bottles were then very gently stirred (approximately 100 rpm) and incubated for five days in a cold room (6°C) in the dark. Gas samples for pCO_2 analysis were withdrawn from the headspace of the experiment using a gas tight syringe with the needle inserted directly through the silicon stopper. The volume was simultaneously replaced with pure N_2 from a needle connected to a gas bottle (<1 atm). Similarly, water samples were withdrawn from the experiments using an acid cleaned syringe and a needle long enough to reach below the water level without inverting the bottles.

Throughout the incubations dissolved NO_3^- was determined as above, and O_2 was measured using a calibrated microelectrode. Total alkalinity (TA) was determined by Gran titration, which along with pH (NBS scale) was used to calculate dissolved inorganic carbon concentrations [DIC] using CO2SYS software (Ernie Lewis, Brookhaven National Laboratory; GEOSECS constants). H_4SiO_4 and PO_4^{2-} were monitored by standard methods (Strickland and Parsons, 1972) and were not present in concentrations large enough to interfere with TA analyses (30 to 60 μM and 1 to 4. μM respectively). DOC was determined by high temperature oxidation, as described by Arnarson and Keil (2000). The pCO_2 in the headspace was measured by isothermal molecular sieve gas chromatography, using a two-point (air and pure N_2) calibration.

The amino acids in particles from the large traps and degradation experiments were analyzed as described by Cowie and Hedges (1992b). Particles were spiked with charge-matched recovery standards: α-aminoadipic acid (AAAA), for acidic amino acids; γ-methylleucine (Mleu), for neutral amino acids; and δ-hydroxylysine (Hlys), for basic amino acids. The samples were then hydrolyzed with 6N HCl under N_2 for 70 min at 150°C. Hydrolysates were neutralized with 0.2N H_3BO_3 buffer (pH = 9.5) and dried under vacuum. The residues were then reconstituted in water and the pH adjusted to 8 to 8.5 with buffer. They were transferred to high-performance liquid chromatography (HPLC) autosampler vials through cleaned cellulose filters. Using the autosampler/derivatization system described by Keil et al. (1998) but without addition of acetic acid, fluorescent (OPA) derivatives of primary amines were injected into a Waters HPLC system. Amino acid OPA derivatives, detected by fluorescence, were quantified by normalizing peak areas to response factors for individual amino acids determined from standard mixtures. Then the three classes of amino acids were further normalized to the recovery of the charge-matched standards. The total quantity of carbon from amino acids in particles is expressed as the fraction of POC (AA/POC). The distribution of individual amino acids is presented as mole percent of the total amino acid yield.

All measurements presented in this paper are given as the mean ± standard deviation. Corrections were made to all data for the slight changes in the volume due to sampling of the degradation experiments.

3. RESULTS

3.1. Water Column Chemistry and POC Fluxes

The ODZ of the ETNP has been well documented by previous workers, and denitrification is the dominant respiratory process in these suboxic waters (Cline and Richards, 1972; Codispoti, 1973; Devol et al., 1976). We also observed the characteristic signature of denitrification in the ODZ (Fig. 1). O_2 rapidly decreased with depth below the mixed layer depth (60 m), and O_2 deficient waters impinged on the sediments (Fig. 1). The NO_3^- concentrations rose sharply bellowed the mixed layer, were fairly constant between ≈150 and ≈350, but increased again below 400m. The 150 to 350 m depth zone is where denitrification was most intense (Codispoti, 1973), and consumption of nitrate was responsible for the diminished NO_3^- accumulation in this profile.

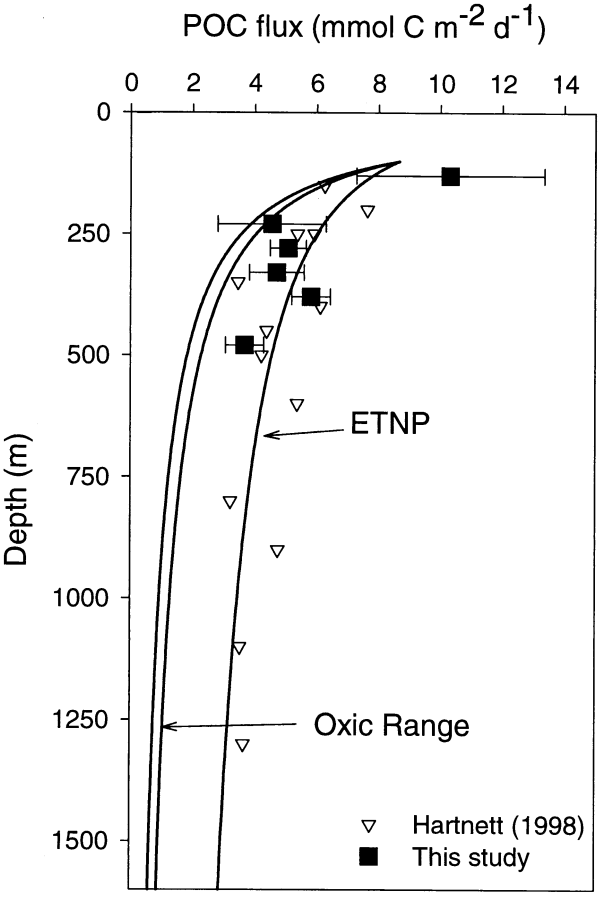

Fig. 2. Profile of the flux of sinking POC in the ETNP. Data from this study are from Station 306 while those of Hartnett (1998) are from stations further offshore. The ETNP line is from Eqn. 1 in the text substituting our values for F_{100} and *b*. The other lines are solutions for Eqn. 3 substituting the range of attenuation coefficients (0.833 to 0.968) given by Martin et al. (1987) from stations outside the suboxic zone in the eastern North Pacific.

Numerous transmissometer profiles (22) were obtained in the vicinity of the traps when they were deployed, and transmission was relatively constant (92 to 93%). Further, at no time was transmission less than 90% at depths above 500m.

Downward fluxes of POC, as determined from the small cylindrical traps, decreased rapidly from 10.3±7.9 mmol C m^{-2} d^{-1} at 130 m to 3.7±0.6 at 480 m (Fig. 2). The C/N ratios of sinking POC showed a concomitant increase from 6.9 to 9.1, similar to what was observed by Martin et al. (1987) throughout the North Pacific. No inorganic carbon ($CaCO_3$) was detected in the particles. Primary production rates at this site have been observed in the range of 22 to 44 mmol Cm^{-2} d^{-1} (Longhurst et al., 1995).

The fluxes are in good agreement with the sediment trap fluxes found previously by Hartnett (1998) and Devol and Hartnett, (2001), which were measured with the same cylindrical traps used in this study. Taken together, POC flux profiles

were fit with a power function of the form adopted by Martin et al., (1987):

$$F_z = F_{100}\,(z/100)^{-b} \quad (1)$$

where F_z is the flux at some depth z in meters, F_{100} is the POC flux at 100m depth, and b is the attenuation coefficient. Our fit yielded an F_{100} of 8.66 ± 0.86 and a b of 0.400 ± 0.079. The attenuation coefficient is a conceptually useful parameter because it quantitatively describes the degradation of sinking POC. The more attenuated a flux is, the more intense the degradation of POC, and hence, the higher the numerical value of b.

3.2. Experimental Degradation of POC Trapped at 75m

At initiation of the first set of degradation experiments, POC collected from the 75m funnel-shaped trap was added to each of the ten total incubation bottles at an average concentration of 252 ± 39 μM. The initial C/N was 8.5 ± 1.0. DIC in the replicate experiments increased from initial average values of 2077 ± 58 μM and 2107 ± 38 μM in the five oxic and five suboxic bottles respectively to 2222 ± 10 μM and 2187 ± 25 μM at their termination (Fig. 3). Initial average pCO_2 increased from 345 ± 52 μatm and 320 ± 15 μatm to 799 ± 62 μatm and 603 ± 82 μatm (Fig. 3). The pCO_2 concentrations determined by gas chromatography were slightly higher (<10%) than those calculated independently from TA and pH measurements. Initial average DOC concentrations were 115 ± 66 μM in the oxic and 97 ± 56 μM in the suboxic experiments and were nearly constant throughout the duration of the experiments; the final DOC concentrations were statistically indistinguishable from the initial concentrations. Consequently, it was assumed that DOC was constant.

The average NO_3^- concentration was constant (26 ± 1 μM) in the five oxic experiments. However in the five suboxic experiments NO_3^- was drawn down from 27 ± 1 μM to detection limit by 1.5 d indicating that denitrification was occurring. During the second day, NO_3^- was added to maintain suboxic conditions in the experiments bringing the concentration up to 61 ± 2 μM and denitrification resumed immediately bringing NO_3^- down to an average of 48 ± 2 μM by the end of the experiment. O_2 concentrations never decreased below 110% saturation in the oxic experiments, and O_2 was below detection limit in all suboxic experiments at all times. At no time was hydrogen sulfide gas detected in samples taken from any of the incubations.

Using volume-normalized initial POC (POC_o) and the time-monitored DIC and pCO_2 data, the degradation of POC was calculated. The ratio of POC at any time during the experiments to initial POC (POC_t/POC_o) was calculated for each separate experiment by the following formula:

$$POC_t/POC_o = 1 - (DIC_t - DIC_o)/POC_o - (pCO_{2t} - pCO_{2o})/POC_o \quad (2)$$

The results of these calculations versus time (Fig. 3) were fit with a kinetic model curve describing the first-order decay of POM as adapted from Westrich and Berner (1984). A two-term equation yielded the best fit to the experimental POC_t/POC_o degradation curves:

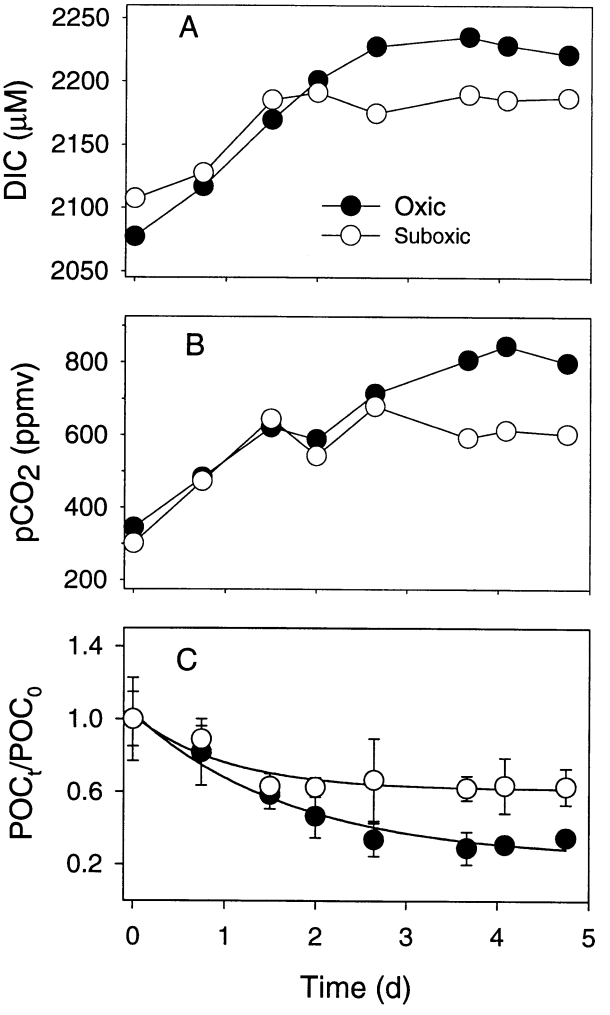

Fig. 3. Mean concentrations of DIC (A), pCO_2 (B), and POC (C) from the five suboxic and five oxic degradation experiments. The curves in the bottom panel are the solutions to Eqn. 6 and 7.

$$POC_t/POC_o = POC_D\, e^{-kt} + POC_{ND} \quad (3)$$

where POC_D is the degradable fraction of POC, k is the first order rate constant in $days^{-1}$, t is the time in days, and POC_{ND}, is the non-degradable fraction of OM. For the five oxic and five suboxic experiments this treatment yielded Eqn. 4 and (5) respectively:

$$POC_t/POC_o = 0.80 \pm 0.08\, e^{(-0.58 \pm 0.15)t} + 0.23 \pm 0.07$$
$$R^2 = 0.92,\ p = 0.0002 \quad (4)$$

$$POC_t/POC_o = 0.41 \pm 0.06\, e^{(-1.00 \pm 0.38)t} + 0.61 \pm 0.04$$
$$R^2 = 0.80,\ p = 0.0035 \quad (5)$$

POC_D and POC_{ND} in Eqn. 4 are statistically different from Eqn. 5 at the 95% confidence interval although the rate constants (k) are not. However, an F-test of these two curves indicated that the functions as a whole were different at the

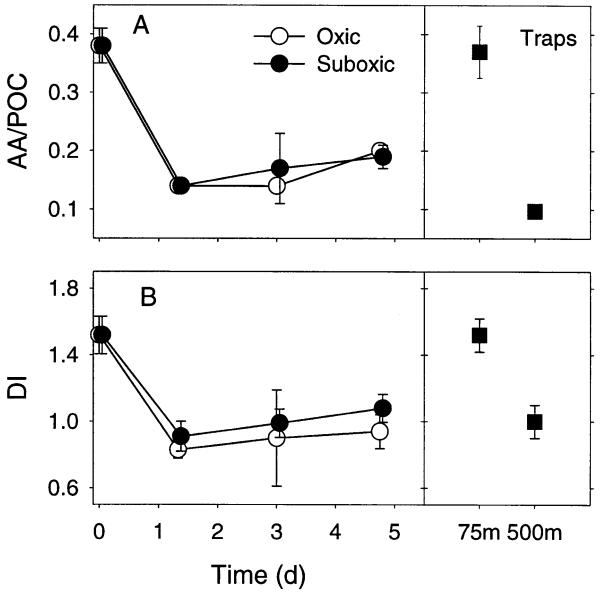

Fig. 4. –Mean AA/POC (A) and DI (B) from POC collected from the five oxic and five suboxic degradation experiments and trap samples.

95% confidence interval and accurately describe two modes of POC degradation.

The AA/POC ratio of POC was observed to decrease with increasing degradation (Fig. 4). The AA/POC was 0.37 ± 0.07 for POM trapped at 75m which served as the inoculant for the degradation experiments. In the degradation experiments the AA/POC was quickly reduced after 1.3 d and stabilized to mean values of 0.17 ± 0.06 and 0.16 ± 0.09 in the five oxic and five suboxic experiments respectively. This decrease during the experiments was very similar to the decrease in the AA/POC of particles sinking in the water column: the AA/POC of POM trapped at 500m was 0.10 ± 0.04

The distributions of individual protein amino acids were typical for sinking particles (Lee et al., 2000) and subtle changes in these distributions were observed with degradation (Table 1). Glycine, alanine, and serine were most abundant, which is typical for organic matter in the marine environment (Keil et al., 2000). Further, glycine and serine were more enriched in the 500m trap than in the 75m trap; these amino acids are frequently observed to become more abundant in organic matter as degradation proceeds (Lee and Cronin, 1984; Keil et al., 2000). Dauwe et al. (1999) compared the distribution of the 14 commonly analyzed amino acids (lysine and non-protein amino acids were not included) in marine organic matter from various settings and computed a degradation index (DI). The DI essentially distills the subtle and complex changes in amino acid distributions into one value that decreases with progress along the early diagenetic continuum from 1.48 phytoplankton to −2.17 for oxidized turbidite sediment (Dauwe et al., 1999)

The DI values of organic matter recovered from the traps and incubations reflected the degradative status of POM (Fig. 4). Values for trapped POM are 1.52 ± 0.10 and 1.00 ± 0.10 for 75m and 500m respectively. In the degradation experiments, the values for oxic and suboxic experiments dropped from the initial 75m values, but stabilized after 1.3 d and remained at average values of 0.90 ± 0.29 and 0.99 ± 0.06.

3.3. Experimental Degradation of POC Trapped at 500 m

In a second set of degradation experiments, POC trapped at 500m was also incubated under the conditions as described above for POC collected at 75m. However, no net degradation of POC was observed on the time-scale of the experiment. Further, the AA/POC and DI did not change.

4. DISCUSSION

Proportionally more particulate organic matter sinks through the suboxic water column of the ETNP than in other parts of the ocean. There is only a slight attenuation in the downward flux of organic matter within the ODZ, and the attenuation coefficient (b = 0.400) is half that of the Pacific VERTEX open ocean composite value (b = 0.858; Martin et al., 1987). Among the nine VERTEX stations (Martin et al., 1987), the three from ODZ regions (Peru margin and two further offshore along the ETNP) also have attenuation coefficients that are low (PERU b = 0. 319; VERTEX II, b = 0.805; VERTEX III, b = 0.648). Thus, our data in conjunction with that of Martin et al. (1987) for the Peru margin and ETNP indicate that a greater proportion of the sinking organic matter escapes degradation while sinking through these major ODZ regions of the modern ocean.

The collection efficiency of a sediment trap is primarily a function of trap geometry and horizontal current velocity (Gardner, 1980b). Since the design of our cylindrical traps was nearly identical to that of Martin et al. (1987), differences in efficiency as a function of trap geometry are probably small (Gardner, 1980a; Gust et al., 1994). These cylindrical traps are one of the most commonly deployed designs (Gust et al., 1996) and their efficiency is comparable to other common trap de-

Table 1. The mole percentages of individual amino acids. The suboxic and oxic results are means from the degradation experiments after 1.3 days.

	Asp	Glu	Ser	His	Gly	Thr	Arg	Ala	Tyr	Met	Val	Phe	Ile	Leu	Lys	nonprot	DI	AA/POC
75m trap	7.44	8.29	9.02	2.35	14.04	6.11	4.82	11.36	4.01	2.00	8.16	3.60	5.29	7.18	5.17	1.15	1.52	0.37
(±)	(0.96)	(0.70)	(0.28)	(0.01)	(0.62)	(0.34)	(0.39)	(0.38)	(0.28)	(0.02)	(0.35)	(0.15)	(0.27)	(0.43)	(0.30)	(0.82)	(0.10)	(0.07)
500m trap	8.89	8.70	9.61	2.07	15.52	5.87	4.67	11.57	4.11	1.50	7.72	3.64	4.09	6.03	4.92	1.11	1.00	0.10
(±)	(0.93)	(0.72)	(0.94)	(0.20)	(0.51)	(0.51)	(0.27)	(0.78)	(0.16)	(0.02)	(0.28)	(0.19)	(0.26)	(0.47)	(0.55)	(1.45)	(0.10)	(0.04)
Suboxic	8.59	8.02	8.57	1.24	13.55	6.74	5.80	12.59	4.30	1.24	7.05	4.03	4.24	7.18	5.38	1.49	0.99	0.16
(±)	(0.02)	(0.42)	(0.34)	(0.34)	(0.61)	(0.01)	(1.06)	(0.29)	(0.12)	(0.24)	(0.66)	(0.12)	(0.44)	(0.18)	(0.50)	(1.87)	(0.06)	(0.09)
Oxic	8.67	7.97	10.36	1.74	14.83	6.19	5.52	11.63	4.02	1.71	6.62	3.78	3.84	6.74	4.70	1.68	0.90	0.17
(±)	(1.20)	(0.73)	(2.72)	(0.30)	(0.64)	(0.69)	(0.28)	(0.77)	(0.34)	(0.06)	(0.56)	(0.41)	(0.51)	(0.83)	(0.14)	(0.93)	(0.29)	(0.06)

signs (Honjo et al., 1992). However, their trapping efficiency has been shown to increase with increasing horizontal flow velocity (Gardner, 1980a; Gust et al., 1996). While layers of suboxia are predicted to occur in marine waters of minimal horizontal flow (Wyrtki, 1962), it is unlikely that basin-scale differences in flow regime between suboxic and oxic water columns may explain the differences in flux attenuation that we observe; sediment traps measure particle flux on much smaller scales and are frequently subject to intermittent current events (Honjo et al., 1992). Gust et al. (1994) found that even within the relatively consistent hydrography of the Sargasso Sea there may be 10-fold differences in horizontal flow velocity. Nonetheless, differences in trapping efficiency are generally small compared to variations in particle flux (Gust et al., 1996) and the differences in the attenuation coefficient (*b*) are unlikely to be the result of systematic differences in hydrodynamic biases.

We have specifically tested the hypothesis that suboxia is responsible, either directly or indirectly, for the relative lack of organic matter degradation during passage through the water column, but there are other possible mechanisms that might also be invoked to explain the observed reduced attenuation. For example, it is possible that the relationship between primary production and particle flux is different along continental margins such that attenuation coefficients may be reduced. However, primary production is no higher at our station than observed on other western North American margins (Hartnett, 1998; Devol and Hartnett, 2001), yet these regions with oxic water columns still have higher attenuation coefficients (Martin et al., 1987, Hartnett, 1998, Devol and Hartnett, 2001). It has also been proposed that off-shelf transport of refractory, shelf-derived organic matter is an important means of delivering organic matter to the slope (Walsh et al., 1981, Ganeshram et al., 1999). This horizontal input could contribute to the POC collected in the trap and skew the sinking flux measurement. However, during our six-week sampling period, we did not observe off-shelf transport of particles. We searched for this phenomenon by monitoring daily surface-to-bottom transmissometer profiles and by collecting and analyzing both trap and large volume filtration samples. While we cannot rule out off-shelf transport as a contribution to the organic carbon content of the sediments in general, it did not contribute substantially to trap fluxes during our observational period. Contamination from zooplankton swimmers could also contribute to the flux measurement, though we made every attempt to manually remove them. However, since zooplankton are less abundant in the ODZ of the ETNP (Saltzman and Wishner, 1997; Wishner et al., 1995), we would not expect any greater input of zooplankton swimmers than elsewhere in the North Pacific. Finally, chemolithotrophic production has also been identified as an important source of sinking POM, (Karl et al., 1984; Naqvi et al., 1993), but the ^{13}C content of POC collected throughout the water column is distinctly planktonic and does not reflect input from the dissolved inorganic carbon reservoir (data not shown). Based on these arguments, it appears that the most likely cause for the reduced attenuation of organic matter in the suboxic zone is the presence of the suboxic zone itself, either directly or indirectly.

There was no difference in the rate constants for the degradable fractions of POC (POC_D) under oxic or suboxic conditions. This is in agreement with the comparisons between oxic and anoxic degradation of labile substrates made by Lee (1992) and Hulthe et al., (1998) but in contrast with those of Harvey et al. (1995) who found that the degradation of plankton was faster under oxic conditions. Additionally, our rates presented here are faster than those observed by Harvey et al. (1995) under either oxic or anoxic conditions. This may arguably be an artifact of our experimental incubation period; shorter experiments yield faster rates (Middelburg, 1989; Hedges and Keil, 1995). Nonetheless, given an estimate for the sinking rate of POC of 90 m d^{-1} (Lorenzen et al., 1983), the timescale of these experiments is appropriate to study the degradation of a sinking particle during the decent from 75 to 500 m depth, the depths where the two funnel-type sediment traps were deployed.

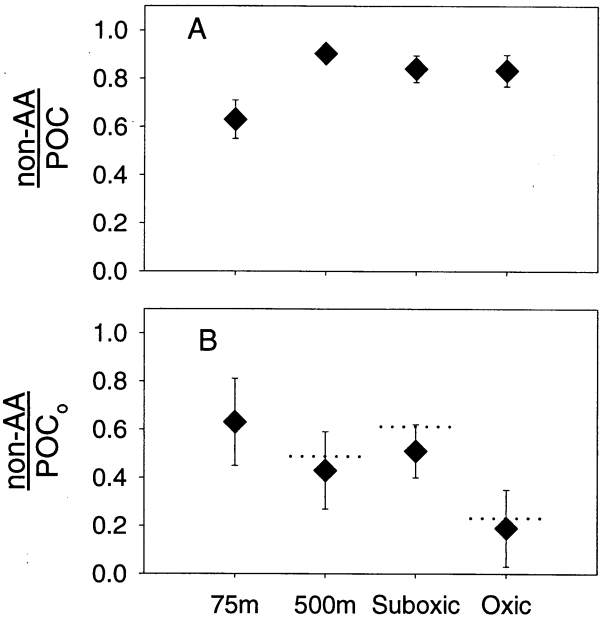

Fig. 5. Non-amino acid POC collected from the degradation experiments and trap samples. In panel A, the mass of non-amino acid carbon divided by the mass of POC from which it was determined. In the panel B, the mass of non-amino acid carbon divided by the mass of POC used to initiate the degradation experiments (from 75m). The dashed lines are values of POC_{ND} from the kinetic model for oxic and suboxic degradation (Eqn. 4 and 5) and the fraction of the 75m flux at 500m as calculated from Eqn. 1.

While the rate constants for the degradation of degradable POC (POC_D) were similar under oxic and suboxic conditions, the fraction of bulk POC composed of POC_D was different (Eqn. 4 and 5). This implies that there was an oxygen-sensitive component of organic matter. The net result of having a smaller fraction of degradable POC is to lower the overall degradation rate for bulk POC. This manifests itself in the water column as a lower attenuation coefficient in the Martin et al. power function (compare Fig. 2 and Fig. 3C)

Our analyses of amino acids indicated that this class of biomolecules did not compose a significant portion of the non-degraded POC. The AA/POC decreased sharply during both oxic and suboxic degradation, and hence the majority of POC at the end of the degradation was composed of non-amino acid carbon (non-AA/POC) (Fig. 5a). However, since bulk POC also decreased with degradation, both the numerator and

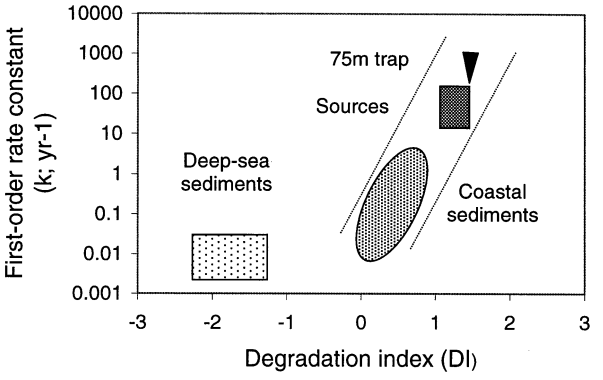

Fig. 6. –A simplified schematic of the relationship between degradation rate and DI as given by Dauwe et al. (1999). Our data from POC recovered from the 75m trap are included.

the denominator of ratio non-AA/POC changed. To account for this, the non-amino acid carbon was normalized to the initial quantity of POC (POC_o), which was a constant (Fig. 5b). This allowed a direct comparison with the kinetic model results that are also normalized to initial POC. The non-degradable fraction (POC_{ND}) of initial POC was 0.23 ± 0.07 and 0.61 ± 0.04 in the oxic and suboxic experiments respectively whereas the non-amino acid fraction (non-AA/POC_o) was 0.19 ± 0.16 and 0.51 ± 0.11 (Fig. 5b). Thus the non-degradable component of POC (POC_{ND}) in the oxic and suboxic experiments was composed almost entirely of non-amino acid carbon.

The non-amino acid component of the POC was degraded only slightly under suboxic conditions, whereas under oxic conditions more than two thirds of the original amount was degraded (Fig. 5b). Intriguingly, when the POC trapped at 500m (preexposed to suboxic conditions) was experimentally degraded, it did not appear to respond to oxic conditions, implying that whatever mechanism retarded degradation was not immediately reversible upon re-exposure to oxygen. This implies that the non-amino acid component may somehow be rendered 'non-degradable' by exposure to suboxic conditions.

The molecular identity of the non-amino acid component that remained at the end of the suboxic experiments is not known, nor is the mechanism that renders it non-degradable under suboxic conditions. One possible mechanism is that the microorganisms that function under suboxic conditions do not possess the ability to degrade this specific type of organic matter. Another possibility is that zooplankton play a critical role in predisposing POC for degradation. Though some zooplankton have been observed in the suboxic ETNP (Wishner et al., 1995), they are not active throughout the ODZ and are concentrated at the upper and lower interface (Saltzman and Wishner, 1997). Perhaps, since sinking particles in the ODZ escape passage through the guts of large zooplankton, a fraction of organic matter is left chemically of physically protected from microbial degradation.

The efficient degradation of amino acids under oxic and suboxic conditions is reflected in the amino acid data. Dauwe et al. (1999) compared the DI with the first-order degradation rate of bulk OC and found a correlation for fresh OC and sedimentary OC from continental margins (Fig. 6). DI and degradation rate for 75m-trap material agree quite well with their observations (Fig. 6) and reflect the lability of this material. The DI and AA/POC ratio decreased similarly under oxic and suboxic conditions indicating that the "quality" of the amino acid fraction remaining after suboxic and oxic degradation was also similar. The relationship between DI and first-order rate of decay (Dauwe et al., 1999; Fig. 6), supports our observation that the degradation rate of OC remaining in the experiments and the POC trapped at 500m (DI ≈ 1, for both), was much too slow to observe in the timescale of our experiments.

Since the POC that was degraded under suboxic conditions in the ETNP was almost exclusively nitrogen-rich amino acids, the stoichiometry of water column denitrification should be reconsidered. Recent analyses of the impact of water column denitrification on the global nitrogen cycle have used the following general equation to represent this metabolism (Gruber and Sarmiento, 1997):

$$C_{106}H_{175}O_{42}N_{16}P + 104\ NO_3^- = 4\ CO_2 + 102\ HCO_3^- + 60\ N_2 + 36\ H_2O + HPO_4^{2-} \quad (6)$$

where $C_{106}H_{175}O_{42}N_{16}P$ represents an ideal OC molecule. The idealized OC molecule in Eqn. 6, has a stoichiometric ratio of carbon to nitrogen of 6.6. This represents a mixture of amino acids that have a C:N ratio of 3.8 and non-amino acid OC that has a much greater C:N. If denitrifying organisms discriminate against non-amino acid OC, and instead use almost exclusively amino acids, then Eqn. 6 is an inaccurate representation of OC degradation via denitrification. We propose the following equation for our observations of denitrification in which an ideal protein (Anderson, 1995) is substituted for the OC molecule:

$$C_{61}H_{97}O_{20}N_{16} + 60.2NO_3^- = 0.8\ CO_2 + 60.2\ HCO_3^- + 38.1\ N_2 + 18.4\ H_2O \quad (7)$$

In this equation, the ratio of N_2 produced to NO_3^- consumed is 0.63 whereas in Eqn. 6 the ratio is 0.58. Therefore, 9% more nitrogen may be lost from the ETNP than is currently accounted for when using Eqn. 6. If our observations are typical for ODZs globally, this could be an underestimation of up to 9 Tg of nitrogen lost from the ocean per annum based on the most recent nitrogen budget of Gruber and Sarmiento (1997). Clearly more studies are required to assure that Eqn. 7 is robust; nonetheless, as global nitrogen budgets are refined, the type of OC that is being consumed during denitrification must be fully considered.

5. CONCLUSIONS

1. The downward POC flux was significantly less attenuated with depth off of the Mexican margin than was observed by Martin et al. (1987) elsewhere in the eastern North Pacific Ocean.
2. In degradation experiments of POC trapped at 75m, the non-degradable fraction of POC (POC_{ND}) was greater under suboxic conditions than under oxic conditions. However, the rate constants of degradation were similar under both conditions. POC trapped at 500m was not observed to degrade under either oxic or suboxic conditions.
3. The AA/POC ratio of material trapped at 75m was the same following degradation under oxic and suboxic conditions. This suggested that the "quality" of POC, as indicated by the

fraction of *N*-rich amino acids, was also similar. Material remaining at the termination of the 75m degradation experiments had an AA/POC ratio similar to the POC trapped at 500m.

4. The degradation index (DI) was the same following oxic and suboxic degradation. This suggested that the remaining POC would degrade at similar rates. The DI of POC trapped at 500 m indicates that degradation rates would be slower than could be observed with our experimental design.
5. Under suboxic conditions, all of the degradation of POC could be accounted for by the degradation of amino acids; the non-AA fraction of POC did not degrade. Analogously, the flux of non-AA POC through the water column was similar at 75 and 500m. Contrastingly, under oxic conditions both the AA and non-AA fractions were observed to degrade.
6. Discrimination against non-AA POC under suboxia indicates that nitrogen-rich OC is preferentially consumed. If these observations are typical of ODZs globally, roughly 9% more fixed nitrogen may be lost via denitrification than is currently being accounted for in global nitrogen budgets.

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