Vertical fluxes of carbon, nitrogen, and phosphorus in the North Pacific Subtropical Gyre near Hawaii

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Abstract. The hypothesized "biological pump" mechanism for removing carbon from the euphotic zone to the deep ocean requires different rates of recycling of C, N, and P in sinking particles. At Station ALOHA in the subtropical North Pacific Ocean (22° 45' N, 158° W), the C/N and C/P ratios in sinking particles increase with depth, while the ratios in the upward mixing flux decrease. An exponential model of the sinking flux as a function of depth is used, which permits remineralization length and time scales (more properly called solubilization scales) to be estimated. Time scales (2.5 days) are consistent with microbiological decomposition, and length scales are greater for C (368 m) than for N and P (249 and 248 m), consistent with the existence of a biological pump for carbon. Assuming that the system is nutrient limited (total upward and downward fluxes of N or P are equal) permits us to estimate vertical eddy diffusivity ($K_z$) and the net export of carbon from the system. Values of $K_z$ range from $5 \times 10^4$ to $4 \times 10^3$ m$^2$ s$^{-1}$ and are consistent with independent estimates for similar environments. We estimate that approximately 20% of the air-to-sea carbon flux at Station ALOHA and a similar fraction of new carbon production are exported to the deep ocean ($\sigma_2 > 27$) by particle sinking. Eddy diffusivities are lower and net carbon export greater if phosphorus is assumed to be the controlling element. This has implications for the role of dinitrogen fixation in the subtropical North Pacific.

1. Introduction

In recent years, the role of the oceanic biota in the global carbon cycle has been a subject of considerable interest [Sarmiento et al., 1988; Shaffer, 1993; Deman et al., 1996]. The downward flux of carbon across the thermocline into the deep ocean (the "biological pump") plays an important role in the upper ocean carbon balance [Epplle and Peterson, 1979]. New production [Dugdale and Goring, 1967] represents the amount of fixed N that can be exported while maintaining the long-term integrity of the ecosystem, and new production expressed in terms of carbon defines the upper limit for carbon export that could in principle be counterbalanced by invasion of atmospheric CO$_2$. In reality the net export is much less, because there is also a substantial upward flux of inorganic carbon [Epplle and Peterson, 1979]. Net carbon export can therefore potentially be zero; that is, a finite rate of new production is a necessary but not sufficient condition for a net flux of carbon out of the surface ocean mediated by biological processes.

The downward flux of organic matter in sinking particles must be balanced by an upward flux of dissolved nutrients to maintain the integrity of the pelagic ecosystem. If elemental ratios are the same in the upward inorganic flux and in the organic export flux, there is no net export of carbon. However, it is well established that the C/N and C/P ratios in sinking particles increase with depth in subtropical oceanic ecosystems [Knauer et al., 1979; Martin et al., 1987; Karl et al., 1996]. A consistently greater remineralization length scale for C will produce a long-term, steady state flux of C from the surface to the deep ocean in this environment, unless elemental ratios in the upward flux show trends with depth identical to those in the sinking flux. Because a significant fraction of loss from the sinking pool may be in the form of dissolved or suspended particulate organic matter (DOM/SPOM), i.e., by particle fragmentation and solubilization rather than remineralization [Azam and Cho, 1987; Karl et al., 1988; Smith et al., 1992], remineralization length and time scales are more properly described as solubilization scales.

Empirical models of particle flux of the form proposed by Martin et al. [1987] describe the flux profile well and show strong consistency in model parameter estimates among various trap deployment experiments [Karl et al., 1996]. However, the physical meaning of the exponent is not clear. Walsh et al. [1988] suggested that a rate constant for losses from the sinking particle flux, or inverse solubilization length scale, could be estimated from a pair of traps, using a negative exponential model for the attenuation of flux between the traps. This exponential model has certain advantages over the form proposed by Martin et al. [1987], notably that the rate of change of flux with increasing depth can be expressed as a linear function of the flux itself (i.e., the order of the function does not change in the differentiation). In addition, the model parameter (exponent) describing the degree of curvature of the flux profile can be expressed in terms of quantities that have physical meaning (sinking rate and solubilization rate coefficient). Although these are not easy to measure in practice and cannot be estimated independently from the data presented in this paper, this formulation is nevertheless preferred over previous formulations with purely empirical coefficients.
Nutrient analyses are given by Karl et al. [1993]. Dissolved inorganic carbon (DIC) was determined coulometrically. DIC samples were preserved with mercuric chloride (0.1 mL of saturated solution per 500 mL of seawater). Details of DIC analysis are given by Winn et al. [1994]. Samples for dissolved organic carbon (DOC) were collected in 15 mL polypropylene tubes and stored frozen until analyzed using a commercial (Ionics model 555) high-temperature catalytic oxidation system [Tupas et al., 1994].

Particulate carbon and nitrogen (PC, PN) in both suspended and sinking fractions were collected on combusted (4 hours at 450 °C) Whatman GF/F glass fiber filters and analyzed in a Perkin-Elmer 2400 Elemental Analyzer (HOT 1-54) or a Europa automated nitrogen and carbon analyzer (HOT 555). Particulate phosphorus (PP) was measured spectrophotometrically following combustion and acid hydrolysis; filters for PP were combusted as for PC/PN, followed by an acid rinse to remove any contaminating inorganic P.

Sinking particles were collected using a free-drifting sediment trap array of the VERTEX (Vertical Transport and Exchange Experiment) design [Knauser et al., 1979]. Twelve cylindrical traps (cross section = 39 cm²) were routinely deployed at 150, 300, and 500 m. Six traps were processed for PC/PN analysis and three for PP. The traps were connected to an array of surface floats outfitted with an Argos transponder and deployed for ~72 hours. Upon recovery, the traps were screened (335 μm) to remove swimmers. On 19 cruises from 1991 to 1993, swimmers passing the screen were manually removed and quantified; these averaged 12.0%, 6.8%, and 2.8% of C flux at 150, 300, and 500 m, respectively [Karl et al., 1996]. A more detailed description of sediment trap protocols is given by Karl et al. [1996].

2.3. Data Analysis

2.3.1. Empirical Models of Particle Flux. Particle fluxes as a function of depth (Fz) were described by a negative exponential function

\[ F_z = F_0 e^{-az} \]  

where \( F_0 \) is the flux at an arbitrary depth less than the trap depths, \( z \) is depth, and \( a \) is an empirically determined coefficient. Alternatively, the hyperbolic expression introduced by Martin et al. [1987] can be used,

\[ F_z = F_{150} \left( \frac{1}{z/150} \right)^b \]  

where \( F_{150} \) is the flux at 150 m, or at the depth of the shallowest set of traps, and \( b \) is an empirically determined coefficient. Because (1) has two model parameters that are not truly independent (solutions with larger \( a \) are more probable for large \( F_0 \) and vice versa, i.e., the two are positively correlated), it is convenient to rewrite it as

\[ F_z = F_{150} e^{-a(z-150)} \]  

This also facilitates comparison of the two models, as they are both constrained to the mean observed value at 150 m. In practice, (1) and (3) return very similar values of \( a \).

2.3.2. Nonlinear Regression. Models were fit using a Gauss-Newton nonlinear least squares algorithm based on Tarantola [1987] and Johnson and Faunt [1992] (see Appendix). This algorithm will converge on the values of the model parameters that minimize the sum of squares of the residuals, which are equivalent to the maximum likelihood values if the standard assumptions of least squares arc met (errors Gaussian and uncorrelated,
errors in independent variable negligible, sufficient data to give representative sample of errors).

2.3.3. Error Propagation. Standard deviations for derived quantities were calculated as

$$\sigma(F) = \left[ \sum_{i=1}^{n} \frac{\partial F}{\partial m_i} \sigma_i^2 + 2 \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{\partial F}{\partial m_i} \frac{\partial F}{\partial m_j} \sigma_{ij} \right]^{1/2}$$

where $F = F(m_1, m_2, \ldots, m_n)$, $m_i$ is the estimated value of the $i$th model parameter, $\sigma_i$ is the standard deviation, and $\sigma_{ij}$ is the covariance of $m_i$ and $m_j$ [Bevington, 1969]. When more than one empirical model was combined, covariances were determined for the parameters of each model; covariances between parameters of different models were assumed to be zero in most cases (see below).

2.3.4. Vertical Eddy Diffusivity. Estimates of vertical eddy diffusivity ($K_z$) were derived from vertical profiles of DIN or DIP and downward fluxes of N or P in sinking particles. The upward and downward fluxes are assumed to be equal for the nutrient that limits biological production; that is, with P limiting, there can be a net flux of N out of the surface ocean. For the limiting nutrient, the total inventory (excluding N for N limiting case) above some depth horizon is assumed to be constant and atmospheric deposition negligible. If eddy diffusion is assumed to dominate the upward flux,

$$F_{\text{down}} = F_{\text{up}} = K_z \frac{dX}{dz}$$

or

$$K_z = \frac{F_{\text{down}}}{\frac{dX}{dz}}$$

where $K_z$ is the vertical eddy diffusivity in m$^2$ d$^{-1}$, $F_{\text{down}}$ is the sinking particle flux in millimoles per square meter per day, and $X$ is the concentration of the limiting nutrient in millimoles per cubic meter. Estimates of $K_z$ were derived for the depths of the two deeper sets of traps (300 and 500 m) from the observed fluxes at these depths and over the entire range from 200 to 500 m from the flux model (equation (3)). For particular depths, the gradient of the nutrient profile was determined using model 1 linear regression; for continuous profiles, second-order polynomials were fit to observed concentration profiles. The variance of $F_{\text{down}}$ was the observed variance of the flux; for other model parameters, variances and covariances were derived from the nonlinear regression algorithm (see Appendix). In the continuous profiles, covariances between model parameters from different models were assumed to be zero.

2.3.5. Net Vertical Flux of Carbon. The difference between upward and downward fluxes of C for an eddy diffusivity calculated from fluxes of N or P can be used to estimate the net flux of C out of the surface ocean by particle sinking.

$$F_{\text{net}} = F_{\text{down}} - F_{\text{up}} = F_{\text{down}} + K_z \frac{d\text{DOC}}{dz} - K_z \frac{d\text{DIC}}{dz}$$

Substituting (6) this gives

$$F_{\text{net}} = F_C + F_X \left( \frac{d\text{DOC}}{dz} \frac{d\text{DIC}}{dz} \right)$$

where $F_C$ and $F_X$ are the sinking particulate fluxes of C and "nutrient" (N or P) and $X$ is the concentration of the dissolved, inorganic form of that element. DOC fluxes were calculated from model 1 linear regression for the discrete-depth solutions but were not considered in the continuous profiles. Covariances between gradients of DOC and inorganic species were assumed to be zero, as were covariances between gradients of DIC and DIN or DIP at 500 m, because there were too few data to calculate statistically meaningful slopes for individual cruises. In the continuous profiles, covariances between model parameters from different models were assumed to be zero.

3. Results

3.1. Particle Flux Models

The two alternative models for the attenuation of particle flux with depth (equations (2) and (3)) gave very similar results for the complete HOT data set from 1988 to 1994. The a posteriori variances on the model parameter estimates ($a$ and $b$) were similar for the two models (Table 1). The exponents $a$ and $b$ were in general greater (as absolute values) for N and P than for C, implying shorter solubilization length scales for N and P.

Table 1. Estimates of Coefficients for (2) ($F = F_{150}/(z/150)^b$) and (3) ($F = F_{150}e^{-(z-150)/150}$) Derived From Gauss-Newton Nonlinear Least Squares

<table>
<thead>
<tr>
<th>Element</th>
<th>Coefficient</th>
<th>Least Squares Optimal Value</th>
<th>Standard Deviation</th>
<th>Coefficient of Variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon$^a$</td>
<td>$F_{150}$</td>
<td>2.30</td>
<td>0.86</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>$a$ (equation (3))</td>
<td>0.00272</td>
<td>0.000030</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>$b$ (equation (2))</td>
<td>-0.78</td>
<td>0.019</td>
<td>2.4</td>
</tr>
<tr>
<td>Nitrogen$^a$</td>
<td>$F_{150}$</td>
<td>0.28</td>
<td>0.11</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>$a$ (equation (3))</td>
<td>0.00401</td>
<td>0.000065</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>$b$ (equation (2))</td>
<td>-1.12</td>
<td>0.015</td>
<td>1.3</td>
</tr>
<tr>
<td>Phosphorus$^b$</td>
<td>$F_{150}$</td>
<td>0.013</td>
<td>0.0053</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>$a$ (equation (3))</td>
<td>0.00403</td>
<td>0.000089</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>$b$ (equation (2))</td>
<td>-1.09</td>
<td>0.018</td>
<td>1.6</td>
</tr>
</tbody>
</table>

$F_{150}$ is the mean flux at 150 m. $F$ is in mmol m$^{-2}$ d$^{-1}$; $a$ is in m$^{-1}$ and $b$ is non-dimensional.

$^a$ Here $n = 172$.

$^b$ Here $n = 173$. 

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The text continues with further discussion and analysis, incorporating equations and data from the research studies. The table provides a structured summary of the coefficients estimated using the Gauss-Newton nonlinear least squares method.
tive exponential model (equation (3)) describes the vertical attenuation of the flux reasonably well but tends to underestimate the flux at 500 m, implying that $a$ is not in fact constant but decreases with increasing depth (Figure 1).

![Graph of carbon, nitrogen, and phosphorus fluxes](image)

Table 2. Elemental Ratios for Particle Fluxes

<table>
<thead>
<tr>
<th></th>
<th>C/N</th>
<th>C/P</th>
<th>N/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression Slope</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 m$^b$</td>
<td>7.76</td>
<td>164.</td>
<td>20.4</td>
</tr>
<tr>
<td>300 m$^b$</td>
<td>9.57</td>
<td>...</td>
<td>18.6</td>
</tr>
<tr>
<td>500 m$^c$</td>
<td>11.6</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Ratio of Means</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 m</td>
<td>8.00</td>
<td>172.</td>
<td>21.5</td>
</tr>
<tr>
<td>300 m</td>
<td>10.3</td>
<td>241.</td>
<td>23.5</td>
</tr>
<tr>
<td>500 m</td>
<td>12.1</td>
<td>232.</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Determined from zero-intercept linear regression for cases where the fluxes of the two elements were significantly correlated and the y intercept was not significantly different from zero, and ratios of the mean flux at each depth. Elemental ratios are in mol/mol.

$^a$ Here n = 52
$^b$ Here n = 45
$^c$ Here n = 46

3.2. Elemental Ratios

Elemental ratios in the sinking particle flux can be estimated by deriving regression equations for each pair of elements at each depth or by a simple ratio of mean values. The slope of a regression equation gives a constant ratio if the intercept is zero. Model 2 regression equations were calculated by the geometric mean method for cases where the fluxes were significantly correlated and intercepts were not significantly different from 0 ($\alpha$=0.05). C/N ratios derived by either method showed a monotonic increase with depth; N/P ratios did not change noticeably with depth (Table 2). Both C/P and N/P ratios were consistently greater than the Redfield ratio.

3.3. Estimation of Solubilization Length Scale

Sinking particles collected in traps form a “population” of particles distinct from the background concentration of suspended particles, whose sinking rates are very low or zero [Fowler and Knauer, 1986]. The steady state concentration of the former group cannot easily be estimated. Calling this steady state concentration $C(z)$, it can be expressed in terms of the standard advection-diffusion equation (for $z$ positive downward)

$$\frac{\partial C}{\partial t} = K \nabla^2 C - w \nabla C - kC = 0$$  \hspace{1cm} (9)

where $K$ is eddy diffusivity ($m^2 s^{-1}$), $w$ is the particle sinking speed ($m s^{-1}$), and $k$ is a first-order rate constant for particle decomposition ($s^{-1}$). Neglecting diffusion as second order, and considering only the vertical dimension, this reduces to

$$-w \frac{\partial C}{\partial z} - kC = 0$$  \hspace{1cm} (10)

in the steady state [cf. Martin et al., 1987; Banse, 1990]. This latter equation defines a solubilization time scale $\lambda/k$ and length scale $w/\lambda$. If the sinking flux is approximated as $F_0 e^{-\mu z}$ (equation (1)), then

$$\frac{\partial F}{\partial z} - w \frac{\partial C}{\partial z} - kC = -a F_0 e^{-\mu z}$$  \hspace{1cm} (11)
DIN and DIP concentration profiles. The resulting profile shows $K_z$ decreasing exponentially with increasing depth (Figure 4). Estimates based on P fluxes are 30-40% lower than those based on N. The value of $K_z$ estimated by this method is 5-10 times greater at 200 m than at 500 m; the gradient is steeper for the N- than for the P-based estimates (Figure 4). Values at 300 m are

![Graphs showing DIN and DIP concentrations](image)

Figure 3. Profiles of dissolved inorganic carbon (DIC), nitrogen (DIN), and phosphorus (DIP) at Station ALOHA showing model 1 regression lines for depth ranges of 200-400 and 400-600 m.

3.4. Vertical Eddy Diffusivity: Discrete Depths

Estimates of eddy diffusivity for the trap reference depths (150, 300, and 500 m) can be derived from estimates of DIN or DIP gradients based on linear approximations to the depth profiles at those depths (Figure 3). However, at 150 m the curvature of the profile is sufficiently great that this linearization is possible only over a very narrow depth range, and there is active biological uptake of DIN and DIP at this depth, which will bias the estimates. Estimates of $K_z$ have therefore been derived in this fashion only for 300 and 500 m (Table 3). Linear approximations to the nutrient profiles are based on a range of 200-400 m for the 300 m traps and 400-600 m for the 500 m traps (Figure 3). These results suggest that the eddy diffusivity decreases by approximately a factor of 2 from 300 to 500 m and that it is greater if N rather than P is assumed to be limiting. However, these differences are small given the variances of the estimates (Table 3).

![Graph showing time scale for sinking particle solubilization](image)

Figure 2. Time scale for sinking particle solubilization as a function of sinking speed and $a$ coefficient for negative exponential model of sinking particle flux, or inverse solubilization length scale; see (3) and (12)).

![Graph showing C(z) = α/F_e^a](image)

and

$$C(z) = \frac{a}{k} F_e e^{-az}$$  \hspace{1cm} (12)

If $F = wC$, then $a = k/w$, i.e., the inverse of the solubilization length scale (see also Banse [1990]). So the exponent ($a$) in (1) and (3) is expressible in terms of quantities that are physically “real,” although difficult to measure in practice. Statistical fitting of these equations gives an estimate of the ratio of these two quantities, although it can not provide estimates of either quantity independently. The solubilization time scale ($1/k$) decreases exponentially for constant $a$ and decreases slowly for $w > 50$ m d$^{-1}$ (Figure 2).

3.5. Vertical Eddy Diffusivity: Continuous Profile

If continuous functions approximating the depth profiles of the relevant quantities can be derived (e.g., equations (1-3)), equation (6) can be used to derive estimates of $K_z$ for a broader range of depths. The negative exponential formulation (equation (3)) was used for particle fluxes, and second-order polynomials were fit.
Table 3. Estimates of Vertical Eddy Diffusivity for 300 and 500 m Trap Reference Depths

<table>
<thead>
<tr>
<th>Element</th>
<th>Depth, m</th>
<th>Vertical Eddy Diffusivity, cm² s⁻¹</th>
<th>Standard Deviation</th>
<th>Coefficient of Variation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>300</td>
<td>0.18</td>
<td>0.087</td>
<td>48</td>
</tr>
<tr>
<td>N</td>
<td>500</td>
<td>0.092</td>
<td>0.032</td>
<td>35</td>
</tr>
<tr>
<td>P</td>
<td>300</td>
<td>0.11</td>
<td>0.070</td>
<td>62</td>
</tr>
<tr>
<td>P</td>
<td>500</td>
<td>0.063</td>
<td>0.040</td>
<td>64</td>
</tr>
</tbody>
</table>

Based on assuming equality of upward (mixing) and downward (sedimentation) fluxes of nitrogen or phosphorus and linearization of dissolved nutrient profiles (see text for depth ranges). Slopes of nutrient profiles were determined using model 1 linear regression.

Figure 4. Profiles of vertical eddy diffusivity estimated from models of sinking particle fluxes of (top) nitrogen and (bottom) phosphorus and polynomial regression equations fit to the inorganic nutrient profiles. Discrete depth solutions from Table 3 are added for comparison. Confidence limits (dot-dashed lines) and error bars on discrete depth solutions are 2 standard deviations from the maximum likelihood value. Alternative confidence limits (dotted lines) assume that the standard deviation of the particle flux at 150 m is equal to 15% of the mean value.

closer to the discrete-depth solutions for these depths than those at 500 m. At 500 m, the continuous profiles give lower values than the discrete-depth solutions, probably because the particle flux model underestimates the mean flux (Figure 4 and Table 3). The variance in estimates of $K_z$ results almost entirely from temporal variance in the flux at 150 m rather than from statistical uncertainty about the parameter estimates for the empirical models; assuming a standard deviation for $F_{up}$ of 15% of the mean value reduces the variance of the estimates of $K_z$ substantially (Figure 4).

Because the gradient in nutrient concentration increases between 200 and 500 m, while particle flux decreases, $K_z$ decreasing with increasing depth follows from the assumptions represented by (3). At 200 m the polynomial approximation overestimates, by about 30%, the concentration gradients at that depth (based on linear regressions on the interval from 175-250 m). The polynomial approximation may therefore be underestimating the increase of $K_z$ in the upper thermocline. However, using a constant value of $a$ in (3) over 150-500 m has the opposite effect; that is, the true value of $a$ for the shallower depths may be larger than that estimated from the entire profile, so the predicted flux at 200 m will be overestimated.

3.6. Net Vertical Flux of Carbon

The net fluxes of C across the 26.0 and 26.7 $\sigma_t$ surfaces (approximately 300 and 500 m, the nominal depths of the traps) are 0.83-1.0 and 0.33-0.51 mmol m⁻² d⁻¹, respectively (Figure 5 and Table 4). The lower and higher values assume that N or P, respectively, is the limiting nutrient. The flux at 500 m represents 17-27% of the net air-to-sea flux of CO₂ at Station ALOHA [Winn et al., 1994]. Continuous profiles of net C flux are uncertain: the flux appears to be at a maximum at ~ 300 m, but large uncertainties make this conclusion tentative (Figure 5). As with estimates of $K_z$, the largest source of uncertainty is the temporal variation in the flux at 150 m (Figure 5). Because the sinking particle flux is nonnegative by definition, the conclusion that the net flux of C is downward is therefore more robust than the calculated confidence intervals suggest.

The gross and net C fluxes at the various depths are listed in Table 4. About 6% of primary production estimated from $^{14}$CO₂ uptake (mean 39 mmol m⁻² d⁻¹; see Karl et al. [1996]) is exported from the euphotic zone (export production) as sinking particles. This primary export flux is slightly larger than the net air-to-sea flux of CO₂. However, most of the C exported from the euphotic zone is remineralized in the upper 500 m and the strong vertical gradient in DIC ensures that much of the carbon remineralized in this depth range will be returned to the surface layer. About 20% of the air-to-sea flux is exported across the 26.7 $\sigma_t$ surface by particle sinking, so the remainder must be exported laterally.
Figure 5. Profiles of net vertical carbon flux (equation (8)) estimated from models of sinking particle fluxes of nitrogen (top) and phosphorus (bottom) and polynomial regression equations fit to the inorganic nutrient profiles. Discrete depth solutions from Table 4 are added for comparison. Confidence limits (dot-dashed lines) and error bars on discrete depth solutions are 2 standard deviations from the maximum likelihood value. Alternative confidence limits (dotted lines) assume that the standard deviation of the particle flux at 150 m is equal to 15% of the mean value.

Whether this export occurs as organic or inorganic carbon and at what depth or density horizon is not known.

4. Discussion

The negative exponential model (equations (1) and (3)) is preferable to the Martin et al. [1987] formulation (equation (2)) because the coefficient \( a \) is expressible in terms of quantities that have physical meaning (sinking speed and decomposition rate) and allows at least a first approximation of a model of the decomposition process. However, it is important to recognize that this model is not statistically preferable to the earlier formulation; that is, it does not necessarily fit the data better. The negative exponential model relates the flux profile to the biological process of particle decomposition and provides an estimate of the rate constant for a first-order model of the decomposition process \( \frac{\partial C}{\partial t} = k_C \). This is not necessarily more biologically plausible than more complex formulations, but higher-order terms cannot be ventured with the data available.

Values of the exponent \( (a) \) in (3) estimated for Station ALOHA suggest solubilization length scales for sinking particles of approximately 368 m for C, 249 m for N, and 248 m for P. For a sinking speed of 100 m d\(^{-1}\) [Fowler and Knaur, 1986], the corresponding values of the decomposition rate constant are in the range of 0.2 0.5 d\(^{-1}\). These are consistent with particle solubilization rates estimated from hydrolytic ectoenzyme activities in unpoisoned traps deployed at Station ALOHA [Christian, 1995]. Smith et al. [1992] estimated the turnover time (for solubilization) of particulate protein in marine snow to be 1.1 days, and showed that time scales for remineralization of POM by particle attached bacteria are much longer than those for solubilization. Ducklow et al. [1985] also estimated long (>1000 days) turnover times for remineralization of POM. Jackson and Eldridge [1992], in an ecosystem-level analysis (flow network inversion) of the Southern California Bight, found, estimated an optimal value of 0.06 day\(^{-1}\) for “detrital dissolution.” Muradian [1994] estimated a rate coefficient of 400 year\(^{-1}\) for particle disaggregation at Ocean Station “P,” from plankton data.

Assuming that all organic C lost from sinking particles passes first through the DOC pool (i.e., no direct remineralization on particles), the steady state reaction-diffusion equation for the highly reactive fraction of DOC is

\[
\frac{\partial C_K}{\partial t} - \frac{\partial}{\partial z} K_z \frac{\partial C_K}{\partial z} - \frac{\partial F}{\partial z} - k_R C_K = 0
\]

with \( F \) defined as in (11). Neglecting diffusion, the concentration of this reactive pool can be calculated from the solutions derived above, e.g., for \( a = 0.003 \) m\(^3\), \( F_{150} = 2 \) mmol C m\(^{-2}\) d\(^{-1}\) m, \( z = 300 \) m and \( k_R = 0.3 \) d\(^{-1}\). \( C_{150} = 13 \) mM, or about 0.02% of total DOC. Values of \( k_R \) or \( C_{150} \) or both, will of course be larger at shallower depths. In addition, it is possible that the diffusive term will become important at shallower depths and would likely be of the same sign as the sedimentation term (i.e., convergence); this is suggested by the results of Emerson et al. [1995]. Diffusion could be significant if either \( K_z \) or \( \partial C_K/\partial z \) decreases with increasing depth. In the absence of flux convergence or divergence, the rates of remineralization of DOM and SPOM must be approximately equal to the rates of production from sinking particles for a temporal steady state to exist. This implies a remineralization time scale similar to the solubilization time scale for sinking particles and much less than that for the total DOM pool [cf. Azam and Cho, 1987; Karl et al., 1988].

The role of the dissolved/suspended organic matter pools in vertical flux is unclear. Estimates of \( K_z \) or net C export based on TDN or TDP are only marginally different from those considering only the inorganic pools. Even at relatively shallow depths (150-250 m) where the dissolved organic pools are larger than the inorganic, the vertical gradients of TDN and TDP are small. Emerson et al. [1995] suggested that ~25% of the vertical flux of C from the euphotic zone is in the dissolved form. However, their estimates of \( K_z \) are relatively high (see below). Deeper in the thermocline (i.e., in the 200 to 500 m range with which this paper is primarily concerned), DOC flux represents a much smaller
Table 4. Components of Vertical Carbon Flux at Station ALOHA (Positive Downward) as Absolute Values and as Percentage of the Air-to-Sea Flux

<table>
<thead>
<tr>
<th></th>
<th>(K_z), From Nitrogen</th>
<th></th>
<th>(K_z), From Phosphorus</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux, mmol m(^{-2}) d(^{-1})</td>
<td>% Air-sea Flux(^a)</td>
<td>Flux, mmol m(^{-2}) d(^{-1})</td>
<td>% Air-sea Flux(^a)</td>
</tr>
<tr>
<td>150 m ((\sigma_r\geq25.0))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC flux (“export production”)</td>
<td>2.23</td>
<td>116</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>300 m ((\sigma_r\geq26.0))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC flux</td>
<td>1.28</td>
<td></td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>DOC flux</td>
<td>0.12</td>
<td></td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>DIC flux</td>
<td>-0.57</td>
<td></td>
<td>-0.34</td>
<td></td>
</tr>
<tr>
<td>Net flux</td>
<td>0.83</td>
<td>43.2</td>
<td>1.00</td>
<td>52.1</td>
</tr>
<tr>
<td>500 m ((\sigma_r\geq26.7))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC flux</td>
<td>0.91</td>
<td></td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>DOC flux</td>
<td>0.07</td>
<td></td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>DIC flux</td>
<td>-0.60</td>
<td></td>
<td>-0.41</td>
<td></td>
</tr>
<tr>
<td>Net flux</td>
<td>0.33</td>
<td>17.2</td>
<td>0.31</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Components of diffusive fluxes assume \(K_z\) calculated for a constant inventory of nitrogen or phosphorus above that depth horizon.

\(^a\) Annual mean air-to-see flux is 1.92 mmol m\(^{-2}\) d\(^{-1}\).

fraction of total flux unless \(K_z\) is considerably greater than our estimates (Table 4). The convergence in the eddy-diffusive DOC flux implied by a flux of 0.56 mmol m\(^{-2}\) d\(^{-1}\) at 150 m (25% of mean particle flux) and 0.12 mmol m\(^{-2}\) d\(^{-1}\) at 300 m (Table 4) is 0.003 mmol m\(^{-2}\) d\(^{-1}\), or about 20% of the rate of solubilization of particles. This implies a mean turnover time for bulk DOC on the order of decades. The contribution of DOC to net C export across density horizons greater than about \(\sigma_r\geq26.3\) (~390 m) should be negligible.

Several investigators have observed that N flux near the base of the euphotic zone in subtropical oceanic waters appears too low to account for N utilization [Lewis et al., 1986; Hayward, 1987; 1991], although this has recently been questioned [Emerson et al., 1995]. The results shown here indicate that no important discrepancy in the nutrient budget exists when a depth horizon significantly below the euphotic zone is treated as the lower boundary of the surface "box." At depths of 300-500 m at Station ALOHA (\(\sigma_r\geq26.0-26.7\)), the upward flux of DIN and DIP can balance the downward flux of biogenic particulates with plausible values of \(K_z\). At shallower depths, the vertical gradient of nutrient concentration is less steep, and demand is greater (at greater depths one must only account for the fraction of export production that sinks to that depth). However, eddy diffusivity may also be significantly greater. The North Atlantic Tracer Release Experiment (NATRE) conducted by Ledwell et al. [1993] provides the best estimates to date for \(K_z\) averaged over fairly long time scales; however, the tracer was released at a single depth (310 m). The values of \(K_z\) obtained cannot necessarily be extrapolated to more energetic environments, such as the base of the euphotic zone, where the microstructure measurements of Lewis et al. [1986] suggested values of \(K_z\) 2 to 4 times greater than the NATRE values, for a similar location in the subtropical Atlantic. At Station ALOHA, the NATRE values can balance the N and P budgets for the depth range where the tracer experiment was conducted. However, it is entirely possible that \(K_z\) in the subtropical Pacific thermocline is greater than at comparable depths in the Atlantic, as, for example, the estimates of White and Bernstein [1981], which are also significantly time averaged. White and Bernstein [1981] also found that \(K_z\) decreased with increasing depth, e.g., by ~60% between the 26.6 and 27.2 \(\sigma_r\) surfaces.

The relationship of \(K_z\) to stratification is not straightforward, as unstratified regions above and below the thermocline have very different energy inputs. In Osborn's [1980] expression, the maximum \(K_z\) is linearly related to turbulent kinetic energy dissipation (\(\varepsilon\)) and to \(N^2\), where \(N\) is the buoyancy (Brunt-Väisälä) frequency; that is, \(K_z\) will be inversely proportional to \(N^2\) for approximately constant \(\varepsilon\). If \(\varepsilon\) decreases significantly below the thermocline, this relationship no longer holds. Quay et al. [1980] observed that \(K_z\) in several lakes was much greater in the hypolimnion than in the thermocline and postulated an expression whereby \(K_z\) was inversely related to \(N^2\). This relationship may result at least in part from boundary friction; similar results have been obtained in a variety of environments, but none of these are remote from basin boundaries. Unstratified regions of the ocean interior have very low values of \(K_z\) (0(10 \(^{-3}\) m\(^{3}\) s\(^{-1}\) )) [Toole et al., 1994], which increase dramatically near the seafloor [Polzin et al., 1996].

The source of energy for mixing in the thermocline remains uncertain. Internal gravity waves are generally believed to play an important role [McGowan and Hayward, 1978; Gargett and Holloway, 1984; Gregg et al., 1986; Gregg, 1987; Large et al., 1994]. The vertical profile for \(K_z\) presented here is consistent with that derived for internal wave breaking by Garrett and Munk [1972]. However, Gargett and Holloway [1984] suggested that the component of dissipation (\(\varepsilon\)) arising from internal wave breaking scales with N such that there is a negative correlation between N and \(K_z\). There are other potential mechanisms of
thermocline mixing [cf. Gregg, 1987; Large et al., 1994], which it is unnecessary to review here; we have presented no data that can elucidate mechanisms. The important point is that the statistically most probable values of $K_z$ are positively, not negatively, correlated with N. Despite the uncertainties in the values obtained, such a vertical profile follows from the assumptions made, i.e., that the upward and downward fluxes of N or P are equal or equivalently that the concentration of dissolved inorganic nutrients in the thermocline at Station ALOHA is governed primarily by local remineralization from sinking particles.

Our estimates of $K_z (\approx 1.5 \times 10^5$ m$^2$ s$^{-1}$) are consistent with other estimates for similar environments. Ledwell et al. [1993] obtained a value of $1.1 \times 10^5$ m$^2$ s$^{-1}$ from tracer release at a depth of 310 m in the subtropical North Atlantic. White and Bernstein [1981] estimated values of $2.4 \times 10^5$ m$^2$ s$^{-1}$ for the main thermocline of the NPSG. Recent estimates by Van Scoy and Kelley [1996] from tritium penetration are also in this range ($\approx 3 \times 10^5$ m$^2$ s$^{-1}$). Emerson et al. [1995] estimated values $> 10^6$ m$^2$ s$^{-1}$ for the region between 100 and 200 m at Station ALOHA; this may reflect the relatively shallow depths considered.

Uncertainties about all of these estimates are large. The vertical profile presented here remains speculative: these results cannot demonstrate conclusively that the variation of $K_z$ with depth has such a form. Expressions describing such a profile have been used in a box model by Siegenthaler and Joos [1992]. Uncertainty about the assumption of nondivergent isopycnal mixing and horizontal advective fluxes must also be considered. Net export of carbon across the 26.7 $\sigma_t$ surface accounts for only about 20% of the mean air-sea flux of CO$_2$, suggesting that this assumption is not met. This could explain at least some of the apparent increase of $K_z$ with decreasing depth.

There are potential lateral fluxes of C, N, and P along the isopycnal surfaces that intersect the sea surface at higher latitudes in the North Pacific. At the point of outcrop the water characteristics will be typical of surface waters: high in organic species and depleted in inorganic species. There is therefore a potential flux of inorganic C, N, and P northward along these isopycnal surfaces and a flux of organic species in the opposite direction. The direction of the gradient in total dissolved N and P is unknown, so it cannot be determined whether the isopycnal mixing flux is a net source or a net sink for these elements in the 200 to 500 m depth range at Station ALOHA. If there is a divergence in the isopycnal mixing flux of N or P at depths of less than 500 m, the net flux of C across the 26.7 $\sigma_t$ surface will be smaller than calculated here. The downward flux of particles is not balanced by an upward flux of DIN or DIP below the oxygen minimum zone, so there is some net export that must be balanced by horizontal advection or diffusion, or in the case of N by dinitrogen (N$_2$) fixation.

The flux of carbon across the 26.7 $\sigma_t$ surface is a potentially long-term sink for atmospheric CO$_2$, as there is little if any area of outcrop to the sea surface of density surfaces greater than 26.7 $\sigma_t$ either in the Pacific equatorial current system or in the subarctic Pacific [Pickard and Emery, 1982; Talley, 1991]. Because the rate of change of the sinking flux is very small below the 26.7 $\sigma_t$ surface, we speculate that the bulk of this particle flux is in fact exported to the interior of the ocean (e.g., below the oxygen minimum zone). Carbon remineralized at shallower depths will be available for exchange with the atmosphere on relatively short time scales (years to decades; cf. Watanabe et al. [1994]).

Nutrient concentrations in the deep ocean (> 400 m) show that the bulk of organic matter remineralization occurs in approximately Redfield ratio [Anderson and Sarmiento, 1994], suggesting that most of the particle flux occurs as pulses of relatively fresh matter that are undersampled by our surface-floating traps. Because of the large variances on the model parameter estimates and uncertainty about the validity of the assumption of nondivergent lateral fluxes, the conclusion of a net downward flux of carbon is tentative. However, it cannot necessarily be assumed either that the particles collected by the floating traps are biochemically identical to the particles that dominate elemental fluxes to the deep ocean or that present ecosystem function does not differ from the historical mean [Karl et al., 1995; Polovina et al., 1995]. The component of particle flux that is remineralized at relatively shallow depths may prove to be biogeochemically highly significant, as improved models of the middepth (200-1000 m) circulation emerge and models of the carbon cycle on the time scale of the present fossil fuel transient incorporate feedbacks between climate and biota [DeMott et al., 1996].

The assumption that the upward and downward fluxes of bioavailable forms of N are equal is invalidated by N$_2$ fixation. If a significant fraction of "new" N comes from the N$_2$ pool, the net flux of C out of the euphotic zone will be greater than the estimates presented above. At Station ALOHA, N$_2$ fixation accounts for significant inputs of "new" N [Karl et al., 1992; 1995], so this may explain the discrepancy between the solutions based on a constant inventory of N versus P. This discrepancy may also be explained by P dissolution in the traps. Because P may dissolve more rapidly in traps than N [U.S. Global Ocean Flux Study, 1989], the mean flux may be underestimated, which will result in lower estimates of $K_z$ and higher estimates of net C export. Either of these, or a combination of the two, could explain the discrepancy between the two sets of solutions. Because of the large variances and these additional uncertainties, the differences between these two sets of solutions should not be considered significant.

It is important to recognize that the large variances on the derived quantities presented here are largely a result of the large variance of the sinking particle flux, which is not analytical but temporal. This is a necessary consequence of combining a 6-year time series to characterize the "mean" condition of the system. Although there are potential collection errors associated with trapping, a large fraction of the variance in trap collections over time at Station ALOHA reflects actual variability in the flux [Karl et al., 1996]. This temporal variance accounts for most of the variance in estimates of $K_z$ and net C flux.

There remains a great deal of uncertainty about the exact value of $K_z$ and its variation with depth, but estimates arrived at by various methods are converging on similar values. That the values presented here, based on particle export measurements, agree reasonably well with independent estimates derived by other methods suggests that our measurements of vertical particle fluxes are not unreasonable. Despite the uncertainty about $K_z$, the conclusion that there is a net flux of C across the 26.7 $\sigma_t$ surface by particle sinking, i.e., that the biological pump in the NPSG is a net sink for atmospheric CO$_2$, is fairly robust. Meteorologically forced variability in the upper ocean biology [Karl et al., 1995; Polovina et al., 1995] suggests that this component of the ocean C sink is potentially sensitive to climatic change, but whether this will constitute a positive or negative feedback can not be determined at this time.

5. Conclusions

The following conclusions are derived from the analyses presented above:

1. Solubilization length scales are significantly less for nitrogen and phosphorus than for carbon. Solubilization length scales
translate into biological turnover times of 2-5 days for particles sinking at a rate of \( \sim 100 \) m d\(^{-1}\). The labile fraction of DOC derived from solubilization of sinking particles accounts for <0.1% of DOC at a depth of 300 m.

2. There is a net flux of carbon across the 26.7 \( \sigma_t \) surface (-500 m at ALOHA) of 0.3-0.5 mmol m\(^{-2}\) d\(^{-1}\), or about 17-27% of the estimated net air-to-sea flux of CO\(_2\). The biological pump is a sink for atmospheric CO\(_2\) in the NPSG. Contribution of DOC to export across the 26.7 \( \sigma_t \) surface is negligible.

3. Vertical eddy diffusivity \( (K_z) \) increases at shallower depths; that is, \( K_z \) is greatest in the region of most intense density stratification. Variances on estimates of \( K_z \) are large but result mostly from temporal variation in particle fluxes.

4. Upward and downward fluxes of N and P are balanced for plausible values of \( K_z \) at depths of 300-500 m, which are the depths that are relevant to net export of C to the abyssal ocean. The mechanism of transport of nutrients across the base of the euphotic zone remains unclear.

Appendix

If (1) is expressed as \( d = g(m, z) \), where \( d = F_z \) are the observed fluxes and \( m = [F_z, a] \), the sum of the squares of the residuals \( d - g(m) \) can be minimized by iteratively applying the equation

\[
\sum \frac{\partial g_i}{\partial m_j} (n_j - m_j) = d_i - g_i(m)
\]

where \( \partial g_i / \partial m_j \) is the derivative of \( g \) with respect to \( m_j \) evaluated at the ith value of the independent variable \( z \) in (1)-(3) and \( g_i(m) \) is the ith value of \( g(m) \), to derive a new value of \( m \) (here called \( m^* \) nearer to the optimal value. This equation can be written in matrix form as

\[
G(n - m) = d - g(m)
\]

where \( G \) is a matrix of the partial derivatives of \( g \) such that \( G_{ij} = \partial g_i / \partial m_j \). This equation is solved for \( m \) by iterating

\[
n = m_{k+1} = m_k + (G^TW^{-1}G + C^{-1})^{-1}G'[d - g(m_k)]
\]

where \( m_i \) is the value at the \( k \)th iteration. \( W \) is a weight matrix (data covariance matrix) where data variances are for samples taken at a particular depth, except for depths where there were only a handful of deployments, in which case the variance for the entire data set was used. Covariances among sampling depths were included for standard sampling depths for cruises where there are data for all three standard depths. \( C \) is a variance-covariance matrix for \( m \) given by

\[
C_{m+1} = (G^TW^{-1}G + C^{-1})^{-1}
\]

The initial value of \( C \) was defined by assigning arbitrarily large \( \sigma \) for parameters permitted to vary freely, arbitrarily small \( \sigma \) for parameters constrained at the initial value (e.g., \( F_{10} \) in (3)), and zero covariance in all cases. Convergence was defined as a change in \( m \) of <0.001%; the number of iterations required varied from 7 to 20.

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References


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