

Flocculation and phytoplankton cell size can alter ^{234}Th -based estimates of the vertical flux of particulate organic carbon in the sea

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Abstract

The deficit of ^{234}Th relative to its radioactive parent ^{238}U in the surface ocean can yield reliable estimates of vertical Particulate Organic Carbon (POC) fluxes to deeper waters, but only when coupled with an accurate ratio of POC concentration to activity of ^{234}Th on sinking matter. Assuming a simple partitioning of suspended phytoplankton mass between single cells and flocs, we calculate the ratio of the POC flux estimated from ^{234}Th deficit to the actual POC flux (p ratio, Smith et al., unpubl.). The p ratios are calculated under the assumption that particle surface area is correlated with ^{234}Th activity and particle volume is correlated with POC concentration. The value of the p ratio depends on the relative contributions of single cells and flocs to the vertical flux. When large single cells make up a significant fraction of the vertical flux, p ratios are less than one, meaning POC fluxes estimated from ^{234}Th deficits underestimate actual

POC fluxes. When large single cells are abundant but do not sink fast enough to contribute to vertical POC flux, p ratios are greater than one (up to 3 X overestimate). Factor analysis of the model indicates that altering the extent of flocculation in suspension and changing the density and maximum size of phytoplankton cells have the greatest effects on the p ratio. Failure to measure the properties of flocs when characterizing the ratio of POC to thorium on sinking matter potentially leads to large overestimation of the POC flux (over 20 X). Failure to characterize the POC to thorium ratio of large particles, by, for example, destruction of phytoplankton cells in pumps, can lead to underestimation of POC flux. Estimates of POC flux should be most reliable in highly flocculated suspensions populated by small cells and rapidly sinking flocs. These conditions are often associated with intense phytoplankton blooms.

Keywords: POC: ^{234}Th , phytoplankton, diatoms, aggregation, flocculation, cell size, sinking rate, sedimentation, vertical flux, carbon

Introduction

Progress in understanding the ocean's role in global climate change requires accurate quantification of the vertical flux of carbon from the surface ocean to depth (Priddle et al., 1992; Boyd et al., 2000; Anderson et al., 2002). The geochemical tracer Thorium-234 (^{234}Th), a particle surface reactive element, adsorbs rapidly to particles in surface waters, and can be used to estimate the flux of particles out of the surface ocean (Coale and Bruland, 1985; Clegg and Whitfield, 1993). This has led to the refinement of ^{234}Th analytical techniques using the modeled ^{234}Th deficit in surface waters, relative to ^{238}U , as an estimator of export flux (Buesseler et al., 1995; Moran and Smith, 2000).

However, while strong empirical correlations can exist between estimates of particulate organic carbon (POC) flux and estimates of ^{234}Th flux (Sigg et al., 1987; Wei and Murray, 1992), the flux of POC per unit ^{234}Th can vary for a given mass by an order of magnitude (Burd et al., 2000; Moran et al., 2003).

The ^{234}Th deficit in surface waters gives an estimate of particle export, and when multiplied by the POC per unit ^{234}Th activity in the sinking material, yields an estimate of POC flux. To be accurate, the measured ^{234}Th deficit in surface waters must be multiplied by the ratio of POC to thorium in the material that dominates the flux. It is difficult, however, to define and isolate this material. Defining and measuring the POC to ^{234}Th ratio of particles that dominate the flux has become a key challenge in geochemical studies (Buesseler et al., 1992; Moran and Buesseler, 1993; Charette et al., 2001). Isolation of the material that dominates flux using sediment traps is appealing conceptually, but it is plagued by uncertainty surrounding collection biases of the sediment traps themselves (Buesseler, 1991). The POC to ^{234}Th ratio in sinking material is often equated with the ratio in the $> 53 \mu\text{m}$ fraction because it is generally assumed that this larger size fraction will dominate particle export. This assumption has basis in theory, but it has not been tested in any general way (Moran et al., 2003).

There is no general agreement on whether the POC to ^{234}Th ratio in the $> 53 \mu\text{m}$ size fraction is a good estimate of the ratio in the particles that dominate vertical flux. Buesseler et al (1992) measured a 2-4 fold lower ratio of POC to ^{234}Th in sediment traps relative to suspended material, and they ascribed this difference to an over-collection in traps of large particles with a lower POC to ^{234}Th ratio. Alternatively, Buesseler and co-workers (1995) suggested that “fresh” biological particles are likely to have a higher POC

to ^{234}Th ratio, and that grazing should cycle POC but not ^{234}Th . Therefore, sinking particles may have lower POC to ^{234}Th ratios than less degraded particles sampled in surface waters. Murray and co-workers (1996) also used the POC to ^{234}Th ratio in the $> 53 \mu\text{m}$ size fraction as an estimate of that in sinking matter. They found the ratio in sediment traps was actually three times *higher* than the ratio in the mixed layer $> 53 \mu\text{m}$ fraction, an artefact they attributed to “swimmer” contamination or inaccurate sampling. Rutgers van der Loeff et al. (2002) pointed out that higher trap ratios could result from the formation of fresh aggregates whose decomposition was minimal en route to the traps. They also indicated that at present it is difficult to constrain or predict how ratios in sinking and $> 53 \mu\text{m}$ particles should differ.

To estimate how robust are POC flux estimates based on measured POC to ^{234}Th ratios and ^{234}Th deficits in the surface ocean, investigators have compared estimates made via such measurements with the actual POC flux in various ways (e.g., via carbon budgets, Quay, 1997). Burd and co-workers (2000) compared the ratio of POC flux estimated from ^{234}Th deficit to the actual POC flux via a theoretical model of bacterial particle dynamics. Dunne and Murray (1999) formulated a ratio called the “over-collection factor” which compared ^{234}Th -based POC flux estimates and actual POC flux measurements in the field; in their case, the POC flux was complicated in practice by any applicable sediment trap biases. We focus here on variations caused by phytoplankton dynamics in the (more theoretical) p ratio, defined as the ratio of POC flux estimated based on ^{234}Th deficit to the actual POC flux (Smith et al., unpubl.).

Phytoplankton are single-celled algae that provide the primary source of fresh organic material in marine systems, and are often the primary organisms driving vertical

carbon flux overall, especially during diatom blooms (Waite et al., 1992; 2005). The size distribution of phytoplankton cells is variable and not always easy to measure (Waite et al., 1997), but in theory ranges from the tiniest picoplankton (1 – 3 μm) to the largest microplankton (300 – 500 μm), the range driven both by species composition and by cell growth rate.

Another key process in determining the *in situ* particle size distribution is flocculation (e.g., Jackson and Burd, 1998). Flocculation describes the collision and adherence of particles in suspension, including phytoplankton, and it transfers some fraction of the suspended particles into relatively large, rapidly sinking aggregates of many particles called “flocs”. Understanding potential inaccuracies in ^{234}Th -based estimates of POC flux in phytoplankton-rich waters therefore requires a systematic understanding of how initial cell size, density and flocculation of particles affect the partitioning of ^{234}Th and POC within the *in situ* particle size distribution (Burd et al., 2000).

Time-dependent models of particle dynamics in flocculating suspensions are complex, since terms describing the interaction of each particle size and type with every other particle size and type appear in the governing equations (Jackson and Burd, 1998). The number of computations required for solution is so large that significant simplifications are required to produce a manageable set of equations. For example, particle diameter is often assumed to be uniquely tied to particle composition, so all particles of the same size, whether floc or single particle, are assigned the same density. Even with substantial simplifications, the accuracy of flocculation models is not well known due to basic lack of understanding of particle stickiness, particle-particle

interaction at small separation distances, and floc disruption by hydrodynamic forces (Jackson and Burd, 1998).

An alternative to modeling the time evolution of particle size via flocculation is to assess the instantaneous partitioning of ^{234}Th and POC by making use of a growing body of observations on *in situ* size distributions and settling velocities (Buesseler et al., this volume). The goal of this paper is to use observations to guide the construction of a range of realistic *in situ* size distributions that include both single phytoplankton cells and flocs (aggregates of phytoplankton cells). Here we investigate the underlying role of particle size, sinking rate and flocculation in causing variation in the p ratio of sinking phytoplankton similar to diatoms. We assume that ^{234}Th adsorbs to phytoplankton surfaces, making its activity proportional to particle area. Particulate organic carbon (POC) content of phytoplankton is proportional to particle volume (Strathmann, 1967), so we use volume as a POC proxy. With flocculated size distributions, phytoplankton density, and floc settling velocity as inputs, the ^{234}Th flux, POC flux, and POC to ^{234}Th ratios of various size fractions can be calculated. These quantities can then be used to calculate the p ratio: Estimated POC flux is calculated by multiplying the ^{234}Th flux by the POC to ^{234}Th ratio in the $> 53 \mu\text{m}$ fraction. To calculate p ratio, this estimated flux is divided by the POC flux.

The approach taken here rests on many simplifying assumptions. It is best viewed as an heuristic designed to investigate specific impact of changes in particle size distribution and flocculation on ^{234}Th -based estimates of POC flux. Lessons learned from this study can be applied to interpretation of data from the much more complex natural world. Overall, this model can be used to understand where and when variations

in particle size and flocculation state should or should not degrade ^{234}Th -based estimates of POC flux.

Methods

Our calculations of ^{234}Th flux, particulate organic carbon (POC) flux, and the POC: ^{234}Th ratio of the $> 53 \mu\text{m}$ fraction are based on several key assumptions. First, ^{234}Th activity on particles is proportional to particle surface area, and POC concentration is proportional to particle volume. Assumptions regarding flocs are supported by observations, many of which derive from field and laboratory studies of inorganic sediments. The physics governing the interaction of particles do not depend, to first order, on the composition of the particles, so it is reasonable to apply some basic observations from inorganic particle suspensions to organic ones. The first assumption is that some fraction f of the suspension is packaged into flocs, while the remainder exists as single particles. This fraction is referred to as the “floc fraction” (Syvitski et al., 1995; Dyer and Manning, 1999; Curran et al., 2004). The second assumption is that the mean settling velocity of the floc fraction, which is distributed among flocs of many sizes and densities (e.g., Diercks and Asper, 1997; Hill et al., 1998), can be used to describe the vertical flux of particles within flocs. This assumption is based on the observation that floc size distributions are relatively well sorted and unimodal (Kranck and Milligan, 1992; Khelifa and Hill, 2005), so a mean settling velocity is an adequate descriptor. Finally, flocs are unbiased samplers of particles in suspension, meaning that certain sizes of particles are not preferentially concentrated in flocs. This assumption is based on observations that show equal removal of all particle sizes from suspension in fully flocculated, sedimenting systems (Kranck, 1980; Kranck et al., 1996).

The parent particle size distribution is described by a power-law function of the form (e.g., Sheldon et al., 1972),

$$n(D) = n(D_o)(D/D_o)^{-4} \quad 1$$

In Equation 1, $n(D)$ is the number per unit volume of particles of size D to $D + dD$. The variable $n(D_o)$ is the number per unit volume of particles of diameter D_o to $D_o + dD$, where D_o is a reference diameter. Herein the reference diameter is equated with the smallest particle size in the model. This size distribution has proven useful for describing biological particle size distributions, inorganic mineral size distributions, and optical properties of the water column (Sheldon et al., 1972; Kranck et al., 1996; Boss et al., 2001).

The volume flux of particles under the above assumptions comprises a term for single cell flux and a term for floc flux:

$$F_v = \int_{D_o}^{D_{max}} (1-f)w_s(D)n(D_o)\left(\frac{D}{D_o}\right)^{-4} \frac{\pi D^3}{6} dD + \int_{D_o}^{D_{max}} fw_f n(D_o)\left(\frac{D}{D_o}\right)^{-4} \frac{\pi D^3}{6} dD \quad 2$$

In Equation 2, F_v is the volume flux, $w_s(D)$ is the settling velocity of particles of diameter D , w_f is mean floc settling velocity, and D_{max} is the size of the largest cell in the simulation. The second term on the right-hand side describes the flux of solids volume within flocs, not the overall floc volume, which includes pore volume as well as solid volume. Single cell settling velocities are related to diameter and particle density via Stokes Law (e.g., Allen, 1985):

$$w_s(D) = \frac{(\rho_s - \rho)gD^2}{18\mu} \quad 3$$

In Equation 3 ρ_s and ρ are the densities of the particles and the fluid, respectively, g is gravitational acceleration, and μ is the dynamic viscosity of the fluid. After integration, Equation 2 takes the form

$$F_v = (1 - f)w_s(D_o)v(D_o)D_o \left[\left(\frac{D_{\max}}{D_o} \right)^2 - 1 \right] + fw_f v(D_o)D_o \ln \left(\frac{D_{\max}}{D_o} \right) \quad 4$$

In Equation 4 $v(D_o)$ is the particle volume concentration of the reference particle size per unit diameter in suspension. The flux of POC is related to the flux of volume by a constant of proportionality, $\beta(\text{POC}:V)$:

$$F_{\text{POC}} = \beta(\text{POC} : V)F_v \quad 5$$

The surface area flux (F_{sa}) is calculated similarly to the volume flux. It also has a term to represent single cell flux and a term to represent floc flux:

$$F_{sa} = \int_{D_o}^{D_{\max}} (1 - f)w_s(D)n(D_o) \left(\frac{D}{D_o} \right)^4 \pi D^2 dD + \int_{D_o}^{D_{\max}} fw_f n(D_o) \left(\frac{D}{D_o} \right)^4 \pi D^2 dD \quad 6$$

Upon integration Equation 6 becomes

$$F_{sa} = (1 - f)w_s(D_o)s(D_o)(D_{\max} - D_o) + fw_f s(D_o) \left(\frac{D_o}{D_{\max}} \right) (D_{\max} - D_o) \quad 7$$

where $s(D_o)$ is the surface area concentration per unit diameter of the reference particle size. As with the equation for volume flux, the second term on the right-hand side of Equation 7 represents the flux of solid surface area within flocs, not total floc surface area. The flux of ^{234}Th is related to the flux of surface area by a coefficient of proportionality as well:

$$F_{Th} = \beta(\text{Th} : \text{SA})F_{SA} \quad 8$$

Solids volume in particles larger than 53 μm (V) comprises a single particle fraction and a floc fraction. It is defined with the equation

$$V = \int_{D_c}^{D_{\max}} (1-f)n(D_o) \left(\frac{D}{D_o}\right)^{-4} \frac{\pi D^3}{6} dD + \int_{D_o}^{D_{\max}} fn(D_o) \left(\frac{D}{D_o}\right)^{-4} \frac{\pi D^3}{6} dD \quad 9$$

In Equation 9, D_c is the cut-off diameter for differentiating particles that contribute to the vertical flux from those that do not. Its value here is 53 μm . Upon integration Equation 9 becomes

$$V = (1-f)v(D_o)D_o \ln\left(\frac{D_{\max}}{D_c}\right) + fv(D_o)D_o \ln\left(\frac{D_{\max}}{D_o}\right) \quad 10$$

The concentration of POC (C_{POC}) is assumed proportional to the volume concentration, so

$$C_{\text{POC}} = \beta(\text{POC} : V)V \quad 11$$

Solids surface area of particles larger than 53 μm (SA), including flocs, is given by

$$SA = \int_{D_c}^{D_{\max}} (1-f)n(D_o) \left(\frac{D}{D_o}\right)^{-4} \pi D^2 dD + \int_{D_o}^{D_{\max}} fn(D_o) \left(\frac{D}{D_o}\right)^{-4} \pi D^2 dD \quad 12$$

which upon integration becomes

$$SA = (1-f)s(D_o)D_o \left(\frac{D_o}{D_{\max}}\right) \left[\left(\frac{D_{\max}}{D_c}\right) - 1 \right] + fs(D_o)D_o \left(\frac{D_o}{D_{\max}}\right) \left[\left(\frac{D_{\max}}{D_o}\right) - 1 \right] \quad 13$$

The activity of ^{234}Th (A_{Th}) is related to SA by the same constant of proportionality that links surface area flux to ^{234}Th flux:

$$A_{\text{Th}} = \beta(A_{\text{Th}} : SA)SA \quad 14$$

The ratio of estimated POC flux to actual POC flux defines the p ratio, given by

$$p = \frac{F_{Th} (C_{POC} : A_{Th})}{F_{POC}} \quad 15$$

The value of p is determined by seven inputs: minimum particle diameter, maximum particle diameter, particle density, fluid density, fluid viscosity, floc settling velocity, and floc fraction (Table 1). The concentration of particulate matter is not an input because concentrations cancel in the equation for p . The coefficients of proportionality between ^{234}Th activity and surface area and POC concentration and volume concentration also cancel in the equation for p ratio. To examine the response of p ratio to changes in the governing variables, minimum particle diameter, maximum particle diameter, particle density, floc settling velocity, and floc fraction were each assigned a high and low value based on literature values. Fluid density and fluid viscosity were not varied because these variables have a limited range of possible values compared to the others. Minimum particle diameter was varied from 0.2 μm to 1 μm to determine how the inclusion of colloidal material affected calculated p ratios (Honeyman and Santschi, 1989; Burd et al., 2000). Maximum particle diameter was varied from 60 to 300 μm to simulate a reasonable range in diatom blooms (Waite et al., 1992; 2005). Particle density was assigned values of 1028 and 1100 based on empirical data of Waite et al. (1997) that showed that for unhealthy or physiologically stressed phytoplankton cells at a diameter of 300 μm , sinking rate can be on the order of 100 m d^{-1} , while for healthy cells sinking rate is low across all particle sizes. Floc settling velocity was given a high value of 1 mm s^{-1} , characteristic of many environments (Hill, 1992; Hill et al., 1998). It was assigned a low value of 0.15 mm s^{-1} , which is at the lower end of observed floc settling velocities (Syvitski et al., 1995; Diercks and Apser, 1997). Floc fraction was varied from 0.1,

typical of low concentration environments, to 1, which has been observed in particle-rich waters (Fox et al., 2004).

The sensitivity of p ratio to the five variables that were given high and low values was conducted in analogy with a factorial experiment. The root mean square difference between p ratios with a variable at its high and low value was used to quantify sensitivity.

Results

Of the five variables examined in the factor analysis, floc fraction and particle density have the strongest effects on p ratios (Figure 1). The effect of maximum cell diameter is one half that of floc fraction. The effect of floc settling velocity is approximately one quarter the magnitude of the floc fraction effect. The effect of minimum particle diameter on p ratios is small (Figure 1).

Floc fraction affects p ratios strongly. When floc fraction is equal to one, p ratios also are equal to one. The result reflects the fact that flocs preserve the parent particle size distribution, so sorting of volume relative to surface area is not possible. If no differential sorting of volume relative to surface area occurs, p ratios equal unity. When floc fraction is small, p ratios deviate from unity. To examine this effect in greater detail, model runs were performed for a range of floc fractions extending from 0 to 1 in increments of 0.1 (Figure 2). Largest and smallest p ratios occur for the lowest non-zero floc fractions. The p ratios converge to one as floc fraction grows (Figure 2).

Particle density has a large effect on p ratio because it is a key variable in determining cell sinking rate, thus determining the relative importance of single cells versus flocs in the vertical flux. When particle density is large, the largest single particles sink faster than flocs and contribute significantly to the flux. Because they have larger

volume to surface area ratios, the largest single particles have higher $C_{POC}:A_{Th}$ ratios than the particles within flocs. The mean $C_{POC}:A_{Th}$ ratio for all particles $> 53 \mu\text{m}$ is also lower than the $C_{POC}:A_{Th}$ ratio for the largest single particles. As a result, when particles are dense, the $C_{POC}:A_{Th}$ ratio of the flux is higher than the $C_{POC}:A_{Th}$ ratio of the $> 53 \mu\text{m}$ fraction, so p ratios are less than one (Figure 2a). If single particles sink slowly because of low density, then flocs dominate the vertical flux. Flocs, because they contain all particle sizes, have a lower V:SA ratio, and therefore lower $C_{POC}:A_{Th}$ ratio, than the $> 53 \mu\text{m}$ fraction. As a result, for low density single particles, p ratios are greater than one (Figure 2a).

It is important to recognize that the p ratios for low density particles are maximum values. If single particles are essentially neutrally buoyant, then flocs sinking at 0.15 or 1 mm s^{-1} must be unrealistically large, or they must be ballasted by denser material. If they are ballasted by denser material, then that same material would contribute to the single particle vertical flux. Inclusion of the ballast in calculations would reduce p ratios. The key point of the low density simulations, then, is that large slowly sinking cells tend to cause estimated flux to exceed actual flux.

The effect of maximum single cell diameter can also be understood through its role in determining the relative magnitudes of single cell and floc flux. When individual cells are dense, they can contribute significantly to the vertical flux, producing p ratios less than unity. The presence of larger cells amplifies the importance of cell sinking to the flux and therefore drives p ratios lower (Figure 2a). When cells are near the density of sea water, they do not contribute significantly to the flux. Their presence in the > 53

μm fraction causes overestimation of $C_{POC}:A_{Th}$ so p ratios are larger than one. Larger cells exacerbate this effect (Figure 2a).

Floc settling velocity affects the relative importance of single cell versus floc settling, so it affects p ratios as well. An increase in floc settling velocity reduces the relative contribution of single cell sinking to the vertical flux. This change produces p ratios nearer to unity when cells are dense. When cells are nearly neutrally buoyant, larger floc settling velocities produce p ratios farther away from one (Figure 2a).

In the field, the determination of $C_{POC}:A_{Th}$ ratios of the $> 53 \mu\text{m}$ fraction is accomplished by filtration of large volumes of water. During filtration, it is possible that flocs, which are fragile, would be disrupted (Alldredge and Gotschalk, 1990; Alldredge, 1998), thereby allowing the finer particles within them to pass through a filter. If flocs were disrupted during sampling, then p ratios would exceed one, sometimes substantially (Figure 2b). This result arises because flocs have low V:SA and $C_{POC}:A_{Th}$ ratios relative to large single particles, so failure to capture them on filters would cause overestimation of $C_{POC}:A_{Th}$ ratios in suspended matter. The potential overestimation of vertical flux by undersampling of flocs can exceed a factor of 10 for the particle size distributions analyzed here (Figure 2b). The greatest potential biases caused by loss of flocs are for highly flocculated suspensions populated with dense single particles and for suspensions of slowly sinking particles in which vertical flux is dominated by flocs.

Loss of large single cells through high-volume pump sampling may also affect p ratios. The high-volume pump sampling often used for bulk geochemical analysis is an excellent sampling method for small phytoplankton ($\sim 5 \mu\text{m}$), even when these cells are fragile (Liu et al., 2005). However, pump sampling does have the potential to disrupt the

carbon content of the very largest single particles such as large diatoms (Smetacek et al., 2002). Some large volume pumping systems cause losses of 15 – 20% of chlorophyll from the particulate phase, along with the physical disruption and breakage of the largest single cells (Waite et al., 2005), while Niskin bottle sampling does not entail such losses (Waite and Nodder, 2001). If large single particles were destroyed during sampling, then p ratios would be significantly reduced (Figure 2c). When particles are dense, the destruction of large particles would cause underestimation of the $C_{POC}:A_{Th}$ in the $> 53 \mu\text{m}$ fraction, so estimated fluxes would be less than the actual fluxes. When single particles sink slowly, the destruction of large particles would actually remove the source of error that makes estimated fluxes greater than actual fluxes. As a result, p ratios would equal one (Figure 2c). Losses of the large single particles would have the largest impact on p ratios where there is a large fraction of unflocculated, relatively dense single cells contributing substantially to the flux.

Discussion

The high affinity of ^{234}Th for particle surfaces makes surface area a reasonable proxy for ^{234}Th activity on suspended particles in the sea (e.g., Burd et al., 2000). Volume is a reasonable proxy for particulate organic carbon (POC) for live cells and other organic-rich particles (Strathmann 1967). The simulations performed here are thus useful for exploring the potential biases caused by changes in particle size distribution and by flocculation processes when using ^{234}Th deficits in the surface ocean to predict vertical flux of particulate organic carbon (POC). The simulations are not intended to reproduce observed ^{234}Th and POC fluxes. They neglect a range of processes such as ^{234}Th adsorption and decay, and POC remineralization. They are intended instead to

build insight into the conditions under which flocculation and/or changes in phytoplankton size and density are likely to reduce the reliability of estimated POC fluxes.

The factors that affect p ratios are controlled by a variety of environmental and biological variables. The fraction of particles in flocs (“floc fraction”) is determined by the balance between aggregation and disaggregation of suspended particles. Because aggregation rate scales approximately with the square of particle number concentration, and disaggregation rate scales only linearly with particle number concentration, large floc fractions should be found in suspensions with large particle concentrations (e.g., Jackson, 1990; Hill, 1992). Disaggregation rate is tied to turbulence levels (Alldredge et al., 1990; Ruiz and Izquierdo, 1997; O’Brien et al., 2004). In energetic water columns, therefore, floc fractions are likely lower than in non-energetic ones, other factors being equal (e.g., Jackson, 1995; Ruiz and Izquierdo, 1997). Under these general guidelines, p ratios should be closest to unity when particle concentrations are high and turbulence is low.

In the simulations described here, particle density is linked conceptually to the physiological status of phytoplankton, particularly diatoms. If diatoms are healthy and not sinking, then p ratios are above one, but not by a large amount. If phytoplankton are stressed and sink rapidly, then p ratios fall significantly below one, especially for suspensions populated by solitary cells (i.e., low floc fractions), and especially when these solitary cells are large. Estimated fluxes will tend to be least reliable for large, physiologically stressed cells at low particle concentrations. Relatively low intensity blooms, like those that occur in oligotrophic oceans (Hill, 1992), would produce the lowest p ratios. An example of such a scenario might be planktonic ecosystems in the

Southern Ocean, such as those sampled during the SOIREE experiment. Sedimentation during SOIREE was dominated by relatively large, single-celled phytoplankton with a very low floc fraction (Jackson, Waite and Boyd, 2005), and no increase in flux was detected in the fertilized patch via the ^{234}Th deficit, while significant (2X) increase in POC flux was measured (Nodder et al., 2001; Nodder and Waite, 2001). Our model clearly predicts low p ratios in systems where such large, unflocculated physiologically stressed (and thus rapidly-sinking) cells dominate the biomass and thus helps both to predict and explain such contradictory results.

The size of the largest single particles depends on species composition. Blooms with larger cells that sink rapidly will tend to produce lower p ratios than those with smaller cells. This means that the occurrence of a single large-celled species such as *Coscinodiscus* sp. (300 -500 μm diameter) could significantly impact the p -ratio of a bloom, especially since such large cells tend to dominate vertical flux against a backdrop of smaller particles with less vertical mobility (Waite et al., 2005). In some cases, chain-formation linking cells will increase effective particle size and significantly impact sedimentation rates of unflocculated cells (Waite et al., 1992), lowering the p ratio. However, because chain formation links numbers of smaller cells, the effect on the p ratio should not be as great as for increases in solitary cell size.

Floc settling velocity may respond to turbulence and particle concentration (e.g. Dyer, 1989; Milligan and Hill, 1998) although these effects are not well documented or understood. Under non-energetic conditions, mean floc settling velocities observed in a variety of environments cluster around 1 mm s^{-1} (cf. Hill et al., 1998). As turbulence grows, floc size decreases, perhaps abruptly (Hill et al., 2001; O'Brien, 2004). Due to the

link between floc size and settling velocity, turbulence likely reduces floc settling velocity as well (e.g., Hill et al., 1998). Smaller floc settling velocities produce smaller p ratios, so error in estimated POC flux is likely to be worst under energetic conditions. High particle concentrations may enhance floc settling velocity (Dyer, 1989; Manning, 2004), so error in estimated POC flux is likely to be least when particle concentrations are high.

In summary, blooms of small phytoplankton cells in highly flocculated suspensions should be least prone to error in estimating POC flux, as long as it is actually these small cells, and not the rarer larger ones, that dominate vertical flux (Waite et al., 2005). Turbulence, therefore, has overall a negative effect on the reliability of flux estimates because it likely reduces floc fraction and settling velocity. Both of these effects would cause p ratios to deviate from unity. On the other hand, large particle concentrations increase floc fraction and may enhance floc settling velocity. Both of these effects would cause p ratios to be nearer to unity. Nutrient stress occurs in stratified waters, leading to higher phytoplankton sinking rates. Higher cell sinking rates cause lower p ratios. This effect may counteract somewhat the hydrodynamic effects of low turbulence on p ratios.

These predictions above are in need of testing. Future studies that use ^{234}Th deficits to estimate POC flux would benefit from characterization of the full particle size distribution and measurement of floc settling velocities. With these measurements it would be possible to estimate floc fraction and to constrain the biases introduced into the estimated flux by differential flux of surface area and volume.

Conclusion

The rapid adsorption of ^{234}Th to particle surfaces in the surface waters of the world's oceans combined with its subsequent removal by particle sinking provides oceanographers with a tool for quantifying the export of particulate organic carbon to the deep ocean. The proper use of this tool, however, requires sound knowledge of the ratio of POC to ^{234}Th on the particles that dominate the vertical flux. This ratio typically is equated with the $C_{\text{POC}}:A_{\text{Th}}$ ratio of large particles in suspension. In partially flocculated suspensions, this assumption can produce erroneous estimates of POC flux. If the largest single particles sink faster than flocs, then ^{234}Th -based estimates of carbon flux should underestimate the actual flux. Under these circumstances, the capture of flocs on filters should cause estimated $C_{\text{POC}}:A_{\text{Th}}$ ratios to be too low. This underestimate arises because flocs contain small particles with small volume to surface area ratios and hence small $C_{\text{POC}}:A_{\text{Th}}$ ratios. If the largest single particles sink slower than flocs, then thorium-based estimates of carbon flux should exceed the actual flux because the capture of large slowly sinking single particles on filters would cause $C_{\text{POC}}:A_{\text{Th}}$ ratios to be too high. Overestimation occurs because the volume to surface area ratios for large single particles are higher than for flocs.

These basic rules governing the effect of cell size, cell settling velocity and flocculation on the reliability of thorium-based estimates of POC flux should hold across a wide range of phytoplankton growth, carbon remineralization, and thorium decay and adsorption characteristics, even when these actively alter the distribution of POC and ^{234}Th among particle size classes. Our model therefore provides a suite of clear, testable hypotheses for use both by modelers, and by large field programs such as VERTIGO that

have the capacity to make, in the field, direct estimates of the parameters we have modeled. Such future attempts to quantify the error associated with thorium-based estimates of POC flux will benefit particularly from careful measurement of the particle size distribution and the settling velocities of flocs and single cells.

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Table 1: Variable values used in model sensitivity analysis.

Variable	Symbol	Model Values
Minimum diameter	D_o	0.2 and 1.0×10^{-6} m
Maximum diameter	D_{max}	60 and 300×10^{-6} m
Particle density	ρ_s	1028 and 1100 kg m^{-3}
Floc settling velocity	w_f	0.15 and $1 \times 10^{-3} \text{ m s}^{-1}$
Floc fraction	f	0.1 and 1.0
Fluid density	ρ	1027 kg m^{-3}
Fluid viscosity	μ	$0.0014 \text{ kg m}^{-1} \text{ s}^{-1}$

Figure Captions

Figure 1. Root-mean-square (rms) difference in p ratios calculated with a high and low value of five variables: minimum particle diameter (D_o), maximum single particle diameter (D_{max}), density of single particles (ρ_s), floc settling velocity (w_f), and floc fraction (f) (Table 1). The rms difference for a given variable is a measure of the sensitivity of p ratio to changes in that variable. This analysis indicates that p ratio is most sensitive to changes in floc fraction and particle density, and least sensitive to changes in minimum particle diameter.

Figure 2. Calculated p ratios as a function of floc fraction for various combinations of maximum particle diameter, particle density, and floc settling velocity. Results are shown for only one minimum particle diameter (1 μm) because of the lack of sensitivity of p ratio to changes in this variable. The *top panel (a)* shows results for simulations that assume that the total volume to surface area ratio of suspended solids is measured accurately. The *bottom left panel (b)* shows results for simulations that assume that flocs are not sampled when estimating volume to surface area ratio of suspended solids. Note that the scale in this panel covers a much larger range than the other two panels. The *bottom right panel (c)* shows the results for simulations that assume that non-flocculated single particles are not sampled when estimating volume to surface area ratio of suspended solids. Symbols indicate various simulations. *Open triangles* show simulations for which particle density was low, and *closed triangles* show simulations for which density was high. *Small triangles* indicate small maximum particle diameter, and *large triangles* indicate large maximum particle diameter. *Upright triangles* show

simulations for which floc settling velocity was small, and *inverted triangles* depict results of simulations for which floc settling velocity was large.

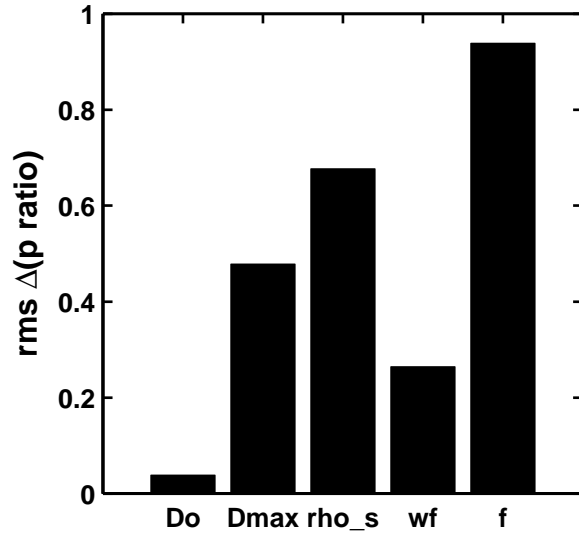


Figure 1.

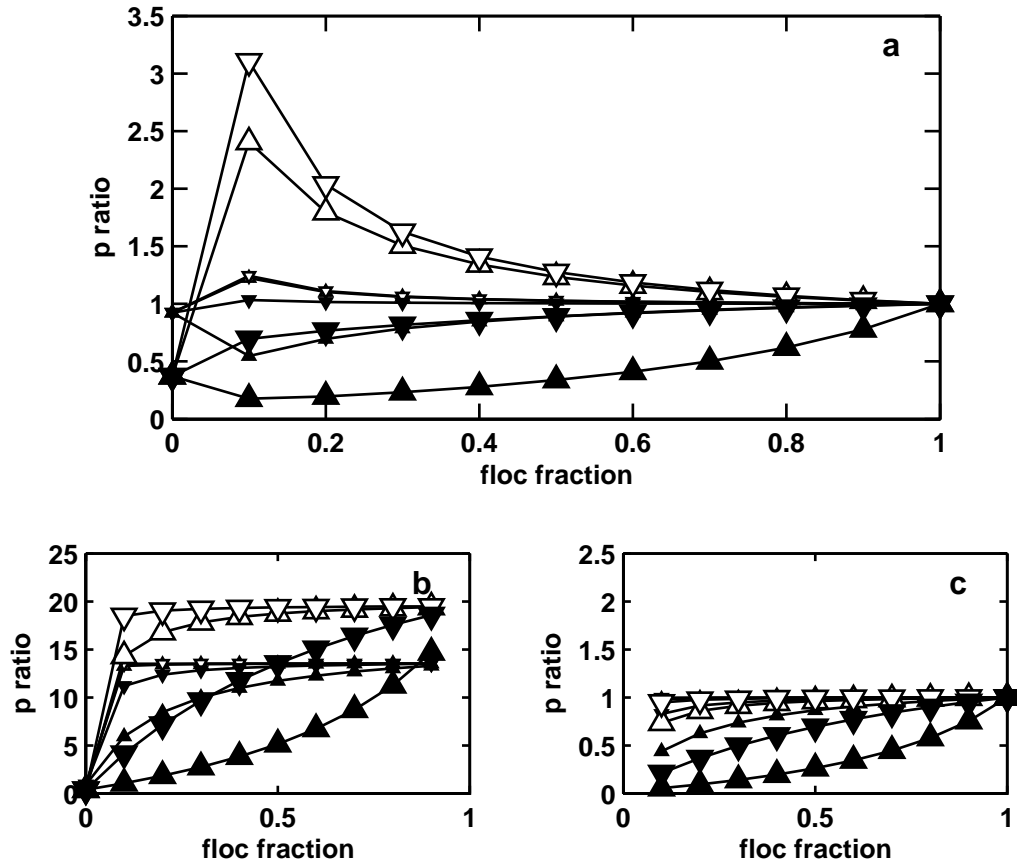


Figure 2.