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Biogeosciences Discussions

Interactive comment on "Particle-associated dissolved elemental fluxes: revising the stochiometry of mixed layer export" *by* A. N. Antia

Anonymous Referee #2

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This is an interesting and well-written paper which I suspect will have a large impact on a wide range of issues in marine biogeochemistry. Dr. Antia's data and presentation put forward a compelling case for the need to study the compositions of supernatants overlying particle samples from sediment traps...a phase which is normally discarded during sample handling. The reason being, if I've understood her manuscript, is that some of the flux which enters sediment traps is ultimately to be found in the solution phase, and not the particle phase. This is observed as an excess of some substance above that in the seawater, brine or preservative solution sent down in the sediment trap cups. By analyzing the supernatant and adding this excess amount to the particulate phase flux, Dr. Antia has demonstrated that not only are the magnitudes of a number of important marine flux components dramatically increased, but that the ratios of these components in the flux are restored to values that have enormous biogeochemical importance. For example, CNP ratios in the downward flux look very much

like classic Redfield values, rather than the N and P depleted values one often finds in the literature when only the particulate phase in the sediment traps are considered. Dr. Antia's abundant data and careful handling of the information leave little doubt in my mind that she has identified a very significant phenomenon and that everyone working with sediment traps needs to be keenly aware of her findings.

I am, however, still unconvinced by her explanation of the mechanism by which this excess of material in the solution phase appears in sediment trap cups. I believe her current hypothesis is that this is a flux of material present in a solution phase that is "trapped" in the interstitial phase of sinking marine particles, and that are dragged into sediment traps. While possible, I believe that she has not completely considered the kinetic limitations of her arguments and therefore she turned away from the more mundane but I think more reasonable explanation: continued particle degradation in sediment trap cups, resulting in an accumulation of material in the solution phase during sediment trap deployment. This is an important distinction to make from an operational point of view, because it implies that traps deployed for a relatively short time (usually shallow water deployments) are not likely to have experienced this effect to a large degree and therefore we may continue to make use of much of the shallow water literature values without a large fear that these values are much too low. For example, on manuscript page 284, Dr. Antia says "diffusive fluxes on the order of ca. 16-50 μm/day (citing Kiorboe et al, 2001; Ploug et al., 2002) would ensure equilibration of interstitial concentrations with the supernatant solution during the long storage times used in this study." If the diffusive fluxes were that large, then sinking particles might also be expected to come to equilibrium with s.w. during the multi-day trip from the surface to her deep moored sediment traps. I was thinking this could be scaled in the following way: Imagine particle degradation from the particle phase (p) as dp/dt=-kVp, where k is the degradation rate constant and V is the particle volume. The rate of diffusive loss from the solution phase (s) trapped within the particle could be modeled as ds/dt = -ADds/dx, where A is the particle area, D is the diffusion coefficient and ds/dx is the gradient of the component from within to without the particle. Let R equal the ratio of

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these two rate laws to one another (degradation on top). If R is greater than 1, then degradation is faster than diffusion and an enriched interstitial fluid can build up. If R is less than 1, then diffusion is faster than degradation and can keep pace, leading to no enrichment in the fluid. Let's also assume that s can be represented as fp, or some fraction of the particle loading (f can be any number greater than or equal to 0), and only represents the excess...thus ds/dx becomes fp/x, where x is the particle radius. Therefore, R = kVp/(ADfp/x), which rearranges to kxV/DfA. Since V/A = r/3 for a spherical particle, R further simplifies to kx^2/3Df. Assuming D=10^-5 cm^2/s (ca. 1 cm^2/d), degradation and diffusion will be comparable when kx^2=3f. As k is going to be at most 30% per day or so, you can see the left hand side will be less than the right (and R will be less than 1) for most instances, unless x gets quite large, or f becomes very small. As particles get big in the real ocean, they are usually big flocs that are very porous and wouldn't trap fluid well, and if f gets small, then the fluids aren't important anyway. Thus, I think particles are degradation limited during their descent.

Dr. Antia countered this possibility by arguing that the material in the cups was poisoned and therefore should have undergone relatively little degradation while in the cup. She cited the work of Lee and others as support. I believe Lee and colleagues demonstrated the effectiveness of their poisons by showing that there was little heterotrophic uptake of radiolabelled glutamic acid. I'm not sure, but I don't believe this precludes cells surviving and continuing to be somewhat active. In addition (and Dr. Antia acknowledged this) there are enzymes released into the supernatant during cell death which could continue to carry out the work of particle degradation in the absence of viable cells. I've been told this is particularly true in the case of Hg-poisoning; formalin-poisoning material does result in some protein denaturing/binding that might slow down extracellular enzymatic activity. Furthermore, she did not make use of a confining brine layer, which would have aided in poison diffusion out of the cups, diminishing their effectiveness. Thus, I think it too premature to suggest that material in sediment trap cups is largely stable.

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I still think this an eminently important paper and should be published immediately...with perhaps some consideration by Dr. Antia on the issue of competition between degradation and diffusion.

Other particular points: There was no deployed blank in the system, and her excess concentrations are determined as the difference between the supernatant and the undeployed, poisoned water used to fill the cups. For whatever reason, this blank might differ from water that spent time at depth in a sample cup. Probably a minor effect. In numerous instances, the notation XX(+x.x)% was used to document the amount of a component that was found in the supernatant. Does this mean XX+/-xx%?

Interactive comment on Biogeosciences Discussions, 2, 275, 2005.