Biogeosciences Discussions, 2, S255–S259, 2005
www.biogeosciences.net/bgd/2/S255/
European Geosciences Union

Biogeosciences
Discussions

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

A. N. Antia

Received and published: 14 June 2005

I appreciate the constructive comments by this reviewer and would like to respond to them in detail as follows:

1. The statement that degradation of material in the traps does not take place cannot be supported since this was not investigated (nor were oxygen measurements done), but is based on the paper by Lee et al. (1992) who tested poisons at various concentrations on particle samples. However, as this reviewer points out, degradation cannot be ruled out, in part since it is unclear as to how fast poison penetrates the aggregates. Additionally, free enzymes within and on the aggregates, although inhibited in their action by poison /fixative, will also degrade some substrate. The manuscript has been ammended to account for this fact and the following inserted: "Concievably, other processes such as continued microbial degradation, the activity of free hydrolytic enzymes, physical destruction of dead organisms and damaged membranes and chemi-

cal dissolution could also contribute to a continued leaching or even production of dissolved elements. Although at the concentration of mercuric chloride used in this study Lee et al. (1992) report complete and almost immediate cesation of microbial activity in a concentrated particle suspension, penetration of the poison into the aggregates would be rate-limited by the diffusivity coefficient applicable. Bezezinski et al. (1987) estimate 2 orders of magnitude slower diffusivity rates for silica from fractal, gel-matrix aggregates than those for elemental silica through a permeous membrane; the effects of poisons are thus unlikely to be instantaneous, though this has not been tested in trap samples. Free enzymes such as phosphatases and proteases are also concentrated in aggregates and though their activity is strongly inhibited by both mercuric chloride and formaldehyde, at the concentrations used to poison trap samples (Christian & Karl 1995; Chen, Chen, Lin, Li, Yang, and Qui, 1997), the same time constraints on penetration of poison as discussed above would apply. In as far as phosphatases degrade larger dissolved organic entities to phosphate and low molecular weight organic material, they would contribute to alteration and not production of dissolved species."

2. The reviewer points out that DIC was not measured or accounted for. This is difficult to do in this type of sample since the solution is buffered, precluding measurements of the carbonate system. However, I attempt to judge the extent of the problem by assuming (as a first approximation) that continual respiration after particles settle in the jars would produce dissolved inorganic carbon (DIC) and nitrogen (DIN) whereas enzymatic degradation and leaching from particles would give out dissolved organic carbon (DOC) and nitrogen (DON), roughly in the Redfield C:N ratio of 6.6:1. If I then multiply the DIN concentration by 6.6 and assume that this (roughly) estimates the contribution of DIC to carbon flux, this ammounts to 2.8 - 4.3 % of particulate organic carbon (POC) flux and 1.7 - 3.3 % of total organic carbon (POC + DOC) flux. This has been ammended in the manuscript: "Dissolved inorganic carbon (DIC) was not measured since the cup water was buffered, precluding measurements of the carbonate system. However, I attempt to judge the extent of the problem by assuming (as a first approximation) that continual respiration after particles settle in the jars would produce dissolved inor-

ganic carbon (DIC) and nitrogen (DIN) whereas enzymatic degradation and leaching from particles would give out dissolved organic carbon (DOC) and nitrogen (DON), roughly in the Redfield C:N ratio of 6.6:1. If I then multiply the DIN concentration by 6.6 and assume that this estimates the contribution of DIC to carbon flux, this ammounts to a mean of 55 - 316 μmol DIC/l in the traps, or 2.8 - 4.3 % of particulate organic carbon (POC) flux and 1.7 - 3.3 % of total organic carbon (POC + DOC) flux.”

3. Since the samples were poisoned with buffered mercuric chloride, pH changes cannot be interpreted to reflect changes in the carbonate chemistry in the cups. However, excess dissolved calcium measured showed little calcium carbonate underwent dissolution. (Table 1, an average of 3 mg Calcium per 400-ml cup was dissolved, corresponding to an alkalinity increment of 330 μmol/l and DIC change of 165 μmol/l. Calculating the potential effect of this calcite dissolution in the cups on cup pH in an unbuffered solution (temperature 4°C, DIC 2100 μmol/kg, Alkalinity 2300 μmol/kg), results in increased pH by an average of 0.2 units. Back-calculating the ammount of respiration that would be needed “balance” this (i.e. bring pH back to the original value) yields 111 μmolDIC/l added due to respiration. This is close to the figure of 55 - 200 μmol DIC/l (316 for OMEX 2 at 600 m) calculated using DIN as a “respiration indicator” in point 2 above. (all calculations using the “CO2SYS” program by E.Lewis). However, these considerations are purely academic where buffered systems are used. The text now includes a short presentation of the point:

“As mentioned, in buffered systems alterations in pH that would summarise changes in the DIC and alkalinity pool due to calcite dissolution and respiration (that have opposing effects on pH) cannot be used. In unbuffered systems however, a rough calculation indicates that these could cancel each other, resulting in loss of DIC and calcite at constant pH values. For example, in these traps the dissolution of calcite, on average 3 mg excess calcium per 400-ml cup was dissolved, corresponding to an alkalinity increment of 330 μmol/l and DIC change of 165 μmol/l. At a temperature of 4°C, DIC of 2100 μmol/kg, and Alkalinity of 2300 μmol/kg, this would increase pH by 0.2 units.

Back-calculating the ammount of respiration that would be needed "balance" this (i.e. bring pH back to the original value) yields 111 μmolDIC/l added due to respiration. This is close to the figure of 55 - 200 μmol DIC/l (316 for OMEX 2 at 600 m) estimated to result from respiration in the cups (see previous paragraph). (All calculations using the "CO2SYS" program by E.Lewis). Nonetheless, these processes would have a small effect on total solubilisation losses since most organic carbon is lost as DOC and little calcite looses are seen. This approach may be useful in shallow, short-term trap deployments where additional mesurements of oxygen depletion could be used to constrain respiration."

4. Trapping efficiency determined by Scholten et al (2001) was indeed for these traps. Since Thorium measurements are not appreciably affected by solubilisation (since Thorium is strongly particle reactive) the "trapping efficiencies" remain unchanged (though aplying them to diferent elements still assumed that there is no particle sorting, which has not been tested). The error due to trapping efficiency is thus for bulk particles (and is bi-directional i.e. under and over-estimation) and includes the fraction that has been solubilised. The error due to solubilisation is both unidirectional (upward correction only) and differs substantially between elements. This has been added to the manuscript. "For the OMEX traps, for example, Scholten et al. (2001) estimate collection efficiencies of ca. 38 % at 600 m at both mooring sites, 90% at 1050 m at OMEX 2 and 113 % and 128% at 1440 m and 3220 m at OMEX 3. As these authors point out, these estimates are to be treated by caution, since no direct measurements in the water column were available and because of their proximity to the shelf edge, where particularly in the deeper traps lateral advection could have caused the "overtrapping" signal. Nonetheless, it should be pointed out that this correction, based on calculated and measured fluxes of 230Th, is unaffected by solubilisation since thorium has a high affinity for particles and is not found in supernatent water (Pohl et al. 2004). The factor of 2.5 "correction" based on the Thorium budgets for the 600 m traps is similar in magnitude to that for organic carbon and nitrogen and slightly lower than that for phosphorus when accounting for solubilisation." 5. Analytical errors are included in

the Results section 6. Will be rectified 7. Conclusions have been added Thanks once again for these comments that have clarified and added value to the manuscript.

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