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Biogeosciences Discussions

Interactive comment on "Does ocean acidification induce an upward flux of marineaggregates?" *by* X. Mari

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General comments: This study investigates the effect of seawater acidification on aggregation and sinking of transparent exopolymer particles (TEP). Natural seawater filtered through 0.2 μm polycarbonate filters was acidified with sulfuric acid (delta_pH of 0.2, 0.4, and 0.8 units). After addition of 6 μm diameter microspheres (beads) the samples were exposed to small-scale turbulence of three different intensities generated by an oscillating grid. TEP size spectra and the adherence of beads were examined microscopically following Alcian Blue staining.

Seawater acidification caused an increase in the size and abundance of TEP. A 100-fold difference in shear stress did not have any detectable effect on TEP formation and bead adhesion. A decrease in sinking velocity and an increase in ascending velocity in response to the acidification treatment was deduced from changes in TEP and bead

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concentrations with time in the top and bottom layer of tissue flask. Implications of these results with respect to ocean acidification and the ocean's biological pump are discussed.

While this study addresses a potentially important and timely issue, the effect of ocean acidification on TEP formation, aggregation and sinking, the experimental approaches used to determine the pH/CO2 sensitivities of these processes raise some questions:

1. Significant differences between TEP size and abundance were obtained between control and pH treatments, however, no difference was observed between the different pH levels, despite a three-fold difference in acid addition. This suggests that the observed effect may be in response to the acid treatment itself rather than the level of acid-induced changes in the carbonate system. Considering that seawater acidification was achieved through the addition of concentrated H2SO4, a transient drastic pH perturbations likely occurred in the sample (or parts of it) upon acid addition. The effect of this on the properties of TEP precursors may have been much stronger than that of the comparatively moderate pH change sustaining after equilibration of the seawater carbonate system. To ensure that the observed responses are not an artifact of the short-term severe pH perturbation, it would have been worthwhile to apply alternative modes of perturbing the carbonate system (e.g. diluting the concentrated acid with organic-free seawater before addition to the samples, applying acid addition of lower molarity or addition of CO2 saturated seawater).

Author Reply: Like Referee #1, I was expecting a linear response to the increasing acid addition. However, the results obtained rather suggest a sigmoidal response to increasing acidification, with an inflexion point for an acidification $<$0.2 units of pH. According to this view, the response of the system to a diminution of pH of 0.4 or 0.8 should not be significantly different from that observed of a diminution of 0.2 units. Referee #1 suggests that the non-linear response to acid addition may be in response of the acid treatment itself. I had forgotten to mention that H2SO4 was first diluted (dilution factor = 1:100) in 0.2-μm filtered seawater prior to addition. I have added a

BGD

5, S814–S820, 2008

comment in the revised version mentioning the dilution.

2. Sinking and ascending rates were measured in 200 ml tissue flasks through sampling of the top and bottom layers after 1, 2, 3, and 4, assuming an initially homogenous sample. According to the author's description, this approach was inappropriate to provide representative samples of the sinking and ascending TEP. As stated on p. 1640, lines 8-10: "...particles 'escape' the surface sampling ... by adhering to the surface microlayer (SML)". And further: "The sampling procedure does not seem to recover satisfactorily the TEP and beads that are likely accumulating in the SML" (p. 1640, lines 12-14). To circumvent the apparent methodological failure, the author modified the data analysis for calculating ascending rates (p. 1640, lines 24-28): "Since the surface sampling apparently failed to detect the surface accumulation of particles, the upward velocity in the pH treatments was calculated from changes in TEP and beads concentrations occurring in the bottom layer during the first hour." Obviously, sampling of the middle layer (missing in this analysis) would have helped to clarify the inconsistency between expected and measured surface layer concentrations. Without this measurement, it is not possible to verify the assumption that the missing material accumulated in the SML. Given the importance of this assumption to the data interpretation, I am surprised that no attempt was taken to analyze the surface microlayer for TEP and bead accumulations. In essence, because this approach relies on some critical but untested assumptions, I think it is not an appropriate method to estimate particle ascending rates.

Author Reply: I agree that the hypothesis that ascending particles accumulated in the SML cannot be proved otherwise than by studying the dynamic of SML formation. However, this hypothesis is only needed to explain the fact that while particles were leaving the bottom layer they were not recovered in the surface layer. Testing this hypothesis is not required to validate the import rate of particles to the bottom layer (i.e., settling velocity) or of the export rate of particles from the bottom layer (i.e., ascending velocity). I do not think it is crucial to study the middle layer in order to estimate the

BGD

5, S814–S820, 2008

velocity at which TEP and beads were leaving (via upward transport) or reaching (via downward transport) the bottom layer. Given that the particles collected in the bottom layer could not be missed (like is the case in the surface layer), variations of particles concentrations in the bottom layer gives a robust estimate of the import rate of particles to this layer (i.e., settling velocity) or of the export rate of particles from this layer (i.e., ascending velocity). The only alternative way settling and ascending velocities could have been misestimated when derived from the variations of particles' concentration in the bottom layer, is if particles accumulated in the middle of the chambers. Such a process is highly unlikely in a water column of less than 9 cm height lacking in a density gradient. In other words, I agree that it would have been useful to have the concentration of particles in the middle layer and in the SML in order to close the budget and to demonstrate that the SML is indeed a sink for ascending particles, but I argue that changes in the concentration of particles in the bottom layer are sufficient to determine the direction of vertical flux and to give estimates of settling and ascending velocities.

Some questions also arise regarding the extrapolation of the experimental results to the natural system:

1. A change in seawater pH of 0.2 units is well in the range of pH variability naturally occurring for example during the seasonal cycle in temperate to high latitude regions or during upwelling events. Is there any field evidence that pH changes of this magnitude influence TEP production, aggregation or sinking (ascending) in areas where pH changes of this magnitude occur naturally?

Author Reply: To my knowledge there is no field study that examined the possibility of an upward flux of particles related to pH variations, or to a larger extent the possibility that pH variations may modulate export rate of particles. I think the present study shows the need for such an investigation. However, some indications suggest that naturally occurring pH variations may indeed favor the ascension of particles and feed the SML, or at least reduce vertical export. In particular, there are two systems

BGD

5, S814–S820, 2008

that experience strong pH variations: estuaries and upwelling. In their study of the TEP-content in SML, Wurl and Holmes (2008) showed that in their estuarine samples, the SML contained a higher fraction of TEP than the SML collected from oceanic samples. Although pH was not mentioned in this study, estuaries are known to experience strong changes in pH. Of course, many other factors may explain such a difference in the composition of the SML between the two systems they investigated, but such a coincidence is rather interesting in the light of the present results. In addition, in upwelling systems, which are known to show pH lower than the average pH (8.16), often lower than 8, it has been shown that vertical fluxes were not directly correlated to the standing stock of suspended POC (Kiorboe et al. 1998). One may hypothesize that the discrepancy observed in upwelling between the standing stock of suspended POC and the vertical export may be related to pH variations and TEP-mediated retention of POC in the surface upper layer. However, to my knowledge the export of particles from the surface upper layer of upwelling systems has never been studied in relation to pH variations. These two points are now discussed in the revised version.

2. Because the maximum effect on TEP formation and aggregation was observed already at a pH decrease of 0.2 units, shouldn't one expect the change in surface ocean pH of 0.12 units since pre-industrial times already have affected these processes? Is there any indication in long-term data sets (e.g. from the time series stations BATS, HOTS, ESTOC) to support this?

Author Reply: I totally agree. It would be very interesting to look into long-term data sets from time series stations to detect any indication of pH induced variation of vertical flux since pre-industrial time. I am not aware of such past or present studies.

3. Given i) the methodological uncertainty (perturbation with concentrated sulfuric acid), ii) the untested assumption about accumulation of TEP and beads in the SML), iii) the surprising finding that a three-fold difference in acidification resulted in identical changes in TEP abundance, size and adherence of beads, is it justified to extrapolate these results to infer about possible future changes in the ocean's biological pump?

BGD

5, S814–S820, 2008

Personally, I think the data interpretation and its extrapolation to the 'real world' requires a more critical evaluation of the results.

Author Reply: I agree that this study does not allow concluding about possible future changes in the ocean's biological pump, but it shows that the matter may not be as simple as the negative feedback postulated by Riebesell et al. (2007). I am aware of the difficulty to extrapolate to the 'real world' the effect of pH variations based of this study. This limit of the present work has been acknowledged in the manuscript, and I try to be as cautious as possible when concluding. For that reason the title is a question rather than a statement.

In summary, I cannot recommend this manuscript for publication in Biogeosciences in its present form.

Minor comments: 1. P. 1632, line 1 of the abstract: Change to "absorption" See also p. 1634, line 5.

Author Reply: Corrected accordingly.

2. P. 1633, lines 2-5, p. 1634, lines 7-9: At present there is no evidence that the biological pump is contributing to fossil fuel CO2 sequestration in the ocean.

Author Reply: I agree that there is no evidence that the ocean is a pump for atmospheric carbon, i.e., that the ocean is a 'sink' rather than a 'source'. However, there is a plethora of evidence that biological activity is pumping down atmospheric carbon and that vertical export of POC is a strong contributor to this drawdown of CO2. This work presents some evidence that changes in pH may actually strengthen the source' hypothesis. As I have written "In such a scheme, the ocean is assumed to play a role in regulating fossil fuel CO2 accumulation by exporting a part of the excess organic carbon produced, provided the DIC fixed during photosynthesis sinks out of the euphotic zone and is buried in sediments."

3. P. 1633, line 10: Projected anthropogenic ocean acidification is not expected to

BGD

5, S814–S820, 2008

exceed a pH decrease of 0.8-1 pH unit over the next few hundred years.

Author Reply: According to the model exercise conducted by Caldeira and Wickett (2005), depending on the CO2 emission scenario used, seawater pH may decrease by up to 1.4 units over the next 300 years. My expertise doesn't allow me to judge whether this is a realistic estimate or not.

4. P. 1636, line 1: Give normality of H2SO4.

Author Reply: The molarity is mentioned and the normality of H2SO4 is twice its molarity.

5. P. 1641, lines 12-14: Doesn't this statement contradict some of the results reported in the previous section?

Author Reply: Referee #1 is perfectly right. The correct sentence is: "In the acidified seawater, the concentration of TEP in the bottom layer always decreased, and their average..." This sentence has been changed accordingly.

6. P. 1643, first paragraph: I don't see how the results of this study specifically relate to the SOIREE iron fertilization experiment. If TEP production indeed reduces particle sinking, shouldn't this be a typical phenomenon after any regular

Author Reply: Referee #1 is right. Referring to this study was not pertinent since it is not linked (at least it is not stated) to pH variations. This reference has been removed.

Interactive comment on Biogeosciences Discuss., 5, 1631, 2008.