Export is not enough: Nutrient cycling and carbon sequestration

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Abstract

The question of whether iron fertilization can yield verifiable carbon sequestration is often cast in terms of whether fertilization results in enhanced particle export. However, model studies show that oceanic carbon storage is only weakly related to global particle export- depending instead on an increase in the carbon associated with the pool of remineralized nutrients. The magnitude of such an increase depends on circulation, stoichiometric ratios and gas exchange. We argue that this puts serious challenges before efforts to properly credit iron fertilization that must be taken into account at the design stage.

Introduction: The role of nutrients in the carbon cycle

One of the most puzzling facts in ocean biogeochemistry is that only about half the inventory of dissolved nitrate and phosphate is directly associated with carbon. This can easily be seen by considering the inventories of phosphate and oxygen in the deep ocean. The ratio of phosphate remineralization to oxygen utilization is around 1:170 for the deep ocean, but the average apparent oxygen utilization is only of order 170

micromolar. Thus only about 1 micromole of the phosphate in the deep ocean is associated with remineralized carbon. Since the concentration of phosphate in the deep ocean is 2.2 micromolar, approximately half of it is then *not* associated with carbon. This biologically unutilized phosphate reaches the deep as a result of surface waters that subduct with high nutrient content and is known as the preformed phosphate, or PO_4^{pref} .

Because the micronutrient iron is used for both chlorophyll synthesis and nitrate reduction, both of which are vital for plankton growth (c.f. Boyd, 2002), much attention has focused on iron limitation as a mechanism to explain the relatively high oceanic concentrations of preformed phosphate. The promise of iron fertilization is that shifting nutrients from the biologically unutilized (or preformed) pool to the biologically utilized (or remineralized) pool allows the ocean to hold more carbon. This carbon will be taken out of the atmosphere. A schematic illustration of how this might work is given in Case 1 in Figure 1- showing how increased productivity and export leads to a reduction in nutrients subducting to depth.

It is common in discussions about iron fertilization for an equivalence to be made between increased nutrient utilization and increased particle export. One of the points of this paper is to reiterate that such a connection need not hold. To take an obvious example if water is flowing through a region where 20% of the nutrients are stripped out, a faster flow of water through the region will lead to a larger export, even though the fraction of nutrient utilized remains constant. A subtler example is shown in Case 2 in Figure 1, where iron fertilization causes nutrients to be consumed locally at point A so that fewer nutrients are advected (on time scales of years to centuries) downstream to point B. This can result in a decrease in export, not only at point B, but also globally

(Marinov et al., 2006). But since the average global concentration of preformed nutrients into the deep ocean drops, so does atmospheric carbon dioxide. A final case (Case 3 in Figure 1) is one in which nutrients are consumed before subduction. By concentrating production near the upwelling, fertilization may then produce "nutrient trapping" (Najjar et al., 1992) increasing the concentration of upwelling nutrients and so resulting in a net increase in production, but *without* significantly changing preformed nutrients and atmospheric carbon dioxide (as noted in Aumont and Bopp, 2006).

Recent work by Marinov et al. (2008a) suggests a more productive way to think about the oceanic carbon storage associated with biology or OCS_{bio} . Disregarding for the present the smaller calcium carbonate pump.

$$OCS_{bio} = \overline{PO_4^{remin}} R_{C:P} + OCS_{bio}^{diseq}$$
(1)

 $\overline{PO_4^{remin}}$ is the globally averaged remineralized phosphate in the ocean and can be written as:

$$\overline{PO_4^{remin}} = \overline{PO_4^{tot}} - \overline{PO_4^{pref}}$$
(2)

where $\overline{PO_4^{tot}}$ is the total phosphate content and $\overline{PO_4^{pref}}$ is the globally averaged unutilized or "preformed" content, i.e. that associated with subducting waters. The oceanic carbon storage then consists of a term proportional to remineralized phosphate and a term associated with disequilibrium (OCS_{bio}^{diseq}) resulting from the fact that ocean water depleted in carbon by biological production (or enriched by upwelling of carbon rich deep waters) may not have time to come into equilibrium with the atmosphere before it is subducted. We focus on phosphate rather than nitrate for two reasons, the first being that its longer residence time and lack of nitrification/denitrification feedbacks makes it more likely to be the ultimate limiting nutrient (Tyrell, 1999; Moore and Doney, 2007), and the second being that C:P ratios appear to be much more variable than C:N ratios.

This basic picture can be used to analyze why different ocean models produce different atmospheric pCO₂ (pCO_2^{atm}). Marinov et al. (2008a,b) examine a range of diagnostic ocean models using a simple representation of biological cycling in which nutrient concentrations near the surface are restored either to the observed value to mimic the natural carbon cycle or to zero to mimic the maximum possible impact of iron fertilization. This must be understood as an upper limit, as both large-scale (100s of km) natural fertilization patches associated with topographic features (c.f. Pollard et al., 2007) and mesoscale (10s of km) purposeful experiments (Boyd et al., 2007) only show drawdowns between 30 and 75% of the initial nutrient inventory. In these models R_{C:P} is set to a constant value of 117 for all time and space. By using a set of models in which the winds and diffusion coefficients differ, we are able to examine the extent to which the response of pCO_2^{atm} to nutrient drawdown depends on the global overturning circulation.

One result that has emerged from these models is that changes in circulation can change pCO_2^{atm} by changing $\overline{PO_4^{pref}}$ (Marinov et al., 2008a). This can be seen by looking at the +-marks in Figure 2a showing results from the control set of the model where surface nutrients are restored to their observed values. As the preformed nutrients go down (implying that remineralized nutrients go up) because of lower vertical mixing, so does pCO_2^{atm} . When nutrients are restored to zero in the Southern Ocean (o-marks) the preformed nutrients drop significantly and so does pCO_2^{atm} . The chain-dotted line in Figure 2a shows the exponential relationship between the two derived by Marinov et al. (2008b) under the limit of infinitely fast gas exchange.

How would we expect pCO_2^{atm} to respond to changes in preformed phosphate? Decreasing $\overline{PO_4^{pref}}$ by 1 micromole/kg corresponds to an increase in remineralized carbon of about 1940 Gt C, given an ocean volume of 1.345 x 10¹⁸ m³. If all of this carbon came out of the atmosphere, it would draw down atmospheric carbon dioxide by ~900 ppmv. However, the actual response in the models is about 20% of this, between 150-200 ppmv per micromole $\overline{PO_4^{pref}}$ depending on the model employed. Note that some of the models on the left of Figure 2b show a global decrease in production even though pCO_2^{atm} drops, just as suggested in Figure 1, Case 2.

This smaller than expected response is due to chemical buffering. Suppose the circulation changes so as to increase preformed nutrients. Much of the carbon pushed out of the ocean by such a change will eventually (over centuries) end up in the ocean as it reacts with carbonate ion- just as most anthropogenic carbon added to the atmosphere today will eventually end up in the ocean. Conversely, much of the carbon that is initially removed from the atmosphere by fertilization will eventually return to the atmosphere.

Within this picture, iron fertilization could increase OCS_{bio} (1) in three ways. 1. Increasing $\overline{PO_4^{remin}}$ (or decreasing $\overline{PO_4^{pref}}$) by increasing photosynthetic uptake and the subsequent remineralization of organic matter. Nutrients which would have gone into the deep ocean as unutilized/preformed are now in the remineralized pool instead. 2. Increasing R_{C:P}, i.e. making nutrient uptake more efficient at sequestering carbon. There is extensive evidence that the C:P ratio in plankton may vary, in large part due to variations in the N:P ratio (Letelier and Karl, 1996; Klausmeier et al., 2004).

3. Increasing OCS_{bio}^{diseq} by making it harder for remineralized carbon to escape from the ocean. This will occur if fertilization redistributes remineralized carbon such that more of it comes to the surface in regions where it does not have time to equilibrate with the atmosphere.

In the following sections we consider some of the complications associated with each of these three mechanisms. Before doing so we note that the preformed nutrient content is essentially independent of the depth of remineralization *so long as one considers an equilibrium situation*. If phosphorus is associated with carbon and iron it does not matter substantially whether it is remineralized at 200m or 2000m, in either case it acts to sequester carbon. Thus Sarmiento and Orr (1991) found that the response to a perpetual fertilization in the Southern Ocean was essentially independent of the depth of remineralization and Gnanadesikan et al. (2003) found a similar result for addition of a "supernutrient" that permanently increased $\overline{PO_4^{remin}}$. If the changes are transient, however, remineralization depth may be important, as it determines the time over which the changes persist.

Changing remineralized phosphate and resulting complications

One simple means of estimating the potential impact of iron fertilization on the carbon cycle is to assume that it will lead to a drawdown of surface nutrients, and to then see how such changes propagate through the system. This was the approach taken by Sarmiento and Toggweiler (1984) in a box model study of fertilization and in studies made using general circulation models by Sarmiento and Orr (1991), Archer et al. (2001),

Gnanadesikan et al., (2003) and Marinov et al. (2006, 2008a,b) among others. While neglecting ecosystem effects and feedbacks through the nitrogen cycle, such an approach does provide a useful means of assessing the potential timescales involved in carbon cycle changes resulting from fertilization and the magnitude of such changes.

We present results from three such simulations in our standard (so-called P2A) ocean model corresponding to nutrient drawdown in the tropics only, south of 30S only and globally (Figure 2c,d). Thinking about the evolution of these runs in terms of changes in preformed nutrients yields some clear insights into their behavior. For example, the much lower impact of drawing down nutrients in the tropics on pCO_2^{atm} is due to the much smaller impact on globally averaged preformed nutrient. The bulk of the atmospheric CO_2 drawdown comes from fertilizing the Southern Ocean (as noted by Marinov et al. 2006) where the impact on preformed nutrients is largest. When preformed nutrient changes are plotted against atmospheric carbon dioxide changes, however (Figure 2d) the picture is much more similar across the simulations. Initially, the bulk of the carbon dioxide comes out of the atmosphere and so the drawdown is more like the idealized 900 ppmv/micromole $\overline{PO_4^{pref}}$. This continues for 50 to 100 years. However, over time (centuries) chemical buffering becomes important, and the final equilibrium slope lies within the range of slopes seen in Figure 1a. If one looks at the ratio between the change in $\overline{PO_4^{pref}}$ and the change in pCO_2^{atm} (not shown), the three simulations collapse to within about 20% of each other.

To a large extent, then, changes in $\overline{PO_4^{pref}}$ or $\overline{PO_4^{remin}}$ are a good metric for evaluating the impact of fertilization on pCO_2^{atm} . This raises a number of important issues when considering the impact of local fertilization. The first issue is that

fertilization may not result in a net change in $\overline{PO_4^{remin}}$ if the nutrients taken up would have been used at some later time or some different location. An example of this can be found in the highly idealized results of Gnanadesikan et al. (2003), which examined the response in a diagnostic ocean model to reducing the target nutrient concentration in a region to zero for a single month over a small patch. Because of the parameterization of production in terms of a restoring to some value, the increased drawdown of nutrients during a "fertilization" event was largely balanced by decreased production in the following months as nutrients recovered to their pre-fertilization values. As a result, the net decrease in unutilized nutrients was relatively small- with only 2-7% of the net additional production during the fertilization event resulting in pCO_2^{atm} drawdown.

It must be emphasized, however, that this case is an extreme one. Essentially the assumption made in Gnanadesikan et al. (2003) is that once fertilization stops the system will return surface nutrients to pre-fertilization levels on a short time scale, something that is unlikely to be true. However, the simulation does highlight the potential importance of post-fertilization declines in productivity. Such declines have been observed by Aumont and Bopp (2006), Jin et al. (2008), and Sarmiento et al. (in prep.) using three different biogeochemical models in which fertilization was applied for a relatively short time period (of order years), then abruptly stopped. The drops in export production across 100m are not nearly as large as in the idealized case, but are potentially significant nonetheless, accounting for as much as a third of the initial production. Aumont and Bopp (2006) attribute the change to a drop in surface nutrient content. Sarmiento et al. (in prep.) find that it is due to enhanced denitrification.

In Gnanadesikan et al. (2003), nutrient drawdown is ineffective at sequestering carbon because productivity at the time of fertilization is essentially "borrowed" from productivity at some time in the future. The displacement of productivity may also happen in the vertical. Jin et al. (2008) find that the greater the depth at which fertilization enhances productivity, the smaller the impact on pCO_2^{atm} . They argue that this occurs because there is less separation between the low pCO₂ anomaly resulting from productivity and the high pCO₂ anomaly resulting from remineralization so that these anomalies are able to cancel each other out before contacting the atmosphere. However, Gnanadesikan (2007) notes that Jin et al. also find a decrease in productivity near the surface, compensating the increase in export at depth. This would act to decrease remineralized nutrients, resulting in no net change in biological carbon storage.

Changing R_{C:P} and resulting complications

There are a number of reasons to believe that iron fertilization could cause changes in the ratio of carbon to phosphate. Higher C:P ratios have been found for nitrogen fixers (Letelier and Karl, 1996) which can be limited by iron (Mills et al., 2004). Hoffman et al. (2006) found an increase in the C:P ratio of micro, nano, and picoplankton during the EiFEX field experiment. They hypothesize that plankton which are iron limited cannot build nitrate reductase and so will tend towards low N:P ratios and (assuming constant C:N ratio), low C:P.

The great advantage of achieving carbon sequestration through changing the C:P ratio in sinking organic matter is that it would be much easier both to evaluate the impact

and to monitor the persistence of the effect by measuring nutrients in situ. Examination of equation (1) shows that a 10% increase in $R_{C:P}$ would be expected to have the same impact on pCO_2^{atm} as a 10% increase in $\overline{PO_4^{remin}}$ (0.1 micromole/kg implying a decrease of 20 ppmv at equilibrium) and far larger variations than this are seen in some regions.

There are, however, some serious complications involved in considering the impact of changing stoichiometric ratios on atmospheric carbon. The most important is that $R_{C:P}$ may go down as well as up with iron fertilization. Arrigo et al. (1999, 2002), point out that $R_{C:P}$ associated with nutrient drawdown is much larger in regions of the Antarctic dominated by phaeocystis blooms ($R_{C:P}$ of 120-154) compared with regions dominated by diatoms ($R_{C:P}$ between 62-100). Additionally, recent work by Klausmeier et al. (2004) points out that the N:P ratio in plankton varies from 8 to 42 over a range of regimes. They argue that in a regime where the plankton are seeking to acquire resources (light and nitrogen) they will tend to build cellular machinery which is rich in N relative to P and will have high N:P (and thus presumably high C:P) ratios, while rapidly growing cells require more ribosomal material with more P and so will have low N:P (and C:P) ratios.

The impacts of iron fertilization on community structure and phytoplankton physiology thus add an additional level of complication. Replacing carbon-rich phaeocystis blooms with carbon-poor diatom blooms would (according to Equation (1) and assuming PO_4^{remin} constant) drive ocean carbon storage down and pCO_2^{atm} up. Similarly, if phytoplankton have high C:P ratios because they are limited by light, adding iron to remove light limitation could reduce C:P ratios and cause pCO_2^{atm} to rise. But if the addition of iron caused an increase in the ability to acquire nutrients (say for example

through allowing nitrogen fixation or shifting the population towards nitrogen fixers as discussed by Doney et al., 2007) C:P ratios could increase, causing pCO_2^{atm} to fall. Such processes are only represented in current ocean ecosystem models at a rudimentary level.

Increasing the efficiency of gas exchange

Gas exchange can play a role in altering the storage of carbon in the ocean. This can clearly be seen in Figure 2a from the difference between the theoretical curve with infinitely fast exchange and the simulations with normal gas exchange. Under infinitely fast gas exchange all the points in Figure 2a lie on the theoretical curve (Marinov et al., 2008b) and $OCS_{bia}^{diseq} = 0$. With realistic gas exchange, however, OCS_{bia}^{diseq} is nonzero. If remineralized nutrients are brought to the surface, converted to preformed nutrients and rapidly (i.e on time scales of weeks to months) reinjected to the deep before biology or gas exchange can act on them the conversion of PO_4^{remin} to PO_4^{pref} occurs without a corresponding change in carbon. OCS_{bio}^{diseq} will be greater than zero because there is no loss of CO₂ to the atmosphere and the biological pump will be more efficient at storing carbon than nutrient fields alone would indicate. This will be particularly the case in convective regions of deep water formation (Toggweiler et al., 2003). Alternatively, one can imagine a case where nutrients are brought to the surface, advected along the surface and taken up by biology just before (weeks or months) they are downwelled. In such a case, the lowered CO₂ associated with enhanced production would not have time to come to equilibrium with the atmosphere, and the biological pump would be *less* efficient at storing carbon than the nutrient fields would indicate ($OCS_{bio}^{diseq} < 0$).

In all of the runs which we have done so far, the first mechanism is the most important and $OCS_{bio}^{diseq} > 0$ (compare all points with the chain-dotted line in Figure 2a). The net impact of gas exchange on fertilization is more complicated. In some of the runs (those associated with higher mixing and higher preformed nutrients), the disequilibrium term increases under depletion. In other runs (those associated with lower mixing and lower preformed nutrients) the disequilibrium term decreases under depletion. These changes can enhance or compensate 10-20% of the pCO_2^{atm} change associated with changing $\overline{PO_4^{pref}}$.

Conclusions

The extent to which the export of organic material from the surface ocean results in oceanic carbon storage is not simply controlled by the magnitude of the export flux or the depth of remineralization. Rather it depends on the extent to which nutrients in the deep ocean are associated with carbon and the extent to which this carbon is able to escape from the deep ocean. As a result, local balances are unlikely to describe the global impact of fertilization. Effects that are remote from the fertilization site in time (monthscenturies) or space (100s-1000s of km), such as reduction in productivity, changes in stoichiometric ratios or changes in the disequilibrium of sinking water can significantly affect the impact of fertilization on atmospheric carbon dioxide. Understanding these effects and constructing models which accurately represent them is thus a crucial part of designing large-scale fertilization projects. Acknowledgements: The authors thank Marian Westley, Robbie Toggweiler, Mike Hiscock, Phil Boyd and an anonymous reviewer for careful reviews of this paper, Jorge Sarmiento for useful discussions and Rick Slater for help in setting up the experiments.

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Figure 1: Schematic illustrating potential decoupling of nutrients and particle export. Case 1: A scenario in which nutrients upwelled at point A on the left of the plot are minimally consumed by the time the water is downwelled at point B. Under fertilization (right-hand column) enhanced productivity is able to take up this nutrient, reducing preformed nutrients and drawing down atmospheric carbon dioxide. This is the classic fertilization scenario. Case 2: A remote impact scenario in which fertilization decreases nutrients locally at A, preventing them from moving to a region (point B) where they can recycle rapidly. The result is to cause global export, global preformed nutrients and atmospheric carbon dioxide to drop (as in some cases in Marinov et al., 2006). Case 3: A local trapping scenario in which preformed nutrient is zero at B. Fertilization will likely trap the nutrient close the point A, decreasing the time it takes to cycle and thus likely increasing production- but as preformed nutrients do not change neither does atmospheric carbon dioxide (Aumont and Bopp, 2006).



Figure 2: Results from a number of models in which nutrients are restored to zero over some area, illustrating the importance of preformed nutrients in understanding the carbon cycle. Runs are made with coarse-resolution, 4-degree models following Gnanadesikan et al. (2004) and Marinov et al. (2006, 2008) with different horizontal and vertical mixing coefficients and wind stresses. (A) Atmospheric pCO₂ versus globally averaged preformed nutrient concentration for six different models. Control runs are shown with a (+), runs in which Southern Ocean nutrients are restored towards zero with an (o). (B) Same as (A) but with particle export at 85m as the independent variable. Notice that the slope is strongly dependent on the intensity of vertical exchange. (C) Three simulations with the P2A model (Marinov et al., 2006) in which nutrients are restored to zero globally (o), over the Southern Ocean (*) and over low latitudes (+). Solid lines show atmospheric pCO_2 change, dashed ones the change in preformed phosphate. Note that the bulk of the difference in atmospheric pCO_2 between runs can be explained in terms of the corresponding difference in preformed phosphate. (D) Absolute change in pCO₂ plotted against preformed phosphate for the runs in Fig. 1c, at 1,51,101,151,201 and 251 years, as well as at equilibrium. Note that the values start close to the theoretical slope and then move rightwards over time as chemical buffering plays more and more of a role.