

# The effect of vertical and horizontal dilution on fertilized patch experiments

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**Abstract.**

A great deal of attention, both negative and positive, has been directed at the potential of large-scale iron fertilization schemes to sequester carbon by inducing phytoplankton blooms that would, in theory, result in significant export of organic carbon to the deep ocean in high nitrogen - low chlorophyll regions. A suite of iron manipulation or ‘patch’ experiments has been performed over length-scales of 10s of km. Here, we use a physical-ecological-chemical model, with prognostic nitrogen, silica and iron dynamics, to study one of the most successful of these experiments, the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES), focusing on the vertical export of organic material, which is difficult to observe in the field. The implications of large-scale fertilization, i.e. increasing patch size, are investigated. Our results agree with the general conclusions obtained from the field experiments. Only a modest export of organic carbon occurs (less than 25% of carbon uptake by phytoplankton) at the base of the mixed layer. Furthermore, we show that lateral and vertical supply of silicic acid is necessary to fuel a sustained phytoplankton bloom. Increasing patch size results in less lateral nutrient supply relative to patch area and so a decrease, not only in total production

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(per unit area), but in the contribution by large phytoplankton due to silica limitation. Most importantly, the export of organic carbon (per unit area) decreases substantially, by nearly an order of magnitude, as scales of 1000 km are approached.

## 1. Introduction

The subarctic northeast Pacific has long been known as a high-nitrogen, low-chlorophyll (HNLC) region. It was originally thought that surface macronutrients were not drawn down to limiting concentrations by phytoplankton because the plants were grazed by small zooplankton, as their growth rates are nearly identical [Frost, 1987]. It has since been shown that, while there is some validity to the grazing hypothesis, the micronutrient iron also limits phytoplankton growth, in both smaller phytoplankton as well as the larger diatoms [Martin and Fitzwater, 1988]. Because it is thought that, if all surface ocean nutrients were utilized by phytoplankton, the ocean would sequester more CO<sub>2</sub> from the atmosphere (e.g., Knox and McElroy [1984]), the idea of mass-scale iron fertilization of HNLC regions was spawned. This idea, and the desire to study factors determining ecosystem productivity, has resulted in at least 10 *in situ* Fe enrichment experiments.

These experiments provided scientists with a wealth of information, as they were well-sampled, often with more than one ship, (although for relatively short periods of time, i.e., weeks). We have learned much about mixing and stirring over the 10 – 100 km spatial-scale of the patch experiments [e.g., Abraham *et al.*, 2000]. Maintenance of enriched chlorophyll (chl) in the patch depends on a balance between confluence and the supply of additional nutrients by diffusion [Abraham *et al.*, 2000; Krishnamurthy *et al.*, 2008]. In addition, it was possible to study the ecological response to a sudden iron addition (e.g. [de Baar *et al.*, 2005] and references within), which occurs naturally on occasion via atmospheric deposition, e.g. Hamme *et al.*, [2010]. Models have benefited from these rich data sets, allowing development and testing of complex ecological models (e.g., cell quota

models [*Fasham et al.*, 2006]) and complex formulations (e.g., aggregation [*Jackson et al.*, 2005]).

None of these experiments have demonstrated exceptional carbon export. In the few experiments that produced blooms and in which vertical export was observed, it was low, about 25% of induced primary production [*de Baar et al.*, 2005]. For comparison, in the northeast Pacific (specifically station P), 25-32% of annual primary production is estimated to be exported [*Peña and Varela*, 2007]. Thus, it appears that significant carbon sequestration (i.e. of order 1 Gt-C yr<sup>-1</sup> on a global scale, e.g. *Pacala and Socolow*, [2004]) by iron fertilization is not likely. However, measuring vertical export in the field is difficult and the patches have not been occupied for long enough periods of time to ensure that the entire flux resulting from a bloom is observed.

The Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) [*Harrison*, 2006] was one of the most successful iron fertilization experiments [*de Baar et al.*, 2005]. Weather was generally calm, so light limitation was not an issue as it had been in several other experiments, particularly in the Southern Ocean (e.g., [*Smetacek and Naqvi*, 2008]). In addition, the patch was occupied for a comparatively long period (26 d). Previous models and budgets of the SERIES data, and of most other enrichment experiments, include either vertical physics (e.g. 1-D vertically resolved models, *Denman et al.*, [2006]) or horizontal dilution (often constant in time), but rarely both.

In this study, we use the SERIES data as a ‘best-case’ scenario. We develop a simple physical model that is able to replicate the physical fluxes during SERIES accurately and explore the importance of both vertical and horizontal exchange using observations of SF<sub>6</sub>. The ecological model of *Denman et al.*, [2006], which is able to successfully predict

annual cycles at the study site, in conjunction with a simple prognostic iron model, is embedded in the physical model. The ability of this relatively simple model to reproduce the ecological data is explored. The vertical export flux of organic material, and its various components (which are simple to determine in a model) are evaluated and compared with observations. The model is then used to test three additional physical scenarios: the first resembles a mesocosm, the second simulates expansion of the experiment to large-scale (order 1000 km or greater), and the last represents optimal physical conditions for maximum ecological response in primary production and export of organic matter.

## 2. Model

Our goal is to keep the physical model as simple as possible while capturing the features critical to the biogeochemistry within the patch. Thus, the physical model is not mechanistic; rather it requires detailed time-dependent forcing functions based on observations (Auxiliary Material, sect. 1). In this case the observations come from the SERIES experiment (July 2002) in the subarctic northeast Pacific [Harrison, 2006]. Within the physical structure, mechanistic ecological and iron models are embedded. Seven chemical tracers (currencies) are tracked by the model in the form of a variety of state variables (Table 1). The system of model equations is solved using a standard Runge-Kutta method [Press *et al.*, 1992] with an adaptive step-size of maximum time-step 0.1 d. Descriptions of each model component used in this study are presented below.

### 2.1. Physical model

The physical model consists of three compartments; the upper mixed layer (1) inside the patch and (2) surrounding the patch and (3) the lower stratified layer (Figure 1).

Model quantities are homogeneous in the upper-layer compartments (1) and (2) but not necessarily the same, so discontinuities in model quantities may exist at the horizontal patch boundary. In the lower layer (3), model quantities vary linearly in the vertical (Figure 1). The boundary between upper and lower layers,  $h_u$ , moves with the mixed layer depth (MLD). The bottom boundary of the lower layer is stationary, specified by the permanent halocline,  $h_{pp}$  (120 m). The horizontal boundaries can also move so that the patch may expand or contract, elongate or shorten. Vertical and horizontal model fluxes are discussed in the following. Physical equations are generalized in Appendix A.1 and parameters are presented in Table 2.

### 2.1.1. Vertical

The vertical structure of the model is 2-level "quasi-homogeneous". We assume that the time-scale for turbulent mixing (roughly 10 min - 1 hr given local conditions; *Denman and Gargett*, [1983]) in the upper mixed-layer is rapid relative to transformations of model quantities so that their distributions are homogeneous above  $h_u$ . In the lower model layer (the halocline), there is less energy (mixing time-scales are expected to be greater than 7 d, *ibid*). We model distributions in this layer varying linearly from the upper-layer concentration to a prescribed concentration (from observations, varying in time) at the base of the permanent halocline (Figure 1). This gradient allows for more realistic entrainment and mixing fluxes between layers, especially when the mixed-layer depth is varying rapidly [*Ianson and Allen*, 2002].

There are two types of vertical fluxes between upper and lower layers, entrained and mixed (equation (A2) - first term, right-hand side). Entrainment occurs when deepening (shoaling) of the mixed layer adds fluid to the upper (lower) layer. We use a turbulence

model to set MLD as a function of time (described below). Mixing occurs continuously and is parameterized by mixing coefficient  $m_v$  (units length/time, Table 2) that, when scaled by vertical length-scale, is of the order of estimated vertical eddy diffusivities in the ocean ( $10^{-5} \text{ m}^2\text{s}^{-1}$ ; *Gregg*, [1989]). The mixing flux is proportional to the difference in concentrations between the upper-layer and a set distance, the mixing depth ( $d_m$ ), below the upper-layer.

### 2.1.2. Horizontal

Horizontal fluxes occur in the upper mixed layer between the patch (compartment 1) and its surroundings (2) (Figure 1). As in the vertical, there are two horizontal flux terms; entrainment and diffusion (equation (A2) - second term).

Horizontal spreading of the patch via mixing and stirring is more complex than its vertical counterpart, “entrainment”. A patch with initial length scale of order 10 km will elongate into a ribbon along the principal axis of strain (confluence) in the local advective field (Figure 2). Diffusion will occur out the sides, perpendicular to this axis [*Ledwell et al.*, 1998]. This ribbon or filament is the true patch (dark area, Figure 2). It may grow in such a way that diffusion balances confluence so that width appears constant while length increases (*sensu Abraham et al.*, [2000]). The ribbon may also fold upon itself in the local mesoscale circulation [*Sundermeyer and Price*, 1998] (Figure 2). Fluid caught between these folds may become part of the apparent patch (as in Figure 2) and is likely to become enriched in patch tracer as a result of diffusion from the filament. The apparent patch is defined here as fluid with a measurable concentration of patch tracer, similar to the objective maps derived from underway surface tracer measurements (e.g., *Law et al.*

[2006]). The model patch is an ellipse, area  $a$ , that approximates the apparent patch (dashed line in Figure 2).

Surface divergence, caused by positive local wind-stress curl and accompanied by upwelling of subsurface fluid, will cause the patch to spread horizontally. In our model horizontal patch spreading (“entrainment”) is caused by three processes; the addition of fluid captured between folds of the true patch, lengthening of a constant-width filament (growth is caused by diffusion that maintains patch width while confluence lengthens it), and surface flow divergence. This spreading term is defined by the change in model patch area,  $a$ , with time and is prescribed based on the analysis of *Law et al.* [2006] (Auxiliary Material, sect. 1.3)

We assume that diffusion out of the model patch (Figure 2) can be approximated by 1-D diffusion out of the sides of the true patch filament [*Ledwell et al.*, 1998]. This diffusion is not accounted for by patch growth (process 2 above). It is the diffused flux of tracer that becomes sufficiently diluted by surrounding water that it is no longer within the patch boundary. The equivalent horizontal diffusion coefficient,  $m_h$  (Table 2 and equation (A2)) used in the model corresponds to a ribbon width of roughly 3-5 km, within estimated ranges in the Southern Ocean Iron Enrichment Experiment (SOIREE) [*Abraham et al.*, 2000] and North Atlantic Tracer Release Experiment (NATRE) [*Sundermeyer and Price*, 1998]. Diffusion from the true patch filament into the additional fluid of the apparent patch (Figure 2) will serve to homogenize the latter, but does not represent a loss from the model patch. In the absence of folding, the apparent patch area and perimeter will be the same as the true patch. Folding will cause the perimeter of the apparent patch to decrease.

The horizontal boundaries of the patch not only expand (patch-spreading), but may also contract during periods of negative local wind-stress curl. Spatial resolution in the observed (and assimilated) local wind field is not sufficient to determine such convergent intervals. The areal patch estimates [Law *et al.*, 2006] are dependent on the effectiveness of the boundary mapping (essentially the cruise tracks available). In the absence of additional data, we assume that the area estimates are correct. At times, these area estimates decrease or remain near constant with time (Figure 8 of Law *et al.*). During these intervals (defined here as patch increase  $< 5\% \text{ d}^{-1}$ ), we found it necessary to model convergence to replicate the observed  $\text{SF}_6$  time series (specifically decreased losses in  $\text{SF}_6$ , see Results). We model no horizontal loss of patch quantities during these convergent times. Model quantities are conserved within the patch by assuming that, as the patch is squeezed horizontally, it becomes deeper, or downwells. Patch volume is conserved. The necessary increase in patch depth does not exceed concurrent increases in estimated MLD. Thus, in the model, a portion of the water below the former MLD comes from the former patch and the rest is entrained from below.

## 2.2. Mixed-layer model

A time-series of mixed-layer depth was used to force the patch model (Figure 3, solid curve). We used the 1-D General Ocean Turbulence Model (GOTM, Auxiliary Material sect. 2) as a diagnostic tool to generate this time-series. The GOTM model was re-stored each day to CTD profiles (both inside and outside the patch) collected during the experiment.

GOTM offers a choice of MLD criterion. The first determines the zone in which properties are homogeneous ( $\Delta T$  criterion: Figure 3, solid curve) and is most suitable for our

slab model. When model quantities are entrained into the lower layer, they are mixed in one time-step. This lower halocline layer is not homogeneous. Model quantities are partitioned into a linear gradient (compartment 2, Figure 1) so that vertical transport is not too rapid or unrealistic when significant shoaling of the upper-layer occurs. To further avoid unrealistic vertical export, the upper-layer is not allowed to shoal above 10 m (Figure 3, solid curve). The second criterion defines the zone of active mixing (TKE criterion: Figure 3, dashed curve). Thus, the model upper-layer reflects the vertical zone in which properties are uniform even though at times they may not be mixing.

### 2.3. Gas exchange

Air-sea exchange of SF<sub>6</sub> and CO<sub>2</sub> was modelled using the standard equations (Auxiliary Material sect. 3) with modelled SF<sub>6</sub> and pCO<sub>2</sub> (the latter calculated from model DIC and Alk) and the gas transfer coefficient relationship of *Nightingale et al.*, [2000]. There are periods when the zone of active mixing shoals above the  $\Delta T$  mixed-layer depth (e.g. days 6–9, Figure 3). During these periods, volatile quantities such as SF<sub>6</sub> below the TKE depth are isolated from the air-sea interface. We experimented with adapting our model to reflect this shoaling for gas exchange (also discussed in Auxiliary Material sect. 3).

### 2.4. Verifying the physical model

Most physical model parameters ( $d_m$ ,  $m_h$ ,  $m_v$ ) were chosen based on theory. The permanent halocline ( $h_{pp}$ ) follows observations (Table 2). Physical forcing functions ( $a$ ,  $h_u$ , model patch perimeter  $p$ ) were derived from data (discussed in 2.1.1 and below); the full ranges over the experiment are shown in Table 2. The inorganic quantities are the simplest to model as they undergo no transformations. Thus, SF<sub>6</sub> and salinity were

used for model-data comparisons to check that the physical model was reasonable. These comparisons began on experiment day 3 to allow time for the initial SF<sub>6</sub> grid to become a coherent patch and are discussed below (Results).

## 2.5. Ecological model

We use the ecosystem model of *Denman et al.* [2006] in the upper mixed layer (boxes 1 and 2, Figure 1), which was designed for the study region and simulates repeatable seasonal cycles. It is based on the nitrogen balance formulated in terms of 6 prognostic state variables; NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, a small (P1) and a large size-class (P2) of phytoplankton (small nano and picoplankton are dominated by flagellates; large represent diatoms), microzooplankton (primarily large ciliates, >20 μm, and dinoflagellates, >10 μm), and detritus. Additionally, the mesozooplankton (>200 μm) concentration, that has a longer life cycle (≥ months), was prescribed based on long-term observations [*Goldblatt et al.*, 1999]. Both diatoms and detritus sink (at different rates), while only diatoms aggregate (with a quadratic formulation; *Ruiz et al.* [2002]). Aggregates are assumed to sink so rapidly that they are removed from the mixed layer within one timestep. Microzooplankton feeds on detritus and on both phytoplankton size-classes (but with a small preference for diatoms), as observed during the SERIES experiment [*Denman et al.*, 2006]. Mesozooplankton, in contrast, feeds only on diatoms and microzooplankton. The uptake of nitrogen by phytoplankton is controlled by the most limiting of inorganic nitrogen, light or iron. Diatoms are also limited by silicic acid. Each limitation is modelled by a Monod kinetics function with unique half-saturation constants for each of the two phytoplankton groups (Table 1 in [*Denman et al.*, 2006]). Additional currencies; carbon, alkalinity, silica and dissolved iron are coupled to the nitrogen cycle assuming fixed elemental ratios in the experiments

presented here. We do not model ecological transformations (which generally have longer time-scales) below the upper layer.

### 2.5.1. Parameter optimization

We used a ‘genetic’ optimization routine [Carroll, 1996] to find the ecological parameter and initial condition set (given the physical model) that would provide the best fit to the observed time evolution of  $\text{NO}_3^-$  and chl (assuming a fixed N:chl ratio) inside and outside the patch (i.e., we did not allow a bloom to occur outside the patch). It was difficult to capture the P2 bloom timing (model P2 bloom earlier than nature) as well as its abrupt onset and crash. The Denman *et al.* [2006] parameter set performed well and the optimal parameters, used in all presented model runs, were only slightly different (only 7 of the 34 parameters were changed - Table 3) as were the results obtained from each parameter set. Most changes reflect the P2 bloom, e.g. lower initial P2 to keep P2 from blooming too early, and reduction of the aggregation coefficient to allow the model bloom to become as large as the natural bloom.

## 2.6. The iron model

Denman *et al.* [2006] used the observed time history of iron concentrations in the patch to prescribe the level of phytoplankton iron limitation. Here, our focus on the effects of patch-spreading, dilution and the impact of changing patch size necessitates a prognostic iron model.

Residence time and availability of iron in seawater are affected by its complicated speciation (organically complexed vs. inorganic compounds, both available in two redox states, coupled with a continuous size distribution over the dissolved, colloidal and particulate

phases; *Weber et al.* [2007], *Ye et al.* [2009]). Modelling speciation requires information such as the concentration of organic ligands. Iron measurements during the SERIES experiment [*Wong et al.*, 2006] included the size distribution (particulate, colloidal and truly dissolved, as defined by filter cutoffs), but did not include redox speciation and/or organic complexation measurements. We therefore opted for a more heuristic approach, much like the empirical model of *Gordon et al.* [1998].

In the model, we distinguish three forms of iron: particulate, colloidal and truly dissolved, and describe the conversion between them by empirical first-order rates, making the assumption that inorganic formation of particulate iron occurs primarily through a colloidal intermediate [*Honeyman and Santschi*, 1989] (Appendix A.2, eqn.s A4 and A5). The rates for colloid formation/dissolution and for the conversion from colloids to filterable particles are not well constrained from laboratory observations. However, *Wong et al.* [2006] have shown that the conversion between the different size classes in the SERIES experiment occurred on the time-scale of days or even less; the rates that we used for our modelling reflect this rapid turnover and are similar to the rates estimated in *Ye et al.* [2009] and *Wagener et al.* [2008] (Table 3).

### 2.6.1. Iron and SF<sub>6</sub> addition

In SERIES as in other fertilization experiments, the background concentration of Fe was low (50 pM [*Wong et al.*, 2006]). Iron was added to the sea in the form of a concentrated solution of Fe(II), which will quickly oxidize to Fe(III) in seawater and, at such high concentration, exceed its solubility considerably. Thus, rapid precipitation and formation of colloids is expected as observed in other iron fertilization experiments (e.g., [*Gordon et al.*, 1998]). In the model, iron injections (two) were uniformly distributed over the mixed

layer upon addition. Between experiment days 0 and 0.7, 365 kg of iron were added. This iron was partitioned in the model so that the dissolved fraction agreed with initial observations and the remainder was instantly passed into the colloidal fraction. Between days 7.625 and 8.375, a further 99 kg of iron were added. We model this addition as purely dissolved.

The tracer SF<sub>6</sub> (5500 L saturated solution) was injected with the first, but not the second, iron addition and was similarly placed into the model patch with a homogeneous distribution. Full details of the injection method are given in *Wong et al.* [2006].

## 2.7. Model experiments

We present 4 experiments using the above model, each with the same absolute amount of iron added, to elucidate the importance of dilution and horizontal nutrient supply, and investigate the potential effects of changing patch size. The ecological and iron models presented above are the same in each experiment; only the physical model changes. Our standard, or ‘baseline’, run includes both the vertical and horizontal physical exchange defined above. Next, we consider a ‘bucket’ run, which resembles a mesocosm experiment. The patch is not allowed to spread or exchange water with its surroundings. The mixed-layer depth does not vary, but is fixed at the value at the beginning of the experiment (shallow - 10.3 m) and there is no vertical exchange. The third experiment, ‘vertical-only’, is our simulation of large-scale fertilization. Similar to the ‘bucket’, the patch is not allowed to expand in the horizontal, as would be the case if the patch were limited by the coast or strong fronts at the boundaries of ocean gyres. (Once a length-scale of 1000km is reached, if patch expansion could occur, the net horizontal nutrient fluxes would be at least 100× less than the net vertical fluxes, given conditions in our study area. At

these scales, horizontal mixing would not be rapid enough for the entire patch to benefit from this horizontal exchange.) While there is no horizontal exchange, the MLD varies and vertical mixing occurs as expected in the ocean and in our baseline run. Finally, the last experiment, ‘horizontal-only’, presents the optimal ecological and export response scenario. In this case, as in the bucket experiment, there is no vertical exchange and the MLD is fixed at 10.3 m so that light conditions will always be favourable. However, the patch is allowed to expand and be diluted by nutrient-rich water from the surrounding surface ocean, somewhat like a chemostat, but with increasing total volume. Although both this last experiment and the ‘bucket’ have fixed MLD, the wind field still changes during the experiments. This feature is not realistic, but it allows comparison of air-sea CO<sub>2</sub> fluxes between runs and does not affect any other model feature (e.g., primary productivity or export of organic matter).

### 3. Results and Discussion

The baseline or standard model is discussed in detail. These results are then contrasted with results from the three different physical forcing scenarios; bucket (or mesocosm), vertical-only (large-scale) and horizontal-only (optimal).

#### 3.1. SF<sub>6</sub> evolution

It was challenging to construct the physical model so that it did not lose SF<sub>6</sub> more rapidly than the data suggested using the patch area estimates of *Law et al.* [2006]. However, after allowing the patch to converge (and so retain SF<sub>6</sub>, sect. 2.1.2), the model results reproduce the observations well (Figure 4a). In particular, the model captures the time evolution; the initial step decrease in SF<sub>6</sub>, followed by the relatively constant

SF<sub>6</sub> observed between days 6 and 9, followed by another (short) rapid decrease days 9-10 (Figure 4a).

The interplay of vertical, horizontal and air-sea fluxes are responsible for this evolution (Figure 4b). Results are easily generalized, as we assume a zero concentration of SF<sub>6</sub> in the atmosphere and ocean, beside and underneath (distributed in a linear gradient see Figure 1) the patch. Horizontal and vertical nutrient (N and Si) fluxes (gains in this case) vary similarly as a function of time (no gas flux), although the amplitudes will increase with time as nutrients get depleted in the patch and horizontal and vertical nutrient gradients increase (in contrast SF<sub>6</sub> losses decrease because gradients are reduced in time).

With the exception of the beginning of the experiment, during which air-sea gas flux dominated, the fluxes are of the same order. These results indicate that both horizontal and vertical dilution must be considered to obtain reasonable physical results in any attempt to model a feature of (10–100 km scale) patch experiments (biological or physical) although, integrated over the whole experiment, horizontal fluxes were larger. Often all three losses are concurrently high and concurrently low (e.g., high days 9–10 and low days 8–9; Figure 4b). This result seems intuitive as times with higher wind have increased gas exchange, increased physical mixing and one might expect more stirring and horizontal spreading. However, the fluxes do not always covary, highlighting the importance of modelling variations in horizontal exchange with time. There are periods of increased winds in which we argue that the patch is convergent so model vertical and air-sea losses are high, but horizontal losses are zero (e.g., days 3–4). Similarly, there are times when vertical fluxes are low despite appreciable air-sea flux and horizontal dilution (e.g. days 12–13) because of increased stratification of the water column.

### 3.2. Ecological Results

In the SERIES experiment, small phytoplankton (also iron-limited) bloomed first (Figure 5a), peaking around day 10, while the diatom bloom followed (peaking around day 17) and was larger. The model was able to reproduce these results reasonably well, especially for the small P, but was limited by its framework (recall that the parameter set was optimized to reproduce the results in Figure 5a). Diatoms bloomed earlier in the model and, as is common, the natural bloom was more dramatic, with a sudden increase and crash. For the model to succeed in capturing the sudden increase, a Droop style, or quota model [Droop, 1973] is necessary, in which phytoplankton are allowed luxury uptake of Fe. This uptake would delay the bloom, and allow subsequent rapid growth. However, it is questionable if such complexity is necessary for larger models to capture the overall fluxes that are important for the evolution of multi-year runs. In addition, at present most larger-scale predictive models (Ocean General Circulation Models) that consider iron do not model it explicitly, but use a set global iron mask, or limitation [e.g. Zahariev et al., 2008], with the exception of few studies that focus on the effects of iron delivery to the ocean [e.g. Parekh et al., 2006; Tagliabue et al., 2009].

In addition, we are comparing observed, size-fractionated, chl with our model phytoplankton, which have units of N. We convert the measured chl to N using a fixed (average) N:chl ratio (Figure 5a). The ratios of N:chl (and C:chl) vary in nature, and can increase significantly during a bloom crash. Thus, it is possible that the observed decrease in diatom (or large P) chl is more rapid than the natural decrease in diatom N. This discrepancy could, at least partially, account for our inability to simulate the steepness of the crash shown in the (large P) chl observations.

### 3.2.1. Export flux

The model predicted export at the base of the mixed layer (Figure 5b) has a similar time evolution to the P2 trace (Figure 5a), although export is affected by the earlier P1 bloom and is generally more dramatic than the bloom itself, primarily because aggregation has a quadratic dependence. The ‘traditional export’, a combination of sinking and aggregation fluxes (dashed curve (Figure 5b), should in theory compare with the flux caught by sediment traps.

During the SERIES experiment, drifting sediment traps were deployed for periods of roughly 2-3 d. The shallowest of these traps (50 m depth) were assumed to have a trapping efficiency near 1.0 (although both under-trapping and over-trapping are possible) [Boyd *et al.*, 2004; Timothy *et al.*, 2006]. Many processes are expected to occur between the base of the mixed layer (often only 10 m in this study, Figure 3) and the traps, including subsequent aggregation with increased sinking rates (which could serve to concentrate or increase a pulse of material) as well as losses due to grazing or horizontal velocity shear. Thus a comparison of model export and trap export is difficult; however, it is reasonable to expect the 50 m trap fluxes to be the same order of magnitude or smaller than in the model. The PON trap flux increased (above background ‘out of patch’ values) a few days after the large plankton bloom began, to 3 mmol m<sup>-2</sup> d<sup>-1</sup>, fluctuated slightly above background levels (minimum 1.5-2 mmol m<sup>-2</sup> d<sup>-1</sup>), then peaked at 5 mmol m<sup>-2</sup> d<sup>-1</sup> during the final trap deployment about 5 d after the abrupt bloom crash (D. Timothy, unpublished data). The magnitude of our model PON fluxes following the bloom are in good agreement (~ 4-6 mmol m<sup>-2</sup> d<sup>-1</sup>; Figure 5b). Estimating the time lag for the flux to reach 50 m from sinking rates, which were estimated to vary from 1-10 m d<sup>-1</sup>

[Figure 7 in *Boyd et al.*, 2005], and distance travelled (25-40 m) following the onset of the observed bloom ( $\sim$  d 13, Figure 3) yields a large range, 3-40 d. If we assume that the final (largest) measured pulse was primarily generated from material aggregating at the time of the bloom crash, when sinking rates were likely maximal and MLD only 10 m, then the transit time would be about 4 d - and the observed lag was  $6\pm 2$  d [D. Timothy unpublished data; *Boyd et al.*, 2004].

We add the flux to higher trophic levels (flux to Z2 in our model) to the traditional (solid curve, Figure 5b) to consider the maximum possible export flux (if the higher trophic levels defecate, respire and die below the surface layer). The flux to higher trophic levels is the dominant flux (relative to sinking and aggregation) until  $\sim$  day 9 when both P1 and P2 concentrations have become anomalously high, in agreement with the theoretical analysis of an earlier version of the same model [*Healey et al.*, 2009]. As expected, aggregation (quadratic) is only important during the peak of the P2 bloom, while sinking flux (linear) is consistent and remains high following the bloom peak (Figure 5b). Even at the end of the field experiment (that sets our model duration), export persists at levels well above initial values.

### 3.2.2. Iron and Silicic Acid

Our iron model is relatively simple and limited by the data that we have to support it. The three model species compare reasonably well with their data counterparts (Table 4), especially the particulate Fe (Figure 5c). The main model weakness occurs following the first few days of the experiment, when the model overpredicts both dissolved and colloidal iron. Either scavenging or uptake of Fe by phytoplankters (assuming that they are capable of luxury uptake) may be underestimated at this time. Modelled silicic acid

concentrations agree well with the observed average patch values (Figure 5d). The timing of increased drawdown occurs earlier in the model (as expected given the timing of the response of large phytoplankton Figure 5a) but the total drawdown during the experiment is the same.

### 3.3. The experiments: 4 physical scenarios

Results from the four model experiments (Section 2.7) show significantly different potentials for exporting carbon and removing carbon from the atmosphere (Figure 6). Each experimental response results from the same amount of iron added, although two of the four experiments expand in area with time. Therefore, when total fluxes (not normalized by area) are compared (e.g. Table 5) some of the disparities amongst experiments become larger.

We focus on the response of P2 rather than P1, as it best defines the response to iron addition. To first order, primary production PP (Table 5) (see also response of large phytoplankton, Figure 6a) drives both the total vertical export (Section 3.2.1) (Figure 6b) and air-sea CO<sub>2</sub> flux (Figure 6c) in the model. Silicic acid plays an important role in all experiments and becomes the most limiting nutrient earlier than iron in all but the baseline case. (Immediately following iron addition, Fe is the most limiting of the nutrients, limitation factor  $\sim 0.8$ , Figure 7a.)

#### 3.3.1. Baseline experiment

The baseline experiment displays the lowest peak in P2 biomass of all cases, and is the only run that resembles the observations (dark green curve, Figure 6a). However, total PP (per unit area) integrated over the duration of the experiment is higher than in any of

the other experiments, and is significantly higher (33%) than the large-scale vertical-only experiment (Table 5). Furthermore, if total PP (integrated over area as well as time) is considered, then PP in the baseline case is  $7\times$  greater than the vertical-only experiment (that does not expand) for the same amount of iron added (Table 5). More importantly, total PON export (integrated over area) is  $9\times$  in the baseline run wrt to the vertical-only (Table 5).

These results depend on the integration time chosen because bloom timing and duration changes with experiment. We present results integrated over 26 d, the period that the patch was occupied by research vessels, however the bloom in two of the experiments is still on-going at that time. Extending the experiment to 34 d (beyond the occupation of research vessels) causes the disparity in total PON export between the baseline and vertical-only to become even greater (over  $10\times$ ) because the baseline bloom continues to be supplied with silicic acid allowing the remaining Fe to be used by phytoplankton.

### 3.3.2. Mesocosm or ‘bucket’ experiment

The bloom in the ‘bucket’ occurs earliest, is largest and most dramatic, which is no surprise, as the upper-layer is shallow and no dilution of biomass occurs. It also crashes first, as the macronutrient silicic acid runs out quickly (after 10 d) and there is no continual delivery from the surrounding water. By day  $\sim 20$ , there is no evidence of a bloom and no export of organic matter above the pre-bloom condition (black curve, Figure 6a and b) or the out-of-patch values (brown curve, Figure 6a and b). There is a brief  $\sim 3$ -d period in which air-sea  $\text{CO}_2$  influx is significantly larger than in other experiments in response to the large bloom, but by day 14, air-sea flux becomes about the same as the baseline run (Figure 6c).

### 3.3.3. Expansion to large-scale experiment

The large-scale or vertical-only run is similar to the bucket run, with the bloom occurring at about the same time, although at a significantly reduced size (blue curve, Figure 6a). Just preceding and during the bloom, wind-mixing was at its peak in the experiment (Figure 3) so that light was more limiting and entrainment caused dilution of biomass. However, the vertical-only bloom runs significantly longer than the bucket scenario due to the vertical supply of silicic acid (see reduction of Si-limitation d 14–17, Figure 7a). Nevertheless, by  $\sim$  day 22, there is no evidence that a bloom has occurred in either P2 concentration or export and, similar to the bucket scenario, increased CO<sub>2</sub> influx from the atmosphere is short-lived so that, by day 14, there is little difference between this run and the baseline run (Figure 6). Also, the peak export flux (Figure 6b) is the same as in the bucket run. The bucket experiment has a constant shallow MLD, causing larger concentrations of biomass relative to the vertical-only experiment, but not larger total biomass or larger vertical flux.

### 3.3.4. Optimal experiment

The optimal or ‘horizontal-only’ run is more similar to the baseline run. Like the baseline case, the P2 bloom occurs later than in the experiments with no horizontal expansion (bright green curve, Figure 6a). The peak response is larger than the baseline, but not as large as the bucket or vertical-only experiments. Despite the higher concentration of P2, PP (both by P2 and total) is actually smaller than the baseline (Table 5) because the MLD is shallower, so that the vertically integrated P2 (and PP) is not higher. The peak export flux is similar to the baseline case but is extended over a larger period of time (Figure 6b), primarily because aggregation fluxes are higher due to the enhanced P2 concentrations in

this run. CO<sub>2</sub> gas flux is only slightly higher than in the baseline experiment during the main wind events (days 10–13, Figure 3) and the subsequent one (days 15–17). Thus, this bloom is optimal in terms of export because of the higher proportion and concentration of diatoms, even though total production is not higher.

In fact, we argue that, relative to other iron enrichment experiments, particularly those in the Southern Ocean (e.g. SOIREE, SOFeX [*deBaar et al.*, 2005]), the SERIES experiment is like this optimal or horizontal-only case. Light was not limiting as the MLD was near 10 m about half of the time, and only ranged as deep as 30 m for a few days (Figure 3) at which time the light-limitation factor dropped only to 0.8 (during day-light hours). It was 1.0, its maximum, the rest of the experiment. Therefore, the vertical export measured during SERIES (25% of PP), described by *Boyd et al.* [2004] as ‘inefficient transfer of carbon’, may be about ‘as good as it gets’. Measuring export flux in the field is difficult; however, our model confirms these results. In any case, the combination of calm conditions with the constant inflow of nutrients was critical to the sustained and substantial response of the experiment.

### 3.3.5. Importance of lateral exchange

Although both the bucket and vertical-only experiments had strong blooms and the largest CO<sub>2</sub> gas fluxes of all of the experiments, this gas-flux was short-lived and insignificant relative to PP and export fluxes (Table 5). Most importantly, the export fluxes (for the same amount of iron added) were relatively small when integrated over patch area (recall that patch area did not increase in these experiments). They were an order of magnitude smaller than in the baseline and horizontal-only scenarios (Table 5). Also, as P2 becomes limited by silicic acid earlier, the proportion of P2 in total PP decreases (to

just under 50%) relative to 70% and 80% in the baseline and horizontal-only, respectively (Table 5). If one were to let the model run for another 8 days (using available wind data and assuming patch expansion at the same rate as at the end of the experiment), the discrepancies in total export (Table 5) diverge further, as the blooms that are enhanced by horizontal supply of silicic acid have not fully diminished by day 26.

The supply of silicic acid plays a critical role. Although significant Si drawdown was observed during SERIES [Boyd *et al.*, 2004] the baseline model run indicates that Fe was always the most limiting of the nutrients (Figure 7a, dark green curves). The physical supply of silicic acid (both vertical and lateral) roughly balance uptake by large P once the bloom is established. This balance has been suggested by Coale *et al.* [2004] under low silicic acid conditions in the Southern Ocean and allows complete use of the iron. When the lateral supply of silicic acid is cut off in the vertical-only experiment that simulates expansion to large scale, Si is quickly depleted. It becomes more limiting than Fe after about a week and completely limiting by about day 10 (Figure 7a, blue curves). Subsequent vertical injections of Si are rapidly taken up by large P ( $\sim$  d 14-16) but without addition lateral supply there is not enough silicic acid to utilize the Fe. Since we expect the remineralization scales for Si to be deeper relative to nitrogen [Nelson *et al.*, 1995], it is expected that, under repetitive fertilization, silicic acid would become increasingly depleted in the surface layers. Thus, the long-term feasibility of fertilization has been questioned [Whitney *et al.*, 2005; Brzezinski *et al.*, 2005].

To test the robustness of our results, particularly the dramatic decrease of carbon export (for the same amount of iron added) when the patch is expanded to large-scale, we performed a suite of sensitivity experiments. Focusing on export flux, we varied the

aggregation coefficient and the sinking rate of large phytoplankton (Table 2) (together and separately) by half to double their baseline values. We also forced the model with the best, max and min constant dilution rates (3 rates during 3 different time periods in each case) suggested by *Law et al.* [2006]. Silicic acid depletion occurred in all of the expansion (no lateral flux) runs while iron was still available. The 1-D (SOFeX) model of *Krishnamurthy et al.* [2008] also indicates silicic acid limitation when there is no lateral dilution, as long as light is not limiting. In contrast, in all the (physical) baseline runs, Fe limitation was greater than Si limitation throughout the experiment. For each sensitivity scenario that produced a diatom bloom in the baseline patch (even if it was small), total vertical export of organic carbon was about  $10 \times$  higher in the baseline patch than in the large-scale experiment.

One could argue that large-scale fertilization would be more easily accomplished as a grid of patches, each behaving more like the baseline patch, so accomplishing a larger export flux, as nutrients between the patches flow into the patches with time. Even if one could accomplish such a feat logistically (e.g., with no poor weather to subduct patches or cause light limitation etc.) then one must reckon with the appropriate area (i.e., that required to provide additional nutrient input) when estimating total potential export.

Additional issues with large-scale iron fertilization exist that have not been explored in this study. For example there are logistical challenges. Most of these experiments required multiple iron injections to produce a bloom and all involved intensive observation of the patch using tracers like the highly volatile greenhouse gas, SF<sub>6</sub> [*Law et al.*, 1998]. Even this experiment, which we argue enjoyed near optimal conditions, required two iron injections. In the very first experiment, the entire patch subducted after only a few days

[*Martin et al.*, 1994]. Furthermore, there may be negative impacts to higher trophic levels associated with manipulating ocean ecosystems and an increased demand on subsurface oxygen [*Chisholm et al.*, 2001; *Strong et al.*, 2009]. In addition, global models suggest that, even if mass-scale fertilization were to be successful, it would only delay the increase in atmospheric carbon by about 10 years [*Aumont and Bopp*, 2006; *Cullen and Boyd*, 2008]. Nonetheless, interest in the potential for large-scale iron fertilization to sequester atmospheric carbon (and possibly obtain carbon credits) remains high [*Güssow et al.*, 2010].

#### 4. Conclusions

Our modelling work with SF<sub>6</sub> demonstrates that both horizontal and vertical fluxes are important in the evolution of a patch, and that these fluxes do not always covary (Figure 4b). The detailed time dependent dilution in our model is necessary to reproduce the subtleties in the observed time-series of SF<sub>6</sub> (Figure 4a). It also exerts a strong influence over bloom timing and duration. Minimal (initial) dilution allows phytoplankton to accumulate sufficiently to produce a bloom, but that bloom requires significant dilution (silicic acid) later to sustain it. In contrast, it is possible to model total primary production and vertical export of carbon (during the experiment) reasonably well with a set of constant (but accurate, e.g. *Law et al.* [2006]) horizontal dilution rates, coupled with our vertical model.

Our results for the baseline experiment indicate that at most 25% of PP is exported below the upper mixed layer (53.4/211 in Table 5), in agreement with field results [*Boyd et al.*, 2004]. This export does not necessarily reach deeper than the depth of winter mixing

(about 120 m) so any organic carbon remineralized above that depth may be reintroduced into the surface layer during the following winter. During peak bloom conditions, phytoplankton aggregation contributes significantly, making up almost half of the total export (Figure 5b). Although the ecological model predicts observed biomass trends well during an annual cycle [Denman *et al.*, 2006], we suggest that a quota model, that allows luxury uptake of iron, is required to more closely reproduce bloom details over time-scales of days. However, it is unclear if such complexity would yield more accurate predictions of total export flux, primary productivity or improved results over time-scales longer than that of a bloom.

The physical conditions during SERIES were optimal relative to those in other fertilization experiments (with the exception of SEEDS, [de Baar *et al.*, 2005]). Thus, our baseline results show a ‘best-case’ scenario in export for a small-scale experiment. Our models of different physical scenarios show that the input of silicic acid from the surrounding ocean is necessary to produce a strong and sustained diatom bloom capable of this best-case export. In particular, without horizontal nutrient supply, silicic acid becomes limiting to diatom growth early in the experiment (Figure 7). The model shows that, in the limit of large-scale patch size, significantly less PP is attainable relative to the small-scale experiments (Table 5). The entire character of the phytoplankton bloom changes without continual supply of silicic acid from surrounding waters. As a result, we predict that export of organic carbon (for the same amount of iron added) would be significantly reduced in a large-scale experiment, by up to an order of magnitude. Thus, if enhanced PP, causing export of carbon, are the goals of iron fertilization, then this study indicates

that expanding to larger scales does not meet these goals, even relative to the modest response of the experimental patch.

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## Appendix A

A generalized model equation is:

$$\frac{dq}{dt} = P + E + F \quad (\text{A1})$$

where  $q$  is the model quantity (state variable) and  $t$  is time. On the right-hand side of the equation,  $P$ ,  $E$  and  $F$  represent physical transport, and the ecological and iron source/sink terms, respectively. All state variables undergo physical transport while only those involved in biological cycles (Table 1) have  $E$  and  $F$  terms. In addition, only upper-layer processes are modelled. In the lower-layer, state variables are prescribed.

### A1. Physical

The physical term,  $P$  is generalized for state variable  $q$  as:

$$P_i(q) = \left( \frac{m_v d_m}{h_{u,i}(h_{pp} - h_{u,i})} + \frac{e_v}{h_{pp} + h_{u,i}} \right) (q_d - q_i) + \frac{(pm_h + e_h)}{a} (q_j - q_i) \quad (\text{A2})$$

for  $h_u \geq h_{pp} - d_m$ . Subscript  $i$  represents the upper-layer (either the inside or outside of the patch),  $j$  – the adjacent box and  $d$  – the average lower layer. Physical parameters are presented in Table 2. Terms on the right-hand side estimate vertical and horizontal

transport, respectively. The entrainment terms,  $e$ , are:

$$e_v = \text{MAX} \left( 0, \frac{dh_u}{dt} \right); e_h = \text{MAX} \left( 0, \frac{da}{dt} \right) \quad (\text{A3})$$

## A2. Iron

The iron term,  $F$  is necessary in two state variable equations; for dissolved and particulate iron,  $Fe_d$  and  $Fe_p$ , respectively.

$$\frac{Fe_d}{dt} = r_{Fe:N} \times Nb_t + k_l Fe_p - scav; \quad \frac{Fe_p}{dt} = -k_l Fe_p + scav \quad (\text{A4})$$

where  $Nb_t$  represents the sum of all ecological fluxes between dissolved inorganic nitrogen ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) and organic nitrogen pools (dominated by biological uptake). Scavenging ( $scav$ ) occurs only when the soluble Fe ( $Fe_d$ ) falls below a threshold value  $L$  (a proxy for the concentration of iron-binding ligand, *Kondo et al.* [2009]);

$$scav = \text{MAX} (0, k_s (Fe_d - L)) \quad (\text{A5})$$

Iron parameters are presented in Table 3. Although both the leached ( $k_l Fe_p$ ) and scavenged ( $scav$ ) fluxes pass through the colloidal pool ( $Fe_c$ ), this passage is not explicitly modelled. These fluxes are rapid (time-scales  $< 1 d^{-1}$ ) and are not constrained by observations. The colloidal pool is subject to physical circulation (above).

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**Figure 1.** Cartoon of model patch (shaded region) in vertical. Upper layer (surface to mixed layer depth,  $h_u$ ) properties in the patch (region 1) and outside the patch (region 2) are homogeneous. The lower or halocline layer (region 3) has a linear gradient in model properties with depth. Concentrations at the bottom of the halocline are prescribed. Physical fluxes occur between upper and lower layers (entrainment and diffusive mixing) and at the horizontal patch boundary (patch growth and diffusive mixing). When the patch converges horizontally, no physical fluxes occur in that plane.

**Figure 2.** Cartoon of patch from above. The patch elongates into a ribbon or filament which is stirred and folded. 1-D diffusive mixing occurs across the boundaries of the ribbon or true patch (dark region). The apparent patch encompasses the true patch and any additional fluid that is caught or "entrained" between the folds of the true patch (dark and medium shaded region). The additional fluid may become enriched in patch tracer. The model patch perimeter and area are estimated from an ellipse that approximates the apparent patch (dashed line).

**Figure 3.** Time-series of the mixed-layer depth (diagnosed using GOTM with 1-day restoring to CTD data) during the experiment. Depths determined from the  $\Delta T$  criterion (solid curve - capped at minimum of 10m) and the TKE criterion (dashed curve) are shown. The  $\Delta T$  curve represents the mixed-layer depth,  $h_u$ , in the model. The TKE depth (dashed curve) shows the zone of active mixing, as estimated by the model. It is often shallower than the  $\Delta T$  mixed-layer depth.

**Figure 4.** (a) A time series of observed average mixed layer (stars) and modelled upper-layer SF<sub>6</sub> (solid curve) in the patch. Observations and model are compared starting at day 3, allowing time for initial grid injection to become a patch. SF<sub>6</sub> remained measurable during the first half of the experiment (to day 13). Vertical profiles were collected where high surface SF<sub>6</sub> concentrations were found (underway loop), estimated as the patch centre. To allow comparison with model SF<sub>6</sub>, these maximum values were adjusted by a factor of 0.7 to approximate the average patch concentration. (b) Model fluxes of SF<sub>6</sub> out of the patch (dotted curve –gas evasion, solid black curve–horizontal loss and dashed curve –vertical loss) as a function of time.

**Figure 5.** (a) The ecological model, standard run for each size class (small P, dashed curve and large P, solid curve) of phytoplankton shown with the observations. Observed small P (x) and large P (o) are estimated from the average chl value in the surface layer and converted to units of N (assuming that the ratio of C:chl by weight is 60 and C:N is 6.625; *Marchetti et al.* [2006]). Surface underway fluorometer data were used to estimate errors for each day assuming that spatial variability contributed most to the uncertainty. (b) The modelled export flux of PON at the base of the mixed layer and its various components as a function of time for the standard model run. The total export (thick solid line) or maximum possible export includes flux to higher trophic levels as well as the ‘traditional export’ (dashed line), comparable to sediment trap flux, that includes sinking (of large phytoplankton and detritus - dotted line) as well as aggregation (of large phytoplankton - thin solid line). (c) Modelled iron species (particulate, dust particles and phytoplankton - dark green curve; colloidal - black curve; truly dissolved - blue curve) are shown with equivalent observations (see Table 4) as a function of time for the standard model run. (d) Modelled silicic acid (solid curve) is shown with observations of average patch silicic acid (o).

**Figure 6.** Model results as a function of time for (a) Large phytoplankton, (b) maximum PON export (sinking, aggregation and flux to higher trophic levels) at the base of the mixed layer and (c) air-sea CO<sub>2</sub> gas flux for 4 different physical experiments: (1) the standard or baseline run (dark green); (2) the bucket run (black) in which the patch does not grow or deepen and there are no horizontal or vertical fluxes; (3) the vertical-only run (blue) in which the patch does not grow and there are no horizontal fluxes, but the upper-layer varies as in the standard run and vertical diffusion and entrainment occurs - the limit of expanding fertilization to large (> 1000km) scale; and (4) horizontal-only run (bright green) in which the patch expands and horizontal fluxes occur as in the standard run but the upper-layer stays constant and there are no vertical fluxes. The model predictions for outside the patch (brown), where there was no iron addition, are also shown.

**Figure 7.** (a) Limitation factors (Nitrogen - dotted; Silicic acid - bold; Iron - dashed) as a function of time for the baseline (dark green) and large-scale (blue) experiments after the iron addition. Limitation factor varies from 0 (completely limiting) to 1 (not limiting). (b) Silicic acid uptake (per unit patch area) as a function of time for the baseline (dark green) and the large-scale (blue) experiments. Uptake occurs only during daylight hours. Horizontal (solid black) and vertical (dashed black) physical supply of silicic acid normalized to patch area is also shown. Vertical supply (per unit patch area) is the same in the baseline and large-scale experiment, while horizontal flux occurs in the baseline experiment but not in the large-scale.

symbol	description	currencies (units)
<b>inorganic (tracers):</b>		
s	salinity	na (psu)
SF <sub>6</sub>	sulphur hexafluoride	na (fM)
<b>inorganic (involved in biological cycles):</b>		
NO <sub>3</sub> <sup>-</sup>	nitrate	N (μM)
NH <sub>4</sub> <sup>+</sup>	ammonium	N (μM)
DIC	dissolved inorganic carbon	C (μM)
SiO <sub>3</sub>	silicic acid	Si (μM)
Fe <sub>d</sub>	dissolved iron	Fe (nM)
Fe <sub>c</sub>	colloidal iron	Fe (nM)
Fe <sub>p</sub>	particulate iron	Fe (nM)
ALK	alkalinity	ALK (μeq)
<b>organic (ecological):</b>		units as above
P1	small phytoplankton	N, C, Fe, ALK
P2	large phytoplankton	N, C, Si, Fe
Z1	microzooplankton	N, C, Si, Fe, ALK
D	detritus	N, C, Si, Fe, ALK

**Table 1.** Model state variables with corresponding currencies. Units are not repeated for the organic state variables, which have multiple currencies.

symbol	description	value
$a$	model patch area	$7.7 \times 10^7 - 1.2 \times 10^9 \text{ m}^2$
$d_m$	mixing depth	2 m
$h_{pp}$	depth of permanent halocline	120 m
$h_u$	upper-layer depth	10–30 m
$m_h$	horizontal mixing coefficient	200 m/d
$m_v$	vertical mixing coefficient	0.2 m/d
$p$	model patch perimeter	$4.2 \times 10^4 - 2.6 \times 10^5 \text{ m}$

**Table 2.** Physical model parameters. For externally forced parameters the range over the course of the experiment is given.

symbol	description	new value	previous value
$\beta$	aggregation coefficient ( $\text{d}^{-1} \mu\text{mol N}^{-1}$ )	0.04	0.1
$ge_{Z1}$	Z1 growth efficiency	0.19	0.3
$ga_{Z1}$	Z1 excretion to $\text{NH}_4$	0.81	0.4
$r_{Z2}$	maximum specific grazing rate for Z2 ( $\text{d}^{-1}$ )	0.8	0.67
$r_{Z1}$	maximum specific grazing rate for Z1 ( $\text{d}^{-1}$ )	1.4	1.3
$v_{m2}$	max large phyto growth rate ( $\text{d}^{-1}$ )	2.2	1.5
$w_{PL}$	large phyto sinking rate ( $\text{m d}^{-1}$ )	1.9	1.2
$k_l$	effective leaching rate ( $\text{d}^{-1}$ )	0.1	n.a.
$k_s$	effective scavenging rate ( $\text{d}^{-1}$ )	0.55	n.a.
$L$	ligand concentration (nM)	0.4	n.a.
$r_{Fe:N}$	Fe to N ratio (nM: $\mu\text{M}$ )	0.033125	n.a.

**Table 3.** Ecological model parameters where different than in *Denman et al.* [2006]; rows 1 – 7. Both our value, resulting from optimization, and the previous value are listed. Iron model parameters for prognostic iron model (not used in *Denman et al.*) rows 8 – 11.

Model	Measured
$Fe_d$	Fe-03
$Fe_c$	(Fe-22 – Fe-03)
$Fe_p$	(Fe-tot – Fe-22)

**Table 4.** Model iron species (Table 2) with equivalent measured quantity. The quantities that are measured directly are: a) the total unfiltered Fe, Fe-tot; b) Fe passing through a  $0.22\mu\text{m}$  filter, Fe-22; c) the “soluble”, Fe passing through a  $0.03\mu\text{m}$  filter, Fe-03 [*Wong et al.*, 2006].

	baseline	bucket	vertical-only	horizontal-only
PP (mmol N m <sup>-2</sup> )	219 (424)	90.3(189)	150 (317)	205 (299)
PON export (mmol N m <sup>-2</sup> )	72.6 (106)	57.9 (78.0)	75.1(108)	101 (124)
CO <sub>2</sub> gas flux in (g C m <sup>-2</sup> )	2.16	3.11	2.77	2.37
total PP (Mmol N)	126 (211)	8.13 (17.1)	13.5 (28.6)	136 (175)
total PON export (Mmol N)	53.4 (73.5)	5.21(7.04)	6.76 (9.72)	79.0 (95.7)
total CO <sub>2</sub> gas flux (Mg C)	1.00	0.280	0.25	1.19

**Table 5.** For each of the model experiments: total primary production (PP), PON export at the base of the mixed layer and air-sea CO<sub>2</sub> gas flux (defined here as positive into the ocean) are shown. In the first 3 rows these quantities are integrated with respect to time over the model experiment (26 d). These same time integrals are then integrated over area (for each model time-step) to obtain the total fluxes (i.e. the total flux for an equivalent fertilization effort) in each experiment (rows 4-6). PP is presented first as the PP by large P followed in parentheses by the total PP (by large and small P). PON export is presented as the traditional export (see Sect. 3.2.1) followed in parentheses by the maximum possible export, which includes flux to higher trophic levels.













