



# **ENHANCEMENT OF OCEANIC UPTAKE OF CO<sub>2</sub> BY MACRO-NUTRIENT FERTILISATION**

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## Background to the Study

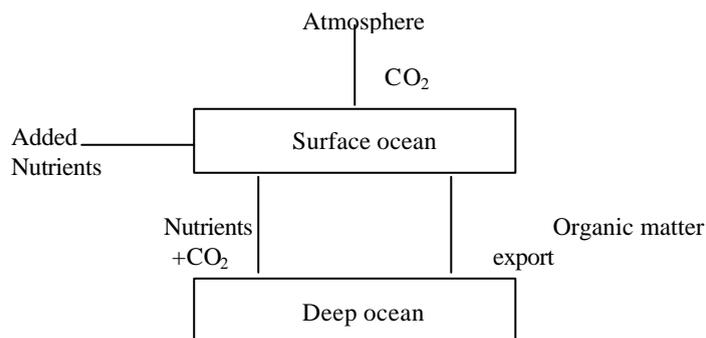
The marine carbon cycle plays a major role in controlling the amount of CO<sub>2</sub> in the atmosphere. The oceans currently remove about 30% of the anthropogenic CO<sub>2</sub> emitted to the atmosphere. An option for increasing the uptake of CO<sub>2</sub> by the oceans, as a means of combating climate change, is to increase biological production by fertilisation. The IEA Greenhouse Gas R&D Programme (IEA GHG) has published a technical review of ocean fertilisation as a CO<sub>2</sub> sequestration option<sup>1</sup>. This review inferred that macro-nutrient fertilisation would be an inefficient means of removing CO<sub>2</sub> from the atmosphere, based on a modelling study by Orr and Sarmiento (1992). The study suggested that as little as 44% of the carbon utilised in the extra biological production resulting from the fertilisation would be derived from atmospheric CO<sub>2</sub>. One worker in the field suggested that recycling of nutrient-enriched water would mean that the effective efficiency of fertilisation would be higher than this. The aim of the study reported here is to resolve some of the uncertainties about the efficiency of macro-nutrient fertilisation for removal of CO<sub>2</sub> from the atmosphere.

This study was carried out for IEA GHG by Richard Matear of CSIRO Marine Research, Australia.

## Approach Adopted

A three-dimensional Ocean Carbon cycle Model (OCM), developed by CSIRO, was used to investigate the potential of macro-nutrient fertilisation to increase biological activity and the amount of CO<sub>2</sub> removed from the atmosphere. A simple 2-box model was also used to illustrate the basic processes taking place in ocean fertilisation.

The published study by Orr and Sarmiento defined the efficiency of macro-nutrient fertilisation as the ratio of increased ocean carbon uptake from the atmosphere to increased export production (carbon transported from the surface layer to the deep ocean). However, this is not a very useful definition of efficiency because export production increases due to the re-supply of nutrient enriched water to the surface layer, while having no effect on the ocean uptake of carbon from the atmosphere. A better definition of efficiency, used in this study, is the increased rate of ocean carbon uptake from the atmosphere compared to the rate of nutrient addition.



<sup>1</sup> Ocean Fertilisation as a CO<sub>2</sub> Sequestration Option, by Bill Ormerod and Martin Angel, IEA GHG report, March 1998, ISBN 1 898373 11 6



**Figure 1** *Flows of carbon and nutrients*

Orr and Sarmiento simulated macro-nutrient fertilisation by imposing a constant increase in export production in the fertilised region. In contrast, this study uses an ocean carbon model where export production is dependent on the surface phosphate concentration and macro-nutrient fertilisation is simulated by adding phosphate at a constant rate to the upper ocean. This formulation of export production allows one to separate the increase in export production due to re-cycling from that due to added phosphate and assess the efficiency of macro-nutrient fertilisation at removing CO<sub>2</sub> from the atmosphere. In this study the efficiency and impact of macro-nutrient fertilisation is investigated in the same 18-50°S region of the ocean as in Orr and Sarmiento's study. Fertiliser was assumed to be added at a constant rate between the years 2000 and 2080 and the results were predicted up to 2200.

The models used in this study assumed that phosphate would be the limiting macro-nutrient. The complexity of the nitrogen cycle and the fact that phytoplankton use nitrogen and phosphorus to form organic matter in a nearly constant ratio (the Redfield ratio) has led to this approach being used in a number of ocean carbon cycle models.

## **Results and Discussion**

### **Efficiency of CO<sub>2</sub> removal from the atmosphere**

The box model indicated that the efficiency of phosphate fertilisation, according to the definition used in this study, would approach 89% for an oligotrophic (macro-nutrient limited) region of the ocean. In the results from the OCM, the maximum efficiency was 62%. The lower efficiency of the OCM results reflects the fact that in 31% of the fertilised region, availability of phosphate is not the factor limiting biological production, so adding more phosphate does not increase biological activity. If the results of the OCM are scaled to account for the fertilised area that is not phosphate-limited, the maximum efficiency is increased to 90%, similar to the result from the box model.

### **Carbonate, DMS and N<sub>2</sub>O production**

Some phytoplankton produce calcium carbonate, which is exported from the surface layer to the deep ocean when they die. Increased export of calcium carbonate from the surface layer reduces alkalinity, which reduces the solubility of dissolved CO<sub>2</sub> gas in seawater, and this reduces CO<sub>2</sub> uptake. The effect of macro-nutrient fertilisation on the amount of calcium carbonate export is uncertain. As a base case, the export of calcium carbonate was held constant. When the calcium carbonate export was assumed to be a constant fraction of the organic carbon export, the efficiency of carbon removal from the atmosphere by fertilisation was reduced from 62% to 47%.

Fertilisation may also increase production of dimethyl sulphate (DMS) in the ocean. DMS from the oceans is oxidised to aerosol particles, which are the main source of cloud condensation nuclei in the marine atmosphere. These can influence the radiative properties of the atmosphere by altering the albedo (reflectance) of clouds and the scattering of incident solar radiation. The types of phytoplankton which produce calcium carbonate also tend to produce much larger quantities of DMS than other species. An increase in atmospheric CO<sub>2</sub> resulting from an increase in calcium carbonate production may therefore be offset by increased DMS production. Our knowledge of the large scale response of ecosystems to macro-nutrient fertilisation is inadequate at present to attempt to quantify changes in DMS production.



The effects of changes in DMS production on the climate are also highly uncertain but may be substantial.

Increased biological production may also increase the sea-to-air flux of  $N_2O$ , a potent long-life greenhouse gas. Using the modelled output, it was estimated that increased  $N_2O$  production could reduce the effective efficiency of macro-nutrient fertilisation for greenhouse gas abatement by a maximum of 20%. This calculation neglects the potential for the ocean to store more  $N_2O$  if the rate of  $N_2O$  production increases. Increased  $N_2O$  storage in the ocean could potentially half this value. These calculations are only approximations and further work is needed to reduce the uncertainties.

### **Other factors influencing efficiency**

The form of the added nutrients may affect the pH of seawater and alter the efficiency of carbon removal from the atmosphere. If nitrogen is obtained from ammonium sulphate, it would have no impact but the use of ammonia or nitrate as the source of nitrogen would reduce the efficiency by 10%.

The OCM was used to simulate the effects of climate change on the oceans and the resulting effects on the efficiency of ocean fertilisation. The effects of climate change on the oceans were predicted to result in a small increase in the amount of carbon sequestered from the atmosphere.

The OCM predicted an increase of 17.5% in the volume of anoxic (oxygen deficient) water after 80 years of fertilisation. The increase in anoxic water was confined to regions that currently have large areas of anoxic water (e.g. eastern equatorial Pacific and Indian Ocean) which suggests that such change would not greatly affect the marine ecosystem in these areas.

### **Effects on phytoplankton community structure**

Phytoplankton communities normally have a near constant C:N:P ratio (the Redfield ratio). However, the possibility that the C:N:P requirement of the phytoplankton community might change in response to macro-nutrient fertilisation limits the ability of current models to describe the ocean carbon cycle. This is a crucial issue to resolve because it has important consequences for both the future ocean uptake of carbon and the sequestration of atmospheric carbon by ocean fertilisation schemes. The impacts of such changes on other parts of the marine ecosystem are uncertain.

It is noted that parts of the ocean that are already experiencing changes in the supply of macro-nutrients would provide valuable sites for studying the impact of macro-nutrient fertilisation on marine ecosystems.

### **Potential quantity of $CO_2$ which could be removed from the atmosphere**

This study did not attempt to predict the ultimate quantity of  $CO_2$  that could be removed from the atmosphere by macro-nutrient fertilisation. The OCM predicted that adding 2.3 Gt P as phosphate to the 18-50°S region of the ocean between 2000 and 2080 would sequester 180 Gt  $CO_2$  (49 Gt C) from the atmosphere by 2200. Based on the typical P:N Redfield ratio (1:16 molar basis), the quantity of nitrogen fertiliser required would be 17 Gt N.  $CO_2$  emitted during production of this nitrogen fertiliser would reduce the net  $CO_2$  removed from the atmosphere to about 40 Gt C.

Effects on ecosystems may limit the ultimate quantity of  $CO_2$  that could be removed from the atmosphere by ocean fertilisation.

## **Expert Group Comments**



The draft version of this report was sent to members of the Programme's Ocean Storage expert group and other researchers who have worked on ocean circulation modelling and ocean fertilisation. The general opinion was that it was a good study and the results were well presented. The main comments were requests for clarification of some aspects of the results and the conclusions. Most of the reviewers highlighted the production of calcium carbonate as an important and uncertain aspect of ocean fertilisation.



## Major Conclusions

- The Ocean Carbon Cycle Model simulations predict that the efficiency of utilisation of added nutrients for removal of CO<sub>2</sub> from the atmosphere is 62%. 31% of the fertilised area in this study is not macro-nutrient limited, so the efficiency may be as high as 90% if only macro-nutrient limited areas were fertilised.
- The efficiencies predicted in this study are higher than the efficiency of 44% quoted in IEA GHG's published review of ocean fertilisation. The definition of efficiency used in this study is different to that used in the earlier review, as it takes into account recycle of nutrients within the ocean. The efficiencies as defined in this study can be used to calculate the quantity of fertiliser required to remove a given quantity of CO<sub>2</sub> from the atmosphere.
- Increased calcium carbonate production with macro-nutrient fertilisation can significantly reduce the efficiency of CO<sub>2</sub> removal from the atmosphere. If calcium carbonate production increases at the same rate as organic production, instead of remaining constant, the efficiency would decrease from 62% to 47%.
- The nitrogen source used to stimulate biological production may affect the pH of seawater and alter the CO<sub>2</sub> removal efficiency. An ammonium sulphate source of nitrogen would have no impact but the use of ammonia or nitrate would reduce the efficiency by 10%.
- Ocean fertilisation may alter the air-sea exchange of two other important greenhouse gases, N<sub>2</sub>O and DMS. We estimate that increased N<sub>2</sub>O production in the ocean with fertilisation would reduce the effectiveness of fertilisation as a greenhouse gas abatement measure by a maximum of 20%. At present it is not possible to predict the effects of changes in DMS production on the climate but they may be substantial.
- Global warming is predicted to result in substantial changes in ocean circulation. However, such predicted ocean circulation changes do not significantly alter the efficiency of CO<sub>2</sub> removal from the atmosphere by macro-nutrient fertilisation.
- The effect on the marine ecosystem of changes in the nature of the phytoplankton or their community structure (e.g. due to changes in the limiting nutrient for biological production) is a fundamental issue for ocean fertilisation.
- Improved knowledge of marine ecosystems may lead to new ways of increasing the CO<sub>2</sub> removal efficiency, such as being able to stimulate biological production without increasing the calcium carbonate production.

## Recommendations

Better understanding of the response of marine systems is needed to improve the prediction of the efficiency of macro-nutrient fertilisation. Particularly important issues are changes to phytoplankton community structures and changes in carbonate and DMS production with ocean fertilisation. The investigation of natural systems that have experienced changes in macro-nutrient should be exploited to provide insight into how ecosystems respond. Such work is beyond the scope of funding for IEA GHG but could become the subject of practical R&D projects.

IEA GHG should carry out an assessment of costs of carbon sequestration by ocean fertilisation when more basic scientific information is available.



## **Enhancement of Oceanic Uptake of CO<sub>2</sub> by Macro-nutrient Fertilization**

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Client :IEA Greenhouse Gas Office

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**TABLE OF CONTENTS**

<b>EXECUTIVE SUMMARY.....</b>	<b>1</b>
<b>1. INTRODUCTION.....</b>	<b>2</b>
<b>2. BOX MODEL.....</b>	<b>3</b>
<b>3. 3-DIMENSIONAL OCEAN CARBON MODEL.....</b>	<b>7</b>
3.1 OCEAN CIRCULATION MODEL.....	7
3.2 OCEAN BIOGEOCHEMICAL MODEL.....	8
3.3 EXPERIMENTS.....	10
<b>4. RESULTS.....</b>	<b>11</b>
4.1 PRESENT CLIMATE.....	11
4.2 CLIMATE CHANGE.....	20
<b>5. DISCUSSION.....</b>	<b>23</b>
5.1 CO <sub>2</sub> SEQUESTRATION EFFICIENCY.....	23
5.2 IMPACT OF MACRO-NUTRIENT FERTILIZATION.....	24
5.2.1 <i>Carbon Chemistry</i> .....	24
5.2.2 <i>Oxygen Limitation</i> .....	24
5.2.3 <i>Phosphate and Silicate Limitation</i> .....	28
5.2.4 <i>Micro-nutrient Limitation</i> .....	29
5.2.5 <i>DMS production</i> .....	30
5.2.6 <i>Marine Ecosystem Impacts</i> .....	31
<b>6. SUMMARY.....</b>	<b>32</b>
<b>7. REFERENCES.....</b>	<b>34</b>



## Executive Summary

This report uses a three-dimensional Ocean Carbon Cycle model for investigating the efficiency of macro-nutrient fertilization to enhance biological export production and sequester atmospheric CO<sub>2</sub>. To simulate macro-nutrient fertilization, phosphate was added to the model in the 18-50°S region of the Southern Ocean. The carbon sequestration efficiency of fertilization is determined from the ratio between increased ocean uptake of CO<sub>2</sub> and the rate of phosphate addition to the upper ocean (converted to carbon units).

### Efficiency of Carbon Sequestration by Macro-nutrient Fertilization

- OCM simulations predicted a maximum efficiency of 90%.
- Increased calcium carbonate production with macro-nutrient fertilization can significantly reduce carbon sequestration efficiency. When calcium carbonate production increases at the same rate as export production, the carbon sequestration efficiency is 75% of the efficiency when calcium carbonate production is held constant.
- Nitrogen source used to stimulate biological production may affect the pH of seawater and alter the sequestration efficiency. An ammonium sulfate source of nitrogen would have no impact but the use of ammonium or nitrate would reduce the efficiency by 10%.
- Ocean fertilization may alter the air-sea exchange of two other important greenhouse gases, N<sub>2</sub>O and DMS. We estimate that increased N<sub>2</sub>O production in the ocean with fertilization would reduce the efficiency of fertilization by a maximum of 20%. Changes in the air-sea exchange of DMS may also occur with ocean fertilization. However, at present one cannot reliably predict the response of marine DMS production to macro-nutrient fertilization.
- Climate simulations with greenhouse warming predicted dramatic changes in ocean circulation. However, the predicted ocean circulation changes did not alter the carbon sequestration efficiency of macro-nutrient fertilization.

### Additional Conclusions

- Carbon sequestration efficiency of macro-nutrient fertilization is site-dependent because macro-nutrient fertilization only increases biological production in regions limited by macro-nutrients.
- Nitrate-limited regions of the surface ocean possess low phosphate concentrations (e.g. in the 18-50°S region the excess phosphate equates to sequestering 0.8 Gt C) and any proposed macro-nutrient scheme would need to consider adding both phosphate and nitrogen to the ocean to stimulate biological production.
- Increased anoxic water with fertilization is confined to areas that already have large anoxic regions hence the impact on the marine ecosystem should be minor.
- Marine ecosystem impacts of changes in the phytoplankton biomass or community structure (i.e. changes in the limiting nutrient for biological production) is a fundamental issue for ocean fertilization. The investigation of natural systems which have experienced changes in macro-nutrient supply (i.e. Hawaii Ocean Time-series Site) should be exploited to provide insight into how ecosystems respond. Better understanding of the system

coupled with improved models are needed to improve our predictions of the response of the system to macro-nutrient fertilization.

## 1. Introduction

The marine carbon cycle plays a major role in controlling atmospheric CO<sub>2</sub> levels. The oceans presently remove about 30% of the annual anthropogenic CO<sub>2</sub> emissions. Eventually the oceans will absorb about 80% of the total anthropogenic CO<sub>2</sub> emissions but this new equilibrium level of atmospheric CO<sub>2</sub> will take several thousand years to attain.

Given the large carbon storage capacity of the ocean and its importance in absorbing anthropogenic CO<sub>2</sub>, it is natural to consider how one could enhance the ocean's uptake of anthropogenic CO<sub>2</sub>. Two proposed strategies exist for increasing the carbon sequestered by the ocean.

One option is the direct deep-sea injection of CO<sub>2</sub>. This option would exploit the long residence time of deepwater and the large storage capacity of the deep ocean. Modeling work of this option has shown that the ocean could absorb all the anthropogenic CO<sub>2</sub> present in the atmosphere and reduce the atmospheric CO<sub>2</sub> levels for many centuries [Bacastow and Dewey, 1996; Wong and Matear, 1996; Wong and Matear, 1997].

A second option is to increase the uptake of carbon by the marine phytoplankton and enhance the biological "pumping" of carbon from the upper ocean into the deep sea [Wong and Matear, 1995]. This would then lower carbon levels in the upper ocean and produce a net flux of CO<sub>2</sub> from the atmosphere into the ocean. This enhancement of the biological pump could be accomplished through either iron fertilization or macro-nutrient fertilization. Iron fertilization is motivated by the observations that 25% of the surface ocean has ample macro-nutrients, which the marine phytoplankton do not completely utilize. Both shipboard incubations and large-scale iron additions have shown that biological production in these regions can be stimulated by adding iron [Boyd *et al.*, 1996; Coale *et al.*, 1996]. Modeling studies have assessed the potential of adding iron to the high-nutrient low-chlorophyll (HNLC) regions to sequester carbon [Sarmiento and Orr, 1991; Matear and Wong, 1999]. Matear and Wong, [1999] calculated that iron fertilization of all HNLC regions for 100 years would enhance the oceanic uptake of CO<sub>2</sub> by 160Gt C. A second way of increasing marine production is to add macro-nutrients to the upper ocean. Low concentrations of macro-nutrients (e.g. nitrate and phosphate) limit biological activity in approximately 70% of the surface ocean. The addition of macro-nutrients to these regions would stimulate biological activity and transfer organic carbon from the surface to the deep ocean.

In the sub-tropical gyres, phytoplankton productivity is typically limited by macro-nutrients. In these regions, the typical limiting nutrient is nitrogen. The difficulty with nitrogen based export production models is the complexity of the nitrogen cycle. With nitrogen, several different pools (e.g. nitrate, ammonium, urea, and N<sub>2</sub>) are available to drive phytoplankton production. In the ocean, the carbon, phosphorus and nitrogen cycles are closely linked because phytoplankton utilizes these elements at nearly constant rates when they form organic matter [Redfield *et al.*, 1963]. The C:N:P ratio for phytoplankton uptake is referred to as the "Redfield ratio". The subsequent remineralization of the organic matter into inorganic material also occurs at approximate Redfield ratios [Anderson and Sarmiento, 1994]. The

complexity of the nitrogen cycle and a nearly constant C:N:P ratio in the production and remineralization of organic matter has prompted the use of phosphate as the limiting nutrient in ocean carbon models [Bacastow and Maier-Reimer, 1990; Maier-Reimer and Bacastow, 1990; Yamanaka and Tajika 1996; Matear and Hirst, 1999]. This has been further justified by recent observations from the oligotrophic North Pacific that demonstrate that nitrogen fixation in the upper ocean by phytoplankton can satisfy phytoplankton nitrogen requirements and make phosphate the limiting nutrient for phytoplankton growth [Karl *et al.*, 1997].

This study uses an Ocean Carbon Model (OCM) to assess the effect of macro-nutrient fertilization on oceanic anthropogenic CO<sub>2</sub> uptake. An earlier modeling study on the effect of macro-nutrient fertilization showed that the atmospheric carbon sequestered by fertilizing the 18-50°S region of the Southern Ocean was only 44% of the increase in export production [Orr and Sarmiento, 1992]. These authors conclude that macro-nutrient fertilization was an inefficient option for sequestering atmospheric CO<sub>2</sub>. Orr and Sarmiento [1992] simulated macro-nutrient fertilization by imposing a constant increase in export production in the fertilized region. In contrast, this study uses an ocean carbon model where export production is dependent on surface phosphate concentration and macro-nutrient fertilization is simulated by adding phosphate at a constant rate to the upper ocean. This formulation of export production allows one to separate the increase in export production due to re-cycling from that due to added phosphate and assess the efficiency of macro-nutrient fertilization at sequestering anthropogenic CO<sub>2</sub>. With this model, efficiency and impact of macro-nutrient fertilization is investigated in the same 18-50°S region of the Southern Ocean as Orr and Sarmiento [1992].

Two ocean carbon models are utilized in this study – 1) box model of carbon and phosphate cycling and 2) a 3-Dimensional Ocean Carbon Model (OCM). The box model provides a simple analytical model to elucidate the response of the ocean to macro-nutrient fertilization. The box model results provide the framework to interpret the results of the more realistic and more complex 3-D model. The 3-D Ocean Carbon Model is used to investigate how the ocean would respond to macro-nutrient fertilization for both the present climate and the climate predicted by greenhouse warming. The simulations are used to assess the efficiency of this option at sequestering anthropogenic CO<sub>2</sub> and the potential impacts of fertilization on ocean biogeochemical cycling and on marine ecosystems.

## 2. Box model

Box models are valuable tools for investigating the response of systems to a perturbation. A two box model of a macro-nutrient-limited region of the ocean is constructed to investigate macro-nutrient fertilization. In the box model, phosphate was the only limiting nutrient and fertilization was simulated by adding phosphate.

The behavior of phosphate (P) and DIC (C) was modeled using the following equations where subscript 1 denotes values in the surface box and subscript 2 denotes values in the deep box:

$$\begin{aligned}
V_1 \frac{dP_1}{dt} &= a(P_2 - P_1) - bP_1 + eV_1 \\
V_2 \frac{dP_2}{dt} &= -a(P_2 - P_1) + bP_1 \\
V_1 \frac{dC_1}{dt} &= a(C_2 - C_1) - brP_1 + f(C_{atm} - C_1) \\
V_2 \frac{dC_2}{dt} &= -a(C_2 - C_1) - brP_1
\end{aligned} \tag{1}$$

The evolution of P and C are affected by the vertical exchange between the two boxes (a), biological export production ( $bP_1$ ), air-sea exchange of carbon dioxide ( $f[C_{atm} - C_1]$ ) and P addition (e). In the box model, export production is a linear function of phosphate concentration in the surface box and the air-sea exchange of CO<sub>2</sub> are determined by restoring the ocean surface box to a value in equilibrium with the atmosphere ( $C_{atm}$ ). In (1), V is the volume of the boxes and r is the carbon to phosphate ratio in the export production.

Without fertilization ( $e=0$ ), the steady-state solution is

$$\begin{aligned}
P_1 &= \frac{aP_2}{a+b} \\
C_1 &= C_{atm} \\
C_2 &= C_{atm} + brP_1/a
\end{aligned} \tag{2}$$

Parameter values appropriate for South Pacific subtropical gyre are  $V_1=1$  and  $V_2/V_1=10$ ,  $r=106$ ,  $a=0.1\text{yr}^{-1}$ ,  $b=1\text{yr}^{-1}$  and  $f=1\text{yr}^{-1}$ ,  $P_2=2\text{ }\mu\text{mol/kg}$ ,  $C_{atm}=1900\text{ }\mu\text{mol/kg}$ .

Now consider perturbation to this model where phosphate is added to the surface box at a constant rate ( $e = \text{constant}$ ). For the values listed above the evolution of the concentrations in the box model rapidly adjust to a new state where  $P_1$ ,  $P_2$  and  $C_2$  increase linearly with time and  $C_1$  drops to a lower value (Figure 1). By assuming box concentrations are a linear function of time, the analytical solution for the change in concentrations due to constant addition of phosphate to the upper box can be found.

$$\begin{aligned}
DP_1 &= \frac{eV_1(a t + V_2)}{a(V_1 + V_2) + bV_2} \\
DP_2 &= \frac{(a+b)eV_1}{a(V_1 + V_2) + bV_2} t \\
DC_1 &= -\frac{berV_1V_2}{(a(V_1 + V_2) + bV_2)f} \\
DC_2 &= \frac{berV_1(ft - V_2)}{(a(V_1 + V_2) + bV_2)f}
\end{aligned} \tag{3}$$

The analytical solution shows that only the carbon concentration in the surface box ( $C_1$ ) does not change with time (consistent with Figure 1 after the initial adjustment period). From the analytical solution, we can express the change in both export production and ocean uptake of carbon due to phosphate addition as follows

$$\begin{aligned}
 \mathbf{DExport} &= rb \mathbf{DP}_1 = \frac{reV_1(at + V_2)}{a(V_1 + V_2) + bV_2} b \\
 \mathbf{DUptake} &= -f \mathbf{DC}_1 = \frac{berV_1V_2}{(a(V_1 + V_2) + bV_2)}
 \end{aligned} \tag{4}$$

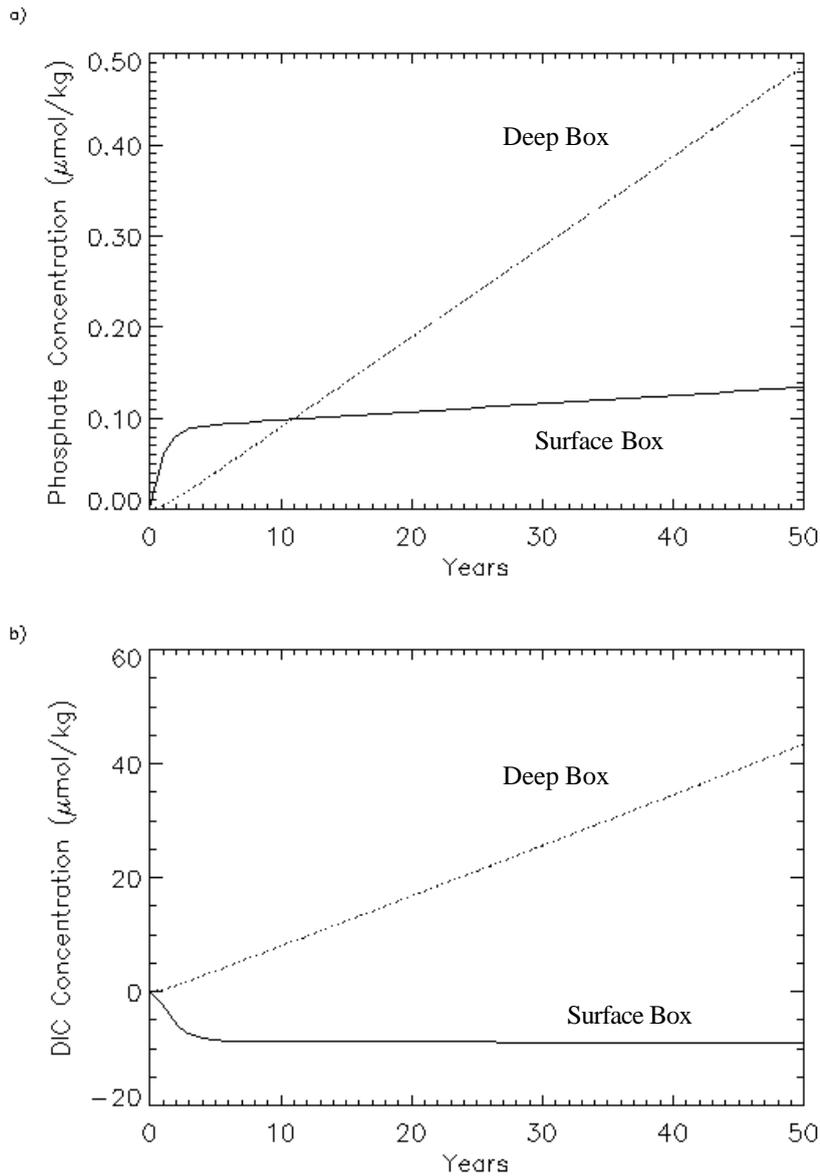


Figure 1. Change in phosphate and dissolved inorganic carbon (DIC) in the box model for a phosphate fertilization rate of  $0.1 \mu\text{mol yr}^{-1}$ . a) Change in the phosphate for the surface box (solid) and the deep box (dotted). b) Change in DIC for the surface box (solid) and the deep box (dotted).

Under constant phosphate addition, the export production will grow linearly with time but the ocean uptake of carbon adjusts to a constant elevated value of uptake. The growth in the

export production with time reflects the increased vertical supply of phosphate to the surface box from the phosphate-enriched deep box. This recycling of phosphate and carbon-enriched water increases export production but does not alter the air-sea exchange of carbon. The increase in export production compared to the rate of phosphate addition is given as

$$\begin{aligned} \frac{DExport}{Padded} &= \frac{eV_1(a t + V_2)}{a(V_1 + V_2) + bV_2} rb / re \\ &= \frac{abV_1 t}{(a(V_1 + V_2) + bV_2)} + \frac{bV_1 V_2}{(a(V_1 + V_2) + bV_2)} \\ &\gg \frac{aV_1}{V_2} t(1 - \frac{a}{b}) + V_1(1 - \frac{a}{b}) \end{aligned} \quad (5)$$

The ratio of the increase in export production to phosphate addition is independent of the rate of phosphate addition ( $e$ ) and it increases slowly with time. For our model parameters, the growth rate is approximately  $0.01 \text{ yr}^{-1}$ . The corresponding numerical solution for a phosphate addition rate of  $0.1 \mu\text{mol yr}^{-1}$  is shown in Figure 2.

*Orr and Sarmiento* [1992] defined the efficiency of macro-nutrient fertilization as the ratio of increased carbon uptake to increased export production. For the box model, this definition of efficiency gives

$$\begin{aligned} Efficiency &= \frac{DUptake}{DExport} \\ &= \frac{V_2}{a t + V_2} \end{aligned} \quad (6)$$

The efficiency decreases with time (Figure 2). However, this definition of efficiency is flawed because export production increases due to the re-supply of phosphate enriched water to the euphotic zone, which increases export production while having no effect on the ocean uptake of carbon. A better definition of the efficiency of phosphate fertilization is to compare the change in ocean CO<sub>2</sub> uptake to the rate of phosphate addition in carbon equivalent units (i.e. phosphate addition multiplied by the C/P ratio,  $r$ , which equals  $r e$ )

$$\begin{aligned} \frac{DUptake}{DPadded} &= \frac{berV_1 V_2}{(a(V_1 + V_2) + bV_2)} / re \\ &= \frac{bV_1 V_2}{(a(V_1 + V_2) + bV_2)} \\ &\gg V_1(1 - a/b - aV_1/bV_2) \end{aligned} \quad (7)$$

This ratio is constant and independent of the rate of phosphate addition. For our model parameters, this ratio is approximately 0.89 (see Figure 2). Therefore, once the box model

has adjusted to the initial perturbation, the increased oceanic CO<sub>2</sub> uptake is approximately 89% of the phosphate addition (in equivalent carbon units).

The box model shows the response of a phosphate-limited ocean to a constant rate of phosphate addition. After an initial adjustment period, a constant rate of phosphate addition produces a linear increase in export production with time and a constant but elevated value for the carbon uptake by the ocean. By defining the efficiency of phosphate addition as in equation 6, one underestimates the efficiency because export production increase with time due to the re-supply of phosphate-enriched water to the surface ocean. Equation 7 is a better definition of the efficiency of phosphate fertilization and it shows that the phosphate addition is effective at sequestering atmospheric CO<sub>2</sub> (89% efficiency).

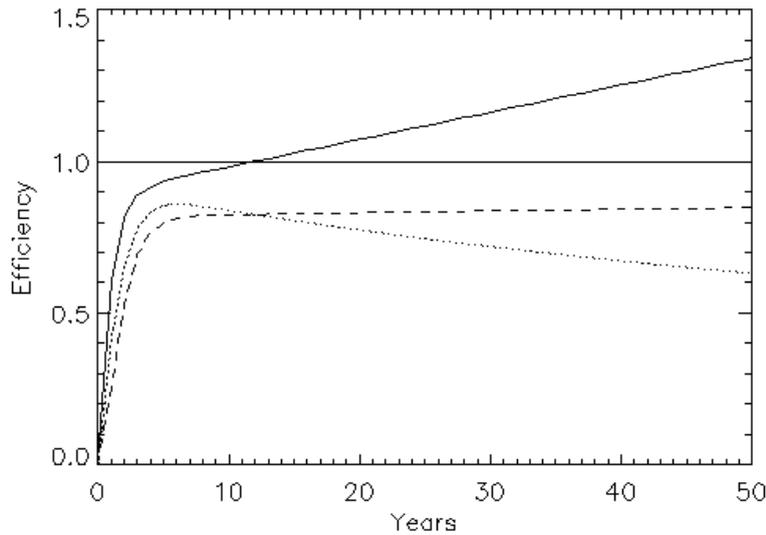


Figure 2. The efficiency of phosphate addition in the box model calculated using the ratio of export production to phosphate addition multiplied by the C:P ratio which is referred to as carbon equivalent units (solid), the ratio of CO<sub>2</sub> uptake to carbon export (dotted) and the ratio of CO<sub>2</sub> uptake to phosphate addition in carbon equivalent units (dashed).

### 3. 3-Dimensional Ocean Carbon Model

The CSIRO Ocean Carbon Model (OCM) was used to make a more realistic assessment of the effectiveness of macro-nutrient fertilization. This OCM determines the seasonal distribution of temperature, salinity, phosphate, oxygen, dissolved inorganic carbon and alkalinity using the combination of an Ocean General Circulation Model (OGCM) and an ocean biogeochemical model.

### 3.1 Ocean Circulation Model

The ocean circulation model is based on the Bryan-Cox OGCM [Bryan, 1984]. The model geometry follows Hirst and McDougall [1996]. The model has horizontal resolution of 3.75° longitude by 4.25° latitude with 21 vertical layers. The model bathymetry is a smoothed discretization of the real ocean bottom topography. In the model, horizontal and vertical viscosities are independent of depth and equal 50 and  $2.5 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$  respectively. The profile of vertical mixing follows Bryan and Lewis [1979] with a value of  $0.3 \text{ cm}^2 \text{ s}^{-1}$  at the surface, increasing to  $1.3 \text{ cm}^2 \text{ s}^{-1}$  at 3500m. Increased vertical diffusivity is used to mix regions of vertical instabilities. The Redi-Cox scheme [Cox, 1987] was used for isopycnal mixing with isopycnal diffusivity,  $K_i$  set to  $10^7 \text{ cm}^2 \text{ s}^{-1}$ . The physical model uses the "GM" scheme [Gent and McWilliams 1990; Gent et al. 1995] for representing the adiabatic transport effects of baroclinic eddies. The diffusivity, which determines the strength of the eddy-induced transports, was set at  $10^7 \text{ cm}^2 \text{ s}^{-1}$  [following Rix and Willebrand 1996]. England and Hirst [1997] indicated that the temperature, salinity and CFC simulations were improved by the use of the GM scheme. Matear [1999] also showed that the natural <sup>14</sup>C simulation was improved with the GM scheme.

The OGCM was forced with the monthly mean wind stress of Hellerman and Rosenstein [1983]. The surface flux of heat and salt were computed by restoring surface temperature and salinity to Levitus [1982] monthly mean values with a time-scale of 30 day<sup>-1</sup> and 50 day<sup>-1</sup> for temperature and salinity respectively. Input from the Mediterranean Sea was included in the model by a diffusive flux from this region [England et al., 1993]. The high latitude salinity of the Southern Ocean was adjusted to reflect observed winter values [England et al., 1993].

### 3.2 Ocean Biogeochemical Model

The structure of the biogeochemical cycle (BGC) model follows Bacastow and Maier-Reimer [1990]. The BGC model was imbedded in the OGCM to determine distributions of dissolved inorganic carbon (DIC), alkalinity, phosphate and dissolved oxygen. The BGC model determined export production and windspeed-dependent gas exchange of CO<sub>2</sub> and O<sub>2</sub>. Export production is parameterized as a function of light, temperature, phosphate and mixed layer depth. The advection-diffusion equation for the BGC tracers was identical to the equation used for the temperature and salinity except the source/sink term,  $Q$ , was different. In an idealized form, the advection-diffusion equation for BGC tracers is

$$\frac{\partial C}{\partial t} + \tilde{N} \times (\mathbf{u}C) = \tilde{N} \times (K_h \tilde{N}C) + \frac{\partial}{\partial z} \left( K_z \frac{\partial C}{\partial z} \right) + Q \quad (8)$$

where  $C$  represents the tracer concentration,  $\mathbf{u}$  is the 3-dimensional velocity,  $K_h$  and  $K_v$  are the horizontal and vertical diffusion coefficients (which include isopycnal and GM mixing terms) and  $Q$  represents the source/sinks due to biological processes and air-sea exchanges.

In the model, biological production (photosynthesis) only occurred in the euphotic zone, which is set to the surface layer of the ocean model (upper 25 m). The export of organic matter (EP) from the euphotic zone was determined using the following equation

$$EP = sA(\mathbf{f}, t_s)B(T)C(h) \frac{P}{P+k}, \quad k = 0.1 \text{ mM}. \quad (9)$$

The term  $A$  is proportional to the seasonally averaged solar radiation, which is a function of latitude ( $\phi$ ) and time of year ( $t_s$ ). The term  $B$  represents the temperature ( $T$ ) dependency and the term  $C$  is a function of the convective depth ( $h$ ). The temperature, light and mixed-layer depth dependency (terms  $A$ ,  $B$  and  $C$ ) followed parameterization used by *Kurz and Maier-Reimer [1993]*. In equation (9),  $k$  is a half saturation constant set to  $0.1 \mu\text{mol kg}^{-1}$ ,  $P$  is the modeled phosphate concentration in the surface layer and  $s$  is the scaling factor for export production. The value of the  $s$  produces an EP flux with a time scale of about one month [*Yamanaka and Tajika., 1996*]. Our formulation of EP saturates at high phosphate concentrations which is consistent with observations that high phosphate regions do not respond to phosphate addition [*Sedwick et al., 1999*]. In the OCM, the limiting nutrient is phosphate and macro-nutrient fertilization was simulated by adding phosphate to the upper ocean.

In the model, the composition of the particulate organic matter (POM) assumed the classical Redfield ratio [*Redfield et al., 1963*]

$$P:N:C:O_2 = 1:16:106:138 \quad (10)$$

The CaCO<sub>3</sub> export was a constant fraction of the organic matter export (8%). The exported POM from the euphotic layer was instantaneously remineralized below the euphotic layer. This implies that the sinking of POM greatly exceeds the effect of horizontal advection and no POM is advected out of the region where it is produced. For a coarse resolution model this is a valid assumption. To remineralize POM, the vertical profile of POM is prescribed by the following equation

$$POM(z) = \left(\frac{z}{100m}\right)^{-a}, \quad (11)$$

where  $z$  is depth in meters and  $a=0.9$ .

This profile of POM is consistent with sediment trap data where observed values of  $a$  varied from 0.988 for particulate organic nitrogen to 0.858 for particulate organic carbon [*Martin et al., 1987*]. In the model, POM that reaches the bottom is remineralized in the bottom layer. The remineralization of POM is allowed to occur under anoxic conditions, which is an important process in the eastern equatorial Pacific and the Gulf of Guinea. In these regions, POM is partly remineralized by denitrification. This is allowed in the model by remineralization of POM according to equation 4 even in the absence of dissolved oxygen. If dissolved oxygen becomes negative during one time iteration, its concentration is reset to zero and the remineralization of POM occurs by denitrification. To remineralize CaCO<sub>3</sub>, the vertical profile of CaCO<sub>3</sub> is given by the following equation

$$CaCO_3(z) = \exp^{-z/3500m} \quad (12)$$

which is based on sediment trap data [Martin *et al.*, 1987]. With these prescribed profiles of POM and CaCO<sub>3</sub>, POM is remineralized at shallower depths than CaCO<sub>3</sub>.

The dissolved oxygen and CO<sub>2</sub> in the ocean are exchanged with the atmosphere. Both the air-sea flux of O<sub>2</sub> and CO<sub>2</sub> were calculated using the wind-speed and species-dependent gas exchange coefficient ( $K_{O_2}$   $K_{CO_2}$ ) from Wanninkhof [1992] multiplied by the air-sea partial pressure difference between the surface ocean and the atmosphere.

$$\begin{aligned} Q_{o_2} &= K_{O_2}(pO_2^{ocean} - pO_2^{atm}) \\ Q_{co_2} &= K_{CO_2}(pCO_2^{ocean} - pCO_2^{atm}) \end{aligned} \quad (13)$$

The partial pressure of O<sub>2</sub> in the atmosphere ( $pO_2^{atm}$ ) was set to 20.85%. The partial pressure of O<sub>2</sub> in the ocean ( $pO_2^{ocean}$ ) was determined using modeled surface ocean temperatures and salinities. The solubility of dissolved oxygen in seawater was calculated using Weiss [1970]. The surface ocean  $pCO_2$  was determined using the full carbon chemistry equations which required modeled temperature, salinity, alkalinity and dissolved inorganic carbon from the surface ocean. The steady-state tracer distributions in the ocean were obtained by running an ocean-only model to steady-state with initial average phosphate and alkalinity set to 2.0  $\mu$ M and 2431  $\mu$ M eq and the atmospheric CO<sub>2</sub> and O<sub>2</sub> set to 280 ppm and 20.85%.

### 3.3 Experiments

The OCM was initially run to a quasi-steady state under pre-industrial atmospheric CO<sub>2</sub> levels. From the pre-industrial state (year 1850), model runs were made using a prescribed evolution of atmospheric CO<sub>2</sub> from the IS92a scenario of the IPCC report [Houghton *et al.* 1996] (Figure 3).

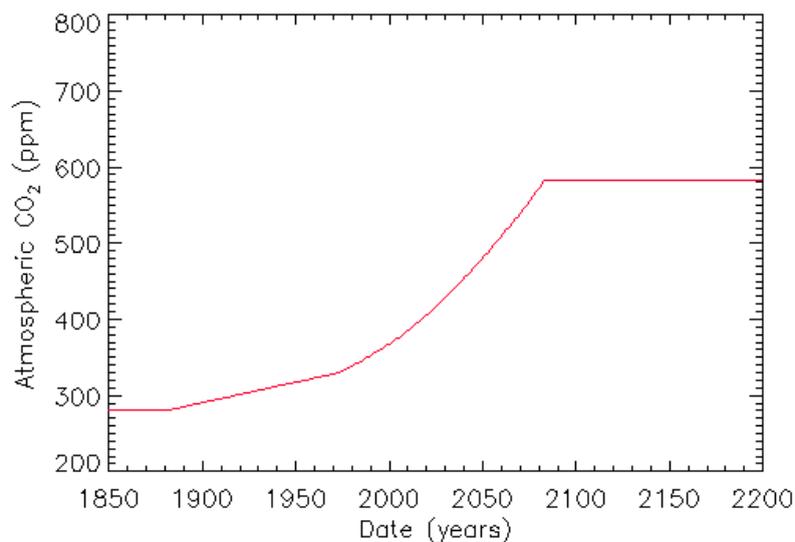


Figure 3. Prescribed evolution of atmospheric CO<sub>2</sub> used in the OCM runs.

The model predicts large regions in the upper ocean where macro-nutrients (phosphate) limit biological production (Figure 4), similar to those observed in the real ocean. The addition of macro-nutrients to these regions would stimulate marine biological export production and allow the ocean to sequester more anthropogenic CO<sub>2</sub>.

Two different sets of experiments were performed with the model. The first set of experiments used the present seasonal climatology of sea surface temperature, salinity, windspeed and sea ice extent as the forcing fields for the OCM. These experiments are referred to as results for the present climate. The second set of experiments used the same OCM but the seasonal fields of sea surface temperature, salinity, windspeed and sea ice extent were predicted using the CSIRO Climate Model under climate change simulation. This allowed investigation of how modifications of the ocean circulation with climate change might alter the efficiency of macro-nutrient fertilization.

## 4. Results

### 4.1 Present Climate

The box model represents the response of a phosphate-limited ocean to the addition of phosphate. The OCM should produce a similar response but with the following two complications. First, like the surface of the real ocean, the OCM has regions where biological production is not limited by macro-nutrients. In these regions, either the addition of phosphate

or the transport of phosphate-enriched water into these regions will not increase the export production. Second, in the OCM, the increased export production of organic matter is coupled to increased export of calcium carbonate. This coupling will reduce oceanic CO<sub>2</sub> uptake of phosphate addition by reducing surface ocean alkalinity.

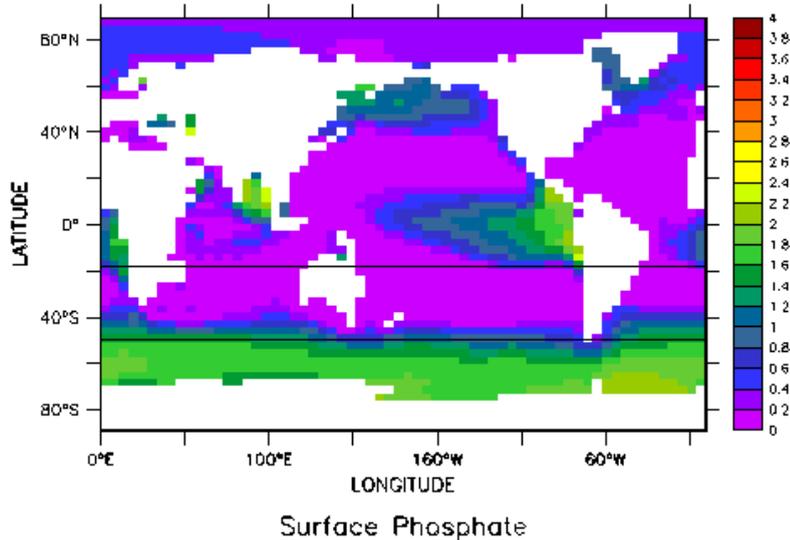


Figure 4. Annual averaged phosphate concentration in the surface ocean for the year 1999 of the control run. The box in the mid-latitudes of the Southern Ocean denotes the fertilized region.

We first performed a set of one-year simulations to assess the response of the modeled export production to phosphate addition. In these simulations, a constant rate of phosphate was added to the upper 25 m of the ocean in the 18°S to 50°S region. The modeled response of export production to added phosphate depended on the rate of phosphate addition (Figure 5). [For convenience all subsequent phosphate units are converted to carbon units by utilizing the carbon to phosphate ratio of the model (106) and quoted as equivalent carbon units]. At low rates of phosphate addition, the export production response was linear but at high rates of phosphate addition, the export production parameterization saturated and the export production deviated from this linear response. For subsequent studies we chose a rate of phosphate fertilization (1.2 equivalent Gt C/yr) that was still in the linear region of Figure 5 hence the non-linear response of export production to phosphate addition is minor.

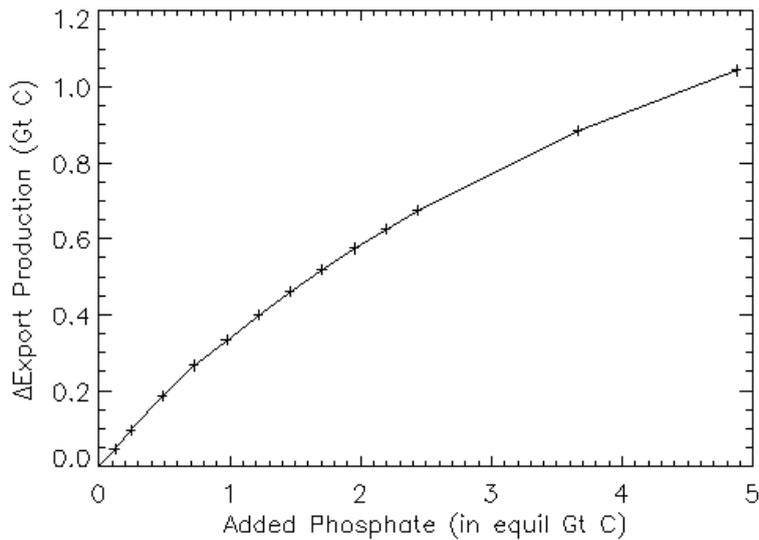


Figure 5. The OCM annual averaged export production after one year fertilization for various rates of phosphate additions to the 18°S-50°S region. Phosphate addition has been converted to “equivalent carbon units” by using the C/P ratio in organic matter (106).

Phosphate fertilization runs were performed to investigate the potential of macro-nutrient fertilization to increase the ocean uptake of anthropogenic CO<sub>2</sub>. For the fertilization runs, phosphate was added to the upper ocean of the 18°S to 50°S region at a constant rate of 1.2 Gt C equivalent /y. Table 1, summarizes the different model runs.

**Table 1. Model Runs showing the total increase in export production, oceanic CO<sub>2</sub> uptake and atmospheric CO<sub>2</sub> change between the years 2000 and 2200.**

Run	Fertilization Period	Enhanced Export Production (Gt C)	Increased CO <sub>2</sub> Uptake (Gt C)	Atmospheric CO <sub>2</sub> Change (matm)
Control	None	–	–	
A	2000-2030	101	19	-9
B	2000-2050	162	31	-15
C	2000-2080	245	49	-24
D	2000-2080 <sup>1</sup>	245	59	-28
E	None <sup>1</sup>	–	–	

<sup>1</sup> Calcium carbon export was held at the pre-fertilization levels. This was accomplished by not modifying the alkalinity equation with time.

In the OCM, phosphate addition stimulated the biological pump, increased the export of organic matter from the upper ocean and increased the ocean uptake of CO<sub>2</sub>. Export production increased dramatically during the first 3 years of fertilization to 0.6 Gt C yr<sup>-1</sup> (Figure 6). Following this period of rapid growth, the increase in export production slowed to a nearly constant rate for the remainder of the fertilization period and after 80 years of fertilization export production had increased by 2.15 Gt C yr<sup>-1</sup>. The stabilization of the growth in export production reflects the balance between the supply of phosphate to the upper ocean by fertilization and ocean transport, and the export of organic matter. The stabilization and subsequent slow growth in export production in the OCM is consistent with the box model. During the fertilization period, several decades are required before the export production equals the rate of phosphate addition (Figure 6b). Once the phosphate fertilization is stopped, export production declines but it takes several centuries for the export production to return to its pre-fertilized value.

Phosphate fertilization increased the oceanic uptake of CO<sub>2</sub> (Figure 7). The increase in the ocean uptake of CO<sub>2</sub> rose dramatically at the start of phosphate fertilization but required 50 years before the oceanic CO<sub>2</sub> uptake stabilized to a new elevated value (Figure 7b). The new elevated oceanic uptake of CO<sub>2</sub> was 0.55 Gt C yr<sup>-1</sup> greater than the value with no fertilization. The behavior of the oceanic uptake of CO<sub>2</sub> in OCM was consistent with the box model. The increase in the cumulative oceanic uptake of CO<sub>2</sub> during the 2000-2200 period from that of the control run is summarized in Table 1. Once phosphate fertilization stopped, the oceanic uptake of CO<sub>2</sub> returned to the pre-fertilization value in less than 100 years. The return of the oceanic CO<sub>2</sub> uptake to the pre-fertilization value was much faster than the return of export production to its pre-fertilized value. The slower adjustment of the export production reflects the recycling of phosphate-enriched water in the upper ocean, which continues to affect export production without altering the oceanic CO<sub>2</sub> uptake.

The key question from these runs is how efficient is macro-nutrient fertilization at increasing oceanic CO<sub>2</sub> uptake. *Orr and Sarmiento [1992]* defined the efficiency of macro-nutrient fertilization as the ratio of the cumulative increase in CO<sub>2</sub> uptake to the cumulative increase in export production. With their definition, the efficiency of our fertilized runs never exceeds 0.5 and it decreases with time (Figure 8). By utilizing the cumulative change in export production to define the efficiency one cannot separate the increase in export production that drives a flux of CO<sub>2</sub> into the ocean from the increase in export production associated with the re-cycling of phosphate-enriched water. This latter effect does not alter the oceanic CO<sub>2</sub> uptake (see section 2.1).

A better definition of the efficiency of phosphate fertilization is the ratio of increased ocean uptake of CO<sub>2</sub> to the added phosphate in equivalent carbon units. For the OCM runs, the efficiency of phosphate fertilization never exceeded 50% (Figure 9). The efficiency of the OCM was significantly less than the 89% efficiency predicted by the box model. One may simply conclude that macro-nutrient fertilization is not an efficient way to sequester anthropogenic CO<sub>2</sub> in the ocean. However, as stated at the start of this section, the OCM

differed from the box model on two points: 1) phosphate addition stimulated both organic and calcium carbonate export from the upper ocean and 2) biological production is not limited by phosphate in all regions of the surface ocean.

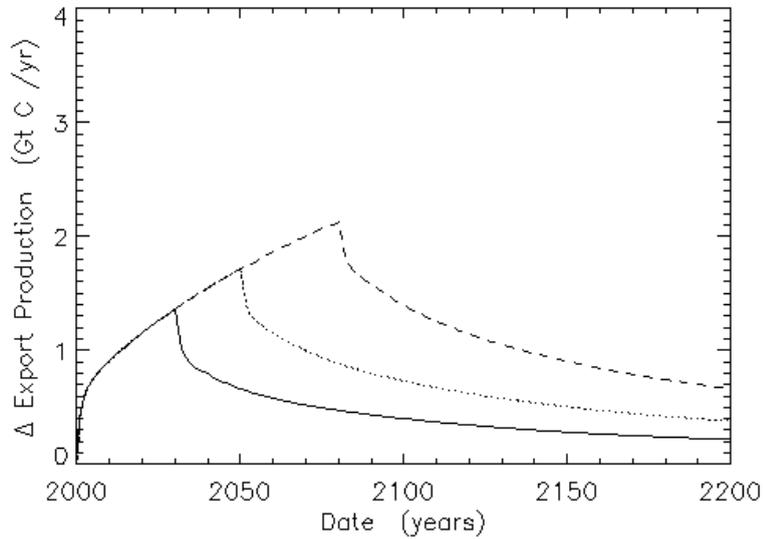
In the OCM, phosphate addition stimulated the export of both organic carbon and calcium carbonate from the upper ocean. Increased calcium carbonate export reduces alkalinity, which reduces the solubility of dissolved CO<sub>2</sub> (gas) in seawater, and this reduces oceanic CO<sub>2</sub> uptake. In the OCM, the effect of increasing the calcium carbonate production was assessed using a model run where phosphate addition did not alter calcium carbonate production. With calcium carbonate production held constant, the maximum efficiency increased from 47% (Run C) to 62% (32% increase) and the total CO<sub>2</sub> sequestered by the ocean increased from 49 Gt C to 59 GtC (20% increase). Calcium carbonate production has an important impact on the efficiency of anthropogenic CO<sub>2</sub> sequestered by phosphate fertilization.

With calcium carbon production held constant, the maximum efficiency (62%) is still significantly less than the value predicted by the box model (89%). In the OCM, not all the phosphate added to the surface ocean stimulated export production. By indiscriminately adding phosphate to the 18°S-50°S region, one adds phosphate to areas where export production was not limited by phosphate. The maps of the change in phosphate concentration and the change in export production due to phosphate fertilization (Figure 10) show that the region of maximum increase in export production is north of the region of maximum increase in phosphate concentration. The regions with large increases in phosphate concentration (0.4 μM) are regions where export production is not phosphate-limited and phosphate addition does not stimulate export production. To assess the consequence of this situation, we separated the fertilized ocean into phosphate-limited and non-phosphate-limited regions. The phosphate-limited region was defined as the ocean region in the 18°S-50°S band where the initial phosphate concentration was less than 0.4 μM. With our definition, the phosphate-limited region accounted for 69% of the surface area of the fertilized ocean. Therefore, a significant portion of the fertilized region (31%) is not phosphate limited and the addition of phosphate to this region would not directly increase export production. Consistent with our definition, export production from the phosphate-limited region dominated the increase in export production while the increase in export production from the non-phosphate-limited region was nearly zero (Figure 11). The corresponding separation of the increase in oceanic CO<sub>2</sub> uptake showed that the phosphate-limited region dominated the oceanic CO<sub>2</sub> uptake. The ocean outside the fertilized region makes a significant contributions to the increased export production (45% by 2080) but accounts for much less of the increased oceanic uptake of CO<sub>2</sub> (17% by 2080) (Figure 11). This reflects the recycling of phosphate and carbon enriched water, which increases export production without affecting increasing the ocean uptake of CO<sub>2</sub>.

Based on separation of the fertilized region into phosphate-limited and non-phosphate-limited areas, our calculated efficiency should be adjusted to reflect the area of the fertilized region that does respond to phosphate addition. By scaling the efficiency by the fraction of the surface area that is phosphate-limited (1/0.69), the efficiency of the phosphate addition becomes consistent with the box model results (Figure 12). This scaling correction is an upper bound adjustment to the efficiency of phosphate fertilization because it assumes that none of

the phosphate added to the non-phosphate-limited region ever stimulates production. Within non-phosphate limited areas this is valid but some of the added phosphate may be transported from these areas to areas where phosphate stimulates production and drives CO<sub>2</sub> flux into the ocean.

a)



b)

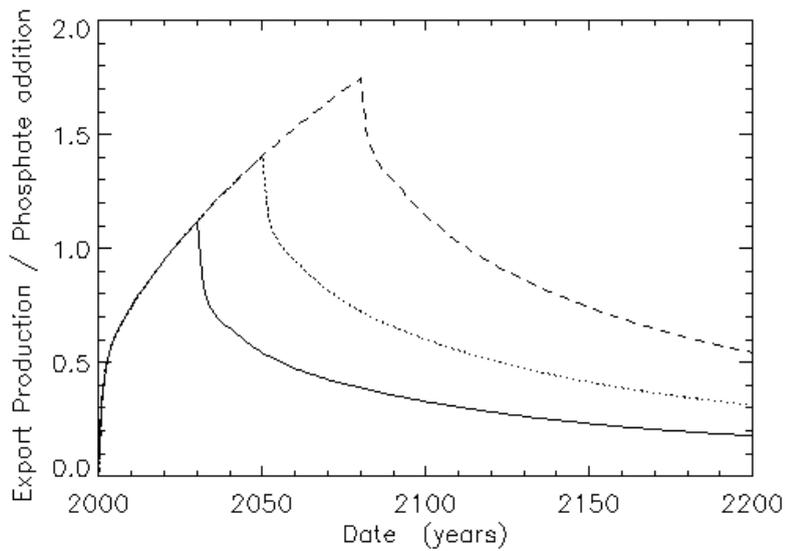
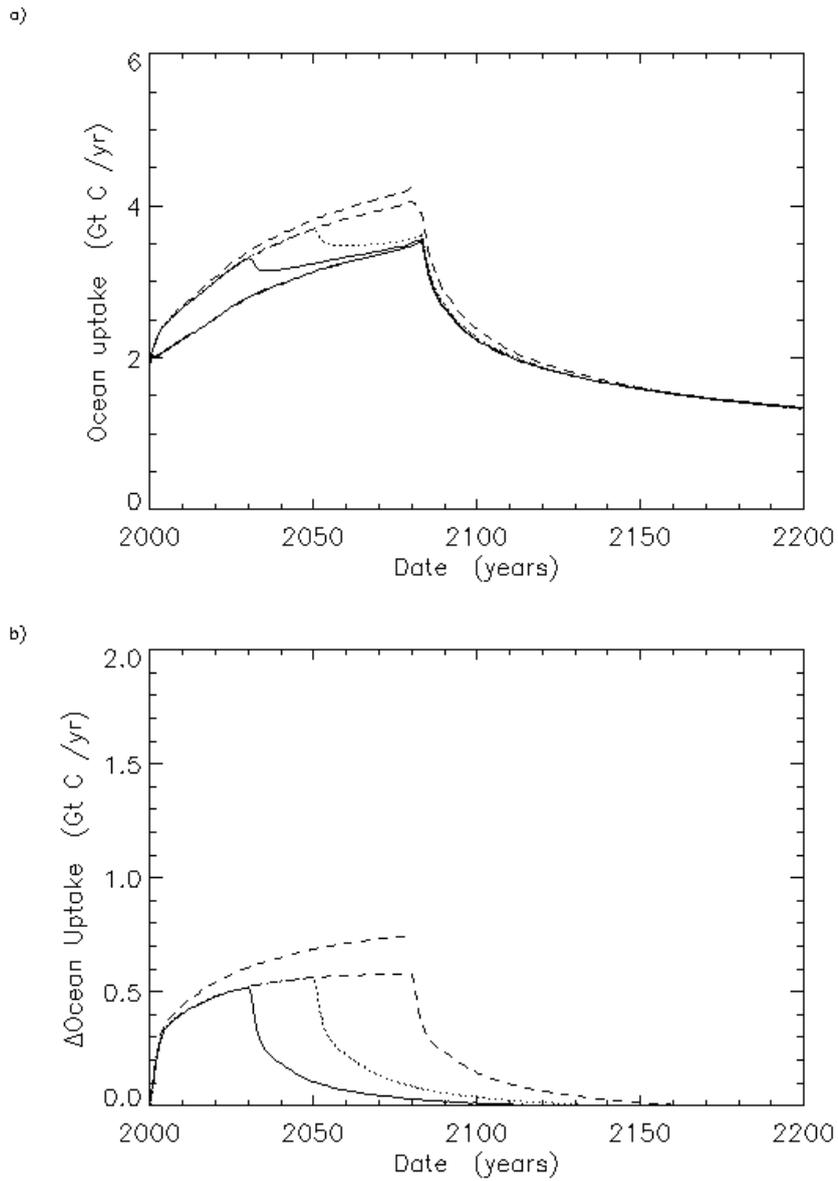


Figure 6. a) Change in annual mean export production with time for run A (solid), run B (dotted) and run C (dashed). b) The ratio of annual mean export to annual phosphate addition (in carbon equivalent units) for run A (solid), run B (dotted) and run C (dashed).



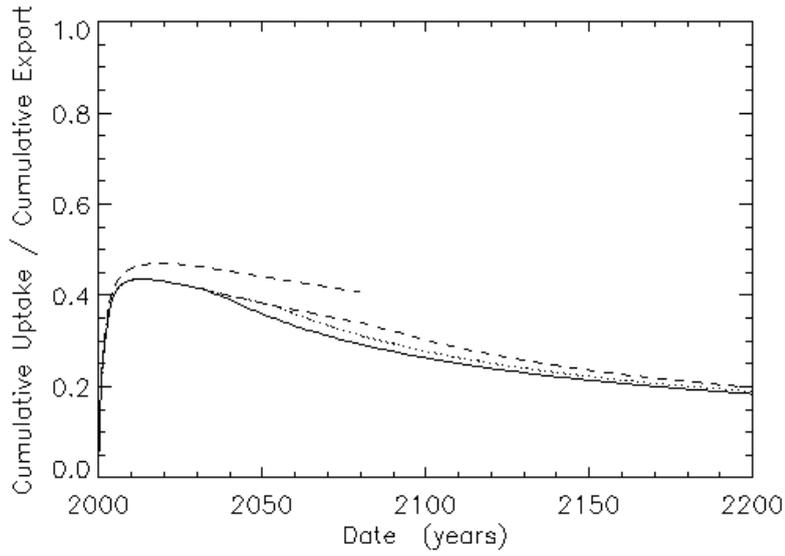


Figure 8. The ratio of the change in the cumulative uptake to change in the cumulative export production between the control run and run A (solid), run B (dashed), run C (dotted) and run E (thick dashed).

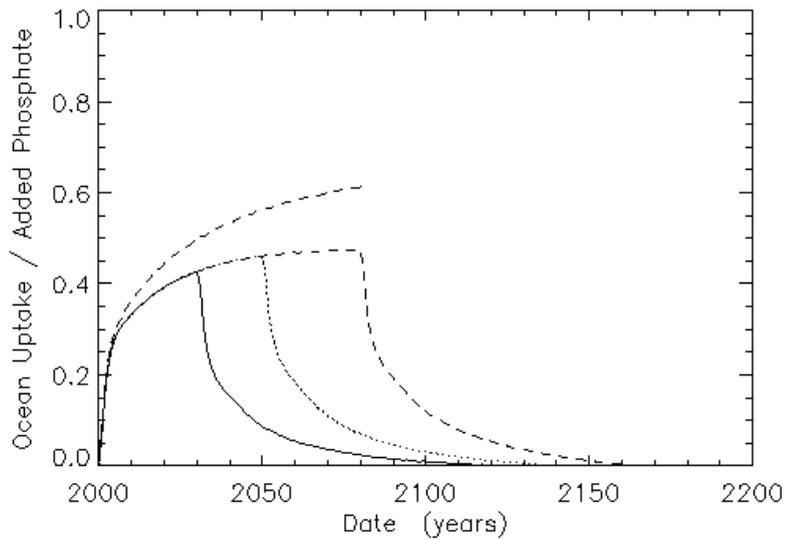


Figure 9. The ratio of the change in annual mean ocean CO<sub>2</sub> uptake to the annual mean phosphate addition in carbon equivalent units for run A (solid), run B (dotted), run C (dashed) and run E (thick dashed).

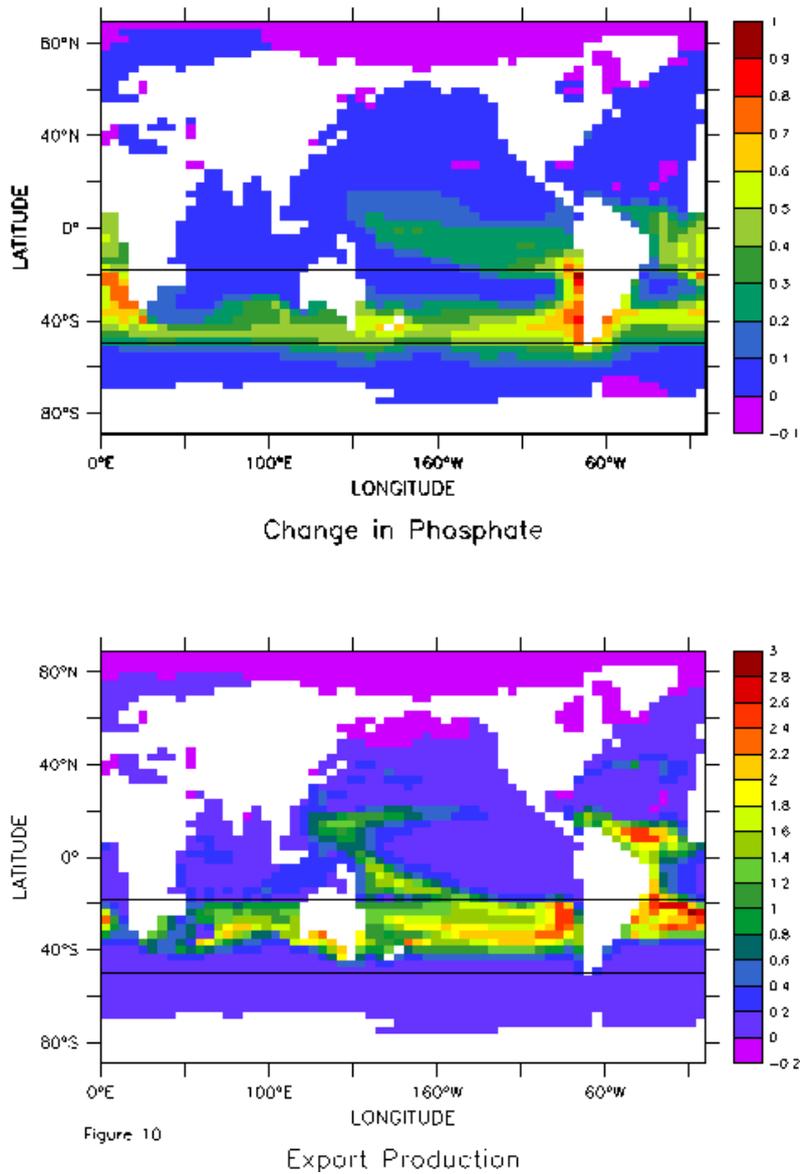


Figure 10. For the year 2080, after 80 years of phosphate addition a) change in the annual mean surface phosphate concentration ( $\mu\text{mol kg}^{-1}$ ) b) change in the annual mean export production. The box in the southern hemisphere denotes the phosphate addition region.

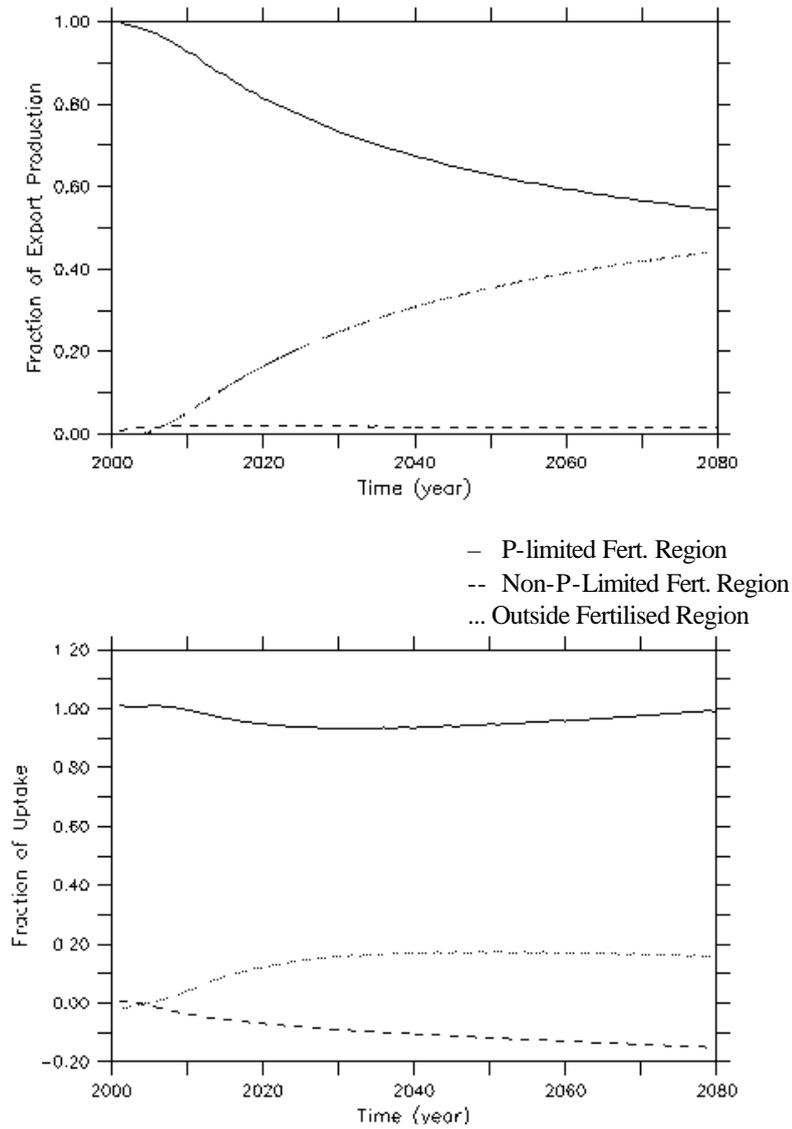


Figure 11. a) The fractional increase in export between run C and the control for the phosphate-limited region of the fertilized ocean (solid), for the non-phosphate-limited region of the fertilized ocean (dashed) and for ocean areas outside the fertilized region (dotted). b) The fractional the increase in oceanic CO<sub>2</sub> uptake of run C - control for the phosphate-limited region of the fertilized ocean (solid), for the non-phosphate-limited region of the fertilized ocean (dashed) and for ocean areas outside the fertilized region (dotted).

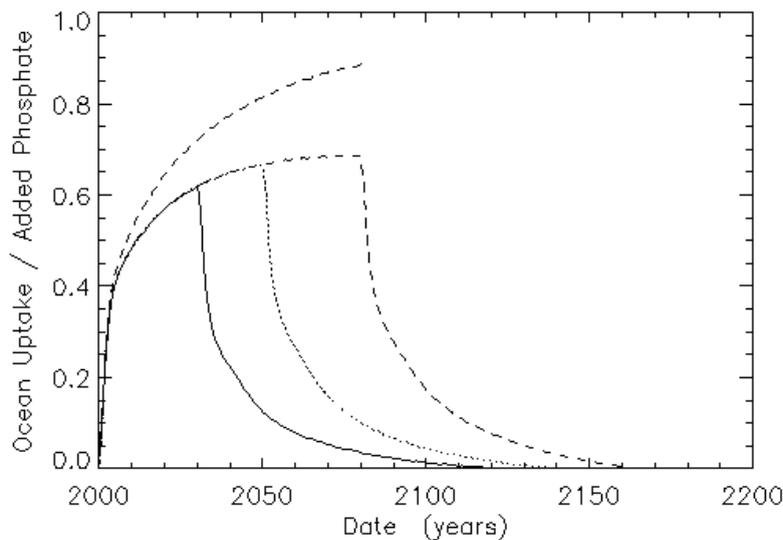


Figure 12. Same as Figure 9 except the efficiency was scaled the fraction of the fertilized region that was phosphate-limited (1/0.69).

#### 4.2 Climate Change

Climate models provide the tools to investigate the impact of greenhouse warming on the climate. Using the CSIRO climate model, *Matear and Hirst* [1999] simulated the climate change impact on the oceanic uptake of CO<sub>2</sub>. With greenhouse warming, *Matear and Hirst* [1999] predicted that the ocean would experience sea surface warming, increased density stratification, reduced ventilation of the deep ocean and reduced supply of nutrient-rich water to the upper ocean. These factors lead to a reduction in the oceanic uptake of anthropogenic CO<sub>2</sub>. Using the same climate model, I assessed whether phosphate fertilization under climate change would differ from the runs done assuming no climate change. For this assessment, three runs of the climate model were used which are summarized in Table 2.

Our fertilization simulation was made using a constant rate of phosphate addition of 1.2 Gt C yr<sup>-1</sup> equivalent to the 18°S-50°S region. Under our climate change scenario, phosphate fertilization more than compensated for the reduction in both export production and oceanic CO<sub>2</sub> uptake predicted with climate change (Figure 13). With climate change, by the year 2080 phosphate fertilization increased export production by 128.6 Gt C and oceanic CO<sub>2</sub> uptake by 43.1 Gt C. This is slightly greater than 120 Gt C and 41.8 Gt C increase in export production and oceanic CO<sub>2</sub> uptake respectively for fertilization using the present day climate. The increased ocean carbon sequestration and export production of the climate change run

reflects the small increase (5%) in the area of the fertilized region that is phosphate-limited in this simulation.

**Table 2. Model runs using the CSIRO climate model. The control climate run has no anthropogenic greenhouse forcing while the climate change runs use IS92a anthropogenic greenhouse gas forcing. The last line in the table summaries how phosphate addition in the 18°S-50°S region changes export production, oceanic CO<sub>2</sub> uptake and atmospheric CO<sub>2</sub> over the period 2000 to 2080.**

<b>Run</b>	<b>Fertilization Period</b>	<b>Enhanced Export Production (Gt C)</b>	<b>Increased CO<sub>2</sub> Uptake (Gt C)</b>	<b>Atmospheric CO<sub>2</sub> Change (matm)</b>
Control Climate	None	–	–	
Climate change	None	-65.3	-36.4	
Climate change with fertilization	2000-2080	63.3	7.4	
Impact of fertilization with climate change	2000-2080	128.6	43.8	-22
With the Present Day Climate	2000-2080	120.0	41.8	-21
Run D- Control Run				

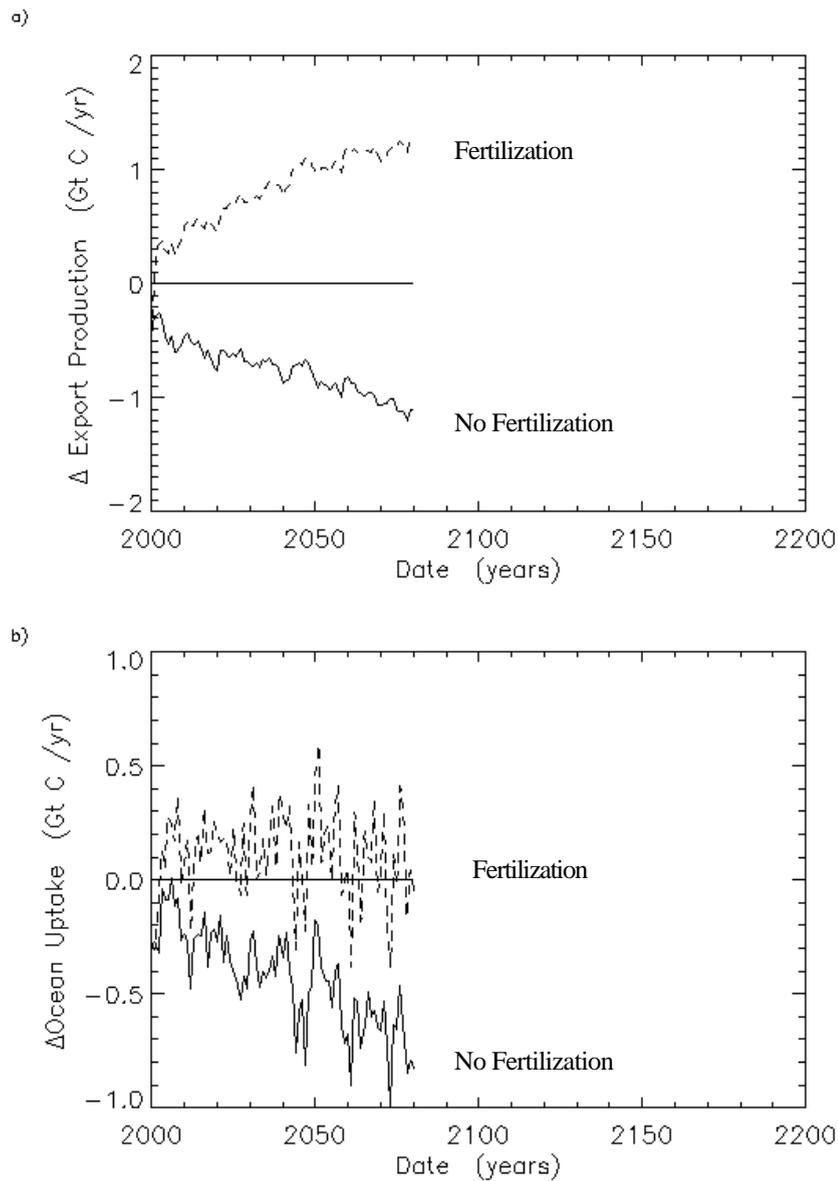


Figure 13. For the climate change simulations a) the change in export production between the climate change run and the control run (solid) and between the climate change run with fertilization and the control run (dashed). b) The change in oceanic CO<sub>2</sub> uptake between the climate change run and the control run (solid) and the climate change run with fertilization and the control run (dashed).

## 5. Discussion

### 5.1 CO<sub>2</sub> Sequestration Efficiency

Macro-nutrient fertilization is one option for increasing the oceanic uptake of anthropogenic CO<sub>2</sub>. *Orr and Sarmiento*, [1992] concluded that this was an inefficient option for increasing oceanic anthropogenic CO<sub>2</sub> uptake because the increase in the oceanic uptake of CO<sub>2</sub> is only 44% of the increase in export production. However, this definition of CO<sub>2</sub> sequestration efficiency cannot separate the increase in export production due to surface addition of macro-nutrients from that due to the re-cycling of macro-nutrient-enriched water. This separation is necessary because only the former process increases the oceanic uptake of CO<sub>2</sub>. This deficiency in the *Orr and Sarmiento* [1992] study motivated a reassessment of the efficiency of macro-nutrient fertilization on the oceanic CO<sub>2</sub> uptake with a global Ocean Carbon Model (OCM).

Prior to running the global OCM, I first investigated the response of a two box model to phosphate fertilization. The box model was configured to represent carbon and phosphate cycling between a surface box and a deep ocean box of an oligotrophic gyre. In the box model, biological production was limited by the phosphate concentration in the surface box. For parameter values that reflected the South Pacific subtropical gyre, the box model predicted that the increase in oceanic CO<sub>2</sub> uptake would be 89% of the rate of phosphate fertilization (phosphate addition in equivalent carbon units). This suggests that macro-nutrient fertilization is an efficient option for increasing oceanic CO<sub>2</sub> uptake. The box model showed that phosphate fertilization would elevate the oceanic CO<sub>2</sub> uptake to a new constant value while export production would increase linearly with time. The increase in export production with time reflects the re-supply of phosphate-enriched water back into the surface box. The re-supply of phosphate-enriched water increases export production with time without changing the oceanic CO<sub>2</sub> uptake.

Guided by the box model results, the impact of macro-nutrient fertilization in a global OCM was investigated. With the OCM, macro-nutrient fertilization was simulated by adding the limiting macro-nutrient in the model, phosphate, to the surface ocean rather than prescribing an increase in export production [i.e. *Orr and Sarmiento* 1992]. Using an OCM that explicitly modeled export production allowed one to assess how phosphate fertilization changes the oceanic CO<sub>2</sub> uptake independent of the associated changes in export production. In the OCM simulations, phosphate was uniformly added to the 18-50°S region of the ocean. The CO<sub>2</sub> sequestration efficiency of phosphate fertilization is defined as the ratio of annual increase in oceanic CO<sub>2</sub> uptake to the annual amount of phosphate added to the surface ocean in equivalent carbon units. The OCM predicted a maximum efficiency of 47% for the case where both the exports of organic matter and calcium carbonate increased with phosphate fertilization. By forcing the calcium carbonate production to remain constant under phosphate fertilization, the maximum efficiency was increased to 62% (32% increase). The efficiency of the OCM simulations was significantly less than the box model because in 31% of the fertilized region, biological production was not limited by phosphate. In the OCM, export production saturates at phosphate concentrations much greater than 0.1 μmol kg<sup>-1</sup>, hence adding phosphate to these regions produced no change in export production. Our export production

formulation is consistent with observations from high-nutrient low-chlorophyll regions that demonstrate macro-nutrient addition to these regions does not stimulate biological production [Boyd *et al.*, 1996]. By scaling our results by the fraction of the fertilized area that was phosphate-limited (1/0.69), one obtained a maximum efficiency of 62% and 90% respectively for runs with and without increased calcium carbonate production. Now, the maximum value predicted by the OCM (90%) is similar to the value calculated from the phosphate-limited box model.

## 5.2 Impact of Macro-nutrient Fertilization

Macro-nutrient fertilization of the ocean would affect biogeochemical cycling of carbon nutrients and oxygen in the ocean with potential impacts on greenhouse gas concentrations in the atmosphere and the behavior of marine ecosystems. Changes in biogeochemical cycling caused by macro-nutrient fertilization and the possible marine ecosystem impacts are discussed in the following sections.

### 5.2.1 Carbon Chemistry

The form of the macro-nutrients added to the seawater could alter the carbon chemistry. The addition of nitrogen as either dissolved nitric acid or dissolved ammonia would lower the seawater alkalinity and raise the fCO<sub>2</sub>. The direct effect of nitric acid or ammonia addition to CO<sub>2</sub> uptake by the ocean can be estimated by determining the amount of CO<sub>2</sub> needed to be absorbed to return the ocean fCO<sub>2</sub> to the initial value. Using values from the surface water of the East Australia Current (total alkalinity of 2335 μM, fCO<sub>2</sub> of 313 μatm and a C/N of 106/16), the addition of nitric acid or ammonia would reduce the CO<sub>2</sub> uptake by 10%. In our macro-nutrient fertilization simulations, we neglect this direct change in alkalinity. This is equivalent to assuming that ammonia sulfate is added to seawater to stimulate biological production which would not change the surface ocean alkalinity. Since this alkalinity change is linked to nitrogen cycling in the ocean, there would be no additional indirect effect on ocean CO<sub>2</sub> uptake.

As summarized in the OCM results, calcium carbonate production associated with macro-nutrient fertilization would increase fCO<sub>2</sub> and offset the reduction in fCO<sub>2</sub> associated with increased export production. The direct effect of increased calcium carbonate production on CO<sub>2</sub> uptake was estimated using the same approach as with nitric acid additions. With a calcium carbonate to organic carbon ratio of 8% (value used in the OCM), the direct reduction in CO<sub>2</sub> uptake is approximately 10%. There are two relevant issues to the impact of calcium carbonate production. One, the value used in the OCM for the CaCO<sub>3</sub>:C<sub>org</sub> ratio was low and an upper-bound estimate for the global-averaged value is approximately 20% [Shaffer 1993]. For a CaCO<sub>3</sub>:C<sub>org</sub> ratio of 20%, the direct change in CO<sub>2</sub> uptake would be 25%. Two, the indirect response of the oceanic CO<sub>2</sub> to changes in carbonate production may be significant because the remineralization of organic carbon is de-coupled from the dissolution of calcium carbonate. In our OCM runs, changes in the calcium carbonate production reduced the maximum oceanic CO<sub>2</sub> uptake by 25% which is much greater than the reduction predicted for the direct effect of changes in calcium carbonate production (10%). This larger

value in the OCM reflects the greater depth of dissolution of calcium carbonate than remineralization of organic carbon, which de-couples the calcium carbonate cycle from the organic carbon cycle and amplifies the effect of changes in calcium carbonate production under phosphate fertilization. Increases in calcium carbonate production with phosphate fertilization significantly reduce the CO<sub>2</sub> uptake efficiency. The OCM results highlight the need to assess the response of calcium carbonate producing organisms to macro-nutrient fertilization.

### 5.2.2 Oxygen Limitation

Macro-nutrient fertilization will increase the flux of organic matter into the ocean. Microbial respiration of this organic material will deplete oxygen. Generally marine animals require oxygen to survive and anoxic regions (no dissolved oxygen) will be devoid of animal life. Mobile animals would avoid anoxic regions, but benthic organisms with limited mobility could die. In the control run, the highly productive equatorial upwelling regions contained layers of anoxic water (Figure 14). The presence of these anoxic layers was consistent with observations. With macro-nutrient fertilization, the thickness and extent of these layers increased.

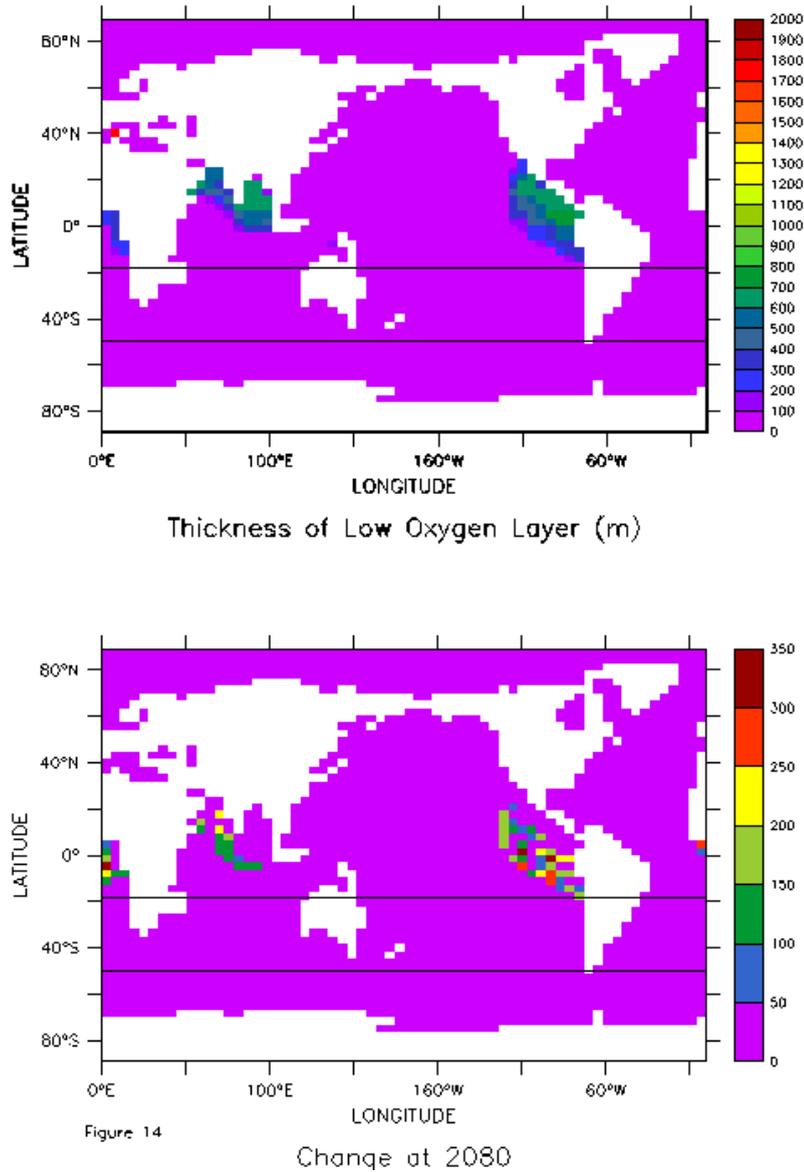


Figure 14. For the year 2080, a) the thickness of the anoxic layer (m) in the control run; b) the change in the thickness of the anoxic layer (m) between run C and the control run.

The change in the volume of anoxic water provided an indication of the impact of macro-nutrient fertilization (Figure 15). After 80 years of fertilization, the volume of anoxic water increased by 17.5%. The increase in anoxic water is generally confined to the equatorial Indian and Pacific oceans in the depth range of 1000-2000 m. The small changes in the volume of anoxic water suggest that the impact of reduced oxygen levels in the ocean is limited.

Changes in the volume of low oxygen or anoxic water will also alter microbial respiration of organic material producing N<sub>2</sub>O and CH<sub>4</sub>. Both N<sub>2</sub>O and CH<sub>4</sub> are greenhouse gases with the ocean contributing 20% and 2% of the global emissions of these gases [Houghton *et al.*, 1995]. Any increased emissions of these greenhouse gases to the atmosphere due to macro-nutrient fertilization will offset the reduction in greenhouse warming of lower atmospheric CO<sub>2</sub>. The weak ocean outgassing of CH<sub>4</sub> to the atmosphere from O<sub>2</sub>-depleted regions indicates that CH<sub>4</sub> sources to the atmosphere are unlikely to increase under macro-nutrient fertilization and this prompts me to neglect this effect.

For global warming, the production of N<sub>2</sub>O is a major concern because one gram of N<sub>2</sub>O has 310 times the greenhouse warming potential of one gram of CO<sub>2</sub> [Houghton *et al.*, 1995]. N<sub>2</sub>O is produced by three microbial processes: denitrification, nitrification, and assimilatory nitrate reduction (the process by which phytoplankton utilizes nitrate) (Figure 16). At present, the upper ocean is super-saturated with N<sub>2</sub>O and the ocean is a source of N<sub>2</sub>O to the atmosphere (3 T g N yr<sup>-1</sup>) accounting for 20% of the current emissions of N<sub>2</sub>O to the atmosphere [Houghton *et al.*, 1995]. It is postulated that increased nitrogen cycling would increase the production of N<sub>2</sub>O and the emissions to the atmosphere [Fuhrman and Capone, 1991]. Fuhrman and Capone [1991] calculated that N<sub>2</sub>O emissions arising from nutrient fertilization of the ocean could completely negate the increased CO<sub>2</sub> uptake of ocean fertilization.

N<sub>2</sub>O production in the ocean primarily occurs in low oxygen environments (less than 10 μmol kg<sup>-1</sup>) where both nitrification and denitrification are occurring. The flux of N<sub>2</sub>O to the atmosphere mainly occurs in regions with extensive oxygen depletion [Codispoti and Christensen, 1985]. The N<sub>2</sub>O production from nitrification is approximately 1% of the remineralized organic nitrogen, but the production of N<sub>2</sub>O increases as the oxygen levels are depleted [Codispoti and Christensen, 1985]. Maximum N<sub>2</sub>O production of 10% of remineralized organic nitrogen have been measured at oxygen levels of 8 μmol kg<sup>-1</sup> [Fuhrman and Capone, 1991]. The production of N<sub>2</sub>O by denitrification also depends on oxygen levels [Seitzinger, 1988]. Production of N<sub>2</sub>O is most efficient at O<sub>2</sub> levels between 1- 10 μmol kg<sup>-1</sup>. A maximum production of 5% N<sub>2</sub>O for every N<sub>2</sub> mole produced have been measured but a more typical value is 1% production levels [Seitzinger, 1988]. In anoxic conditions the denitrification process produces no N<sub>2</sub>O [Codispoti and Christensen, 1985].

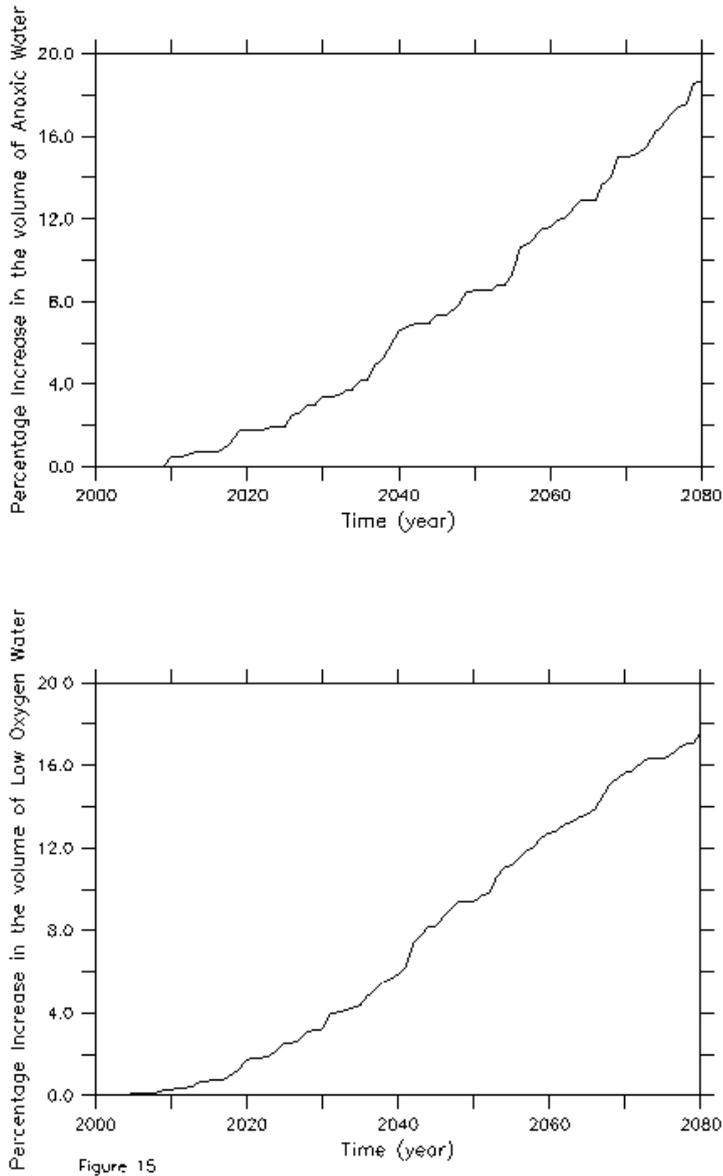


Figure 15

Figure 15. a) The percentage increase in the volume of anoxic water ( $O_2$  levels less than  $1\mu\text{mol/kg}$ ) between run C and the control run; b) percentage increase in the volume of low Oxygen water ( $O_2$  levels between 1 and  $10\mu\text{mol/kg}$ ) between run C and the control run.

We estimated the increased production of N<sub>2</sub>O with macro-nutrient fertilization using two approaches. First, we related the increase in the N<sub>2</sub>O production to the modeled increase in export production [e.g. *Fuhrman and Capone* 1991]. With phosphate fertilization, export production increased by a maximum of 30%. Multiplying the current emissions of N<sub>2</sub>O (3 Tg N yr<sup>-1</sup>) by the increase in export production and converting this into the mass of N<sub>2</sub>O (1.57) gave an increased emission of N<sub>2</sub>O of 1.4 T g yr<sup>-1</sup>. The change in N<sub>2</sub>O emission can be converted to an equivalent amount of CO<sub>2</sub> emission by multiplying by 310 and by the carbon content of CO<sub>2</sub> (12/44) to yield 0.12 Gt C yr<sup>-1</sup>. For the second calculation, the observation that N<sub>2</sub>O is largely produced in low oxygen water is used to assume that the change in the volume of low oxygen water determined the increased production of N<sub>2</sub>O. From the OCM runs, the volume of low oxygen water increased by a maximum of 20% and this equated to an increase in N<sub>2</sub>O emissions of 1 T g yr<sup>-1</sup>, equivalent to 0.08 Gt C yr<sup>-1</sup> of CO<sub>2</sub> emissions. The emissions of N<sub>2</sub>O would offset the increased oceanic CO<sub>2</sub> associated with phosphate fertilization runs by a maximum of 20%. Both the previous calculations of increased N<sub>2</sub>O emissions assumed an instantaneous release of N<sub>2</sub>O back into the atmosphere with no increased storage in the ocean. However, if N<sub>2</sub>O production primarily occurs in low oxygen water a finite time is required to transport this water to the surface before it can be exchanged with the atmosphere. Furthermore, an increase in N<sub>2</sub>O in the atmosphere will cause a repartitioning of N<sub>2</sub>O between the ocean and the atmosphere with corresponding increased N<sub>2</sub>O in the ocean. Presently, the pool of N<sub>2</sub>O in the ocean is comparable to the atmospheric N<sub>2</sub>O pool (1.3 Gt N). This suggests that approximately half of the additional N<sub>2</sub>O produced by macro-nutrient fertilization may reside in the ocean. This would reduce the negative impact of N<sub>2</sub>O production to approximately 10% of the sequestered carbon. Also, increased N<sub>2</sub>O outgassing from the ocean may continue even after fertilization has stopped because elevated export production would persist for several more centuries after the cessation of fertilization (Figure 6).

### 5.2.3 Phosphate and Silicate Limitation

In the OCM, phosphate was the limiting macro-nutrient; biological production was increased by adding phosphate. In reality, nitrate usually limits biological production and biological production would be stimulated by adding nitrate or ammonia to the surface ocean. Throughout the world oceans, the nitrate to phosphate ratio (N:P ratio) in deep water is nearly constant (N:P ratio equals 16:1). This agrees with the ratio of nutrient utilization by phytoplankton in the surface water [*Redfield et al.* 1963]. At present in the surface waters of the oligotrophic gyres, there is a small excess of phosphate available after utilization of all the nitrate. For nitrate limited regions of the 18-50°S Southern Ocean the excess phosphate in the euphotic zone is approximately 65 x 10<sup>10</sup> moles P. For a C:N:P ratio of 106:16:1, the nitrogen required to deplete all the phosphate would be approximately 1040 x 10<sup>10</sup> moles N and this would sequester approximately 0.8 Gt C. To justify fertilization of the ocean with macro-nutrients, one would want to sequester considerably more than 0.8 Gt C. Any re-supply of intermediate water to the upper ocean would contain a N:P ratio that was approximately Redfield hence would not provide excess phosphate. Therefore, any nitrate only fertilization scheme could rapidly deplete all available phosphate.

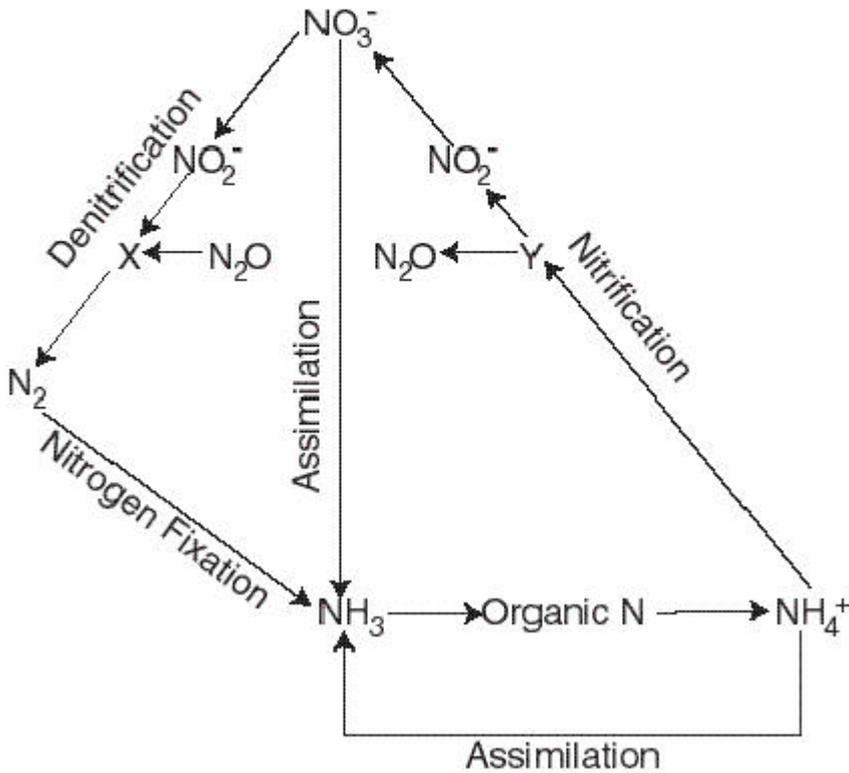


Figure 16. Diagram of the marine nitrogen cycle (adopted from *Codispoti and Christensen* [1985]). X and Y represent intra-cellular intermediates that do not appear to accumulate in sea water. Photochemical processes that occur near the sea surface are not include in this figure.

The response of phytoplankton to phosphate depletion and excess nitrate is unclear. Under laboratory conditions, phytoplankton can reduce their phosphorous requirements relative to nitrogen and carbon by an order of magnitude. If natural populations respond in the same way, nitrate and carbon uptake would still occur at depleted phosphate levels. With such a response, nitrate fertilization might exhaust the available silicate and the phytoplankton may become silicate-limited. If one drove the ecosystem from nitrate-limited to either silicate-limited or phosphate-limited, it would be expected that the species composition of the phytoplankton would change. The addition of both nitrate and phosphate would provide one option to avoid phosphate limitation but the potential for silicate limitation would still exist and needs to be assessed.

#### 5.2.4 Micro-nutrient Limitation

Extensive areas of the surface ocean have high nitrate and phosphate concentrations and these macro-nutrients do not limit biological production. These high-nutrient low-chlorophyll regions appear to be limited by the combination of grazing pressure and iron [Coale *et al.*, 1996]. In the subtropical gyres there is ample evidence to suggest that nitrate limits production but it is not clear if iron concentrations are close to limiting in such regions. The iron concentration in any fertilized region and its control on phytoplankton production would need to be known to ensure that one does not rapidly deplete the iron and switch the system from nitrate-limited to iron-limited.

#### 5.2.5 DMS production

Most species of phytoplankton in the ocean produce dimethylsulphide (DMS) which is the dominant volatile sulphur-containing compound in the ocean and the major natural source of sulphur to the atmosphere [Liss *et al.*, 1997]. Global sulphur emissions to the atmosphere are approximately 12-58 TgS/yr from the oceanic DMS production, 3-9 TgS/yr from volcanoes, 75-100 TgS/yr from anthropogenic sources and 1-11 Tg S from the terrestrial biosphere [Moller, 1995]. DMS outgassed from the ocean into the atmosphere is oxidized to produce aerosol particles. In the Southern ocean, these aerosol particles are the principal (80%) cloud condensation nuclei (CCN) in the marine atmosphere [Charlson *et al.*, 1987]. The reflectance of clouds (albedo) and the scattering of incident solar radiation is influenced by the CCN. Marine DMS production can influence the radiative properties of the atmosphere by altering the albedo of clouds and by scattering incident solar radiation [Liss *et al.*, 1997]. Changes in biological production in the ocean due to macro-nutrient fertilization could alter the DMS production in the ocean. To assess the possible climatic impact of changes in DMS production with macro-nutrient fertilization, one first needs to describe the processes controlling DMS production in the ocean. Then, I will comment on how macro-nutrient fertilization may alter DMS production.

In the marine environment, living phytoplankton cells excrete DMS. The biological function of DMS is unclear but the pre-cursor to DMS, dimethylsulphonium propionate (DMSP) is an important osmoregulator [Vairavamurthy *et al.*, 1985] and cryoprotectant [Karsten *et al.*, 1996] in a number of phytoplankton species. DMSP is also released by phytoplankton when they die or are grazed by zooplankton and its breakdown in the seawater produces additional DMS. Although DMS is excreted by phytoplankton, its concentration in seawater is only weakly correlated with either phytoplankton biomass or productivity [Andreae, 1990]. DMS flux to the atmosphere appears independent of primary productivity for two reasons. First, DMS concentrations in seawater depend on both the rate of production and the rate of removal. The important removal mechanisms for DMS are outgassing to the atmosphere and the photochemical and microbial breakdown in the seawater. In the tropical and temperate Pacific, DMS removal by microbial consumption is more than 10 times faster than atmospheric outgassing [Kiene and Bates, 1990]. Second, different phytoplankton species have over three orders of magnitude variability in their DMS production [Andreae *et al.*, 1983]. Coccolithophorids, which are abundant in the tropical and oligotrophic surface ocean, produce several orders of magnitude more DMS than diatoms. The phytoplankton species composition

and the activity of the microbial foodweb combined with primary productivity controls DMS production and its rate of release to the atmosphere.

The iron fertilization experiments performed in the eastern equatorial Pacific (IronEx I and II) provide insight into how DMS production may change under enhanced biological production. Both these experiments showed that iron addition stimulated DMSP which increased the production of DMS [Turner *et al.*, 1996]. Although IronEx I and II observed similar increases in the DMSP concentrations, only IronEx II showed elevated seawater DMS concentrations. Turner *et al.* [1996] concluded that the response of the microbial community was responsible for the differences between the two experiments. The IronEx experiments demonstrate that changes in the ocean DMS production are linked to how the ecosystem responds to fertilization. Therefore, it is inappropriate to extrapolate changes in phytoplankton production to changes in DMS production. Rather, one must consider how the phytoplankton and bacteria populations will respond and use this to infer changes in DMS production. Our knowledge of the large-scale response of ecosystem to macro-nutrient fertilization is inadequate at present to attempt to quantify changes in DMS production with ocean fertilization.

### 5.2.6 Marine Ecosystem Impacts

Macro-nutrient fertilization driven changes in biogeochemical cycling in the ocean have the potential to alter the composition and behavior of the marine ecosystem. If large-scale macro-nutrient fertilization was undertaken large increases in the plankton biomass could occur. As the phytoplankton bloom decays either through sinking or zooplankton grazing, there would be a high vertical flux of organic matter out of the euphotic zone. Much of this organic material would be remineralized in the upper 500m. If one drove the ecosystem from nitrate-limited to phosphate-limited or silicate-limited, the species composition of the phytoplankton could change. Silicate limitation would favor dinoflagellates and flagellates with potential nuisance or toxic blooms of these organisms becoming more common. If nitrate fertilization led to the eutrophication of shelf water, nuisance or toxic algal blooms could occur (e.g. North Sea has extensive toxic algal blooms in eutrophied shelf waters).

The grazing community would also respond to both the elevated phytoplankton growth rate and potential changes in the phytoplankton composition. The impact on higher trophic levels however is more difficult to predict. Dramatic impacts on the benthic biology community are also possible particularly if the enhanced biological production occurs over the continental shelf or slope.

The addition of macro-nutrients to oligotrophic regions would enhance biological production. Oligotrophic areas are regions of low biological production and high biodiversity. These regions are characterized as high recycling environments where the organic matter is efficiently recycled providing the nutrients to maintain biological production. In contrast, regions with high biological production and low biodiversity characterize eutrophic areas. These regions display less recycling of nutrients and greater export of organic material into the ocean than oligotrophic waters. Macro-nutrient fertilization of oligotrophic regions (these are the regions that are macro-nutrient-limited) would increase biological production and tend to make the

region more eutrophic. The increased production may lead to increased fish catches but possible loss of species diversity. This may also alter the types of fish (i.e. shift from species typically caught in oligotrophic waters to species common in coastal or high nutrient waters).

Observations from the Baltic Sea and Hawaii Ocean Times-Series Sites provide guides to the possible marine ecosystem impacts of macro-nutrient fertilization. The Baltic Sea provides an example where large quantities of anthropogenic nitrate and phosphate have entered the sea. This has increased both primary production and pelagic fish catches. Associated with the increased biological production is the decline in oxygen levels in the deep water and the development of anoxic areas devoid of marine animals. Coastal regions of the Baltic Sea have experienced more frequent harmful blooms of algae (e.g. toxic bloom of *Chrysocromulina* [Nielsen *et al.*, 1990]). The consequences of anthropogenic macro-nutrients in the Baltic Sea are both positive and negative making it difficult to deduce the net benefit of anthropogenic nutrient enrichment.

The Hawaii Ocean Time-Series (HOTS) provides insight into how marine ecosystems could respond to a shift from nitrate limitation to phosphate limitation. At HOTS, the marine ecosystem has undergone a shift from nitrate limitation to phosphate limitation in the last decade [Karl *et al.*, 1997]. This switch is the result of cyanobacteria (*Trichodesmium*) using N<sub>2</sub> fixation to satisfy their nitrate requirements [Karl *et al.*, 1995]. At present, the cyanobacteria supply half of the nitrogen required for new production [Karl *et al.*, 1997]. Cyanobacteria, like *Trichodesmium*, can grow with a reduced cell quota of phosphorous which enables the ecosystem to drift to phosphorous limitation as the supply of new nitrogen switches from upwelling to the inexhaustible pool of N<sub>2</sub> dissolved in the surface ocean. Although *Trichodesmium* never dominate the phytoplankton population, they provide nitrogen essential for the non-nitrogen-fixing phytoplankton to grow more efficiently [Karl *et al.*, 1997]. With the switch from nitrate limitation to phosphate limitation, primary production at HOTS increased by 50% but particulate export production decreased by 30% [Karl *et al.*, 1997]. The switch to phosphate limitation increased the capacity of the ecosystem to recycle nutrients in the euphotic zone, which reduced the export of particulate organic matter and increased the accumulation of dissolved organic matter. For ocean fertilization, this suggests that driving the ecosystem to phosphate limitation may change the behavior of the ecosystem. An increase in dissolved organic matter may partially counter the desired goal of fertilizing, which is to increase the oceanic uptake of CO<sub>2</sub> by increasing export production, by locking up some macro-nutrients in a form of dissolved organic matter that takes centuries to breakdown.

## 6. Summary

The CO<sub>2</sub> sequestration efficiency of macro-nutrient fertilization of the ocean was investigated using a box model and a 3-dimensional OCM. Both models employed phosphate as the only limiting macro-nutrient. The box model demonstrated that the efficiency of phosphate fertilization would approach 89% for an oligotrophic region. In the OCM, the maximum efficiency of phosphate addition at stimulating CO<sub>2</sub> uptake was 62%. The lower efficiency of the OCM reflects that in 31% of the fertilized region, phosphate did not limit biological production. If the results of the OCM are scaled to account for the fertilized area that is not phosphate-limited, the maximum efficiency is increased to 90%. Macro-nutrient fertilization

can efficiently increase the oceanic uptake of CO<sub>2</sub>. Table 3 compares the amount of phosphate added to the OCM to the amount of carbon sequestered. Since the OCM used phosphate as the limiting nutrient, the equivalent amount of nitrate was determined by using the P:N Redfield ratio (1:16). The estimated cost of sequestering carbon by macro-nutrient fertilization may be calculated from these numbers.

**Table 3. For the OCM simulations, the added macro-nutrients are compared to the additional carbon that is sequestered by 2200. The added nitrate was calculated by multiplying the added phosphate by 16.**

Run	Fertilization Period	Added Phosphate (moles P)	Added Nitrate (moles N)	Increased CO <sub>2</sub> Uptake (moles C)
A	2000-2030	$2.8 \times 10^{13}$	$4.5 \times 10^{14}$	$1.6 \times 10^{15}$
B	2000-2050	$4.7 \times 10^{13}$	$7.5 \times 10^{14}$	$2.6 \times 10^{15}$
C	2000-2080	$7.5 \times 10^{13}$	$12.0 \times 10^{14}$	$4.0 \times 10^{15}$
D	2000-2080 <sup>1</sup>	$7.5 \times 10^{13}$	$12.0 \times 10^{14}$	$4.9 \times 10^{15}$

The study presents new results that affect the implementation of large-scale macro-nutrient fertilization in the ocean. The OCM simulations showed that the macro-nutrient fertilization would be site-dependent; adding macro-nutrients to regions where these nutrients do not limit biological production would not stimulate production or increase oceanic CO<sub>2</sub> uptake. The form of the added nutrients could reduce the efficiency of the sequestered carbon. By adding nitrogen in the form of either nitrate or ammonium one would reduce the alkalinity of the surface water and decrease the efficiency of carbon sequestration by 10%. The OCM simulations revealed the potential for calcium carbonate export to alter the carbon sequestration efficiency of macro-nutrient fertilization. When calcium carbonate export was fixed at 8% of organic carbon export, the efficiency of carbon sequestered by macro-nutrient fertilization was reduced by 25% from the case where calcium carbonate production was held constant. The OCM predicted an increase of 17.5% in the volume of anoxic water after 80 years of fertilization. These increases in anoxic water were confined to regions that presently have large areas of anoxic water (e.g. eastern equatorial Pacific and Indian Ocean) which suggests that these changes would not greatly impact the marine ecosystems in these areas. Finally, the OCM simulations under modeled climate change suggest that the dramatic changes in ocean circulation predicted with climate change would not alter the amount of carbon sequestered after 80 years of macro-nutrient fertilization.

The general discussion of the potential impact of macro-nutrient fertilization on biogeochemical cycling in the ocean and marine ecosystem identified a number of issues that need further study.

One key question to address for any macro-nutrient fertilization scheme is whether both phosphate and nitrogen are required to enhance biological production in the ocean. Hypothesized macro-nutrient fertilization of the ocean has focused on adding only nitrogen to the ocean [Jones, 1999]. For regions of the Southern Hemisphere where nitrate limits production, the present available phosphate in the euphotic zone is approximately  $65 \times 10^{10}$  moles. Using the Redfield P:C ratio of 1:106, this suggests that only 0.8 Gt C can be sequestered before phosphate is exhausted. To sequester more than 0.8 Gt C requires the addition of both nitrogen and phosphate or phytoplankton must increase their N:P ratio. The latter response is highly speculative but ongoing work at the HOTS may provide further insight into the response of an oligotrophic ecosystem to the switch from nitrate limitation to phosphate limitation. The potential for the C:N:P requirement of phytoplankton to change greatly reduces our ability to model the ocean carbon cycle. This is a crucial issue to resolve [Wong and Matear, 1999] because it has important consequences on both the future ocean uptake of carbon and ocean fertilization schemes aimed at sequestering atmospheric carbon. Potential changes in the "Redfield ratios" may simply reflect changes in phytoplankton composition in the ocean.

Macro-nutrient fertilization will affect the radiative properties of the atmosphere by sequestering atmospheric CO<sub>2</sub> but there are a number of potential ocean feedbacks. Changes in carbonate production with macro-nutrient fertilization could directly influence the amount of atmospheric carbon that is sequestered. Our simulations demonstrate a large negative (25% reduction in sequestered carbon) influence of increased carbonate production on the amount of atmospheric carbon sequestered. Increased carbonate production may increase DMS production in the ocean, which may offset radiative effects of higher CO<sub>2</sub> in the atmosphere with higher DMS levels. Both these potential feedbacks are uncertain and require further investigation.

An additional change in the radiative properties of the atmosphere could be accomplished by altering the amount of N<sub>2</sub>O transferred from the ocean into the atmosphere. Fuhrman and Capone [1991] hypothesized that increased biological production would increase the sea-air flux of N<sub>2</sub>O. Using the modeled output, it was estimated that increased N<sub>2</sub>O production could reduce the efficiency of macro-nutrient fertilization by a maximum of 20%. This calculation neglects the potential for the ocean to store more N<sub>2</sub>O if the rate of N<sub>2</sub>O production increases. Increased N<sub>2</sub>O storage in the ocean could potentially half this value. These calculations are only approximations and further work is needed to reduce the uncertainties.

Macro-nutrient fertilization has the potential to alter the structure of the phytoplankton community by increasing the biomass of phytoplankton or by shifting ecosystem production from a nitrogen-limited system to a phosphate-limited, a silicate-limited, or an iron-limited system. The impact of these changes on higher trophic levels is uncertain. Ecosystems that are experiencing changes in the supply of macro-nutrients (i.e. HOTS and Baltic Sea) provide

valuable sites to study the impact of macro-nutrient fertilization on marine ecosystems. Time-series data from the Southern Hemisphere site would provide further insights into this impact.

In conclusion, this study suggests a large range in carbon sequestration efficiency of macro-nutrient fertilization of 48% to 90%. Although, extreme values in this range are considered unlikely the large uncertainty demonstrates that better understanding of the response of the marine system is needed to predict the carbon sequestration efficiency. Improved knowledge will enable better assessment of the potential impacts of macro-nutrient fertilization and better models to predict the efficiency of fertilization. Improved understanding of the marine system may also lead to new ways of increasing the carbon sequestration efficiency, such as being able to stimulate biological production without increasing the calcium carbonate production.

**Comment:** Efficiency minimum is .90% \* .75 \* .9 \* .8 = 48%

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