

## **Ocean Fertilisation: a potential means of geo-engineering?**

Lampitt R.S., Achterberg E.P., Anderson T.R., Hughes J.A., Iglesias-Rodriguez M.D., Kelly-Gerreyn B.A., Lucas M\*, Popova E.E., Sanders R., Shepherd J.G., Smythe-Wright D., Yool A.

All authors except \* at:  
National Oceanography Centre,  
European Way  
Southampton SO14 3ZH,  
UK

\* Department of Oceanography,  
University of Cape Town,  
Rondebosch, Cape Town, 7701,  
South Africa

### **Abstract**

The oceans sequester carbon from the atmosphere partly as a result of biological productivity. Over much of the ocean surface this productivity is limited by essential nutrients and we discuss whether it is likely that sequestration can be enhanced by supplying limiting nutrients. Various methods of supply have been suggested and we discuss the efficacy of each and the potential side effects that may develop as a result. Our conclusion is that these methods have the potential to enhance sequestration but that the current level of knowledge from the observations and modelling carried out to date does not provide a sound foundation on which to make clear predictions or recommendations. For ocean fertilisation to become a viable option to sequester CO<sub>2</sub> we need more extensive and targeted field work and better mathematical models of ocean biogeochemical processes. Models are needed both to interpret field observations and to make reliable predictions about the side effects of large scale fertilisation. They would also be an essential tool with which to verify that sequestration has effectively taken place. There is considerable urgency to address climate change mitigation and this demands that new field work plans are developed rapidly. In contrast to previous experiments, these must focus on the specific objective which is to assess the possibilities of CO<sub>2</sub> sequestration through fertilisation.

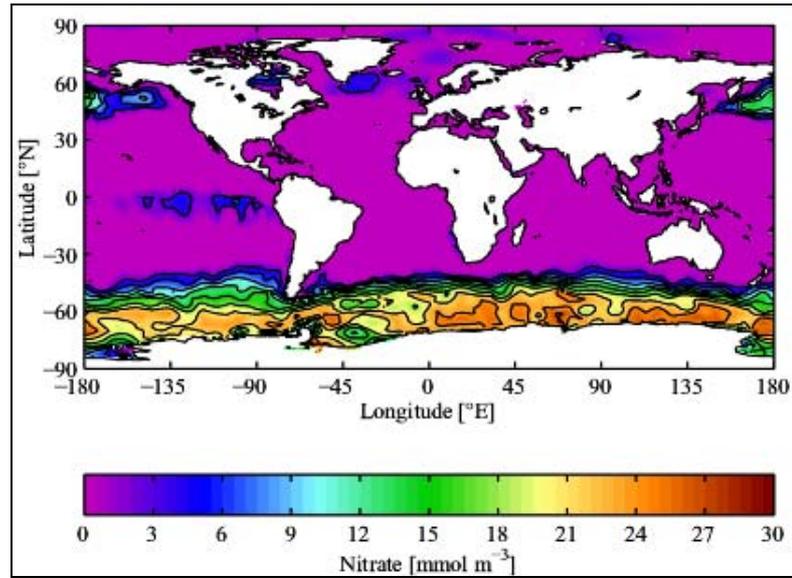
### **Keywords:**

Ocean fertilisation, iron, nutrients, carbon sequestration.

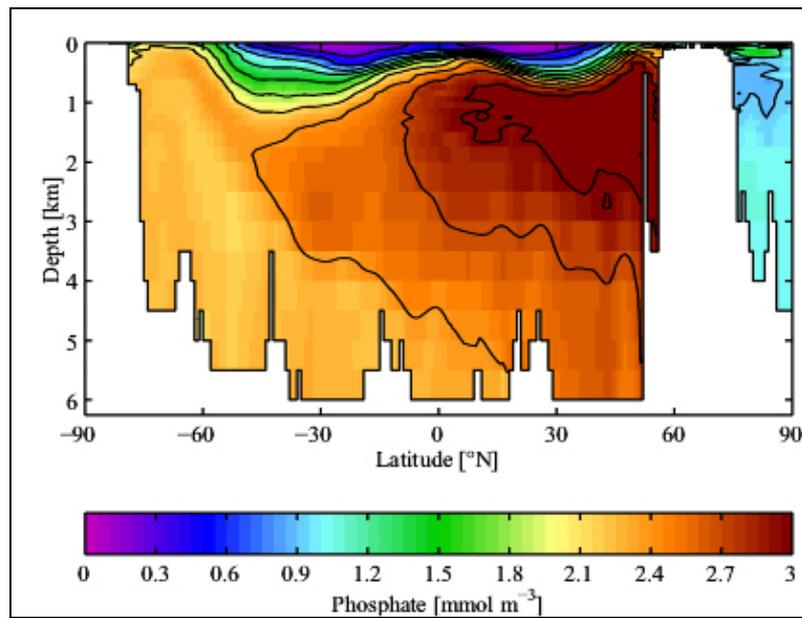
## 1. Background:

It is now generally accepted (IPCC 2007) that emissions of CO<sub>2</sub> to the atmosphere are the dominant cause of global warming, and that cuts in these emissions (currently about 8 GtC/yr and rising) are needed in the next few years. Concurrent with these cuts it may be possible to develop technological strategies to enhance sequestration of carbon dioxide from the atmosphere. Within the ocean, carbon is cycled between the surface and deep waters as part of a natural cycle and this has two major components that are of similar magnitude (Sarmiento et al 1995). One is the “solubility pump” driven by ocean circulation and by the solubility of CO<sub>2</sub> in seawater and the other the “biological pump”. This biological pump is driven by the primary production of plant (phyto-) plankton and subsequent gravitational settling of carbon-rich detrital particles or dispersion of dissolved organic carbon. The solubility pump has increased since pre-industrial times as a result of increasing atmospheric CO<sub>2</sub> concentration and this historically-recent ocean sink for anthropogenic CO<sub>2</sub> is currently estimated to be about 2 GtC/yr (IPCC 2007). Ways in which direct action can be taken to enhance the ocean solubility pump still further have been considered with the final conclusion that they are “highly unlikely to ever be a competitive method of sequestering carbon in the deep ocean.” (Zhou and Flynn 2005) because the CO<sub>2</sub> cost of implementing them will outweigh the benefits.

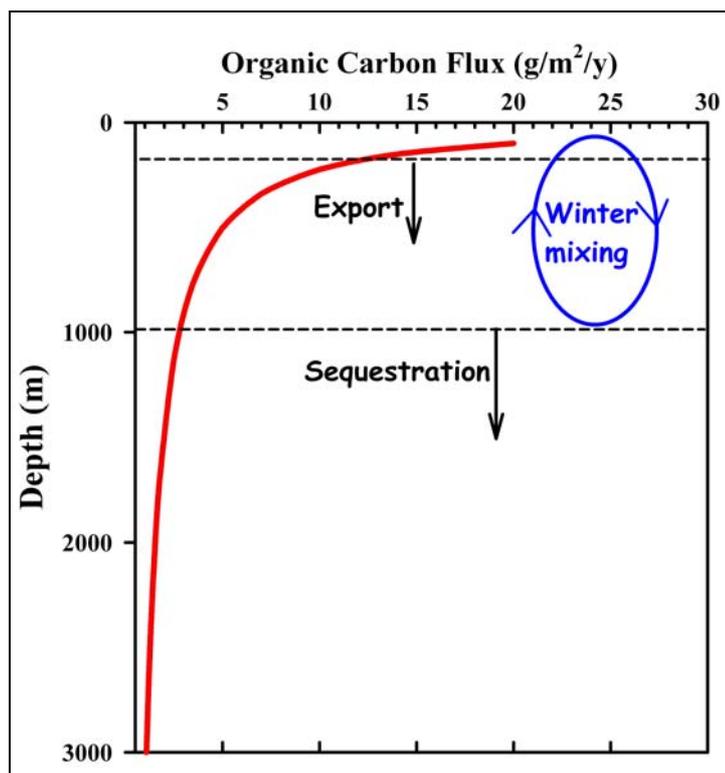
With regard to the biological pump the production of organic matter by phytoplankton absorbs CO<sub>2</sub> from solution, lowering its concentration in the surface zone thus leading to uptake from the atmosphere as a result of an increased concentration gradient. Over almost the entire ocean, primary production of phytoplankton is limited by light and by nutrient supply and in the sunlit surface ocean, (the “euphotic zone” approximately the top 100m) one or other of the essential nutrients is almost always exhausted at some time during the growing cycle (Figure 1). An important point is that the relief of limitation by one nutrient will normally allow production to increase only to the point where it is limited by another. Concentrations deeper in the water column remain high and upward mixing of these nutrients is responsible for much of the productivity (Figure 2). It is this surface feature of nutrient deficiency which underlies the suggestion that ocean fertilisation could be used to enhance the productivity of the euphotic zone, stimulate the biological pump and hence increase the uptake of anthropogenic CO<sub>2</sub>. In this paper the relevant component of productivity is that which is based on a nutrient supply from outside the euphotic zone. This is termed “new production” and is in effect that production available for export. Production which is based on nutrients which are recycled within the euphotic zone such as ammonia are not relevant here but are an important component of the total productivity often referred to simply as “primary production”.



**Figure 1** Global annual minimum distribution of surface concentrations of nitrate, one of the principal macronutrients limiting primary production (Levitus world ocean atlas 1994).



**Figure 2** Distribution of phosphate from south to north in the Pacific along 170 deg West showing the near-surface depletion and increase in concentration with depth.



**Figure 3.** Schematic of the decrease in downward flux of organic carbon as a function of depth in the water column. This is based on Martin et al (1987) depicting the values that may be encountered in the temperate North Atlantic Ocean but the general principle is common to other regions. The two factors that determine the shape of the curve are the sinking rate of the particles and their rate of degradation.

If ocean fertilisation is to be useful as a geo-engineering option, any carbon removed from the atmosphere must remain separated from the sea surface and hence out of contact with the atmosphere for periods in excess of a century (IPCC 2007). This requirement demands that any enhanced production must lead to “sequestration” of the material by settling into the deeper water masses (200-1000m) below the depth of winter mixing. Losses by sinking from the euphotic zone are referred to as the “export flux” as distinct from this “sequestration flux” to deep water (Figure 3).

The process of biological production generates either Particulate Inorganic Carbon (PIC) (calcite) or Particulate Organic Carbon (POC) (or both) and these two pathways are significantly different in terms of the uptake of CO<sub>2</sub>. Production of organic matter removes CO<sub>2</sub> from solution, whilst the process of calcification decreases surface ocean alkalinity, and in addition releases CO<sub>2</sub> to solution thereby partly counteracting the biological pump (Zeebe and Wolf-Gladrow 2001, Iglesias-Rodriguez et al 2002). The potential for carbon sequestration is therefore influenced by the balance between calcifying and non-calcifying organisms. The majority of synthesised POC is remineralised to Dissolved Inorganic Carbon (DIC) in the upper few hundred meters of the ocean

as a result of biological degradation leading inevitably to the decrease in flux with depth (Figure 3). However a small fraction of it escapes into the zone below the depth of winter mixing and it is this component that can be considered as sequestered. This depth exhibits considerable regional variability from about 200 to 1000m.

In this paper we present the background to the suggestion that it may be possible to enhance ocean sequestration of carbon from the atmosphere. We provide a brief account of the role of nutrients in the oceans and their supply routes and the modelling approaches that are required to understand these complex interactions of physical, chemical and biological processes. Such models are central to any discussions about the efficacy of any proposed strategy for ocean fertilisation and the potential side effects. We review in Section 2 the four means that have so far been suggested in order to enhance sequestration and comment on their likelihood of success. In Section 3 we discuss the side effects that may occur and in Section 4 we describe the research that is required to provide a basis for rational decisions about the way forward.

A crucial issue for all of these methods is whether (and to what extent) they can be demonstrated to enhance carbon sequestration to the international scientific community, to policy makers and to the commercial sector. Before carbon credits could be granted or traded, the extent of sequestration must be adequately *verified*. There is no single method that must be adopted for verification but considerable discussion is required in order to agree upon the principles and practices to be adopted. It is likely that verification will involve direct measurement of the downward flux of particulate carbon to deep oceanic layers, the measurement of the concentrations of elements affected by enhanced sequestration flux such as oxygen and nitrogen and good satellite images. Furthermore, and crucially, all this must be supported by a suitable modelling framework within which the observations can be adequately interpreted and the confidence in the level of sequestration expressed in an objective and analytical manner. This difficulty of establishing a means of verification is by no means new and, for instance, the agricultural livestock industry is facing very similar problems (DEFRA report 2006: RCCF 06/09). Nevertheless the principles need to be addressed and agreement reached between the industrial, policy making and scientific communities as to what constitutes appropriate verification.

### **1.1 Macro- and micro-nutrients**

A variety of nutrients are essential for the growth of phytoplankton (Arrigo, 2005). These can be divided into macro-nutrients such as nitrate and phosphate that are required in relatively

high concentrations, and micro-nutrients such as iron and zinc that are required in much smaller quantities. Some elements such as silicon are essential for growth of certain phylogenetic groups (diatoms) but do not necessarily limit overall production. Nutrients are supplied to the euphotic zone by a variety of mechanisms (Table 1) all of which are relevant to this discussion.

Macro-nutrients below the euphotic zone generally occur in a constant “Redfield ratio” of N:P of 16:1 (Redfield et al., 1934) and the elemental ratio of particulate matter in surface waters often does not deviate far from this (e.g. Chen et al., 1996). With regard to carbon, the vast majority is DIC but the particulate matter in the surface and subsurface has a ratio of C:N:P of about 106:16:1 while Dissolved Organic Matter (DOM) has a ratio of 199:20:1 (Hopkinson and Vallino 2005). The implication from this is that **if** nutrients were provided solely from deep water, and **if** the settling biogenic particles (or DOM) had the same composition as the upwelled water, sequestration could not be enhanced in any sustained way. However such simple first order statements are not precisely correct and second order effects allow some scope for sequestration by artificial ocean fertilisation. For example, as seen from Table 1, some nutrients are not associated with carbon such as the nitrogen gas from the atmosphere and furthermore settling particles do not always have a Redfield composition.

The availability of nutrients in the oceans and their means of supply vary considerably from one region to another due largely to differences in physical characteristics. For example about 25% of the ocean surface has consistently high concentrations of macro-nutrients but still the plant biomass (as defined by chlorophyll) is low. Production in these High Nutrient Low Chlorophyll (HNLC) waters are primarily limited by micro-nutrients especially iron. In contrast, Low Nutrient Low Chlorophyll (LNLC) waters can be found in the sub-tropical gyre systems of the oceans. These oligotrophic regions comprise about 40% of the ocean surface and are characterised by wind-driven downwelling and a strong thermocline (both of which impede the nutrient supply from deeper water by vertical mixing) and hence exhibit very low surface water nutrient concentrations. To overcome the deficiency in nitrogen, fixation of nitrogen gas (diazotrophy) by cyanobacteria forms a crucial component of the biogeochemical cycle in many of these waters as it provides a major source of available nitrogen. In effect diazotrophy ultimately prevents the ocean from losing the nitrogen required for photosynthesis (Falkowski, 1997, Tyrrell, 1999). For phosphorus, there is however no alternative supply route and it can therefore be considered as the ultimate limiting macronutrient (Tyrrell 1999). The only sources available to fuel primary production are the stocks in deep water or those supplied from rivers or on airborne dust and unless such sources exist, productivity will cease once local production exhausts the upper ocean pool.

	Upwelling and mixing of deep water	Atmospheric supply as gas	Atmospheric supply as dust	Conc. Limiting productivity	Conc. range in the oceanic euphotic zone
<b><u>Phosphorus</u></b>	◆◆◆◆		◆	<0.01 $\mu\text{M}$	0.005-2.0 $\mu\text{M}$
<b><u>Nitrogen</u></b>	◆◆◆	◆	◆	<0.02 $\mu\text{M}$	0.002-30.0 $\mu\text{M}$
<b><u>Silicon</u></b>	◆◆◆◆		◆	0.2 $\mu\text{M}$	0.05-130 $\mu\text{M}$
<b><u>Iron</u></b>	◆◆◆		◆◆	0.2 nM	0.005-1.0 nM
Zinc	◆◆◆◆◆				0.01-1.0 nM
Carbon (DIC)	◆◆◆◆	◆			2.0 mM

**Table 1 Elements important for oceanic new primary production and their principal supply routes. Elements that generally limit new production in some areas are emphasised. The concentration limiting productivity is not a fixed value as co-limitation is a frequent occurrence during which a low concentration of one nutrient can render the community more sensitive to limitation by another. Silicon does not affect the total annual new production directly but will alter the temporal trend of new production during the growing season (earlier peak in presence of silica). However the presence or absence of Si will affect the community structure which will probably affect the remineralisation length scale of settling particles. This in turn will affect the vertical distribution of nutrients in the mesopelagic which will then change subsequent new production levels. Note that in contrast to terrestrial ecosystems, carbon (as DIC) is not usually a limiting nutrient.**

## 2. Efficacy of ocean fertilisation for carbon sequestration

To date four distinct ways have been proposed to fertilise the oceans in order to enhance carbon sequestration. Two of these involve the supply of large quantities of macro-nutrients (or nutrient cocktails) and two involve micro-nutrient supply designed to facilitate the efficient utilisation of existing macro-nutrients. We now consider the potential efficacy of each of the schemes. Where possible we present costs of implementing these schemes which can then be compared to other geo-engineering proposals and to the current trading value of carbon emissions which at present is of the order \$75/tonne carbon [note that 1t (C) corresponds to 3.67t (CO<sub>2</sub>)]. Clearly it is the net sequestration that must ultimately be calculated after taking into account the energetic costs of the technology concerned. Although such a cost comparison may seem the

correct approach, not all industrial components are involved in carbon trading and the cost is not always the appropriate comparator. Potential side effects are considered in Section 3.

An aspect which is often overlooked is that although fertilisation may be carried out in a particular area leading to sequestration, the efficacy of this action must be considered in a global context and on a timescale of at least 100 years (as defined by IPCC; see above in background section). The rationale behind this statement is that if a water mass is fertilised and leads to local sequestration, this may not be globally significant if that water mass would, over the subsequent weeks and months, have been fertilised naturally. While the process of fertilisation may be local (eg  $10^4$  -  $10^6$  Km<sup>2</sup>) and of limited duration (1-10 years), the assessment of the effects must be global and address the 100-year time period adopted by the IPCC.

This demands that the macro- and micro-nutrient cycles with associated ecosystem interactions are embedded in high resolution 3D global circulation models. When combined with appropriate field observations this will be the only effective way of assessing the long term efficiency and remote consequences of any type of ocean fertilisation.

## **2.1 Nutrient supply from land.**

It has been proposed that fertiliser cocktails of macro- and micro-nutrients should be manufactured on land and transported by submarine pipe to a region significantly beyond the edge of the continental shelf. The nutrient ratios and the temporal supply rates could be controlled so that biological populations develop which optimise sequestration. Such environmental manipulation is today carried out in a sophisticated manner in terrestrial glasshouses where the physical conditions can be controlled but with close monitoring, there is no *a priori* reason why this should not also be possible in an environment such as the open ocean where control of the physical environment is unlikely to be possible.

Empirical support for this approach has been based largely on the observations that the substantial leakage of agricultural fertiliser to coastal seas increases production greatly (with the associated problems of excessive eutrophication- see Section 3.1). In the open oceans, observations have been limited to a purposeful release of phosphate and iron (Rees et al 2006) and to various modelling studies that highlight the intimate and intricate relationships between the various essential elements and the forms in which they are present in the ocean (Dutkiewicz, et al 2005, Parekh et al 2005).

On the face of it, macro-nutrient supply from land has much to recommend it. We believe that if properly implemented it is likely that such a scheme would lead to enhanced oceanic

carbon sequestration. The drawback of the scheme is that the energetic costs of producing the cocktail and piping it from the land to regions of nutrient limitation are likely to be large with a carbon footprint that may be greater than the carbon sequestered. Nevertheless it is worthwhile assessing the approximate costs of this proposal as there is a likelihood of successful sequestration.

As phosphorus is the ultimate limiting nutrient in the oceans, mining of phosphate-bearing rocks would have to be substantially increased. This is a demanding process and some sources currently used for fertiliser have a phosphate content as low as 4% with many sources highly enriched in carbonate (Zapata and Roy 2004). One of the most common water-soluble fertilisers is diammonium phosphate (DAP) [  $(\text{NH}_4)_2\text{HPO}_4$  ] which currently has a market price of about \$420/tonne FOB ([http://www.icispricing.com/il\\_shared/Samples/SubPage181.asp](http://www.icispricing.com/il_shared/Samples/SubPage181.asp)) or \$1700/tonne of phosphorus. Costs of purification and injection to nutrient-poor regions of the ocean are likely to be large but if one excludes these costs and uses the C:P Redfield ratio of 106:1 one obtains a sequestration cost of the order \$45/tonne carbon, a figure that is substantially less than the current trading price for carbon emissions. However, such a simple calculation may not be appropriate as a result of the details of timing. Although new production would increase rapidly in response to this nutrient supply (days),  $\text{CO}_2$  is absorbed by the ocean slowly (months) and depending on the local physics of the water column there is a possibility this mismatch would prevent sequestration of atmospheric  $\text{CO}_2$ .

Extraction of nitrogen gas from the atmosphere and conversion to urea has already been proposed and small scale applications carried out (Ocean Nourishment Corporation <http://www.oceannourishment.com/>). Initial studies of the cost of this process suggested it was a viable proposition (Shojia and Jones 2001) with about 12 tonnes of  $\text{CO}_2$  captured per tonne of ammonia provided and a cost of about \$25/tonne of carbon claimed to be “sequestered”. However, these calculations were based on the assumption that phosphate would always be present in unlimited quantities at the site of injection, an assumption that is incorrect in almost all regions of the oceans. As mentioned above, relief of limitation by one nutrient will normally allow production to increase only to the point where it is limited by another. Thus unless persuasive data are released demonstrating that this is likely to lead to sustained sequestration, we conclude that it will only provide a short term and localised enhancement of the biological pump and possibly no effective sequestration of atmospheric  $\text{CO}_2$ .

The issue of distance from the shelf edge is an important one and obviously affects the economic and engineering viability of this scheme substantially. From the modelling perspective this raises particular problems that will need to be addressed. Shelf zones have rarely been

included in ocean general circulation models and there are some very particular difficulties accurately representing the physics in areas where the shelves meet the open ocean. Until recently, large-scale ocean circulation and shelf sea modelling have progressed in parallel with little interaction between the two. Recent increases in computational resources have however allowed refinement of finite difference grids and application of the finite element approaches which allow increase of the resolution towards the shelf and accurate representation of the shallow topography and the coast line (e.g. Davies and Xing, 2005). Thus although some of the ocean circulation models encompass the shelf edge it will be a major challenge to embed in these models the appropriate ecosystem dynamics and carbon cycle.

## ***2.2 Macro-Nutrient supply from the deep ocean***

An alternative method proposed to supply nutrients to the oceanic euphotic zone is the use of local wave power to pump deep nutrient-rich water from depths of several hundred meters to the surface (<http://www.atmocean.com/sequestration.htm>, Lovelock and Rapley 2007). It is claimed that this would lead to enhanced production and sequestration of organic carbon via a direct stimulation of the biological carbon pump. This claim has been disputed on the grounds that deep waters also contain elevated concentrations of dissolved carbon dioxide which may be released to the atmosphere when these deep waters reach the surface (Shepherd et al 2007).

To first order, assuming Redfield stoichiometry, the net supply of DIC in the upwelled water will be just sufficient to supply the carbon required for the additional photosynthesis generated by the upwelled nutrients, without requiring drawdown of CO<sub>2</sub> from the atmosphere. However, there are second-order effects to be considered, the most significant of which is the way in which the composition of the water pumped from depth (C:N:P) differs from that of the settling particles. It is widely accepted that nitrogen is preferentially remineralised relative to carbon from sinking organic material (e.g. Anderson and Sarmiento 1994, Christian et al., 1997). Consequently upward flux of this relatively nitrate-rich water will allow a sinking flux of carbon larger than that contained in the upwelled water, thus potentially allowing a net air-sea flux of CO<sub>2</sub> to occur. Whether the offset between the ratio of these two elements, C and N, in the upwelled water and in the sinking particles could be sufficiently large for this strategy to become a plausible means to sequester CO<sub>2</sub> from the atmosphere is unclear at present.

As far as we are aware, no comprehensive studies have examined the effects of these pipes at the time and space scales most pertinent to the anticipated effects. Preliminary calculations (Yool et al., submitted) using upper limit assumptions for the effective translocation of nutrients

indicate that the efficiency of sequestration is low. A very large number of pipes (approaching 1000 km<sup>2</sup> in total area) would therefore be needed to achieve sequestration of 1GtC/yr.

An inherent part of this scheme's design is that the pipes will not only supply nutrients but will also supply denser water to the surface. This leads to a statically unstable situation: denser fluid overlying lighter fluid. Depending on the upward flow rate and the rate of lateral surface mixing, this will increase mixing and deepening of the upper mixed layer, with consequences for the light field experienced by phytoplankton. These detailed concerns may best be assessed by high resolution, non-hydrostatic physical models or finite element models with adaptive mesh.

Although early results suggest that the utility of the pipes scheme may be limited by its efficiency, large uncertainties still exist in their precise operation at the local scale, and how this translates to their ability to enhance oceanic uptake of CO<sub>2</sub>. We believe that this scheme cannot be dismissed as a potential solution yet and that further research is warranted.

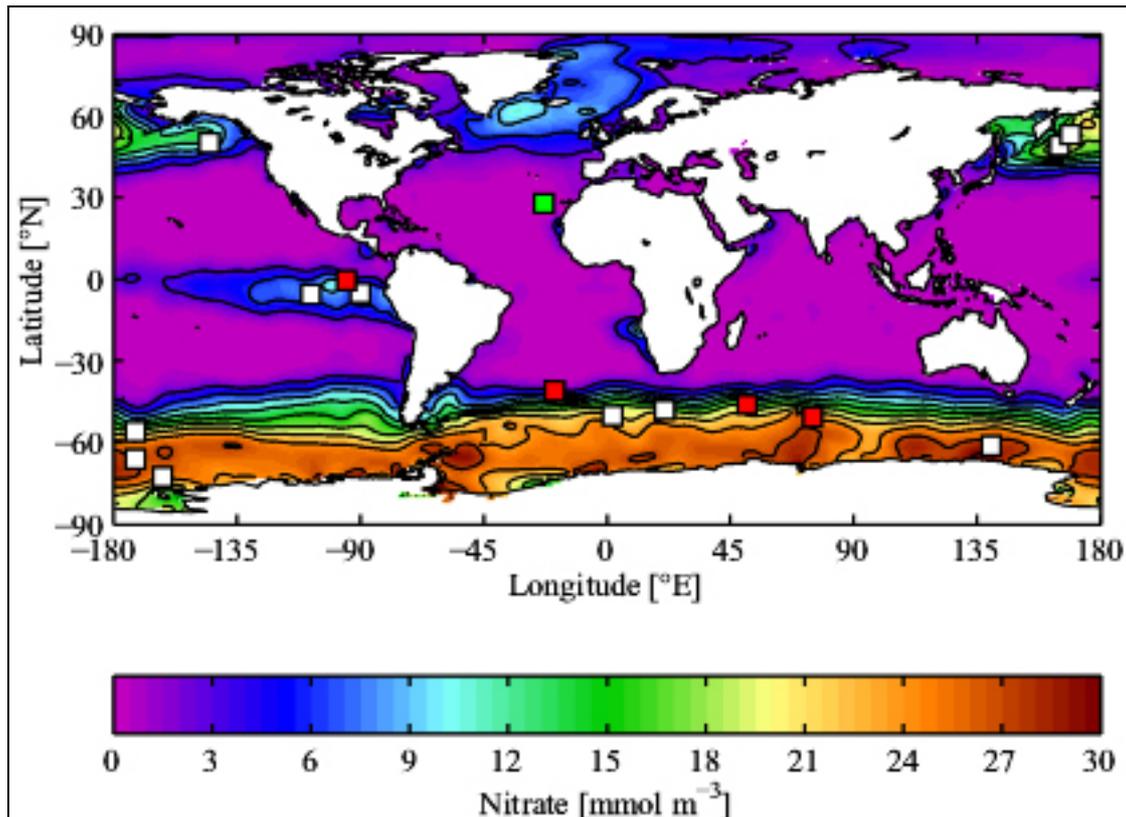
### **2.3 Iron supply to HNLC regions (enhance macro-nutrient uptake).**

Ice core records indicated that during past glacial periods, naturally occurring iron fertilisation had repeatedly drawn massive amounts of carbon from the atmosphere. Several observational programmes have been carried out in present-day HNLC regions where there are regionally restricted natural supplies of iron and it has been suggested that this supply of iron is sufficient to relieve macro-nutrient limitation and hence enhance local productivity (Figure 4: red squares). The two most recent observational programmes, both in the Southern Ocean, examined the region around the Crozet islands, and that associated with a shallow plateau near Kerguelen Island (Pollard *et al.*, 2007, Blain *et al.*, 2007). These studies have shown that not only is there enhanced surface production and nitrate reduction as a result of the local iron supply, but that this enhancement leads to increased fluxes of organic carbon below the euphotic zone, some of which reaches the sediments. The conclusion has been that natural iron fertilisation in such HNLC regions promotes carbon export and sequestration by measurable amounts.

The amount of carbon sequestered per unit addition of iron is of considerable interest and is termed the iron fertilisation efficiency (IFE). Results from the field programs indicate that the value of IFE at Crozet is four times lower than that calculated from Kerguelen although the uncertainties at both locations are large and the difference between them probably not statistically significant. A key goal of future observational programmes must be to refine this value.

Twelve artificial iron fertilisation experiments have been carried out since 1993 to examine the effects of *in situ* addition of this micro-nutrient on upper ocean biogeochemistry (summarised

in De Baar et al 2005, Boyd et al 2007). These experiments have shown that supplementing these areas with iron has a significant effect on biological processes in these regions and on the cycles of the major elements such as carbon, nitrogen, silicon and sulphur. Although all experiments enhanced the growth of phytoplankton, they were not all designed to measure export from the upper ocean and none was designed to measure sequestration. There was nevertheless evidence of enhanced export flux in several of the experiments, and one may expect this led to enhanced sequestration though to an unknown extent.



**Figure 4.** Annual average surface nitrate showing the locations of iron experiments referred to in Boyd et al. (2007) (red = natural Fe studies; white = Fe addition experiments; green = Fe + P addition experiments).

This fertilisation method has been the focus of more publicity than other methods, largely stemming from an informal sound-bite by John Martin in 1988 that an ice age could be initiated with “half a tanker full of iron”. The laboratory experiments that formed the basis for Martin’s comments indicated that every ton of iron added to HNLC regions could sequester 30-100 thousand tonnes of carbon.

Models of progressively increasing resolution and realism have been used during the last twenty years in order to evaluate the potential for iron fertilisation of HNLC regions as a means of consuming nutrients and sequestering carbon. Early simplistic models (e.g. Peng and Broecker 1985) indicated a possible reduction in atmospheric CO<sub>2</sub> of 50-100 ppm, however recent studies with higher resolution 3D models coupled to ecosystem dynamics including iron suggested that

iron addition is much less efficient (order of 10ppm) because the other limiting factors of light and grazing become dominant (e.g. Dutkiewicz et al., 2005; Aumont and Bopp, 2006).

The link between nutrient supply and ecosystem dynamics is complex, especially for micro-nutrients. Formulations suitable for global ecosystem models are only now becoming available with detailed physiological models of iron cycling (e.g. Flynn, 2001) being implemented in ecosystem models (e.g. Fasham et al., 2006). However modellers still face many problems in representing aspects of iron cycling such as the complex speciation of iron in the marine environment, bioavailability (e.g., binding by organic ligands), photochemical processes, and interactions with colloids (Weber et al., 2005).

Global biogeochemical models are not yet capable of accurately predicting both upper ocean production and consequent export of organic matter to deep waters (e.g. Gehlen et al., 2006), let alone the impact of a perturbation due to iron fertilisation on the system. Our understanding of the mechanisms contributing to export remains incomplete, compromising the ability to successfully predict the ecosystem response to perturbations in iron supply. The data from the iron fertilisation experiments are in themselves inconclusive, further contributing to the difficulties in reducing uncertainties in IFE through modelling.

The final conclusion from Aumont and Bopp (2006) was that “the tool used in this study is a..... simplified (and simplistic) representation of reality. Thus large uncertainties remain concerning the efficiency of iron fertilization that should be explored using more observations and/or other models”. We concur entirely with this conclusion and until these other studies are carried out it will be impossible to state with confidence whether iron fertilisation in HNLC regions is likely to be effective in sequestering anthropogenic carbon. Only after these studies are completed will it be possible to determine the net benefit of the activity after taking into account the carbon costs.

## ***2.4 Iron supply to LNLC regions (enhance nitrogen fixation)***

In areas of the ocean where surface waters contain residual phosphate but are deficient in nitrate, nitrogen fixation (which has an especially high dependency on iron) is limited by this micronutrient (eg Falkowski, 1997). Supply of iron could, if supported by sufficient local supplies of phosphorus facilitate nitrogen fixation leading to enhanced productivity and thus possibly also carbon sequestration. As for HNLC areas, an important question regarding the efficacy of iron fertilisation in LNLC regions is the extent to which other limiting factors, notably phosphorus, become limiting. The problem is exacerbated by our relatively poor understanding of the mechanisms of nutrient supply, including P, to the oligotrophic gyres. The addition of more

“plankton functional types” such as N<sub>2</sub>-fixers in marine ecosystem models is fraught with difficulty given our limited understanding of plankton physiology (Anderson, 2005) but this is clearly a crucial task in the context of iron fertilisation of LNLC regions.

The good correlation between the diazotroph *Trichodesmium sp.* abundance and estimated dust deposition (Tyrrell et al, 2003) in the sub-tropical North Atlantic Ocean gives further support to this notion. Similarly the South Atlantic oligotrophic gyre has low nitrate and iron concentrations but with residual phosphate. The effect of this on carbon sequestration has yet to be determined through large scale field experiments although the evidence is strong that iron and phosphorus provide pivotal co-limitation of nitrogen fixation (Mills et al 2004).

## **2.5 Conclusions:**

None of these four methods has yet been fully explored either by adequate field experimentation or by appropriate computational modelling of the system. Both are required to determine the likelihood that sequestration can be enhanced and by how much but there is definite potential that some or all of the proposed methods could enhance sequestration. However no serious and detailed assessments have been published on the full economic and/or energetic costs required in order to implement any of the methods. At present the carbon trading market is developing at great speed (\$10.9 billion in 2005, \$30.2 billion in 2006) but not all industrial sectors are involved. The consequence of this partial involvement of industry is that a direct comparison of costs between the various fertilisation methods is much more difficult and will require detailed and thorough analyses. Nevertheless, it seems likely that iron fertilisation would be the most cost-effective, simply because the quantity and cost of the fertilising material required are both small.

## **3. Side-effects of ocean fertilisation**

Before any commercial application of ocean fertilisation is considered, it is essential that adequate attention be given to potential unintended consequences, some of which may be deleterious to the marine environment or its users (*sensu* London convention and protocol) either in the short term (1-10 years) or in the longer term (centuries). Here we can only provide a brief description of these potential side effects, but subsequently they must be explored in detail so that any benefits of sequestration can be balanced against any potential damage. There will be significant uncertainties in the scientific assessment of several of these side effects. Nevertheless

it will be necessary to estimate probabilities so that a cost-benefit-risk analysis can be carried out in a rational and well-informed manner. We identify and briefly discuss seven areas of potential side effect that will require specific attention in the future although we can not discount the possibility that others will occur.

### **3.1 Eutrophication and anoxia**

Defined as the detrimental response of an ecosystem to excess macronutrients, eutrophication is a coastal phenomenon of worldwide concern (UNEP 2004, Diaz et al. 2004). Key features of eutrophication of relevance here include reductions in oxygen levels, changes in phytoplankton species including development of harmful algal blooms (HABs) and a lowering of biological diversity. It is important to note that the degree to which eutrophication might occur in artificially fertilised areas of the open ocean is debatable on account of differences in circulation patterns, nutrient supply mechanisms and biological communities compared to coastal seas.

Responses of marine organisms to low oxygen are almost entirely negative (Diaz et al. 2001, Levin et al 2001, Cowie 2005, Domenici et al 2007). While physiological adaptation can occur (Diaz and Rosenberg, 1995), extended exposure (> 60 days) to anoxia leads to total mortality (Knoll et al 2007). The likelihood of such prolonged exposure will depend on how well different parts of the deep sea are ventilated. Closer to the continental margins, artificially enhanced POC fluxes may combine with the already higher productive shelf systems to increase the risk of low oxygen conditions in bottom waters. Such changes potentially reduce the capacity of the system to support commercial fisheries. Prolonged (> 1 year) anoxia promotes burial of organic carbon into the long-term geological record (Hedges and Keil, 1995) and may be a means to sequester carbon but the degree of success will again depend on circulation patterns and/or proximity to the higher productive shelf-ocean margin systems. However, the promotion of bottom water anoxia as a sequestration strategy has to be judged against its serious detrimental effects on marine life. Furthermore, purposefully lowering the oxygen content of waters increases the risk of enhanced release of N<sub>2</sub>O - a greenhouse gas more potent than CO<sub>2</sub> - negating any potential benefit from fertilisation (Fuhrman and Capone, 1991; Jin and Gruber 2003). In more extreme situations, “sulphur eruptions” can occur and so called “black tides” of H<sub>2</sub>S-laden water can cause extensive and prolonged mortality for almost all marine organisms (Weeks et al, 2002). Interestingly, susceptibility of organisms to hypoxia is also tied to temperature ranges (i.e. a thermal envelope that varies from species to species) (Pörtner et al, 2005) suggesting the possibility of identifying, by latitude, higher and lower risk regions for fertilisation.

Changes in nutrient input ratios (N:P:Si) can alter phytoplankton community composition (Radach et al 1990). Enrichment of N relative to Si has been accompanied by shifts in species dominance from diatoms to dinoflagellates (see Cloern 2001) whereas changes in N:P ratios (below Redfield) may have promoted “nuisance” phytoplankton species such as *Phaeocystis* sp. (Riegman et al, 1992). Eutrophication also causes HABs (e.g. *Chrysochromulina polylepsis*), which in productive fishery regions has serious economic impacts (Underdal et al, 1989) and can lead to human fatalities through consumption of contaminated shellfish (Hallegraeff, 1993). Hence, tampering with natural oceanic nutrient ratios through fertilisation may promote phytoplankton which are harmful to marine life and human health.

In oligotrophic oceanic regions, artificially enhanced POC fluxes may have a positive effect on the benthic biomass (see Section 3.8). However, closer to the productive continental shelves, increase in productivity due to eutrophication may reduce diversity in the benthos. Consequently, ocean fertilisation strategies need to consider ecosystem characteristics (e.g. Biological community structure) and both proximity to shallower shelf environments and circulation patterns which can transport organic matter horizontally over large (>100km) distances.

### **3.2 Modification of ocean pH**

Ocean pH has fluctuated between 8.0 and 8.3 for the last 25 million years and since industrialisation, the rate of increase in atmospheric CO<sub>2</sub> has caused unprecedented changes in seawater pH and carbonate chemistry (Caldeira and Wickett 2003, Bellerby et al., 2005; Orr et al., 2005). These changes are predicted to impact on biological functions, including calcification, reproduction and physiology (Raven et al, 2005). The effects of fertilisation are likely to be to reduce the current trend of decreasing pH in the euphotic zone although in deeper water the increased POC supply would tend to lower pH although to only a small degree.

Understanding the effect of increasing anthropogenic  $p\text{CO}_2$  on marine biota is both ecologically relevant and of major significance for managing the global carbon cycle on human time scales. Ocean acidification may shift the phytoplankton community and this has important implications for sinking particulate organic matter as this may be partly controlled by ballast materials such as dust, silica, and calcium carbonate (Klaas and Archer, 2002). The available evidence suggests that the increase in atmospheric CO<sub>2</sub> absorbed by the oceans will increase photosynthesis by coccolithophores (Riebesell et al., 2000, Leonardos and Geider, 2005) but is generally assumed to be detrimental for calcification although there are substantial discrepancies among laboratory results. Additionally, evidence from the geological record suggests that past

periods of ocean acidification such as the Paleocene-Eocene Thermal Maximum did not result in a productivity crisis (Stoll et al., 2007) and calcification appeared insensitive to changes in pH (Gibbs et al., 2006). Controls on calcification under high CO<sub>2</sub> are extremely complex (eg Riebesell et al., 2007) and probably influenced by other environmental parameters that naturally co-vary with pCO<sub>2</sub>.

### **3.3 Modification of global macro-nutrient balance**

Any attempt to fertilise the ocean with nutrients to stimulate production and hence carbon sequestration will inevitably result in a redistribution of nutrients on a global scale. The significance of this statement is that some areas may subsequently experience a decrease in nutrient supply leading to a reduction of biological productivity and possibly a reduction in economic activities such as fisheries. It is therefore important in any discussion of the side effects of purposeful fertilisation that the down-stream effects of nutrient redistribution are adequately considered.

Once again the crucial requirement is the development of global models with sufficient resolution and appropriate parameterisation to examine each potential method of fertilisation. Results to date (Sarmiento and Gruber 2002) indicate that, for example, a side effect of HNLC iron fertilisation around Antarctica will be to reduce macronutrient concentrations in the equatorial and coastal upwelling regions some decades to centuries later. This may cause a reduction in productivity leading to reduction in fishery yield. It is essential that such “costs” are considered in the cost-benefit-risk analyses which will be carried out when appropriate data are available.

### **3.4 Modification of global Iron balance**

It has been suggested that we should not alter the global balance of this essential trace element as it will become scarce elsewhere. The alternative view has been expressed that addition of iron to specific regions should be considered as pollution. We demonstrate below that neither of these concerns is justified.

Iron is supplied to the surface ocean via the atmospheric transport of dust and its deposition, as well as by the upwelling, entrainment, or mixing of deeper waters that are relatively rich in iron and other nutrients (Watson, 1997). These sources supply new iron to the euphotic zone (ie not acquired via recycling). Rivers and continental margin sediments are also a significant source of iron to coastal waters (Tappin, 2002; Laës et al., 2003). However, uptake by coastal phytoplankton

and sedimentation of the fluvial inputs are likely to render this iron supply inaccessible to oceanic phytoplankton. In the oceanic euphotic zone, iron is also recycled from living matter to sustain regenerated biological production. The currently projected iron additions by the OIF industries are estimated as 10,000 tonnes per year, which is less than 0.1% of the amount delivered to the ocean by dust ( $15.5 \times 10^6$  tonnes per year) or rivers ( $650 \times 10^6$  tonnes per year). Consequently, the projected OIF activities will not significantly upset the global oceanic balance of iron.

Iron is a highly reactive element, and is subject to very rapid removal through inorganic precipitation and scavenging processes, in addition to biological uptake. Iron added to the ocean by natural or anthropogenic processes will consequently be rapidly removed from the ocean surface waters. A consequence of this strong removal mechanism is that oceanic surface waters are depleted of iron, with increasing concentrations with depth (Measures and Landing, 2008). Iron added through OIF will hence be rapidly removed from the surface waters (Sarhou et al. 2003) (1 - 5 months), and continual additions would be required to replenish iron concentrations.

### **3.5 Generation of other climate-relevant gases** (greenhouse/cloud forming)

It is important to consider ocean fertilisation in the context of radiative forcing and not simply in terms of the carbon cycle. CO<sub>2</sub> is only partially responsible for greenhouse warming and although this gas is intimately linked to the biological production of the oceans, others are also controlled to a large extent by the biological and chemical processes taking place in the oceans. Some of these processes increase radiative forcing while others cause a reduction and in Table 2 we provide an overview of the processes involved in the budgets of these various gases and the factors that are likely to be affected by ocean fertilisation.

Gas	Radiative forcing (W/m <sup>2</sup> )	Ocean to atmosphere supply rate (mol/y)	Factors causing increase or decrease.	References
CO <sub>2</sub>	1.6	-1.4 x 10 <sup>14</sup>	Increased sequestration and carbon export will reduce forcing but not well constrained.	IPCC Climate Change 2001. The Scientific Basis
Methane	0.5	8.0 x 10 <sup>12</sup>	Anoxia increases production	Houweling et al., 2000
Halocarbons	0.3	>1x10 <sup>11</sup>  (summation of various compounds)	Enhanced production due to phytoplankton metabolic processes. Bromo and Chloro compounds increase forcing. Iodine compounds may lead to increases in aerosols and albedo enhancing cooling (cf DMS).	Quack and Wallace, 2003; Harper, 2000; Smythe-Wright et al., 2006
Ozone	0.3		Reduction in stratospheric ozone due to increased halocarbons will reduce its negative effect on global warming. Conversely depletion of tropospheric ozone will reduce its radiative forcing.	Solomon et al., 1994; Dvortsov et al., 1999; Vogt et al., 1999;
Nitrous oxide	0.1	1.2x10 <sup>11</sup>	Increase forcing due to biological production by phytoplankton	Jin and Gruber, 2003
Aerosols (direct)	-0.5	3.3x10 <sup>15</sup> (g/yr)	Any increase in sea salt input will increase aerosol production	IPCC Climate Change 2001.
DMS (Albedo)	-0.7	6.9x10 <sup>11</sup>		

**Table 2 Gases and aerosols affecting the radiative balance of the earth, their current effects, the fluxes to and from the ocean and the ways in which ocean fertilisation are likely to alter their influence.**

Fluxes are potentially large particularly if the anticipated decrease in oxygen concentration are sufficient to generate larger quantities of methane and nitrous oxide. The interactions are complex and not well constrained with potentially a number of both positive and negative feedbacks. The critical research now needed is to determine and model the production rates of

these gasses in response to fertilisation and hence to determine the influence on greenhouse forcing

### **3.6 Change to pelagic ecosystem structure.**

While the purpose of ocean fertilisation is to enhance carbon sequestration, one likely consequence is a change to the structure and function of the biological communities especially in the euphotic zone. These changes may affect fisheries directly or indirectly or they may alter the details of the export process such as by modifying the characteristics of the settling particles produced by the euphotic zone communities (chemical composition, sinking rates, palatability for sub-euphotic zone communities etc).

About 1.3 billion people depend on fisheries for a major part of their sustenance and economic welfare (FAO 2004: 169-174) so it is appropriate we should consider ecosystem changes that might be a consequence of ocean fertilisation and which might affect such human communities either negatively or positively. Although most fisheries are on the continental shelves and the OF schemes we discuss are in oceanic areas, it has been claimed by enthusiasts of OF that such schemes will inevitably enhance both carbon sequestration and fisheries yield. Computational models have to date been extremely poor at predicting community structure and in spite of the massive efforts over the past century at providing accurate predictions of fish yield, the uncertainties are usually very large even in relatively well constrained coastal environments. This hope of double benefit seems optimistic.

There are various examples where environmental change appears to have caused alterations in community structure. For example it has been suggested that jellyfish replace bony fish in some ecosystems in response to climate change (Mills 2001, Purcell et al., 2007). Elsewhere for example, the Salp, *Salpa thompsonii* appears to be replacing Antarctic Krill in the Southern Ocean (Atkinson, 2004). Similarly the decline in the cod population of the North Sea is thought to be due largely to subtle changes in the timing of the zooplankton communities that are the staple diet of juvenile cod (Beaugrand et al 2003). This latter case is a classic example of the match-mismatch hypothesis whereby the food for larval growth and hence adult recruitment is required at precisely the correct time (Cushing 1975). Similarly, changes in global environmental indicators such as the North Atlantic Oscillation (NAO) or the El Nino Southern Oscillation (ENSO) have been shown to elicit ecosystem changes albeit ones that are hard to predict (Stenseth et al. 2002).

In addition to the direct effects on fisheries, indirect impacts such as by the promotion of harmful algal blooms (HABs) should not be ignored. As described above, HABs sometimes occur in response to coastal eutrophication and although unlikely to become a feature of fertilisation of the open ocean they provide examples of major community changes that are demonstrably difficult to predict with confidence (Cloern 2001). The possibility that ocean fertilisation will elicit comparable effects cannot be ruled out although we think it unlikely.

As mentioned above, ecosystem changes in response to ocean fertilisation may also affect the nature of the export process. The biological pump is mediated by the members of the euphotic zone community and changes to that community will necessarily change the nature of the settling particles in terms of their morphology (eg marine snow aggregates vs faecal pellets as the principal vehicles for flux) or the chemical composition of the particles affecting for instance the Redfield ratio of these particles and the balance between the production of POC and PIC.

It is widely accepted that changes in nutrient input ratios (N:P:Si) affect phytoplankton community composition (Arrigo, 2005). For example, long-term regime shifts in species dominance from diatoms to dinoflagellates in the North Sea are thought to be a reflection of nitrogen enrichment relative to silicon (see Cloern 2001) whereas changes in N:P ratios (below Redfield) may have promoted undesirable phytoplankton species such as *Phaeocystis* sp. in north-west European coastal waters (Riegman et al, 1992).

Similarly during the natural fertilisation CROZEX project, iron fertilisation had the somewhat unexpected result of increasing the abundance, diameter and biomass of the colonial forms of *Phaeocystis antarctica* which proved both unpalatable to mesozooplankton and were inefficiently exported (Lucas et al., 2007).

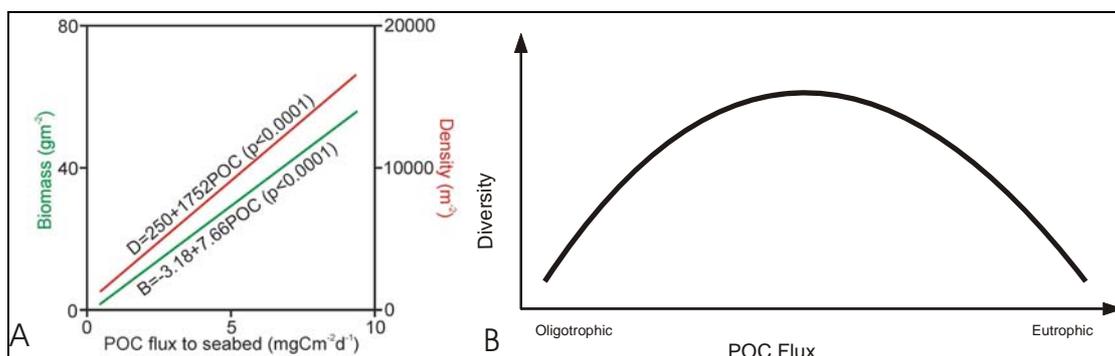
Our conclusion is that ocean fertilisation is likely to change pelagic ecosystem structure and function. This may have a direct effect on fisheries and will certainly modify the details of the biological pump. The types of change will depend heavily on the proposed method of fertilisation but a clear conclusion about either of these is not possible until the large scale field work and associated modelling has been completed.

### **3.7 Change to benthic ecosystem structure**

Approximately 0.4Gt of carbon is deposited on the abyssal seafloor each year, the end member of the biological pump (Jahnke 1996). Of this, about 96% dissolves or is remineralised each year to DIC and hence influences air-sea CO<sub>2</sub> exchange on a time scale of a few centuries (Tyson 1995). The remaining 4% is buried and incorporated into the geological sediment and

hence removed from atmospheric interaction for many millions of years. The processes that determine the proportion of the sedimented material that is buried are largely driven by the benthic biota and it is therefore of importance to determine potential effects on this community. With this in mind, it will be possible to estimate the effects of ocean fertilisation on sequestration on the centennial time-scale agreed upon by the IPCC and on the much longer timescales of geological significance. From the strict perspective of the 100-year time scale we are considering here the effects of changes to the benthic communities can probably be ignored.

The abundance, biomass and diversity of the deep-sea benthos are intimately linked to inputs of organic matter from the euphotic zone (Gage & Tyler 1991). In general, there is a decrease in benthic biomass and abundance with decreasing organic carbon flux (Figure 5A; Rowe 1983; Rex *et al.* 2006). Diversity generally increases from regions of low to moderate productivity, and then declines towards regions of higher productivity (Figure 5B). The response of the benthos to increases in organic carbon inputs will therefore depend on where it sits on this continuum. In the characteristically low productivity oligotrophic gyres where ocean fertilisation has been suggested, it is likely that enhanced POC fluxes to the seafloor would result in increased biomass and abundance (Glover *et al.* 2002) and enhanced diversity (Levin *et al.* 2001). This change in the assemblages may influence ecosystem functioning (Sokolova, 2000; Danovaro *et al.* 2008). However, the relationship between POC fluxes and benthic response is not simple; for example, recent changes in megafaunal species dominance in the abyssal North Atlantic (Billett *et al.* 2001) appear to be related to changes in the composition of the organic matter (Wigham *et al.* 2003), and not simply to changes in total export flux (Lampitt *et al.* 2001).



**Figure 5 A.** The relationship between estimated POC flux and wet weight biomass and abundance of the deep-sea macrobenthos in the western North Atlantic (Adapted from Johnson *et al.* 2007). **B.** Schematic diagram showing the pattern of diversity change with POC flux (Adapted from Levin *et al.* 2001).

Benthic ecosystems are in a complex state of dynamic equilibrium. While this equilibrium may be altered by enhanced fluxes (e.g. seasonal phytodetritus, Beaulieu 2002), after the period of fertilisation has ceased, the system may revert back to the earlier equilibrium. It is not clear what will happen to the carbon that was contained in the increased biomass; Some of this may be incorporated into the geological record although the majority will be released into the water column by remineralisation.

## **4. Research and developments required to reduce uncertainties**

As is apparent above, the commercial and engineering sectors urgently need to carry out a substantive assessment of the financial and energetic costs of each method but necessarily in parallel with further scientific research. Although not the principal focus of this paper we can identify here the scientific approaches that are required in order to assess the efficacy of the various proposed methods and the likelihood of unacceptable side effects. We divide these into experiments carried out in the laboratory, in mesocosms, in the field, and with computational models. Each approach has advantages and disadvantages and provides complementary insights into the complex biogeochemical interactions implicated in any ocean fertilisation proposal.

### **4.1 Laboratory experiments**

Experiments in the laboratory cannot simulate many aspects of the natural world such as diurnal changes in mixing but they have the great advantage of providing environments that can be controlled and manipulated to simulate a wide variety of conditions. Changes in climate-driven biogeochemical processes such as photosynthesis, calcification, nitrogen fixation, silicification have been investigated in the laboratory (on land and at sea) by manipulating environmental variables including macro- (Krauk et al., 2006) and micro-nutrients (Hudson and Morel, 1989, Timmermans et al., 1994, Yoshida et al., 2002), and carbonate chemistry (Zondervan et al., 2001). However, we face two main problems in interpreting the laboratory data. The first is the different experimental approaches used, for example, continuous *versus* batch-mode cultures, different media compositions and nutrient concentrations. Secondly, the available measurements are mostly limited to biogeochemical rates or the ecological/biogeochemical function at the cellular level, frequently for single species although some contain detailed and comprehensive information at several levels of biological organization. The use of relevant organisms and (if possible) communities will be required for laboratory experiments (Brewer et al., 2000).

Understanding long-term (chronic) effects of eutrophication and increased concentrations of carbon dioxide on organisms are a prerequisite in addition to *in situ* field observations and manipulations. For example, these could include, amongst others, long-term (chronic) effects of Fe-fertilisation, vertical macro-nutrient flux, eutrophication, anoxia, changing pH, a changing light environment, changing temperature and increased concentrations of carbon dioxide on organisms including appropriate combinations of the above.

Laboratory and field experiments are required to assess the effect of nutrients, CO<sub>2</sub>, iron availability on the community structure of phytoplankton taxa, and how these changes may alter biogeochemical fluxes. Particularly, observations should be made where time series are available in regions that have undergone changes in pCO<sub>2</sub> or in nutrient dynamics, and tests should be conducted to assess to what extent these processes have played a role in determining trophic interactions and carbon fluxes.

## **4.2 Mesocosm experiments**

Mesocosms are containers currently with volumes 1- 400m<sup>3</sup> which may (or may not) contain a benthic sediment environment (Harada et al 1996). They represent an approximation of a natural environment that can be controlled by the addition of nutrients, pollutants, predators or CO<sub>2</sub> and hence are intermediate between laboratory and field experiments. They have proven useful in providing information about trophic interactions and biogeochemical functions (Howarth, 1988, Dam and Drapeau, 1995, Riemann et al., 2000, Delille et al., 2005). They enable scaling from the individual organism up to the community level and interdisciplinary programs which involve manipulative experiments using benthic and pelagic mesocosms can begin to address the complexity of the responses of the biota. Problems associated with mesocosm experiments include their predominantly coastal location and inevitable uncertainty as to whether the response of the community is really representative of open ocean environments. Furthermore they do not reflect some key processes such as variations in physical mixing. To overcome the first of these problems, off-shore pelagic mesocosms experiments can be used to quantify the effects of manipulations on species composition and succession, photosynthesis, macro- and micro-nutrient, and carbon removal, nitrogen fixation, organic matter production, and gas exchange in natural open sea plankton communities. Some technical problems remain to be solved but this approach offers significant opportunities for simulated open ocean fertilisation experiments. As discussed above, sequestration is defined as the removal of carbon from the

system for over a century and this demands flux to depths of 200-1000m, which are probably impossible to replicate in any future design of mesocosm.

### **4.3 Field experiments**

Of the four potential means of ocean fertilisation identified above, significant field experiments have only been carried out to address the effects of iron fertilisation and almost all have been in HNLC regions. As described above, these studies were not designed to address the issue of sequestration and if the feasibility of all four potential strategies is to be evaluated, further relevant experiments in the field will need to be undertaken. In order to address issues of natural spatial and temporal variability, these would need to be of sufficient duration (> 10 weeks) and scale (in excess of 100 x 100km). Because such experiments potentially have considerable social and economic importance, they need be carried out by well-qualified and experienced teams of independent oceanographers skilled in the state-of-the-art observations that will be necessary to verify that sequestration has been globally enhanced as a result of the localised fertilisation. This will involve oceanographers from the disciplines of physics, biology, biogeochemistry and chemistry and the observations will need to be interpreted rigorously by assimilation into an appropriate modelling framework (see below). The cost of such experiments will be large (millions of pounds), including ship-time on suitably equipped research vessels.

The scientific and commercial communities are now ready to collaborate in the pursuit of appropriate field experiments. Given the appropriate financial and legal support we are optimistic that major advances can and should be made using large scale field experiments which will address explicitly the effects of various types of ocean fertilisation on carbon sequestration.

### **4.4 Modelling**

Modelling studies addressing the issue of artificial ocean fertilisation broadly fall into two categories: regional modelling of localised field experiments and global modelling to assess the long term and remote consequences of proposed fertilisation schemes. A new generation of ecosystem models is being developed that includes the cycling of iron and other elements, providing the link to carbon export. It is important that the models in question are sufficiently complex to reproduce the essential features of the experiments, yet without including complexity beyond that which can be verified by observation. Effective model verification is then possible, the aim being to provide accurate simulations of the ecosystem dynamics as observed in the field. By successfully modelling fertilisation experiments, the models provide a formal assessment of

our understanding of marine ecosystems and their potential response to nutrient enrichment. Important processes and nutrient budgets are constrained in a way that could not be done solely on the basis of measurements. The results of these models, focusing on particular field experiments, then provide the basis for the GCMs addressing impacts at the global scale.

Modelling the long term and large-scale (remote) effects of iron fertilisation requires high resolution global GCMs coupled with suitable ecosystem models. A necessary prerequisite is good physics, biogeochemical models only being “as good as the physical circulation framework in which they are set” (Doney, 1999). Further, a full description of the ocean carbon system and carbon exchange with the atmosphere, spun up to the equilibrium (involving model runs of thousands of years), is required. One such model for this purpose, at the forefront of the field, is that of Aumont and Bopp (2006), which has been used to study the global effects of iron enrichment experiments. With a resolution of  $2 \times 2^\circ$ , the model suffers deficiencies in reproducing biophysical interactions, particularly in the oligotrophic gyres where mesoscale effects play an important role in nutrient budgets. The resolution required for a good representation of nutrients and carbon in the ocean (e.g. a few kilometres) is currently unachievable. Improvements may however be made through alternative approaches, notably developments in numerical methods of accelerations of global models (e.g. Li and Primeau, 2008) and finite element modelling on adaptive meshes (e.g. Piggott et al., 2008). The latter is a promising new method that allows increased resolution where and when it is required as simulations are run.

Finally, the need for experimental and observational data to underpin modelling studies cannot be overemphasised. In order to be effective as management tools, models need to undergo rigorous validation to ensure that the assumptions employed are realistic and lead to reliable predictions.

## 5. Conclusion

The proposition that the biological pump could be stimulated by the purposeful supply of essential nutrients is sound in principle. There are several methods which have been proposed in order to achieve this and it is very likely that some or all of these could lead to enhanced flux of carbon into the deeper layers of the ocean in a localised area. We have considered the two main issues surrounding these proposals, the first being “will they work?” By this we question whether a particular scheme will sequester more carbon than the scheme consumes when the timescale of consideration is 100 years and the spatial scale is global. Local or short term sequestration is irrelevant if counteracted by carbon release when the scale of time or space is enlarged.

The second consideration is whether there are likely to be unacceptable side-effects of the proposed scheme. All methods of ocean fertilisation must, by design, substantially modify the natural biological processes of the marine ecosystem. Without doubt the effects of fertilisation will extend far beyond any sequestration of carbon from the atmosphere. It is possible that some of these effects will be significant and may be considered as an unacceptable cost for the calculated benefits in terms of carbon sequestration.

There is at present a clear and urgent need for tightly focussed research into the effects of ocean fertilisation. The critical areas of research will involve large scale field experiments (100 x 100Km) tightly coupled to high resolution 3D computational models with embedded biogeochemistry. This is required for each of the four classes of fertilisation scheme that have been proposed. Until completed satisfactorily it is impossible to provide a rational judgement about whether the schemes proposed are (a) likely to be effective and (b) likely to cause unacceptable side effects. Once this research has been carried out, it will be the responsibility of the science community to perform appropriate cost-benefit-risk analyses in order to inform policy. At the same time discussions between the commercial, regulatory and scientific communities must take place so that the principles and practices of verification can be established.

## 6. References

- Anderson, L. A., and Sarmiento, J. L. 1994. Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochemical Cycles*, **8**, p 65-80.
- Anderson, T.R. 2005. Plankton functional type modelling: running before we can walk? *J. Plankton Res.* **27**, 1073-1081.
- Arrigo, K.R., 2005. Marine micro-organisms and global nutrient cycles. *Nature* **437**: 349-355.
- Atkinson, A., Siegel, V., Pakhomov, E. and Rothery, P. 2004. Long-term decline in krill stocks and increase in Salps within the Southern Ocean. *Nature* **432**, 100-103.
- Aumont O. and L. Bopp, 2006. Globalizing results from ocean in situ iron fertilization, *Global Biogeochemical Cycles*, 20 2. GB2017: 1-15.
- Beaugrand G, Brander KM, Lindley JA, Souissi S, Reid PC. 2003. Plankton effect on cod recruitment in the North Sea. *Nature* : **426** : 6967: 661-664
- Beaulieu, S.R. 2002. Accumulation and fate of phytodetritus on the sea floor. *Oceanography and Marine Biology Annual Review* **40**, 171-232.
- Bellerby, R. G. J., Olsen, A., Furevik, T., and Anderson, L. A., 2005. Response of the surface ocean CO<sub>2</sub> system in the Nordic Seas and North Atlantic to climate change, in: Climate Variability in the Nordic Seas, edited by: Drange, H., Dokken, T. M., Furevik, T., Gerdes, R., and Berger, 20 W., *Geophysical Monograph Series, AGU*, 189–198.
- Billett, D.S.M., Bett, B.J., Rice, A.L., Thurston, M.H., Galéron, J., Sibuet, M. & Wolff, G.A. 2001. Long-term change in the megabenthos of the Porcupine Abyssal Plain NE Atlantic. *Progress in Oceanography* **50**, 325-348.
- Blain S et al 2007. Effect of natural iron fertilization on carbon sequestration in the Southern Ocean. *Nature* **446** : 1070-U1

- Boyd PW et al 2007. Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions. *Science* **315**: -617
- Brewer, P.G., Peltzer, E.T., Friederich, G., Aya, I. and Yamane, K., 2000. Experiments on the ocean sequestration of fossil fuel CO<sub>2</sub>: pH measurements and hydrate formation, *Marine Chemistry* **72**: 83-93.
- Caldeira, K. and Wickett, M. E.: 2003. Anthropogenic carbon and ocean pH, *Nature* **425**: 365–365.
- Chai, F., Jiang, M.-S., Chao, Y., Dugdale, R.C., Chavez, F., Barber, R.T. 2007. Modeling responses of diatom productivity and biogenic silica export to iron enrichment in the equatorial Pacific Ocean. *Global Biogeochemical Cycles* **21**, GB3S90.
- Chen, C.-T.A., Lim, C.-M., Huang, B.-T., Chang, L.-F. 1996. Stoichiometry of carbon, hydrogen, nitrogen, sulfur and oxygen in the particulate matter of the western North Pacific marginal seas. *Marine Chemistry* **54**, 179-190.
- Christian JR, Lewis MR, Karl DM 1997. Vertical fluxes of carbon, nitrogen, and phosphorus in the North Pacific Subtropical Gyre near Hawaii *Journal of Geophysical Research-Oceans* **102** Issue: C7 : 15667-15677
- Cloern JE 2001. Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology-Progress Series* **210**:223-253
- Coles, V.J., Hood, R.R. 2007. Modeling the impact of iron and phosphorus limitations on nitrogen fixation in the Atlantic Ocean. *Biogeosciences* **4**, 455-479.
- Cowie G 2005. The biogeochemistry of Arabian Sea surficial sediments: A review of recent studies. *Progress in Oceanography* **65**:260-289
- Cushing DH 1975. Natural mortality of plaice. *Journal Du Conseil* **36** : 150-157
- Dam, H.G. and Drapeau, D.T., 1995. Coagulation efficiency, organic-matter glues and the dynamics of particles during a phytoplankton bloom in a mesocosm study, *Deep Sea Research Part II* **42**: 111-123.
- Danovaro, R., Gambi, C., Dell'Anno, A., Corinaldesi, C., Fraschetti, S., Vanreusel, A., Vincx, M. & Gooday, A.J. 2008. Exponential Decline of Deep-Sea Ecosystem Functioning Linked to Benthic Biodiversity Loss. *Current Biology* **18**, 1-8.
- Davies A.M. and J. Xing, 2005. Modelling process influencing shelf edge exchange of water and suspended sediment, *Continental Shelf Research* **25**, 973–1001
- de Baar, H.J.W., Boyd, P.W., Coale, K.H., Landry, M.R., Tsuda, A., Assmy, P., et al., 2005. Synthesis of iron fertilization experiments: From the iron age in the age of enlightenment. *Journal of Geophysical Research-Oceans* **110** C9.
- Delille, B., Harlay, D. and Zondervan, I. 2005. Response of primary production and calcification to changes of pCO<sub>2</sub> during experimental blooms of the coccolithophorid *Emiliana huxleyi*, *Global Biogeochemical Cycles* **19**: GB2023, doi:10.1029/2004GB002318
- Diaz RJ, Solan M, Valente RM 2004. A review of approaches for classifying benthic habitats and evaluating habitat quality. *Journal of Environmental Management* **73**: 165-181
- Diaz RJ 2001. Overview of hypoxia around the world. *Journal of Environmental Quality* **30**:275-281
- Domenici P, Lefrancois C, Shingles A 2007. Hypoxia and the antipredator behaviours of fishes. *Philosophical Transactions of the Royal Society B-Biological Sciences* **362**:2105-2121
- Doney, S.C. 1999. Major challenges confronting marine biogeochemical modelling. *Global Biogeochem. Cycles* **13**, 705-714.
- Dutkiewicz, S., Follows, M.J., Parekh, P. 2005. Interactions of the iron and phosphorus cycles: A three-dimensional model study. *Global Biogeochem. Cycles* **19**, GB1021.
- Dvortsov, V. L., M. A. Geller, S. Solomon, S. M. Schauffler, E. L. Atlas, and D. R. Blake 1999., Rethinking reactive halogen budgets in the midlatitude lower stratosphere, *Geophys. Res. Lett.*, **26**, 1699-1702.

- Falkowski PG 1997. Evolution of the nitrogen cycle and its influence on the biological sequestration of CO<sub>2</sub> in the ocean. *Nature*: 387: 272-275
- Fasham, M.J.R., Flynn, K.J., Pondaven, P., Anderson, T.R., Boyd, P.W. 2006. Development of a robust ecosystem model to predict the role of iron on biogeochemical cycles: a comparison of results for iron-replete and iron-limited areas, and the SOIREE iron-enrichment experiment. *Deep-Sea Research I* **53**, 333-366.
- Flynn KJ 2001. A mechanistic model for describing dynamic multi-nutrient, light, temperature interactions in phytoplankton. *Journal of Plankton Research* **23**: 977-997
- Fuhrman JA, Capone DG 1991. Possible biogeochemical consequences of ocean fertilization. *Limnology and Oceanography* 36:1951-1959
- Gage, J.D. & P.A. Tyler 1991. *Deep Sea Biology. A Natural History of Organisms at the Deep-Sea Floor*. Cambridge University Press, Cambridge, 504pp.
- Gehlen M, Bopp L, Ernprin N, Aumont O, Heinze C, Raguencau O 2006. Reconciling surface ocean productivity, export fluxes and sediment composition in a global biogeochemical ocean model. *Biogeosciences* **3** : 521-537
- Gibbs, S.J., Bown, P.R., Sessa, J.A., Bralower, T.J. and Wilson, P.A., 2006. Nannoplankton Extinction and Origination Across the Paleocene-Eocene Thermal Maximum, *Science* **314**: 1770-1773.
- Glover, A.G., Smith, C.R., Paterson, G.L.C., Wilson, G.D.F., Hawkins, L. & Sheader, M. 2002. Polychaete species diversity in the central Pacific abyss: local and regional patterns, and relationships with productivity. *Marine Ecology Progress Series* **240**, 157-170.
- Gnanadesikan, A., J. L. Sarmiento, and R. D. Slater 2003. Effects of patchy ocean fertilization on atmospheric carbon dioxide and biological production. *Global Biogeochem. Cycles*, **17** 2., doi: 10.1029/2002GB001940.
- Harada S, Watanabe M, Kohata K, Ioriya T, Kunugi M, Kimura T, Fujimori S, Koshikawa H, Sato K 1996. Analyses of planktonic ecosystem structure in coastal seas using a large-scale stratified mesocosm: A new approach to understanding the effects of physical, biochemical and ecological factors on phytoplankton species succession. *Water Science and Technology* **34**: 219-226
- Harper, D. 2000., The global chloromethane cycle: biosynthesis, biodegradation and metabolic role, *Nat. Prod. Rep.*, **17**, 337-348.
- Hedges JI, Keil RG 1995. Sedimentary organic-matter preservation - an assessment and speculative synthesis. *Marine Chemistry* 49:81-115
- Houweling, S., F. Dentener, J. Lelieveld, B. Walter, and E. Dlugokencky 2000., The modeling of tropospheric methane: how well can point measurements be reproduced by a global model?, *J. Geophys. Res.*, **105**, 8981-9002.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems, *Annual Review of Ecology and Systematics* **19**: 89-110.
- Hudson, R.J.M. and Morel, F.M.M., 1989. Distinguishing Between Extra- and Intracellular Iron in Marine Phytoplankton, *Limnology and Oceanography* **34**: 1113-1120.
- Hughes, J.A., Smith, T., Chaillan, F., Bett, B.J., Billett, D.S.M., Boorman, B., Fisher, E.H., Frenz, M. & Wolff, G.A. 2007. Two abyssal sites in the Southern Ocean influenced by different organic matter inputs: environmental characterization and preliminary observations on the benthic foraminifera. *Deep-Sea Research II* **54**, 2275-2290.
- Iglesias-Rodriguez, M.D., Armstrong, R., Feely, R., Hood, R., Kleypas, J., Sabine, C. and Sarmiento, J., 2002. Progress made in Study of Ocean's Calcium Carbonate Budget. *EOS, Transactions, American Geophysical Union*. **83**, 365, 374, & 375.
- IPCC, *Climate Change 2001: the Scientific basis*, Cambridge University Press, Cambridge, 2001.
- Jahnke RA 1996. The global ocean flux of particulate organic carbon: Areal distribution and magnitude. *Global Biogeochemical Cycles*. **10**: 71-88

- Jin X, Gruber N 2003. Offsetting the radiative benefit of ocean iron fertilization by enhancing N<sub>2</sub>O emissions. *Geophysical Research Letters* **30**:4
- Klaas, C. and Archer, D. E., 2002. Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cy.*, **16**: 1116, doi:10.1029/2001GB001765.
- Krauk, J.M., Villareal, T.A., Sohm, J.A., Montoya, J.P. and Capone, DG., 2006. Plasticity of N:P ratios in laboratory and field populations of *Trichodesmium* spp., *Aquat Microb Ecol* **42**: 243–253.
- Laës, A., Blain, S., Laan, P., Achterberg, E. P., Sarthou, G., De Baar, H. J. W., 2003. Deep dissolved iron profiles in the eastern North Atlantic in relation to water masses. *Geophysical Research Letters*, **30**, 1902, doi:10.1029/2003GL017902.
- Lampitt, R.S., Bett, B.J., Kiriakoulakis, K., Popova, E.E., Ragueneau, O., Vangriesheim, A. and Wolff G.A. 2001. Material supply to the Abyssal seafloor in the Northeast Atlantic. *Progress in Oceanography*. **50**: 27-63.
- Leonardos, N. and Geider, R.J., 2005. Elevated atmospheric carbon dioxide increases organic carbon fixation by *Emiliana huxleyi* Haptophyta., under nutrient-limited high-light conditions, *Journal of Phycology* **41**: 1196–1203.
- Levin LA, Etter RJ, Rex MA, Gooday AJ, Smith CR, Pineda J, Stuart CT, Hessler RR, Pawson D 2001. Environmental influences on regional deep-sea species diversity. *Annual Review of Ecology and Systematics* **32**:51-93
- Li X. and F.W.Primeau, in press. A fast Newton-Krilov solver for seasonally varying global ocean biogeochemistry models suitable for automatic parameter optimisation, *Ocean Modelling*.
- Lovelock, J.E. and Rapley, C.G. 2007. Ocean pipes could help the Earth to cure itself. *Nature* **449**: 403.
- Lucas M, Seeyave S, Sanders R, Moore CM, Williamson R, Stinchcombe M 2007. Nitrogen uptake responses to a naturally Fe-fertilised phytoplankton bloom during the 2004/2005 CROZEX study. *Deep-Sea Research II* **54**: 2138-2173
- Martin, J.H., Knauer, G.A., Karl D.M., Broenkow W.W., 1987. VERTEX: Carbon cycling in the northeast Pacific. *Deep-Sea Research* **34**, 267-285.
- Measures CI, Landing WM, Brown MT, Buck CS 2008. High-resolution Al and Fe data from the Atlantic Ocean CLIVAR-CO<sub>2</sub> repeat hydrography A16N transect: Extensive linkages between atmospheric dust and upper ocean geochemistry. *Global Biogeochemical Cycles* **22** 1: GB1005.
- Mills MM, Ridame C, Davey M, La Roche J, Geider RJ 2004. Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature*: **429** 6989: 292-294.
- Mills, C.E., 2001. Jellyfish blooms: Are populations increasing globally in response to changing ocean conditions? *Hydrobiologia* **451**:55–68.
- Orr, J. C., Fabry V. J., Aumont, O., et al., 2005. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*: **437**: 681–686.
- Parekh, P . Follows, M. J . Boyle, E. A . 2005. Decoupling of iron and phosphate in the global ocean. *Global Biogeochemical Cycles* **19** 2. p:GB2020
- Peng TH, Broecker WS 1985. the utility of multiple tracer distributions in calibrating models for uptake of anthropogenic co<sub>2</sub> by the ocean thermocline. *Journal of Geophysical Research-Oceans* **90**: 7023-7035
- Piggott MD, Gorman GJ, Pain CC, Allison PA, Candy AS, Martin BT, Wells MR, 2008. A new computational framework for multi-scale ocean modelling based on adapting unstructured meshes, *International Journal for Numerical Methods in Fluids*,
- Pollard R, Sanders R, Lucas M, Statham P 2007. The CROzet natural iron bloom and EXport experiment CROZEX. *Deep-Sea Research Part II* **54**: 1905-1914

- Portner HO, Langenbuch M, Michaelidis B 2005. Synergistic effects of temperature extremes, hypoxia, and increases in CO<sub>2</sub> on marine animals: From Earth history to global change. *Journal of Geophysical Research-Oceans* 110
- Purcell, J.E., Uye, S., Lo, W.-T., 2007. Anthropogenic causes of jellyfish blooms and their direct consequences for humans: a review, *Mar Ecol Prog Ser* **350**: 153–174.
- Quack, B., and D. W. R. Wallace 2003., Air-sea flux of bromoform: control rates and implications,, *Global Biogeochemical Cycles*, 17, 1023, doi:10.1029/202GB001890.
- Raven, J. A. et al. 2005. Ocean acidification due to increasing atmospheric carbon dioxide. *Policy document 12/05*. London: The Royal Society UK.
- Redfield AC. 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In: James Johnstone Memorial Volume, pp. 176-92. Liverpool: University of Liverpool.
- Rees, A. P., Law, C. S., Woodward, E. M. S . 2006. High rates of nitrogen fixation during an in-situ phosphate release experiment in the Eastern Mediterranean Sea. *Geophysical Research Letters* 0094-8276: 33 10. p:L10607-L10608
- Rex MA et al 2006. Global bathymetric patterns of standing stock and body size in the deep-sea benthos. *Marine Ecology-Progress Series* **317** : 1-8
- Riebesell, U. Schulz, K. G, Bellerby, R. G. J., Fritsche, P., Meyerhofer, M., Neill, C., Nondal, G., Oeschies, A., Wohlers, J., and Zollner, E.: 2007. Enhanced biological carbon consumption in a high CO<sub>2</sub> ocean, *Nature* **450**: 545–549, doi:10.1038/nature06267
- Riegman R, Noordeloos AAM, Cadee GC 1992. Phaeocystis blooms and eutrophication of the continental coastal zones of the North-Sea. *Marine Biology* 112:479-484
- Riemann, L. Steward, G.F. and Azam, F., 2000. Dynamics of bacterial community composition and activity during a mesocosm diatom bloom, *Applied and Environmental Microbiology* **66**: 578-587.
- Rowe, G.T. 1983. Biomass and production of the deep-sea macrobenthos. In: *The Sea, Vol. 8*. Ed: Rowe, G.T.. Wiley Interscience, New York, pp. 97-121.
- Sarmiento JL, Gruber N 2002. Sinks for anthropogenic carbon. *Physics Today* **55** : 30-36
- Sarmiento JI, Murnane R, Lequere C 1995. Air-sea CO<sub>2</sub> transfer and the carbon budget of the north-Atlantic. *Philosophical Transactions of the Royal Society -Biological Sciences* **348** : 211-219
- Sarmiento, J.L. and Orr, J.C., 1991. Three-dimensional simulations of the impact of Southern Ocean nutrient depletion on atmospheric CO<sub>2</sub> and ocean chemistry, *Limnology and Oceanography* **36**, 1928-1950.
- Sarthou, G., Baker, A. R., Blain, S., Achterberg, E. P., Boye, M., Bowie, A. R., Croot, P., Laan, P., De Baar, H. J. W., Jickells, T. D. and Worsfold, P. J., 2003., Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean. *Deep Sea Research I*, **50**, 1339-1352.
- Shepherd, J.G., Inglesias-Rodriguez, D. and Yool, A. 2007. Geo-engineering might cause, not cure, problems. *Nature* **449**, 781.
- Shojia K. and Jones I S F 2001. The costing of carbon credits from ocean nourishment plants *The Science of The Total Environment* **277**, 1-3., 28: 27-31
- Smythe-Wright , D., S. M. Boswell, P. Breithaupt, R. D. Davidson, C. H. Dimmer, and L. Eiras Diaz 2006., Methyl iodide production in the ocean : Implications for climate change, *Global. Biogeochem. Cycles*, 20, GB3003, doi:10.1029/2005GB002642.
- Sokolova, M.N. 2000. Feeding and Trophic Structure of the Deep-Sea Macrobenthos. Smithsonian Institution Libraries, Washington, D.C., 264 pp.
- Solomon, S., R. R. Garcia, and A. R. Ravishankara 1994., On the role of iodine in ozone depletion, *J. Geophys. Res.*, **99**, 20491-20499.
- Stenseth N.C., Mysterud A., Ottersen G., Hurrell J.W., Chan K-S., Lima M. 2002. Ecological

- Effects of Climate Fluctuations. *Science*: **297** 5585. 1292 – 1296.
- Stoll, H.M., Shimizu, N., Archer, D. and Ziveri, P. 2007. Coccolithophore productivity response to greenhouse event of the Paleocene–Eocene Thermal Maximum, *Earth and Planetary Science Letters* **258**: 192-206.
- Tappin, A.D., 2002. An Examination of the Fluxes of Nitrogen and Phosphorus in Temperate and Tropical Estuaries: Current Estimates and Uncertainties. *Estuarine, Coastal and Shelf Science* **55**, 885-901
- Timmermans, K. R., Stolte, W. and de Baar, H.J.W., 1994. Iron-mediated effects on nitrate reductase in marine phytoplankton, *Marine Biology* **121**: 389-396.
- Tyrrell, T., Maranon, E., Poulton, A.J., Bowie, A.R., Harbour, D.S. and Woodward, E.M.S. 2003. Large-scale latitudinal distribution of *Trichodesmium* spp. in the Atlantic Ocean. *Journal of Plankton Research*, **25**: 405-416.
- Tyrrell T., 1999. The relative influences of nitrogen and phosphorus on oceanic primary production *Nature*, **400**: 525-53.
- Tyson, R.V., 1995. *Sedimentary Organic Matter*. Chapman and Hall, London, 615pp.
- UNEP United Nations Environment Programme. 2004. GEO Year Book 2003. GEO Section/UNEP, Nairobi.
- Vogt, R., R. Sander, R. V. Glasow, and P. J. Crutzen 1999., Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: a model study, *J. Atmos. Chem.*, **32**: 375-395.
- Watson AJ 1997. Volcanic iron, CO<sub>2</sub>, ocean productivity and climate. *Nature*: 385: 587-588
- Weber L, Volker C, Schartau M, Wolf-Gladrow DA. 2005. Modeling the speciation and biogeochemistry of iron at the Bermuda Atlantic Time-series Study site. *Global Biogeochemical Cycles* **19** : GB1019
- Weeks S.J., B. Currie, and A. Bakun, 2002. Satellite Imaging: massive emissions of toxic gas in the Atlantic. *Nature*, **415**, 493-494
- Wigham, B.D., Hudson, I.R., Billett, D.S.M. & Wolff, G.A. 2003. Is long-term change in the abyssal Northeast Atlantic driven by qualitative changes in export flux? Evidence from selective feeding in deep-sea holothurians. *Progress in Oceanography* **59**, 409-441.
- Yool A., Shepherd J.G., Bryden H.L. Oschlies A. Submitted. The efficiency of nutrient traslocation for enhancing oceanic uptake of carbon dioxide.
- Yoshida, T., Hayashi, K. and Ohmoto, H., 2002. Dissolution of iron hydroxides by marine bacterial siderophore, *Chemical Geology* **184**: 1-9.
- Zapata F., Roy . R.N. 2004. Use of Phosphate Rocks for Sustainable Agriculture. *Fertilizer and Plant Nutrition Bulletin* 13. A joint publication of the FAO Land and Water Development Division and the International Atomic Energy Agency. Food and Agriculture Organization of the United Nations. Rome.
- Zeebe RE, Archer D 2005. Feasibility of ocean fertilization and its impact on future atmospheric CO<sub>2</sub> levels. *Geophysical Research Letters* **32**: L09703.
- Zeebe, R.E. and Wolf-Gladrow, D. 2001. *CO<sub>2</sub> in seawater: equilibrium, kinetics, isotopes*. Elsevier, 346 pp.
- Zhou, S. Flynn, P. 2005. Geoengineering Downwelling Ocean Currents: A Cost Assessment *Climatic Change*, **71**, 1-2: 203-220.
- Zondervan, I., Zeebe, R.E., Rost, B., Riebesell U., 2001. Decreasing Marine Biogenic Calcification: A Negative Feedback on Rising Atmospheric pCO<sub>2</sub>, *Global Biogeochemical Cycles* **15**: 507-516.