Ocean fertilization: a potential means of geoengineering?

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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 fertilization to become a viable option to sequester CO₂, we need more extensive and targeted fieldwork 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 fertilization. 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 fieldwork plans are developed rapidly. In contrast to previous experiments, these must focus on the specific objective which is to assess the possibilities of CO_2 sequestration through fertilization.

Keywords: ocean fertilization; iron; nutrients; carbon sequestration

1. Background

It is now generally accepted (IPCC 2007) that emissions of CO_2 to the atmosphere are the dominant cause of global warming, and that cuts in these emissions (currently approx. 8 GtC yr⁻¹ 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 *Author for correspondence (r.lampitt@noc.soton.ac.uk).

One contribution of 12 to a Theme Issue 'Geoscale engineering to avert dangerous climate change'.



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

similar magnitude (Sarmiento *et al.* 1995). One is the 'solubility pump' driven by ocean circulation and by the solubility of CO_2 in seawater and the other is the 'biological pump' that 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_2 concentration and this historically recent ocean sink for anthropogenic CO_2 is currently estimated to be approximately 2 GtC yr⁻¹ (IPCC 2007). The 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 & Flynn 2005) because the CO_2 cost of implementing them will outweigh the benefits.

With regard to the biological pump, the production of organic matter by phytoplankton absorbs CO_2 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 nutrient supply and in the sunlit surface ocean (the 'euphotic zone', approx. the top 100 m) 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 fertilization could be used to enhance the productivity of the euphotic zone, stimulate the biological pump and hence increase the uptake of anthropogenic CO_2 . 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



Figure 2. Distribution of phosphate from south to north in the Pacific along 170° 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.

'new production' and is in effect that production available for export. Production that is based on nutrients that are recycled within the euphotic zone such as ammonia is not relevant here but is an important component of the total productivity often referred to simply as 'primary production'.

If ocean fertilization is to be useful as a geoengineering 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 (200–1000 m) 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_2 . The production of organic matter removes CO_2 from solution, while the process of calcification decreases surface ocean alkalinity, and in addition releases CO_2 to solution thereby partly counteracting the biological pump (Zeebe & 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 synthesized POC is remineralized to dissolved inorganic carbon (DIC) in the upper few hundred metres 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 approximately 200 to 1000 m.

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 fertilization and the potential side effects. We review in §2 the four means that have so far been suggested in order to enhance sequestration and comment on their likelihood of success. In §3, we discuss the side effects that may occur and, in §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 Table 1. Elements important for oceanic new primary production and their principal supply routes. (Elements that generally limit new production in some areas are in italics. 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 remineralization 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.)

	upwelling and mixing of deep water	atmospheric supply as gas	atmospheric supply as dust	conc. limiting productivity	conc. range in the oceanic euphotic zone
phosphorus nitrogen silicon iron zinc carbon (DIC)	• • • • • • • • • • • • • • • • •	 	* * *	$\begin{array}{c} < 0.01 \; \mu \mathrm{M} \\ < 0.02 \; \mu \mathrm{M} \\ 0.2 \; \mu \mathrm{M} \\ 0.2 \; \mathrm{nM} \end{array}$	0.005–2.0 μM 0.002–30.0 μM 0.05–130 μM 0.005–1.0 nM 0.01–1.0 nM 2.0 mM

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.

(a) Macro- and micronutrients

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

Macronutrients below the euphotic zone generally occur in a constant 'Redfield ratio' of N:P of 16:1 (Redfield 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 approximately 106:16:1, while dissolved organic matter (DOM) has a ratio of 199:20:1 (Hopkinson & 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 fertilization. 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, approximately 25 per cent of the ocean surface has consistently high concentrations of macronutrients but still the plant biomass (as defined by chlorophyll) is low. The production in these high-nutrient lowchlorophyll (HNLC) waters is primarily limited by micronutrients especially iron. By contrast, low-nutrient low-chlorophyll (LNLC) waters can be found in the subtropical gyre systems of the oceans. These oligotrophic regions comprise approximately 40 per cent of the ocean surface and are characterized by winddriven 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 of 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.

2. Efficacy of ocean fertilization for carbon sequestration

To date four distinct ways have been proposed to fertilize the oceans in order to enhance carbon sequestration. Two of these involve the supply of large quantities of macronutrients (or nutrient cocktails) and two involve micronutrient supply designed to facilitate the efficient usage of existing macronutrients. We now consider the potential efficacy of each of the schemes. Where possible, we present costs of implementing these schemes that can then be compared with other geoengineering proposals and with the current trading value of carbon emissions which at present is of the order \$75 tonne⁻¹ carbon (note that 1 t (C) corresponds to $3.67 \text{ t (CO}_2)$). 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 §3.

An aspect that is often overlooked is that although fertilization 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 time scale of at least 100 years (as defined by IPCC; see §1). The rationale behind this statement is that if a water mass is fertilized and leads to local sequestration, this may not be globally significant if that water mass would, over the subsequent weeks and months, have been fertilized naturally. While the process of fertilization may be local (e.g. 10^4-10^6 km²) 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 micronutrient cycles with associated ecosystem interactions are embedded in high-resolution three-dimensional 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 fertilization.

(a) Nutrient supply from land

It has been proposed that fertilizer cocktails of macro- and micronutrients 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 that optimize 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 fertilizer to coastal seas increases production greatly (with the associated problems of excessive eutrophication; \$3a). 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, macronutrient 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 fertilizer have a phosphate content as low as 4 per cent with many sources highly enriched in carbonate (Zapata & Roy 2004). One of the most common water-soluble fertilizers is diammonium phosphate (DAP), $(NH_4)_2HPO_4$, that currently has a market price of approximately \$420 tonne⁻¹ FOB (http://www.icispricing.com/il_shared/Samples/SubPage181.asp) or \$1700 tonne⁻¹ of phosphorus. The 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 of \$45 tonne⁻¹ 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), CO_2 is absorbed by the ocean slowly (months) and depending on the local physics of the water column there is a possibility that this mismatch would prevent sequestration of atmospheric CO_2 .

The 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 that it was a viable proposition (Shoji & Jones 2001) with approximately 12 tonnes of CO_2 captured per tonne of ammonia provided and a cost of approximately \$25 tonne⁻¹ 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 previously, 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 localized enhancement of the biological pump and possibly no effective sequestration of atmospheric 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 in 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 shelf and accurate representation of the shallow topography and the coast line (e.g. Davies & 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.

(b) Macronutrient 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 metres to the surface (http://www.atmocean.com/ sequestration.htm; Lovelock & 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 that 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_2 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 remineralized relative to carbon from sinking organic material (e.g. Anderson & 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 CO₂ 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 CO₂ 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 km² in total area) would therefore be needed to achieve sequestration of 1 GtC yr⁻¹.

An inherent part of this scheme's design is that the pipes will supply not only nutrients but also 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 usefulness 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_2 . We believe that this scheme cannot be dismissed as a potential solution yet and that further research is warranted.

(c) Iron supply to HNLC regions (enhance macronutrient uptake)

Ice core records indicated that during past glacial periods, naturally occurring iron fertilization had repeatedly drawn massive amounts of carbon from the atmosphere. Several observational programmes have been carried out in presentday 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 macronutrient 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 (Blain *et al.* 2007; Pollard *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 fertilization 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 fertilization efficiency (IFE). Results from the field programmes indicate that the value of IFE at Crozet is four times lower than that



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).

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 fertilization experiments have been carried out since 1993 to examine the effects of *in situ* addition of this micronutrient on upper ocean biogeochemistry (summarized 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.

This fertilization 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 30 000–100 000 tonnes of carbon.

Models of progressively increasing resolution and realism have been used during the last 20 years in order to evaluate the potential for iron fertilization of HNLC regions as a means of consuming nutrients and sequestering carbon. Early simplistic models (e.g. Peng & Broecker 1985) indicated a possible reduction in atmospheric CO₂ of 50–100 ppm; however, recent studies with higher resolution three-dimensional models coupled to ecosystem dynamics including iron have suggested that addition of iron is much less efficient (order of 10 ppm) because the other limiting factors of light and grazing become dominant (e.g. Dutkiewicz *et al.* 2005; Aumont & Bopp 2006). The link between nutrient supply and ecosystem dynamics is complex, especially for micronutrients. 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 fertilization 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 fertilization experiments are in themselves inconclusive, further contributing to the difficulties in reducing uncertainties in IFE through modelling.

The final conclusion from Aumont & 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 fertilization 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.

(d) 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 (e.g. Falkowski 1997). The 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 fertilization 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_2 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 fertilization of LNLC regions.

The good correlation between the diazotroph *Trichodesmium* sp. abundance and estimated dust deposition (Tyrrell *et al.* 2003) in the subtropical 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).

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(e) 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 and \$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 fertilization methods is much more difficult and will require detailed and thorough analyses. Nevertheless, it seems likely that iron fertilization would be the most cost-effective, simply because the quantity and cost of the fertilizing material required are both small.

3. Side effects of ocean fertilization

Before any commercial application of ocean fertilization 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 wellinformed manner. We identify and briefly discuss seven areas of potential side effect that will require specific attention in the future although we cannot discount the possibility that others will occur.

(a) Eutrophication and anoxia

Defined as the detrimental response of an ecosystem to excess macronutrients, eutrophication is a coastal phenomenon of worldwide concern (Diaz *et al.* 2004; UNEP 2004). The 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 fertilized areas of the open ocean is debatable on account of differences in circulation patterns, nutrient supply mechanisms and biological communities compared with coastal seas.

Responses of marine organisms to low oxygen are almost entirely negative (Diaz 2001; Levin *et al.* 2001; Cowie 2005; Domenici *et al.* 2007). While physiological adaptation can occur, extended exposure (more than 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 lowoxygen conditions in bottom waters. Such changes potentially reduce the capacity of the system to support commercial fisheries. Prolonged (more than 1 vear) anoxia promotes burial of organic carbon into the long-term geological record (Hedges & 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_2O , a greenhouse gas more potent than CO₂, negating any potential benefit from fertilization (Fuhrman & Capone 1991; Jin & Gruber 2003). In more extreme situations, 'sulphur eruptions' can occur and the so-called 'black tides' of H_2S 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 fertilization.

The changes in nutrient input ratios (N : P : Si) can alter phytoplankton community composition. Enrichment of N relative to Si has been accompanied by shifts in species dominance from diatoms to dinoflagellates (see Cloern 2001) whereas the 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 polylepis*), which in productive fishery regions has serious economic impacts (Underdal *et al.* 1989) and can lead to human fatalities through the consumption of contaminated shellfish (Hallegraeff 1993). Hence, tampering with natural oceanic nutrient ratios through fertilization 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 (\$3g). However, closer to the productive continental shelves, increase in productivity due to eutrophication may reduce diversity in the benthos. Consequently, ocean fertilization 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 (more than 100 km) distances.

(b) Modification of ocean pH

Ocean pH has fluctuated between 8.0 and 8.3 for the last 25 Myr, and, since industrialization, the rate of increase in atmospheric CO_2 has caused unprecedented changes in seawater pH and carbonate chemistry (Caldeira & 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 fertilization 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 pCO_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 & Archer 2002). The available evidence suggests that the increase in atmospheric CO_2 absorbed by the oceans will increase photosynthesis by coccolithophores (Leonardos & Geider 2005; Riebesell et al. 2007) and some studies also demonstrate an associated decrease in calcification (Riebesell et al. 2000). Other studies confirm the increase in photosynthesis but also show an increase in calcification in response to elevated pCO_2 (Iglesias-Rodriguez *et al.* 2008). Additionally, evidence from the geological record suggests that past periods of ocean acidification such as the Palaeocene–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_2 are extremely complex (e.g. Riebesell et al. 2007) and probably influenced by other environmental parameters that naturally covary with pCO_2 .

(c) Modification of global macronutrient balance

Any attempt to fertilize 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 fertilization that the downstream effects of nutrient redistribution are adequately considered.

Once again the crucial requirement is the development of global models with sufficient resolution and appropriate parametrization to examine each potential method of fertilization. Results to date (Sarmiento & Gruber 2002) indicate that, for example, a side effect of HNLC iron fertilization 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 that will be carried out when appropriate data are available.

(d) 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 (i.e. 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 per cent of the amount delivered to the ocean by dust $(15.5 \times 10^6 \text{ tonnes yr}^{-1})$ or rivers $(650 \times 10^6 \text{ tonnes yr}^{-1})$. 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 *et al.* 2008). Iron added through OIF will hence be rapidly removed from the surface waters (Sarthou *et al.* 2003; 1–5 months), and continual additions would be required to replenish iron concentrations.

(e) Generation of other climate-relevant gases (greenhouse/cloud forming)

It is important to consider ocean fertilization in the context of radiative forcing and not simply in terms of the carbon cycle. CO_2 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 fertilization.

Fluxes are potentially large particularly if the anticipated decrease in oxygen concentration is 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 fertilization and hence to determine the influence on greenhouse forcing.

(f) Change to pelagic ecosystem structure

While the purpose of ocean fertilization is to enhance carbon sequestration, one probable 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 and palatability for sub-euphotic zone communities, etc.).

Approximately 1.3 billion people depend on fisheries for a major part of their sustenance and economic welfare so it is appropriate we should consider ecosystem changes that might be a consequence of ocean fertilization 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

gas	radiative forcing $(W m^{-2})$	ocean to atmosphere supply rate $(mol yr^{-1})$	factors causing increase or decrease	references
$\overline{\mathrm{CO}_2}$	1.6	-1.4×10^{14}	increased sequestration and car- bon export will reduce forcing	IPCC (2001)
methane	0.5	8.0×10^{12}	anoxia increases production	Houweling <i>et al.</i> (2000)
halocarbons ozone	0.3	greater than 1×10^{11} (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) reduction in stratospheric ozone	Harper (2000), Quack & Wallace (2003) and Smythe-Wright <i>et al.</i> (2006) Solomon <i>et al.</i> (1994),
			due to increased halocarbons will reduce its negative effect on global warming. Conversely depletion of tropospheric ozone will reduce its radiative forcing	Dvortsov <i>et al.</i> (1999) and Vogt <i>et al.</i> (1999)
nitrous oxide	0.1	1.2×10^{11}	increase forcing due to biological production by phytoplankton	Jin & Gruber (2003)
aerosols (direct)	-0.5	3.3×10^{15} (g yr ⁻¹)	any increase in sea salt input will increase aerosol production	IPCC (2001)
DMS (albedo)	-0.7	6.9×10^{11}		

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 fertilization are likely to alter their influence.

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 thompsoni* appears to be replacing Antarctic krill in the Southern Ocean (Atkinson *et al.* 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 HABs should not be ignored. As described above, HABs sometimes occur in response to coastal eutrophication and although unlikely to become a feature of fertilization 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 fertilization will elicit comparable effects cannot be ruled out although we think it unlikely.

As mentioned above, ecosystem changes in response to ocean fertilization 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 (e.g. marine snow aggregates versus 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 northwest European coastal waters (Riegman *et al.* 1992).

Similarly during the natural fertilization CROZEX project, iron fertilization 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 fertilization 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 fertilization but a clear conclusion about either of these is not possible until the large-scale fieldwork and associated modelling has been completed.

(g) Change to benthic ecosystem structure

Approximately 0.4 Gt of carbon is deposited on the abyssal seafloor each year, the end member of the biological pump (Jahnke 1996). Of this, approximately 96 per cent dissolves or is remineralized each year to DIC and hence influences air– sea CO_2 exchange on a time scale of a few centuries (Tyson 1995). The remaining 4 per cent 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 fertilization on sequestration on the centennial time scale agreed upon by the IPCC and on the much longer time scales of geological



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 showing the pattern of diversity change with POC flux (adapted from Levin *et al.* 2001).

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 benchos 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 benchos 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 fertilization has been suggested, it is likely that enhanced POC fluxes to the seafloor would result in increased biomass and abundance (Glover et al. 2002; Hughes et al. 2007) 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).

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 fertilization has ceased, the system may revert 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 remineralization.

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 fertilization proposal.

(a) 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 and silicification have been investigated in the laboratory (on land and at sea) by manipulating environmental variables including macro- (Krauk et al. 2006) and micronutrients (Hudson & 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 medium compositions and nutrient concentrations. Second, 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, among others, long-term (chronic) effects of Fe fertilization, vertical macronutrient flux, eutrophication, anoxia, changing pH, 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_2 , 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_2 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.

(b) Mesocosm experiments

Mesocosms are containers currently with volumes $1-400 \text{ m}^3$, 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 CO₂ 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 & Drapeau 1995; Riemann *et al.* 2000; Delille *et al.* 2005).

They enable scaling from the individual organism up to the community level and interdisciplinary programmes that 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, offshore pelagic mesocosm experiments can be used to quantify the effects of manipulations on species composition and succession, photosynthesis, macro- and micronutrients 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 fertilization 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 200–1000 m, which are probably impossible to replicate in any future design of mesocosm.

(c) Field experiments

Of the four potential means of ocean fertilization identified above, significant field experiments have only been carried out to address the effects of iron fertilization 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 (more than 10 weeks) and scale (in excess of 100×100 km). Because such experiments potentially have considerable social and economic importance, they need to 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 localized fertilization. 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 that will address explicitly the effects of various types of ocean fertilization on carbon sequestration.

(d) Modelling

Modelling studies addressing the issue of artificial ocean fertilization broadly fall into two categories: regional modelling of localized field experiments and global modelling to assess the long-term and remote consequences of proposed fertilization 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 fertilization 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 fertilization 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 & 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 & 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 overemphasized. In order to be effective as management tools, the 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 that 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 localized 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 time scale 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 fertilization must, by design, substantially modify the natural biological processes of the marine ecosystem. Without doubt, the effects of fertilization 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 focused research into the effects of ocean fertilization. The critical areas of research will involve large-scale field experiments $(100 \times 100 \text{ km})$ tightly coupled to high-resolution threedimensional computational models with embedded biogeochemistry. This is required for each of the four classes of fertilization schemes that have been proposed. Until completed satisfactorily, it is impossible to provide a rational judgement about whether the schemes proposed are (i) likely to be effective and (ii) 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.

References

- Anderson, T. R. 2005 Plankton functional type modelling: running before we can walk? J. Plankton Res. 27, 1073–1081. (doi:10.1093/plankt/fbi076)
- Anderson, L. A. & Sarmiento, J. L. 1994 Redfield ratios of remineralization determined by nutrient data analysis. *Glob. Biogeochem. Cycles* 8, 65–80. (doi:10.1029/93GB03318)
- Arrigo, K. R. 2005 Marine micro-organisms and global nutrient cycles. Nature 437, 349–355. (doi:10.1038/nature04159)
- Atkinson, A., Siegel, V., Pakhomov, E. & Rothery, P. 2004 Long-term decline in krill stocks and increase in Salps within the Southern Ocean. *Nature* 432, 100–103. (doi:10.1038/nature02996)
- Aumont, O. & Bopp, L. 2006 Globalizing results from ocean in situ iron fertilization. Glob. Biogeochem. Cycles 20, GB2017. (doi:10.1029/2005GB002591)
- Beaugrand, G., Brander, K. M., Lindley, J. A., Souissi, S. & Reid, P. C. 2003 Plankton effect on cod recruitment in the North Sea. *Nature* 426, 661–664. (doi:10.1038/nature02164)
- Beaulieu, S. R. 2002 Accumulation and fate of phytodetritus on the sea floor. Oceanogr. Mar. Biol. Annu. Rev. 40, 171–232.
- Bellerby, R. G. J., Olsen, A., Furevik, T. & Anderson, L. A. 2005 Response of the surface ocean CO₂ system in the Nordic Seas and North Atlantic to climate change. In *Climate variability in* the Nordic Seas, vol. 20 (eds H. Drange, T. M. Dokken, T. Furevik, R. Gerdes & W. Berger). Geophysical Monograph Series, AGU, pp. 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. Prog. Oceanogr. 50, 325–348. (doi:10.1016/S0079-6611(01)00060-X)
- Blain, S. et al. 2007 Effect of natural iron fertilization on carbon sequestration in the Southern Ocean. Nature 446, 1070–1074. (doi:10.1038/nature05700)
- Boyd, P. W. et al. 2007 Mesoscale iron enrichment experiments 1993–2005: synthesis and future directions. Science 315, 612–617. (doi:10.1126/science.1131669)
- Brewer, P. G., Peltzer, E. T., Friederich, G., Aya, I. & Yamane, K. 2000 Experiments on the ocean sequestration of fossil fuel CO₂: pH measurements and hydrate formation. *Mar. Chem.* 72, 83–93. (doi:10.1016/S0304-4203(00)00074-8)
- Caldeira, K. & Wickett, M. E. 2003 Anthropogenic carbon and ocean pH. *Nature* **425**, 365. (doi:10. 1038/425365a)

- Chen, C.-T. A., Lim, C.-M., Huang, B.-T. & Chang, L.-F. 1996 Stoichometry of carbon, hydrogen, nitrogen, sulfur and oxygen in the particulate matter of the western North Pacific marginal seas. *Mar. Chem.* 54, 179–190. (doi:10.1016/0304-4203(96)00021-7)
- Christian, J. R., Lewis, M. R. & Karl, D. M. 1997 Vertical fluxes of carbon, nitrogen, and phosphorus in the North Pacific Subtropical Gyre near Hawaii. J. Geophys. Res.-Oceans 102, 15 667–15 677. (doi:10.1029/97JC00369)
- Cloern, J. E. 2001 Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol.-Prog. Ser. 210, 223–253. (doi:10.3354/meps210223)
- Cowie, G. 2005 The biogeochemistry of Arabian Sea surficial sediments: a review of recent studies. *Prog. Oceanogr.* **65**, 260–289. (doi:10.1016/j.pocean.2005.03.003)
- Cushing, D. H. 1975 Natural mortality of plaice. J. Du Conseil 36, 150-157.
- Dam, H. G. & Drapeau, D. T. 1995 Coagulation efficiency, organic-matter glues and the dynamics of particles during a phytoplankton bloom in a mesocosm study. *Deep Sea Res. II* 42, 111–123. (doi:10.1016/0967-0645(95)00007-D)
- 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. *Curr. Biol.* 18, 1–8. (doi:10.1016/j.cub.2007.11.056)
- Davies, A. M. & Xing, J. 2005 Modelling process influencing shelf edge exchange of water and suspended sediment. *Continental Shelf Res.* 25, 973–1001. (doi:10.1016/j.csr.2004.12.006)
- de Baar, H. J. W. et al. 2005 Synthesis of iron fertilization experiments: from the iron age in the age of enlightenment. J. Geophys. Res.-Oceans 110, C9. (doi:10.1029/2004JC002601)
- Delille, B., Harlay, D. & Zondervan, I. 2005 Response of primary production and calcification to changes of pCO_2 during experimental blooms of the coccolithophorid *Emiliania huxleyi*. Glob. Biogeochem. Cycles **19**, GB2023. (doi:10.1029/2004GB002318)
- Diaz, R. J. 2001 Overview of hypoxia around the world. J. Environ. Qual. 30, 275–281.
- Diaz, R. J., Solan, M. & Valente, R. M. 2004 A review of approaches for classifying benthic habitats and evaluating habitat quality. J. Environ. Manage. 73, 165–181. (doi:10.1016/ j.jenvman.2004.06.004)
- Domenici, P., Lefrançois, C. & Shingles, A. 2007 Hypoxia and the antipredator behaviours of fishes. *Phil. Trans. R. Soc. B* 362, 2105–2121. (doi:10.1098/rstb.2007.2103)
- Doney, S. C. 1999 Major challenges confronting marine biogeochemical modelling. Glob. Biogeochem. Cycles 13, 705–714. (doi:10.1029/1999GB900039)
- Dutkiewicz, S., Follows, M. J. & Parekh, P. 2005 Interactions of the iron and phosphorus cycles: a three-dimensional model study. *Glob. Biogeochem. Cycles* **19**, GB1021. (doi:10.1029/ 2004GB002342)
- Dvortsov, V. L., Geller, M. A., Solomon, S., Schauffler, S. M., Atlas, E. L. & Blake, D. R. 1999 Rethinking reactive halogen budgets in the midlatitude lower stratosphere. *Geophys. Res. Lett.* 26, 1699–1702. (doi:10.1029/1999GL900309)
- Falkowski, P. G. 1997 Evolution of the nitrogen cycle and its influence on the biological sequestration of CO₂ in the ocean. *Nature* **387**, 272–275. (doi:10.1038/387272a0)
- 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 Res. I* 53, 333–366. (doi:10.1016/j.dsr.2005.09.011)
- Flynn, K. J. 2001 A mechanistic model for describing dynamic multi-nutrient, light, temperature interactions in phytoplankton. J. Plankton Res. 23, 977–997. (doi:10.1093/plankt/23.9.977)
- Fuhrman, J. A. & Capone, D. G. 1991 Possible biogeochemical consequences of ocean fertilization. Limnol. Oceanogr. 36, 1951–1959.
- Gage, J. D. & Tyler, P. A. 1991 Deep sea biology. A natural history of organisms at the deep-sea floor. Cambridge, UK: Cambridge University Press.
- 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. & Wilson, P. A. 2006 Nannoplankton extinction and origination across the Paleocene–Eocene Thermal Maximum. *Science* 314, 1770–1773. (doi:10.1126/science.1133902)
- 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. *Mar. Ecol. Prog. Ser.* 240, 157–170. (doi:10.3354/meps240157)
- Hallegraeff, G. M. 1993 A review of harmful algal blooms and their apparent global increase. *Phycologia* **32**, 79–99.
- 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 Sci. Technol.* 34, 219–226. (doi:10.1016/S0273-1223(96)00748-2)
- Harper, D. 2000 The global chloromethane cycle: biosynthesis, biodegradation and metabolic role. Nat. Prod. Rep. 17, 337–348. (doi:10.1039/a809400d)
- Hedges, J. I. & Keil, R. G. 1995 Sedimentary organic-matter preservation—an assessment and speculative synthesis. Mar. Chem. 49, 81–115. (doi:10.1016/0304-4203(95)00008-F)
- Hopkinson, C. S. & Vallino, J. J. 2005 Efficient export of carbon to the deep ocean through dissolved organic matter. *Nature* 433, 142–145. (doi:10.1038/nature03191)
- Houweling, S., Dentener, F., Lelieveld, J., Walter, B. & Dlugokencky, E. 2000 The modeling of tropospheric methane: how well can point measurements be reproduced by a global model? J. Geophys. Res. 105, 8981–9002. (doi:10.1029/1999JD901149)
- Howarth, R. W. 1988 Nutrient limitation of net primary production in marine ecosystems. Annu. Rev. Ecol. Syst. 19, 89–110. (doi:10.1146/annurev.es.19.110188.000513)
- Hudson, R. J. M. & Morel, F. M. M. 1989 Distinguishing between extra- and intracellular iron in marine phytoplankton. *Limnol. Oceanogr.* 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 Res. II* 54, 2275–2290. (doi:10.1016/j.dsr2.2007.06.006)
- Iglesias-Rodriguez, M. D., Armstrong, R., Feely, R., Hood, R., Kleypas, J., Sabine, C. & Sarmiento, J. 2002 Progress made in study of ocean's calcium carbonate budget. *EOS*, *Trans. Am. Geophys. Union* 83, 365. (doi:10.1029/2002EO000267)
- Iglesias-Rodriguez, M. D. et al. 2008 Phytoplankton calcification in a high-CO₂ world. Science 320, 336–340. (doi:10.1126/science.1154122)
- IPCC 2001 Climate change 2001: the scientific basis. Cambridge, UK: Cambridge University Press.
- IPCC 2007 Climate change 2007: synthesis report. Contribution of working groups I, II and III to the fourth assessment report of the Intergovernmental Panel on Climate Change. IPCC, Geneva.
- Jahnke, R. A. 1996 The global ocean flux of particulate organic carbon: areal distribution and magnitude. Glob. Biogeochem. Cycles 10, 71–88. (doi:10.1029/95GB03525)
- Jin, X. & Gruber, N. 2003 Offsetting the radiative benefit of ocean iron fertilization by enhancing N₂O emissions. *Geophys. Res. Lett.* **30**, 4. (doi:10.1029/2003GL018458)
- Johnson, N. A., Campbell, J. W., Moore, T. S., Rex, M. A., Etter, R. J., McClain, C. R. & Dowell, M. D. 2007 The relationship between the standing stock of deep-sea macrobenthos and surface production in the western North Atlantic. *Deep Sea Res.* 154, 1350–1360. (doi:10.1016/j.dsr.2007.04.011)
- Klaas, C. & Archer, D. E. 2002 Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio. *Glob. Biogeochem. Cycle* 16, 1116. (doi:10.1029/2001GB001765)
- Knoll, A. H., Bambach, R. K., Payne, J. L., Pruss, S. & Fischer, W. W. 2007 Paleophysiology and end-Permian mass extinction. *Earth Planet. Sci. Lett.* 256, 295–313. (doi:10.1016/j.epsl.2007.02.018)
- Krauk, J. M., Villareal, T. A., Sohm, J. A., Montoya, J. P. & Capone, D. G. 2006 Plasticity of N:P ratios in laboratory and field populations of *Trichodesmium* spp. Aquat. Microb. Ecol. 42, 243–253. (doi:10.3354/ame042255)

- 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. *Geophys. Res. Lett.* **30**, 1902. (doi:10.1029/2003GL017902)
- Lampitt, R. S., Bett, B. J., Kiriakoulakis, K., Popova, E. E., Ragueneau, O., Vangriesheim, A. & Wolff, G. A. 2001 Material supply to the Abyssal seafloor in the Northeast Atlantic. *Prog. Oceanogr.* 50, 27–63. (doi:10.1016/S0079-6611(01)00047-7)
- Leonardos, N. & Geider, R. J. 2005 Elevated atmospheric carbon dioxide increases organic carbon fixation by *Emiliania huxleyi* Haptophyta, under nutrient-limited high-light conditions. J. Phycol. 41, 1196–1203. (doi:10.1111/j.1529-8817.2005.00152.x)
- Levin, L. A., Etter, R. J., Rex, M. A., Gooday, A. J., Smith, C. R., Pineda, J., Stuart, C. T., Hessler, R. R. & Pawson, D. 2001 Environmental influences on regional deep-sea species diversity. Annu. Rev. Ecol. Syst. 32, 51–93. (doi:10.1146/annurev.ecolsys.32.081501.114002)
- Li, X. & Primeau, F. W. 2008 A fast Newton-Krilov solver for seasonally varying global ocean biogeochemistry models. Ocean Model. 23, 13–20. (doi:10.1016/j.ocemod.2008.03.001)
- Lovelock, J. E. & Rapley, C. G. 2007 Ocean pipes could help the Earth to cure itself. *Nature* 449, 403. (doi:10.1038/449403a)
- Lucas, M., Seeyave, S., Sanders, R., Moore, C. M., Williamson, R. & Stinchcombe, M. 2007 Nitrogen uptake responses to a naturally Fe-fertilised phytoplankton bloom during the 2004/2005 CROZEX study. *Deep Sea Res. II* 54, 2138–2173. (doi:10.1016/j.dsr2.2007.06.017)
- Martin, J. H., Knauer, G. A., Karl, D. M. & Broenkow, W. W. 1987 VERTEX: carbon cycling in the northeast Pacific. *Deep Sea Res. A* 34, 267–285. (doi:10.1016/0198-0149(87)90086-0)
- Measures, C. I., Landing, W. M., Brown, M. T. & Buck, C. S. 2008 High-resolution Al and Fe data from the Atlantic Ocean CLIVAR-CO₂ repeat hydrography A16N transect: extensive linkages between atmospheric dust and upper ocean geochemistry. *Glob. Biogeochem. Cycles* 22, GB1005. (doi:10.1029/2007GB003042)
- Mills, C. E. 2001 Jellyfish blooms: are populations increasing globally in response to changing ocean conditions? *Hydrobiologia* 451, 55–68. (doi:10.1023/A:1011888006302)
- Mills, M. M., Ridame, C., Davey, M., La Roche, J. & Geider, R. J. 2004 Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature* 429, 292–294. (doi:10. 1038/nature02550)
- Orr, J. C. et al. 2005 Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437, 681–686. (doi:10.1038/nature04095)
- Parekh, P., Follows, M. J. & Boyle, E. A. 2005 Decoupling of iron and phosphate in the global ocean. *Glob. Biogeochem. Cycles* 19, GB2020. (doi:10.1029/2004GB002280)
- Peng, T. H. & Broecker, W. S. 1985 The utility of multiple tracer distributions in calibrating models for uptake of anthropogenic CO₂ by the ocean thermocline. J. Geophys. Res.-Oceans 90, 7023–7035. (doi:10.1029/JC090iC04p07023)
- Piggott, M. D., Gorman, G. J., Pain, C. C., Allison, P. A., Candy, A. S., Martin, B. T. & Wells, M. R. 2008 A new computational framework for multi-scale ocean modelling based on adapting unstructured meshes. *Int. J. Numer. Methods Fluids* 56, 1003–1015. (doi:10.1002/fld. 1663)
- Pollard, R., Sanders, R., Lucas, M. & Statham, P. 2007 The CROzet natural iron bloom and EXport experiment CROZEX. Deep Sea Res. II 54, 1905–1914. (doi:10.1016/j.dsr2.2007.07.023)
- Pörtner, H. O., Langenbuch, M. & Michaelidis, B. 2005 Synergistic effects of temperature extremes, hypoxia, and increases in CO₂ on marine animals: from Earth history to global change. J. Geophys. Res.-Oceans 110, C09S10. (doi:10.1029/2004JC002561)
- 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. (doi:10.3354/meps07093)
- Quack, B. & Wallace, D. W. R. 2003 Air-sea flux of bromoform: control rates and implications. Glob. Biogeochem. 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, the Royal Society, London, UK.

- Redfield, A. C. 1934 On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In: *James Johnstone memorial volume*, pp. 176–192. Liverpool, UK: 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. Geophys. Res. Lett. 33, L10607–L10608. (doi:10.1029/2006GL025791)
- Rex, M. A. et al. 2006 Global bathymetric patterns of standing stock and body size in the deep-sea benthos. Mar. Ecol.-Prog. Ser. 317, 1–8. (doi:10.3354/meps317001)
- Riebesell, U., Zondervan, I., Rost, B., Tortell, P. D., Zeebe, R. E. & Morel, F. M. M. 2000 Reduced calcification of marine plankton in response to increased atmospheric CO₂. *Nature* 407, 364–367. (doi:10.1038/35030078)
- Riebesell, U. *et al.* 2007 Enhanced biological carbon consumption in a high CO₂ ocean. *Nature* **450**, 545–549. (doi:10.1038/nature06267)
- Riegman, R., Noordeloos, A. A. M. & Cadee, G. C. 1992 Phaeocystis blooms and eutrophication of the continental coastal zones of the North-Sea. *Mar. Biol.* **112**, 479–484. (doi:10.1007/ BF00356293)
- Riemann, L., Steward, G. F. & Azam, F. 2000 Dynamics of bacterial community composition and activity during a mesocosm diatom bloom. *Appl. Environ. Microbiol.* 66, 578–587. (doi:10.1128/ AEM.66.2.578-587.2000)
- Rowe, G. T. 1983 Biomass and production of the deep-sea macrobenthos. In *The sea*, vol. 8 (ed. G. T. Rowe), pp. 97–121. New York, NY: Wiley Interscience.
- Sarmiento, J. L. & Gruber, N. 2002 Sinks for anthropogenic carbon. *Phys. Today* 55, 30–36. (doi:10.1063/1.1510279)
- Sarmiento, J. L., Murnane, R., Lequere, C., Keeling, R. & Williams, R. G. 1995 Air-sea CO₂ transfer and the carbon budget of the north-Atlantic. *Phil. Trans. R. Soc. B* 348, 211–219. (doi:10.1098/rstb.1995.0063)
- Sarthou, G. et al. 2003 Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean. Deep Sea Res. I 50, 1339–1352. (doi:10.1016/S0967-0637 (03)00126-2)
- Shepherd, J. G., Inglesias-Rodriguez, D. & Yool, A. 2007 Geo-engineering might cause, not cure, problems. *Nature* 449, 781. (doi:10.1038/449781a)
- Shoji, K. & Jones, I. S. F. 2001 The costing of carbon credits from ocean nourishment plants. Sci. Total Environ. 277, 27–31. (doi:10.1016/S0048-9697(01)00832-4)
- Smythe-Wright, D., Boswell, S. M., Breithaupt, P., Davidson, R. D., Dimmer, C. H. & Eiras Diaz, L. 2006 Methyl iodide production in the ocean: implications for climate change. *Glob. Biogeochem. Cycles* 20, GB3003. (doi:10.1029/2005GB002642)
- Sokolova, M. N. 2000 Feeding and trophic structure of the deep-sea macrobenthos. Washington, DC: Smithsonian Institution Libraries.
- Solomon, S., Garcia, R. R. & Ravishankara, A. R. 1994 On the role of iodine in ozone depletion. J. Geophys. Res. 99, 20 491–20 499. (doi:10.1029/94JD02028)
- Stenseth, N. C., Mysterud, A., Ottersen, G., Hurrell, J. W., Chan, K.-S. & Lima, M. 2002 Ecological effects of climate fluctuations. *Science* 297, 1292–1296. (doi:10.1126/science.1071281)
- Stoll, H. M., Shimizu, N., Archer, D. & Ziveri, P. 2007 Coccolithophore productivity response to greenhouse event of the Paleocene–Eocene Thermal Maximum. *Earth Planet. Sci. Lett.* 258, 192–206. (doi:10.1016/j.epsl.2007.03.037)
- Tappin, A. D. 2002 An examination of the fluxes of nitrogen and phosphorus in temperate and tropical estuaries: current estimates and uncertainties. *Estuar. Coast. Shelf Sci.* 55, 885–901. (doi:10.1006/ecss.2002.1034)
- Timmermans, K. R., Stolte, W. & de Baar, H. J. W. 1994 Iron-mediated effects on nitrate reductase in marine phytoplankton. *Mar. Biol.* 121, 389–396. (doi:10.1007/BF00346749)
- Tyrrell, T. 1999 The relative influences of nitrogen and phosphorus on oceanic primary production. Nature 400, 525–553. (doi:10.1038/22941)

- Tyrrell, T., Maranon, E., Poulton, A. J., Bowie, A. R., Harbour, D. S. & Woodward, E. M. S. 2003 Large-scale latitudinal distribution of *Trichodesmium* spp. in the Atlantic Ocean. J. Plankton Res. 25, 405–416. (doi:10.1093/plankt/25.4.405)
- Tyson, R. V. 1995 Sedimentary organic matter. London, UK: Chapman and Hall.
- Underdal, B., Skulberg, O. M., Dahl, E. & Aune, T. 1989 Disastrous bloom of *Chrysochromulina polylepis* (Prymnesiophyceae) in Norwegian coastal waters 1988—mortality in marine biota. *Ambio* 18, 265–270.
- UNEP 2004 United Nations Environment Programme 2004. GEO year book 2003. GEO Section/UNEP, Nairobi.
- Vogt, R., Sander, R., Glasow, R. V. & Crutzen, P. J. 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. (doi:10.1023/A:1006179901037)
- Watson, A. J. 1997 Volcanic iron, CO₂, ocean productivity and climate. Nature 385, 587–588. (doi:10.1038/385587b0)
- Weber, L., Volker, C., Schartau, M. & Wolf-Gladrow, D. A. 2005 Modeling the speciation and biogeochemistry of iron at the Bermuda Atlantic time-series study site. *Glob. Biogeochem. Cycles* 19, GB1019. (doi:10.1029/2004GB002340)
- Weeks, S. J., Currie, B. & Bakun, A. 2002 Satellite imaging: massive emissions of toxic gas in the Atlantic. Nature 415, 493–494. (doi:10.1038/415493b)
- 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. *Prog. Oceanogr.* 59, 409–441. (doi:10.1016/j.pocean. 2003.11.003)
- Yool, A., Shepherd, J. G., Bryden, H. L. & Oschlies, A. Submitted. The efficiency of nutrient translocation for enhancing oceanic uptake of carbon dioxide.
- Yoshida, T., Hayashi, K. & Ohmoto, H. 2002 Dissolution of iron hydroxides by marine bacterial siderophore. *Chem. Geol.* 184, 1–9. (doi:10.1016/S0009-2541(01)00297-2)
- 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, R. E. & Wolf-Gladrow, D. 2001 CO_2 in seawater: equilibrium, kinetics, isotopes. Amsterdam, The Netherlands: Elsevier.
- Zhou, S. & Flynn, P. 2005 Geoengineering downwelling ocean currents: a cost assessment. Clim. Change 71, 203–220. (doi:10.1007/s10584-005-5933-0)
- Zondervan, I., Zeebe, R. E., Rost, B. & Riebesell, U. 2001 Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO₂. *Glob. Biogeochem. Cycles* **15**, 507–516. (doi:10. 1029/2000GB001321)