



THEME SECTION

Implications of large-scale iron fertilization of the oceans

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CONTENTS

Boyd PW Introduction and synthesis.....213–218	de Baar HJW, Gerringa LJA, Laan P, Timmermans KR Efficiency of carbon removal per added iron in ocean iron fertilization.....269–282
Denman KL Climate change, ocean processes and ocean iron fertilization.....219–225	Law CS Predicting and monitoring the effects of large-scale ocean iron fertilization on marine trace gas emissions.....283–288
Freestone D, Rayfuse R Ocean iron fertilization and international law.....227–233	Gnanadesikan A, Marinov I Export is not enough: nutrient cycling and carbon sequestration.....289–294
Orbach MK Cultural context of ocean fertilization.....235–242	Cullen JJ, Boyd PW Predicting and verifying the intended and unintended consequences of large-scale ocean iron fertilization.....295–301
Huesemann MH Ocean fertilization and other climate change mitigation strategies: an overview.....243–250	Watson AJ, Boyd PW, Turner SM, Jickells TD, Liss PS Designing the next generation of ocean iron fertilization experiments.....303–309
Leinen M Building relationships between scientists and business in ocean iron fertilization.....251–256	
Karl DM, Letelier RM Nitrogen fixation-enhanced carbon sequestration in low nitrate, low chlorophyll seascapes.....257–268	

Introduction and synthesis

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ABSTRACT: A historical perspective of the scientific study of ocean iron fertilization (OIF) over the last 15 yr prefaces a short synthesis of the multi-faceted issues raised by the 11 contributions to this Theme Section. These issues, which range from ethical to logistical, must be aired in discussions surrounding OIF and its commercial application as a potential climate mitigation tool. Two other issues, not considered in detail by the contributors, are also addressed: (1) the importance of the rate of change in atmospheric CO₂ following sustained global OIF (other than model simulations, the only data presently available to assess this comes from the geological record, e.g. Vostok ice core record of dust supply and atmospheric CO₂); and (2) the necessity of making realistic estimates of the cost of OIF (i.e. carbon sequestered per unit of iron added) to provide comparisons of the ratio of cost:environmental risk of OIF with other mitigation strategies.

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HISTORICAL PERSPECTIVE

Ocean fertilization with nutrients is one of 2 potential methods of using the ocean to mitigate atmospheric CO₂ concentrations that have received both wide media interest (Young 2007) and considerable scientific scrutiny (Boyd et al. 2007, Glibert et al. 2008). (The other method is deep ocean CO₂ disposal; Parks 1999, Brewer et al. 1999, Tamburri et al. 2000). Initial discussion of the use of ocean iron fertilization (OIF) as a CO₂ mitigation strategy resulted from John Martin's iron hypothesis (Martin 1990), in which he linked contemporary findings of the limitation of phytoplankton growth rates by iron supply (in 3 large oceanic regions) with variations in dust supply, anti-correlated with changes in atmospheric CO₂, in the geological record. Prior to the publication of Martin's study, the release of a report on OIF by the US National Research Council Board on Biology resulted in a wave of publicity that included front-page headlines about OIF and climate mitigation in newspapers including the Washington Post.

The first comprehensive scientific evaluation of OIF as a mitigation strategy came at a meeting sponsored by the American Society of Limnology and Oceanography (ASLO) in San Marcos, California, in February 1991. More than 30 papers on aspects of OIF were published in a special issue of *Limnology and Oceanography* (Chisholm & Morel 1991). Over 15 yr later, many of the issues raised and questions they posed remain: the motivation for OIF (a 'cheap, fast and easy' solution), the ethics of 'a massive intervention in the earth's biogeochemical cycle,' and how to devise 'philosophical and/or political frameworks for decision making about conducting OIF globally' (Chisholm & Morel 1991, Preface). The outcome of this ASLO meeting was a consensus resolution of the participants that highlighted the scientific uncertainty of OIF as a mitigation strategy, which, even if implemented globally would probably have a short-term (years) and a relatively small effect that would merely delay the rise of atmospheric CO₂ by several years, and thus be ineffectual in contributing to a long-term reduction on atmospheric CO₂ levels. ASLO also advocated further research into OIF effects on the regulation of ocean productivity and its role in the carbon cycle, and advised against using OIF as a policy option for climate mitigation.

In the ensuing 15 yr there has been a large body of research conducted, ranging from laboratory culture experiments (Sunda & Huntsman 1995), to shipboard studies (Hutchins et al. 2001) and OIF modelling simulations (Aumont & Bopp 2006). However, the most thorough investigation has come from eleven 10 km length-scale OIF experiments in subtropical, subpolar and polar high-nitrate, low-chlorophyll

(HNLC) waters between 1993 and 2005 (de Baar et al. 2005, Boyd et al. 2007). There have been OIF tests conducted by commercial companies (Markels & Barber 2001, Schiermeier 2003). These OIF studies by commercial stakeholders were viewed as controversial and resulted in widespread debate within the scientific community (Chisholm et al. 2001, Johnson & Karl 2002) that is still ongoing as evidenced during a symposium on OIF at Woods Hole Oceanographic Institution in October 2007 involving scientists, policy makers and commercial stakeholders (Powell 2008).

AIMS OF THIS THEME SECTION

Within this Theme Section there are commentaries and research articles by a wide range of academics, each of whom brings expertise on aspects of the many scientific, technical, legal, commercial, environmental and ethical issues that encompass OIF. It is hoped that their counterpoint and breadth of discussion will provide a valuable tool for research scientists policy makers, educators and students to both grasp the complexity of the issues involved, and to assist with attaining a clearer picture of the key issues and the way forward.

The Theme Section commences with Denman, who examines OIF within the context of the ocean carbon cycle and global climate (Denman 2008, this Theme Section). He does this by stepping through 4 central issues (from mitigation objectives to side-effects) related to OIF. This assessment is followed by commentaries from Freestone & Rayfuse on legal and environmental considerations of OIF and how these considerations relate to existing legislation for the ocean (e.g. the Law of the Sea [LOSC]) and the environment (Kyoto Protocol) (Freestone & Rayfuse 2008, this Theme Section), and from Orbach on the ethics of altering the ocean commons by using global-scale manipulations such as OIF (Orbach 2008, this Theme Section). Huesemann then puts OIF into the context of other mitigation schemes, such as geological carbon sequestration and renewable energy generation from biomass (Huesemann 2008, this Theme Section). Such schemes were discussed at a geoengineering symposium at Harvard University (Kintisch 2007). Huesemann's article leads on to a commentary by Leinen (of the company CLIMOS, www.climos.com), who describes how scientists and business can better align themselves to carry out OIF studies at scales larger than the 10 km length scale of the first-generation experiments (Leinen 2008, this Theme Section). Such studies are required to better understand the longer term and larger scale impacts of OIF (Buesseler et al. 2008).

The remainder of the Theme Section focuses on some key unresolved scientific questions. Karl & Lete-

lier explore whether fertilization—either via iron and/or phosphate enrichment or stimulation of the upwelling of nutrient-rich waters (Lovelock & Rapley 2007)—of the oligotrophic low-latitude ocean will result in blooms of nitrogen fixers, ultimately resulting in the net transport of carbon to the deep sea (Karl & Letelier 2008, this Theme Section). De Baar et al. discuss the efficiency of OIF at removing CO₂ from the atmosphere and the range of factors that determine this efficiency (De Baar et al. 2008, this Theme Section). Law provides insights into how the concentrations of other biogenic gases in the upper ocean, which have potentially negative (i.e. nitrous oxide) or positive (dimethylsulphide) effects on radiative forcing and hence climate, might be altered during the proposed larger scale (>10 km) and longer (months) OIF studies (Law 2008, this Theme Section).

In the only modelling study in this Theme Section, Gnanadesikan & Marinov present simulations of the longer-term (years to decades) biogeochemical trajectory (and the interplay with ocean circulation) and fate of a large-scale (4° × 4°) OIF study (Gnanadesikan & Marinov 2008, this Theme Section). They conclude that the veracity of OIF as a mitigation strategy is more closely aligned to the fate of the nutrients taken up by the biota than to the export of carbon to depth. The 2 concluding papers deal with logistical and technical issues. Cullen & Boyd comment on the difficulties posed by verification of the outcomes from OIF (Cullen & Boyd 2008, this Theme Section) and Watson et al. provide an analysis of what will be required (from both modellers and observationalists) to devise, design and implement the second generation of OIF (at a 100 km length scale) (Watson et al. 2008, this Theme Section).

OTHER ISSUES

Despite the breadth of issues tackled and the wider range of views aired in this Theme Section, 2 important topics receive less attention than they merit: (1) the utility of the geological record in assessing the time-scales of carbon sequestration resulting from global OIF, and (2) the financial cost of carbon sequestration during large-scale OIF studies.

Geological records of the temporal relationship between OIF and climate

In a recent policy statement on OIF, Buesseler et al. (2008) indicate that if widespread (i.e. global) OIF was to be viewed as a wedge to help stabilise atmospheric CO₂ concentrations (Pacala & Socolow 2004), the rate of change in atmospheric CO₂ due to global OIF will be

just as critical as its magnitude. Buesseler et al. (2008) reported an upper bound for sequestration of 0.5 Gt C yr⁻¹, corresponding to a reduction of 0.24 ppmv atmospheric CO₂ yr⁻¹ (Cullen & Boyd 2008). However, this sequestration estimate was based on a modelling study of global OIF (Aumont & Bopp 2006). Given the critical importance of estimating the rate of OIF-mediated C sequestration in order to assess whether it can be viewed as a climate stabilisation wedge, there is one dataset—from the geological past—that can be used to evaluate the predictions from models of global OIF.

The Vostok ice core record of dust and atmospheric CO₂ concentrations across 4 glacial–interglacial cycles was the centrepiece of the iron hypothesis (Martin 1990) and led to OIF being considered as a potential climate mitigation tool (Keith & Dowlatabadi 1992). Much of the subsequent debate on the Vostok record has focussed on (1) what mechanism(s) caused the 80 ppmv change in atmospheric CO₂ concentrations and their relative contribution to this change (Watson et al. 2000, Toggweiler et al. 2006), and (2) the timing of changes in the dust flux relative to those in atmospheric CO₂ (Watson et al. 2000). It has been suggested that up to 30% of the 80 ppmv atmospheric CO₂ drawdown could be attributed to OIF (Sigman & Boyle 2000) and modelling studies indicate that increased dust supply probably caused the initial decrease (i.e. up to 25 ppmv) in atmospheric CO₂, and was then superseded by other causative mechanisms that drew down a further 55 ppmv (Watson et al. 2000). Thus, the magnitude of atmospheric CO₂ drawdown due to global OIF has an upper bound of ca. 25 ppmv.

The temperature–CO₂ relationship from Vostok has been interpreted as a marked alteration of global climate to which OIF made a significant contribution; therefore the magnitude of this signal has been cited widely by observationalists (Martin 1990, de Baar et al. 2005), modellers (Aumont & Bopp 2006) and commercial ventures (e.g. www.climos.com) interested in the OIF debate. However, there has been little emphasis to date on the equal importance of the rate of change in atmospheric CO₂ due to global OIF (Boyd et al. 2007).

Given the difficulties in planning and conducting an OIF event at the 100 km length scale (Watson et al. 2008), the Vostok record is a valuable resource that provides the most robust data available for the likely outcome from a sustained (i.e. millennia) global OIF event (termed here Vostok OIF), and thus gives a low-cost snapshot (relative to the outlay of doing a large scale OIF event, Watson et al. 2008) of the biogeochemical and climatic signature of such a global OIF event. Examination of the highest resolution (<500 yr) data of the Vostok record (Petit et al. 1999) reveals a ca. 20 ppmv drawdown in atmospheric CO₂ concentrations over roughly 5000 to 10 000 yr (Fig. 1). This yields

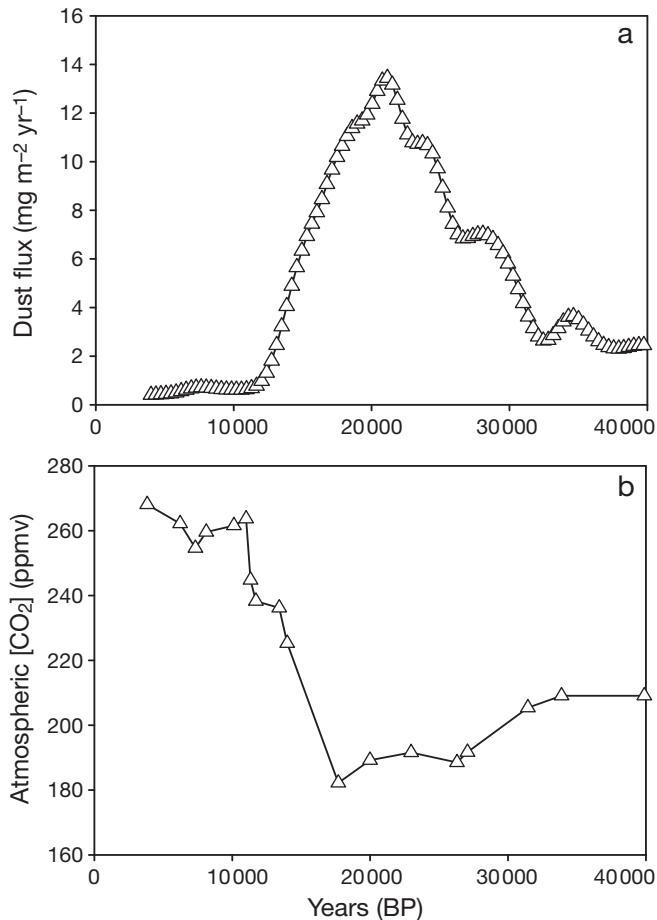


Fig. 1. High-resolution plots of the (a) dust flux and (b) atmospheric CO₂ concentrations from the Vostok ice core record for the most recent glacial termination (i.e. the highest resolution data in the record were available for this period; Petit et al. 1999). The plots clearly indicate the 5000–10 000 yr timescale for decreases in atmospheric CO₂ due to significant increases in the dust flux. The asymmetry in the atmospheric CO₂ record, relative to that for dust, is due to ocean iron fertilization (OIF) being only one of the mechanisms responsible for the observed changes in atmospheric CO₂; see modelling simulations by Watson et al. (2000), their Fig. 2b. Note, alternative hypotheses for the changes in the atmospheric CO₂ records have been proposed (e.g. intensity of upwelling, Toggweiler et al. 2006)

a C sequestration rate of 0.01 to 0.005 Gt C yr⁻¹, which is significantly less than that estimated from modelling studies of global OIF (Aumont & Bopp 2006) and would therefore not represent a 'Pacala & Socolow' climate stabilization wedge (Pacala & Socolow 2004). Hence, a better understanding of the underlying reasons for the disparity between the modelling study (Aumont & Bopp 2006) and the Vostok record (Fig. 1) is urgently required.

The outcome of the Vostok OIF is the integral of a wide range of oceanic processes over millennia that may be altered directly (primary and export produc-

tion) or indirectly (biogenic gas production, foodweb structure) due to OIF and about which little is known on scales >1000 km² and >1 mo (Boyd et al. 2007). The impact of the Vostok OIF is reported to be greater in the Southern Ocean than in low latitude regions (Winckler et al. 2008); nonetheless, it does represent a global OIF event where dust supply increased worldwide—albeit by different magnitudes in each HNLC region (Winckler et al. 2008).

In models such as that of Aumont & Bopp (2006) (see also Table 1 in Denman 2008), there are marked differences in how OIF is parameterized relative to what is evident from the Vostok record, such as dissolved iron being maintained at 2 nM following an instantaneous increase at onset of the model run (cf. our Fig. 1). This and other factors prescribed in the model, such as the relatively high efficiency of carbon sequestration may in part explain the up to 100-fold difference in the C sequestration rate between the simulations and Vostok. An additional distinction between Vostok and the Aumont & Bopp (2006) model is that the latter is run under elevated atmospheric CO₂ concentrations (due to climate change). A global OIF simulation by Aumont & Bopp (2006) with no increase in atmospheric CO₂ (i.e. comparable to the geological past) resulted in a <10 ppmv CO₂ drawdown, but note this occurs within 100 yr and so is still much more rapid than reported for Vostok. To determine whether global OIF could be a stabilization wedge, the reasons for the 100-fold difference in the rates of iron-mediated C sequestration between models and geological records require better resolution of the timescales and modes of control of global OIF.

Evaluating the cost of sequestering carbon via OIF

The principal attraction of using OIF as a mitigation strategy is the notion that it is a 'cheap, fast and easy' solution to climate change. This notion has been propagated through the popular press since the early 1990s and was discussed in Chisholm & Morel (1991). It has been proposed that OIF could be carried out at low cost relative to other mitigation strategies (Keith et al. 2005, Huesemann 2008); this was based on \$US 2 US ton⁻¹ C (1 US ton = 0.9072 t) sequestered (Markels & Barber 2001). Other estimates of \$US 5 US ton⁻¹ C sequestered are reported online (www.en.wikipedia.org/wiki/Iron_fertilization). The calculations of Markels (see <http://www.patentstorm.us/patents/6440367.html>) appear to be based on several assumptions: (1) that 'each US ton of iron dumped could pull 30 000 US tons of carbon from the atmosphere' (i.e. an Fe:C molar ratio of 7.27×10^{-6}) (http://www.wired.com/wired/archive/8.11/ecohacking_pr.html); and (2) that 53% of the iron-

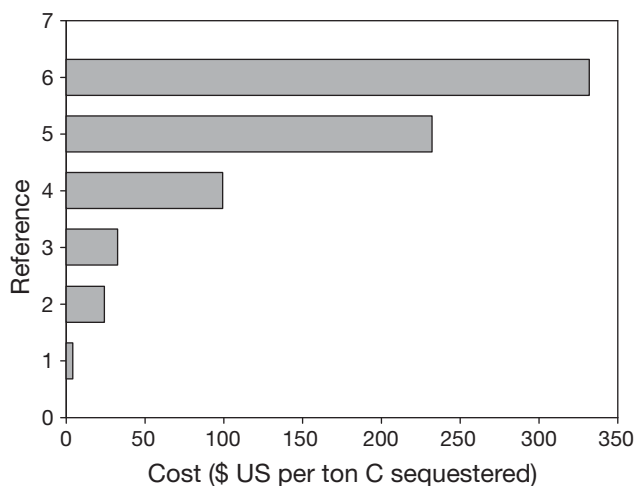


Fig. 2. Revised estimates of the cost of C sequestration by ocean iron fertilization (OIF). The estimates are based on the range of Fe:C molar ratios reported for mesoscale OIF studies and from naturally occurring blooms. These ratios are converted to a cost by simply scaling them using the Markels' Fe:C ratio of 1.37×10^{-5} as equivalent to \$US 2 US ton⁻¹ C sequestered. Reference 1: Markels' original estimate (http://www.wired.com/wired/archive/8.11/ecohacking_pr.html); 2: Fe:C from Southern Ocean phytoplankton (Twining et al. 2004); 3: mixed layer particulate Fe:C from the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) OIF (Boyd et al. 2004); 4: Fe:C in sinking particles from the North Atlantic Bloom Experiment (Martin et al. 1993); 5 and 6: Fe:C in sinking particles, 5: exiting the mixed layer, and 6: sinking through the permanent pycnocline (120 m depth) during the SERIES OIF, respectively (Boyd et al. 2004). These Fe:C ratios are summarized in Boyd et al. (2007), their Fig. 3. Note these estimates do not include other potential costs, such as fisheries loss levy that are listed in the main text. 1 US ton = 0.9072 t

mediated increases in algal carbon are sequestered, based on the study of Hansell et al. (1997) in the equatorial Pacific (P. Lam & S. W. Chisholm unpubl. data)¹. Taken together, this information suggests that each US ton of iron dumped could sequester 15 900 US tons of carbon (i.e. an Fe:C molar ratio of 1.37×10^{-5}). Evidence from a mesoscale OIF event where the fate of the iron-mediated increase in algal carbon was measured directly (Boyd et al. 2004) and from natural open ocean blooms (Martin et al. 1993, de Baar et al. 2008) reveal that the C sequestration efficiency assumed by Markels is a significant overestimate; therefore the cost of sequestering carbon using OIF has so far been underestimated (Fig. 2).

Furthermore, the revised cost of C sequestration must also take into account other factors not included in the original estimate by Markels, including any deleterious downstream effects of OIF on the produc-

tivity of commercial fisheries, where a fisheries loss levy could be up to \$US 150 US ton⁻¹ C sequestered (Gnanadesikan et al. 2003). From discussion of how 100 km length scale second generation OIF studies will be conducted (Watson et al. 2008) it is clear that the requisite OIF delivery systems (multiple vessels or aircraft), monitoring (remote-sensing), research and development (modelling), and verification (employment of independent evaluators) will also have to be included in such a cost estimate. These costs, when applied to a 100 km length-scale OIF event will probably not scale linearly but increase as a step function (Watson et al. 2008). There are also potentially hidden costs depending on the eventual outcome of OIF, including deduction of C offsets due to unanticipated side effects, such as greenhouse gas production (Law 2008). Although uncertainties remain, revised estimates—based simply on scaling Markel's original cost estimate to the C sequestration or export measured during first-generation OIF studies, such as SERIES (NE Pacific), indicate that the cost of C sequestered using OIF is between \$US 30 and \$US 300 t⁻¹ (Fig. 2).

This more realistic evaluation of the cost of the carbon sequestered using OIF suggests that the initial attraction—the estimated low cost of this approach—is not valid. The revised estimate of the cost of OIF requires a reappraisal of the ratio of cost:environmental risk relative to other mitigation strategies. For OIF the degree of risk is reported as medium (Keith et al. 2005, Huesemann 2008), due to issues such as the possibility of unintended environmental side effects and difficulties in verification. Thus, OIF can be classified as a medium-risk, medium-cost mitigation strategy that may have similar costs to other, lower-risk mitigation strategies (for example, biomass with carbon capture, which Keith et al. 2005 estimated as costing \$US 300 t⁻¹ C).

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Climate change, ocean processes and ocean iron fertilization

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ABSTRACT: Observations indicate that the rate of increase in concentration of atmospheric CO₂ is increasing faster than projected in any of the Intergovernmental Panel on Climate Change (IPCC) emission scenarios. Several mitigation measures, referred to as 'geoengineering options', have been proposed to remove CO₂ from the atmosphere. To be successful, such a mitigation operation must remove 'significant' CO₂ from the atmosphere for many decades, be verifiable, and not cause deleterious side effects. One option, purposeful addition of iron to fertilize photosynthetic uptake of CO₂ by phytoplankton in regions of the ocean where iron is a limiting nutrient, has received considerable scientific attention. In the last 15 yr, a dozen small-scale open ocean iron fertilization experiments have been performed and a succession of models of large-scale fertilization have been developed. As successive models have become more realistic, the amounts of CO₂ forecast to be sequestered have dropped, and in all cases are small relative to the amounts of CO₂ projected to be released through fossil fuel burning over the next century for any of the IPCC emission scenarios. Possible side effects include a long term reduction in ocean productivity, alteration of the structure of marine food webs, and a more rapid increase in ocean acidity. Most importantly, increased remineralization associated with the increased downward export of organic carbon particles would result in increased production of the third most important long-lived greenhouse gas, N₂O. The magnitude of this effect is poorly known.

KEY WORDS: Climate change · Iron fertilization · Mitigation · Ocean carbon cycle

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BACKGROUND

Recent assessment reports of the Intergovernmental Panel on Climate Change (IPCC) have documented the increasing concentrations of CO₂ in the atmosphere due to anthropogenic activities and their causal link with global warming. The preferred mitigation measure to reverse the rise in atmospheric CO₂ is to reduce emissions of CO₂ from anthropogenic activities, primarily burning fossil fuels and cement production. However, recent studies demonstrate that CO₂ released from fossil fuel emissions is accelerating and the rate of increase of emissions since 2000 exceeds all IPCC Special Report on Emissions Scenarios (SRES) for various human development paths (e.g. projections of population growth, energy use, rate of adaptation of new technology, land use change) over the next century (IPCC 2000, Raupach et al. 2007).

To limit climate change to an 'acceptable' level, e.g. an increase in global surface temperature of 2°C relative to 2000, or a leveling off of atmospheric CO₂ concentration at say 450 ppm, recent model results indicate that we must eventually reduce emissions by at least 90% (Weaver et al. 2007, Matthews & Caldeira 2008). The Kyoto Protocol commits 38 industrialized countries to cut their emissions by 5.2% relative to 1990 levels by the period 2008 to 2012. Given the rapid approach of this deadline and the continuing acceleration of fossil fuel emissions, there is intense discussion (e.g. Crutzen 2006, Kintisch 2007) over proposed mitigation actions, such as injecting sulphate aerosols or other reflecting particles into the stratosphere, establishing large-scale plantations of trees or other plants to sequester CO₂, and iron fertilization of large areas of the ocean, also to sequester CO₂.

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Since the hypothesis of Martin (1990), that ice ages cause increased iron deposition to the ocean via increased dust, which results in increased primary production and sequestration of CO₂, fertilization of the ocean with iron has been proposed as a 'geoengineering' mechanism to mitigate climate change by increasing ocean sequestration of CO₂ through purposeful large-scale fertilization of high-nitrogen, low-chlorophyll (HNLC) regions of the ocean. The scientific community responded to this proposal first with a workshop sponsored by the American Society of Limnology and Oceanography (ASLO) on controls on phytoplankton production (Chisholm & Morel 1991) that included results from the first global model 'thought experiment.' Subsequently, a dozen purposeful, small-scale field experiments were performed, where areas of the open ocean of order of 10 km per side were fertilized from moving ships with ferrous sulphate dissolved in water of appropriate salinity to be neutrally buoyant in the surface waters (de Baar et al. 2005, Boyd et al. 2007). Several recent studies with global ocean carbon-climate models have addressed the efficacy of large-scale fertilization. These models employ increasingly explicit biogeochemistry, incorporating the recent scientific understanding of the physiological and ecological response of the planktonic ecosystem to purposeful fertilization that has been obtained from these open ocean experiments and associated laboratory studies. In September 2007, an Ocean Iron Fertilization workshop was held at Woods Hole Oceanographic Institution, bringing together people representing the scientific, policy, economics, commercial and environmental protection aspects of the issue (www.whoi.edu/page.do?pid=14617). Based on the workshop, Buesseler et al. (2008) have produced a summary of the key issues relating to purposeful ocean iron fertilization.

To evaluate the viability of purposeful open ocean iron fertilization as a mitigation option to slow down the increase in atmospheric CO₂, we need to consider at least 5 issues: (1) state a clear mitigation objective, (2) estimate the amounts of CO₂ being released into the atmosphere, (3) review the ability of the ocean to sequester comparable amounts, (4) identify possible side effects, and (5) determine whether ocean sequestration of CO₂ through iron fertilization can be unambiguously verified. I will only consider the first 4 issues. The final issue, verification, is discussed in a separate article (Cullen & Boyd 2008, this Theme Section).

MITIGATION OBJECTIVE

Based on the above issues, an objective for meaningful mitigation of climate change through purposeful ocean iron fertilization may be stated:

To sequester CO₂ in sufficient quantity and for a sufficient time period to make a significant reduction in the rate of increase of atmospheric CO₂ in a verifiable manner, without deleterious unintended side effects.

SCENARIOS FOR FUTURE RELEASE OF FOSSIL FUELS THROUGH HUMAN ACTIVITIES

From pre-industrial times (before 1750) up to 2000, anthropogenic activities have released about 286 Pg C as CO₂ through the burning of fossil fuels and cement production from limestone (from data of Marland et al. 2007). This value is small compared with what is likely to be released over the next century: the IPCC has produced 40 scenarios for future development of global society, the so-called SRES scenarios (IPCC 2000). For several of the most commonly used scenarios¹, Table 1 gives the cumulative CO₂ emissions from 2000 to 2050 and to 2100. Up to 2100 they range from 918 to 2058 Pg C (for the mean scenarios tabulated in IPCC 2001).

Actual emissions for the 5 yr period 2000 to 2004, estimated at 36.7 Pg C, demonstrate the rapid increase in recent emissions, being ~13% of all emissions for the 250 yr up to 2000. Raupach et al. (2007) showed that since 1999, the rate of increase in fossil fuel emissions exceeds even the highest scenario, A1FI (Table 1), and most likely the annual emissions themselves now exceed those for the A1FI scenario (www.globalcarbonproject.org/carbontrends/index.htm). In addition, results from global coupled carbon cycle climate models (Friedlingstein et al. 2006) indicate that for the A2 SRES scenario, more than 1°C of additional warming by 2100 is projected (because of climate-driven release of additional carbon to the atmosphere), relative to the suite of 'standard' climate models used in the recent IPCC AR4 (IPCC 2007, Chap. 10). For 1 of these models, Matthews (2005) shows that for eventual stabilization of atmospheric CO₂ at say 1000 ppm, an additional 94 Pg C by 2050 and 160 Pg C by 2100 (from 2005) must be sequestered beyond that projected by the model without the carbon cycle–climate feedback, i.e. beyond the amounts given in Table 1.

OCEAN CARBON CYCLE

To help understand the projections of fertilization by global models, I describe next the most relevant characteristics of the ocean carbon cycle, as shown schematically in Fig. 1. When CO₂ enters the surface

¹The IPCC requires all scenarios to be treated as equally probable. The 4 scenarios in Table 1 span the range of fossil fuel emissions given by all the SRES scenarios

Table 1. Cumulative emissions of CO₂ (Pg C) from fossil-fuel burning for several IPCC future emission scenarios (from IPCC 2001, WG1: Appendix 2, Table II.I.I)

IPCC SRES scenario	1751–2000 ^a	2001–2050	2001–2100
A1B	286	622	1367
A1FI	286	681	2058
A2	286	597	1702
B1	286	842	918

^aBased on annual emissions from Marland et al. (2007), available at: http://cdiac.ornl.gov/ftp/ndp030/global.1751_2004.ems

ocean from the atmosphere, it is rapidly dissolved and chemically distributed among the 3 components that comprise dissolved inorganic carbon (DIC): aqueous [CO₂], bicarbonate [HCO₃⁻], and carbonate [CO₃⁼] ions, the latter 2 with negative charge. Corresponding H⁺ ions, released through the dissociation of water molecules, lower the pH of the water simultaneously. Through photosynthetic primary production, CO₂ is taken up by phytoplankton and converted to organic molecules (with some species also forming CaCO₃, referred to in Fig. 1 as particulate inorganic carbon

[PIC]). Photosynthesis requires sunlight and nutrients (nitrogen, phosphorous, iron, etc.) in approximately fixed proportions known as the Redfield ratios. Phytoplankton are grazed by zooplankton and they excrete dissolved organic carbon (DOC) and respire organic carbon back to DIC. In Fig. 1, all particulate ecosystem carbon, living and dead, is grouped together as particulate organic carbon (POC) plus PIC. Much of this carbon, with the associated nutrients, is respired or remineralized within the ocean surface layer on short timescales.

A fraction of this carbon, referred to as export production, sinks out of the surface layer as particles (Fig. 1, sinking POC + PIC) or is transported from the surface layer by mixing and advection of DOC. Most of the POC and DOC are remineralized through the action of bacteria in the top 500 m back into DIC. This remineralization also requires dissolved oxygen when it is available. During remineralization, especially at very low concentrations of dissolved oxygen, some 'denitrification' occurs, producing the gases N₂ and N₂O, which may outgas to the atmosphere when the water parcel enters the surface layer again. A small fraction of POC and PIC reaches the sediments, where some is buried and some is released back into the water column after transformation, i.e. 'diagenesis,' back into dissolved nutrients and DIC.

Large-scale physical advective and mixing processes eventually return the DIC (and associated dissolved inorganic nutrients) in the ocean interior back to the surface layer, where the CO₂ comes into contact with the atmosphere once more. For sequestration to reduce the rate of increase of atmospheric CO₂, this return time-scale must be long enough (at least decades) and the associated dissolved nutrients must be returned as soon as, or sooner than, the DIC, which is possible, as they appear to remineralize at shallower depths than the organic carbon, except for silica.

The first key point is that biological processes set the rate of sequestration of carbon to the ocean interior, but physical processes regulate the time-scale over which the sequestered CO₂ is returned to the surface ocean where it again comes in contact with the atmosphere. The second key point is that fertilization will only work where there are unutilized macronutrients in the sunlit surface layer; these unused macronutrients occur at large concen-

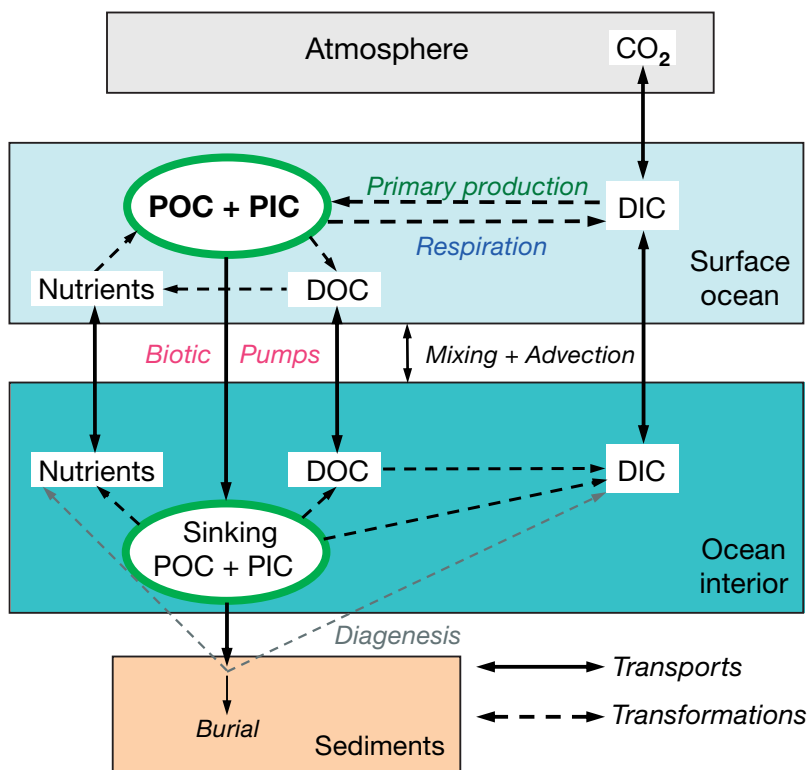


Fig. 1. Schematic of the main components of the ocean carbon cycle, including interactions with the atmosphere and bottom sediments

trations only in the Southern Ocean, the sub-arctic North Pacific, and in the equatorial Pacific, although the return cycle seems to be much shallower and shorter, and therefore less effective at keeping the sequestered CO₂ out of contact with the atmosphere.

RESULTS OF LARGE-SCALE MODEL SIMULATIONS

Sarmiento & Orr (1991) and Kurz & Maier-Reimer (1993) used global models with minimal biology to simulate large-scale fertilization of primarily the Southern Ocean (10 to 15% of the global ocean) continuously for 50 or 100 yr starting in 1990 with the 'business-as-usual' (BaU) scenario (similar to the SRES A2 scenario). Sarmiento & Orr (1991) modelled export production by restoring modelled surface phosphate back to observations with a restoring timescale of 1 mo (standard run). The rate of reduction in surface nutrients (through restoration) was set equal to export production of phosphate and organic carbon. Kurz & Maier-Reimer (1993) included simple biological constraints on the sequestration, due to light and temperature regulation of photosynthetic production, which reduced the total carbon sequestered after 100 yr from 152 Pg C (Sarmiento & Orr 1991) to 106 Pg C (Table 2) and for constant emissions from 127 to 93 Pg C. Both models responded similarly, with an initial peak in CO₂ uptake by the ocean, followed over the next decade or so by a reduction in increased uptake with an offset that appears to be related to the increased carbon being transported around the oceanic carbon conveyor belt described above.

For these 2 idealized model experiments, the total carbon sequestered after 100 yr was on the order of 10% of that which would be released under the BaU/A2 scenario. Hence, the IPCC Second Assessment Report (SAR) concluded (Denman et al. 1996) that iron fertilization was not a feasible mitigation option because of (1) the difficulty of scaling up to such a level (15 to 25% of the global ocean being fertilized continuously for 100 yr), (2) the unknown realized efficiency, and (3) possible unintended ramifications of such a procedure, in particular increased production and outgassing of N₂O (Fuhrman & Capone 1991). N₂O is the third most important long-lived anthropogenic greenhouse gas, with an atmospheric lifetime now estimated to be ~115 yr (IPCC 2007, Chap. 2). Subsequent to the SAR, the Kyoto Protocol was negotiated by member countries of the United Nations Framework Convention on Climate Change (FCCC), but it did not include ocean fertilization as a sequestration method that would qualify for offset credits.

Recent global models incorporating increasingly explicit biology give much reduced sequestration relative to the 2 earlier models (Table 2). Aumont & Bopp (2006), with a more realistic ecosystem and biogeochemical cycles, obtain a cumulative uptake by 2100 of 70 Pg C. If they cease fertilization after 10 yr, the cumulative uptake by 2100 is less than 7 Pg C (their Fig. 7c). Zahariev et al. (2008), with a 4-component ecosystem that has nitrogen and light limitation of primary production even when iron limitation is removed, have conducted a simulation of the 'pre-industrial' ocean (no fossil fuel emissions) similar to that of Kurz & Maier-Reimer (1993). Zahariev et al. (2008) obtained a

Table 2. Global cumulative increased uptake of CO₂ (Pg C) after 100 yr for iron fertilization, forced by IPCC 'Business as usual' (BaU) or A2 scenarios, or Pre-industrial (no emissions); phyto.: phytoplankton, zoopl.: zooplankton, POM: particulate organic matter, DOM: dissolved organic matter, NPZD: nutrient + phytoplankton + zooplankton + detritus

Scenario	Fertilization protocol	Representation of the marine ecosystem	Total carbon sequestered (Pg C)	Source
BaU	Global, continuous	Complete nutrient restoring	152 (98–180) ^a	Sarmiento & Orr (1991)
BaU <i>Pre-industrial</i>	Southern Ocean, 6 mo	Nutrient restoring: rate a function of light, temperature, and 'turbulence'	106 72	Kurz & Maier-Reimer (1993)
BaU	20% ocean area, 15 ^b times yr ⁻¹	Ratio of C-export to Fe-added from Buesseler et al. (2004)	32	Zeebe & Archer (2005)
A2	Global, continuous	Complex ecosystem model: 5 nutrients, 2 phyto., 2 zoopl., 2 POM, 1 DOM (Aumont et al. 2003)	70	Aumont & Bopp (2006)
Pre-industrial	Global, continuous	NPZD + simple calcifiers and N-fixers	26	Zahariev et al. (2008)

^aRange of results for different remineralization depth scales, restoring times, and gas exchange coefficients
^bRepresents twice the Earth's surface each year

much-reduced CO₂ sequestration after 100 yr of only 26 Pg C, as compared to 72 Pg C in Kurz & Maier-Reimer (1993).

In most of the recent small-scale fertilization experiments, iron injection was repeated several times over the course of 10 to 14 d because of rapid loss of bioavailable iron beyond what can be accounted for through uptake by phytoplankton (de Baar et al. 2005, Boyd et al. 2007). The small scales of these experiments, the requirement for multiple injections of iron, and the low efficiency of carbon sequestration all make the scenario of 15 to 25% of the global ocean being fertilized continuously for 50 to 100 yr even more difficult to imagine.

To mimic the effects of the recent fertilization experiments, modellers have simulated these patch experiments. Gnanadesikan et al. (2003), with a nutrient-restoring representation of fertilized primary production, estimated that after 100 yr the loss from the atmosphere would be only 2 to 44% of the initial uptake pulse for patches of a few 100s of km per side fertilized for limited periods of order 1 mo. Amounts of carbon sequestered after 100 yr are at most 10s of Tg C, compared with expected cumulative emissions of order 10⁶ Tg C (1000 Pg C = 10⁶ Tg C, Table 1). Furthermore, the initial fertilization reduces nutrients in the upper few hundred meters over several years, leaving the remaining high nutrients at greater depths and increasing the time scale of their return to the surface layer, thereby reducing century-scale export biological productivity by a factor of up to 30. This reduced export production due to more carbon and nutrients being transported to greater depths has been found in other studies (e.g. Zahariev et al. 2008). From a recent purposeful iron fertilization experiment, Zeebe & Archer (2005) estimated an efficiency for iron fertilization of ~10 to 25%. Using a global model and this efficiency, they found that fertilizing 20% of the global ocean 15 times yr⁻¹ until 2100 would sequester less than 32 Pg C. This procedure is equivalent to fertilizing about twice the area of the Earth's surface each year.

The results of the studies summarized in Table 2 are highly dependent on the representation of critical biological, chemical and physical processes in the models. Jin et al. (2008), with the most comprehensive biogeochemical/ecological model of the studies described here, and with a highly resolved euphotic zone, obtained results that contrast with the other studies. They fertilized patches in the eastern tropical Pacific of various sizes and under various temporal schedules. Because the fertilization and enhanced primary production occur just below the sea surface (as in the shipborne fertilization experiments to date), their model gives high atmospheric uptake efficiencies (the ratio of the perturbation in air-sea CO₂ flux to the perturba-

tion in export flux across 100 m integrated over 10 yr) of 0.75 to 0.93. Larger area fertilizations, especially those when light profiles were adjusted to give the greatest increase in fertilized primary production near the bottom of the euphotic zone, give much lower atmospheric uptake efficiencies. Even with their high efficiency of fertilization, for a simulation of fertilization of the entire north and tropical Pacific, the air to sea flux over 10 yr is only 3.4 Pg C (small relative to the range of expected fossil fuel emissions for the 4 SRES scenarios of Table 1 of 92 to 109 Pg C for the 10 yr period 2011 to 2020).

POSSIBLE SIDE EFFECTS

There are several known possible side effects of large-scale iron fertilization, but we have little knowledge of their potential magnitudes. (1) Increased remineralization, mostly within the 500 m below the euphotic zone, requires dissolved oxygen at a rate of O₂:C near 1.5:1 (mol:mol). Box models (and Sarmiento & Orr 1991) predicted wide areas of the subsurface ocean becoming anoxic under large-scale continuous fertilization, but as the magnitude of projected sequestration has decreased, anoxic regions have been replaced by low oxygen regions. (2) More importantly for climate change, increased remineralization results in increased denitrification and production of N₂O, the third most plentiful long-lived greenhouse gas affected by anthropogenic activities. We do not yet have reliable estimates of magnitudes of this source at the global scale (Law 2008, this Theme Section). (3) The productivity and structure of marine ecosystems would change. Projections by Gnanadesikan et al. (2003), Aumont & Bopp (2006), and Zahariev et al. (2008) all indicate a reduction in primary production and in biological export of carbon on the multi-decadal to century timescale, due to the reduction in available macronutrients returning to the surface ocean. Over large scales this reduction could translate into a reduction in harvestable marine resources. Iron fertilization also alters the species composition of phytoplankton (at least temporarily in the short-term fertilization experiments conducted to date). Initially, there may be an increase in smaller phytoplankton abundance, but after a week or more, the increasing biomass of diatoms dominates that of all other phytoplankton groups (Marchetti et al. 2006, for the 2002 Subarctic Ecosystem Response to Iron Enrichment Study [SERIES]). Sustained fertilization would favour diatoms and hence, through grazing transfers, copepods over smaller microzooplankton; towards the end of the SERIES observation period, Tsuda et al. (2006) observed a migration upwards into the patch of some

species of mesozooplankton, as well as an increase in nauplii and larvae of some species, hypothesized to be due to reduced grazing on them. A shift to diatoms results in greater drawdown of silicic acid relative to nitrate (Boyd et al. 2004), a process that could not continue over an extended fertilization.

Production of the climate-active gas dimethylsulfide (DMS) is also altered by iron fertilization. Its precursor, dimethylsulfoniopropionate (DMSP), is produced by some species of phytoplankton. Some DMS outgasses to the atmosphere and is the largest natural source term in the global atmospheric sulphur budget. DMS stimulates the formation of cloud condensation nuclei (Liss et al. 2005). Several of the iron fertilization experiments showed a short-term increase in surface ocean DMS concentrations (Boyd et al. 2007), but following that initial increase, the SERIES experiment showed a decrease of DMS in the patch relative to concentrations outside the patch (Levasseur et al. 2006). As the diatoms (which produce little DMSP) out-competed other functional groups of phytoplankton, they apparently displaced DMSP-producing species (Steiner & Denman 2008). Because most iron-fertilized patches have been observed for less than 1 mo, we have no information on what magnitude longer-term changes in ecosystem structure and function might be. Boyd et al. (2008) conclude that our quantitative understanding of the adaptability of phytoplankton based on observations from field and laboratory studies is inadequate to forecast their responses to 'slow' changes in their environment, such as those forecasted for the Southern Ocean over the next 2 decades.

The fourth known possible side effect of large-scale iron fertilization is the issue of increasing ocean acidity; CO₂ added to the ocean rapidly dissolves and dissociates into bicarbonate and carbonate ions, adding H⁺ ions (i.e. protons) to the oceans, thereby reducing pH and increasing acidity. Stimulating increased sequestration of CO₂ to the oceans through widespread successful iron fertilization would increase the cumulative acidity more rapidly and would change the depth distribution of remineralization back to DIC. Arguments that this CO₂ will end up in the ocean eventually even without fertilization ignore the scientific issue of how quickly marine organisms can adapt, through diversity of species occupying an ecological niche (e.g. calcifiers such as coccolithophores), diversity within species (physiological 'plasticity'), and through genetic mutations. The more rapidly pH decreases, either in the surface layer or at depth where there is increased remineralization due to fertilization, the more likely it is that organisms will be unable to adapt, both to the increased acidity and, in the subsurface zones of increased remineralization, to the related decrease in dissolved oxygen.

WHAT IS THE PROSPECT OF IRON FERTILIZATION AS AN EFFECTIVE MITIGATION MEASURE?

In IPCC AR4 (Denman et al. 2007), the IPCC again dismissed purposeful fertilization as a viable mitigation measure, primarily because of lack of feasibility. Perhaps based on the proposal by Pacala & Socolow (2004) of 'stabilization wedges' of mitigation measures, a collection of small measures, each reaching ~1 Pg C yr⁻¹ within 50 yr, can result in a cumulative sequestration large enough to stabilize emissions. Under this scenario of a collection of mitigation measures, CO₂ sequestration through iron fertilization remains a potential mitigation measure for consideration. But the tendency for the magnitude of sequestration to decrease over time, the small amounts of CO₂ likely to be sequestered relative to the large amounts to be released through fossil fuel burning, the difficulty with verification, and the possible negative side effects—none of which have known magnitudes—all must be thoroughly addressed in any future iron fertilization experiments (e.g. Watson et al. 2008, this Theme Section) before iron fertilization should be attempted at large scales for climate mitigation.

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Climate change, ocean processes and ocean iron fertilization

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ABSTRACT: Observations indicate that the rate of increase in concentration of atmospheric CO₂ is increasing faster than projected in any of the Intergovernmental Panel on Climate Change (IPCC) emission scenarios. Several mitigation measures, referred to as 'geoengineering options', have been proposed to remove CO₂ from the atmosphere. To be successful, such a mitigation operation must remove 'significant' CO₂ from the atmosphere for many decades, be verifiable, and not cause deleterious side effects. One option, purposeful addition of iron to fertilize photosynthetic uptake of CO₂ by phytoplankton in regions of the ocean where iron is a limiting nutrient, has received considerable scientific attention. In the last 15 yr, a dozen small-scale open ocean iron fertilization experiments have been performed and a succession of models of large-scale fertilization have been developed. As successive models have become more realistic, the amounts of CO₂ forecast to be sequestered have dropped, and in all cases are small relative to the amounts of CO₂ projected to be released through fossil fuel burning over the next century for any of the IPCC emission scenarios. Possible side effects include a long term reduction in ocean productivity, alteration of the structure of marine food webs, and a more rapid increase in ocean acidity. Most importantly, increased remineralization associated with the increased downward export of organic carbon particles would result in increased production of the third most important long-lived greenhouse gas, N₂O. The magnitude of this effect is poorly known.

KEY WORDS: Climate change · Iron fertilization · Mitigation · Ocean carbon cycle

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BACKGROUND

Recent assessment reports of the Intergovernmental Panel on Climate Change (IPCC) have documented the increasing concentrations of CO₂ in the atmosphere due to anthropogenic activities and their causal link with global warming. The preferred mitigation measure to reverse the rise in atmospheric CO₂ is to reduce emissions of CO₂ from anthropogenic activities, primarily burning fossil fuels and cement production. However, recent studies demonstrate that CO₂ released from fossil fuel emissions is accelerating and the rate of increase of emissions since 2000 exceeds all IPCC Special Report on Emissions Scenarios (SRES) for various human development paths (e.g. projections of population growth, energy use, rate of adaptation of new technology, land use change) over the next century (IPCC 2000, Raupach et al. 2007).

To limit climate change to an 'acceptable' level, e.g. an increase in global surface temperature of 2°C relative to 2000, or a leveling off of atmospheric CO₂ concentration at say 450 ppm, recent model results indicate that we must eventually reduce emissions by at least 90% (Weaver et al. 2007, Matthews & Caldeira 2008). The Kyoto Protocol commits 38 industrialized countries to cut their emissions by 5.2% relative to 1990 levels by the period 2008 to 2012. Given the rapid approach of this deadline and the continuing acceleration of fossil fuel emissions, there is intense discussion (e.g. Crutzen 2006, Kintisch 2007) over proposed mitigation actions, such as injecting sulphate aerosols or other reflecting particles into the stratosphere, establishing large-scale plantations of trees or other plants to sequester CO₂, and iron fertilization of large areas of the ocean, also to sequester CO₂.

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Since the hypothesis of Martin (1990), that ice ages cause increased iron deposition to the ocean via increased dust, which results in increased primary production and sequestration of CO₂, fertilization of the ocean with iron has been proposed as a 'geoengineering' mechanism to mitigate climate change by increasing ocean sequestration of CO₂ through purposeful large-scale fertilization of high-nitrogen, low-chlorophyll (HNLC) regions of the ocean. The scientific community responded to this proposal first with a workshop sponsored by the American Society of Limnology and Oceanography (ASLO) on controls on phytoplankton production (Chisholm & Morel 1991) that included results from the first global model 'thought experiment.' Subsequently, a dozen purposeful, small-scale field experiments were performed, where areas of the open ocean of order of 10 km per side were fertilized from moving ships with ferrous sulphate dissolved in water of appropriate salinity to be neutrally buoyant in the surface waters (de Baar et al. 2005, Boyd et al. 2007). Several recent studies with global ocean carbon-climate models have addressed the efficacy of large-scale fertilization. These models employ increasingly explicit biogeochemistry, incorporating the recent scientific understanding of the physiological and ecological response of the planktonic ecosystem to purposeful fertilization that has been obtained from these open ocean experiments and associated laboratory studies. In September 2007, an Ocean Iron Fertilization workshop was held at Woods Hole Oceanographic Institution, bringing together people representing the scientific, policy, economics, commercial and environmental protection aspects of the issue (www.whoi.edu/page.do?pid=14617). Based on the workshop, Buesseler et al. (2008) have produced a summary of the key issues relating to purposeful ocean iron fertilization.

To evaluate the viability of purposeful open ocean iron fertilization as a mitigation option to slow down the increase in atmospheric CO₂, we need to consider at least 5 issues: (1) state a clear mitigation objective, (2) estimate the amounts of CO₂ being released into the atmosphere, (3) review the ability of the ocean to sequester comparable amounts, (4) identify possible side effects, and (5) determine whether ocean sequestration of CO₂ through iron fertilization can be unambiguously verified. I will only consider the first 4 issues. The final issue, verification, is discussed in a separate article (Cullen & Boyd 2008, this Theme Section).

MITIGATION OBJECTIVE

Based on the above issues, an objective for meaningful mitigation of climate change through purposeful ocean iron fertilization may be stated:

To sequester CO₂ in sufficient quantity and for a sufficient time period to make a significant reduction in the rate of increase of atmospheric CO₂ in a verifiable manner, without deleterious unintended side effects.

SCENARIOS FOR FUTURE RELEASE OF FOSSIL FUELS THROUGH HUMAN ACTIVITIES

From pre-industrial times (before 1750) up to 2000, anthropogenic activities have released about 286 Pg C as CO₂ through the burning of fossil fuels and cement production from limestone (from data of Marland et al. 2007). This value is small compared with what is likely to be released over the next century: the IPCC has produced 40 scenarios for future development of global society, the so-called SRES scenarios (IPCC 2000). For several of the most commonly used scenarios¹, Table 1 gives the cumulative CO₂ emissions from 2000 to 2050 and to 2100. Up to 2100 they range from 918 to 2058 Pg C (for the mean scenarios tabulated in IPCC 2001).

Actual emissions for the 5 yr period 2000 to 2004, estimated at 36.7 Pg C, demonstrate the rapid increase in recent emissions, being ~13% of all emissions for the 250 yr up to 2000. Raupach et al. (2007) showed that since 1999, the rate of increase in fossil fuel emissions exceeds even the highest scenario, A1FI (Table 1), and most likely the annual emissions themselves now exceed those for the A1FI scenario (www.globalcarbonproject.org/carbonrends/index.htm). In addition, results from global coupled carbon cycle climate models (Friedlingstein et al. 2006) indicate that for the A2 SRES scenario, more than 1°C of additional warming by 2100 is projected (because of climate-driven release of additional carbon to the atmosphere), relative to the suite of 'standard' climate models used in the recent IPCC AR4 (IPCC 2007, Chap. 10). For 1 of these models, Matthews (2005) shows that for eventual stabilization of atmospheric CO₂ at say 1000 ppm, an additional 94 Pg C by 2050 and 160 Pg C by 2100 (from 2005) must be sequestered beyond that projected by the model without the carbon cycle–climate feedback, i.e. beyond the amounts given in Table 1.

OCEAN CARBON CYCLE

To help understand the projections of fertilization by global models, I describe next the most relevant characteristics of the ocean carbon cycle, as shown schematically in Fig. 1. When CO₂ enters the surface

¹The IPCC requires all scenarios to be treated as equally probable. The 4 scenarios in Table 1 span the range of fossil fuel emissions given by all the SRES scenarios

Table 1. Cumulative emissions of CO₂ (Pg C) from fossil-fuel burning for several IPCC future emission scenarios (from IPCC 2001, WG1: Appendix 2, Table II.I.I)

IPCC SRES scenario	1751–2000 ^a	2001–2050	2001–2100
A1B	286	622	1367
A1FI	286	681	2058
A2	286	597	1702
B1	286	842	918

^aBased on annual emissions from Marland et al. (2007), available at: http://cdiac.ornl.gov/ftp/ndp030/global.1751_2004.ems

ocean from the atmosphere, it is rapidly dissolved and chemically distributed among the 3 components that comprise dissolved inorganic carbon (DIC): aqueous [CO₂], bicarbonate [HCO₃⁻], and carbonate [CO₃⁼] ions, the latter 2 with negative charge. Corresponding H⁺ ions, released through the dissociation of water molecules, lower the pH of the water simultaneously. Through photosynthetic primary production, CO₂ is taken up by phytoplankton and converted to organic molecules (with some species also forming CaCO₃, referred to in Fig. 1 as particulate inorganic carbon

[PIC]). Photosynthesis requires sunlight and nutrients (nitrogen, phosphorous, iron, etc.) in approximately fixed proportions known as the Redfield ratios. Phytoplankton are grazed by zooplankton and they excrete dissolved organic carbon (DOC) and respire organic carbon back to DIC. In Fig. 1, all particulate ecosystem carbon, living and dead, is grouped together as particulate organic carbon (POC) plus PIC. Much of this carbon, with the associated nutrients, is respired or remineralized within the ocean surface layer on short timescales.

A fraction of this carbon, referred to as export production, sinks out of the surface layer as particles (Fig. 1, sinking POC + PIC) or is transported from the surface layer by mixing and advection of DOC. Most of the POC and DOC are remineralized through the action of bacteria in the top 500 m back into DIC. This remineralization also requires dissolved oxygen when it is available. During remineralization, especially at very low concentrations of dissolved oxygen, some 'denitrification' occurs, producing the gases N₂ and N₂O, which may outgas to the atmosphere when the water parcel enters the surface layer again. A small fraction of POC and PIC reaches the sediments, where some is buried and some is released back into the water column after transformation, i.e. 'diagenesis,' back into dissolved nutrients and DIC.

Large-scale physical advective and mixing processes eventually return the DIC (and associated dissolved inorganic nutrients) in the ocean interior back to the surface layer, where the CO₂ comes into contact with the atmosphere once more. For sequestration to reduce the rate of increase of atmospheric CO₂, this return time-scale must be long enough (at least decades) and the associated dissolved nutrients must be returned as soon as, or sooner than, the DIC, which is possible, as they appear to remineralize at shallower depths than the organic carbon, except for silica.

The first key point is that biological processes set the rate of sequestration of carbon to the ocean interior, but physical processes regulate the time-scale over which the sequestered CO₂ is returned to the surface ocean where it again comes in contact with the atmosphere. The second key point is that fertilization will only work where there are unutilized macronutrients in the sunlit surface layer; these unused macronutrients occur at large concen-

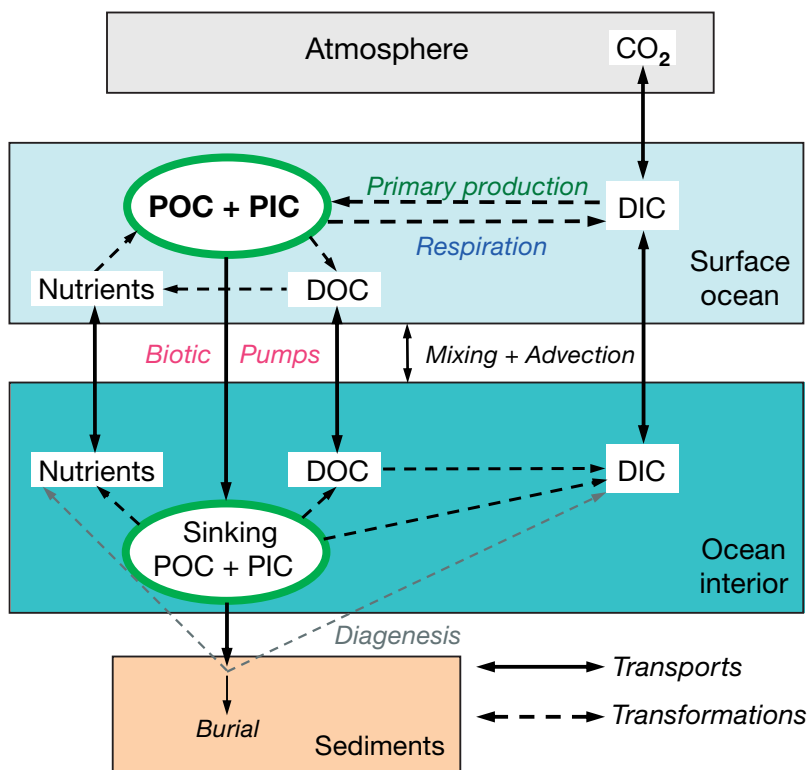


Fig. 1. Schematic of the main components of the ocean carbon cycle, including interactions with the atmosphere and bottom sediments

trations only in the Southern Ocean, the sub-arctic North Pacific, and in the equatorial Pacific, although the return cycle seems to be much shallower and shorter, and therefore less effective at keeping the sequestered CO₂ out of contact with the atmosphere.

RESULTS OF LARGE-SCALE MODEL SIMULATIONS

Sarmiento & Orr (1991) and Kurz & Maier-Reimer (1993) used global models with minimal biology to simulate large-scale fertilization of primarily the Southern Ocean (10 to 15% of the global ocean) continuously for 50 or 100 yr starting in 1990 with the 'business-as-usual' (BaU) scenario (similar to the SRES A2 scenario). Sarmiento & Orr (1991) modelled export production by restoring modelled surface phosphate back to observations with a restoring timescale of 1 mo (standard run). The rate of reduction in surface nutrients (through restoration) was set equal to export production of phosphate and organic carbon. Kurz & Maier-Reimer (1993) included simple biological constraints on the sequestration, due to light and temperature regulation of photosynthetic production, which reduced the total carbon sequestered after 100 yr from 152 Pg C (Sarmiento & Orr 1991) to 106 Pg C (Table 2) and for constant emissions from 127 to 93 Pg C. Both models responded similarly, with an initial peak in CO₂ uptake by the ocean, followed over the next decade or so by a reduction in increased uptake with an offset that appears to be related to the increased carbon being transported around the oceanic carbon conveyor belt described above.

For these 2 idealized model experiments, the total carbon sequestered after 100 yr was on the order of 10% of that which would be released under the BaU/A2 scenario. Hence, the IPCC Second Assessment Report (SAR) concluded (Denman et al. 1996) that iron fertilization was not a feasible mitigation option because of (1) the difficulty of scaling up to such a level (15 to 25% of the global ocean being fertilized continuously for 100 yr), (2) the unknown realized efficiency, and (3) possible unintended ramifications of such a procedure, in particular increased production and outgassing of N₂O (Fuhrman & Capone 1991). N₂O is the third most important long-lived anthropogenic greenhouse gas, with an atmospheric lifetime now estimated to be ~115 yr (IPCC 2007, Chap. 2). Subsequent to the SAR, the Kyoto Protocol was negotiated by member countries of the United Nations Framework Convention on Climate Change (FCCC), but it did not include ocean fertilization as a sequestration method that would qualify for offset credits.

Recent global models incorporating increasingly explicit biology give much reduced sequestration relative to the 2 earlier models (Table 2). Aumont & Bopp (2006), with a more realistic ecosystem and biogeochemical cycles, obtain a cumulative uptake by 2100 of 70 Pg C. If they cease fertilization after 10 yr, the cumulative uptake by 2100 is less than 7 Pg C (their Fig. 7c). Zahariev et al. (2008), with a 4-component ecosystem that has nitrogen and light limitation of primary production even when iron limitation is removed, have conducted a simulation of the 'pre-industrial' ocean (no fossil fuel emissions) similar to that of Kurz & Maier-Reimer (1993). Zahariev et al. (2008) obtained a

Table 2. Global cumulative increased uptake of CO₂ (Pg C) after 100 yr for iron fertilization, forced by IPCC 'Business as usual' (BaU) or A2 scenarios, or Pre-industrial (no emissions); phyto.: phytoplankton, zoopl.: zooplankton, POM: particulate organic matter, DOM: dissolved organic matter, NPZD: nutrient + phytoplankton + zooplankton + detritus

Scenario	Fertilization protocol	Representation of the marine ecosystem	Total carbon sequestered (Pg C)	Source
BaU	Global, continuous	Complete nutrient restoring	152 (98–180) ^a	Sarmiento & Orr (1991)
BaU <i>Pre-industrial</i>	Southern Ocean, 6 mo	Nutrient restoring: rate a function of light, temperature, and 'turbulence'	106 72	Kurz & Maier-Reimer (1993)
BaU	20% ocean area, 15 ^b times yr ⁻¹	Ratio of C-export to Fe-added from Buesseler et al. (2004)	32	Zeebe & Archer (2005)
A2	Global, continuous	Complex ecosystem model: 5 nutrients, 2 phyto., 2 zoopl., 2 POM, 1 DOM (Aumont et al. 2003)	70	Aumont & Bopp (2006)
Pre-industrial	Global, continuous	NPZD + simple calcifiers and N-fixers	26	Zahariev et al. (2008)

^aRange of results for different remineralization depth scales, restoring times, and gas exchange coefficients
^bRepresents twice the Earth's surface each year

much-reduced CO₂ sequestration after 100 yr of only 26 Pg C, as compared to 72 Pg C in Kurz & Maier-Reimer (1993).

In most of the recent small-scale fertilization experiments, iron injection was repeated several times over the course of 10 to 14 d because of rapid loss of bioavailable iron beyond what can be accounted for through uptake by phytoplankton (de Baar et al. 2005, Boyd et al. 2007). The small scales of these experiments, the requirement for multiple injections of iron, and the low efficiency of carbon sequestration all make the scenario of 15 to 25% of the global ocean being fertilized continuously for 50 to 100 yr even more difficult to imagine.

To mimic the effects of the recent fertilization experiments, modellers have simulated these patch experiments. Gnanadesikan et al. (2003), with a nutrient-restoring representation of fertilized primary production, estimated that after 100 yr the loss from the atmosphere would be only 2 to 44% of the initial uptake pulse for patches of a few 100s of km per side fertilized for limited periods of order 1 mo. Amounts of carbon sequestered after 100 yr are at most 10s of Tg C, compared with expected cumulative emissions of order 10⁶ Tg C (1000 Pg C = 10⁶ Tg C, Table 1). Furthermore, the initial fertilization reduces nutrients in the upper few hundred meters over several years, leaving the remaining high nutrients at greater depths and increasing the time scale of their return to the surface layer, thereby reducing century-scale export biological productivity by a factor of up to 30. This reduced export production due to more carbon and nutrients being transported to greater depths has been found in other studies (e.g. Zahariev et al. 2008). From a recent purposeful iron fertilization experiment, Zeebe & Archer (2005) estimated an efficiency for iron fertilization of ~10 to 25%. Using a global model and this efficiency, they found that fertilizing 20% of the global ocean 15 times yr⁻¹ until 2100 would sequester less than 32 Pg C. This procedure is equivalent to fertilizing about twice the area of the Earth's surface each year.

The results of the studies summarized in Table 2 are highly dependent on the representation of critical biological, chemical and physical processes in the models. Jin et al. (2008), with the most comprehensive biogeochemical/ecological model of the studies described here, and with a highly resolved euphotic zone, obtained results that contrast with the other studies. They fertilized patches in the eastern tropical Pacific of various sizes and under various temporal schedules. Because the fertilization and enhanced primary production occur just below the sea surface (as in the shipborne fertilization experiments to date), their model gives high atmospheric uptake efficiencies (the ratio of the perturbation in air-sea CO₂ flux to the perturba-

tion in export flux across 100 m integrated over 10 yr) of 0.75 to 0.93. Larger area fertilizations, especially those when light profiles were adjusted to give the greatest increase in fertilized primary production near the bottom of the euphotic zone, give much lower atmospheric uptake efficiencies. Even with their high efficiency of fertilization, for a simulation of fertilization of the entire north and tropical Pacific, the air to sea flux over 10 yr is only 3.4 Pg C (small relative to the range of expected fossil fuel emissions for the 4 SRES scenarios of Table 1 of 92 to 109 Pg C for the 10 yr period 2011 to 2020).

POSSIBLE SIDE EFFECTS

There are several known possible side effects of large-scale iron fertilization, but we have little knowledge of their potential magnitudes. (1) Increased remineralization, mostly within the 500 m below the euphotic zone, requires dissolved oxygen at a rate of O₂:C near 1.5:1 (mol:mol). Box models (and Sarmiento & Orr 1991) predicted wide areas of the subsurface ocean becoming anoxic under large-scale continuous fertilization, but as the magnitude of projected sequestration has decreased, anoxic regions have been replaced by low oxygen regions. (2) More importantly for climate change, increased remineralization results in increased denitrification and production of N₂O, the third most plentiful long-lived greenhouse gas affected by anthropogenic activities. We do not yet have reliable estimates of magnitudes of this source at the global scale (Law 2008, this Theme Section). (3) The productivity and structure of marine ecosystems would change. Projections by Gnanadesikan et al. (2003), Aumont & Bopp (2006), and Zahariev et al. (2008) all indicate a reduction in primary production and in biological export of carbon on the multi-decadal to century timescale, due to the reduction in available macronutrients returning to the surface ocean. Over large scales this reduction could translate into a reduction in harvestable marine resources. Iron fertilization also alters the species composition of phytoplankton (at least temporarily in the short-term fertilization experiments conducted to date). Initially, there may be an increase in smaller phytoplankton abundance, but after a week or more, the increasing biomass of diatoms dominates that of all other phytoplankton groups (Marchetti et al. 2006, for the 2002 Subarctic Ecosystem Response to Iron Enrichment Study [SERIES]). Sustained fertilization would favour diatoms and hence, through grazing transfers, copepods over smaller microzooplankton; towards the end of the SERIES observation period, Tsuda et al. (2006) observed a migration upwards into the patch of some

species of mesozooplankton, as well as an increase in nauplii and larvae of some species, hypothesized to be due to reduced grazing on them. A shift to diatoms results in greater drawdown of silicic acid relative to nitrate (Boyd et al. 2004), a process that could not continue over an extended fertilization.

Production of the climate-active gas dimethylsulfide (DMS) is also altered by iron fertilization. Its precursor, dimethylsulfoniopropionate (DMSP), is produced by some species of phytoplankton. Some DMS outgasses to the atmosphere and is the largest natural source term in the global atmospheric sulphur budget. DMS stimulates the formation of cloud condensation nuclei (Liss et al. 2005). Several of the iron fertilization experiments showed a short-term increase in surface ocean DMS concentrations (Boyd et al. 2007), but following that initial increase, the SERIES experiment showed a decrease of DMS in the patch relative to concentrations outside the patch (Levasseur et al. 2006). As the diatoms (which produce little DMSP) out-competed other functional groups of phytoplankton, they apparently displaced DMSP-producing species (Steiner & Denman 2008). Because most iron-fertilized patches have been observed for less than 1 mo, we have no information on what magnitude longer-term changes in ecosystem structure and function might be. Boyd et al. (2008) conclude that our quantitative understanding of the adaptability of phytoplankton based on observations from field and laboratory studies is inadequate to forecast their responses to 'slow' changes in their environment, such as those forecasted for the Southern Ocean over the next 2 decades.

The fourth known possible side effect of large-scale iron fertilization is the issue of increasing ocean acidity; CO₂ added to the ocean rapidly dissolves and dissociates into bicarbonate and carbonate ions, adding H⁺ ions (i.e. protons) to the oceans, thereby reducing pH and increasing acidity. Stimulating increased sequestration of CO₂ to the oceans through widespread successful iron fertilization would increase the cumulative acidity more rapidly and would change the depth distribution of remineralization back to DIC. Arguments that this CO₂ will end up in the ocean eventually even without fertilization ignore the scientific issue of how quickly marine organisms can adapt, through diversity of species occupying an ecological niche (e.g. calcifiers such as coccolithophores), diversity within species (physiological 'plasticity'), and through genetic mutations. The more rapidly pH decreases, either in the surface layer or at depth where there is increased remineralization due to fertilization, the more likely it is that organisms will be unable to adapt, both to the increased acidity and, in the subsurface zones of increased remineralization, to the related decrease in dissolved oxygen.

WHAT IS THE PROSPECT OF IRON FERTILIZATION AS AN EFFECTIVE MITIGATION MEASURE?

In IPCC AR4 (Denman et al. 2007), the IPCC again dismissed purposeful fertilization as a viable mitigation measure, primarily because of lack of feasibility. Perhaps based on the proposal by Pacala & Socolow (2004) of 'stabilization wedges' of mitigation measures, a collection of small measures, each reaching ~1 Pg C yr⁻¹ within 50 yr, can result in a cumulative sequestration large enough to stabilize emissions. Under this scenario of a collection of mitigation measures, CO₂ sequestration through iron fertilization remains a potential mitigation measure for consideration. But the tendency for the magnitude of sequestration to decrease over time, the small amounts of CO₂ likely to be sequestered relative to the large amounts to be released through fossil fuel burning, the difficulty with verification, and the possible negative side effects—none of which have known magnitudes—all must be thoroughly addressed in any future iron fertilization experiments (e.g. Watson et al. 2008, this Theme Section) before iron fertilization should be attempted at large scales for climate mitigation.

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Ocean iron fertilization and international law

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ABSTRACT: Intentional ocean fertilization and the commercial sale of associated carbon offsets raise a number of issues in international law. On the one hand, states are obliged to adopt adaptation and mitigation measures to prevent dangerous climate change. On the other hand, international law obliges states to protect and preserve the marine environment and to act in a precautionary manner in the face of scientific uncertainty. In this article, we examine the application of the international Law of the Sea to ocean fertilization, with particular reference to the law's dumping regime, which prohibits the dumping of wastes or other materials from vessels into the ocean. We then examine the application of the international legal regime on climate change to ocean fertilization and assess the international legal basis for the sale of carbon offsets or carbon credits associated with ocean fertilization. We conclude that ocean fertilization is governed by the dumping regime and that its commercialization is inconsistent with international law unless and until independent, internationally peer-reviewed scientific research and assessment demonstrates that it is effective and that its benefits outweigh the risks to the marine environment.

KEY WORDS: International law · Law of the sea · Ocean fertilization · Ocean dumping · London Convention · London Protocol

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INTRODUCTION

Ocean fertilization through the intentional introduction into the ocean of substances such as iron, urea or phosphorous, or by the mechanical or technological perturbation of natural marine systems, presents something of a dilemma for international law. On the one hand, through the 1992 United Nations Framework Convention on Climate Change (UNFCCC 1992) the international community has accepted that a range of mitigation and adaptation measures is necessary if we are to avoid exceeding the capacity of natural, managed and human systems to adapt to climate change. On the other hand, the international community has long agreed on the obligations of states to protect and preserve the marine environment and to act in a precautionary manner in the face of scientific uncertainty.

Ocean fertilization, particularly ocean iron fertilization (OIF), has been suggested by some as a simple, quick, effective and environmentally friendly fix to the world's CO₂ emissions problems. Extrapolating from results obtained during experiments in the early 1990s,

oceanographer J. H. Martin suggested that a mere 430 000 tons of iron deposited into the Southern Ocean would result in the removal of 3×10^9 tons of atmospheric carbon annually (Martin 1990, Martin et al. 1990, 1994). Most others, however, including the highly regarded Intergovernmental Panel on Climate Change (IPCC) consider ocean fertilization to be 'speculative and unproven, and with risks of unknown side effects' (IPCC 2007, p. 20). Nevertheless, despite scientific uncertainty as to its efficacy as well as its environmental risks, a number of commercial operators are preparing to engage in ocean fertilization activities with the intention of reaping financial benefits through the sale of associated carbon credits or offsets. The first vocal proponent of the commercialization of OIF, the USA-based company Planktos, recently abandoned its plans to conduct 6 fertilization cruises from 2007 to 2009, each of which would have dissolved up to 100 t of iron over a 10 000 km² tract of ocean (Planktos 2007). Nevertheless, other firms, including USA-based Climos and GreenSea Ventures, and the Australia-based Ocean Nourishment Corporation, are proceed-

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ing with their own plans to engage in iron and urea fertilization activities, respectively. These companies promote ocean fertilization as a tool to buffer ocean acidity, replenish the marine food chain, and sequester CO₂, and they invite investors and green co-sponsors to finance their activities in return for the provision of carbon credits to offset investors' CO₂ emissions (Salleh 2007, Glibert et al. 2008, Gunther 2008).

In June 2007 the Scientific Working Groups of the London (Dumping) Convention (1972) (LC) and its 1996 London Protocol (1996) (LP) issued a Statement of Concern noting 'the potential for large-scale ocean iron fertilization to have negative impacts on the marine environment and human health' and requesting the 29th Consultative Meeting of the LC and the 2nd Meeting of Contracting Parties to the LP 'to consider the issue ... with a view to ensuring adequate regulation of large-scale ocean fertilization operations' (IMO 2007a). At their meeting in November 2007, the contracting parties to the LC and LP endorsed the Statement of Concern, agreeing that ocean fertilization activities fall under the competence of the Convention and the Protocol, in particular in relation to their objectives of protecting the marine environment. It was agreed that planned operations for large-scale fertilizations were not currently justified and that the issue would continue to be studied from both the scientific and legal perspectives, with a view to its regulation (IMO 2007b). Precisely what is meant by 'large-scale' was not defined. However, the clear inference to be drawn is that 'large-scale' would certainly refer to operations on the scale then planned by Planktos. Whether it would apply to smaller-scale operations remains to be determined.

In any event, for any project, including an ocean fertilization project, to generate so-called 'carbon credits' that can be used by states to meet their greenhouse gas (GHG) emission reduction targets, it must meet the rigorous requirements of the UNFCCC and its Kyoto Protocol (1997) (KP). The KP envisages industrialized states reducing their GHG emissions by an average of 5.2% from 1990 levels between 2008 and 2012. Although the UNFCCC envisages the use of all types of carbon sequestering techniques, or 'sinks,' as well as reductions of GHG emissions in order to achieve 'stabilization' of the earth's climate, this is not reflected in the KP regime. The strict rules established by the KP Parties (the famous Marrakech Accords 2001) to approve and monitor projects which might generate tradable credits do not accept any form of carbon sink project—except afforestation or reforestation projects. The huge European Emission Trading Scheme (ETS), with carbon trades worth more than \$US 24 billion in 2006 (Capoor & Ambrosi 2007), does not accept any sink projects at all.

Parallel with the official trading schemes there are a number of informal, voluntary schemes. Some of these are industry based, but others rely primarily on a 'feel good' approach of their investors, who believe they are financing climate friendly activities, such as tree-planting or conversion to energy-efficient light-bulbs, to off-set their individual or corporate carbon foot-print. These voluntary schemes are currently unregulated at both the national and the international levels, although they are subject, like all other commercial activities, to national laws relating to trade practices, securities regulation and consumer protection. There is now increasing recognition of the need to develop national verification mechanisms to ensure the veracity of the carbon reduction claims made (Pearce 2007).

This article examines the international law issues arising from ocean fertilization activities. In particular, it focuses on the issues arising from fertilization by anthropogenic introduction of fertilizing agents into the ocean. Similar but different legal considerations apply in the case of fertilization by anthropogenic manipulation of the ocean environment through mechanical or other means, such as ocean pumps, as suggested by Lovelock & Rapley (2007) and the USA-based company Atmocean (see www.atmocean.com). The issues to be considered here relate not only to the regulation of the activity itself—which is governed by the international law of the sea and possibly a range of other sectoral and regional treaties (for example, the Antarctic Treaty System, which includes the Madrid Protocol 1991 on protection of the Antarctic environment, which requires prior environmental impact assessments [EIA] for all activities south of 60° S)—but also to the way in which such activity might generate carbon credits or off-sets under the international treaty regime established by the UNFCCC and the KP.

LAW OF THE SEA ISSUES

The basic legal framework for protection and preservation of the marine environment is set out in the United Nations Convention on the Law of the Sea (LOSC 1982), which gives content to the customary international law obligation binding on all states (including non-parties to the LOSC, such as the USA) to ensure that activities under their jurisdiction or control do not cause damage to the environment of other states or to areas beyond national jurisdiction. To that end, all states are obliged to take individually and jointly all measures necessary to prevent, reduce and control pollution of the marine environment, to prohibit the transfer, either directly or indirectly, of damage or hazards from one area to another, and to pro-

hibit the transformation of one type of pollution to another (Articles 192 to 195 LOSC).

Pollution is defined in LOSC Article 1(4) as 'the introduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, which results or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the seas, impairment of quality for use of sea water and reduction of amenities'. In other words, it is not the nature of the substance per se that matters, but rather its potential for deleterious effects.

Pursuant to Article 196 of the LOSC, states are to prevent, reduce and control pollution from all sources, whether generated from scientific research or from commercial operations, including from land based sources, through the atmosphere, and from vessels, including from 'dumping'. Dumping is defined in Article 1(5) as 'any deliberate disposal of wastes or other matter from vessels, aircraft, platforms or other man-made structures at sea'. Article 210 of the LOSC requires all states to adopt national laws to prevent and regulate dumping that must be no less effective than internationally agreed global rules and standards. These rules and standards are currently found in the LC (to which the USA is party) and the LP. For states parties to the former, dumping of non-prohibited substances is only allowed subject to the requirements of prior environmental impact assessment, permitting and ongoing monitoring set out in Annex III of the LC. For parties to the latter, dumping of all waste and other matter is prohibited, except for 5 categories of substances listed in Annex 1, the dumping of which is, nevertheless, subject to the stringent assessment, permitting and ongoing monitoring requirements of Annex 2 of the LP. Wastes and other matter listed in Annex 1 are dredged material, sewage sludge, fish waste or material resulting from industrial fish processing operations, vessels and platforms or other man-made structures at sea, inert, inorganic geological material, organic material of natural origin, and bulky items comprising iron, steel, concrete and similar harmless materials whose disposal is otherwise impractical or impossible. It is questionable whether the 'fertilizers' used in ocean fertilization can come within these categories. However, even if they do, the Annex 2 requirements must be met.

The central issue for ocean fertilization is whether it is exempt from the ban on dumping by virtue of the operation of the exception to the definition of dumping found in the LOSC, LC and LP, all of which state that dumping does not include 'placement of matter for a purpose other than the mere disposal thereof, provided that such placement is not contrary to the aims of' the

LOSC or the LC/LP, respectively. Neither 'placement' nor 'matter' are defined further. Nevertheless, the plain meaning of the words indicates that human introduction of a substance into the oceans would constitute 'placement.' Additionally, iron is clearly 'matter.' However, while iron deposited during fertilization activities is abandoned with no intention of it being recovered, 'mere disposal thereof' is not the objective of the operation. It is therefore necessary to determine whether there are other reasons why placement of matter for ocean fertilization activities would be regulated by the LC/LP. To do this it is necessary to consider both the purposes of ocean fertilization and the aims of the LOSC and the LC/LP.

With respect to the former, the purpose of ocean fertilization is to stimulate a phytoplankton bloom. This may be for scientific research, or to draw down CO₂ from the atmosphere for storage in the ocean. While the oceans are a natural sink for CO₂, the point of ocean fertilization (apart from any commercial motive) is to sequester into the oceans a greater percentage of atmospheric CO₂ than would occur naturally. Ocean fertilization could therefore be viewed as the placement, by indirect means, into the oceans of excess atmospheric CO₂ for the purpose of disposing of that CO₂ in the medium to long term.

With respect to the latter, marine scientific research (MSR) is one of the 'freedoms' protected by the LOSC. However, the conduct of MSR is subject to the marine environmental protection provisions of the LOSC, including the provisions on dumping. In that respect, the aims of the LOSC, LC and LP are to prevent, reduce and eliminate pollution that is liable to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea. A wide range of side effects have been observed and predicted as being likely to accompany ocean fertilization. In terms of marine ecology these include the potential for changes to natural speciation of phytoplankton, thereby causing changes in species that depend on it, alteration of ocean chemistry leading to deep ocean hypoxia or anoxia, and changes to nutrient balance and availability, which could lead to adverse changes in primary production patterns globally, resulting in unforeseen, cumulative, and long term adverse consequences that could disrupt marine food webs with potentially devastating effects on open water communities and seabed ecosystems throughout the oceans (cf. Chisholm et al. 2001, Dalton 2002, Buesseler & Boyd 2003, Gnanadesikan et al. 2003, Buesseler et al. 2004). Other observed and predicted side effects relate to changes in emissions of climate-relevant gases into the atmosphere, including dimethylsulfide (DMS), halogenated organic compounds, isoprene and nitrous oxide, a greenhouse

gas with a greenhouse warming potential much greater than that of CO₂. The absorption of solar radiation by plankton may also have a substantial warming effect on the ocean surface over the fertilized area comparable to the radiative forcing from anthropogenically enhanced CO₂ (Lawrence 2002, Jin & Gruber 2003, Meskhidze & Nenes 2006, Lutz et al. 2007). Given the range of observed and predicted adverse side effects, and the concerns expressed by many scientists, including the IPCC, as to its efficacy and environmental safety, it is currently not possible to say that ocean fertilization, and the placement, by indirect means, of excess CO₂ into the ocean, will not result in increased harm to living resources and marine life, potential harm to humans or interference with other legitimate uses, such as fishing, bio-prospecting, MSR, and navigation (Gnanadesikan et al. 2003). In fact, the preponderant scientific view is that the jury is still out and that the onus is now on proponents of the practice to demonstrate through rigorous, transparent, carefully regulated and internationally peer-reviewed scientific examination that it is effective, and that it does not do more harm than good (Buesseler et al. 2008, Glibert et al. 2008).

It could, therefore, be said that ocean fertilization is, *prima facie*, contrary to the aims of the LOSC, the LC and the LP and is not saved by the exception. If this is the case, for states parties to the LP, ocean fertilization would be prohibited, unless the fertilizer and the CO₂ sequestered fall within the definition of 'inert, inorganic geological material' or 'organic material of natural origin,' both of which may be considered for dumping subject to permitting requirements; while for states parties to the LC, ocean fertilization would be subject to the permitting requirements set out therein. This is, in fact, the position adopted by the states parties to the LC and LP in their November 2007 statement 'recognising that it is within the purview of each state to consider proposals [for ocean fertilization] on a case-by-case basis in accordance with the Convention and/or Protocol' (IMO 2007b). In other words, for any ocean fertilization activity conducted under the jurisdiction or control of states parties to the LC or the LP, permits issued by national authorities in accordance with the terms of the Convention or the Protocol (as relevant) will be required.

Admittedly, the characterization of ocean fertilization as within the jurisdiction of the LC/LP does not guarantee its effective regulation and control, particularly where the activities take place on the high seas in areas beyond national jurisdiction. As a legal matter, it is arguable that the provisions of the LC are binding on all states parties to the LOSC as a result of the latter's incorporation of generally agreed international standards (de La Fayette 1998, Birnie & Boyle 2002). How-

ever, a strict interpretation of the law of treaties holds that the LC and LP are only binding on their parties. Nevertheless, all states party to the LOSC are bound by its general prohibitions on pollution of the marine environment, dumping, transfer or transformation of one type of pollution to another, and use of technologies which cause significant and harmful changes to the marine environment. However only LC/LP parties are bound by the specific rules on permitting, assessment and monitoring.

In addition, state responsibility for protection of the marine environment is allocated on the basis of jurisdictional competencies to enforce ascribed to coastal states, port states and flag states. Coastal states have jurisdiction to enforce their dumping laws within their territorial sea and exclusive economic zone or on their continental shelf. Port states have jurisdiction to enforce in respect of loading of waste or other matter to be dumped within their territory or at their offshore terminals. Nevertheless, where a coastal or port state is unwilling or unable to adopt, implement and enforce, at a minimum, the internationally agreed rules and standards, the marine environment may suffer. This situation is particularly exacerbated in the case of activities conducted on the high seas, where primary jurisdiction to regulate and enforce rests with the flag state, which may not be party to the relevant treaties or may otherwise be unable or unwilling to enforce against its vessels.

As a practical matter, therefore, reliance on flag state and port state jurisdiction gives rise to the very real threat, common to all areas of the Law of the Sea, of use of 'flags of convenience' and 'ports of convenience.' No matter how strict an approach is taken by the parties to the LC/LP, the very real potential exists for proponents of ocean fertilization to undermine the LC/LP regulatory efforts by simply incorporating their companies, flagging their vessels, and loading their fertilizer in non-LC/LP party states. The standing of other states to bring claims against these recalcitrant states, in respect of damage to the formers' interests in the high seas, its resources and amenities as a result of ocean fertilization, is still uncertain.

UNFCCC/KYOTO PROTOCOL ISSUES

The UNFCCC was opened for signature in June 1992 as a part of the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, Brazil. It now has near universal membership of 192 states. The basic objective of the UNFCCC, set out in Article 2, is to stabilize GHG emissions 'at a level that would prevent dangerous anthropogenic interference with the climate system' and 'within a time frame

sufficient to allow eco-systems to adapt naturally to climate change, to ensure that food production is not threatened and to enable economic development to proceed in a sustainable manner'.

The UNFCCC imposes an obligation on its parties to 'promote and cooperate in the conservation and enhancement, as appropriate, of sinks and reservoirs of all greenhouse gases ... including biomass, forests and oceans' (Article 4[1][d]). Moreover, parties are urged to take precautionary measures to, inter alia, mitigate the adverse effects of climate change, and lack of scientific certainty should not be used as a reason for postponing such measures (Article 3[3]). However, they are also obliged to use appropriate methods, such as impact assessments, with a view to minimizing adverse effects on the quality of the environment of projects designed to mitigate, or adapt to climate change (Article 4[1][f]).

Neither time frames nor modalities for achieving these objectives are set out in the UNFCCC. Rather, these were negotiated in the context of the KP, which was the first of what was envisaged as a series of protocols that would add substance to the UNFCCC framework. The KP imposes binding obligations on developed countries (set out in its Annex B) to reduce emissions of GHG by agreed amounts within the 2008 to 2012 commitment period. The KP also envisages developing countries using the so-called 'flexibility mechanisms' in order to assist them in meeting these targets.

There are 3 flexibility mechanisms provided for in the KP. The first, carbon trading between Annex I developed countries (Article 17), does not concern us here because this relates to the trading of allowances allocated by the Protocol, and not to project-based activities. The second is Joint Implementation (JI), whereby 2 developed countries collaborate in a project to reduce emissions in 1 country, with investment from the other that can then claim carbon credits for achieved emission reductions (Article 6). Most radical, however, is the Clean Development Mechanism (CDM) whereby developed countries invest in GHG emission reduction projects in developing countries (Article 12). These projects must also contribute to sustainable development in the host country. Once an independent auditor certifies that reductions have actually occurred, the developed country can claim 'certified emission reductions' and set these off against its own GHG reduction targets. In order to prevent abuse of this mechanism, a CDM Executive Board oversees these projects and must approve the methodology by which emissions reductions are calculated. The Board also licenses the auditors (or certifiers). CDM projects need to meet established criteria: participation must be voluntary; all countries—or entities acting under their authority—must be parties to the

KP; the projects must manifest real measurable and long-term benefits relating to mitigation of climate change; and a project activity must be 'additional' to that which would have occurred in its absence.

Participation in the CDM is open to the involvement of private as well as public entities, as long as they act under the authority of a KP state party and subject to the guidance of the CDM Executive Board. It is a relatively bureaucratic process which, to date, has approved more than 800 projects since they opened for business some 7 years ago. It is also worth noting that to date only one of these has been a 'sink' project. The reason is that carbon sequestration projects have long been controversial in the negotiations of parties to the UNFCCC. In 2001, in Marrakech, it was decided that only reforestation and afforestation projects would qualify for consideration by the CDM. Although the recent Conference of the Parties in Bali in December 2007 decided that any successor to the KP would consider avoided deforestation, these are the only forms of sequestration that are currently even on the radar screen of the negotiators.

Carbon sequestration in the oceans therefore seems highly unlikely to be eligible for the generation of credits under the KP regime. The UNFCCC parties have never considered how sequestration by ocean fertilization might figure in the national inventories developed countries are required to submit, nor does it seem likely to be on their agenda given the skepticism of the IPCC regarding fertilization. The situation is not the same for CO₂ capture and storage activities, which could be part of a national strategy where CO₂ generated in one country might be captured and stored in ocean floor reservoirs in areas under national jurisdiction. Indeed, the LP was amended in 2006 specifically to contemplate such activities. Ocean fertilization, by contrast, is very different, particularly where the fertilization activity takes place in areas outside of national jurisdiction so there is no 'host' country to certify that this contributes to their sustainable development (a difficult task in any event). Moreover, there is no real evidence that carbon is actually captured and retained in the oceans for a reasonable period and that there is no leakage of other GHG, such as nitrous oxide, in the process. Indeed, there are problems with virtually all the other current requirements for CDM and JI project registration.

Outside the ambit of the KP regime, there are few restrictions on the ability of national authorities or the private sector to offer national, or in the case of the private sector voluntary, carbon offset schemes. Voluntary carbon offset schemes do not affect states' commitments under the UNFCCC/KP. These schemes and the credit or off-set generating projects included in them are subject to domestic laws rather than interna-

tional regulation, although a number of national and international certification programs are being developed to enhance vigilance by national authorities in states where these markets flourish and to ensure these projects offer real environmental benefits in return for the substantial investments that are being made (Pearce 2007). The private sector is also seeking to develop its own self-regulation through codes of conduct (Climos 2007). Nevertheless, under the rules on state responsibility, states may still be internationally responsible if projects under their jurisdiction or control cause damage to the rights and interests of other states.

CONCLUSIONS

Based on IPCC assessments, the Stern Report suggests there is a 10 to 15 yr window in which to make major reductions in global GHG concentrations to avoid dangerous climate change. In this environment, all the available tools should be on the table. Certainly, the characterization of ocean fertilization as within the competence of the LC/LP does not relieve the international community of the obligation expressed in Article 3 of the UNFCCC to take precautionary measures to mitigate the adverse effects of climate change, including through the use and development of greenhouse gas sinks, of which the oceans are, by far, the largest and most important on earth. Indeed, lack of full scientific certainty is not to be used as a reason for postponing such measures where there are threats of serious or irreversible damage. However, where the mitigation measures themselves may result in serious or irreversible damage, the precautionary principle requires, at the very least, that these need to be subject to proper and rigorous assessment to minimize unwanted adverse impacts on the environment in order to ensure the potential benefits outweigh the potential harms. Indeed, both the LOSC (Article 204) and the UNFCCC (Article 4[1][f]) mandate prior assessment.

The states parties to the LC and the LP have rightly recognized that ocean fertilization falls under the competence of the LC/LP regime and have agreed to study the need for further regulation. While they do so, they have urged states to 'use the utmost caution when considering proposals for large-scale fertilization operations' and have taken the view that, 'given the present state of knowledge ... such large-scale operations are currently not justified' (IMO 2007b). The parties to the LC/LP have therefore recognized that in order to avoid conflict and minimize interference with other legitimate uses of the oceans, with the rights and interests of all states in protection of the marine environment of the high seas, and with the rights and interests of

coastal states in areas under national jurisdiction, ocean fertilization should be subject to internationally agreed regulations and permitting requirements. It goes without saying that these regulations will need to incorporate 'best practice' prior and cumulative EIA, as well as ongoing monitoring and, if necessary, remediation requirements. Given scientific uncertainty about possible adverse effects of ocean fertilization, it would also be sensible to require that applicants for permits for ocean fertilization include research on the broader effects of fertilization on the marine and atmospheric environments. As with all such procedures, where those effects are unknown or likely to be severe, modification to experimental design can be required to minimize possible adverse effects (Verlaan 2007).

In addition, given the significant practical and technological difficulties encountered in previous fertilization experiments in containing and monitoring the algal bloom and in verifying the amount of carbon draw down, consideration could be given to restricting the size and number of future experiments unless and until the process is shown to be effective and that its benefits outweigh the risks involved. Finally, consideration will need to be given to addressing liability issues that may well arise if the rights and interests of other states are adversely affected by ocean fertilization activities.

Regulation by the LC/LP does not answer all the questions posed by ocean fertilization. In this respect ocean fertilization highlights the inadequacies inherent in the decentralized and fragmented international legal system, which, for effective implementation, requires co-ordination between different international treaty regimes such as the LC/LP and the UNFCCC — no formal mechanism for which exists — and the informed collaboration of national authorities. As has been discussed above, this devolved implementation may present unfortunate opportunities for exploitation. However, it should be borne in mind that all states and their nationals are under a legal obligation not to cause damage to the marine environment of other states or to areas beyond national jurisdiction. States not party to the LC/LP could therefore also consider adopting domestic legislation regulating the activity. Other multilateral treaty bodies, such as the various Regional Seas conventions, the OSPAR Convention (OSPAR 1992), and the Antarctic Treaty Consultative Parties, may also wish to consider its regulation. Climate change institutions such as the UNFCCC and the KP may also need to address the role of the oceans in global climate processes as well as the issue of ocean fertilization, particularly as regards its commercialization and the sale of associated credits or off-sets.

In conclusion, the main message seems to be that ocean fertilization has yet to be shown to work as a

serious climate change mitigation strategy (Buesseler et al. 2008). Until such time as independent, internationally peer-reviewed scientific research and assessment has demonstrated that it is effective and that its benefits outweigh the risks to the marine environment, it is premature for commercialization of ocean fertilization and for carbon credits or offsets generated by ocean fertilization activities to be offered on either the regulated or the voluntary market.

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Cultural context of ocean fertilization

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ABSTRACT: All environmental law and policy, including potential policy governing ocean fertilization, involves trade-offs between the state of the world's biophysical ecology, by which we mean all of the non-human elements, and the state of the world's human ecology, by which we mean humans and their relationships with one another, including their governance institutions. All rules of governance affect—and only directly affect—human behavior, and through that behavior shape the biophysical world. All law is an expression of human culture. Legal statutes and rules are those elements of culture that we feel strongly enough about and share enough with each other that we write them down as rules of behavior and create some form of sanction for their transgression. In this paper I will discuss the broad-brush history of human value-based governance with respect to human use of the ocean and the kinds of decisions that face us with respect to the question of ocean fertilization. The general thesis is that ocean fertilization is essentially a 'cultivation' activity, even if done for the purpose of carbon sequestration for environmental conservation or market (carbon trading) purposes, and that such 'cultivation' is a new arena for ocean policy and regulation.

KEY WORDS: Ocean fertilization · Ocean policy · Carbon sequestration

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INTRODUCTION

All environmental law and policy, including potential policy governing ocean fertilization, involves trade-offs between the state of the world's biophysical ecology, i.e. all of the non-human elements, and the state of the world's human ecology, i.e. humans and their relationships with one another, including their governance institutions. All rules of governance affect—and only directly affect—human behavior and through that behavior shape the biophysical world. The configuration of the biophysical environment, in turn, defines the form of the costs and benefits that can be incurred or received by humans in the use of that environment. Every decision regarding our relationship with the biophysical environment involves some form of tradeoff and all of the tradeoffs we make in our policy-making and implementation are guided by some set of human values. For example, achieving a higher standing stock of fish means extracting less through fishing, with attendant social and economic effects. In the present case, fertilizing the ocean to achieve higher productivity or for carbon

sequestration and attendant 'credits' means altering the biophysical ecosystem and perhaps other social and economic benefits we presently enjoy from it. We do not always do this with will full knowledge or forethought, but there is at least a presumptive tradeoff made with each decision based on some human value structure.

In this paper I will discuss the broad-brush history of human value-based governance with respect to human use of the ocean and the kinds of decisions that face us with respect to the question of ocean fertilization.

LAW AND CULTURE

All law is an expression of culture. Legal statutes and rules are those elements of culture that we feel strongly enough about and share enough with each other that we write them down as rules of behavior and create some form of sanction for their transgression (Nader 1969). Culture varies throughout the world, and accordingly, so does law. Different local governments, different states, and different nations have

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different laws reflecting their common culture within their particular governance structure.

In general, when we set out to 'conserve' a part of the biophysical environment, we mean to be able to sustain its use or enjoyment by humans over time. Some of this use or enjoyment may be extractive, other, non-extractive. If we decide to enjoy part of the biophysical environment in a non-extractive way and develop rules accordingly, we often use the term 'preservation' rather than 'conservation,' as in the terms 'preservation ethic' and 'conservation ethic' associated with John Muir and Gifford Pinchot, respectively (Miller et al. 1987). The form of law and policy we construct reflects our cultural values and our preferred 'ethic' of interaction with the biophysical environment.

One of the significant questions we face with ocean fertilization is: How should we use the oceans? As I discuss below, humans have addressed this question, if imperfectly, for terrestrial—and even atmospheric—environments, but not yet for ocean environments. Should we, given both the similarities and the differences between them, treat the sea as we have the land, to be subject to private ownership and large-scale cultivation and alteration? Or should we treat it differently? Whatever law and policy we adopt for ocean fertilization will reflect our commonly-held cultural values with regard to this question, which itself is inherently international because of the biophysical nature of the ocean. Thus I will tend to use the terms 'law' and 'culture' somewhat interchangeably in this article.

HUMAN GOVERNANCE INSTITUTIONS

For most of the world's human population, the ocean is 'out of sight, out of mind.' Not only do most people not live or work on or in the ocean, but it is in fact an extremely hostile environment for humans. It is too salty to drink or to irrigate crops. Its density both smothers us if we are immersed in it and crushes us if we go too deep without elaborate protection. Its waves bash us on beaches and in boats, and its biochemical characteristics foul and corrode our machines and structures. Even though an increasing number of us live or work near the ocean, it is still not an 'intimate environment' for most people (Revelle 1969, Orbach 1982).

Governance on land and ocean

In the earliest days of human society most terrestrial space was 'open access, common pool,' owned or controlled by no-one. After the Neolithic Revolution

around 10 000 to 14 000 yr BP and, especially with the aggregation of human populations into cities around 3000 to 5000 yr BP and the subsequent growth of major centers of 'civilization' in what are now Greece, China, Mexico, Peru and North Africa, human terrestrial governance institutions grew exponentially in number and complexity. One of the most important of these is the notion of 'private property', under which space and resources may be held, and their use dictated, exclusively by certain individuals or groups of individuals. The last 10 000 yr of human history have seen the complete carving up of terrestrial space and resources into property, some of which is held in trust for aggregates of people under institutions called governments under the general term 'public trust'. Our cultural understandings regarding this property have been codified over time through 'natural', Roman Civil, and English Common law (Coastal States Organization 1990, McCay 1998). An important point with respect to ocean fertilization is that on land we made the cumulative, but explicit decision to 'cultivate' the land and its resources. We set aside some portions of the terrestrial environment for parks, wildernesses and other special designations, but by and large we bought into the idea that it is permissible, even desirable, for humans to manipulate large portions of the terrestrial environment.

Not so with the ocean. With few exceptions, until the late 1700s nation-states did not even claim exclusive governance authority over any portion of the ocean (Eckert 1979, Wilder 1998). The exceptions were societies that depended heavily on ocean resources and were in the position to exert some form of control over the use of those resources. In the age of low technology, this was not very common, and the reach of such societies did not extend very far from shore. Even if a state claimed 'territory' or control over ocean resources, it was difficult, if not impossible, to enforce such claims. The areas in which such claims were most in evidence were in smaller, more enclosed, ocean areas such as the Mediterranean or North Seas, or in smaller, more remote insular areas such as the Pacific Islands (Johannes 1981). In virtually none of these situations was the decision made to cultivate ocean resources, but rather to make claims for purposes of extraction or other uses such as shipping or military transport.

Emergence of the 'freedom of the seas'

Long before fishing developed as a significant ocean use, merchant and military shipping were prominent (Revelle 1969, Wenk 1972). During the first half of the second millennium, attempts were made by many

countries and coalitions of countries to assert control over shipping. Beginning around the midpoint of the second millennium, large-scale attempts were made to carve up the ocean in terms of shipping access.

It was the inability of any nation or group of nations to actually control ocean use or access that led, in 1609, to the treatise by the Dutchman Hugo de Grotius titled, 'Mare Liberium', or 'freedom of the seas' (Wilder 1998). Under the commonly accepted doctrine that developed pursuant to this treatise, the world ocean remained 'open access, common pool', with no nation or group of nations controlling use or access. Combined with this doctrine was the notion of the ocean as a source of inexhaustible resources, the use of which need not be restricted. This also created, in essence, the exact opposite of the 'precautionary principle'.

This remained generally the situation until the late 1700s, when the then-new USA declared a 3 nautical mile (n mile) territorial sea off its shores, the term 'territorial sea' meaning the portion of the ocean that nation-states have the right to treat as they do their land areas, with all the attendant rights and responsibilities (Wilder 1998). Soon all ocean-adjacent nations had followed suit and the first phase of the 'ocean enclosure' movement, out to 3 n miles, was complete. This 3 n mile limit remained in effect in the USA as the main ocean enclosure until 1945, when President Harry Truman issued a presidential proclamation claiming the resources of the outer continental shelf adjacent to its shore for the USA. This proclamation, later codified in the Outer Continental Shelf Lands Act of 1953, had the effect of extending the USA's jurisdiction over certain ocean resources much farther than the traditional 3 n miles, to the outer limit of the continental shelf. It was, however, not a 'territorial' zone, but a 'resource control' zone. That is, neither the proclamation nor the act extended the sovereign territory of the USA, only its control over the use of certain space and resources for extractive purposes (Cicin-Sain & Knecht 2000).

Two more major steps bring us to our current formal enclosure situation. The first was the passage by the U.S. Congress of the Magnuson Fishery Conservation and Management Act (now the Magnuson-Stevens Act, or M-SFCMA) of 1976. The M-SFCMA extended the jurisdiction of the USA over fishery resources to 200 n miles. Most ocean-adjacent nations followed suit soon thereafter. Then, in 1983, in part in reaction to the then-recently completed United Nations 'Law of the Sea' convention, President Ronald Reagan, again by presidential proclamation, declared a 200 n mile Exclusive Economic Zone (EEZ) off the USA shores. This proclamation, which has still not been codified by the U.S. Congress, essentially turned a continental shelf and fishery resource jurisdictional system into

an exclusive access system for all ocean and shelf resources within 200 n miles, including the water column itself. Again, most ocean-adjacent nations followed (and in some cases, led) suit (Cicin-Sain & Knecht 2000).

Thus, by the end of the second millennium the ocean enclosure movement had reached 200 n miles out to sea, and farther in cases of continental shelves that exceeded that distance. Once again, throughout this process little consideration was given to the question of large-scale manipulation of ocean environments, except perhaps in the context of fisheries extractions or oil and gas development. To fully understand the context of this situation, however, we must recount a parallel and somewhat broader international discussion regarding ocean spaces and resources that began in the early 1900s.

OCEAN SPACE AND RESOURCES IN THE BROADER PERSPECTIVE

Although merchant and military shipping had dominated ocean access discussions for most of the second millennium, in the latter part of that millennium extractive ocean uses became much more prominent. Ocean fisheries and offshore oil and gas, in particular, grew quickly in the wake of the industrial revolution of the 1800s, and by World War I extractive uses of the ocean had achieved the beginnings of their current (in some cases devastating) status. The technological advances of World War II completed this advance, and by the 1990s, for example, world ocean fish catches had leveled off in the face of ever-increasing fishing effort (Stone 1997). Offshore oil and gas, the other major extractive ocean use, continues to rise, as does world ocean shipping.

It was also clear, especially in the face of the open access, common pool character of ocean resources, that these issues had significant international dimensions. Not only are many of the resources of the ocean themselves mobile across national boundaries, but the human users themselves (fishermen, oil and gas activities, shipping) crossed those boundaries with increasing regularity as extractive technology (steam and diesel power, steel ships, radar, sonar, synthetic fibers, deep-sea engineering) developed. Beginning with the League of Nations early in the 1900s; through the Treaty of Paris in the 1930s; the 3 United Nations 'Law of the Sea' conventions (UNCLOS) beginning in 1958; and finally, in broader environmental discussions beginning in Stockholm in 1972 and continuing through Rio de Janeiro, Kyoto and Johannesburg, attempts have been made to further develop human governance institutions for ocean space and resources

(Hollick 1981, Cicin-Sain & Knecht 2000, Johannesburg Summit 2002).

These discussions have all had a curious dimension, owing to the culturally defined open access, common pool nature of ocean space and resources. Humans have always treated ocean space and resources differently from terrestrial resources. From time to time 'scientific' justifications have been given for this circumstance—for example, that many of the resources are mobile—but these justifications ring a bit hollow when exposed to scrutiny. Many terrestrial resources, for example, are (or were) also mobile, often highly migratory. Because of the density and intimacy of the use of terrestrial resources humans developed the notion of property on land (including many natural resources, such as forests and water) and governance institutions developed accordingly. There are, of course, categories of terrestrial or avian resources that under our governance institutions are formally called wildlife, which generally are not subject to private property access (Bean 1983). However, virtually all of the terrestrial space and resources have been divided up into property of either the private or public trust variety. This is opposed to the ocean, where even under the 200 n mile EEZ, some 60% of the ocean and its resources are 'high-seas' and thus principally open-access, common pool.

What was remarkably different in this history of ocean use and policy from the history of terrestrial use and policy, was that although the 'frontier' notion of the ability of anyone to enter the fray was the same, the ability of individuals and private sector organizations to make formal claims on ocean spaces and resources was absent. That is, there was no notion of private property in the oceans, and also—once again—virtually no discussion of the idea of actively cultivating the ocean.

One aspect of this distinction between land and sea became focused in the idea of ocean space and resources as the 'common heritage of mankind,' a phrase coined by Arvid Pardo, the United Nations Ambassador from Malta, in a speech to the United Nations in 1967 (Borgese 1998). That phrase, and a companion phrase, 'the new international economic order,' (NIEO) became common parlance in the third UNCLOS Convention (UNCLOS III) between 1973 and 1982 (Hollick 1981, Wilder 1998). These 2 phrases perpetuated the idea of ocean space and resources as different from the terrestrial; in particular, that they are and should remain common pool, if not open access. Significantly, however, they also advanced the notion that the governance of ocean space and resources should be institutionalized for the benefit of all humankind, not only those in ocean-adjacent nations or with ocean exploitation capability. More particu-

larly, the idea was advanced that the benefits of ocean resources should be directed to those humans most in need of them on some sort of social equity basis, rather than simply to those with the ability to exploit them. This discussion remains prominent today, as evidenced recently in Johannesburg at the United Nations World Summit on Sustainable Development (Johannesburg Summit 2002).

In general, the common heritage principle has not been implemented, with 1 exception: ocean mining. In this case, those supporting the 'common heritage of mankind/NIEO' made an effort to both extend the notion of resource control beyond 200 n miles and to ensure the benefits of the exploitation of ocean minerals for the good of all humankind, not only those with exploitation capacity (International Seabed Authority 2000).

Even with ocean mining, however, the discussion was in the context of extracting some natural resource, in general with the idea that such extraction should be done in the most environmentally sound, if not benign, way possible. That is, the discussion did not consider, much less accept, the idea that human activity would create large scale alteration of ocean environments.

Who owns the ocean? As noted above, some 60% of the ocean space lies outside of the 200 n mile EEZ of individual nation-states. Within 200 n miles there are 3 different states of governance. The first is the 'territorial sea', now out to 12 n miles (again, in the USA, by presidential proclamation), within which the ocean is treated as sovereign territory of the adjacent nation as is the land (customs authority, etc.). The second is the area from 12 to 200 n miles, which is officially classed as EEZ, within which access to resources is controlled by the adjacent nation. The third governance situation involves resources that are migratory, meaning either common pool resources, such as migratory fish or ships registered to individual nation-states that cross international boundaries in their travels. In the case of migratory fish stocks the governing institution is the Convention on Straddling Stocks, which places the burden for cooperation in conservation for such stocks in the hands of nations within whose jurisdiction the fish occur, or whose fishermen take them either within or outside of any national jurisdiction (Burke 1994, Balton 1996). In the case of shipping, the 1996 Protocol for the London Convention places a similar burden in the hands of the nations of registry of the ships, again either within or outside of national jurisdiction (Van Dyke 2000).

Thus, in summary: (1) Shoreline to 12 n miles, territorial sea, (2) 12 to 200 n miles, EEZ, (3) outside of 200 n miles, high seas, and (4) special provisions for migratory resources and shipping.

It is useful in this regard to review the history of marine fisheries policy and management in the USA. Until 1976 there was no effective federal management of marine fisheries. Virtually all management, with the exception of international treaties, was done by the individual states within 3 n miles of their shorelines. There were various coordination mechanisms, such as the Interstate Marine Fisheries Commissions initiated in the 1940s, but the basic management authority existed in individual states and their respective jurisdictions. Until the advent of the Alaska Salmon Limited Entry system in the early 1970s, the management of marine fisheries had operated under an open-access principle. The Magnuson-Stevens Act created for the first time a uniform, authoritative marine fishery policy and management presence and included a provision for the development of 'limited access' systems. As of 2002, most of the USA's major marine fisheries are under some form of limited access system. Some of these systems, termed generally individual fisherman quota (IFQ) systems, create a form of property right of access to a certain portion of the fish harvest. These IFQ systems are controversial, in large measure because they introduce both the notions of restricted access and property rights to ocean spaces and resources (NRC 1998). However, I submit that they are becoming ubiquitous for exactly the same reasons that terrestrial space and resources eventually came under some form of private property (Christy 1996) — increased density of human use.

The question is: Should ocean resources be different from the terrestrial—in particular in the areas of access and property rights—and if so, in what ways? There is also the overarching general question of whether we should allow the large-scale manipulation of ocean environments through actions such as ocean fertilization.

DIFFERENCES BETWEEN OCEAN AND TERRESTRIAL SYSTEMS AND IMPLICATIONS FOR GOVERNANCE

I would suggest that there are 3 basic reasons that ocean and terrestrial space and resources require different systems of governance. The first is that ocean space and resources are intrinsically different from the terrestrial. The second is that practical aspects of dealing with ocean space and resources justify, and perhaps require, a governance system different from those on land. The third is what I will call the cultural preference rule: humans simply believe that ocean space and resources should be treated differently from those of the land, ideally for reasons that we can articulate clearly. Let us consider these 3 possibilities.

Are ocean space and resources intrinsically different?

In a special issue of *Scientific American* in 1969 dealing with the ocean, Roger Revelle and his colleagues enumerated the distinctive features of ocean space and resources: depth, density, fluidity, salinity, viscosity, organismal metabolism and mobility (Revelle 1969). Why, however, would these characteristics lead us to govern human behavior differently in the ocean realm? The atmosphere, also, has characteristics different from the land and we have developed governance institutions for activities such as aircraft, radio transmission, satellites, air space and air pollution that mimic, in principle, governance institutions for terrestrial space and resources (Wiener 1999a, Torres 2001, Sagarin et al. 2007).

Take, for instance, migratory resources such as terrestrial and avian wildlife. In both cases—similar to ocean resources—the populations themselves are mobile across jurisdictional (including national) boundaries. For many of them we created a specific category with specific legal standing: wildlife. In the case of most, if not all, of these resources we have developed a subsidiary cultural rule, translated into law, allocating these resources to recreational, as opposed to commercial, harvest. For those resources that remain the realm of commerce, we have applied the notions of private property and developed appropriate governance institutions. For those we consider wildlife, we also develop elaborate governance institutions, including rules of access, and many of these institutions are robust across national boundaries (Holt & Talbot 1978, Bean 1983). Why should we not do the same for ocean resources, throughout ocean space?

To the question at hand, one could also query whether manipulations such as ocean fertilization are appropriate uses of ocean environments. One goal of ocean fertilization, for example, is to stimulate phytoplankton growth in order to draw carbon out of the atmosphere and into the ocean, and in some cases to stimulate further ocean productivity. This would be achieved by spreading substances such as iron in the ocean in those locations where iron is currently in such low concentrations that it limits phytoplankton growth. The closest parallel to this process is probably the addition of feed to ocean environments during the process of ocean aquaculture, but the addition of the feed itself is ancillary to the overall process of catching, penning and harvesting the fish themselves, and the policy and regulatory process for ocean aquaculture itself is not well-developed (Cicin-Sain & Knecht 2000, USCOP 2004).

As with any issue that combines complex science, policy and economic drivers, different cultural value systems also come to bear on people's views about the

wisdom of iron fertilization. For example, every group of scientists consulted for this report will express a range of viewpoints based on their particular cultural value orientation. While all may address the need to be cautious with ecosystem engineering at any significant scale, some might also suggest that such engineering projects may be useful as part of a larger portfolio of ideas to reduce greenhouse gas concentrations, while others may express strong opposition to manipulating ocean ecosystems in this manner. Aside from the specific biophysical, economic, or social effects of such systems, these cultural value orientations reflect personal and organizational attitudes and perceptions regarding the appropriateness of different courses of action.

My conclusion from this general discussion is that ocean resources generally and ocean fertilization specifically are not intrinsically different from terrestrial or avian resource and environmental uses from a governance point of view. However, these above questions would have to be answered to yield a rational and effective regime for governance of ocean fertilization.

Do ocean space and resources have practical management conditions or constraints?

It is certainly true that 100, or even 50, yr ago technology and management systems did not exist to monitor ocean fish harvests, or the movements of merchant or military ships, or processes such as ocean fertilization. It is also true that even now there may be people who perceive the ocean and its resources to be inexhaustible, or its environments infinitely adaptable and resilient. I submit that neither of these circumstances is true today.

In the current era of computers, satellites and remote-sensing technology we can monitor the movements of, if not detailed behavior aboard, every boat and ship in the sea. There are, of course, economic factors and issues of confidentiality and privacy involved, but no more so than on the land or in the air. Although the ocean remains a difficult biophysical space for humans to deal with, for purposes of the monitoring of major ocean uses the technology is generally available, as is the underpinning of a legal framework for their governance (Wiener 1999b). With some technological development we certainly could monitor ocean fertilization experiments and, assuming effective theories and methods, their effects.

The question of whether we have the capability to effectively monitor and enforce whatever rules we might devise with respect to ocean fertilization is a very significant question. Because of the basic nature of the proposed process itself, the scientific uncertain-

ties involved, and the presumed broad scale impact of the activity, the question of our ability to monitor and enforce would be significant.

The resources of the ocean are not inexhaustible and while it is technologically possible to monitor—and control—human behavior in the major extractive ocean uses with sufficient resources applied to that end, the question is less certain with respect to ocean fertilization.

The cultural preference rule

Just as humans have developed special governance institutions for such categories of resources as wildlife (and in the case of the USA, even more particular institutions in the case of marine mammals), we could decide that ocean space and resources simply deserve (read 'humans would prefer them') to be treated differently (Earle 1995). In the governance sense, this is a premise of the common heritage of mankind approach—that all humankind should share in some equitable way in the use of ocean resources in a way they do not with terrestrial resources, largely because of the existence of the pervasive notion of private property on land, which to a certain extent subverts equitable public purpose. In our present discussion of ocean fertilization, one significant question that we face is whether the ocean should be used for such purposes. There are, of course, overarching political, social and economic philosophies regarding this question, the discussion of which has reached across the millennia.

In a more practical vein, though, it may simply be a matter of deciding. The current discussion of the concept of marine protected areas (MPA) is an example of this. In one sense the MPA discussion involves the best way to conserve or protect specific ocean resources or ecosystems, but in a larger sense the question is simply how do we prefer to treat ocean space and resources? This is akin to the questions that John Muir and Teddy Roosevelt asked about terrestrial resources that led to the establishment in the USA of the national park system. Conservation is a consideration, yes, but so are aesthetics, existence value, perceptions of individual and societal well being and all of the other concepts that have emerged as we have developed governance institutions for our cities, farms, forests rivers and wildlife (Miller et al. 1987). The analogous question could be asked of the idea of active cultivation of ocean resources and environments.

My own conclusion from this brief exploration of these issues is that ocean space and resources are not significantly different from the terrestrial and atmospheric from the point of view of functionally appropriate governance institutions. It is our own cultural

assumptions that lead us to treat them differently. In this sense, the question of ocean fertilization is a cultural question. It is not until the cultural questions—the human values we wish to apply—are answered that we can begin to answer the rest of the questions pertaining to ocean fertilization.

DESIGNING THE OCEAN ENVIRONMENT

The answer to all of these questions lies in 2 areas. The first is increased knowledge of the biophysical ecology of the world's oceans and of the human ecology of our use of the oceans, in order that the tradeoff inherent in different rules of governance might be accurately estimated. The second is the ability to format the discussion in a reasonable and productive way and to use our increased knowledge to rationally construct law and policy.

In making public policy regarding ocean fertilization, we must necessarily choose among many different possible governance rules, all of which are interactive with human behavior, and law and policy in related policy arenas such as fisheries, shipping, oil and gas, etc. This is a case of what we might define as 'ecosystem management,' a much bandied-about term but useful in the present context. The important point is that we need to know as much in a documented way about the human ecological configuration as we do about the biophysical ecological configuration, including the structure of human values that underlie our current—and potential future—law and policy.

Following from this point, all of the resulting governance rules will be based on some set of human cultural values. These values will reflect our perceptions and attitudes regarding our desired state of the biophysical and human environments. In this sense, we are engaged in a design exercise for both the biophysical and human ecology, and the ways in which the two map onto one another. As we stated at the outset, we will have to decide whether to treat the ocean as we have the land and even the atmosphere—to be divided up into private property or exclusive access privileges and/or cultivated on a mass scale. In any event, to manage human behavior effectively at the scale necessary for the world ocean, we will have to proceed towards a 'policy enclosure' of the world ocean, in order that the resulting governance rules for all parts of the ocean ecosystem, both inside and outside of areas of national jurisdiction, can be effectively developed and applied (Orbach 2002). The future of ocean fertilization will be guided by the tradeoffs we make, the design we select for ocean environments and resources, and the pattern of human uses resulting from that design.

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Ocean fertilization and other climate change mitigation strategies: an overview

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ABSTRACT: In order to evaluate ocean fertilization in the larger context of other proposed strategies for reducing the threat of the global warming, a wide range of different climate change mitigation approaches are compared in terms of their long-term potential, stage of development, relative costs and potential risks, as well as public acceptance. This broad comparative analysis is carried out for the following climate change mitigation strategies: supply-side and end-use efficiency improvements, terrestrial and geological carbon sequestration, CO₂ ocean disposal and iron fertilization, nuclear power, and renewable energy generation from biomass, passive solar, solar thermal, photovoltaics, hydroelectric and wind. In addition, because of the inherent problems of conducting an objective comparative cost–benefit analysis, 2 non-technological solutions to global warming are also discussed: curbing population growth and transitioning to a steady-state economy.

KEY WORDS: Ocean fertilization · Climate change mitigation technologies · Efficiency · Carbon sequestration · Renewable energy · Cost–benefit analysis · Population growth · Economic growth

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INTRODUCTION

Anthropogenic emissions of carbon dioxide from the combustion of fossil fuels have significantly increased atmospheric CO₂ concentrations during the last century, which, in turn, is expected to bring about climate change together with both predictable and unforeseen negative consequences for both humans and the environment. In order to reduce the threat of global warming, drastic reductions in carbon emissions, currently amounting to ~7.1 Gt C yr⁻¹, are needed. According to the so-called 'Kaya' equation, the magnitude of net carbon emissions to the atmosphere (Net C) is a function of multiple driving forces (Huesemann 2006):

$$\text{Net C} = P (GDP/P) (E/GDP) (C/E) - S \quad (1)$$

where P is the size of the human population, GDP/P is the per capita gross domestic product, often referred to as 'affluence', E/GDP is the energy required per gross domestic product, also called energy intensity, which is the inverse of energy efficiency, C/E is the carbon emitted per unit energy generated, i.e. the carbon

intensity of the fuel mix used to drive the economy, and S is the natural and induced removal of carbon as CO₂ from the atmosphere, also referred to as carbon sequestration. In summary, the Kaya equation states that the size of total carbon emissions is the product of a nation's population, its per capita economic output, its energy utilization efficiency, and the carbon quality of the fuel used, minus any carbon that is sequestered in terrestrial biomass, geologic formations, or oceans. It is the objective of this paper to provide a broad comparative cost–benefit analysis of all climate change mitigation technologies, including ocean fertilization, and also consider non-technological solutions to global warming, such as curbing population growth and transitioning to a steady-state economy.

COMPARISON OF CLIMATE CHANGE MITIGATION STRATEGIES

A comparison of different climate change mitigation technologies, in terms of their long-term potential,

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Table 1. Comparison of different climate change mitigation in terms of their long-term potential, stage of development, relative costs and potential risks. R&D: research and development, C: carbon, tech: technology, med: medium

Mitigation technology	Long-term potential	Stage of development	Relative cost ^a	Potential risks	Other issues
Efficiency improvements					
Supply-side efficiency	2-fold improvement	Current tech	Low to med	None	Market imperfections
End-use efficiency	>10-fold (?) improvement	R&D	Low to med	None	Market imperfections
Carbon sequestration					
Terrestrial	Approx. 200 Gt C	Current tech	Low	None	Competition with food, fiber and fuel wood
Geological					
Coal seams, Oil & gas fields	Several 100 Gt C	R&D, pilot study	Med to high	Environmental health	Leakage, only power plants
Saline aquifers	Up to 10 000 Gt C	R&D, pilot study	Med to high	Environmental health	Leakage, only power plants
Ocean					
CO ₂ disposal	Several 1000 Gt C	R&D, pilot stopped	Med to high	Acidification of marine biota	Public resistance, legality
Iron fertilization	~0.2 Gt C/yr ⁻¹	R&D, pilot study	Low to med	Marine environment	Public resistance, legality
Carbon intensity reduction					
Decarbonization of fossil fuels	Decarbonize all fossil fuels	Current tech	Low to med	Carbon sequestration	–
Renewable energy sources					
Biomass	Several-fold increase	Current tech, some R&D	Low	Environment, food availability	Land-use conflicts
Passive solar	>10-fold increase	Current tech	Very low	None	Market imperfections
Solar thermal	>10-fold increase	Current tech, some R&D	Low to med	Desert ecosystems	–
Photovoltaics	>10-fold increase	Current tech, some R&D	Low to med	None or very limited	–
Hydroelectric	No further increase	Current tech	Low	Aquatic ecosystems	Public resistance
Wind power	>10-fold increase	Current tech, some R&D	Low to med	Noise, bird kills	Aesthetics, public resistance
Nuclear energy	Several-fold increase	Current tech, some R&D	Low to med	Radioactivity, catastrophe	Waste proliferation

^aThe quantification of exact costs or cost ranges is difficult for the following reasons: (1) for many currently existing technologies (e.g. solar photovoltaics), costs are expected to decrease substantially due to economies of scale if they were to be widely adopted; (2) for mitigation strategies that exhibit some type of saturation phenomenon (e.g. planting trees on limited land), marginal costs increase as opportunities for applying them decrease; (3) for technologies that are still in the research and development stage (e.g. geological sequestration, iron fertilization), costs are difficult to estimate because the final system or end-product is not yet known; (4) for technologies that transfer costs and risks to future generations (e.g. nuclear energy, geological sequestration), present-day cost estimates may be significantly underestimated

stage of development, relative costs and potential risks, is given in Table 1. As indicated by Eq. (1), climate change mitigation technologies fall into 3 general categories: energy efficiency improvements, carbon sequestration and carbon intensity reduction. Within each of these 3 general categories, a number of different technologies or mitigation approaches exist. For example, energy efficiency improvements can further be classified as either supply-side or end-use efficiency improvements. Supply-side efficiency is defined as the ratio of useful energy output (e.g. work, heat, electric-

ity) to primary energy input (e.g. coal, oil, uranium, biomass) and is currently about 37% at the global scale (Jochem 2000), but could in theory be further increased ~2-fold (Jochem 1991). Further improvements are unlikely, given intrinsic thermodynamic and practical constraints (Jochem 1991). Most increases in supply-side efficiency could be achieved with current technologies, making them relatively cost effective and risk free.

End-use efficiency is defined as the ratio of economic output resulting from energy services (measured as

gross domestic product, or GDP) to useful energy input and could, in certain specific cases, be increased substantially, possibly by 1 order of magnitude or more. For example, compared to traditional incandescent lights, the amount of lighting service (lumens) provided per electric energy input has risen significantly with the use of light-emitting diodes (LEDs). Since continued research and development will be needed to further increase end-use efficiencies, relative costs are intermediate, but risks are low or nonexistent.

Despite the fact that efficiency improvements are a risk-free solution to climate change and that many could easily be implemented at no additional cost (Lovins & Lovins 1991), there are a number of barriers, such as absence of economic incentives, lack of consumer information, insufficient capital, slow technology diffusion, and general cultural inertia (Huesemann 2006). However, the primary reason for not realizing theoretically achievable efficiencies are market imperfections that are created when the cost of energy is kept artificially low by subsidies or by externalizing environmental and national security costs, thereby encouraging wasteful energy use by consumers and providing no incentives for energy conservation via efficiency measures (Sioshansi 1991, Jochem 2000). Finally, it is important to note that energy efficiency improvements alone will not reduce total energy use and carbon emissions if the size of the global economy continues to grow (see also Huesemann 2006, Huesemann & Huesemann 2008).

Carbon sequestration involves either the capture and secure storage of power plant CO₂ emissions in geologic formations or deep oceans, or the removal of CO₂ from the atmosphere by terrestrial or marine photosynthesis and the subsequent, long-term storage of the carbon-rich biomass (US DOE 1999). Terrestrial carbon sequestration consists of the photosynthetic fixation of atmospheric CO₂ by plants (e.g. trees, crops, grasses, etc.) and the long-term accumulation and storage of both standing and below-ground biomass. Rates of terrestrial carbon sequestration can be increased by reforestation and afforestation, and by implementing alternative soil management practices, such as no-till agriculture to promote the formation and retention of soil organic matter. The terrestrial biosphere currently stores approximately 2000 Gt C (ca. 600 Gt in plant biomass and 1400 Gt in soil humus) (US DOE 1999) and this carbon pool could possibly be increased by approximately 200 Gt C, to its pre-1750 size, via reforestation and improved farming practices (Scholes & Noble 2001). Terrestrial carbon sequestration can be carried out with current technology, is low in cost and carries few risks—in fact, it should result in a significant improvement in previously degraded ecosystems. The main challenge to implementing terrestrial carbon

sequestration on a large scale is the ever-increasing and competing demand for food, fiber, and fuel wood by growing human populations.

Geological carbon sequestration involves the storage of CO₂ in deep underground reservoirs, such as depleted oil and gas fields, unmineable coal seams, and saline aquifers (US DOE 1999, Bruant et al. 2002). Prior to sequestration, the CO₂ must first be separated from the flue gases of centralized fossil fuel-fired power plants and then transported via pipeline to geologic reservoirs. The total world-wide carbon storage capacity is estimated to be tens to hundreds Gt C for coal seams, hundreds to 10 000 Gt C for saline aquifers, and several hundred Gt C for depleted oil and gas fields (Herzog 2001, Bruant et al. 2002). The primary difficulty with geologic carbon sequestration is the potential leakage of CO₂ from the reservoirs and subsequent adverse effects to human health and the environment (Herzog 2001, Bruant et al. 2002, Wilson et al. 2003). Thus, given that some leakage is unavoidable—because it would be very difficult, if not impossible, to detect, monitor and to control all potential CO₂ escape routes—geologic carbon storage is not truly permanent. Slow, chronic leakage could result in the dissolution of CO₂ in shallow aquifers, causing the acidification of groundwater and undesirable changes in geochemistry (e.g. mobilization of toxic metals), water quality (e.g. leaching of nutrients), and ecosystem health (e.g. pH impacts on organisms) (Bruant et al. 2002). A sudden catastrophic release of large amounts of CO₂, as a result of either reservoir fracturing by earthquakes or pipeline failures, could result in the immediate death of both people and animals, particularly since CO₂ is odorless, colorless, and tasteless, and thus is likely to escape detection (Bruant et al. 2002). The US Department of Energy is currently conducting a number of field pilot studies to evaluate the efficacy and safety of geologic carbon sequestration (US DOE 2007). Because of the need for gas separation, transport, injection and long-term monitoring, sequestration costs will likely be intermediate to high.

Two different types of ocean carbon sequestration schemes have been proposed: (1) the disposal of CO₂ in mid- or deep oceans, and (2) the addition of fertilizers to stimulate the growth of phytoplankton, part of the latter is expected to sink to the ocean floor and thus sequester C there. Proposed CO₂ ocean disposal strategies include the release of dry ice cubes from a stationary ship, the introduction of liquid CO₂ onto a seafloor depression forming a 'deep lake,' the release of CO₂-enriched seawater at 500 to 1000 m depth, and the injection of liquid CO₂ at 1000 to 1500 m depth from a stationary outlet or from a pipe towed by a moving ship (Herzog et al. 1996, Caulfield et al. 1997, US DOE 1999). The rationale for injecting CO₂ into the

oceans, which have a combined storage capacity of several thousand Gt C (Herzog 2001), is to accelerate the transfer of CO₂ from the atmosphere to the deep ocean, a process which occurs naturally at an estimated rate of 2 Gt C yr⁻¹. The main problem with CO₂ ocean disposal is that the resulting seawater acidification and pollution with CO₂ impurities such as NO_x, SO_x, and trace metals (US DOE 1999) could adversely affect highly sensitive marine organisms, many of which have adapted to the very stable deep sea environment and therefore are ill-suited to adjust to drastic changes in seawater chemistry (US DOE 1999, Tamburri et al. 2000, Seibel & Walsh 2001). In addition, CO₂ disposal may also negatively affect microbial populations and thus cause changes or disruptions in marine biochemical cycles (Seibel & Walsh 2001, Huesemann et al. 2002), which may have large negative consequences, many of them secondary and difficult to predict (US DOE 1999). Because of these environmental issues, mounting public opposition and legal concerns, 2 proposed small-scale CO₂ disposal experiments off the coasts of Hawaii and Norway were cancelled in 2002 (Burke 2002), making the future of CO₂ ocean dumping uncertain.

Ocean fertilization involves the addition of limiting micronutrients, such as iron, to stimulate the growth of phytoplankton (US DOE 1999, Chisholm et al. 2001). While most of the additional photosynthetically fixed biomass carbon will be recycled in the photic zone, a small fraction will sink to the ocean floor, where it will become incorporated into deep-sea sediments, thereby preventing its reentry into the global carbon cycle for some time. Although there are significant scientific and technical problems with quantifying the exact amounts of carbon that would be sequestered in deep-ocean sediments (Gnanadesikan et al. 2003, Buesseler et al. 2004), it is estimated that about 200 × 10⁶ t C (i.e. ca. 3% of current annual CO₂ emissions) could be sequestered per year by fertilizing 10⁸ km², an area corresponding to the size of the entire Southern Ocean (Buesseler & Boyd 2003). Because large-scale ocean fertilization would involve the manipulation of immense expanses of ocean surface waters, there are serious concerns about potential unexpected negative consequences to marine ecosystems and biogeochemical cycles. For example, large-scale eutrophication could result in the depletion of oxygen, leading to deep ocean anoxia, which, in turn, would shift the microbial community structure towards organisms that produce methane and nitrous oxide, i.e. greenhouse gases with much higher warming potentials than CO₂ (US DOE 1999, Chisholm et al. 2001, Gnanadesikan et al. 2003). In addition, it will be difficult to predict all secondary and higher order effects of ocean fertilization on the ocean food web structure and dynamics, including

changes in the biogeochemical cycling of important elements, such as carbon, nitrogen, phosphorus, silicon and sulfur (US DOE 1999, Boyd et al. 2007). Despite increasing interest by private companies in selling carbon credits by fertilizing large expanses of ocean, the International Maritime Organization recently announced at their 2007 London Convention that, 'knowledge about the effectiveness and potential environmental impacts of ocean fertilization is currently insufficient to justify large-scale operations.' (IMO 2007).

In addition to efficiency improvements and carbon sequestration, a third climate mitigation approach is to reduce the carbon intensity of the energy mix¹, which can be brought about by (1) decarbonization of fossil fuels, (2) increased use of renewable energy, and (3) greater utilization of nuclear power (see Table 1). Decarbonization of fossil fuels involves the generation of the carbon-free energy carrier hydrogen and CO₂, the latter of which must be sequestered in geologic formations or deep oceans, an approach that is neither inexpensive nor risk-free (see above). The increased use of renewable energy sources such as biomass, wind, photovoltaic, solar thermal, and hydroelectric energy is often seen as an easy and obvious solution to climate change but, as has been reviewed in great detail elsewhere (Huesemann 2003, Huesemann 2006), there are likely to be significant environmental impacts if renewable energy generation were to be implemented on a large scale.

Biomass energy can be generated in many cases at relatively low cost using technologies that are already available or currently under development. The main problem with biomass energy is that large areas of productive land are required. Consider, for example, that anthropogenic activities already appropriate 30 to 40% of the terrestrial primary productivity (i.e. photosynthetically fixed carbon) worldwide (Vitousek et al. 1986, Rojstaczer et al. 2001), indicating that two-fifths of the land's productive capacity is tightly controlled and managed for supplying food, fiber and energy. In the USA, total energy use (ca. 100 quads) is almost twice as large as the energy captured by all vegetation (58 quads), about half of which (28 quads) is already harvested as agricultural crops and forest products and therefore not available for energy production (Huesemann 2006). For example, if ethanol from corn were to be substituted for 100% of the gasoline consumption in the USA, all of the available USA cropland would have to be devoted to ethanol production, leaving no land for food production (Kheshgi et al. 2000). Thus, increased biomass energy production will lead to com-

¹Energy mix is defined as the proportional relationship between all utilized energy sources

petition for scarce agricultural land and will intensify ethical conflicts regarding the use of crops for food versus fuel. Indeed, in response to the rising demand for corn-based ethanol, prices for corn and other basic staples have already increased significantly, placing the world's poorest people at serious risk of malnutrition and starvation (Muller et al. 2008). A possible solution to these problems is to cultivate microalgal biomass for biofuel conversion employing land and water resources not used for agriculture. Because of the high solar conversion efficiencies of microalgae, their cultivation has a 10-fold smaller environmental footprint than agricultural biomass; however, significant research and development will be needed to make biofuels from microalgae economically competitive (Huesemann & Benemann 2008). According to a recent analysis by van Harmelen & Oonk (2006), approximately 100×10^6 t CO₂ (27×10^6 t C) could be removed annually by microalgae starting around 2020. If microalgal biofuels were to be produced at this scale for 50 yr, about 1.35 Gt C would be abated, which amounts to approximately 5% of the climate stabilization wedge proposed by Pacala & Socolow (2004).

Another extremely cost-effective way of providing renewable energy for space heating and hot water is through 'passive' solar energy capture by buildings specifically designed for this purpose. Tremendous potential exists for capturing more solar energy by buildings with current technologies with no or minimal environmental impacts. Solar energy can also more 'actively' be captured by either solar thermal receivers consisting of computer-controlled sun-tracking parabolic mirrors that focus sunbeams to generate steam for electric power generation or by photovoltaic cells that convert light into electricity. While some limited amount of energy is already being generated with these active solar capture technologies, more research and development will be needed to make them economically competitive. For significant fractions of the total energy demand to be supplied by these technologies, very large land areas (e.g. thousands of square miles) would have to be covered with these solar energy capture devices, which could potentially result in adverse environmental impacts (Huesemann 2006). Hydroelectric dams generate annually about 3% of the USA's total energy demand, but hydropower generation is unlikely to be expanded because all suitable sites have already been exploited and there are increasing concerns about deleterious environmental impacts to aquatic species (Huesemann 2006). Finally, large windmills—if deployed by the millions—could also provide a fraction of carbon-free power. However, given that millions of ha would have to be covered with windmills to provide even a small fraction of the USA's electricity demand, it is unlikely that the public will

tolerate huge wind farms, given concerns about blade noise and aesthetics (Huesemann 2006).

In addition to renewable solar energy generation, carbon-free energy can also be produced in a relatively cost-effective way by nuclear power plants using existing technologies. Although nuclear power currently supplies about 6% of energy in the form of electricity worldwide, further expansion of nuclear energy generation will be problematic because of limited uranium reserves, waste disposal and weapons proliferation concerns associated with breeder reactors, nuclear reactor safety, long-term storage of radioactive wastes, and intense public resistance against the construction of new nuclear power plants (Huesemann 2006).

Finally, a number of innovative 'geo-engineering' or 'planetary engineering' approaches have been proposed to counteract global warming by reducing the quantity of sunlight reaching the earth surface. More commonly proposed geoengineering strategies include (1) the dispersal of sulphate aerosols and/or dust into the atmosphere, thereby effectively simulating volcanic eruptions that have historically been demonstrated to cause 'global cooling,' (2) large-scale cloud seeding to increase cloud cover, and (3) the installation of a 2000 km diameter space-mirror deflecting about 2% of earth-bound solar radiation (Teller et al. 1997, Hoffert et al. 2002). Although these geoengineering technologies are presently only at the conceptual stage of development, there is already considerable concern about potentially unknown and even intrinsically unknowable negative long-term consequences of the large-scale modification of planetary processes (Kintisch 2007).

INHERENT PROBLEMS OF COMPARATIVE COST-BENEFIT ANALYSIS

Based on the above cursory analysis of potential climate change mitigation options (Table 1), it appears that the best approaches are those which can employ existing technologies, are low cost, and have minimal risk, thereby being readily acceptable to the public. Using these selection criteria, efficiency improvements, terrestrial carbon sequestration, passive solar, and a very cautious expansion of renewable solar energy sources such as biomass, active solar, and wind power are probably some of the best choices for reducing the risk of global climate change. However, because of the limited potential of these few options, it will be necessary to carry out a more rigorous comparative cost-benefit analysis (CBA) of all climate change mitigation approaches.

As shown in Fig. 1, a comprehensive and systematic CBA involves at least 9 different steps (Boardman et

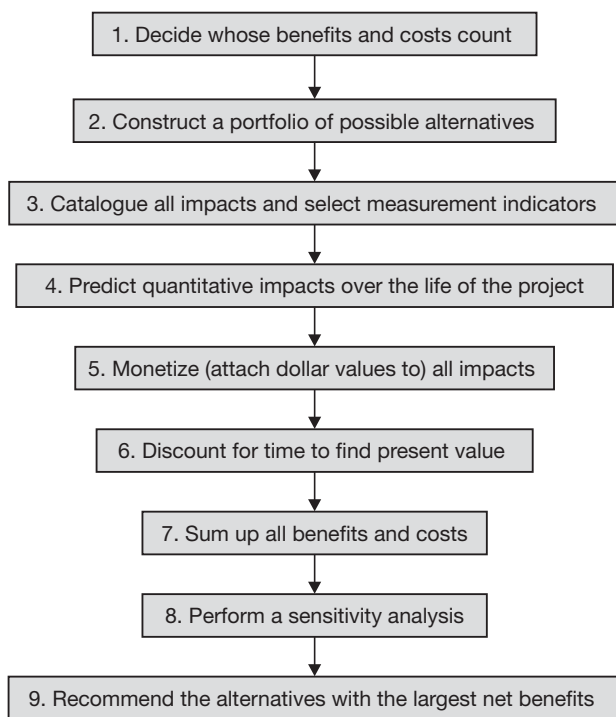


Fig. 1. Procedural steps involved in performing comprehensive and systematic cost-benefit analyses (Boardman et al. 1996)

al. 1996). Although this step-wise procedure appears to be straightforward at first sight, many difficult problems arise as soon as one actually tries to carry out a particular comparative CBA. (1) It is difficult to determine whose benefits and costs should be counted (Step 1). Should it be a selected group of people, all people presently living, future generations, certain animal species, all animals, all plants, etc.? The answer to these questions cannot be found by an objective analysis but depends on value judgments, thus greatly increasing the probability of value conflicts among different stakeholders. (2) The cataloging of all potential impacts and the selection of measurement indicators (Step 3) is affected by the boundaries of the analysis. Should local or global, present or future impacts be considered? In addition, many impacts may not be foreseeable. Similarly, the selection of measurement indicators depends on our current state of knowledge, which, because of its perpetual incompleteness, could result in a situation in which the most important impacts would not be measurable. (3) Even if all potential effects could be identified and measured, quantitative prediction (Step 4), from the present into the distant future, is almost certainly impossible given the inherent limitations of current mechanistic, reductionist science (Huesemann 2001). (4) The monetization of all costs and benefits

(Step 5) is highly problematic because it is exceedingly difficult to assign a price for non-marketed values such as the life of humans or animal species. (5) The discounting of the future to obtain the present value (Step 6) is ethically questionable because potential negative consequences to future generations may be greatly underestimated. (6) The entire process of CBA, which is based on utilitarian philosophy, is an attempt to maximize overall benefits to society (Step 7) while at the same time ignoring issues of equity and justice, i.e. CBA is insensitive to the fact that benefits may accrue to some individuals or groups at the expense of others.

Because of these inherent procedural uncertainties, it is intrinsically impossible to conduct a truly objective, comparative CBA of different climate change mitigation technologies. Instead, the most powerful stakeholders often define the problem and influence the procedure in such a way that the outcome of the CBA will be biased towards a particular favored technology. Thus, the selection of the best climate change mitigation approaches is not just a technical exercise but a highly political process.

CURBING POPULATION GROWTH AND TRANSITIONING TO A STEADY-STATE ECONOMY

According to Eq. (1), net carbon emissions are affected to a significant degree by the size of the human population (P) and per capita affluence (GDP/P), 2 factors that are rarely considered in the climate change mitigation debate. Several studies have shown that the projected population growth between 1985 and 2100 accounts for more than 33% of the future growth in CO_2 emissions globally and close to 50% in developing nations (Bongaarts 1992, UNPC 1994). If global fertility could be reduced by only 0.5 births per woman to achieve the United Nation's low variant population projection of 5.6×10^9 (Gaffin 1998), the projected population would decrease by 18% in 2050 and by 46% in 2100, which could translate into similar reductions in energy demand and greenhouse gas emissions (Gaffin & O'Neill 1998).

Respecting human rights, global fertility could be easily and cost-effectively reduced by (1) increasing the education of women, (2) offering financial incentives for small families and disincentives for large ones, (3) providing social security and universal health care in order to reduce dependence on adult children, (4) making family planning services available, and (5) changing cultural norms with regard to ideal family size (Huesemann 2006, Huesemann & Huesemann 2008). Compared to most climate change technologies discussed above (Table 1), controlling population

growth is one of the cheapest methods to avoid future CO₂ emissions. According to the analysis of Birdsall (1994), the costs of reducing births through family planning and female education are \$US4 to \$US11 and \$US3 to \$US9 t⁻¹ of carbon avoided, respectively, which is lower than the US Department of Energy's ambitious goal of \$10 per ton of carbon sequestered or avoided (US DOE 2007).

All other things being equal, the size of the per capita GDP, commonly referred to as 'affluence' or 'material standard of living,' is directly related to the magnitude of net carbon emissions (see Eq. 1). According to estimates by the Intergovernmental Panel on Climate Change (IPCC), the size of the world economy is expected to increase 12- to 26-fold by 2100, and per capita affluence 4- to 19-fold, depending on scenario conditions (Huesemann 2006). This continuing growth in economic output and material affluence is likely to significantly lessen any gains in net carbon emission reductions that will be made by the various technological mitigation approaches discussed above (see Table 1). Thus, unless there is a conscious effort to transition from our current growth-oriented economy to a steady-state economy in which material affluence is maintained at constant and sustainable levels, it will be extremely difficult to reduce carbon emissions sufficiently to achieve permanent climate stabilization.

It could be argued that it is practically and politically impossible to abolish our addiction to infinite economic growth and ever-rising material affluence. That may be so. But it should be kept in mind that as soon as basic material needs have been satisfied, further increases in the material standard of living do not result in greater happiness (Lane 2001). For example, although the average income after taxes more than doubled in the USA from 1960 to 1990, the fraction of people who consider themselves 'very happy' remained virtually constant at around 35% (Myers & Diener 1996). The reasons for this paradox are that (1) human desires are inherently insatiable, (2) relative rather than absolute income determines one's social position and feeling of achievement, and (3) the pursuit of materialism deprives people of opportunities to engage in social, cultural, and spiritual activities that are known to promote feelings of happiness and well-being (Huesemann & Huesemann 2008).

In conclusion, while there are a number of promising climate change mitigation technologies, it is highly unlikely that global warming will be successfully averted unless we seriously reconsider our commitment to unlimited economic growth and consumption, and instead find fulfillment in less materialistic ways. Should we continue along a path that not only aggravates global warming but also does not improve our sense of well-being? It is time to re-examine our priorities.

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Building relationships between scientists and business in ocean iron fertilization

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ABSTRACT: The potential use of ocean iron fertilization (OIF) as a tool for either carbon reduction projects like those used to generate carbon credits or offsets, or for larger-scale mitigation to remove a significant percentage of CO₂ from the atmosphere has interested the private sector. Scientists have highlighted the additional research that must be completed to understand the efficacy and impact of OIF at either scale. Carbon markets also place requirements on the nature of the credits generated if they are to be trusted and valued. The challenge for the future is to find effective ways for the science, business and carbon market communities to collaborate in ways that adhere to the high standards of scientific research. A code of conduct that recognizes the needs for scientific excellence and transparency, carbon market quality controls, and regulatory requirements like permitting can facilitate collaboration.

KEY WORDS: Ocean iron fertilization · Carbon mitigation · Carbon markets

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INTRODUCTION

Scientists working in the Joint Global Ocean Flux Study (JGOFS) and the Surface Ocean Lower Atmosphere Study (SOLAS) have forged not only a new understanding of the way the biology, chemistry and physics of the ocean interact to control primary productivity in the ocean, but also new tools for studying biogeochemistry. The ocean iron fertilization (OIF) experiments of the last 15 yr are unique examples of such a tool, the active manipulation of the ocean environment to study biogeochemical processes. These ambitious experiments, built on 10 successful bottle experiments that demonstrated the potential of iron to stimulate phytoplankton growth (e.g. Buma et al. 1991, Zettler et al. 1996), allowed the community to test hypotheses about controls on primary productivity in the open ocean. Several experiments also discussed their results in the context of hypotheses related to ocean productivity during glacial times (e.g. Coale et al. 1996, Boyd & Law 2001), when dust fluxes to the open ocean were greater than during interglacial periods (Rea 1994, Winckler et al. 2008). While the experi-

ments did not explicitly focus on the potential of OIF to sequester anthropogenic CO₂, this possibility was clearly under discussion in symposia and workshops, as well as in the peer-reviewed literature (Spencer 1992). But the experiments were not well designed to answer fundamental research questions about carbon export and sequestration (e.g. de Baar et al. 2005, Boyd et al. 2007, Buesseler et al. 2008), much less CO₂ mitigation.

Over the last 5 yr the pace of scientific research demonstrating global change impacts due to anthropogenic greenhouse gases has been accelerating; e.g. Intergovernmental Panel on Climate Change (IPCC) summaries of warming (Solomon et al. 2007), syntheses of research on ocean acidification (Raven et al. 2005), and evidence of rapid changes in the extent of Arctic sea ice (see: nsidc.org/news/press/2007_seaiceminimum/20071001_pressrelease.html). The slow response of the global policy community to develop strategies for abating fossil fuel emissions (Canadell et al. 2007) and the emergence of the European Trading System (ETS) and Clean Development Mechanism (CDM) of the Kyoto Protocol (KP) (Harrison & Radov 2002) led to increased

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interest in global change mitigation from the private sector and a surge of investment in clean technology and mitigation—for example an 18% increase in venture investment in the first quarter (Q1) of 2008 over Q1 2007 (see: renewable.energystocks.com/news/051608.asp). The scale of the problem, together with these sources of funding and an emerging market for CO₂ abatement (Bayon et al. 2007) have renewed interest in the potential of OIF as a mechanism for carbon sequestration.

The carbon markets—regulated and voluntary—want to assure that carbon credits are real and reflect true sequestration of carbon or abatement of emissions. The biogeoscience community brings specific concerns about carbon credits for OIF: sequestration must go beyond simple increases in gross primary production and must reflect new production, it must also account for any other greenhouse gases that are generated (e.g. N₂O and CH₄), the air/sea exchange of CO₂ must be considered, and the length of time that the carbon is sequestered must be defined. Both groups are also concerned that the impact of OIF on the ocean be understood and that it be acceptable and responsible. The community has highlighted the fact that many questions related to sequestration and impact cannot be inferred from small-scale experiments (10s of km per side) because many processes do not scale linearly. This implies the need for a new set of OIF experiments that are in part justified by questions related to commercialization. A recent Science policy forum (Bueseler et al. 2008) emphasized these needs and called for new experiments at larger and longer time scales. These experiments must be of the highest scientific quality and they are, in part, motivated by research questions related to application, in addition to basic research questions.

The participation of private capital in funding experimentation is common in other fields, including some fields of oceanography (e.g. genomic prospecting, aquaculture), but is relatively new to ocean biogeochemistry. Although a recent community workshop expressed an openness to working on experiments motivated by commercial interest (Holmes 2008), it is clear that a strong set of guiding principles for such work are necessary to ensure that the results can be evaluated and that the researchers involved are not compromised. Some of the concerns can and are being addressed by the mechanisms of the regulated carbon market; others can be addressed by a strong scientific interaction between the biogeochemistry and marine ecology science communities and the community of businesses interested in the OIF process. I discuss some of the market regulating mechanisms that assist in this process as well as the roles that scientists and commercial interests can play in ensuring that questions on sequestration and impacts of OIF are addressed.

CARBON MARKET CONTROLS ON QUALITY OF OFFSETS

The regulated carbon markets established under the KP—the CDM and Joint Implementation (JI)—have a set of criteria for carbon credits or 'offsets' (Grubb et al. 1999):

(1) The markets require that credits are real, that they represent actual reductions in atmospheric CO₂, and that they are measurable.

(2) The measurement of CO₂ in the regulated market under the KP requires a methodology (see: cdm.unfccc.int/Reference/Procedures/index.html for a description of procedures), a rigorous, formula-based description of the measurements by which CO₂ or other greenhouse gases are shown to be reduced. Each methodology undergoes an extensive review by a panel with expertise in many forms of CO₂ reduction (see: cdm.unfccc.int/Panels/meth/index.html for the current Methodology Panel and its activities) and with the capability of engaging outside discipline experts (see: cdm.unfccc.int/Panels/meth/CallForExperts for the criteria used by the Methodology Panel to choose outside experts). OIF might well use models to describe aspects of sequestration. Methodologies can be based on model output, as in the case of forestation, where statistical models of growth, disease, age distribution, etc. are used to estimate total CO₂ sequestered. Methodologies are typically revised multiple times to address concerns of the Methodology Panel and its experts. Some methodologies are rejected (the methodology portion of the CDM website provides information on methodologies that have been accepted, those being considered, and those that have been rejected: cdm.unfccc.int/methodologies/index.html).

(3) Credits are also required to be 'additional,' that is, credit cannot be claimed for reductions that would have happened anyway because of regulation or planned technological upgrades. OIF would, of course, be 'additional' because carbon mitigation is the primary reason that it is contemplated, and the carbon market is the only rationale for commercial funding. This is not a minor point, as a common problem with carbon credit projects has been that they would have been done anyway. For example, some projects to sequester CO₂ in oil wells would have been done to enhance oil recovery; some landfill gas projects were mandated by law.

(4) Credits must be permanent and markets rely on the IPCC definition of 100 yr as permanent for sequestration projects (United Nations Framework Convention on Climate Change, UNFCCC 1997). The permanence definition is important because it sets the minimum age for carbon to be sequestered from any OIF project. The 100 yr choice was a policy decision, informed from scientific and policy deliberations on global warming potential (GWP), a method to normal-

ize the heat trapping capabilities of the important greenhouse gases (e.g. N₂O, CH₄, hydrofluorocarbons [HFCs]). GWP divides the cumulative lifetime radiative forcing per molecule of each gas against a reference time period of cumulative radiative forcing of a molecule of carbon dioxide (IPCC 1995). The IPCC (1995) calculated GWP for time periods of 20, 100, and 500 yr, and characterized the choice of 'time horizon' as a policy decision. In discussion of this, they noted:

'Policy-relevant climate-change phenomena exist at both ends of the climate-change time spectrum:

- (1) *If the policy emphasis is to help guard against the possible occurrence of potentially abrupt, non-linear climate responses in the relatively near future, then a choice of a 20-year time horizon would yield an index that is relevant to making such decisions regarding appropriate greenhouse gas abatement strategies. In addition, if the speed of potential climate change is of greatest interest (rather than the eventual magnitude), then a focus on shorter time horizons can be used.*
- (2) *Similarly, if the policy emphasis is to help guard against long-term, quasi-irreversible climate or climate-related changes (e.g. the very slow build up of and recovery from sea level changes that are controlled by slow processes such as warming of the ocean), then a choice of a 100-year or 500-year time horizon would yield an index that is relevant to making such decisions regarding appropriate greenhouse gas abatement strategies.*

With this awareness, policies could choose to be a mix of emphases. GWPs with differing time horizons can aid in establishing such a mix. Indeed, that was the case in the Montreal Protocol deliberations, in which the long-lived, high-ODP [ozone depleting potential] gases were the initial focus and the shorter-lived, lower-ODP gases were subsequent focus.'
(IPCC 1995)

The KP adopted 100 yr as the only time horizon for calculating GWP (UNFCCC 1997). All subsequent carbon credits have been normalized by this standard, including emissions reductions from sinks (e.g. forestry) as defined by the UNFCCC Reporting Guidelines:

'Annex I Parties should report aggregate emissions and removals of greenhouse gases, expressed in CO₂ equivalent terms at summary inventory level, using GWP values provided by the IPCC in its Second Assessment Report.'
(UNFCCC 1996)

Subsequent discussion by the IPCC on the definition of permanence for forestry projects shows how the GWP approach can also be applied for calculating the benefit of any sequestration project of variable length as compared to a reference time period of 100 yr:

'Absolute Global Warming Potentials (AGWPs) are calculated by integrating the total radiative forcing of an emissions pulse over a 100-year time horizon with no discounting. Relative GWPs are the ratio of this integral for a given GHG [greenhouse gas] to that of CO₂, which serves as the reference gas. This approach could be applied to compare carbon sequestration projects of different lengths, although there is no requirement in the Protocol to use the same conventions in this context. The reference is 'permanent' (more than 100 years) removal (or emission) of 1 t CO₂.' (Watson et al. 2000)

Future regulation could choose a different permanence standard, or like the Montreal Protocol, change permanence standards with time. However, it is important to understand the reasons behind the choice of 100 yr for permanence.

(5) Credits must also account for 'leakage' (e.g. carbon emissions generated in the process of creating reductions, increase in carbon emissions as a result of emission reductions elsewhere, etc.). OIF projects would certainly have to account for fuel used to transport iron to the site, but they would also have to account for any greenhouse gases generated as a result of fertilization (e.g. N₂O, CH₄) and potentially for downstream nutrient depletion.

(6) Finally, a third party must verify credits to ensure that the CO₂ reduction took place and that the methodology was followed. While no framework for quality can assure complete accuracy in measurement of carbon reductions, or complete compliance, the methodology and verification requirements of the KP have developed considerable trust in the applicable markets.

While OIF credits would not be eligible for KP markets at present because they are not generated within signatory countries, both voluntary markets and emerging regulated markets are sensitive to the need for 'quality' (referring to the degree to which credits meet the criteria discussed above) and are moving quickly toward adoption of standards. Starting in 1998, a partnership between the World Business Council for Sustainable Development (WBCSD) and the World Resources Institute (WRI) convened The Greenhouse Gas Protocol Initiative (GHG Protocol), a multi-stakeholder partnership of businesses, non-governmental organizations (NGOs), governments, and others. This effort resulted in Corporate Accounting and Reporting Standards (Corporate Standard, WBCSD & WRI 2004) and the Greenhouse Gas Protocol for Project Accounting (GHG Protocol, WBCSD & WRI 2006). The GHG Protocol provides guidance on best practices for development on projects. A group of other products of the process provide guidance for accounting in land use and forestry projects, grid electricity projects and other specialized sectors.

Both the KP and the GHG Protocol have benefited by substantial scholarly activity devoted to developing statistical methods for dealing with estimated carbon in credit situations in which CO₂ is not captured permanently, but is stored temporarily (e.g. Godal et al. 2003) in soils (e.g. Smith et al. 1997) and forests (e.g. Noble & Scholes 2001). Natural sinks for carbon such as soil, forest and deepwater ocean carbon (whether in the form of particulate or dissolved, organic or inorganic) also require modeling to determine the duration of sequestration. The scientific communities studying soils and forest carbon (cf. Noble & Scholes 2001, Smith

2004) have also had to address such challenges. Commercial entities in forestry have methodologies that have been accepted to measure permanence using models.

All voluntary markets currently do not require adherence to the GHG Protocol, but credits that have not adhered to the protocol requirements have been criticized publicly. The voluntary market has expanded very quickly from 1 Mt CO₂ during 2005 to 25 Mt CO₂ during 2006 (Capoor & Ambrosi 2007) and nearly tripled in 2007 to 65 Mt CO₂ (Capoor & Ambrosi 2008). These figures represent only credits traded on exchanges like the Chicago Carbon Exchange (CCX) and not credits purchased in private transactions, such as the highly publicized requests for credits by major USA corporations Google and Yahoo or those transactions that would fulfill the agreements of power plants to offset CO₂ emissions. Large 'bilateral' or off-exchange transactions are estimated to be many times the exchange-traded volume (Capoor & Ambrosi 2008) and generally adhere to the GHG Protocol requirements or even more stringent requirements established by the buyers to ensure that they are not embarrassed by negative publicity. Thus, sale of any substantial carbon credit pool from OIF activities is likely to have the same requirements from buyers because its size would draw public scrutiny. A new effort to establish a Voluntary Carbon Standard (VCS) for projects selling carbon credits in a voluntary market was initiated by The Climate Group, the International Emissions Trading Association and the World Economic Forum in late 2005. After the release of 2 consultation documents, the VCS 2007 was released in November 2007 (www.v-c-s.org/documents.html).

The scientific community can play a powerful role in ensuring that any OIF carbon credits to offset CO₂ emissions in emerging markets and future markets adhere to standards. Legislators developing emerging regulated markets in the USA (e.g. the Regional Greenhouse Gas Initiative, the market mandated by California's AB32, and markets proposed in current national legislation) are also keenly aware of the GHG Protocol requirements and have incorporated quality factors from the Protocol into pending legislation. Negotiations concerning the incorporation of OIF into any international regulated trading scheme, such as the ETS or any UNFCCC protocol that would follow the KP period (post-2012) would also consult with scientists familiar with OIF. Regulators will look to the scientific community for guidance on the means of quantifying CO₂ sequestered by this technique. It is important that the ocean science policy research community and the ocean science research community familiarize themselves with the processes and standards for carbon credits to understand how best to interact with the markets on the issue of standards and

quality if OIF does prove to be an acceptable mechanism for sequestering carbon.

CONDUCTING OIF EXPERIMENTS WITH COMMERCIAL FUNDING

Capital from private sources can fulfill 2 important requirements necessary to advance the investigation of OIF as a potential climate mitigation or carbon credit project technique. First, it can provide venture funding for costly initial moderate-scale demonstration experiments (~200 × 200 km) that are, at least in part, commercial development research difficult to justify for government research support. Second, it could provide a potentially sustainable source of funding for research into sequestration and impacts if conservative, verified results from initial demonstrations justify funding subsequent cruises.

The interest of the commercial community in funding moderate-scale experiments or demonstrations in order to address questions of sequestration and/or impact has led to an active discussion of the best way to ensure that the results of such experimentation can be evaluated by the scientific community. The elements of a code of conduct proposed by Climos (www.climos.com) were an early contribution to this discussion. The code addresses 3 aspects of commercial activity: regulatory concerns, carbon market concerns, and scientific/environmental concerns

The code proposes that any commercially funded activity should be in full compliance with applicable regulatory requirements (including the use of permits required under the London Convention of 1972), should include an environmental impact assessment, and should avoid sensitive areas such as marine protected areas, world heritage sites, etc. The purity of the iron compound being used for fertilization should also be known to ensure that it does not introduce concentrations of other elements or organic compounds that would endanger marine ecosystems.

The code proposes that commercial activities should also use the best practices of the carbon markets. These would include the development of a published, validated methodology that provides detailed information on the methods of determining the carbon sequestration and allows independent verification of results by third parties. Other quality aspects of carbon credits, such as calculation of baselines before and after fertilization (as well as in and out of the fertilized patch), calculation of all leakage, adherence to additionality and permanence criteria, should also be characteristics of the projects. Any credits derived from experiments or demonstrations should also be tracked and registered to prevent duplicate sale.

The Climos code of conduct also proposes that scientific concerns about conduct of experiments should be addressed: measurements should be made using state-of-the-art techniques by individuals who are appropriately trained (i.e. experienced scientists and their graduate students and post-docs). All project specifications, including location, size, details of iron application, pre- and post-fertilization conditions and observed responses, including measured export, should be published immediately in an open format so that results are accessible to the public. Measurement techniques and raw data should also be provided if possible. Results should be available for publication in the open literature.

A recent 'Science' editorial (Buesseler et al. 2008) also contributes suggestions for the conduct of projects done with a view toward future commercialization, emphasizing the need for a broader range of measurements than were characteristic of most of the early fertilization experiments, the need for active collaboration between researchers and those with commercial interests, and consideration of partnerships between commercial interests as well as philanthropic and government sources of funding. These types of formal dialog (published codes of conduct, editorials/policy fora, workshops, documents) are important contributions toward building relationships of trust between the research and business communities interested in OIF.

TIMELINE FOR BUILDING A RELATIONSHIP BETWEEN BUSINESS AND RESEARCH

The evolving landscape of OIF for carbon sequestration has 3 phases: basic research experimentation, focused research and development, and potential deployment. The early experiments between 1993 and 2004 certainly fit into the basic research/experimentation phase. They were small in scale (most about 10 × 10 km), financed by research grants. These experiments definitively showed that OIF would result in phytoplankton blooms and provided some important insights into the role of iron in biogeochemical cycling. Because most experiments were limited in duration and small in scale, they often did not observe the termination of the blooms and export of carbon.

The science community has called for a new phase of moderate-scale experiments with explicit suggestions about the types of measurements necessary to determine whether OIF is an effective mechanism for removing atmospheric CO₂ (Boyd et al. 2007, Buesseler et al 2008). Such experiments could be funded in partnership with commercial interests with the objective of understanding controls on sequestration, assessment of environmental impact and modeling of permanence,

and atmospheric drawdown (Holmes 2008). Because the goals of credible carbon markets are congruent with those of researchers (proof of sequestration by accepted techniques, knowledge of the permanence of the sequestration, accounting for leakage and environmental impact, etc.), if sequestration is demonstrated, carbon offsets from these experiments can be validated, verified and marketed without impacting the quality of the science that is done or creating intellectual conflicts for researchers. This is certainly the case in forest carbon sequestration. This focused research or development phase is critical to understanding the potential of OIF to sequester carbon.

Only after such focused research—and only with knowledge and acceptance of environmental impacts—should more routine (e.g. repetitive yearly projects in a certain area under a single permit) and/or larger-scale deployment be undertaken. By larger-scale deployment I refer to fertilization of large patches several degrees of latitude/longitude per side or fertilization of significant percentages of specific ocean areas such as have been considered in some models (e.g. Gnanadesikan et al. 2003, Jin et al. 2008). This larger scale would almost certainly require regulated market acceptance for finance. The scientific community would also need to participate actively in the definition of limits to deployment to ensure that environmental impacts would be acceptable.

SUMMARY

While private sector funding for OIF development presents challenges, the desire of both oceanographic researchers and carbon markets for high standards of excellence are complementary. These common cultures can be leveraged to ensure that OIF development research is carried out in a responsible and transparent way even if funded by the private sector.

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Nitrogen fixation-enhanced carbon sequestration in low nitrate, low chlorophyll seascapes

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ABSTRACT: The magnitude of fluxes in the carbon cycle of subtropical and tropical marine habitats is determined by the supply of inorganic nutrients. These habitats have low sea-surface concentrations of nitrate (NO_3^-) and chlorophyll (dubbed LNLC regions), sustain relatively low rates of organic matter production and export, and represent global ocean minima in carbon sequestration potential. The low NO_3^- resupply should select for nitrogen (N_2)-fixing bacteria, termed diazotrophs, provided all other growth-limiting nutrients are available. Several recent field efforts have been aimed at enhancing N_2 fixation in LNLC regions through mesoscale fertilization with iron and phosphorus (or both) and we hypothesize herein that controlled upwelling of nutrient-enriched deep water may also be effective. Based on a quantitative assessment of the vertical distribution of NO_3^- , phosphate (PO_4^{3-}) and dissolved inorganic carbon (DIC) at Station ALOHA ($22^\circ 45' \text{ N}$, 158° W), we hypothesize that the process of controlled upwelling of low $\text{NO}_3^-:\text{PO}_4^{3-}$ seawater may lead to enhanced N_2 fixation, organic matter production and net carbon sequestration. Furthermore, based on a long-term (20 yr) data set from Station ALOHA, we predict that the upwelling of water from a depth of 300 to 350 m during summer months will trigger a 2-stage phytoplankton bloom. The first stage will be characterized by a NO_3^- -supported Redfield ratio (e.g. $\text{C}_{106}:\text{N}_{16}:\text{P}$ by atoms) diatom bloom. Following quantitative NO_3^- removal, the residual PO_4^{3-} from the low N:P (<16:1) upwelled nutrient pulse will stimulate a N_2 -fixing bacterial bloom, leading to net sequestration of carbon. However, any strategic benefit of controlled upwelling for enhancing the long-term carbon sequestration will depend on the spatial and temporal uncoupling of organic matter production and remineralization, which is ultimately controlled by the microbial response to these perturbations.

KEY WORDS: N_2 fixation · Diazotroph · Nutrients · Carbon sequestration · North Pacific gyre

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N_2 FIXATION IN OCEANIC HABITATS

Nearly 80% of the surface waters of the global ocean are considered nitrate (NO_3^-)-depleted ($\leq 1 \mu\text{M NO}_3^-$). These regions, located between 30° N and 30° S in every ocean basin, are characterized by low NO_3^- delivery, low standing stocks of particulate matter (including living organisms) and low rates of new and export production (Longhurst 1998). A strong vertical stratification insulates the upper layers of these vast seascapes from the large pool of NO_3^- in deeper waters; e.g. in the North Pacific subtropical gyre (NPSG) a maximum concentration of approximately $42 \mu\text{M NO}_3^-$ is observed at 1000 m depth, whereas

NO_3^- concentrations in the upper 100 m are generally $< 5 \text{ nM}$ (Fig. 1). Chronic NO_3^- limitation in the upper layer of the water column, where light is available to support photosynthesis, should select for microorganisms that are able to utilize the fairly large, but as yet poorly characterized, pool of dissolved organic nitrogen (DON, $\sim 5 \mu\text{M}$) or the unlimited supply of dissolved N_2 ($> 400 \mu\text{M}$) as a source of cellular N; the latter process is termed N_2 fixation and the microorganisms responsible for it are termed diazotrophs.

N_2 -based new production requires an ample supply of energy, iron (Fe) and phosphorus (P). In marine ecosystems, the primary source of energy appears to be light; i.e. most marine diazotrophs are also phototrophs

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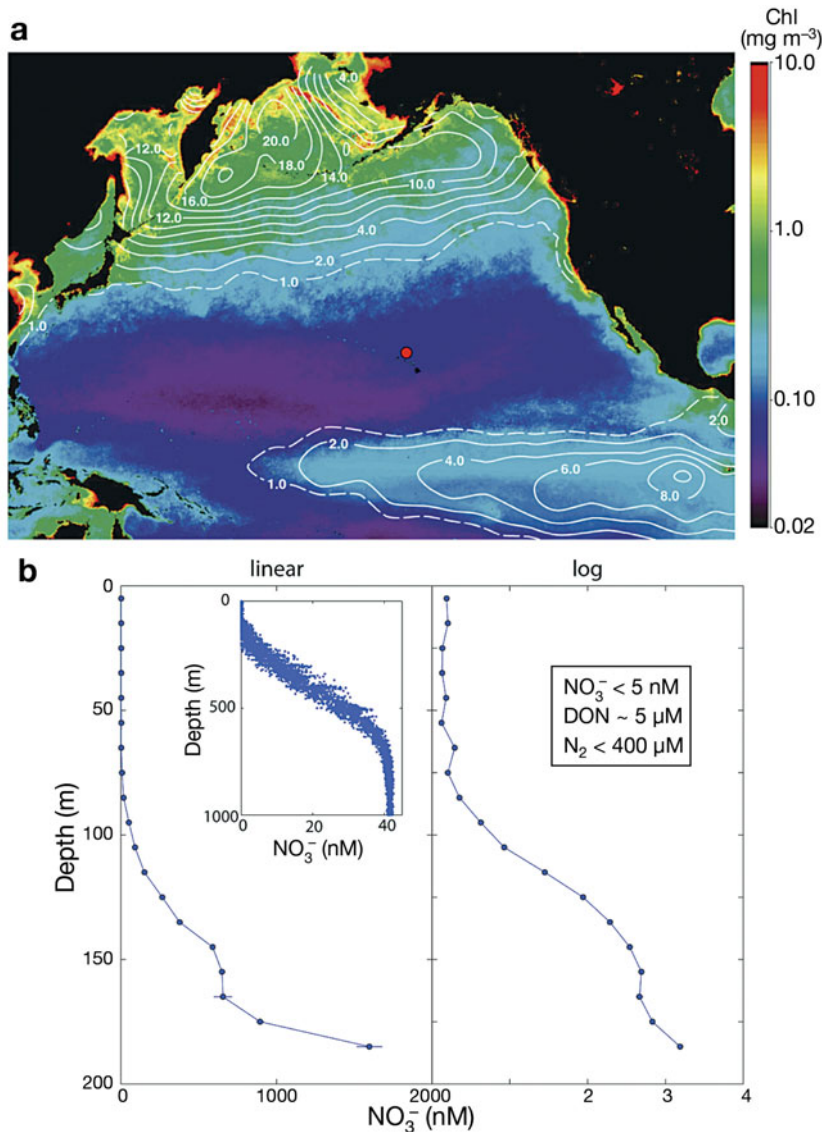


Fig. 1. (a) North Pacific Ocean with sea surface distributions of chlorophyll (mg m^{-3}) derived from the AQUA MODIS satellite-based sensor system (4 km resolution). Superimposed on ocean color, in white contour lines, is the mean annual surface nitrate concentration ($\text{mmol NO}_3^- \text{ mg m}^{-3}$) based on the World Ocean Atlas Ocean Climate Laboratory/NOEC (<http://www.nodc.noaa.gov/OC5/>). Areas of high NO_3^- (and presumably NO_3^- flux) correspond to regions that are enriched in chlorophyll as a result of phytoplankton growth. Red circle indicates the approximate location of Station ALOHA $22^\circ 45' \text{N}$, 158°W , a typical low-nitrate, low-chlorophyll (LNL) habitat. (b) Mean concentrations of NO_3^- versus water depth for samples collected at Station ALOHA during 1989–2006 plotted on both linear and logarithmic (\log_{10}) scales to show details of the profile. Inset (left-hand plot) shows the NO_3^- concentration profile to 1000 m. Compared to the low ($< 5 \text{ nM}$) surface water concentrations of NO_3^- , dissolved organic nitrogen (DON) and dissolved N_2 are in ample supply but not readily available (see box in right-hand plot)

(Karl et al. 2002). Fe is an obligate co-factor for the enzyme nitrogenase and it has been estimated that diazotrophs may require an order of magnitude more Fe for growth than eukaryotic phytoplankton growing on ammonium as a source of nitrogen (Kustka et al. 2003). Although phosphate (PO_4^{3-}) is considered to be the pre-

ferred P substrate for the growth of marine microorganisms (including diazotrophs), selected P-containing organic compounds can also be used. In this study, we will use measured PO_4^{3-} concentrations as a lower limit on bioavailable P, acknowledging that the true concentrations may be at least twice as high (Björkman & Karl 2003). If solar energy, Fe and P all were present in excess, phototrophic diazotrophs would have a competitive growth advantage in low NO_3^- habitats worldwide. As diazotrophs grow, their metabolism decouples the N and P cycles by providing new N in the absence of deep mixing and, over time, their net growth would remove all bioavailable P from the ecosystem as long as Fe and all other required nutrients are in sufficient supply. Any P remaining is termed residual P (r-P). Therefore, based on the constraints imposed by the C:P stoichiometry in the production of organic matter, the concentration of r-P in a given habitat can be used as a measure of the potential for CO_2 sequestration by N_2 fixation.

The pathways for Fe and P resupply to the surface ocean are governed by distinct environmental forcings (Karl 2002). Whereas both Fe and P are delivered from deep water to the surface by diffusion and turbulent mixing in the upper thermocline, Fe is also supplied from atmospheric deposition of dust. Furthermore, some dust sources (e.g. selected Saharan desert soils) contain both Fe and P (Ridame & Guieu 2002). Because the atmosphere-to-ocean Fe flux is approximately an order of magnitude larger in the northern hemisphere than in the southern hemisphere and is larger in the North Atlantic than in the North Pacific (Duce & Tindale 1991, Jickells et al. 2005), NO_3^- -stressed environments in the South Pacific gyre tend to have much higher r-P ($> 150 \text{ nM}$; Moutin et al. 2008) than either the

NPSG ($10\text{--}100 \text{ nM}$; Karl et al. 2001) or the North Atlantic subtropical gyre ($< 1 \text{ nM}$; Wu et al. 2000). Consequently, rates of N_2 -based new and export production can vary geographically and may have regionally distinct environmental controls. Dissolved Fe concentrations in the NPSG exhibit 'nutrient-like' profiles with

minimum concentrations (0.2 to 0.4 nM) in near-surface waters, increasing to values of 0.7 to 1.0 nM at approximately 1000 m (Johnson et al. 1997, Wu et al. 2001). In addition, and as a result of the atmospheric deposition of Fe-containing dust, near-surface waters have elevated—but much more time-variable—Fe concentrations relative to those found in the lower portion of the euphotic zone (Boyle et al. 2005). Nevertheless, quantifying bioavailability of Fe in marine ecosystems is difficult due, in part, to the presence of colloidal Fe-binding organic ligands (Wu et al. 2001) of unknown availability to microorganisms.

Superimposed on this complex network of Fe sources and sinks, r-P concentrations within the euphotic zone of the NPSG also display significant intra-seasonal as well as decadal-scale variability (Karl 2007a), emphasizing the temporal context of nutrient control of microbial dynamics. Ultimately, the concentration of r-P in low NO₃⁻ seascapes will depend on the extent of N₂-based new production, which, in turn, constrains carbon export and sequestration, and is controlled by both the availability of energy (e.g. solar radiation and upper water column stratification) and the resupply of Fe.

In theory, there are at least 2 experimental manipulations that could be employed to stimulate the growth of marine diazotrophs in well-stratified low-NO₃⁻, low-chlorophyll (LNLC) subtropical pelagic habitats and promote the sequestration of CO₂: (1) fertilization of the surface ocean with Fe, PO₄³⁻ or both, depending upon the ambient concentrations and *in situ* fluxes of both elements relative to cell needs and (2) controlled upwelling of Fe-enriched deep waters that have a low NO₃⁻:PO₄³⁻ molar ratio (<16:1) and, therefore, a relative excess of P. Successful application of either nutrient perturbation for the purpose of net CO₂ sequestration would be site- and depth-specific, and perhaps seasonally dependent. While the theory of N₂-based CO₂ sequestration appears sound, field application might not be as straightforward and the outcomes are difficult to predict given our current understanding of microbial biogeochemical processes and ecosystem function in LNLC habitats. For this reason, nutrient manipulations should be treated as hypotheses that are amenable to direct field experimentation and quantification.

OCEAN Fe/P FERTILIZATION

In well-illuminated and stratified NO₃⁻-depleted oceanic regions that contain r-P, the addition of Fe should enhance the growth of diazotrophs and promote N₂-based carbon export and sequestration. Target regions for these studies include Fe-depleted, denitrified water masses (e.g. eastern tropical North Pacific)

or oceanic gyres far removed from continental dust sources (e.g. South Pacific subtropical gyre). Alternatively, the addition of PO₄³⁻ to Fe-containing, P-depleted waters also should stimulate N₂ fixation. Regions with these characteristics include oligotrophic waters downwind from continental dust sources (e.g. eastern Mediterranean Sea, North Atlantic subtropical gyre, South China Sea) or areas impacted by hydrothermal inputs of Fe from shallow underwater volcanoes. Furthermore, it is important to emphasize that PO₄³⁻ fertilization of Fe-sufficient regions may require much larger nutrient loads than Fe fertilization of P-sufficient habitats because of the relatively high P:Fe molar stoichiometry of living organisms (P:Fe ≥ 10²; Ho et al. 2003). The addition of PO₄³⁻ for the purpose of enhancing N₂-based carbon export and sequestration would, therefore, impose a significant logistical constraint and greater expense compared to Fe fertilization. However, even in seascapes that contain measurable r-P, the impact of Fe fertilization would be enhanced if additional PO₄³⁻ was added simultaneously due to the possibility of Fe and PO₄³⁻ co-limitation of N₂ fixation (Sañudo-Wilhelmy et al. 2001, Mills et al. 2004). Consequently, the autotrophic biomass response and concomitant CO₂ sequestration potential will ultimately scale on the total P, i.e. the sum of the r-P plus added PO₄³⁻ concentrations.

To date, there have been 2 open ocean field trials designed to assess the Fe/P fertilization effects on microbial assemblages and elemental fluxes: (1) PO₄³⁻ addition to an Fe-sufficient portion of the eastern Mediterranean Sea (CYCLOPS project; Thingstad et al. 2005) and (2) Fe and Fe/PO₄³⁻ additions to a region in the Northeast Atlantic Ocean (FeeP project; Rees et al. 2007).

Cycling of phosphorus in the Mediterranean (CYCLOPS) project

Following the addition of PO₄³⁻ to increase the r-P concentration by nearly 2 orders of magnitude (to 110 nM) in an approximately 16 km² patch within an ultraoligotrophic warm-core eddy, there was a 40% decrease (rather than a predicted 40-fold increase) of chlorophyll during the first 6 d, relative to an unfertilized control station (Thingstad et al. 2005). However, while parallel on-deck incubations amended with PO₄³⁻ did not display significant changes, those amended with PO₄³⁻ plus ammonium yielded a >9-fold increase in chlorophyll (Zohary et al. 2005), suggesting N and P co-limitation in selected non-diazotrophic phytoplankton taxa. Furthermore, *in situ* N₂ fixation was enhanced by only 48% following PO₄³⁻ addition and was unaffected by Fe addition (Rees et al. 2006), indicating that P, rather than Fe, was the primary limit-

ing factor for N_2 fixation. These unexpected and still unexplained results from the CYCLOPS project require further elaboration and perhaps the development of a new trophic model (Thingstad et al. 2005). Additional considerations include the competition between phytoplankton and heterotrophic bacteria and the coupling to higher trophic levels, as well as the potential role of other essential trace metals and organic compounds (e.g. vitamins) in establishing the carrying capacity of the pelagic ecosystem.

FeeP project

During FeeP, 2 experimental patches, each approximately 25 km², were created and studied over a 3 wk period. The first patch contained only PO_4^{3-} while the second was seeded with Fe at first, followed by a pulse of PO_4^{3-} after 24 h. The experimental concentrations were ~200 nM PO_4^{3-} and 3 nM Fe:200 nM PO_4^{3-} in Patch 1 and Patch 2, respectively, compared to background concentrations of approximately 10 nM PO_4^{3-} and 0.3 nM Fe (Rees et al. 2007). Whereas total primary production showed only small deviations from the unamended control site, rates of PO_4^{3-} uptake and N_2 fixation in the 2 experimental treatments increased 6-fold and 4.5-fold, respectively (suggesting that only a small fraction of the photoautotrophic assemblage, probably composed of diazotrophs, responded initially to the nutrient enrichments); the dominant diazotroph in this habitat was a unicellular cyanobacterium (Rees et al. 2007). Particulate matter export to the deep sea was not measured during either the CYCLOPS or FeeP, so the potential impact on CO_2 sequestration from these fertilization experiments and the enhanced N_2 fixation they triggered is currently unknown.

CONTROLLED UPWELLING

Lovelock & Rapley (2007) recently suggested that the purposeful delivery of deep-water nutrients to the euphotic zone (i.e. artificial or controlled upwelling) might enhance primary and export production and thereby constitute an effective mechanism for CO_2 se-

questration in the open sea. Upwelling of deep waters could be implemented using a passive, wave-powered pump (Isaacs et al. 1976) or via conventional mechanical pumping. Critics of this procedure for the purpose of CO_2 sequestration (e.g. Shepherd et al. 2007) were quick to point out that, along with the production-supporting nutrients (e.g. NO_3^- , PO_4^{3-} , Fe), deep waters also contain elevated concentrations of dissolved inorganic carbon (DIC, also referred to as total CO_2) derived from the long-term decomposition of sinking particulate matter (Fig. 2). Consequently, most natural upwelling regions are net sources of CO_2 to the atmosphere (Takahashi et al. 1997).

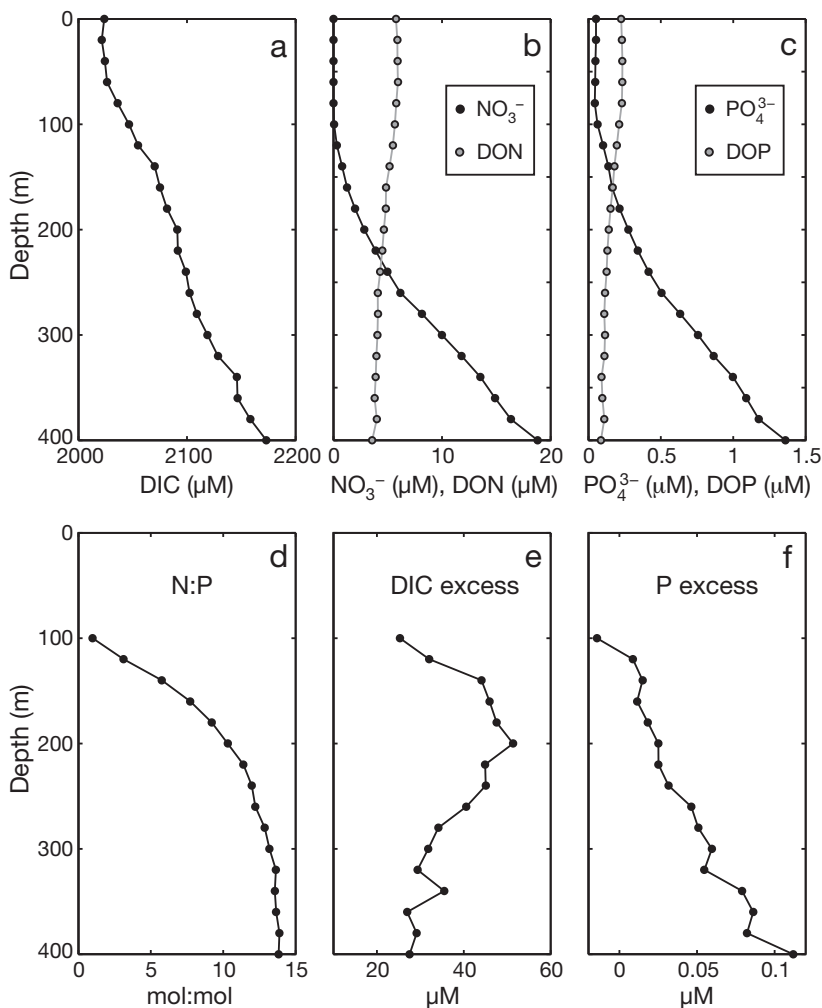


Fig. 2. Vertical profiles (a–c) of dissolved inorganic carbon (DIC) and dissolved nitrate and phosphate (NO_3^- and PO_4^{3-} , respectively) and dissolved organic nitrogen and phosphorus (DON and DOP, respectively) concentrations for the upper 400 m at Station ALOHA. (d–f) $NO_3^-:PO_4^{3-}$ (N:P) molar ratios and excess DIC and excess P in the upper 400 m at Station ALOHA. Excess DIC and PO_4^{3-} were calculated as described in Table 1, and represent the DIC and P concentrations that would remain if the NO_3^- from each reference depth were assimilated into organic matter with a Redfield stoichiometry ($C_{106}:N_{16}:P_1$). All values shown are based on the long-term climatology (1989–2006) for this low-nitrate, low-chlorophyll (LNLC) station (data available at <http://hahana.soest.hawaii.edu>)

However, since the ratio of DIC:NO₃⁻:PO₄³⁻ (C:N:P) in deep-sea waters is variable, the ecological consequences of a controlled upwelling experiment is predicted to be site- and depth-specific and, for some regions, seasonally dependent due to local variations in solar irradiance, surface mixed layer depth and temperature.

Based on our current understanding of marine microbial biogeochemistry, if deep waters are introduced to the surface ocean, a phytoplankton bloom (i.e. enhancement in the growth rate of one or more species leading to an increase in biomass; Richardson 1997) will result, following the stratification of the upper water column. It is well known that a sudden pulse of inorganic nutrients into the euphotic zone selects for rapidly growing, mostly eukaryotic phyto-

plankton (especially diatoms). Although the background microbial loop continues to be active, it is overprinted by larger phytoplankton species that can respond quickly to the introduction of allochthonous nutrients and have few predators, at least initially, allowing accumulation and subsequent sedimentation out of the euphotic zone (Karl 1999, Cullen et al. 2002). The nature of the upwelling nutrient supply, for example whether it is continuous or pulsed, can also influence the dynamical behavior and trophic structure of the resultant community (Wiegert & Penas-Lado 1995) and ultimately affect the C:N:P stoichiometry of the organic matter that is exported from the system. For any controlled upwelling experiment, the nutrient supply rate is a key design criterion.

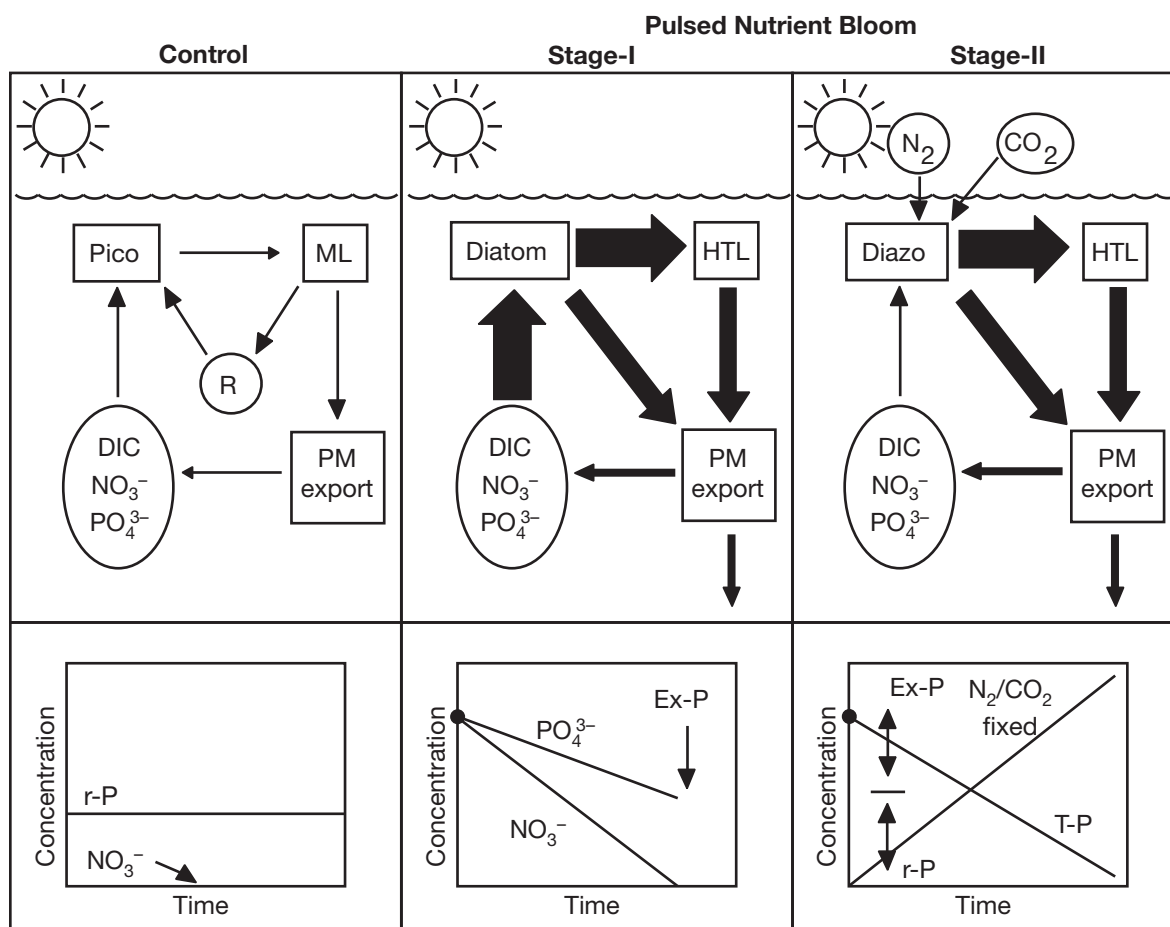


Fig. 3. Hypothesized ecosystem processes following a controlled nutrient upwelling event: (left) unamended control region, with low background nutrient fluxes from below the euphotic zone, a remineralization (R)-intensive picophytoplankton-based (Pico) microbial loop (ML) and low rates of particulate matter (PM) export mostly remineralized back to inorganic nutrients (dissolved inorganic carbon [DIC], NO₃⁻ and PO₄³⁻) in the upper mesopelagic zone (plot at the bottom depicts the hypothesized time-dependent changes in NO₃⁻ and residual P [r-P]); (center) Stage I of the inorganic nutrient (DIC, NO₃⁻, PO₄³⁻) supported phytoplankton bloom of diatoms (~C₁₀₆:N₁₆:P₁) that exports additional PM partly by the combination of aggregation/sinking of intact cells and coupled higher trophic level (HTL) processes—based on the PM composition and sinking rates, a larger portion penetrates deeper into the water column facilitating long-term CO₂ sequestration (plot at the bottom depicts the excess P [Ex-P] that remains after all the NO₃⁻ in the upwelled water has been assimilated); (right) total P (T-P Ex-P + r-P) supports the Stage II N₂-based bloom of diazotrophs (~C₃₃₁:N₅₀:P₁) that assimilate N₂ and CO₂ and enhance the potential for CO₂ sequestration as described in section 'Controlled upwelling' and in Table 1

Based on field observations and experiments conducted at Station ALOHA (22° 45' N, 158° W) over the past 2 decades (e.g. Karl 1999) and recent results of shipboard experiments that simulate upwelling (McAndrew et al. 2007), we hypothesize that controlled upwelling of Fe-replete deep water containing excess P (low $\text{NO}_3^-:\text{PO}_4^{3-}$) into the surface layers of the NPSG (a LNLC ecosystem) will lead to a 2-staged phytoplankton bloom (Fig. 3). Stage I is characterized by an immediate (hours to a few days) bloom of rapidly growing phytoplankton (typically diatoms; McAndrew et al. 2007) that assimilate DIC, NO_3^- and PO_4^{3-} , and trigger the export of particulate organic matter with a predictable stoichiometry of $\text{C}_{106}:\text{N}_{16}:\text{P}_1$ (so-called Redfield ratio), leaving excess P (and possibly excess DIC, depending on the $\text{DIC}:\text{PO}_4^{3-}$ ratio and concentration of NO_3^- in the upwelled waters) in its wake. The excess PO_4^{3-} supplements the r-P, if any, already present in the surface waters, leading to a N_2 -fixing cyanobacterial bloom, as described above. This Stage II bloom imports new N through the process of N_2 fixation, resulting in an enhanced sequestration of CO_2 over and above the DIC that was initially introduced to the euphotic zone by the upwelling event, depending upon the $\text{DIC}:\text{PO}_4^{3-}$ ratio of the upwelled water and the C:P ratio of the exported organic matter (Fig. 3). The production of excess bioavailable N in the form of ammonium and dissolved organic nitrogen, a feature that is characteristic of diazotroph growth in general (Capone et al. 1994, Mulholland et al. 2004), will ensure the efficient scavenging of total P and lead to efficient carbon export, provided adequate light and Fe are both available. *In situ* observations of summer blooms dominated by diazotrophs in LCLN regions lend support to this hypothesis (Karl et al. 1992, Uz 2007, Dore et al. 2008).

The efficacy of C sequestration by N_2 -based new production is enhanced by growth in P-limited environments. Diazotrophic growth is characterized by variable C:P stoichiometry in both the laboratory and the field, with C:P ratios ranging from 100 to 1000, with significantly reduced P cell quota under conditions of P stress (Karl et al. 1992, White et al. 2006). Even non-diazotrophic phytoplankton exhibit a P-sparing effect and synthesize new cell materials with elevated C:P when P becomes limiting (Bertilsson et al. 2003, Van Mooy et al. 2006). Consequently, this altered, C-enriched stoichiometry enhances the P-specific CO_2 sequestration potential of the Stage II N_2 -based bloom. Characterizing and understanding the processes governing the plasticity of elemental coupling (stoichiometry) in the biologically mediated production, remineralization and export of organic matter in these oligotrophic environments is critical if we are to assess potential CO_2 sequestration by these ecosystems. From a biogeochemical perspective, there is nothing as fundamental as the elemental

stoichiometry defined by biological systems through the coupling, storage and transport of nutrients.

N_2 FIXATION CASE STUDY: STATION ALOHA

The key to net CO_2 sequestration by controlled upwelling is the selection of an appropriate source water (geographic location and depth). Station ALOHA is the deep-water benchmark site of the Hawaii Ocean Time-series (HOT) program, where systematic observations of microbial biogeochemistry have been made since October 1988 (Karl & Lukas 1996). It is a typical LNLC, moderate r-P (30 to 50 nM) habitat with non-limiting total dissolved Fe concentrations (0.2 to 0.8 nM; Boyle et al. 2005). Assuming that a significant portion of the Fe is bioavailable, the well-illuminated surface waters of Station ALOHA should be a favorable habitat for the proliferation of N_2 -fixing microorganisms. This prediction has been confirmed by direct measurements, including: (1) the abundances of the putative diazotrophs, (2) quantitative estimation of *nifH* gene abundances and expression, (3) $^{15}\text{N}_2$ tracer assimilation experiments, (4) N isotopic abundance of suspended and exported particulate matter, and (5) C:N:P stoichiometrics of dissolved and particulate matter pools (Karl et al. 1992, Letelier & Karl 1996, Karl et al. 1997, Church et al. 2005a,b). An intriguing observation from this ongoing 20 yr program is the reduction in r-P in the upper 60 m of Station ALOHA from a depth-integrated inventory of approximately 5 mmol P m^{-2} in 1989 to <2 mmol P m^{-2} in 2005 (Fig. 4). Within this long-term trend we also observe strong sub-seasonal variability in 0 to 60 m depth-integrated P with the lowest values observed following summer blooms of diazotrophs (White et al. 2007). Between 1989 and 2005 the total pool of particulate phosphorus (PP) has also decreased significantly, and the C:P and N:P ratios of the suspended particulate matter have systematically increased to values well in excess of the Redfield ratios that were observed 20 yr ago (Fig. 4). This long-term, decadal process can be viewed as a 'slow motion' bloom of N_2 -fixing microorganisms controlled by some process other than P availability, possibly grazing, viral lysis, the bioavailability of Fe, or increased water column stratification (Karl 2007b). Top-down control by grazing or viral lysis is very likely in remineralization-intensive habitats like Station ALOHA. Bottom-up biomass control by Fe, or any other growth-limiting substrate, could occur independently or in conjunction with top-down control.

Based on our current understanding of this oligotrophic habitat, we predict that the addition of Fe to waters surrounding Station ALOHA may trigger a diazotroph bloom; if both Fe and P are added, the

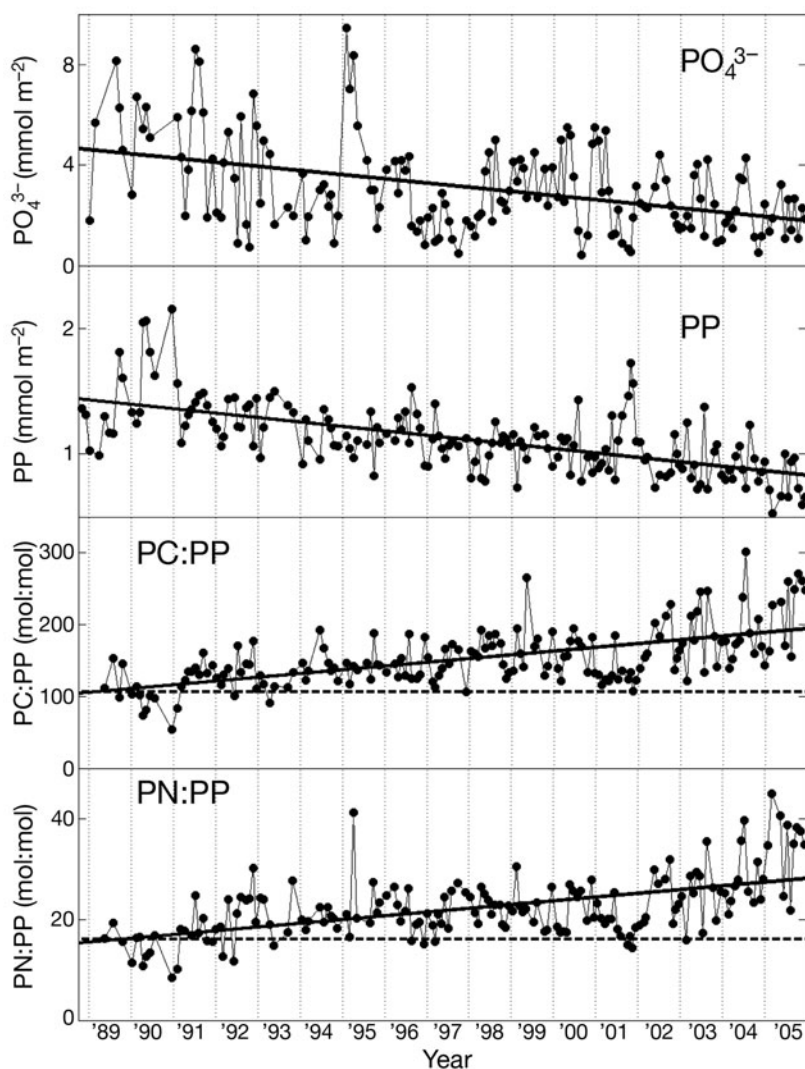


Fig. 4. Station ALOHA phosphorus pool dynamics. Shown is the 17 yr time-series of PO_4^{3-} integrated over the upper 60 m of the water column, particulate phosphorus (PP) integrated over the upper 75 m of the water column, and the average (0–75 m) C:P and N:P ratios of the particulate matter pools (PC:PP and PN:PP, respectively). Solid lines represent the best-fit linear regression analyses for each data set and the dashed line in the PC:PP and PN:PP plots is the global average stoichiometry ($\text{C}_{106}:\text{N}_{16}:\text{P}_1$) for marine particulate matter. The decreasing concentrations of SRP and PP, and increasing PC:PP and PN:PP ratios are all predicted from the hypothesized enhancement of N₂ fixation at Station ALOHA over the past 2 decades (Karl 2007a)

probability of a N₂-based bloom is even greater. However, it is obvious from the field observations at Station ALOHA that this seascape is not in biogeochemical steady state, but rather, supports a dynamic and time-variable ecosystem.

An important characteristic of the vertical nutrient structure at Station ALOHA is the low $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio in the upper 200 m of the water column (Fig. 2). Consequently, as deep waters are introduced into the near surface, whether by natural eddy-diffusion processes or by controlled upwelling, NO_3^- will be rapidly assim-

lated by phytoplankton along with DIC and PO_4^{3-} in relative proportions that approximate the Redfield ratio of $\text{C}_{106}:\text{N}_{16}:\text{P}_1$, the stoichiometry of average marine particulate matter (Stage I bloom; Figs. 3 & 5). Depending upon the depth of origin of the upwelled waters (controlled by experimental design) the complete assimilation of NO_3^- will leave behind excess PO_4^{3-} to supplement the r-P already present in the surface waters (Fig. 2, Table 1). Fe is also introduced as water is upwelled. However, both the biological requirements for Fe and the availability of the Fe upwelled are difficult to estimate, given the large range of Fe requirements reported in the literature (Sunda 1991) and the observation at Station ALOHA that a significant proportion of 'dissolved' Fe may be chelated with Fe-binding organic ligands (Wu et al. 2001). Nevertheless, the recurrent observation of diazotrophic summer blooms at Station ALOHA, followed by a significant reduction in r-P (White et al. 2007), suggests that Fe does not limit N₂-fixation at this site; most likely, there may be a temporal oscillation between Fe and P nutrient limitation, or co-limitation (Grabowski et al. in press).

The upwelled waters at Station ALOHA contain excess DIC (relative to NO_3^- , assuming Redfield stoichiometry) and variable excess DIC: excess P ratios depending on water depth (Fig. 2, Table 1). If the partial pressure of CO_2 in the surface waters is at or above equilibrium with the atmosphere, the addition of excess DIC may result in an ocean-to-atmosphere transfer of CO_2 . However, at Station ALOHA, the surface waters are nearly always undersaturated with respect to atmospheric CO_2

(although the extent of undersaturation appears to have decreased between 1990 and 2000; Dore et al. 2003), so the excess DIC in upwelled waters (up to approximately 20 to 30 μM) will be retained unless the surface ocean warms. Furthermore, recent laboratory studies of N₂ fixation as a function of pCO_2 suggest that *Trichodesmium* spp. displays CO_2 limitation under present-day conditions (Hutchins et al. 2007). Consequently, an increase in surface pCO_2 by controlled upwelling may even stimulate nitrogen fixation in a well-stratified water column.

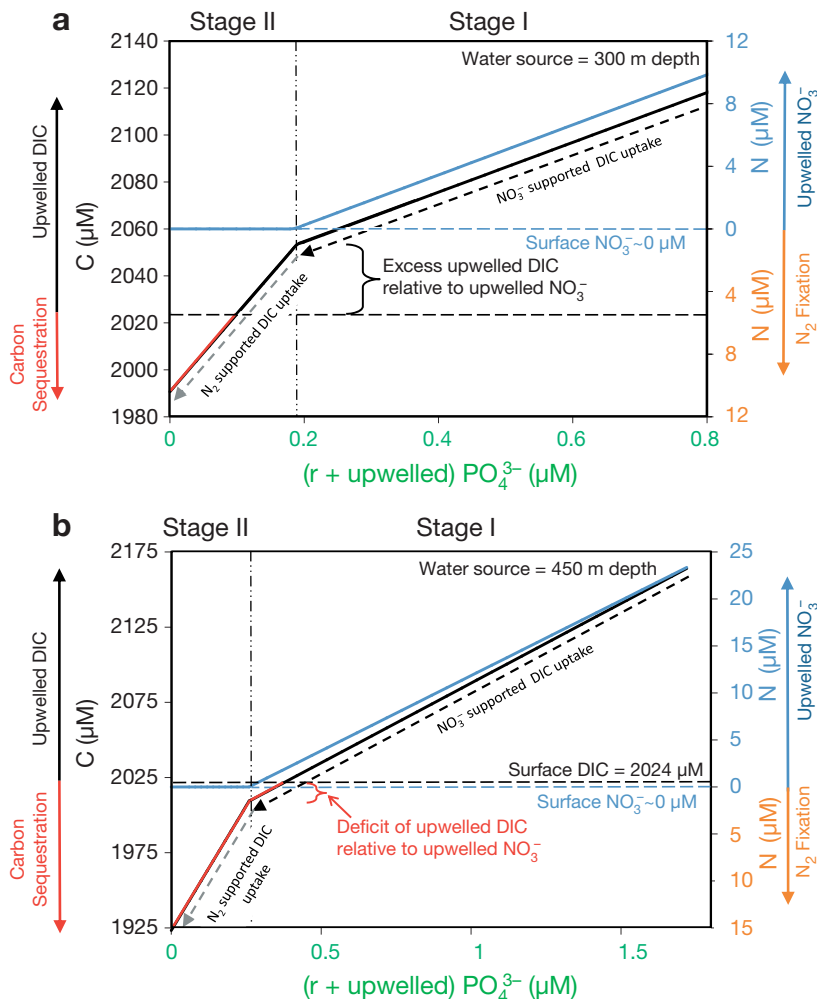


Fig. 5. Hypothetical evolution of DIC and NO_3^- concentrations as a function of total PO_4^{3-} concentration following the upwelling of (a) 300 m and (b) 450 m deep water into the upper euphotic zone at Station ALOHA. The increase of DIC (black arrow along left axis) and NO_3^- (blue arrow along white axis), relative to background surface ocean concentrations (horizontal dashed lines) will support a NO_3^- -based bloom characterized by Redfield stoichiometry (Stage I bloom), reducing DIC and PO_4^{3-} until NO_3^- is depleted. Following NO_3^- depletion, the remaining PO_4^{3-} should support a N_2 -based bloom (Stage II bloom and brown right axis) with an enhanced C:P and N:P stoichiometry, leading to the net sequestration of DIC in surface waters (red line within the graph). The vertical dash-dotted line marks the transition between Stage I and Stage II of the bloom. Note that while the 300 m upwelled water has excess DIC relative to NO_3^- , the water from 450 m has a deficit of DIC relative to NO_3^- leading to the removal of DIC even in the absence of N_2 fixation

Regardless of excess DIC concentration, excess P in the upwelled waters would most likely control the dynamics of N_2 -based new production and carbon export (Figs. 2 & 3, Table 1). Therefore, the key factors for determining CO_2 sequestration via N_2 -fixation in subtropical oligotrophic regions based on the long-term observations at Station ALOHA are (1) the excess DIC:excess P ratio in the upwelled waters, (2) the r-P concentration, (3) the saturation state of the surface

ocean with respect to atmospheric CO_2 , (4) the stratification of the upper water column, and (5) the C:P ratio of exported organic matter. The relative excess of P in upwelled waters (Fig. 2, Table 1) would ensure a significant net sequestration of CO_2 as long as N_2 -based production and remineralization of the organic matter are uncoupled in time and with depth. Furthermore, the surface waters at Station ALOHA always contain r-P (although the amount appears to be decreasing over the past 2 decades), so the excess P delivered via upwelling would supplement the r-P, further enhancing N_2 -based production and export, especially following the initial Redfield bloom, until either P or Fe becomes limiting for diazotrophic growth.

Based on well-constrained environmental observations at Station ALOHA (<http://hahana.soest.hawaii.edu>), we can provide estimates of the CO_2 sequestration potential following controlled upwelling from a variety of target depths using reasonable biogeochemical assumptions (Table 1). The derived values reported are CO_2 sequestered m^{-3} of upwelled water, provided sufficient Fe is available. There is an important tradeoff in the selection of the optimal source water between the $\text{NO}_3^-:\text{PO}_4^{3-}$ and the excess DIC:excess P ratios (Table 1). If our assumptions and calculations are reasonable, then the delivery of deeper waters (>300 m) would appear to be more efficient at removing CO_2 than delivery of waters from immediately below the euphotic zone (e.g. 140 to 200 m), where dissolved Fe is at a minimum (Johnson et al. 1997) and the excess DIC:excess P ratio is at maximum. Zonal and meridional transects in the region surrounding Station

ALOHA, as well as long-term observations at this benchmark confirm that low $\text{NO}_3^-:\text{PO}_4^{3-}$ concentration ratios in subeuphotic-zone water depths are a characteristic feature of the NPSG (Fig. 6); hence, it is likely that the calculations from Station ALOHA might be appropriate for the regional gyre scale. However, over extended temporal scales (decades to centuries) of continuous upwelling, the export and remineralization of particulate organic matter with elevated C:P

Table 1. Nutrient balance and net CO₂ sequestration potential for precision upwelled waters at Station ALOHA. DIC: dissolved inorganic carbon; r-P: residual phosphorus

Source Water (m)	Total nutrient concentration (μM)			Excess nutrient concentration ^a			Total P (excess plus r-P, μM)	Total N ₂ fixation ^b (μM)	Net C sequestered (mmol C m ⁻³ upwelled) ^c
	DIC	NO ₃ ⁻	PO ₄ ³⁻	DIC (μM)	P (μM)	DIC:P (mol:mol)			
100	2046	0.06	0.062	22	0.058	371:1	0.111	5.6	15.2
120	2055	0.32	0.101	29	0.081	357:1	0.134	6.7	15.5
140	2070	0.79	0.137	41	0.088	465:1	0.141	7.0	5.8
160	2075	1.26	0.163	43	0.084	512:1	0.137	6.8	2.5
180	2082	1.98	0.215	45	0.091	492:1	0.144	7.2	2.9
200	2091	2.84	0.276	48	0.099	489:1	0.152	7.6	2.0
250	2100	5.58	0.461	39	0.112	348:1	0.165	8.3	15.7
300	2119	9.99	0.757	29	0.133	217:1	0.186	9.3	32.7
350	2146	14.22	1.044	28	0.155	179:1	0.208	10.4	41.2
400	2173	18.82	1.361	24	0.185	132:1	0.238	11.9	54.5
450	2164	23.35	1.667	-15	0.208	-71:1	0.261	13.0	101.1
500	2199	28.00	2.033	-11	0.283	-37:1	0.336	16.8	121.8
750	2313	40.90	2.985	18	0.429	42	0.482	24.1	141.5
1000	2337	41.58	3.006	38	0.407	92	0.460	23.0	114.9

^aExcess nutrient is defined as concentration of DIC and PO₄³⁻ at the target depth that would remain in the surface if all the upwelled NO₃⁻ is removed during the hypothesized Stage I bloom with Redfield stoichiometry (C₁₀₆:N₁₆:P₁) after correcting for the average nutrient concentration that is observed in the upper 25 m at Station ALOHA between 1989 and 2005 (DIC = 2024 μM, r-P = 0.053 μM). For example, excess DIC at 300 m is: (2119 μM - 2024 μM) - (9.99 × [106 ÷ 16]) = 29 μM

^bTotal N₂ fixed = total P × (N:P ratio); assumes a molar N:P ratio of 50 (White et al. 2006)

^cNet C sequestered = total P × (C:P ratio) - excess DIC for that depth; assumes a molar C:P ratio of 331 (White et al. 2006)

and N:P ratios may eventually alter the nutrient ratios of subeuphotic zone waters, thereby reducing the efficacy of controlled upwelling as a method of net CO₂ sequestration (Karl 2002).

The primary uncertainties in these first-order calculations of CO₂ sequestration potential are: (1) the role of dissolved organic N and P (DON and DOP, respectively) in supporting bloom dynamics or, for DOP, as a supplemental reservoir of r-P to further enhance N₂/CO₂ fixed, (2) the type of diazotroph community that is established during Stage II of the upwelling-induced bloom and (3) the C:N:P stoichiometry of the organic matter that is produced and exported. With respect to the role of DON/DOP, it is important to emphasize that these organic nutrient pools are the dominant reservoirs of N and P in surface waters at Station ALOHA (Fig. 2). However, their bioavailability, especially for DON, and the N:P ratio of the bioavailable fraction are not known or even well-constrained at present. Nevertheless, it has been demonstrated that approximately 50% of the total P assimilated in the surface waters at Station ALOHA is derived from DOP (Björkman & Karl 2003), so at least a fraction of the fairly large DOP pool in surface waters is also expected to support net CO₂ uptake and a concomitant carbon export to the deep sea.

There are at least 3 fundamentally different groups of diazotrophs at Station ALOHA: (1) small, free-living unicellular cyanobacteria (*Crocospaera*-like), (2)

large filamentous and colonial morphologies of the cyanobacteria *Trichodesmium* spp. and (3) *Richelia*-like cyanobacteria living as ecto- and endosymbionts with several species of large, aggregate-forming diatoms (e.g., *Rhizosolenia* spp., *Hemiaulus hauckii*). The N₂ and CO₂ fixed by each of these groups will have a different impact on export, despite the fact that all belong to the same diazotroph guild. Finally, the C:P ratio of newly synthesized and exported organic matter is a critical consideration for CO₂ sequestration. As mentioned previously, diazotrophs, as well as many eukaryotic phytoplankton, exhibit a P-sparing effect (a reduction in P cell quota) under conditions of P limitation, thereby increasing the P-specific sequestration of CO₂.

The best proof of this concept is to 'study nature, not books,' as Louis Agassiz advised many years ago. N₂-based, high C:P export/efficient CO₂ sequestration Stage II phytoplankton blooms occur at Station ALOHA, usually in summer when the water column is well stratified (White et al. 2007, Dore et al. 2008, Fong et al. 2008). While the mechanisms that establish and sustain the periodic greening of the oligotrophic oceanic desert are not yet known, nutrient loading, especially of Fe and PO₄³⁻, either from above (dust deposition) or below, is the most likely cause (Dore et al. 2008). However, the dynamical coupling between nutrient delivery and excess carbon export is not well constrained either for Station ALOHA or for any other

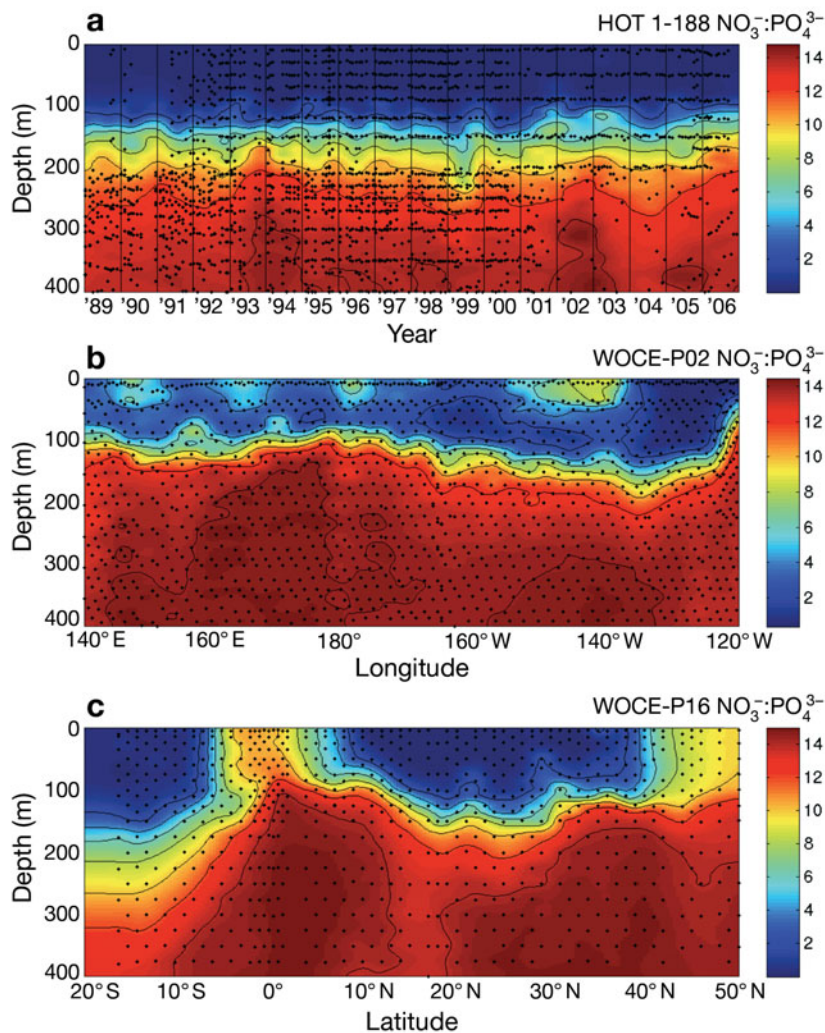


Fig. 6. Contour plots of $\text{NO}_3^-:\text{PO}_4^{3-}$ for the North Pacific Ocean: (a) time-series of $\text{NO}_3^-:\text{PO}_4^{3-}$ ratio at Station ALOHA for 1989–2006; (b) meridional section along 30°N , World Ocean Circulation Experiment (WOCE) line P02; (c) section along 150°W , WOCE line P16. Hawaii ocean time-series (HOT) data from <http://hahana.soest.hawaii.edu> and WOCE data from <http://WOCE.nodc.noaa.gov/wdiu>

marine ecosystem. Recently, Rodier & Le Borgne (2008) proposed a similar nutrient-trigger hypothesis to explain aperiodic blooms of *Trichodesmium* spp. in coastal waters of New Caledonia. In their study, *Trichodesmium* spp. blooms followed phosphate and chlorophyll enrichments with a 3 to 7 d lag, not unlike our hypothesized Stage I/Stage II progression.

FUTURE PROSPECTS

In promoting natural seascape engineering projects to enhance the efficiency for the ocean's biological carbon pump, one must always be vigilant of unintended consequences (Fuhrman & Capone 1991, Powell 2008). For the application of N_2 fixation-based methods, po-

tential secondary impacts might include the production of nitrous oxide (N_2O) via coupled N_2 fixation-nitrification ($\text{N}_2 \rightarrow \text{NH}_4^+ \rightarrow \text{N}_2\text{O}$) and the aerobic production of methane (CH_4) from enhanced cycling of methylphosphonate, a likely component of the DOP pool (Karl et al. 2008). Either one of these unintended consequences, or others not yet considered, could negate the impact of CO_2 sequestration because both N_2O and CH_4 are potent greenhouse gases. Toxin production by both of the probable bloom-forming algal assemblages, diatoms and diazotrophs, is also possible and may have significant ecological consequences. Well-designed and comprehensive nutrient perturbation experiments that examine all aspects of microbial metabolism likely to be influenced by controlled upwelling, not just the intended consequences, need to be conducted before diazotroph manipulation can be promoted as a potential climate stabilization wedge (Socolow & Pacala 2006).

Human-induced climate change is already having measurable environmental consequences that need to be addressed by the scientific community. Sitting idle or criticizing those who do take a position on geo-engineering are not good options, in our opinion. The global scale and trajectory of climate change suggest that it may not be possible to address the problem without further affecting natural ecosystems. For this reason, understanding the ecosystem response to human-induced

perturbations at a local scale must be a priority in order to develop the bases for risk assessment analyses and to minimize the impacts of geoengineering implementation on a basin-wide or global scale.

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Efficiency of carbon removal per added iron in ocean iron fertilization

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ABSTRACT: The major response to ocean iron fertilization is by large diatoms, which at Fe-replete ambient seawater show an optimum C:Fe elemental ratio of ~23 000 and a higher ratio of ~160 000 or more under Fe-limited conditions. The efficiency of CO₂ drawdown during the several weeks of artificial fertilization experiments with concomitant observations is in the range of 100 < (CO₂:Fe) < 1000 and is unknown in direction (positive or negative) and magnitude in the period after observations. The efficiency of biogenic carbon export into deeper water layers ranges from ~650 < (C:Fe)_{export} < ~25 000 for reported export depths in the 100 to 250 m range. Variations in ocean initial conditions and variable weather during an experiment cause this range of ~2 orders of magnitude. Approximately 75% of Fe added in fertilization experiments is lost very rapidly. Hence the above efficiencies can be multiplied 4-fold, to ~2600 < (C:Fe)_{export} < ~100 000, for the sake of comparison with natural fertilization with Fe-organic complexes, which stabilize Fe in solution. Quantification of the Fe source of natural fertilization is difficult, leading to an export efficiency in the ~2400 < (C:Fe)_{export} < ~800 000 range. Due to severe under-sampling, the existing datasets of artificial experiments and natural fertilizations may allow a wider range of alternative assessments than reported here.

KEY WORDS: Iron · Fertilization · Ocean · Efficiency · Carbon · Export · Diatoms

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INTRODUCTION

This study assessed the efficiency (or efficacy) of carbon removal from the upper ocean and atmosphere by natural or artificial Fe fertilization of ocean surface waters. The high-nutrient, low-chlorophyll regions (HNLC) of the oceans have been shown to suffer from the lack of essential trace nutrient iron, but other factors, notably light limitation (Smith & Nelson 1985, Mitchell et al. 1991, de Baar et al. 2005) also play a key role. Among the 3 major HNLC regions of the World ocean (the Antarctic Ocean, the equatorial Pacific upwelling region and the subarctic North Pacific Ocean), it is only in the Antarctic Ocean that Fe stimulation of CO₂ fixation would, in principle, yield long-term C storage in deeper waters (Sarmiento & Orr

1991). Fertilization of the Antarctic Ocean with extra Fe has been suggested both as an explanation for the past glacial periods (Martin 1990) and as an option for solving the present day fossil-fuel CO₂ problem. The latter intentional, large-scale, ocean iron fertilization (OIF) concept is the subject of this article, which focuses on the efficiency (effectiveness, efficacy) of carbon removal, with emphasis on the most relevant lines of evidence, i.e. relevance for the Antarctic Ocean.

PARAMETERIZATION

Universal response of large diatoms. Briefly, from all Fe-limitation and Fe-fertilization observations and experiments in bottles (reviewed by de Baar & Boyd

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2000), in natural fertilization systems (de Baar et al. 1995, Blain et al. 2007, Pollard et al. 2007), and in artificial *in situ* fertilizations (de Baar et al. 2005, Hoffmann et al. 2006, Tsuda et al. 2007), it is known that the supply of Fe strongly favors and stimulates the larger size-class (typically >10 μm) diatoms (de Baar & Boyd 2000). One key parameter is the cellular requirement (C:Fe)_{large-diatoms-optimal} of C versus Fe for healthy well-growing large diatoms in optimal Fe-replete conditions (Table 1).

Efficiency of net dissolved inorganic carbon (DIC) removal. Overall, the DIC decrease presently observed from *in situ* Fe fertilization experiments thus far tends to be ~51% (±26%, SD) of total primary production, ranging between 16 and 87% across 7 *in situ* fertilizations (de Baar et al. 2005). For these experiments, the ratio

$$(\Delta\text{DIC}:\text{Fe})_{\text{NCP}} = [(\Delta\text{DIC}_{\text{in-patch}} - \Delta\text{DIC}_{\text{control-station}}):\text{Fe}] \quad (1)$$

of observed DIC decrease versus added Fe serves as one of the efficiency parameters. The DIC loss is taken over the complete patch (i.e. lateral patch dilution has been taken into account). The DIC loss represents net community production (NCP) and is useful well beyond the plankton ecosystem, i.e. in larger ocean or global biosphere contexts.

Efficiency of atmosphere to ocean CO₂ flux. Net uptake of DIC leads to a decrease in the equilibrium value of pCO₂ in surface waters, and as result an influx of CO₂ into the ocean can be compared with the gas flux at a control site, leading to an efficiency for CO₂ drawdown:

$$(\text{C}:\text{Fe})_{\text{gas-flux efficiency}} = \text{CO}_2:\text{Fe} = (\text{Flux}_{\text{fertilized-patch}} - \text{Flux}_{\text{control-station}}) / \text{Fe}_{\text{added}} \quad (2)$$

as another efficiency parameter to be compared between experiments (Table 1). This gas flux tends to be slow, partly due to slow chemical equilibration of the

CO₂ system in seawater, such that after the period of observation there may or may not be considerably more gas exchange taking place in subsequent weeks or even months. This CO₂ gas exchange may continue to be from the atmosphere into the ocean, but may also become reversed due to the common sequence of net community production being succeeded by collapse of the phytoplankton bloom which is followed in turn by a stage of net community respiration which tends to drive excess CO₂ back into the atmosphere. However, we only assess the observed gas exchange flux during the actual period of shipboard observation of an experiment.

Efficiency of particle export into deeper waters. The export of settling organic matter (i.e. organic carbon) into deeper water layers has been assessed using the ²³⁴Th deficiency method (Buesseler et al. 2004, 2005, Blain et al. 2007, Morris et al. 2007) and sediment traps (Boyd et al. 2004, Salter et al. 2007). This export is often defined just below the euphotic zone at a depth of 100 m, leading to an export efficiency

$$(\text{C}:\text{Fe})_{\text{export-efficiency-100m}} = [(\text{C}_{\text{export-in-patch}} - \text{C}_{\text{export-control-site}})_{100\text{m}}:\text{Fe}] \quad (3)$$

However, Buesseler et al. (2004) reckon that on average >50% of the particles sinking at 100 m depth are remineralized before they reached 250 m depth and thus an extrapolated efficiency is defined at 250 m (Table 1). For the Kerguelen Ocean and Plateau Compared Study (KEOPS), an observed export is reported for 200 m depth (Blain et al. 2007).

Fate in deep ocean waters. Once exported below the 100 to 250 m depth horizon, the fate of this carbon is not further quantified in this paper, but a brief qualitative prediction of its fate is as follows. From settling fluxes into sediment traps, it is known that the downward flux of particulate matter (i.e. biogenic C, N and P; often accompanied by Si opal and CaCO₃ skeletons) decreases exponentially with increasing depth due to its utilization as substrate by bacteria where most is respired into CO₂, nitrate and phosphate. For the soft tissue components (C, N, P) some differentiation exists of the apparent first-order rate of remineralization (i.e. dissolution) as function of depth (Wakeham et al. 1980, de Baar et al. 1983), but we take the simplified view that decomposition delivers DIC, nitrate and phosphate in standard Redfield proportions (C:N:P = ~106:~16:1) into the intermediate and deep waters. Exponential function fits

Table 1. Parameters for comparison between fertilization experiments. Export at 250 m is by extrapolation from export at 100 m depth. Not listed are the actual observed export at 200 m in the Kerguelen Ocean and Plateau Compared Study (KEOPS) and 150 m in the European Iron Fertilization Experiment (EIFEX)

True element ratio values	Complete equation	Eq. no.
(C:Fe) _{large-diatoms-optimal}		
Efficiency ratio values		
(ΔDIC:Fe) _{NCP}	(ΔDIC _{in-patch} - ΔDIC _{control-station}):Fe	(1)
(C:Fe) _{gas-flux efficiency}	(Flux _{fertilized-patch} - Flux _{control-station}) / Fe _{added}	(2)
(C:Fe) _{export-efficiency-100m}	(C _{export-in-patch} - C _{export-control-site}) _{100m} :Fe	(3)
(C:Fe) _{export-efficiency-250m}	(C _{export-in-patch} - C _{export-control-site}) _{250m} :Fe	

to sediment trap fluxes versus depth (Knauer & Martin 1981, de Baar et al. 1983, Martin et al. 1987) typically show that of the export across a ~100 m depth horizon, some 90 % or more is remineralized in the 100 to 1000 m depth range, and that between 1000 m and ~4000 m depth, half or more of the C particle flux is lost once again. Combining such exponential loss function with ocean circulation modeling provides a prediction of how long the DIC, nitrate and phosphate will remain in the ocean interior before eventually (e.g. due to upwelling) returning to the surface ocean. Excess CO₂ then will be outgassed into the atmosphere, while the parallel excess nitrate and phosphate create high nutrient regions, where the recycled nutrients are suitable for once again supporting phytoplankton growth, provided there is adequate Fe and favorable light conditions. The problem is that trace-nutrient Fe does not follow Redfield stoichiometry during re-mineralization; Fe is very particle-reactive and due to adsorptive scavenging is lost from deep ocean waters (de Baar & de Jong 2001). This is shown by modeling of the ocean Fe cycle versus the regular nutrient phosphate cycle (Parekh et al. 2005, Bergquist & Boyle 2006). Thus, each time new upwelled water rich in DIC and major nutrients reaches the surface, it has lost most or virtually all of its remineralized Fe content and only by new Fe addition (e.g. dust, anoxic margin sediments, artificial OIF) can the plankton bloom and subsequently start the biological cycle all over again.

Combining these concepts of particle flux and remineralization with ocean circulation modeling provides an assessment of the fate of carbon sequestered below 100 m depth (chosen as the standard depth for export in this paper). From these modeling approaches we know that among the major HNLC regions, only the Antarctic Ocean would yield significant long term (>100 yr) carbon storage (Sarmiento & Orr 1991). Moreover, the deeper the defined horizon of particle flux, the lower the $(C:Fe)_{\text{export-depth(m)-efficiency}}$. At ~1000 m the efficiency will be an order of magnitude lower than at 100 m depth, at ~4000 m the efficiency may well be ~40-fold lower than at 100 m. In general, deep ocean waters tend to have a longer deep residence time than intermediate depth waters, hence a longer storage time of sequestered carbon before the water mass reaches the surface again and exchanges its excess CO₂ with the atmosphere. However, with increasing depth the C:Fe efficiency is less. Thus, with increasing depth the expected longer storage time is countered by the expected lower C:Fe efficiency. Quantification by deep ocean simulation modeling of this fate and storage time in the deep oceans of the here quantified OIF-driven export at ~100 m depth is recommended.

RESULTS

When aiming to resolve an issue in biological oceanography, Lalli (1991) and Lalli & Parsons (1993) have suggested a combination of 3 lines of approach: (1) observations in the field; (2) mesoscale size experiments (e.g. mesocosms); and (3) controlled experiments in the laboratory; and these 3 approaches interlinked by modeling and interpretation. No single approach in itself can provide the final answer, but the combination may. For the role of Fe in ocean ecosystems, Fe fertilization experiments and CO₂ transfer in the global oceans, this has been further developed by de Baar & Boyd (2000). Accordingly, to assess the effectiveness of OIF, the several lines of evidence (Approaches 1 to 3 above) as well as modeling (e.g. Gnanadesikan & Marinov 2008) need consideration, as does the spectrum of response to added Fe from a single species to a complete plankton community.

Iron requirement of large diatoms

Determining the Fe content of plankton cells is complicated by the fact that Fe is extremely reactive towards particles and tends to adsorb on the outside of the cell. Analyses of whole plankton would yield a severe overestimation. Attempts have been made to avoid this by gentle washing of the external Fe fraction with, for example, Ti-citrate solution (Hudson & Morel 1989, Tovar-Sanchez et al. 2003, Tang & Morel 2006). Unfortunately, it is not certain that washing removes all adsorbed Fe; and the process can rupture the cells, leading to an overall underestimation of cellular Fe content. Recently, these problems have been overcome by the application of synchrotron X-ray radiation and detection, which allows quantification of the truly intracellular Fe, distinct from the surface-bound Fe (Twining et al. 2004). Moreover, the method examines individual cells, thus permitting taxonomic and size classification. For large diatoms in the Fe-enriched patch of the Southern Ocean Iron Experiment (SOFeX)-South experiment, an intracellular C:Fe ratio of ~23 000 was reported and, thus, we consider ~23 000 representative of $(C:Fe)_{\text{large-diatoms-optimal}}$ as well (Table 2). The optimal Fe conditions for optimal growth rate were confirmed independently by the very high (virtually theoretical maximum) value $F_v/F_m = 0.65$, confirming very healthy phytoplankton cells (Coale et al. 2004). In the natural Fe-depleted region outside the fertilized SOFeX patch, i.e. at the control station, the cellular C:Fe ratio of ~160 000 for diatoms is considered sub-optimal, due to ambient Fe depletion, also confirmed by the low $F_v/F_m = 0.25$ before the Fe addition.

Table 2. The thus-far best estimate of $(C:Fe)_{\text{large-diatoms-optimal}}$, ~23 000, as well as various other estimates from the literature for C:Fe of diatoms and whole plankton assemblages (Bruland et al. 1991, based on Martin & Knauer 1973, Martin et al. 1976, Collier & Edmond 1983) and their deep ocean debris and mineralization ratios (Martin et al. 1989). Literature values of diatoms for the 84% (n = 21) lower percentile of all published values, after Sarthou et al. (2005). Using all sources (n = 25), including 4 more outlier ratio values, the average increases to C:Fe = $68\,863 \pm 112\,167$ (mean \pm SD). GFAAS: graphite furnace atomic absorption spectrometry. See 'Results' for definitions of study area acronyms

Description	C:Fe ratio value	Method	Source
$(C:Fe)_{\text{large-diatoms-optimal}}$	~23 000	SOFeX IN patch; synchrotron X-ray	Twining et al. (2004)
$(C:Fe)_{\text{large-diatoms-Fe-limited}}$	~100 000–160 000	SOFeX OUT patch	Twining et al. (2004)
$(C:Fe)_{\text{diatoms-literature}}$	$28\,571 \pm 24\,440$	84% percentile (n = 21)	Sarthou et al. (2005)
$(C:Fe)_{\text{diatoms-literature}}$	$68\,863 \pm 112\,167$	100% percentile (n = 25)	Sarthou et al. (2005)
$(C:Fe)_{\text{whole-plankton-tows}}$	~21 000	GFAAS	Bruland et al. (1991)
$(C:Fe)_{\text{excess-deep-particles}}$	~33 000	Debris by GFAAS	Martin et al. (1989)
$(C:Fe)_{\text{Thalassiosira oceanica}}$	~30 000–100 000	Optimal growth rate	Sunda et al. (1991)
$(C:Fe)_{\text{Thalassiosira oceanica}}$	~500 000	Suboptimal 90% growth	Sunda et al. (1991)
$(C:Fe)_{\text{nitricline}}$	~483 000	Linear regression	Martin et al. (1989)
$(C:Fe)_{\text{oxycline}}$	~384 000	Linear regression	Martin et al. (1989)
$(C:Fe)_{\text{plankton-content}}$	$227\,000 \pm 5\,000$ (n = 10) 175 000–333 000 range	KEOPS shipboard; ^{55}Fe radiotracer, with oxalate washing off the extracellular Fe	Sarthou et al. (2008)

Another approach to assess iron requirement is by assessing growth rate as a function of the ambient concentration of dissolved trace-nutrient Fe. As there is no good understanding yet on the effect of Fe chemical speciation (notably Fe-organic complexes) on the growth rate of a given phytoplankton species, it is best to simply take the dissolved Fe concentration as the growth-rate-controlling parameter in otherwise natural, unperturbed, Antarctic seawater (Timmermans et al. 2004). Timmermans et al. (2004) demonstrated that the K_m values for growth of large Antarctic oceanic diatoms *Fragilariopsis kerguelensis*, *Chaetoceros dictyota*, *Thalassiosira sp.*, *Corethron pennatum* and *Actinocyclus sp.* range from 0.19 nM to 1.14 nM, i.e. generally well above the average concentration of dissolved Fe in Antarctic surface waters. Moreover, these K_m values have been shown to be inversely related to the surface:volume ratio of these diatoms (de Baar et al. 2005). These results are consistent with the observation that large diatoms bloom only occasionally in the open Antarctic Ocean, presumably upon an event of Fe supply either from below (de Baar et al. 1995) or from above by wet deposition of Fe-rich dust. Notably in the Southern Ocean Iron Enrichment Experiment (SOIREE) fertilization, the (inside-patch) dissolved Fe was always above ~0.2 nM, allowing *Fragilariopsis kerguelensis* to maintain at least its half maximum growth rate (de Baar et al. 2005) and eventually become the dominant species in response to the Fe fertilization.

The above independent estimates of intracellular Fe concentration (Twining et al. 2004) and large diatoms

growth rates (Timmermans et al. 2004) were shown to be in perfect agreement with the diffusion limitation of growth rate of these diatoms (de Baar et al. unpubl. data). At increasing size the less favorable surface:volume ratio prescribes a necessary higher ambient Fe concentration for growth continuation. Conversely, small cells with the same intracellular Fe concentration, i.e. spheres with a typical diameter less than ~8 μm , are never Fe-limited in an ocean where dissolved Fe always exceeds an 0.01 nM concentration (de Baar et al. unpubl. data). This is consistent with the observation that small *Chaetoceros brevis* is never Fe-limited (Timmermans et al. 2001).

While Fe enrichments thus far have shown a response from the larger size class of diatoms, from decades of independent field observations we know that major blooms in the Antarctic Ocean are due to either such large diatoms, or the colony-forming *Phaeocystis antarctica*. For example, in the Ross Sea there are blooms of either diatoms or *P. antarctica* in distinct regions and seasons, and the cause for this distinction is of great interest (Arrigo et al. 2003, Tagliabue & Arrigo 2005). Recently, Sedwick et al. (2007) have shown from *P. antarctica* cultures in natural Antarctic seawater the K_m value for growth of ~0.45 nM dissolved Fe. This is in the same range as for the above large diatoms. Previous estimates for incubations of Ross Sea Prymnesiophytes were about one order of magnitude lower (Coale et al. 2003), the latter presumably solitary *P. antarctica* cells (diameter ~4 to 6 μm ; Rousseau et al. 2007) with a more favorable surface:volume ratio for diffusive Fe assimilation.

Other literature estimates of iron requirement of diatoms

In context of the Iron Resources and Oceanic Nutrients: Advancement of Global Ecosystem Simulations (IRONAGES) project, reviews based on previous studies have focused on the limitations by light, major nutrients and iron, of major bloom-forming groups, the diatoms (Sarhou et al. 2005), *Phaeocystis* spp. (Schoemann et al. 2005), diazotrophs (La Roche & Breitbarth 2005), and picoplankton (Timmermans et al. 2005), while fine reviews already existed for the coccolithophorids (Iglesias-Rodríguez et al. 2002, Paasche 2002). Briefly, the cell quota for diatoms have an average (mean \pm SD) C:Fe = $28\,571 \pm 24\,440$ based on 21 publications of laboratory incubation studies (Sarhou et al. 2005).

Several of the previous studies, while novel at the time, may in retrospect require caveats for the following reasons. Firstly, the problem of measuring true intracellular Fe content as mentioned above renders many old C:Fe values questionable. Secondly, in the pioneering days of metal–phytoplankton interaction experiments, it was not yet possible to achieve the ultraclean dissolved metal concentrations we know to exist in the real ocean. In order to overcome this, the culture media were overdosed with 10^{-4} M EDTA, which binds all dissolved metal ions; by then overdosing with the metal of interest, a ‘free metal’ concentration similar to the total metal in the real ocean was achieved (Provasoli et al. 1957). This method has led to many breakthroughs (e.g. Sunda & Guillard 1976). For Fe limitation, the inherent paradigm has become (de Baar 1994) that the calculated free Fe’ is the controlling agent for phytoplankton growth. However, these experiments were conducted in EDTA media. Since the 1994 discovery of >99% organic complexation of dissolved Fe in the real ocean (Gledhill & van den Berg 1994), EDTA media now are known to be not representative of the real ocean (Gerringa et al. 2000). Moreover, with the ultraclean methods of today, it is not necessary anymore to add EDTA to circumvent inadvertent contamination.

From a comparison of the cellular Fe requirements of the coastal diatom *Thalassiosira pseudonana* and the oceanic diatom *T. oceanica* (Sunda et al. 1991), one can determine from the reported growth curve that at the optimum growth rate of $\sim 1.2\text{ d}^{-1}$ of *T. oceanica*, the corresponding suggested cell ratio is in the range of C:Fe = $\sim 30\,000$ to $100\,000$. At suboptimal ($\sim 90\%$ of maximum) rate of growth the corresponding cell ratio presumably is in the order of C:Fe = $\sim 500\,000$. However, these experiments were in EDTA media and not relevant for the real ocean. Otherwise, (Sunda et al. 1991) reported that it was not possible to drive *T. oceanica*

into Fe limitation, at most a suppression to 90% of maximum growth was realized. This is consistent with the fact that *T. oceanica* is a very small diatom and therefore will never be Fe diffusion limited in real ocean waters (de Baar et al. 2008), akin to the similarly small oceanic diatom *Chaetoceros brevis* which could not be driven into Fe limitation in natural Antarctic seawater either (Timmermans et al. 2001), except after the addition of very strong siderophore DFOB (desferrioxamine-B) making Fe unavailable for uptake. Quite remarkably, addition of DFOB to natural Antarctic seawater cannot even drive *T. oceanica* into Fe limitation (K. R. Timmermans et al. unpubl. data). Somehow, DFOB-bound Fe appears to be available to *T. oceanica*, but not at all available to *C. brevis* (Timmermans et al. 2001). Similarly, Hutchins et al. (1999) reported that different phytoplankton species can access different Fe-organic species, i.e. something more than just inorganic Fe’(III) is affecting growth. Sedwick et al. (2007) also report that DFOB bound Fe somehow is partly available for *Phaeocystis antarctica*. Researchers are only beginning to unravel the intriguing interactions between several organic ligands and several different phytoplankton species (Rijkenberg et al. 2006, 2008), as natural iron–plankton interactions can only be assessed in natural seawater.

Efforts to derive C:Fe ratio values from the deep ocean

One of the first reliable vertical profiles of dissolved Fe in the deep ocean was in the north Pacific Ocean at 50°N , 145°W (Ocean Station Papa) which appeared to exhibit similarity to the vertical distribution of nitrate (Martin et al. 1989) but, linear correlation, akin to e.g. phosphate versus nitrate (Redfield et al. 1963), between Fe and nitrate was not successful. However, by combining data only in the nitricline of 50°N , 145°W (Ocean Station Papa) and adjacent stations at 40°N , 140°W (Vertex T-5) and 45°N , 143°W (Vertex T-6) a linear relation was achieved (Martin et al. 1989). Conversion of N to C by classical Redfield (C:N = 106:16 = ~ 6.6) yielded C:Fe = $\sim 483\,000$ (de Baar & de Jong 2001, p. 164). Similarly, versus the oxycline, C:Fe = $\sim 384\,000$ was obtained. On the other hand, excess Fe on deep particles (excess over lithogenic Fe) presumably represents biogenic Fe and led to a C:Fe = $\sim 33\,000$ (Martin et al. 1989). This is similar to the C:Fe = $\sim 21\,000$ of whole plankton tows (Bruland et al. 1991).

With some more recent vertical profiles of dissolved Fe in other ocean basins (de Baar & de Jong 2001, Parekh et al. 2005, Bergquist & Boyle 2006), it now appears that dissolved Fe in the deep oceans is within a narrow band of concentrations and does not show the general in-

crease from young deep Atlantic to old deep Pacific waters as do the micronutrients N, P and Si. This is likely due to net removal of dissolved Fe from deep waters by adsorptive scavenging, while there is no net removal of micronutrients (Parekh et al. 2005). Hence, it appears that each ocean basin has its own Fe cycle and that there is little exchange of Fe between basins (de Baar & de Jong 2001). It seems there is no straightforward relationship between deep Fe and deep micronutrients. Most likely the deep ocean ratio of dissolved Fe versus major nutrient (e.g. nitrate or phosphate) tends to decrease with the age of deep water; hopefully, the ongoing Geotraces global mapping project will provide new insight into this area in the near future.

Values of C:Fe ratio derived from the 1993–2002 *in situ* fertilization experiments

By comparison of the *in situ* fertilization experiments, a compilation of efficiency values ($\Delta\text{DIC}:\text{Fe}$)_{NCP} has been reported before (de Baar et al. 2005, their Table 3) and is given in Table 3. Moreover, we have calculated the other efficiency ratio values for gas influx during the observation period of each experiment, as well as the export efficiency at the 100 m depth horizon. Note that in most ocean regions, the export efficiency at the 250 m depth horizon would be about half that at 100 m, as observed and applied by Buesseler et al. (2004) in the context of the SOFeX-South experiment in the Antarctic Ocean.

The (C:Fe)_{gas-flux-efficiency} varies between 100 and 1000 mol CO₂ gas influx into the ocean mol⁻¹ Fe added. This estimate may, on the one hand, be considered a lower limit, as gas influx would presumably continue

when the bloom continued after the period of observation, i.e. after the ships had left. On the other hand, it may just as well be considered an upper limit. For example, upon the collapse of a bloom (e.g. at end of SERIES), the ecosystem would most likely tend to shift to net community respiration, eventually accompanied by outgassing of CO₂ in this post-bloom period. Such a major shift has been reported for the final observation period at the natural Kerguelen Plateau study (Lefèvre et al. 2008).

The estimates of export flux efficiency (C:Fe)_{export-efficiency-100m} or (C:Fe)_{export-efficiency-250m} are very modest compared to those that have been suggested in geo-engineering proposals (C:Fe > 100 000) for reducing the greenhouse effect by removing CO₂ from the atmosphere (Buesseler et al. 2004). These efficiency values are in the range 650 < (C:Fe)_{export-efficiency} < 6600; much lower than initial suggestions derived directly from assumed cellular composition ratio of plankton of C:Fe = ~100 000 or more (Table 2). The low export efficiencies may partly be ascribed to the fact that ~75 % of the added fresh Fe(II) is removed rapidly into fine colloids (Nishioka et al. 2005) within 24 to 48 h after each fertilization:

$$[\text{Colloidal Fe}] = 0.76 [\text{Dissolved Fe}] + 0.052 \quad (4)$$

$$(R^2 = 0.93)$$

This removal is likely the first step towards the next stage of aggregation into larger particles, which then are lost due to settling into deeper water layers. This would appear consistent with ~63 % of added Fe (1100 out of 1740 kg Fe) that cannot be accounted for in an Fe budget of SOIREE (Bowie et al. 2001). Such major loss does not only require repeated fertilizations, but also causes a ~4-fold decrease of efficiency. During

Table 3. Calculated values of efficiency ratio of C versus total added Fe in each experiment for total estimates over complete period of each experiment for net community production, CO₂ gas influx from the air, carbon export across 100 m depth horizon into deeper waters, and by extrapolation, export across 250 m depth horizon (Buesseler et al. 2004). Each value has large uncertainty. Compilation of best estimates following de Baar et al. (2005) with many incompatibilities between experiments and inherent uncertainties (de Baar et al. 2005, their Fig. 22 & Table 3). For SOFeX-South the ($\Delta\text{DIC}:\text{Fe}$)_{NCP} estimate is integrated over a 225 km² patch area, while the ($\Delta\text{DIC}:\text{Fe}$)_{NCP} Option 2 is integrated over a 1000 km² patch area, following Buesseler et al. (2004). For some other experiments, other ($\Delta\text{DIC}:\text{Fe}$)_{NCP} options have also been published (de Baar et al. 2005, their Table 3, italics), but these were considered not the best estimates. If nothing else, the variations between presumed best estimates and other-option estimates for any one experiment underlines the intrinsic difficulty of quantification. Moreover, in some experiments it is not clear if the published changes of terms in the carbon budget are truly by difference between the fertilized in-patch and the control site (as here defined in Table 1, 'Complete equation'), or only for the fertilized in-patch, i.e. without correcting for simultaneous changes of terms in the the carbon budget at the unfertilized control site

Efficiency ratio	IronEx II	SOIREE	EisenEx	SEEDS I	SOFeX-South	SOFeX-North	SERIES
($\Delta\text{DIC}:\text{Fe}$) _{NCP}	9672	3701	2847	15 000	8028	4110	16 887
($\Delta\text{DIC}:\text{Fe}$) _{NCP} Option 2	–	–	–	–	35 680	–	–
(C:Fe) _{gas-flux-efficiency}	630.5	100.8	219.0	853.7	1003.5	548.0	–
(C:Fe) _{export-efficiency-100m}	3150	Negligible	–	766	6648	–	650
(C:Fe) _{export-efficiency-250m}	–	–	–	–	3300	–	–

the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS) I experiment, the over 75% colloid Fe fraction tended to remain in the surface waters (Nishioka et al. 2003), at least during the 13 d of observations, nevertheless being colloids this fraction would remain inaccessible for direct uptake by phytoplankton.

Fine colloidal Fe is itself deemed unavailable for uptake by phytoplankton, but reduction by daytime photochemistry, or perhaps also in the vicinity of the cell wall due to membrane-bound reductases (Salmon et al. 2006), may bring colloidal Fe back into a soluble state suitable for plankton uptake. The diurnal physical chemistry of Fe colloids (Nishioka et al. 2005, Croot et al. 2005) requires further investigation.

Perhaps in future experiments, when adding dissolved Fe in a dissolved organic-complexed form (e.g. bound with excess EDTA), this could be overcome and 4-fold higher export efficiencies (ranging from $2600 < (C:Fe)_{\text{export-efficiency}} < 27000$) would not be inconceivable. As a matter of fact, this strategy has been used in 2 experiments (GreenSea 1 and 2) in the Gulf of Mexico, where researchers added extra lignopolysulfonate (cheap by-product of paper industry); however, the brief report does not have information on carbon export (Markels & Barber 2001).

C:Fe ratio derived from SEEDS II and the European Iron Fertilization Experiment (EIFEX)

The SEEDS II fertilization in 2004 was at the same location as SEEDS I, but had very different initial conditions and responses (Tsuda et al. 2007). This, in itself, illustrates the lack of predictability of ocean iron fertilization. Moreover, the fertilized patch was surrounded by a non-uniform water mass of different characteristics and this makes comparison between the fertilized patch and the control site less reliable (A. Tsuda pers. comm.). Upon addition of 322 kg Fe (5760 mol) in a 64 km² patch at Day T = 0 and an additional 160 kg (2842 mol) at Day T = 6 in a 200 km² patch, the particulate organic carbon (POC) export flux collected in a sediment trap at 100 m depth was variable, increasing from ~26 to ~35 mmol m⁻² d⁻¹. At the control site the export flux at 100 m depth was lower at ~17 mmol m⁻² d⁻¹ (A. Tsuda & H. Saito unpubl. results). During the first 25 d, the total POC export at 100 m depth was 640 mmol m⁻² in the fertilized patch and 423 mmol m⁻² at the control site. By difference the excess POC export at 100 m depth was 217 mmol m⁻². Meanwhile, the detectable patch size increased to 1000 km² by Day 15 and then decreased to 830 km² by Day 22. This lateral patch dynamics is a major challenge for deriving carbon budgets and

excess carbon export. Nevertheless, the excess POC export of 217 mmol m⁻² would yield lower and upper limits for the export efficiency at 100 m depth in the range of $\sim 1600 < (C:Fe)_{\text{export-efficiency-100m}} < \sim 25\,000$ for an assumed 64 or 1000 km² patch size, respectively. This efficiency at 100 m depth in SEEDS II is more than the $(C:Fe)_{\text{export-efficiency-100m}} = 766$ (Table 3) at 100 m depth in SEEDS I. An exciting finding of SEEDS II is the importance of mesozooplankton. The initial copepod biomass in SEEDS II was 3-fold higher than in SEEDS I and SERIES; the copepod biomass also increased strongly, some days earlier inside the patch than outside. On the other hand, an observed relationship between copepod biomass and export flux collected at 40 m depth in sediment traps shows no significant difference between in-patch and outside patch (out-patch) of SEEDS II (Tsuda et al. 2007). These observations suggest that the POC export flux collected in sediment traps at 40 m depth was a function of the copepod biomass and the iron-enhanced growth of phytoplankton had a minor effect on the export flux collected in 40 m depth sediment traps in SEEDS II (Tsuda et al. 2007). Moreover, vertical migration of mesozooplankton causes an extra carbon export flux which is not collected in sediment traps. In SEEDS II this vertical migration increases the excess carbon export at 40 m depth with ~70% (H. Saito unpubl. results) leading to an ~70% increase of the $(C:Fe)_{\text{export-efficiency-40m}}$ at 40 m depth. Similarly the $(C:Fe)_{\text{export-efficiency-100m}}$ at 100 m depth may increase due to vertical migration.

The 2004 EIFEX in the Southern Ocean (Hoffmann et al. 2006) was twice fertilized with 25 180 mol Fe, once in a 150 km² patch and once in a 400 km² patch. Currently, we have no information on whether or not and to what extent the second fertilization overlapped with the water mass of the first fertilization. In between the first and the second fertilization, the size of the patch was reportedly observed to be ~600 km². Initial export fluxes at 150 m depth were high at $\sim 21 \pm 5$ mmol C m⁻² d⁻¹ and remained high and constant at both in-patch and out-patch stations during the first 21 d (Jacquet et al. 2008, their Fig. 3). Export production increased slightly during Day 17 to Day 34 at out-patch stations, while at in-patch stations it decreased to the lowest values at Day 20 to Day 24. From Day 25 to Day 32, a massive increase of carbon export to as high as $\sim 54 \pm 14$ mmol C m⁻² d⁻¹ occurred at the in-patch stations (Jacquet et al. 2008, after their Fig. 3), coinciding with massive sinking of large diatoms. During that final period, the excess total flux appears to have been on the order of ~ 350 mmol C m⁻², which, with an assumed average patch size of ~ 400 km² and a total Fe addition of 50 360 mol would lead to an estimate of $(C:Fe)_{\text{export-efficiency-150m}} = \sim 2780$ for EIFEX.

Values of C:Fe ratio in natural fertilization

The Fe supply in natural Fe fertilizations at both the Kerguelen plateau and the Crozet Island plateau comes from suboxic or anoxic sediments. These sediments can be just below the surface waters exhibiting enhanced phytoplankton, i.e. there may be an upward transport of dissolved Fe from the sediments to the surface waters, as suggested for the Kerguelen Plateau (Blain et al. 2007). Alternatively, dissolved Fe from sediments at an adjacent island plateau might be transported laterally by horizontal currents and water mass mixing to a site with observed enhanced phytoplankton, as suggested for the Crozet Island region (Planquette et al. 2007). Due to the >99% organic complexation (Gerringa et al. 2008), this Fe is maintained in solution far better than the artificial fresh Fe(II) additions of the *in situ* fertilization experiments, where within 12 to 48 h some 75% of the added Fe (II) is lost very rapidly due to oxidation into colloids (Eq. 4) which in turn may aggregate into large particles. Hence, for natural fertilization the efficiency ratio values may well be on the order of 4-fold higher (or more) than for the experimental fertilizations.

Values of C:Fe in natural fertilization at the Crozet Plateau

At the Crozet Plateau, high carbon export rates have been reported from sediment trap collection. Normalized to 100 m depth these export rates range from ~1 to ~36 mmol C m⁻² d⁻¹ in the productive region north of the plateau and ~2 to 4 mmol C m⁻² d⁻¹ in the HNLC control region south of the plateau (Salter et al. 2007). These values are in good agreement with independent estimates by the ²³⁴Th deficiency method, ranging from initially 15 mmol C m⁻² d⁻¹ in the high-chlorophyll bloom region, compared with 5 mmol C m⁻² d⁻¹ in the low-chlorophyll, non-bloom region (Morris et al. 2007). After a moderately small bloom and export event at the southern control stations, the POC export became more uniform, resulting in equally high levels of POC export (~20 mmol C m⁻² d⁻¹) throughout the study region.

The magnitude of Fe influx from various sources is very difficult to quantify. For the blooming area of the Crozet Natural Iron Bloom and Export Experiment (CROZEX) the soluble Fe influx from aerosols has been assessed at 100 nmol m⁻² d⁻¹, the vertical influx from below sediments at 61 nmol m⁻² d⁻¹, and the horizontal influx from the nearby islands at 390 nmol m⁻² d⁻¹ (Planquette et al. 2007). Each of these values is based on a suite of estimates and inherent assumptions (see Planquette et al. 2007); assuming that the atmo-

spheric and vertical fluxes are also present at the HNLC control site, and that the horizontal flux continues for 100 d of winter, then the estimated stock of Fe available at the start of spring is equivalent to 0.039 mmol m⁻² yr⁻¹ (Pollard et al. unpubl. data).

Next, by comparing the ²³⁴Th-deficiency-derived export (mmol m⁻² d⁻¹) of biogenic Si (i.e. diatoms) with the seasonal deficit (mmol m⁻²) of dissolved silicate in the upper water layer, Pollard et al. (unpubl. data) arrive at an estimated bloom duration of 61 d. This yields an excess C export of the productive bloom region compared to the low production control region of 670 mmol m⁻² per growing season, which, divided by the excess Fe supply of 0.039 mmol m⁻² yr⁻¹ yields their reported best estimate efficiency (C:Fe)_{export-efficiency-100m} = ~17 200 for export across the 100 m depth horizon (Pollard et al. unpubl. data). Furthermore, by using upper and lower limits of C export and Fe supply, upper and lower limits of efficiency of (C:Fe)_{export-efficiency-100m} = ~60 400 and ~5400, respectively, are achieved (Pollard et al. unpubl. data).

The vertical POC flux collected in a deep sediment trap at 3000 m depth was found to have only 4% of the above-mentioned downward-POC flux across the 100 m depth horizon, i.e. 96% of the downward-settling POC flux was lost in the 100 to 3000 m depth interval. This is consistent with the expectations mentioned in the above subsection 'Parameterization—Fate in deep ocean waters' for the fate of POC in the deep ocean and yields an efficiency ratio at 3000 m of (C:Fe)_{export-efficiency-3000m} = ~730. For intermediate depths in the 100 to 3000 m range the efficiency ratio would be between ~17 200 and ~730. When combining this with an ocean circulation model, the *a priori* expectation is that the deepest regenerated CO₂ (with lowest C:Fe efficiency) will have the longest ocean storage time, while the major regeneration in the 100 to 1000 m depth 'ocean twilight zone' (Buesseler et al. 2007), with its relatively high C:Fe efficiency, will have shorter deep ocean storage time. Thus for a range of depth intervals the more favorable C:Fe efficiency tends to be coupled with less favorable storage time. However, regional circulation and mixing—as well as rapid deep sedimentation events with or without enhancement-by-ballast effects of Si opal and CaCO₃ skeletons—will cause deviations from this simple *a priori* expectation.

Natural fertilization at the Kerguelen plateau

The Kerguelen plateau consistently shows elevated chlorophyll *a* (chl *a*) levels (as observed by satellite) and this 'ocean island effect' has been investigated in KEOPS (Blain et al. 2007). The diffusive upward flux of Fe from sediments below was 31 nM m⁻² d⁻¹ (partly due to

Table 4. Ratio values of plankton uptake rate, plankton content, and various efficiency values derived for the KEOPS field study of natural fertilization processes (Blain et al. 2007). The reported $200\,000 \pm 118\,000 \text{ mol mol}^{-1}$ value (Blain et al. 2007) apparently slightly deviates from the actual value of $274\,000 \pm 142\,000 \text{ mol mol}^{-1}$ (range is 131 000 to 416 000) in the more recently published article of the shipboard experiments (Sarhou et al. 2008). Export efficiencies at 100 and 200 m reported by Blain et al. (2007); alternative export efficiency values (Invoked 2) calculated in this study. Ratio values C:Fe of plankton uptake rate and plankton content after inversion of ratio values Fe:C reported by Sarhou et al. (2008). Also shown is an Invoked 3 scenario for sake of comparison with diatom C:Fe composition under optimal Fe-replete conditions, see 'Discussion—Concordia'

Ratio values	KEOPS	KEOPS Invoked 1 (Blain et al. 2007)	KEOPS Invoked 2 (present study)	KEOPS Invoked 3 (present study)
Plankton uptake rate				
(C:Fe) _{plankton-uptake-rate}	–	$200\,000 \pm 118\,000^a$	–	–
	–	131 000 to 416 000 (n = 6) ^b	–	–
Plankton content				
(C:Fe) _{plankton-content}	–	$227\,000 \pm 5000$ (n = 10) ^b	–	–
		175 000 to 333 000		
(C:Fe) _{large-diatoms-Fe-limited}	–	–	$\sim 160\,000^c$	–
(C:Fe) _{large-diatoms-optimal}	–	–	–	$\sim 23\,000^c$
Efficiency ratios				
Excess Fe supply rate ($\text{nM m}^{-2} \text{d}^{-1}$)	27	204 ± 77 (Invoked 1)	~ 289 (Invoked 2)	~ 2013 (Invoked 3)
($\Delta\text{DIC:Fe}$) _{NCP}	668 000	–	–	–
	Seasonal budget	–	–	–
($\Delta\text{DIC:Fe}$) _{NCP}	–	149 000	–	–
		Seasonal budget including lithogenic Fe supply		
(C:Fe) _{export-efficiency-100m}	$400\,000 \pm 180\,000$	21 000 to 123 600	16 800 to 98 880	2415 to 14 214
(C:Fe) _{export-efficiency-200m}	$526\,000 \pm 290\,000$	$70\,000 \pm 46\,000$ 22 400 to 174 000	$56\,000 \pm 37\,000$ 17 920 to 193 200	8050 ± 5290 2576 to 20 010

^aBlain et al. (2007); ^bSarhou et al. (2008); ^cTwining et al. (2004)

enhanced vertical diffusivity) as compared to $4 \text{ nM m}^{-2} \text{d}^{-1}$ at the off-plateau control site. The mean excess of ^{234}Th -derived export production on the plateau versus at the control site was $10.8 \pm 4.9 \text{ mmol C m}^{-2} \text{d}^{-1}$ at 100 m depth and $14.2 \pm 7.9 \text{ mmol C m}^{-2} \text{d}^{-1}$ at 200 m depth. Dividing by the excess upward diffusive Fe flux of $27 \text{ nM m}^{-2} \text{d}^{-1}$ leads to $(\text{C:Fe})_{\text{export-efficiency-100m}} = 400\,000$ and $(\text{C:Fe})_{\text{export-efficiency-200m}} = 526\,000$. Presumably these record high export efficiencies were deemed non-realistic by the authors. Therefore, an additional Fe

Table 5. Export efficiency at 100 m depth during SEEDS II, estimated after A. Tsuda et al. (unpubl. data), and the export efficiency at 150 m during EIFEX following Smetacek (2005) and Jacquet et al. (2008) for the two 7 t iron-sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) enrichments (in $\sim 150 \text{ km}^2$ and $\sim 400 \text{ km}^2$ patches). One mol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ equals 278 g, 1 mol Fe equals 55.847 g. Upon publication of findings for dissolved inorganic carbon (DIC) and pCO_2 , differences between in-patch and out-patch stations the $(\Delta\text{DIC:Fe})_{\text{NCP}}$ and $(\text{C:Fe})_{\text{gas-flux-efficiency}}$ may also be assessed

Efficiency ratio	SEEDS II	EIFEX
(C:Fe) _{export-efficiency-100m}	$\sim 1600\text{--}25000$	–
(C:Fe) _{export-efficiency-150m}	–	~ 2780

supply term was invoked. Shipboard ^{55}Fe uptake and regeneration experiments would lead to a hypothesized excess Fe input of $204 \pm 77 \text{ nM m}^{-2} \text{d}^{-1}$ over the plateau, but the source of this excess Fe is unaccounted for. With the same above carbon export at 200 m depth, we calculate a range of $22\,400 < (\text{C:Fe})_{\text{export-efficiency-200m}} < 174\,000$ —not dissimilar to the reported $(\text{C:Fe})_{\text{export-efficiency-200m}} = 70\,000 \pm 46\,000$ (Blain et al. 2007).

In general, the reported efficiency values of the KEOPS (Table 4) natural environment exceed those reported from the *in situ* experiments. Taking into account the 75% loss term in the latter experiments, we simply (if not simplistically) multiply the $(\Delta\text{DIC:Fe})_{\text{NCP}}$ values (Table 3) of *in situ* experiments by a factor of 4 and arrive at a range of 11 388 to 67 548 from low EisenEx to high SERIES. This range is still well below the range 149 000 to 668 000 for the reported $(\Delta\text{DIC:Fe})_{\text{NCP}}$ seasonal budget estimates of KEOPS (Table 4). Similarly, multiplying the export efficiency values 4-fold, we obtain a range of 2600 (SERIES at 100 m) to 26 592 (SOFeX-South at 100 m), which just overlaps with the wide range from 21 000 to 916 000 for various export efficiency estimates of KEOPS (Table 4). Apart from this somewhat arbitrary 4-fold adjustment, there remains the challenge to

bridge the gap between the very high efficiency ratio values reported for KEOPS (Blain et al. 2007) and lower efficiency ratio values for the artificial fertilizations (Tables 3 & 5). Below, we will show how these, at first glance inconsistent, findings can be reconciled.

DISCUSSION

Concordia

The excess Fe input of $204 \pm 77 \text{ nM m}^{-2} \text{ d}^{-1}$ over the Kerguelen plateau invoked on the basis of shipboard ^{55}Fe uptake experiments, inevitably yields high C:Fe efficiencies which are consistent with the ratio values of these shipboard ^{55}Fe -based experiments (Blain et al. 2007). In other words, the reported (Blain et al. 2007) consistency of high efficiencies of short and seasonal budgets with shipboard observations of C:Fe uptake rate ratios ($200\,000 \pm 118\,000 \text{ mol mol}^{-1}$) is a circular argument. Otherwise, the latter $200\,000 \pm 118\,000 \text{ mol mol}^{-1}$ value apparently slightly deviates from the actual value of $274\,000 \pm 142\,000 \text{ mol mol}^{-1}$ (range is 131 000 to 416 000) in the more recently published article of the shipboard experiments (Sarhou et al. 2008). Nevertheless, the plankton content ratio range $175\,000 < (\text{C:Fe})_{\text{plankton content}} < 333\,000$ reported for the Kerguelen plateau is not dissimilar to the $(\text{C:Fe})_{\text{large-diatoms-Fe-limited}} = \sim 160\,000$ for large diatoms of the unfertilized control site of SOFeX-South (Table 2) as determined by the reliable synchrotron X-ray method (Twining et al. 2004). This value of $\sim 160\,000$ now may be used as a second approach for another invoked Fe supply scenario leading to efficiency ratio values (Table 4, KEOPS Invoked 2) similar (but somewhat lower) to the first invoked scenario (Table 4, KEOPS Invoked 1). As the result of this second invoked scenario one finds similar efficiency ratio values for the export, conversely suggesting the large diatoms at Kerguelen Plateau were as Fe-limited as at the SOFeX oligotrophic control site. Finally, when assuming truly Fe-replete large diatoms, one may invoke the best estimate, $(\text{C:Fe})_{\text{large-diatoms-optimal}} = \sim 23\,000$ (Table 2), and thus arrive at much lower C:Fe efficiency values for the Invoked 3 scenario (Table 4). The values obtained in this fashion, ranging from 2415 to 20 010, are closer to the 650 to 6648 export efficiency of the artificial *in situ* experiments (Table 3). Moreover, when taking into account the $\sim 75\%$ immediate loss of added Fe in the *in situ* fertilization experiments, multiplying the latter export efficiencies by 4 would yield a range of 2600 to 25 600, which overlaps with the Invoked 3 scenario of a 2415 to 20 010 export range at KEOPS for truly Fe-replete diatoms driving this export.

Indeed, the mean dissolved Fe concentration in the surface waters over the Kerguelen plateau is low ($0.090 \pm 0.034 \text{ nM}$) and only slightly higher than at the oligotrophic control site ($0.073 \pm 0.014 \text{ nM}$) (Blain et al. 2008). These dissolved Fe concentrations are similar to those found elsewhere in the oligotrophic Antarctic Ocean; for example, 0.04 to 0.06 nM at the beginning of EisenEx (Nishioka et al. 2005). At the out-patch stations of SOFeX-South, values were somewhat higher, at $\sim 0.1 \text{ nM}$ (and perhaps occasionally higher, at $\sim 0.5 \text{ nM}$), and at these out-patch stations, $(\text{C:Fe})_{\text{large-diatoms-Fe-limited}}$ values = $\sim 100\,000$ to $160\,000$ were found. In contrast, the fertilized patch of SOFeX-South had a typical dissolved Fe of $\sim 1.2 \text{ nM}$, an order of magnitude higher than at Kerguelen Plateau, thus stimulating more rapid growth of large diatoms. Indeed, the cell division rates of key large diatom species in seawater of the Kerguelen Plateau are $\sim 0.2 \text{ d}^{-1}$ (Timmermans et al. 2008) which is about half of the optimal rate of growth (Timmermans et al. 2004).

Nevertheless, at the Kerguelen Plateau, the slight difference of $\sim 0.02 \text{ nM}$ extra dissolved Fe compared to the SOFeX-South out-patch station, as well as the likely more steady supply from below, would be beneficial for long term maintenance of an elevated abundance and elevated rate of growth (but by no means optimal in the sense of Monod growth). The F_v/F_m values, indicative of more or less adequate supply of Fe for healthy state of growth, were reported somewhat higher, at 0.55 over the Plateau, as compared to ~ 0.3 at the KEOPS control site (Blain et al. 2007, their supplement). Over the complete spring and summer season, a modest increase of cell division rate (say from 0.15 d^{-1} to 0.2 d^{-1}) may yield the 'cumulative interest' effect for the significant difference between steady blooms at Kerguelen versus the generally low chlorophyll abundance (HNLC) of open Antarctic Ocean waters. In other words, it appears that the large diatoms in surface waters of the Kerguelen plateau are only somewhat less Fe-limited than elsewhere in the open Antarctic Ocean, yet nevertheless, by steady moderate rate of growth, do make an impact on budgets of C and Si. This might explain the reported very high, $175\,000 < (\text{C:Fe})_{\text{plankton-content}} < 333\,000$, values for algae growing in Fe = $\sim 0.09 \text{ nM}$ surface waters of Kerguelen Plateau, as compared to the $(\text{C:Fe})_{\text{large-diatoms-optimal}} = \sim 23\,000$ in the Fe-replete $\sim 1.2 \text{ nM}$ waters of the in-patch of SOFeX-South. Indeed, in the Fe-enriched patch of SOFeX-South, the F_v/F_m was at its virtual theoretical maximum ratio, ~ 0.65 (Coale et al. 2004).

Uncertainties

For both the *in situ* fertilization experiments and the natural fertilizations the approaches or methodologies

for quantification of the carbon C stocks and turnover rates are the same or similar, hence the inherent uncertainties likely are similar. On the other hand, the quantifications of the Fe supply, stocks and turnover rates are vastly different. For the *in situ* experiments, the total amount of added Fe is accurately known, but the fate of this Fe is very poorly quantified due to some 60 to 75 % being lost, somehow, somewhere. Budget estimations of the fate of added Fe are difficult and only one budget assessment has been published (Bowie et al. 2001). For the natural fertilization experiments, the quantification of Fe supply from below sediments is difficult and in KEOPS was shown to be far lower than desirable.

Ranges of estimates

The oceans are dynamic regions, with much variability in time and place, where day-to-day variability of the weather (wind, insolation) is a major driver of variability of any one upper ocean plankton ecosystem. In every single fertilization experiment or natural fertilization study, the complete 3D mapping every day of all key variables cannot be achieved with merely 1 (or at most 3) ships and their shipboard observers. For each experiment the ensuing dataset, therefore, is very limited in space, in time, and in a very restricted number of key variables. Thus, we are only scratching the surface. Nevertheless, for each study, the overarching synthesis article (e.g. Tsuda et al. 2003, 2007, Boyd et al. 2004, Coale et al. 2004, Blain et al. 2007) very cleverly combines these limited observations into an overall coherent interpretation, based on the underlying more specific reports (e.g. Buesseler et al. 2004, Nishio et al. 2005, Gerringa et al. 2008) of that 1 study.

Previously (de Baar et al. 2005, Boyd et al. 2007) and in this article, an effort has been made to combine these individual field projects (IronEx II through CROZEX, KEOPS) into a synthesis, where inevitably its conclusions carry the sum of all uncertainties of the single studies. Moreover, the various estimates as cited here from work by others, as well as in this article, are all based on many inevitable assumptions, as required due to lack of data or knowledge, where a large number of these assumptions are highly debatable, if not questionable. In other words, due to the limited datasets, there is much room for alternative interpretations and conclusions.

CONCLUSIONS

The most reliable estimate of $(C:Fe)_{\text{large-diatoms-optimal}}$ is to date $\sim 23\,000$ for *in situ* large Antarctic diatoms

within the Fe-replete SOFeX-South patch. This is in good agreement with the diffusion limitation (de Baar et al. unpubl. data) of the rate of growth of large Antarctic diatoms in shipboard and laboratory experiments of incubations of single species diatoms in filtered ultraclean natural Antarctic seawater (Timmermans et al. 2004). In the Fe-limited, suboptimal growth conditions of the open Antarctic Ocean, large diatoms survive at very low, but likely persistent, rates of growth and may have lower suboptimal intracellular C:Fe ratio values, from $\sim 160\,000$ at out-patch stations of SOFeX-South to $\sim 227\,000$ in the ambient 0.09 nM Fe surface waters of Kerguelen Plateau.

In the artificial Fe fertilization experiments, the 4 estimates thus far of $(C:Fe)_{\text{gas-flux-efficiency}}$ range from 100 to 1000 (Table 3). In the period after observation ships have left, this efficiency may either increase or decrease, due to either continued net community production or a shift to final net community respiration, respectively.

The estimates of carbon export efficiency at 100 m depth range from 650 (SERIES) to 6648 (SOFeX-South) with an extrapolated value at 250 m of ~ 3300 for SOFeX-South (Tables 3 & 5). For EIFEX the export efficiency at 150 m depth is estimated at ~ 2780 (Table 5).

For these artificial fertilizations the $\sim 75\%$ immediate loss of added Fe may be corrected for by a factor of ~ 4 when assuming future or natural fertilization as a more stable Fe-organic complex. This would increase the CO_2 drawdown efficiency in the 400 to 4000 range and the various export efficiency estimates to a range from ~ 2600 (SERIES) to $\sim 26\,600$ (SOFeX-South), or even $\sim 100\,000$ when including the high estimate of SEEDS II based on an assumed very large 1000 km^2 patch size.

For the artificial *in situ* Fe fertilization experiments, at least the amount of added Fe is accurately known, such that the uncertainty in the above estimations of C:Fe efficiency is due solely to uncertainty in the assessment of the C budgets. For natural Fe fertilizations the supply of Fe also must be derived from field observations, such that the derived supply of Fe has an uncertainty equal or larger than the uncertainty in the parallel estimation of the C budget. Therefore, the $(C:Fe)_{\text{export-efficiency}}$ of natural fertilizations has an inherently larger uncertainty than that of the artificial fertilization experiments.

In the natural Fe fertilization at the Crozet Plateau the $(C:Fe)_{\text{export-efficiency}}$ at 100 m depth was reported to be $\sim 17\,200$, within reported upper and lower estimates of $\sim 60\,400$ and ~ 5400 , respectively (Pollard et al. 2008). In the natural Fe fertilization at the Kerguelen Plateau, the derived $(C:Fe)_{\text{export-efficiency}}$ at either 100 m or 200 m depth ranged from ~ 8050 to $\sim 526\,000$, largely depending on the assumed or invoked Fe supply term.

RECOMMENDATIONS

When delivering the iron fertilizer in a more stable organic-complexed dissolved form, the efficiency of carbon export into deeper ocean waters may range from ~2600 to ~26 600 per added amount of iron. Laboratory research is needed to unravel which specific Fe-organic complexing chemical molecule would both stabilize Fe in solution and leave it available for uptake by the target group of phytoplankton, e.g. large diatoms. This will be influenced by photochemistry (notably Fe photoreduction) which should be part of such studies.

The wide variability of export efficiency is due to wide variations of initial ocean conditions before iron addition and wide variation of weather conditions after iron addition. Initial conditions of major influence are the initial abundance of phytoplankton and its major taxonomic groups and size classes, micro- and mesozooplankton, water column stratification, and temperature. For nutrient-rich HNLC regions, the initial concentrations of major nutrients are deemed in ample supply, yet the weather strongly controls the light climate for photosynthesis, not only by the variations of cloud cover controlling incoming solar irradiance at the ocean surface, but perhaps even more by wind forcing algae to be mixed deeper down, where light conditions are unfavorable. This strong weather-dependence renders the outcome of commercial-scale OIF unpredictable, its statistics more akin to gambling than prudent financial investment. Moreover, even the very highest efficiency value of ~25 000 is far less than the first-hypothesized values in the ~500 000 range and OIF business plans should at least use a 20-fold higher amount of Fe than initially hypothesized.

The iron fertilization experiments done thus far were by no means designed for assessing commercial-scale OIF. When pursuing commercial-scale OIF, far more extensive quantification of carbon export (e.g. by far more intensive ^{234}Th mapping, many more sediment trap deployments, or other methods yet to be designed and validated) is required for accurate accountability of the carbon storage, which in turn is required for appropriate accountability of intended financial carbon credits.

Beyond the efficiency of CO_2 influx from the atmosphere into the ocean and efficiency of export below a defined 100 m or 250 m depth horizon, there are additional factors beyond the scope of this paper (some even beyond the scope of oceanography). These have been considered elsewhere and in companion articles of this Theme Section and include (1) longevity of deep ocean storage in relation to the ventilation time of underlying waters (after how many years, decades, or perhaps centuries, will the temporarily stored deep

ocean CO_2 surface again and ventilate back into the atmosphere); (2) negative feedbacks (i.e. enhanced production of stronger greenhouse gases methane and nitrous oxide); (3) the financial and energy expenditure and CO_2 emission (e.g. by ships) of OIF; (4) environmental protection; (5) international treaties (the London 'Dumping' Convention, Antarctic Treaty, etc.); and last, but not least, (6) the ethics of OIF in, for example, the precautionary principle and the trans-generational principle. Briefly, even when ignoring the latter two factors (international treaties and ethics) perhaps the question to ask a proponent of OIF is whether or not one would invest his or her own personal savings in an OIF enterprise, or advise his or her children to invest their money as a means of securing their personal future financial security.

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Predicting and monitoring the effects of large-scale ocean iron fertilization on marine trace gas emissions

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ABSTRACT: Large-scale (>40 000 km², >1 yr) ocean iron fertilization (OIF) is being considered as an option for mitigating the increase in atmospheric CO₂ concentrations. However OIF will influence trace gas production and atmospheric emissions, with consequences over broad temporal and spatial scales. To illustrate this, the response of nitrous oxide (N₂O) and dimethylsulphide (DMS) in the mesoscale iron addition experiments (FeAXs) and model scenarios of large-scale OIF are examined. FeAXs have shown negligible to minor increases in N₂O production, whereas models of long-term OIF suggest significant N₂O production with the potential to offset the benefit gained by iron-mediated increases in CO₂ uptake. N₂O production and emission will be influenced by the magnitude and rate of vertical particle export, and along-isopycnal N₂O transport will necessitate monitoring over large spatial scales. The N₂O–O₂ relationship provides a monitoring option using oxygen as a proxy, with spatial coverage by Argo and glider-mounted oxygen optodes. Although the initial FeAXs exhibited similar increases (1.5- to 1.6-fold) in DMS, a subsequent sub-arctic Pacific experiment observed DMS consumption relative to unfertilized waters, highlighting regional variability as a complicating factor when predicting the effects of large-scale OIF. DMS cycling and its influence on atmospheric composition may be studied using naturally occurring blooms and be constrained prior to OIF by pre-fertilization spatial mapping and aerial sampling using new technologies. As trace gases may have positive or negative synergistic effects on atmospheric chemistry and climate forcing, the net effect of altered trace gas emissions needs to be considered in both models and monitoring of large-scale OIF.

KEY WORDS: Iron fertilization · Trace gases · Nitrous oxide · Dimethylsulphide · Remineralization

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INTRODUCTION

Enhancing ocean productivity and vertical carbon export by increasing iron supply will indirectly influence the production of a range of trace gases, often via a complex web of biogeochemical interactions. The resulting change in oceanic emissions may alter atmospheric composition with positive or negative feedbacks on radiative forcing, tropospheric oxidation capacity and ozone concentration (Liss et al. 2005). However, the response of oceanic trace gas emissions to iron fertilization is currently uncertain, primarily as indirect effects and biogeochemical feedbacks have received limited attention in the 12 mesoscale iron addition experiments (FeAXs) to date (Boyd et al. 2007). This is a reflection of the priority of FeAXs to test the 'iron hypothesis' (Martin 1990) by focussing on phytoplankton productivity

and carbon export and of the relatively short-term nature and scale of FeAXs relative to the temporal and spatial scales of trace-gas cycling. For example, dimethylsulphide (DMS), non-methane hydrocarbons and halocarbons are influenced during the phytoplankton growth phase and generally show a short-term response in the surface mixed layer within days to weeks; conversely, production of trace gases that are influenced by remineralization of sinking particulate matter during the bloom decline and export phase occurs over greater temporal and spatial scales (Fig. 1). With the current consideration of large-scale ocean iron fertilization (OIF) (here defined as continuous fertilization over areas >40 000 km² for periods of >1 yr) as a strategy for lowering atmospheric CO₂, there is a need to consider potential trace-gas responses, using FeAX observations, natural analogues and model scenarios, for pre-

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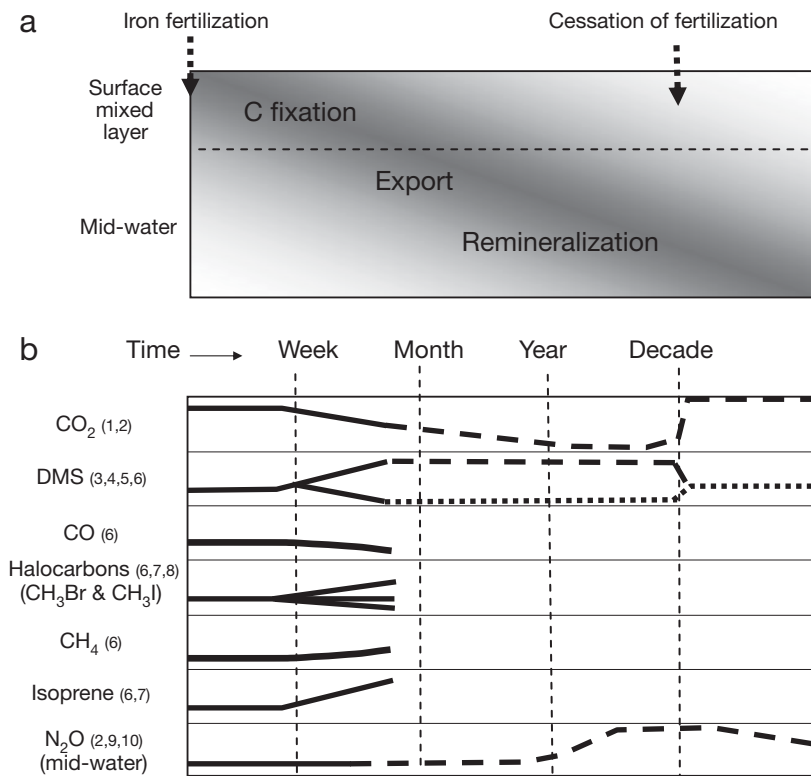


Fig. 1. (a) Conceptual response to iron fertilization showing the temporal evolution from carbon fixation during the bloom phase to remineralization in the mid-water column, with cessation of iron fertilization after 10 yr. (b) Temporal response of CO₂ and trace gases in surface waters and N₂O in the mid-water column based on the FeAX observations (solid lines) and model output and extrapolations (dashed and dotted lines) of (1) Wong et al. (2006), (2) Jin & Gruber (2003), (3) Turner et al. (2004), (4) Takeda & Tsuda (2005), (5) Levasseur et al. (2006) (observed DMS results extrapolated as dotted line), (6) Wingenter et al. (2004) (observed DMS results extrapolated as dashed line), (7) Moore & Wang (2006), (8) Liss et al. (2005), (9) Law & Ling (2001), and (10) Walter et al. (2005)

diction and development of monitoring strategies (London Convention 2007).

N₂O RESPONSE TO OIF

Nitrous oxide (N₂O) is an example of a trace gas that may respond to OIF on greater temporal and spatial scales. The oceans are a major contributor to the global N₂O budget, providing 5.6 to 14 Tg N yr⁻¹ (Bange 2006) of the total 7.6 to 41 Tg N yr⁻¹ (IPCC 2007), primarily from coastal, shelf and upwelling regions. Nitrification is the main source of N₂O in the open ocean, with the yield increasing with decreasing oxygen (Goreau et al. 1980), as evidenced by an anti-correlation between dissolved N₂O and oxygen throughout the oceans (Nevison et al. 2003). A N₂O maximum in intermediate waters is apparent throughout much of the ocean; this maximum shoals and intensifies in upwelling regions, which act as 'natural chimneys' by contributing dispro-

portionately to total marine N₂O emissions (Law & Owens 1990). Upwelling systems may be regarded as natural large-scale OIF analogues as they are characterized by enhanced vertical particle export. Elevated mid-water remineralization and oxygen consumption not only supports N₂O production but also leads to anoxia, as observed in the Californian and Namibian coastal upwelling systems (Monteiro et al. 2006, Chan et al. 2008). Denitrification is a minor source but the primary microbial sink for N₂O and occurs in anoxic sediments and water bodies. As surface and most intermediate waters do not experience hypoxia or contact sediments, N₂O loss to denitrification will be minimal, so the ultimate fate of this N₂O is ventilation to the atmosphere. N₂O is relatively long-lived in the atmosphere and has a global warming potential (GWP) 310 times that of CO₂ (Forster et al. 2007). The potential then exists for N₂O emissions to offset the radiative decrease achieved by iron-mediated phytoplankton CO₂ uptake and consequently monitoring and verification of N₂O response should be a priority in any large-scale OIF.

Upscaling of observations from FeAXs to large-scale OIF is limited by the paucity of N₂O measurements to date. No significant increase in mixed layer N₂O concentration and emissions was observed on 2 Southern Ocean FeAXs (Law & Ling 2001, Walter et al. 2005); however, an increase in N₂O saturation of 7% was identified in the upper pycnocline in the Southern Ocean Iron Release Experiment (SOIREE) iron patch that co-varied with column-integrated chlorophyll *a*, suggesting iron-induced stimulation of N₂O production (Law & Ling 2001). Excess N₂O was not observed during a subsequent FeAX in the Southern Ocean, the European Iron Fertilization Experiments (EIFEX), although water column sampling was limited and did not focus upon density discontinuities where particles may accumulate (Walter et al. 2005). Measurements during the initial 13 d of the Sub-arctic Ecosystem Response to Iron Enrichment Study (SERIES) FeAX in the Gulf of Alaska identified an increase in N₂O saturation of 8% at 30 to 50 m (C. Law unpubl. data)—coincident with increases in ammonium and nitrite—suggesting, but not confirming, nitrification as the source. Nitrification in the lower euphotic zone is a significant N₂O source, contributing

40 to 75 % of atmospheric emissions from the sub-tropical gyres (Dore et al. 1998, Popp et al. 2002). Although generally considered insignificant in surface waters due to light inhibition, nitrification rates have recently been shown to be uniform throughout the surface mixed layer (Yool et al. 2007). These observations indicate the potential for local N_2O production in surface waters—and hence atmospheric emissions—to increase following OIF on short timescales.

N_2O production is not confined to surface waters, with the rate of vertical particle export determining the subsequent timeframe, magnitude and location of N_2O emissions. Although few FeAXs have been of sufficient duration to record the export phase (Boyd et al. 2007), those that were, provide a range of findings. Vertical export below the thermocline was relatively insignificant during SERIES due to bacterial remineralization of the diatom bloom in near-surface waters (Boyd et al. 2005), whereas vertical export of a diatom bloom during EIFEX was rapid, with aggregate sinking rates of several hundred $m\ d^{-1}$ (V. Smetacek pers. comm.). This rapid export to the seafloor may account for the reported absence of N_2O accumulation below the EIFEX patch (Walter et al. 2005), although the higher and more variable N_2O concentrations between 500 to 2000 m depth beneath the iron fertilized waters suggest potential N_2O production. Rapid sinking of particles would limit N_2O production in the upper water column and maximize the time period before ventilation. Consequently, the vertical particle export rate is critical to OIF, not just in terms of the efficacy of carbon sequestration and effectiveness, but also with respect to the timeframe to subsequent N_2O emission. At present, the majority of N_2O turnover occurs in the upper 300 m (Codispoti et al. 2001) and so ventilation to the atmosphere will be within a 100 yr timeframe.

LONGER-TERM EFFECTS ON N_2O

Extrapolations and models provide some insight into the longer-term effects of OIF that defy observational capability. For example, remineralization of the additional carbon fixed during SOIREE was estimated to subsequently produce 2.1 to 4.1 t of N_2O (Law & Ling 2001), assuming Redfield stoichiometry and a nitrification: N_2O production rate of 0.25 to 0.5 % (Goreau et al. 1980). Due to the high GWP of N_2O , this would offset the reduction in radiative forcing achieved through increased carbon fixation by at least 6 to 12 % (Law & Ling 2001). Initial model estimates of long-term (100 yr) iron fertilization of the Southern Ocean, based on the assumption of complete macronutrient drawdown, suggested that increases in N_2O production could completely offset the benefit gained by increased carbon

fixation (Fuhrman & Capone 1991, Law & Ling 2001). More recent analysis of Southern Ocean iron fertilization using 3D models suggests a more conservative offset of 6 to 18 % due to downstream far-field effects, as iron-stimulated macronutrient utilization increases local N_2O production, but reduces production in the tropics due to decreased macronutrient supply (Jin & Gruber 2003). However, Jin & Gruber (2003) identify a more significant N_2O offset of 37 to 47 % from fertilization of the tropics, increasing to 58 to 194 % when fertilization was limited to 10 yr. The latter arises from the disproportionate effect of long-term decreases in dissolved oxygen and associated N_2O production relative to a shorter period of CO_2 drawdown. These examples illustrate the necessity to consider long-term N_2O production when determining potential sites and duration of OIF. In particular, for assessment of any future OIF should address the model predictions that (1) small-scale and/or shorter-term fertilization may not reduce N_2O production and emissions proportionally, (2) cessation of fertilization will not bring N_2O production back to baseline levels in the short-term, and (3) N_2O production hotspots may relocate (Jin & Gruber 2003).

Monitoring of potential adverse effects is a key issue for future OIF, as identified by the recent London Convention (2007) statement, which recommended evaluation of 'potential impacts of gases that may be produced by the expected phytoplankton blooms or by bacteria decomposing the dead phytoplankton' (London Convention 2007, p. 2). This presents a challenge for N_2O , as any perturbation will be small relative to a background signal that exhibits natural spatial variability; for example, N_2O at 200 m to 800 m may exceed 1000 % saturation in upwelling regions (Law & Owens 1990). In addition, N_2O will be responsive to climate change as warming of the ocean will decrease oxygen solubility and increase bacterial remineralization (Schmittner et al. 2008), thus complicating attribution of increases in N_2O to OIF. Current technology limits the capacity for monitoring, as autonomous *in situ* N_2O sensors are insufficiently sensitive to measure N_2O concentrations (5 to 30 $nmol\ l^{-1}$) in the open ocean. Shipboard techniques using electron capture detector gas chromatograph (ECD-GC) provide sufficient sensitivity but limited vertical resolution and areal coverage; they are sufficient for surface mapping of N_2O distribution, but not for following mid-water N_2O production and along-isopycnal transport over distances of 1000s of km. An alternative approach for monitoring over large spatial and temporal scales is to use O_2 concentration as a proxy for N_2O , by utilizing the parameterization for N_2O as a nonlinear function of O_2 and depth (Nevison et al. 2003). O_2 optode measurements on Argo floats show considerable promise

for broad-scale mapping of oxygen in intermediate and deep waters (Roemmich et al. 2004, Riser & Johnson 2008), and provision of a large pre-fertilization database against which post-OIF changes in oxygen and N_2O could be assessed. This approach could be augmented using oxygen optodes on gliders for repeat transect measurements and by the use of passive and deliberate tracer distributions on isopycnals for attribution of changes in oxygen and N_2O to OIF. Use of dissolved O_2 as a proxy would require further validation of the N_2O – O_2 relationship and its regional variability. For example, variability may arise from changes in iron availability; iron is a component of ammonium monooxygenase and hydroxylamine oxidase enzymes (Moir et al. 1996, Zahn et al. 1996) and so may influence both nitrification rate and N_2O yield. In addition, N_2O yield may be influenced by nitrogen fixation (Nevison et al. 2003), which warrants further investigation as iron availability is a limiting factor for nitrogen fixation in low latitude waters (Mills et al. 2004).

DMS AND OIF

DMS represents a potential link between the iron and Charlson-Lovelock-Andreae-Warren (CLAW) hypotheses (Charlson et al. 1987, Martin 1990), which have together dominated surface ocean biogeochemical research over the last decade. DMS has a short atmospheric lifetime and may influence climate change via particle formation and alteration of atmospheric albedo. The CLAW hypothesis (Charlson et al. 1987), which invokes oceanic regulation of climate via phytoplankton production of DMS precursors, DMS emission, and aerosol and cloud condensation nuclei (CCN) production that influences atmospheric albedo, still remains to be proven some 20 yr after inception (Harvey 2007). This reflects both its inherent complexity and the logistical difficulty of relating a variety of biogeochemical, physical and photochemical processes occurring at different spatial and temporal scales, as recently summarized in a series of papers in *Environmental Chemistry* (2007, Vol. 4). Nevertheless, as the DMS precursor dimethylsulphonopropionate (DMSP) is produced by certain phytoplankton groups and initial paleoceanographic evidence indicated a sulphur–iron–climate link (Legrand et al. 1988), the potential for iron-mediated DMS production has been well studied, with DMS measurements on 9 of the 12 FeAXs (Boyd et al. 2007). Initial confirmation was provided by the first 4 FeAXs in the equatorial Pacific and Southern Oceans, which exhibited similar trends of increased production of DMSP followed by DMS increases (1.5- to 6.5-fold) associated with a decline in nanophytoplankton (2 to 20 μm) stocks 12 to 14 d after

fertilization (Turner et al. 2004). Consistent with this, a 5-fold increase in DMS was observed during the subsequent Southern Ocean Iron Experiment (SOFEX) campaign and extrapolated regionally to suggest that iron fertilization of the Southern Ocean could potentially double global DMS emissions (14 Tg S yr^{-1} , Wingenter et al. 2004). A subsequent more conservative estimate, based upon iron fertilization of 2% of the Southern Ocean, suggested a 20% DMS increase that could produce a 2°C decrease over the Southern Ocean via the CLAW hypothesis (Wingenter et al. 2007).

However, subsequent FeAXs in the north Pacific exhibited significant departures from the initial experiments (Fig. 1), with no significant change in DMS during SEEDS (Sub-Arctic Pacific Experiment for Ecosystem Dynamics Study) despite the highest response in chlorophyll concentration observed in a FeAX (Takeda & Tsuda 2005, Boyd et al. 2007). Furthermore, in the most detailed FeAX study of DMS cycling during SERIES, the initial increase in nanophytoplankton stocks and DMSP was instead followed by only a minor increase in DMS, with a subsequent decline to concentrations one order of magnitude lower than surrounding unfertilized waters (Levasseur et al. 2006, Merzouk et al. 2006). Instead of DMS production initiated by herbivory, as in previous FeAXs, increases in bacterial production and associated sulphur demand resulted in DMSP and DMS utilization. This variability in DMS response to iron addition, with Southern Ocean waters representing a significant DMS source and the sub-arctic Pacific a sink, indicates the need for comparative studies to determine the origin of regional variation. It is also a good illustration of the importance of extrapolating individual FeAX results on a regional basis, rather than to the global ocean. Recent palaeorecord analysis found no co-variation of non-sea salt sulphate, a DMS proxy, with glacial–interglacial variations in dust supply (Wolff et al. 2006). As the role of iron as a major control of DMS has become less certain, other factors such as UV-radiation have been identified as important drivers of DMS seasonality (Vallina & Simo 2007). Indeed, the potential myriad responses of DMS to the interaction of climate-reactive physical and biogeochemical drivers (Harvey 2007) presents large uncertainty in the prediction of future DMS emissions, even without the confounding influence of OIF.

Monitoring of DMS in the ocean is currently limited to shipboard measurement as autonomous sensors of sufficient sensitivity are not available. However, recent analytical advances include the Membrane Inlet Mass Spectrometer, which has the capacity for sampling dissolved DMS at high spatial resolution (Tortell 2005), and the Atmospheric Pressure Ionization Mass Spectrometer (APIMS), which provides direct measurement

of atmospheric DMS (Huebert et al. 2004) on both research vessels and aircraft. Verification and attribution of changes in aerosol concentrations and CCN arising from iron-induced DMS production is more challenging. Atmospheric sulphur measurements during SERIES attempted to characterize downwind aerosol composition, but were complicated by the size of the patch relative to the large wind fetch (Phinney et al. 2007). This reflects the difficulty of positioning and scaling shipboard air measurements relative to a small-scale (100 to 500 km²) patch, and thus the requirement for rapid and adaptive airborne measurements on timescales of <24 h. Characterization of seasonal and regional variability in marine DMS and atmospheric sulphur and aerosol composition (Boers et al. 1998) should be a pre-requisite of future OIF. 'Natural laboratories,' such as phytoplankton blooms at open-ocean frontal regions and island wakes, offer potential for studying both DMS cycling and associated aerosol production prior to OIF. Such natural laboratories would be ideally sited in the southern hemisphere, due to the favourably low background aerosol concentration at accessible locations for repeat aircraft sampling.

NET IMPACT OF OIF ON ATMOSPHERIC PROCESSES

DMS and N₂O have been used above to illustrate the issues relating to prediction and monitoring of trace gas response to OIF. Other trace gases monitored during FeAXs include carbon monoxide and methane, which decreased and increased, respectively, during SOFeX, and isoprene, which increased 5- to 6-fold during SOFeX and SERIES (Fig. 1) (Wingenter et al. 2004, Moore & Wang 2006). These trace gases react with hydroxyl radicals in the troposphere, so variation in their marine emission will influence the atmospheric lifetime of other short-lived OH-reactive gases, such as DMS and halocarbons. Consequently, altered emissions of different trace gases could have positive or negative synergistic effects on atmospheric processes. Halocarbons have also exhibited a range of responses in FeAXs (Fig. 1), with positive, negative and negligible responses observed in methyl bromide and methyl iodide concentrations (Wingenter et al. 2004, Liss et al. 2005, Moore & Wang 2006), potentially reflecting regional variations in photochemistry and plankton community composition. Secondary effects on atmospheric chemistry and climate may also arise from OIF via changes in halocarbon emissions, for example, with increased methyl bromide emissions in the Southern Ocean potentially delaying the recovery of stratospheric ozone (Wingenter et al. 2004). For comprehen-

sive monitoring and modeling of OIF, it is then essential to determine the net effect of changes in emissions of different trace gases on atmospheric processes and climatic forcing, with priority on the radiative balance and tropospheric oxidation capacity. This information should then be summarized in a similar manner to the IPCC radiative forcing components (IPCC 2007), an approach that would facilitate assessment of both iron-mediated changes on individual trace gases and the net impact on climate and atmospheric composition, and so assist monitoring bodies and policy makers in determining the impacts of ocean iron fertilization.

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Export is not enough: nutrient cycling and carbon sequestration

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

KEY WORDS: Ocean iron fertilization · Preformed nutrients · Carbon sequestration

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ROLE OF NUTRIENTS IN THE CARBON CYCLE

One of the most puzzling facts in ocean biogeochemistry is that only about half the inventory of dissolved nitrate and phosphate is directly associated with carbon. This can easily be seen by considering the inventories of phosphate and oxygen in the deep ocean. The ratio of phosphate remineralization to oxygen utilization is around 1:170 for the deep ocean, but the average apparent oxygen utilization is only of order 170 μM . Thus only about 1 μM of the phosphate in the deep ocean is associated with remineralized carbon. Since the concentration of phosphate in the deep ocean is 2.2 μM , then approximately half of it is not associated with carbon. This biologically unutilized phosphate reaches the deep as a result of surface waters that subduct with high nutrient content and is known as preformed phosphate, or $\text{PO}_4^{\text{pref}}$.

Because the micronutrient Fe is used for both chlorophyll synthesis and nitrate reduction, both of which are vital for plankton growth (cf. Boyd 2002), much attention has been focused on iron limitation as a mechanism to explain the relatively high oceanic concentrations of $\text{PO}_4^{\text{pref}}$. The promise of ocean iron fertilization (OIF) is that shifting nutrients from the biologically unutilized (or preformed) pool to the biologically uti-

lized (or remineralized) pool allows the ocean to hold more carbon. This carbon will be taken out of the atmosphere. A schematic illustration of how this might work is given in Fig. 1a, which shows how increased productivity and export leads to a reduction in nutrients subducting to depth.

It is common in discussions about OIF for an equivalence to be made between increased nutrient utilization and increased particle export. One of the points of this paper is to reiterate that such a connection need not hold. To take an obvious example, if water is flowing through a region where 20% of the nutrients are stripped out, a faster flow of water through the region will lead to a larger export, even though the fraction of nutrient utilized remains constant. A subtler example is shown in Fig. 1b, where iron fertilization causes nutrients to be consumed locally at point A, so that fewer nutrients are advected (on time scales of years to centuries) downstream to point B. This can result in a decrease in export, not only at point B, but also globally (Marinov et al. 2006). But since the average global concentration of preformed nutrients into the deep ocean drops, so does atmospheric carbon dioxide. A final case (Fig. 1c) is one in which nutrients are consumed before subduction. By concentrating production near the upwelling, fertilization may then produce

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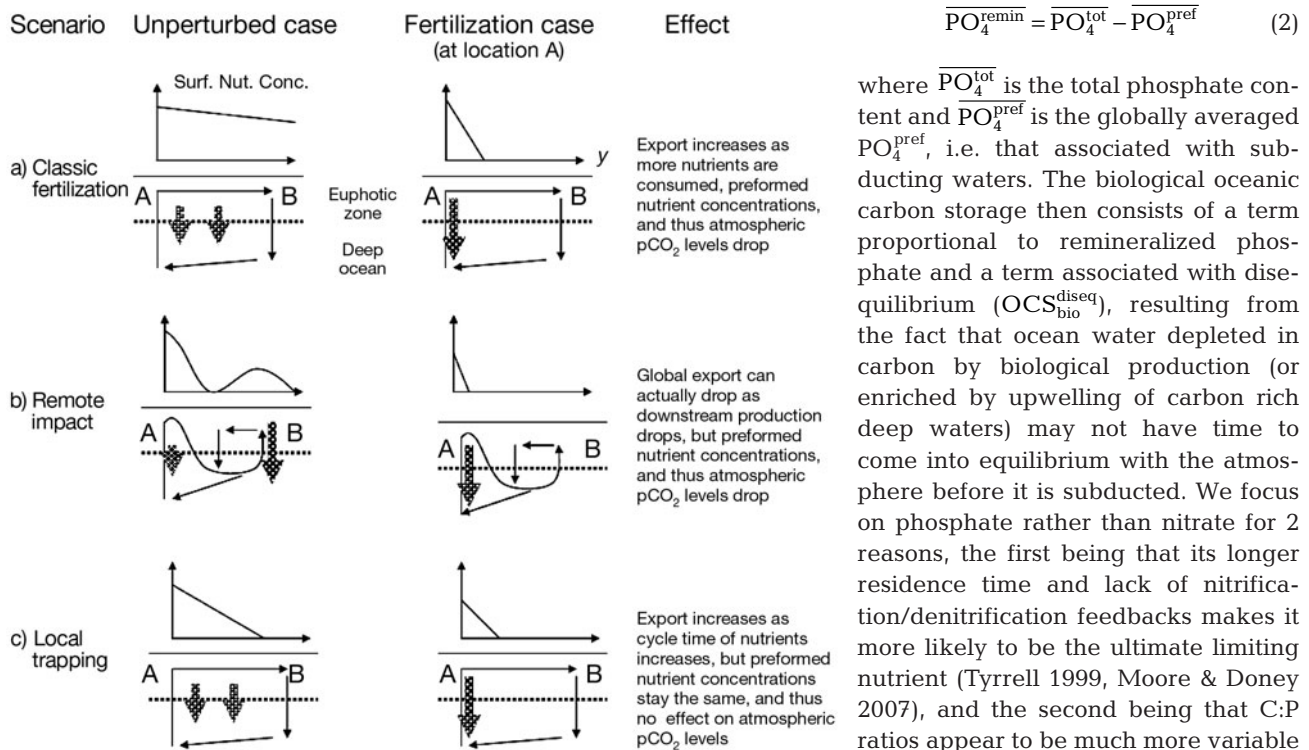


Fig. 1. Potential decoupling of nutrients and particle export. For each row, the upper diagram shows the surface nutrient concentration, the lower diagram the euphotic zone and deep ocean flow (thin arrows) and organic matter fluxes (striped arrows). (a) Nutrients upwelled at Point A are minimally consumed by the time the water is downwelled at Point B. Under fertilization (right-hand column), enhanced productivity is able to take up this nutrient, reducing preformed nutrient concentrations and thus causing atmospheric pCO₂ to drop. This is the classic fertilization scenario. (b) Remote impact scenario in which fertilization decreases preformed nutrient concentrations locally at Point A, preventing them from moving to a region (Point B) where they can recycle rapidly. The result is to cause a reduction in global export, global preformed nutrient concentrations and atmospheric pCO₂ (as in some cases in Marinov et al. 2006). (c) Local trapping scenario in which preformed nutrient is 0 at Point B. Fertilization will likely trap nutrient close to Point A, decreasing the time it takes to cycle and thus likely increasing production, but as preformed nutrient concentrations do not change, neither does atmospheric pCO₂ (Aumont & Bopp 2006)

‘nutrient trapping’ (Najjar et al. 1992), increasing the concentration of upwelling nutrients and so resulting in a net increase in production, but without significantly changing preformed nutrients and atmospheric CO₂ (as noted in Aumont & Bopp 2006).

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

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

where $\overline{PO_4^{remin}}$ is the globally averaged remineralized phosphate in the ocean, and $R_{C:P}$ is the C:P ratio and can be written as

where $\overline{PO_4^{tot}}$ is the total phosphate content and $\overline{PO_4^{pref}}$ is the globally averaged PO_4^{pref} , i.e. that associated with subsiding waters. The biological oceanic carbon storage then consists of a term proportional to remineralized phosphate and a term associated with disequilibrium (OCS_{bio}^{diseq}), resulting from the fact that ocean water depleted in carbon by biological production (or enriched by upwelling of carbon rich deep waters) may not have time to come into equilibrium with the atmosphere before it is subducted. We focus on phosphate rather than nitrate for 2 reasons, the first being that its longer residence time and lack of nitrification/denitrification feedbacks makes it more likely to be the ultimate limiting nutrient (Tyrrell 1999, Moore & Doney 2007), and the second being that C:P ratios appear to be much more variable than C:N ratios.

This basic picture can be used to analyze why different ocean models produce different atmospheric pCO₂ (pCO₂^{atm}). Marinov et al. (2008a,b) examine a range of diagnostic ocean models using a simple representation of biological cycling in which nutrient concentrations near the surface are restored either to the observed value to mimic the natural carbon cycle or to 0 to mimic the maximum possible effects of OIF. This must be understood as an upper limit, as both large-scale (100s of km) natural fertilization patches associated with topographic features (cf. Polard et al. 2007) and mesoscale (10s of km) purposeful experiments (Boyd et al. 2007) only show drawdowns between 30 and 75% of the initial nutrient inventory. In these models, $R_{C:P}$ is set to a constant value of 117 for all time and space. By using a set of models in which the winds and diffusion coefficients differ, we are able to examine the extent to which the response of pCO₂^{atm} to nutrient drawdown depends on the global overturning circulation.

One result that has emerged from these models is that changes in circulation can change pCO₂^{atm} by changing PO_4^{pref} (Marinov et al. 2008a). This can be seen in Fig. 2a, which shows results from the control set of the model, where surface nutrients are restored to observed values. As the preformed nutrients

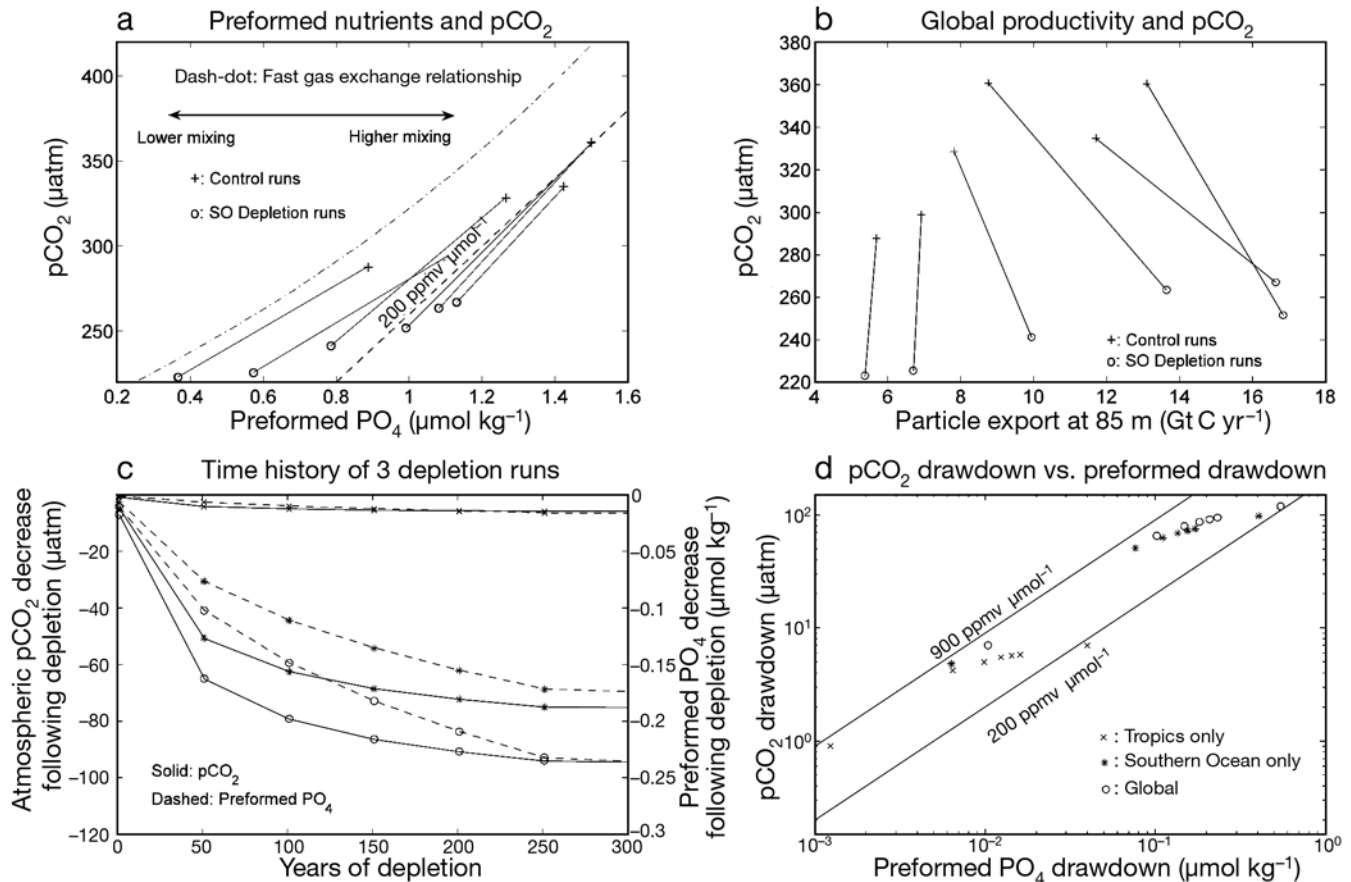


Fig. 2. Results from a number of models in which nutrients are restored to 0 over some area, illustrating the importance of preformed nutrients in understanding the carbon cycle. Runs are made with coarse-resolution, 4° models following Gnanadesikan et al. (2004) and Marinov et al. (2006, 2008a,b), with different horizontal and vertical mixing coefficients and wind stresses. (a) Atmospheric $p\text{CO}_2$ versus globally averaged preformed nutrient concentration for 6 different models. Control runs are shown by (+), runs in which Southern Ocean nutrients are restored towards 0 by (o). (b) Same as (a), but with particle export at 85 m as the independent variable. Note the slope is strongly dependent on the intensity of vertical exchange. (c) 3 simulations with the P2A model (Marinov et al. 2006), in which nutrients are restored to 0 globally (o), over the Southern Ocean () and over low latitudes (). Solid lines show atmospheric $p\text{CO}_2$ change, dashed lines the change in preformed phosphate. Note the bulk of the difference in atmospheric $p\text{CO}_2$ between runs can be explained in terms of the corresponding difference in preformed phosphate. (d) Absolute change in $p\text{CO}_2$ plotted against preformed phosphate for the runs in Fig. 1c, at 1, 51, 101, 151, 201 and 251 yr, as well as at equilibrium. Note the values start close to the theoretical slope and move rightward over time as the role of chemical buffering increases

decrease (implying that remineralized nutrients increase) because of lower vertical mixing, so does $p\text{CO}_2^{\text{atm}}$. When nutrients are restored to 0 in the Southern Ocean (Fig. 2a, O-marks) the preformed nutrients decrease significantly and so does $p\text{CO}_2^{\text{atm}}$. The dash-dotted line in Fig. 2a shows the exponential relationship between the two, derived by Marinov et al. (2008b) under the limit of infinitely fast gas exchange.

How would we expect $p\text{CO}_2^{\text{atm}}$ to respond to changes in preformed phosphate? Decreasing $\text{PO}_4^{\text{pref}}$ by $1 \mu\text{mol kg}^{-1}$ corresponds to an increase in remineralized carbon of about 1940 Gt C, given an ocean volume of $1.345 \times 10^{18} \text{ m}^3$. If all of this carbon came out of the atmosphere, it would draw down atmospheric CO_2 by $\sim 900 \text{ ppmv}$. However, the actual response in the models is about 20% of this, between 150 and

$200 \text{ ppmv } \mu\text{mol}^{-1} \overline{\text{PO}_4^{\text{pref}}}$ depending on the model employed. Note that some of the models on the left of Fig. 2b show a global decrease in production even though $p\text{CO}_2^{\text{atm}}$ drops, just as suggested in Fig. 1b.

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

Within this picture, OIF could increase $\overline{\text{PO}_4^{\text{remin}}}$ (Eq. 1) in 3 ways: (1) Increasing $\overline{\text{PO}_4^{\text{remin}}}$ (or decreasing $\overline{\text{PO}_4^{\text{pref}}}$)

by increasing photosynthetic uptake and the subsequent remineralization of organic matter. Nutrients which would have gone into the deep ocean as unutilized/preformed are now in the remineralized pool instead. (2) Increasing $R_{C:P}$, i.e. making nutrient uptake more efficient at sequestering carbon. There is extensive evidence that the C:P ratio in plankton may vary, in large part due to variations in the N:P ratio (Letelier & Karl 1996, Klausmeier et al. 2004). (3) Increasing OCS_{bio}^{diseq} by making it harder for remineralized carbon to escape from the ocean. This will occur if fertilization redistributes remineralized carbon such that more of it comes to the surface in regions where it does not have time to equilibrate with the atmosphere.

In the following sections we consider some of the complications associated with each of these 3 mechanisms. Before doing so we note that the preformed nutrient content is essentially independent of the depth of remineralization, so long as one considers an equilibrium situation. If phosphorus is associated with carbon and iron it does not matter substantially whether it is remineralized at 200 m or 2000 m, in either case it acts to sequester carbon. Thus, Sarmiento & Orr (1991) found that the response to a perpetual fertilization in the Southern Ocean was essentially independent of the depth of remineralization and Gnanadesikan et al. (2003) found a similar result for addition of a 'supernutrient' that permanently increased PO_4^{remin} . If the changes are transient, however, remineralization depth may be important, as it determines the time over which the changes persist.

CHANGING REMINERALIZED PHOSPHATE AND RESULTING COMPLICATIONS

One simple means of estimating the potential effects of OIF on the carbon cycle is to assume that it will lead to a drawdown of surface nutrients and to then see how such changes propagate through the system. This was the approach taken by Sarmiento & Toggweiler (1984) in a box model study of fertilization and in studies made using general circulation models by Sarmiento & Orr (1991), Archer et al. (2000), Gnanadesikan et al. (2003) and Marinov et al. (2006, 2008a,b), among others. While neglecting ecosystem effects and feedbacks through the nitrogen cycle, such an approach does provide a useful means of assessing the potential timescales involved in carbon cycle changes resulting from fertilization and the magnitude of such changes.

We present results from 3 such simulations in our standard (so-called P2A) ocean model, which corresponds to nutrient drawdown in the tropics only, south of 30° S only, and globally (Fig. 2c,d). Thinking about the evolution of these runs in terms of changes in pre-

formed nutrients yields some clear insights into their behavior. For example, the much lower effect of drawing down nutrients in the tropics on pCO_2^{atm} is due to the much smaller effect on globally averaged preformed nutrient. The bulk of the atmospheric CO_2 drawdown comes from fertilizing the Southern Ocean (as noted by Marinov et al. 2006), where the effect on preformed nutrients is largest. When preformed nutrient changes are plotted against atmospheric CO_2 changes, however (Fig. 2d), the picture is much more similar across the simulations. Initially, the bulk of the carbon dioxide comes out of the atmosphere and so the drawdown is more like the idealized $900 \text{ ppmv } \mu\text{mol}^{-1} PO_4^{pref}$. This continues for 50 to 100 yr. However, over time (centuries), chemical buffering becomes important and the final equilibrium slope lies within the range of slopes seen in Fig. 1a. If one looks at the ratio between the change in PO_4^{pref} and the change in pCO_2^{atm} (not shown), the 3 simulations collapse to within about 20% of each other.

To a large extent, then, changes in PO_4^{pref} or PO_4^{remin} are a good metric for evaluating the effect of OIF on pCO_2^{atm} . This raises a number of important issues when considering the impact of local fertilization. The first issue is that fertilization may not result in a net change in PO_4^{remin} if the nutrients taken up would have been used at some later time or some different location. An example of this can be found in the highly idealized results of Gnanadesikan et al. (2003), which examined the response in a diagnostic ocean model to reducing the target nutrient concentration in a region to zero for a single month over a small patch. Because of the parameterization of production in terms of a restoration to some value, the increased drawdown of nutrients during a fertilization event was largely balanced by decreased production in the following months as nutrients recovered to their pre-fertilization values. As a result, the net decrease in unutilized nutrients was relatively small, with only 2 to 7% of the net additional production during the fertilization event resulting in pCO_2^{atm} drawdown.

It must be emphasized, however, that this case is an extreme one. Essentially the assumption made in Gnanadesikan et al. (2003) is that once fertilization stops the system will return surface nutrients to pre-fertilization levels on a short time scale, something that is unlikely to be true. However, the simulation does highlight the potential importance of post-fertilization declines in productivity. Such declines were observed by Aumont & Bopp (2006), Jin et al. (2008), and J. L. Sarmiento et al. (unpubl. data), using 3 different biogeochemical models in which fertilization was applied for a relatively short time period (<10 yr), then abruptly stopped. The drops in export production across 100 m are not nearly as large as in the idealized case, but are potentially significant nonetheless, accounting for as much as

one-third of the initial production. Aumont & Bopp (2006) attributed the change to a drop in surface nutrient content. J. L. Sarmiento et al. (unpubl. data) found that this drop is due to enhanced denitrification.

In Gnanadesikan et al. (2003), nutrient drawdown was ineffective at sequestering carbon because productivity at the time of fertilization was essentially 'borrowed' from productivity at some time in the future. The displacement of productivity may also happen in the vertical. Jin et al. (2008) found that the greater the depth at which fertilization enhances productivity, the smaller the effect on $p\text{CO}_2^{\text{atm}}$. They argue that this occurs because there is less separation between the low $p\text{CO}_2$ anomaly resulting from productivity and the high $p\text{CO}_2$ anomaly resulting from remineralization so that these anomalies are able to cancel each other out before contacting the atmosphere. However, Gnanadesikan (2007) notes that Jin et al. (2008) also found a decrease in productivity near the surface, compensating for the increase in export at depth. This would act to decrease remineralized nutrients, resulting in no net change in biological carbon storage.

CHANGING $R_{\text{C:P}}$ AND RESULTING COMPLICATIONS

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

The great advantage of achieving carbon sequestration through changing the C:P ratio in sinking organic matter is that it would be much easier both to evaluate the impact and to monitor the persistence of the effect by measuring nutrients *in situ*. Examination of Eq. (1) shows that a 10% increase in $R_{\text{C:P}}$ would be expected to have the same effect on $p\text{CO}_2^{\text{atm}}$ as a 10% increase in $\overline{\text{PO}}_4^{\text{remin}}$ ($0.1 \mu\text{mol kg}^{-1}$, implying a decrease of 20 ppmv at equilibrium) and far larger variations than this are seen in some regions.

There are, however, some serious complications involved in considering the effect of changing stoichiometric ratios on atmospheric carbon. The most important is that $R_{\text{C:P}}$ may go down as well as up with OIF. Arrigo et al. (1999, 2002) point out that $R_{\text{C:P}}$ associated with nutrient drawdown is much larger in regions of the Antarctic dominated by phaeocystis blooms ($R_{\text{C:P}}$ of 120 to 154) compared with regions dominated by

diatoms ($R_{\text{C:P}}$ between 62 and 100). Additionally, recent work by Klausmeier et al. (2004) observes that the N:P ratio in plankton varies from 8 to 42 over a range of regimes. They argue that in a regime where the plankton are seeking to acquire resources (light and nitrogen) they will tend to build cellular machinery rich in N relative to P and that they will have high N:P (and thus presumably high C:P) ratios, while rapidly growing cells require more ribosomal material with more P and so will have low N:P (and C:P) ratios.

The effects of OIF on community structure and phytoplankton physiology thus add an additional level of complication. Replacing carbon-rich phaeocystis blooms with carbon-poor diatom blooms would (according to Eq. [1] and assuming $\overline{\text{PO}}_4^{\text{remin}}$ is constant) drive ocean carbon storage down and $p\text{CO}_2^{\text{atm}}$ up. Similarly, if phytoplankton have high C:P ratios because they are limited by light, adding iron to remove light limitation could reduce C:P ratios and cause $p\text{CO}_2^{\text{atm}}$ to rise. But if the addition of iron caused an increase in the ability to acquire nutrients (say, for example, through allowing nitrogen fixation or shifting the population towards nitrogen fixers as discussed by Moore & Doney 2007) C:P ratios could increase, causing $p\text{CO}_2^{\text{atm}}$ to fall. Such processes are only represented in current ocean ecosystem models at a rudimentary level.

INCREASING THE EFFICIENCY OF GAS EXCHANGE

Gas exchange can play a role in altering the storage of carbon in the ocean. This can clearly be seen in Fig. 2a from the difference between the theoretical curve with infinitely fast exchange and the simulations with normal gas exchange. Under infinitely fast gas exchange all the points in Fig. 2a lie on the theoretical curve (Marinov et al. 2008b) and $\text{OCS}_{\text{bio}}^{\text{diseq}} = 0$. With realistic gas exchange, however, $\text{OCS}_{\text{bio}}^{\text{diseq}}$ is non-zero. If remineralized nutrients are brought to the surface, converted to preformed nutrients and rapidly (i.e. on time scales of weeks to months) reinjected to the deep before biology or gas exchange can act on them, the conversion of $\overline{\text{PO}}_4^{\text{remin}}$ to $\overline{\text{PO}}_4^{\text{pref}}$ will occur without a corresponding change in carbon. $\text{OCS}_{\text{bio}}^{\text{diseq}}$ will be >0 because there is no loss of CO_2 to the atmosphere and the biological pump will be more efficient at storing carbon than nutrient fields alone would indicate. This will be particularly the case in convective regions of deep water formation (Toggweiler et al. 2003). Alternatively, one can imagine a case where nutrients are brought to the surface, advected along the surface and taken up by biology just before (weeks or months) they are downwelled. In such a case, the lowered CO_2 associated with enhanced production would not have time

to come to equilibrium with the atmosphere, and the biological pump would be less efficient at storing carbon than the nutrient fields would indicate ($\text{OCS}_{\text{bio}}^{\text{diseq}} < 0$).

In all of the runs we have done so far, the first mechanism is the most important and $\text{OCS}_{\text{bio}}^{\text{diseq}} > 0$ (compare all points with the dash-dotted line in Fig. 2a). The net effect of gas exchange on OIF is more complicated. In some of the runs (those associated with higher mixing and higher preformed nutrients), the disequilibrium term increases under depletion. In other runs (those associated with lower mixing and lower preformed nutrients) the disequilibrium term decreases under depletion. These changes can enhance or compensate for 10 to 20% of the $\text{pCO}_2^{\text{atm}}$ change associated with changing $\text{PO}_4^{\text{pref}}$.

CONCLUSIONS

The extent to which the export of organic material from the surface ocean results in oceanic carbon storage is not simply controlled by the magnitude of the export flux or the depth of remineralization. Rather, it depends on the extent to which nutrients in the deep ocean are associated with carbon and the extent to which this carbon is able to escape from the deep ocean. As a result, local balances are unlikely to describe the global impact of OIF. Effects remote from the fertilization site in time (months to centuries) or space (100s to 1000s km)—such as reduction in productivity, changes in stoichiometric ratios or changes in the disequilibrium of sinking water—can significantly affect the impact of OIF on atmospheric carbon dioxide. Understanding these effects and constructing models that accurately represent them is thus a crucial part of designing large-scale OIF projects.

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Predicting and verifying the intended and unintended consequences of large-scale ocean iron fertilization

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ABSTRACT: Ocean iron fertilization (OIF) is being considered as a strategy for mitigating rising atmospheric CO₂ concentrations. One model for implementation is the sale of carbon offsets. Modeling studies predict that OIF has the potential to produce a material difference in the rise of atmospheric CO₂ over the next several decades, but this could only be attained by alteration of the ecosystems and biogeochemical cycles of much of the world's oceans. The efficacy of OIF on this scale has not been proven. However, the consequences of successful implementation must be considered now, for 2 important reasons: (1) to determine if the environmental effects would be predictable and verifiable, and if so, acceptable; and (2) to establish whether the basis for valuing carbon offsets—an accurate audit of net reductions in cumulative greenhouse gas potential over 100 yr—can be met. Potential side-effects of widespread OIF that must be considered include a reduced supply of macronutrients to surface waters downstream of fertilized regions, increased emissions of the potent greenhouse gases nitrous oxide and methane, and changes in the extent or frequency of coastal hypoxia. Given the uncertainties inherent in ocean models, predictions of environmental effects must be backed up by measurements. Thus, to go forward with confidence that the effects of rising CO₂ could indeed be mitigated through OIF over the next century, and to establish the foundations for auditing carbon offsets, it must be explicitly demonstrated that methods exist to predict and detect downstream effects of OIF against the background of both climate variability and global warming. We propose that until the side-effects of widespread OIF can be shown to be verifiable—and there is good reason to believe that they cannot—OIF should not be considered a viable technology for climate mitigation.

KEY WORDS: Ocean fertilization · Climate change · Climate change mitigation · Carbon offsets · Ecological effects · Hypoxia · Nitrous oxide

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INTRODUCTION

The relentless rise of atmospheric CO₂ concentrations presents us with one of the greatest challenges of our times. It has been established that fossil-fuel emissions must be drastically reduced to stabilize atmospheric CO₂ soon enough to avoid rapid climate change with very serious consequences for humanity (IPCC 2007). It is also clear that a broad range of strategies for capturing and sequestering CO₂ must be pursued. Direct manipulation of the radiative balance of Earth, for

example through stratospheric sulfur injections (Crutzen 2006), is also being considered. The latter, and other proposals that involve large-scale manipulations of the planet, are sometimes termed 'geoengineering'; they merit special scrutiny because they would impose pervasive changes to earth systems with inherently uncertain consequences (Kintisch 2007). Here, we examine one geoengineering proposal: fertilization of the ocean on a scale large enough to make a significant difference to the rise of atmospheric CO₂ over the next several decades.

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PROPOSED STRATEGY FOR MITIGATING CLIMATE CHANGE

Despite profound uncertainties about its ultimate consequences, widespread fertilization of the ocean is being seriously considered as a strategy for mitigating climate change (Buesseler et al. 2008). One reason for contemplating this potentially risky manipulation of marine ecosystems on an unprecedented scale is that the consequences of taking no action could be worse. The same reasoning is used to justify consideration of a broad range of geoengineering proposals (Kintisch 2007). The premise of these arguments is that the geoengineering activity could slow the rise of atmospheric CO₂ concentrations or otherwise modify global warming enough to significantly mitigate greenhouse-gas driven climate change. Pacala & Socolow (2004) describe a portfolio of technologies they claim could solve the carbon and climate problem for the next half century. Each of seven 'stabilization wedges' would rise over 50 yr to account for 1 Gt C yr⁻¹ of sequestered atmospheric CO₂ or reduced CO₂ emissions—corresponding to 0.47 ppm of atmospheric CO₂ yr⁻¹ (Lassey et al. 1996). Such wedges would stabilize net CO₂ emissions for long enough to permit a plateau at 500 ppm to be achieved by substantially reduced fossil fuel emissions in subsequent years. These technologies are identified as having 'the potential to produce a material difference by 2054' (Pacala & Socolow 1968, p. 968). Consistent with the time scale of this scenario, technologies for sequestering atmospheric CO₂ should do so for at least 100 yr—the standard for permanence of carbon sequestration strategies (Powell 2008).

In principle, ocean iron fertilization (OIF) could represent a stabilization wedge; modeling studies predict that sustained fertilization (for decades) of so-called high-nutrient, low-chlorophyll (HNLC) regions of the ocean (i.e. up to 30% of the World Ocean) would sequester at most 0.5 Gt C yr⁻¹ (Buesseler et al. 2008). Fertilization of some oligotrophic waters (which in total account for nearly 50% of ocean area) with iron or a mix of iron and macronutrients (i.e. via induced upwelling) could lead to more sequestration of carbon in the ocean by enhancing the growth of phytoplankton and/or stimulating nitrogen fixation, with subsequent sinking of organic material to the deep sea (Karl & Letelier 2008, this Theme Section). Thus, although it is by no means proven, the potential exists for OIF to make a significant difference to atmospheric CO₂ concentrations (e.g. carbon sequestration of about 0.5 Gt C yr⁻¹), but this could only be attained by intentional alteration of the ecosystems and biogeochemical cycles of much of the world's oceans for a century or more.

It has been argued that implementation of an OIF strategy would depend on there being 'acceptable and

predictable environmental impacts' (Buesseler et al. 2008). We agree and add that, as with essentially all predictions of complex earth processes involving the biosphere, projections of the consequences of OIF are inherently uncertain. What, then, is the standard for predictability? Reasonably, predictions would have to be sufficiently accurate to exclude the possibility of unacceptable environmental impacts. In turn, they would have to be validated by comparison with appropriate environmental observations. Since the model of OIF as a climate mitigation strategy is widespread implementation, sustained for decades and leading to carbon sequestration for at least 100 yr, the requirement for prediction and verification of environmental impacts must be applied not only to individual applications or pilot programs, but also to global alteration of the ocean for a century or more. To do less would be to embark on this course of global environmental manipulation, trusting—without adequate foundation—that unacceptable consequences could be detected in time to halt this activity. We feel that it is necessary to rely on more than trust.

OIF AND CARBON OFFSETS

OIF is controversial not only because of its uncertain effects, but also because commercial interests are pursuing a market-driven strategy for implementation: multiple nutrient applications (e.g. roughly 200 × 200 km) for carbon offsets sustained for decades. The feasibility of this strategy has been pointedly questioned (Zeebe & Archer 2005), and issues such as the effect of frequency of OIF (sporadic versus continuous) on carbon sequestration (Arrigo & Tagliabue 2005) appear to have been ignored. However, if OIF could reach its potential for carbon sequestration and cause a material difference in atmospheric CO₂ (a major justification for considering such action despite uncertainties that may never be resolved), the resulting carbon offsets would be worth many billions of euros and if the process were as simple as some proponents have suggested, revenues would greatly exceed costs. This raises many concerns, including the worry that the cumulative, large-scale effects of many market-driven implementations would lead to a classic 'tragedy of the commons' (Hardin 1968, Chisholm et al. 2001). The response of proponents is a clear acknowledgement that OIF should be subject to international oversight, with requirements for careful validation of carbon sequestration and other environmental side-effects

It follows that, whether the objective is to evaluate OIF comprehensively as a strategy for mitigating climate change or more specifically as a technology for generating carbon offsets (i.e. through a series of com-

mercially funded nutrient applications ultimately leading to large-scale changes in the ocean), the effects of OIF must be shown to be acceptably predictable and verifiable, locally and globally. Here, we describe intended and unintended effects of OIF that must be predicted and discuss the accuracy that would be required to verify these predictions effectively enough to exclude the possibility of materially significant counteracting or negative environmental effects.

INTENDED AND UNINTENDED EFFECTS OF OIF

The central objective of OIF is alteration of the structure and function of pelagic ecosystems and the associated biogeochemical cycles. This is not meant to imply that today's ocean is pristine; we know that climate variability influences ocean ecosystems in many ways and that anthropogenic activities are already affecting climate (IPCC 2007). Also, humans have polluted coastal systems (GESAMP 2001) and fundamentally altered marine food webs by fishing down top predators and depleting fish stocks world-wide (Jackson et al. 2001, Myers & Worm 2003). Regardless, OIF merits very careful evaluation because using it broadly enough to mitigate climate change would ultimately result in the manipulation of ocean ecosystems on basin scales.

Simply, OIF is intended to promote nutrient utilization in surface layers of the ocean to produce organic matter that will sink and decompose in the deep sea, isolated from the atmosphere. Iron would be added to HNLC areas of the ocean, where the availability of this trace element limits the accumulation of phytoplankton and thus the utilization of macronutrients. Local effects of individual applications are well recognized and have been studied over weeks at relatively small scales (i.e. 10×10 km) of experimental ocean fertilization (Boyd et al. 2007b). Addition of iron to oligotrophic (low-nutrient, low-chlorophyll [LNLC]) waters would be intended to stimulate nitrogen fixation supported by utilization of residual phosphate (and possibly, added nutrients), ultimately resulting in the export of organic material from the surface layer (Karl & Letelier 2008). To date, the efficacy of LNLC fertilization has not been demonstrated; open ocean enrichment experiments with iron have had a minor impact on nitrogen fixation (Rees et al. 2006, unpubl. data), and global models (e.g. Tagliabue et al. 2008) suggest a relatively small effect of aerosol iron supply on LNLC regions. But questions of scale and modes of implementation remain unexplored (Karl & Letelier 2008) and there are unknowns surrounding what environmental factors stimulate nitrogen fixers (Deutsch et al. 2007, Hutchins et al. 2007). If LNLC fertilization does sequester car-

bon, we must know if the consequences would be predictable, verifiable and acceptable. It is thus appropriate at this time to conduct the heuristic exercise of exploring the potential effects of successful, widespread ocean fertilization.

Direct effects of individual applications

If effective, each application of iron to the ocean would have several direct results that are described and discussed elsewhere in this Theme Section (see Law 2008, Watson et al. 2008): (1) Phytoplankton would bloom, leading to depletion of macronutrients in the surface layer. (2) After varying degrees of repackaging through food web processes and the formation of aggregates (marine snow), a proportion of the organic matter produced by the bloom would sink from the surface layer, roughly the upper 100 m. (3) Below the surface layer, the downward flux of organic matter would decrease with depth, approximating a power law function (Buesseler et al. 2007), due primarily to decomposition by microbes—consuming oxygen and regenerating nutrients and CO_2 in the process—and the grazing of particles by zooplankton. (4) Consequently, only a portion of the organic matter that sank out of the surface layer would reach deep waters that are likely to stay out of contact with the atmosphere for 100 yr or more, i.e., beyond the '100 yr horizon'. This is the carbon that would be considered to be sequestered. (5) Some fertilizations could stimulate blooms of communities that produce dimethylsulfide (DMS), the principal natural source of sulfur to the atmosphere, which influences climate by its role in cloud formation and modifying radiative properties of the earth (Andreae 1990). Enhanced DMS emissions could potentially reinforce the climate-mitigation effects of OIF by increasing the earth's albedo (Law 2008). Except perhaps for enhanced production of DMS, these general predictions should apply to LNLC (Karl & Letelier 2008), as well as HNLC waters.

It is seldom recognized explicitly, but has nonetheless been observed, that at the end of an effective fertilization, surface waters would be depleted of nutrients (Boyd et al. 2004) and plankton biomass would be low because a proportion of the organic matter produced by fertilization would have sunk to deeper layers.

Direct effects of sustained and widespread OIF

As assumed in models used to predict the efficacy of OIF in a climate mitigation scenario (e.g. Aumont & Bopp 2006, Tagliabue et al. 2008), sustained and widespread fertilization would lead to replacement of iron

limitation with iron sufficiency in broad expanses of the ocean. The previously unused macronutrients in the surface layer would have been stripped from the water by phytoplankton and delivered to depth—along with carbon—as sinking particulate organic matter. Given the stoichiometry of synthesis and regeneration of organic material in the sea, several biogeochemical and ecological consequences would be expected from this iron-induced pumping of organic particles to depth across broad expanses of ocean: (1) Lower concentrations of macronutrients in the surface layer, likely leading to the limitation of new production by the vertical flux of nitrate, or if nitrogen fixation is stimulated, phosphate. The engineered iron-sufficient, macronutrient-limited pelagic ecosystems would thus be structured in a fundamentally different way from their present state, in which upper limits to the growth of phytoplankton are hypothesized to depend on supplies of iron from atmospheric deposition as well as from below (Jickells et al. 2005). The new state is intended to mimic what is thought to have occurred naturally during glacial periods (Martin 1990). (2) Higher concentrations of carbon at depth, associated with the organic material that sank from the surface layer. Most of this would be dissolved inorganic carbon (DIC) associated with decomposition of that organic matter, and much of the DIC would accumulate below the surface layer but above the 100 yr horizon, i.e. in waters that would come in contact with the atmosphere in less than 100 yr. (3) Lower concentrations of oxygen below the surface layer, corresponding directly to the extra DIC produced by decomposition. (4) Higher concentrations of macronutrients at depth, roughly in stoichiometric proportion to the OIF-induced excess DIC and deficiency in oxygen.

It is important to remember that the products of OIF that do not reach the 100 yr horizon—likely the majority of that which sinks below 100 m—still affect the chemistry and biology of subsurface waters by increasing nutrients and DIC and decreasing oxygen. A comprehensive audit of the effects of OIF would have to include careful assessment of these changes in mid-depth waters.

Downstream effects of sustained and widespread OIF

Expected results of OIF have qualitatively (and in sufficiently detailed models, quantitatively) predictable ecological and biogeochemical consequences that can be referred to as downstream effects: (1) OIF would reduce the surface nutrient inventory, and thus the productivity of plankton communities, in large expanses of ocean downstream of the fertilizations. This might severely diminish their ability to support

fisheries (Gnanadesikan et al. 2003, Gnanadesikan & Marinov 2008, this Theme Section). (2) As recognized early on by Fuhrman & Capone (1991), increased particle flux from widespread OIF would promote oxygen depletion and the regeneration of nutrients and CO₂ in subsurface waters, which could lead generally to increased production and efflux of greenhouse gases such as N₂O and methane (with 300× and 23× the global warming potential of CO₂, respectively, calculated by molecular weight). (3) Fertilization-induced oxygen depletion and regeneration of nutrients at mid-depths could alter source waters for some coastal upwelling systems. Effects of similar alterations are illustrated by examples from the coast of Oregon influenced by anomalous high-nutrient, low-oxygen upwelled source water in 2002 (Grantham et al. 2004) and very low O₂ water in 2006 (Chan et al. 2008); effects included nearshore hypoxia with fish kills and transients of increased emissions of CO₂ and N₂O from the ocean associated with upwelling (Lueker 2004). Through its incremental influence on mid-depth oxygen and nutrients, OIF-induced alteration of source waters for coastal upwelling should increase the frequency or extent of coastal hypoxia, but by what amount, we do not know. As the events of 2002 and 2006 illustrate, incompletely understood natural processes will always be a factor. If dramatic anoxia like that observed in 2006 (Chan et al. 2008) occurred several years after OIF had even slightly altered source waters, there would likely be an active discussion of the extent to which those who applied fertilizer might be liable. (4) Higher nutrients in source waters for coastal upwelling can have positive effects, especially if the system is not driven to hypoxia; enhanced delivery of nutrients to upwelling systems influenced by OIF-enriched source waters should lead to increased productivity in the surface layer and export of production from it, although supplies of N would likely be reduced by the conversion of ammonium and nitrate to N₂ by denitrification and anammox in suboxic waters (Arrigo 2005). (5) For enrichment of oligotrophic waters to stimulate N-fixation, alteration of subsurface N:P nutrient ratios is expected—and indeed will be exploited (Karl & Letelier 2008). This could have important, and at present unknown, influences on the structure of the pelagic food web (Arrigo 2005).

A common feature of these downstream effects is that they would be expected to build up gradually over time in response to the cumulative influence of repeated fertilizations, ultimately altering much of the ocean. As we discuss below, capabilities exist to model the effects and to make measurements relevant to validation of model predictions, but quantifying perturbations directly attributable to OIF on a global scale during coming decades of changing climate presents a

huge challenge (Denman 2008, this Theme Section, Watson et al. 2008). Indeed, modeling studies indicate the difficulties that exist in discerning the signal of global climate change over that of climate variability during the coming decades (Boyd et al. 2007a); assessing the influence of OIF will require detecting its direct and indirect effects over the 2 sources of climate-related variability — with confidence.

CRITERIA FOR EFFECTIVE VERIFICATION

Now that we have identified the expected (but not necessarily easily quantifiable) influences of wide-scale OIF, we can return to the conclusion that it is premature to sell carbon offsets for OIF unless it can be demonstrated to have 'acceptable and predictable environmental impacts' (Buesseler et al. 2008). It is useful to start with a list of what should be predicted.

- Reduced vertical export of carbon from waters immediately downstream, due to depletion of surface water nutrients, should be assessed and deducted from the vertical carbon flux associated directly with each fertilization. To do so, we would need to quantify the extent to which nutrients were depleted and the effect of that depletion on vertical carbon fluxes that would have occurred had the patch of water been left alone. Knowledge of the mean state and variability envelope (around the mean) of the nutrient fields prior to OIF is a prerequisite for this quantification (see Watson et al. 2008). The use of autonomous sensor systems on floats and gliders (Riser & Johnson 2008) would assist with large-scale quantification of changes in nutrients and dissolved oxygen.
 - Changes in the emissions of N_2O to the atmosphere during the 100 yr after fertilization would have to be predicted and any net increases — multiplied by a global warming potential of 300 times that of CO_2 — would have to be deducted from the estimate of net carbon sequestration. Given that waters below the surface layer but above the 100 yr horizon will be enriched with nitrogen and somewhat depleted in oxygen, increased emissions to the atmosphere are expected (Gnanadesikan et al. 2003). Thus, N_2O production would have to be assessed for these mid-depth waters, along with atmospheric exchange (Nevison et al. 2004). To estimate the required limit of detection, consider that the global warming benefit associated with ocean carbon sequestration of 0.5 Gt C yr^{-1} would be diminished 20% by incremental emission of $0.8 \text{ Tg N as } N_2O \text{ yr}^{-1}$. This difference is coincidentally about 20% of the estimated ocean production of N_2O (Nevison et al. 2004) and well within the uncertainty of the estimate. For further discussion, see Law (2008).
 - Alterations to methane emissions from the global ocean should also be assessed. However, simple calculations indicate that even large changes in methane production may not be a problem in this context; emissions of methane would have to increase by $16 \text{ Tg CH}_4 \text{ yr}^{-1}$ to offset 20% of a 0.5 Gt C yr^{-1} carbon sequestration. This is well over 10× the estimated marine source of methane to the atmosphere (Kock et al. 2008), so, unless other relevant facts arise, increases in methane production might safely be considered an acceptable consequence of OIF.
- Other expected effects of OIF cannot be quantified in terms of CO_2 greenhouse gas equivalents, but would have economic and societal impacts that should be assessed to evaluate net benefits of ocean fertilization.
- In some regions of the ocean, purposefully nutrient-depleted surface waters would be subducted, then upwelled into the thermocline hundreds or thousands of km away. These upwelled waters would have lower concentrations of nutrients, limiting their potential to support productive ecosystems (Carr & Kearns 2003). It will be important to estimate not only the reduction of carbon sequestration, but also the impacts on food webs and on the yields of fisheries in particular. Using calculations they recognized to be uncertain, Gnanadesikan et al. (2003) related regional fisheries landings to export production (transport of organic carbon to depth) and estimated that 1 US ton of reduced export flux corresponded to \$US5 of fisheries value. Applying this estimate to results of one of their 100 yr simulations of OIF, Gnanadesikan et al. (2003) calculated that the long-term cost to fisheries of the southeast Pacific region associated with sequestering 1 US ton C through fertilization of the tropical ocean would be \$US150 US ton⁻¹ C sequestered. If history is any guide, regardless of uncertainties in the cost estimate, we should expect major repercussions if fisheries yields decline in regions predicted to be starved of nutrients due to upstream OIF. Attributing causality to a major change in fisheries is notably difficult, and the compounding effects of climate variability and global warming promise to make determinations even harder to make.
 - As discussed above, alteration of subsurface waters has its own consequences. Widespread OIF above waters that impinge on coastal regions should lead to increased extent, and possibly frequency, of hypoxia in coastal ecosystems supplied by artificially enriched mid-depth waters, but we have little basis on which to predict the degree of increase. Major hypoxic events have significant ecological and economic impact, so it will be important to determine how much influence OIF might have. Comprehensive ocean surveys with autonomous sensor systems (nitrate and oxygen) informing detailed ocean models should help. It will nonetheless be very difficult to

determine the degree to which OIF may have contributed to coastal hypoxia during coming decades of climate variability and major anthropogenic inputs of nutrients to coastal waters (GESAMP 2001).

We conclude that predicting the effects of OIF will be a formidable challenge and validating the predictions will be very difficult. These obstacles to effective auditing of OIF impacts are compounded by the possibility of unpredictable effects.

UNPREDICTABLE EFFECTS

The preceding discussion has been based on the heuristic assumption — by no means proven — that OIF would be broadly effective at stimulating the growth of phytoplankton and utilization of surface nutrients, leading to globally significant sequestration of carbon. We have done this because it is imprudent to embark on a course of action that could influence the whole world without considering the consequences of complete implementation with expected results. In turn, we should consider the consequences of unexpected results.

It has been argued that we cannot predict the ecological and biogeochemical responses to OIF (Chisholm et al. 2001). This argument is supported by a range of unanticipated outcomes of OIF experiments to date. Specifically, markedly different algal community composition of blooms were reported from the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS) I and II experiments at the same site in the northwest Pacific (Boyd et al. 2007b). A large-scale phosphate fertilization in the phosphorus-poor eastern Mediterranean resulted, surprisingly, in a decrease in phytoplankton stocks. After careful analysis, this result was attributed to other food web components out-competing phytoplankton for the added phosphate (Thingstad et al. 2005). The result was entirely unexpected and appreciated only in retrospect; it illustrates that when complex marine ecosystems are manipulated, the most obvious prediction, e.g. a phytoplankton bloom in response to P-fertilization or a bloom of fast-settling diatoms sequestering carbon in response to iron fertilization, cannot be guaranteed.

Larger-scale changes of ecosystems must also be considered. There is now considerable evidence that environmental forcing, associated with climate variability and/or climate change, results in unexpected changes in ecosystems — so-called 'regime shifts' that can alter phytoplankton community structure and also indirectly impact on higher trophic levels (see Boyd & Doney 2003, their Table 7.1). One example of such a shift is the sudden appearance of extensive coccolithophore blooms in the Bering Sea, with subsequent large-scale changes of regional biogeochemistry and

food web structure (Stockwell et al. 2001). OIF for climate mitigation will alter regions of similar scale and it may not be possible to assess unwanted effects until after they happen.

UNCERTAINTY, ACCOUNTABILITY AND THE SCALE OF OIF

We agree with Buesseler et al. (2008) that uncertainties surrounding OIF are too great to justify the selling of carbon offsets for ocean fertilization at this time and we add that some uncertainties will never be fully resolved. But when it comes to the recognized threat of climate change, arguments can be made for going forward in the face of uncertainty. That is, acceptance of risk — and perhaps a relaxation of the standards for carbon offset valuation — might be tolerated if OIF showed great promise for mitigating climate change and thereby reducing the recognized risks of increasing atmospheric CO₂. However, this justification for accepting uncertainty and associated risks diminishes greatly when proposals for OIF are scaled back to much more modest levels that, on their own, would not make a substantial difference to climate (for example, as recently presented by one company, Climos, on their site, http://www.climos.com/faq.html#solve_global_warming, accessed April 28, 2008). It follows that as the ultimate objectives of OIF are scaled back, the tolerance of uncertainty and the assessment of benefits as compared to risks should be adjusted accordingly. At the same time it should be recognized that there is no guarantee that one company's restraint will be mimicked by others in a carbon-offset market. Further, no proposals have been made to define the conditions under which restrictions on cumulative fertilization should be imposed. We therefore feel that assessment of OIF as a climate mitigation strategy should consider the effects of widespread fertilization as discussed above.

CONCLUSIONS

We conclude that if OIF is pursued as a climate mitigation strategy, it will affect much of the ocean over 100 yr or more. So its effects should be predicted on the scale of the global ocean and verified against the background of climate variability and climate change over coming decades. This is also required for comprehensive auditing of carbon offsets. We propose that until the capability for predicting and detecting downstream side-effects of OIF can be demonstrated — and there is good reason to believe that it cannot — OIF should not be considered a viable technology for climate mitigation.

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Designing the next generation of ocean iron fertilization experiments

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ABSTRACT: The first generation of open-ocean iron enrichments (1993 to 2005) have all had broadly the same design. Enrichment of patches of ocean was typically on a 10 km length-scale, and experiments were of a duration of weeks. These scales were dictated by what could conveniently be achieved from research vessels, using tracers to track Lagrangian patches. The extrapolation of experimental findings to the larger scales required for carbon sequestration by ocean iron fertilization (OIF) leaves many uncertainties, to answer which, longer duration (i.e. months) and larger scale observations (100 to 200 km length-scale) are required. However, to extrapolate to a timescale of decades and to the scale of ocean basins, such observations must be conducted in parallel (and where possible assimilated into) detailed models of the physics and biogeochemistry of the fertilized waters. Our present understanding suggests that any carbon sequestration will occur as the net result of changes in the air–sea flux integrated over millions km² and many years, and can only realistically be assessed by modelling. A central role of the observational studies will be to make such models as accurate as possible in their simulations and predictions. We present a scheme for the design of a second generation of ocean iron-enrichments and discuss the challenges that are evident in linking the modelling and observational components of such studies.

KEY WORDS: Carbon · Sequestration · Climate · Mitigation · Southern Ocean · HNLC · Nutrient · Chlorophyll

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UNANSWERED QUESTIONS FROM PREVIOUS RELEASES

Open-ocean iron addition experiments (FeAXs) have been performed in each of the high-nutrient, low-chlorophyll (HNLC) regions of the World Ocean—the equatorial Pacific Ocean, Southern Ocean and north Pacific Ocean—and have established the fundamental role of iron limitation in all these regions (de Baar et al. 2005, Boyd et al. 2007). These experiments have all followed a similar design (Watson et al. 1991), in which patches on the order of 10 km long are initially seeded with both inorganic iron and the inert tracer sulphur hexafluoride, and the chemical and biological consequences of enrichment are followed over an ensuing period of several weeks. The time scale and conse-

quently the spatial dimension of the experiments have been set by very practical concerns and logistical constraints; a campaign from even the largest research vessels can rarely last more than 2 mo. The endurance of the ships and the scale of funding available (not to mention the reluctance of scientists and seagoers to spend many months away from home) set this time scale. In turn, this means that patches reach only a few tens of km in length-scale before the studies end. Using 2 or more research cruises, recent experiments have increased the duration somewhat (e.g. Coale et al. 2004), but exercises such as the Southern Ocean Iron Experiments (SOFeX) and the European Iron Fertilization Experiment (EIFEX) (Hoffmann et al. 2006) are at the upper limit of what can be achieved by conventional oceanography.

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Though much has been learned from these experiments about the effects of iron addition at the ecosystem level, if we are interested in the effects of deliberate ocean iron fertilization (OIF) as a method for sequestration of carbon, or for that matter, in the climatic effects of increased iron availability on glacial–interglacial time scales, then we need to upscale our results to longer times and larger space scales. Difficulties quickly become apparent when this is attempted. Recent reviews (de Baar et al. 2005, Boyd et al. 2007) have summarized where our knowledge is still inadequate for this extrapolation and the major remaining questions are summarized in Table 1.

HOW IS CO₂ SEQUESTERED FROM THE ATMOSPHERE BY OIF?

In order to understand the likely influences on the efficiency of sequestration, it is helpful to describe the carbon balance of a parcel of water that upwells into the surface layer of the ocean. Suppose we take some typical deep ocean water and bring it to the surface in an HNLC region—consider first the polar Southern Ocean or sub-antarctic. In the absence of iron fertilization, biological uptake of nutrients and carbon takes place, fixing carbon and macronutrients to the extent allowed by the iron (and light) availability. After some

Table 1. Major uncertainties in the effects of deliberate ocean iron fertilization

Process	Issue	Finding	Comments
Carbon sequestration efficiency	Carbon fixation in surface water	Variable ^a	Latitude, mixed layer depths + light co-limitation
	Carbon export	None/little/significant ^b	Limited duration of studies
	Depth of carbon export	Poorly constrained	
	Duration of carbon sequestration	Unknown	Unanswerable by observations alone
	Fraction fixed from atmosphere	Poorly known	Likely unanswerable by observations alone
Influence on dissolved oxygen	Formation of subsurface O ₂ minima	Poorly known ^c	Potentially harmful, depth dependent
Production of other climate-active gases	Methane & nitrous oxide	No effect/possible enhancement ^{d,e,f}	Significant warming potential
	Dimethylsulphide	No change/ increase ^b	Some evidence that enhancement is transient
	Biogenic halocarbons	Reduction/no change/ increase ^g	Pertinent to atmospheric oxidation chemistry & particle formation
	Biogenic hydrocarbons, including alkyl nitrates	No change/increase ^{e,g}	Pertinent to atmospheric oxidation chemistry & particle formation
Effects on ecosystems and biogeochemistry	Phytoplankton species shifts	Mainly towards diatoms ^b	Are shifts transient?
	Mesozooplankton stocks	No change/increase ^b	Localised increases within Fe patch due to arrested vertical migration: duration of study & longer reproductive cycles
	Higher trophic levels	Unknown	Limited duration of studies. Possibility of enhanced secondary and higher-level production ^j
	Macronutrient uptake	Small to significant ^b	Mixed layer depths + light co-limitation
	Reduction of nutrient transport	Important in upwelling regions ^h	Supply flows to other areas cut off, e.g. sub-tropical gyres
	Nutrient remineralization	May affect global distributions	At present only evident from modelling studies ⁱ

^ade Baar et al. (2005); ^bBoyd et al. (2007); ^cNatural O₂ minima: e.g. Arabian Sea & east subtropical Pacific, anthropogenic minima: e.g. Gulf of Mexico eutrophication; ^dLaw & Ling (2001); ^eWingenter et al. (2004); ^fWalter et al. (2005); ^gLiss et al. (2005); ^hCooper et al. (1996); ⁱGnanadesikan et al. (2003); ^jTsuda et al. 2006

period at the surface, which is typically of the order of 1 or 2 yr and probably depends very much on proximity to frontal regions, the water is subducted or transported by deep winter mixing out of the surface layer. As relatively cold, dense water, it can mix into the deep or intermediate waters and may not surface again for 100s of yr. If we now imagine that this water is fertilized with iron while it is at the surface and that its $p\text{CO}_2$ decreases as the iron-stimulated bloom develops, it will begin to take up atmospheric CO_2 , or to decrease the outgassing flux if the region is a net source of CO_2 to the atmosphere. When this water is subducted, any CO_2 it has removed from the atmosphere, or that it retains when, without fertilization, it would have been lost to the atmosphere, will be transported into the ocean's interior ocean and sequestered until that water is again brought to the surface.

It is notable that in this description the sequestration of carbon from the atmosphere is not dependent on having an export flux to any particular depth. Provided the biologically fixed carbon is not quickly respired back to CO_2 while the water is still at the surface, sequestration could occur even if there were no export flux. The export flux is only important in that, since remineralization of the phytoplankton carbon is often quite fast (days, Boyd et al. 2004), export ensures that a proportion of this remineralization would occur at depths where the water is out of contact with the atmosphere. The important point is that the fertilized water has a limited residence time at the surface before subduction and that during this time fertilization induces enhanced lowering of its $p\text{CO}_2$. Efficient sequestration will be dependent on this time scale. In particular, if the cumulative natural iron supply to this water (from the atmosphere, for example) is sufficient to cause the carbon fixation to occur in any case during the time it is at the surface, the deliberate iron fertilization is largely redundant; its only effect is to speed up by 1 or 2 yr a sequestration that would have occurred even without the artificial fertilization, focusing enhanced productivity into a bloom at the expense of reduced production in the waters downstream. The condition for efficient sequestration is therefore that the residence time at the surface, τ_r , must satisfy:

$$\tau_e < \tau_r < \tau_{\text{Fe}} \quad (1)$$

where τ_e is the air–sea equilibration time for CO_2 , which is typically 1 yr (Broecker & Peng 1982) and τ_{Fe} is the time that would be required for the natural iron flux to supply iron equivalent to that needed for the fertilization. This second time scale depends on poorly known variables, such as the C:Fe ratio assumed necessary for open ocean phytoplankton and (if the iron source is atmospheric dust) the solubility of the iron in aerosol. As an example, using figures from Jickells et

al. (2005) for the iron flux to the Southern Ocean, a solubility of iron in dust of 3% (Baker & Jickells 2006), a mixed layer depth of 50 m and a molar C:Fe ratio of 10^5 , we calculate a τ_{Fe} of about 10 yr.

This discussion suggests that sequestration efficiency due to iron fertilization may be less in the equatorial Pacific, as models tend to show (e.g. Sarmiento & Orr 1991, Cooper et al. 1996). Water that upwells into the surface layer in this region is strongly heated and therefore much less dense than most subsurface water, and it is unlikely to be permanently subducted below the thermocline until it has been transported to cooler regions, requiring decadal or longer residence time at or near the surface. This residence time will usually exceed τ_{Fe} (which in most regions is shorter than that calculated for the Southern Ocean, since the atmospheric iron flux is at its lowest in polar waters). The net effect of OIF in such warm water regions would then be simply to replace the slow uptake of macronutrients and carbon that would normally take place over a period of years after the water has upwelled with an artificially induced bloom. Alternatively, recent models suggest some subduction to comparatively shallow depths may occur from the equatorial Pacific (F. Chai pers. comm.). In that case, fertilization here would provide some sequestration, though of a less permanent nature than in the sub-antarctic. In the sub-arctic Pacific some intermediate water (North Pacific Intermediate Water) is formed and efficient sequestration might be possible if waters feeding into this water mass were fertilized.

This description should make clear why realistic physical-biogeochemical modelling of a given OIF event must be an intrinsic part of any strategy to investigate the sequestration of carbon. The C sequestered cannot be measured by any simple means. It is certainly not equal to the export flux deriving from a bloom triggered by the fertilization, for example. Rather, it is the difference between the net air–sea flux of carbon dioxide due to the iron fertilization and that which would have occurred in its absence. Calculation of this flux involves integration over periods of years and an area of ocean that rapidly grows to cover millions of km^2 . Clearly this can only be determined by modelling. The problem is that the model must correctly simulate the physics, chemistry and biology, and their interplay in such HNLC open-ocean provinces. But our models are not currently this good. The best we can do is likely to be to guide, improve and make more accurate the models by well-chosen measurements, not only of inorganic carbon but of all the relevant variables that we can measure. Thus, we see the program as being a joint effort of modellers and field experimentalists, with the observational program improving the models by validating any variable that

can be both modelled and measured. Observations alone cannot determine the carbon sequestration and models should not be believed unless they consistently reproduce observations.

NEED FOR A JOINT MODELLING-OBSERVATIONAL STRATEGY

It is clear that to reduce the uncertainties about the effects of iron fertilization, observations on scales larger than used those up to now are needed, and we assume here that the initial fertilization in Generation 2 experiments would be on the order of 200×200 km. However, as discussed in the previous section, it is evident that observations alone are insufficient. Rather, we need a joint modelling-observational strategy, because there are several crucial questions that direct observation alone cannot answer, as follows: (1) The outcome of the release, including its eventual efficiency at removing carbon from the atmosphere, will be strongly dependent on the initial physical, chemical and biological conditions at the potential site. These will vary with location and also with factors such as mixed-layer depth, proximity to oceanic fronts and degree of eddy activity. Assessment of all these will require models resolving eddies and fronts (typically the model resolution should be less than 10 km). (2) The assessment of the lateral trajectory of the iron patch also requires assimilating remote sensing and *in situ* observations into eddy resolving models, which will constrain the initial conditions of physical, biological and chemical state, as well as keep the modelled physics realistic. (3) Assessment of these outcomes will require integration up to scales that are too large and long for any ship-based observation programme. (4) Finally, this assessment requires evaluation of the 'control' case — what would have happened in the absence of a release — which can be provided by observations of a site within the surrounding HNLC waters for small experiments, but only by a model for larger experiments.

Model studies would need therefore to be carried out before, during and after a given FeAX. Adequately integrating such detailed model simulations with an observational program is likely to be as challenging as the practical logistics of the experiment at sea.

SITE SELECTION

In the first generation of experiments, the criteria for site selection were appropriate biogeochemical conditions (HNLC, low iron, iron-limited phytoplankton, seasonal mean mixed layer depth) and relatively quiescent physical conditions (to permit a coherent

labelled patch of ocean to persist). For larger experiments that rely less on tracking a tracer, this basis for site selection will no longer be so relevant. Modelling should be used to help select the site, considering not just the large-scale dynamics (e.g. what part of the world ocean to do the release in) but also the mesoscale: proximity to fronts, eddy scales and kinetic energy. For this purpose, high resolution models and observations (from satellite altimetry, for example) would be useful and could help determine the best strategy for the iron release. The 'confined patch' strategy used up until now may well not be the best way to begin a larger and longer-scale experiment (see later), which might be better initiated by an elongated streak.

DESIGN OF THE OBSERVATIONAL PHASE OF THE EXPERIMENT

Following the selection of a suitable site based on an ensemble of model simulations, the next step is to design a comprehensive survey of the variability exhibited by the properties that may be altered by the iron release. This survey should cover both the waters upstream (i.e. into which the iron will eventually be released) and downstream (i.e. the waters that will interact with the labelled iron patch as it evolves). The variables to be measured would include biogenic gases, downward export flux, biological productivity and nutrients. The areal extent of this survey will be dictated by the expected final areal extent of the iron release. Modelling will also be essential to provide some constraints on the probable trajectory (e.g. Coale et al. 1996) and evolution (dilution rate) of the iron-labelled patch over the subsequent 6 to 12 mo.

During the first generation of experiments, around 12 to 14 h was required to add the dissolved iron so that it formed a coherent patch of 10 km length-scale. However, logistics dictate that for iron enrichment of a 200×200 km patch, multiple vessels would be required if a coherent enrichment patch is to be accomplished within a few days. Such a challenge would require making the iron addition in a carefully co-ordinated manner, which would involve monitoring a suite of Lagrangian (i.e. moving with the net flow of the upper ocean currents, etc.) drifters both in surface and subsurface waters (the latter ensuring the water at depth below the patch is moving in concert with the iron-enriched surface layer). A possible alternative to iron addition using multiple ships might be to use aircraft to spread the iron, though this would inevitably mean the iron would be added at the very surface, rather than homogenized into the mixed layer. We also foresee some operational difficulties in spreading >10 t of material from the air in remote regions of the ocean.

Previous experiments have used the conservative chemical tracer sulphur hexafluoride as a proxy for the concurrently added iron (Watson et al. 1991); however, the use of such a tracer, which is a powerful approach, is impractical on larger spatial scales because the lifetime of the tracer in the surface water is too short and mapping a large patch would take too much ship time. It might be possible to label the centre of this 200 km long patch (and if multiple vessels were adding the iron, this might be very useful), but mapping a patch this large as it evolves would require other approaches including aircraft or helicopters with bio-optical sensors to monitor chlorophyll fluorescence or CO₂ (Boyd et al. 2007). As the patch evolved onto larger scales, satellite remote-sensing could be used to assess its areal extent, as was done on some of the first generation iron enrichments at scales of 500 to 1000 km² (Boyd et al. 2007).

The first set of iron enrichments made very wide-ranging ancillary measurements over and above the core physical, chemical and biological approaches. Generation 2 experiments will no doubt do likewise, but discussion of the full suite of measurements is beyond the scope of this short commentary. In Table 2 we present examples of approaches that provide data streams of different resolution, from remotely sensed to discrete measurements. As data assimilation into models is advocated as part of this multi-stranded experimental design, resolving how best to assimilate a range of datasets with different characteristics (frequency of observations, data quality) requires considerable thought and development, as do issues of

free parameter space versus computation needs for conducting eddy resolving physical-biogeochemical model simulations.

EVOLUTION OF THE IRON-STIMULATED BLOOM

Previous experience during earlier FeAXs suggests that monitoring the latter stages of the bloom (i.e. after it terminates due to resource limitation) and the fate of the algal carbon are problematic. The main issue here is that much of the export, transformation and recycling of this algal carbon takes place in the waters underlying the surface layer that was initially iron-enriched. Hence the need for Lagrangian drifters in the surface and subsurface layers and some means to ensure that there is no lateral slippage between these layers, as is sometimes observed (Savidge et al. 1992), that would uncouple the processes occurring in each layer. Other important issues include defining the depth of carbon sequestration and the areal extent of the source region for particles settling out of the surface ocean (the so-called 'statistical funnel') and how it compares areally with that of the iron-enriched patch (Siegel et al. 2008). A further challenge at this time will be tracking the fate of the dissolved constituents of the bloom signature (i.e. after recycling by microbes and zooplankton). Some of these are climate-reactive gases with very high greenhouse warming potential (see Law 2008, this Theme Section), which could potentially offset the effects of C storage resulting from the bloom. This challenge becomes greater with a longer

Table 2. Sampling resolution of techniques used to obtain measurements of properties prior to, during, and after an FeAX. Range of datasets will pose problems for assimilating observations into a model that will be used to investigate the longer-term (decades) fate of the FeAX. Due to the large number of techniques used on the first generation of experiments, here we provide a small subset of techniques and properties. T: temperature; S: salinity; LIDAR: light detection and ranging; DMS: dimethylsulfide; DMSP: dimethylsulphoniopropionate. Note, in some cases analysis of samples—e.g. thorium for high-resolution estimates of export fluxes—would take months

Approach	Technique	Property	Temporal resolution
Remote-sensing	Glider	T, S, O ₂ , nutrients, particle optics	Hours
	Instrumented buoy	T, S, O ₂ , bio-optics, particle optics	10s of min
	Satellite	Chlorophyll, eddies (altimetry), temperature	Daily images
	Airborne LIDAR	Chlorophyll, photosynthetic competence	Min
Vessel—underway survey	Undulating tow-body	Chlorophyll, nutrients	Min
	Pumped seawater supply	Biogenic gases (e.g. DMS, CO ₂ , CH ₄ & DMSP), dissolved iron	Min
Vessel—discrete measurements	CTD vertical profiles	T, S, chlorophyll	Hours
	Water bottles/net tow	Water samples for N ₂ O, phytoplankton (microscopy), grazing (experiments), thorium (export)	6 d ⁻¹
Moored instrumentation	Sediment traps	C export and C sequestration	1 measurement 2–3 d ⁻¹

experiment because of the impact of ocean currents/physical transports in diluting these signals as the patch gets larger. There is also the added difficulty of detecting such by-products of the decaying algal bloom over the background variability in these downstream waters (hence the need for some downstream survey before commencing the initial iron release).

The logistical challenges in an experiment such as we describe are formidable. They include the need for multiple ships (for the pre-release survey, experiment and post-bloom monitoring). This will necessitate the frequent replacement of vessels (occupation of a site for longer than 2 mo is not possible, as mentioned earlier) and the associated standardization and intercalibration exercises required to ensure uniformity during multiple vessel occupations. Besides using multiple ships for surveying the iron patch and adjacent areas, the emerging autonomous ocean sampling techniques should be used for monitoring and surveying processes inside the iron patch. For example, a set of sophisticated robotics vehicles (autonomous underwater vehicles, gliders and floats) equipped with optical and chemical sensors (Riser & Johnson 2008) will be useful not only to provide 3-dimensional distribution of physical and biogeochemical properties during initial release of iron and onset of phytoplankton bloom, but also for following the iron patch and detecting the decreasing signature of enhanced carbon production for months after the initial addition (Bishop et al. 2002). Finally, there will be a time lag in getting samples and data analysed and in ensuring quality control, prior to assimilation into the model.

A high-resolution eddy-resolving model, preferably guided by assimilation of real-time data, would be used to guide and simulate the release and the first phase of observations. It could be used to interpret the data being returned and to assess how representative the measurements taken at any one point are, which will be particularly important given that it will not be possible to obtain comprehensive observational coverage of the large area to be monitored using *in situ* measurements. Through near real-time iterations between observations and the model, it may be possible to command robotic vehicles to locales where their data will be most useful for assessing water and carbon movement. Finally, the model could be run forward after the main observation phase has ended, to predict the probable long term effects.

CONCLUSIONS

It is evident that to conduct a second generation of experiments on the scales needed to address the issue of the utility of carbon sequestration and monitoring of

unintended side effects, a step increase in the scale of developmental work, costs, lead-in time, co-ordination and logistics will be necessary. We advocate a joint modeling-observational approach as the only means to conduct these second-generation studies. However, even at this early stage of development, it is clear that linking a wide range of measurements, many made on disparate time and/or spatial scales with models (via data assimilation) will be problematic. It may be necessary to use some of the observational results from the first generation of iron fertilization experiments to develop and improve physical-biogeochemical models (Fujii et al. 2005, Chai et al. 2007).

Modelling studies based on results from the first generation of studies point to the complex interplay of physics, photochemistry and biology in setting the concentrations of biogenic gases such as DMS (Le Clainche et al. 2006). It is not possible to have this level of detail in the regional or basin-scale circulation models needed to assimilate observations from the experiments, so a variety of different types of model studies will be necessary to fully interpret the experiments.

Modellers may be horrified by the faith that we are apparently placing in their codes. They will point out that the state of our knowledge is currently insufficient to place much confidence in their predictions and that different models presently give substantially different pictures of the effect of iron fertilization. Nevertheless, this is the state of our knowledge at the present: in this complex area the models represent our best synthesis of current understanding and the outcomes that they agree on are the only ones for which we can claim any certainty.

The program we advocate is a formidable challenge. However, it does not necessarily all have to be achieved in a single, massive effort. Many of the steps on the road to such a project are happening already—e.g. improvements in models, observational techniques and data assimilation methods. Implementation of second-generation iron fertilization experiments will become progressively more tractable in the coming years as we make progress in these related fields. The major challenge will then be to integrate all of these advances into a coherent program at the large scales necessary for the next generation of experiments.

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