



# Climate change, ocean processes and ocean iron fertilization

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**ABSTRACT:** Observations indicate that the rate of increase in concentration of atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> from the atmosphere. To be successful, such a mitigation operation must remove 'significant' CO<sub>2</sub> 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 CO<sub>2</sub> 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 successful models have become more realistic, the amounts of CO<sub>2</sub> forecast to be sequestered have dropped, and in all cases are small relative to the amounts of CO<sub>2</sub> 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, N<sub>2</sub>O. 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 CO<sub>2</sub> in the atmosphere due to anthropogenic activities and their causal link with global warming. The preferred mitigation measure to reverse the rise in atmospheric CO<sub>2</sub> is to reduce emissions of CO<sub>2</sub> from anthropogenic activities, primarily burning fossil fuels and cement production. However, recent studies demonstrate that CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>, and iron fertilization of large areas of the ocean, also to sequester CO<sub>2</sub>.

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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  $\text{CO}_2$ , fertilization of the ocean with iron has been proposed as a 'geoengineering' mechanism to mitigate climate change by increasing ocean sequestration of  $\text{CO}_2$  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](http://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  $\text{CO}_2$ , we need to consider at least 5 issues: (1) state a clear mitigation objective, (2) estimate the amounts of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  in sufficient quantity and for a sufficient time period to make a significant reduction in the rate of increase of atmospheric  $\text{CO}_2$  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  $\text{CO}_2$  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 scenarios<sup>1</sup>, Table 1 gives the cumulative  $\text{CO}_2$  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](http://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  $\text{CO}_2$  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  $\text{CO}_2$  enters the surface

<sup>1</sup>The 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 CO<sub>2</sub> (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 <sup>a</sup>	2001–2050	2001–2100
A1B	286	622	1367
A1FI	286	681	2058
A2	286	597	1702
B1	286	842	918

<sup>a</sup>Based on annual emissions from Marland et al. (2007), available at: [http://cdiac.ornl.gov/ftp/ndp030/global.1751\\_2004.ems](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 [CO<sub>2</sub>], bicarbonate [HCO<sub>3</sub><sup>-</sup>], and carbonate [CO<sub>3</sub><sup>=</sup>] ions, the latter 2 with negative charge. Corresponding H<sup>+</sup> ions, released through the dissociation of water molecules, lower the pH of the water simultaneously. Through photosynthetic primary production, CO<sub>2</sub> is taken up by phytoplankton and converted to organic molecules (with some species also forming CaCO<sub>3</sub>, 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 N<sub>2</sub> and N<sub>2</sub>O, 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 CO<sub>2</sub> comes into contact with the atmosphere once more. For sequestration to reduce the rate of increase of atmospheric CO<sub>2</sub>, 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 CO<sub>2</sub> 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-

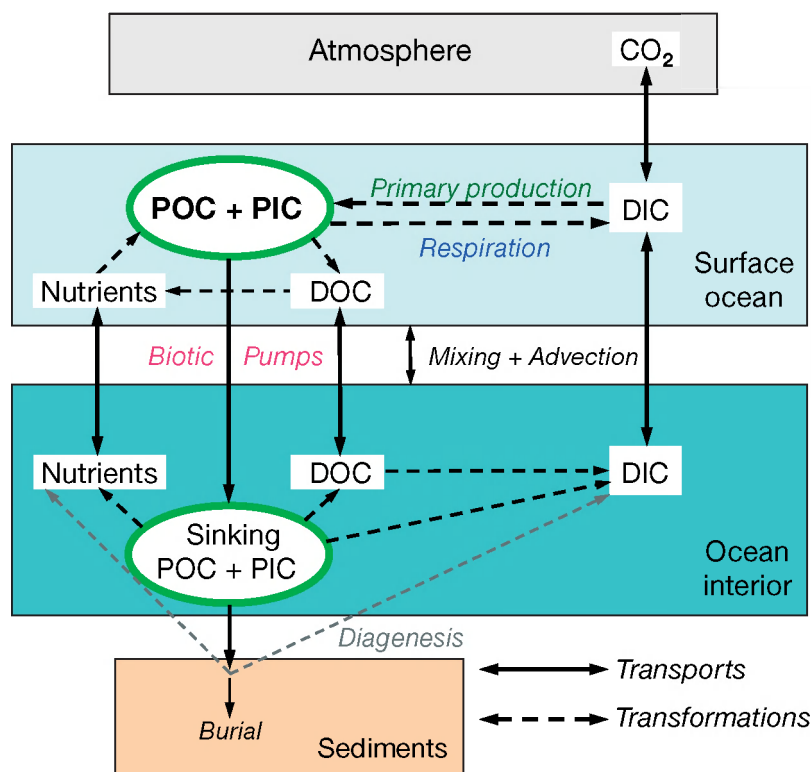


Fig. 1. Schematic of the main components of the ocean carbon cycle, including interactions with the atmosphere and bottom sediments

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 N<sub>2</sub>O (Fuhrman & Capone 1991). N<sub>2</sub>O 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 CO<sub>2</sub> (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) <sup>a</sup>	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 <sup>b</sup> times yr <sup>-1</sup>	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)

<sup>a</sup>Range of results for different remineralization depth scales, restoring times, and gas exchange coefficients  
<sup>b</sup>Represents twice the Earth's surface each year

much-reduced CO<sub>2</sub> 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 10<sup>6</sup> Tg C (1000 Pg C = 10<sup>6</sup> 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<sup>-1</sup> 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 ship-borne fertilization experiments to date), their model gives high atmospheric uptake efficiencies (the ratio of the perturbation in air-sea CO<sub>2</sub> 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 O<sub>2</sub>: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 N<sub>2</sub>O, 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; CO<sub>2</sub> added to the ocean rapidly dissolves and dissociates into bicarbonate and carbonate ions, adding H<sup>+</sup> ions (i.e. protons) to the oceans, thereby reducing pH and increasing acidity. Stimulating increased sequestration of CO<sub>2</sub> 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 CO<sub>2</sub> 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<sup>-1</sup> within 50 yr, can result in a cumulative sequestration large enough to stabilize emissions. Under this scenario of a collection of mitigation measures, CO<sub>2</sub> 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 CO<sub>2</sub> 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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