A scientific critique of oceanic iron fertilization as a climate change mitigation strategy

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EXECUTIVE SUMMARY

Iron is an essential trace element for almost all living organisms. For phytoplankton, microscopic photosynthetic organisms dominated by single-celled algae that inhabit the surface waters of the oceans, iron is necessary for a number of cellular functions including the synthesis of chlorophyll, a pigment required for photosynthesis.

In about one third of the world ocean, the major nutrients required for phytoplankton growth, such as nitrates and phosphates, are in plentiful supply and yet the abundance of phytoplankton remains lower than would be expected. These areas have been called high-nutrient, low chlorophyll (HNLC) regions and include the equatorial Pacific, the sub-Arctic Pacific and the Southern Ocean. Initial scientific investigations of this phenomenon led to a hypothesis by Martin in 1990 that phytoplankton growth is limited in HNLC regions by a lack of iron. Martin further proposed an experiment which could be used to check the 'iron hypothesis' – the addition of iron to the ocean in an HNLC area, and monitoring of the plankton response. Since 1993, a total of 12 such mesoscale iron enrichment experiments have taken place in different HNLC regions of the oceans to investigate the iron hypothesis and, more recently, to determine whether iron can influence carbon export (the sinking of dead plankton and faecal matter to the deeper ocean). This research has shown that the growth of phytoplankton in HNLC regions is indeed stimulated by iron and has verified the 'iron hypothesis' insofar that growth of phytoplankton in HNLC regions is limited by a lack of iron.

When phytoplankton rapidly increase their population they are said to bloom. During the process of photosynthesis, dissolved inorganic carbon in the surrounding water is 'fixed' by phytoplankton, using energy from sunlight, to produce organic carbon. Because dissolved inorganic carbon is consumed in the photosynthetic process, its levels in the water are replenished by carbon dioxide from the atmosphere to maintain the chemical equilibrium. This results in a drawdown of carbon dioxide from the atmosphere into the oceans until equilibrium is restored. Thereafter, the organic carbon produced by the phytoplankton is subject to a number of fates. For example, if the phytoplankton are consumed by other organisms, much of the organic carbon can be rapidly regenerated into carbon dioxide as these 'grazing' organisms respire. In addition, some phytoplankton exude a proportion of the carbon they fix as dissolved organic carbon (DOC), which can also be regenerated quickly through microbial processes. Alternatively, dead phytoplankton, dead zooplankton or their faecal matter (collectively known as particulate organic matter) sink to shallow or intermediate depths and are consumed by microbes that convert it back to inorganic nutrients and carbon dioxide in a process known as remineralization. Sometimes, particulate organic matter originating from the phytoplankton escapes the remineralization process in surface waters and sinks to depths below 200 metres before it decays. Upon decay, the carbon dioxide that is released remains at these depths for longer periods of time because the lower temperature and higher density of the water prevents it mixing with warmer waters above. This process involving phytoplankton removing carbon dioxide from surface waters to storage in the deep ocean is known as the "biological pump". A small proportion of this particulate organic carbon may reach the seafloor where it ultimately may become deposited in sedimentary rocks and, over geological timescales, contribute to hydrocarbon deposits.

With the scientific discovery that phytoplankton growth can be stimulated by the addition of iron to HNLC waters, some have proposed that the 'biological pump' could be enhanced by fertilizing the oceans with iron, as a way of drawing down more carbon dioxide from the atmosphere into the oceans and, in so doing, helping mitigate climate change. However, such proposals are founded on an incomplete understanding and highly simplified interpretation of current scientific knowledge. They have not taken properly into account the results of the 12 mesoscale iron enrichment scientific studies carried out to date which suggest that the amount of carbon sequestered in this way would be very small, nor the fundamental influence of hydrodynamics and large uncertainties and indeterminacies in ecosystem response which those studies highlight.

Furthermore, such schemes would be virtually impossible to carry out in practice because of the colossal areas that would have to be fertilized to result in significant atmospheric carbon removal. The proposals also do not give due consideration to the high probability and consequences of major ecological perturbations to the oceans through the alteration of plankton communities upon which most marine life is dependent. Neither do they take account of the unpredictable and potentially dangerous geophysical changes that could occur with large-scale ocean fertilization.

This scientific review discusses each of these issues in some detail. highlighting the current areas of uncertainty and ignorance and the concomitant dangers inherent in proposals to carry out iron fertilization of the oceans on a commercial scale.

Ecological Concerns

Results of mesoscale iron enrichment studies have generally shown that, after iron is added to HNLC waters, the initially predominant smaller phytoplanktonic species increase their growth rate. However, their growth soon becomes checked by the microzooplankton that consume them. The larger phytoplanktonic diatoms are initially low in abundance in the phytoplankton community but, upon the addition of iron, their growth rate also increases. However, unlike the smaller phytoplanktonic species, the diatoms bloom because they largely escape the grazing pressure of the mesozooplankton that consume them and whose rate of replication is too slow to keep pace.

- It is evident from mesoscale iron enrichment studies that, after iron addition to HNLC waters, the phytoplankton community commonly changes from one dominated by smaller phytoplanktonic species to one dominated by diatoms. This is of great concern from an ecological viewpoint because phytoplankton form the base of the marine food chain. *Any changes in the phytoplankton community will have unknown and poorly predictable, but potentially highly damaging, impacts on marine ecosystems.*

- Iron fertilization results in other essential nutrients, such as nitrates, phosphates ad silicates, being used up as the phytoplankton bloom progresses. Consequently, this could result in a reduction of these nutrients down-current from an iron- fertilized area. In turn, a lack of nutrients would cause a negative impact on phytoplankton down-current resulting in a reduction in overall biological productivity. This would be likely to have a knock-on negative impact on all other marine life because phytoplankton underpin the marine food web. Indeed, because of this phenomenon, modelling studies have predicted that commercial-scale iron fertilization of the oceans could have a significant detrimental impact on important fisheries.

- Iron addition and subsequent phytoplankton blooms, associated with increased particulate organic export and remineralization, could reduce oxygen levels in subsurface waters. Low oxygen levels would lead to a negative impact on many marine organisms because they need oxygen to breathe. Indeed, an early modelling study of large-scale iron fertilization predicted that it would lead to significant deep ocean oxygen depletion in one region of the oceans studied.

- Commercial iron fertilization could, in some circumstances, lead to harmful algal blooms, forms of algal growth which can impact very negatively on other organisms. Although the mesoscale iron enrichment studies to date have not resulted in any such harmful algal blooms, it is known, for example, that wind-blown dust containing iron can lead to the promotion of harmful algal blooms in some areas of the ocean. Commercial iron fertilization therefore carries the associated risk of initiating such blooms.

Geophysical Concerns

A number of climate-active gases were found to be released during some of the mesoscale iron enrichment studies. In a commercial iron fertilization scenario, the release of such gases could have unpredictable impacts and could initiate positive feedback effects on atmospheric chemistry and global climate. For example:

- There is a risk that iron fertilization could result in increased production of nitrous oxide, a greenhouse gas far more powerful than carbon dioxide. It is of great concern that one modelling study predicted that any benefits of carbon sequestration by commercial iron fertilization could be outweighed by nitrous oxide production. In two mesoscale studies which tested for the production of nitrous oxide, one found a small but significant increase in nitrous oxide while the other did not detect the gas.

- Dimethylsulphoniopropionate (DMSP) is produced by certain classes of phytoplankton. It degrades to dimethylsulfide (DMS), a climate-active gas that contributes to reducing the radiative flux to the Earth's surface. DMS increased in some but not all mesoscale iron enrichment studies. Its effect would be to reduce atmospheric temperature but the scale of any change following commercial iron fertilization is hard to predict.

Inadequate Carbon Sequestration and Impracticalities

To be effective as a carbon sequestration technology, particulate organic carbon (dead plankton and faecal matter) has to be exported efficiently to deeper waters (at least 200 metres). However, published results from the mesoscale iron enrichment studies showed that the amount of carbon exported was either very low or not detectable. This inefficient export of particulate organic carbon to deep waters does not favour iron fertilization as a carbon sequestration technology. For example, during the Southern Ocean Iron Experiment (SOFeX) iron enrichment study, an area of 15 km^2 was seeded with iron, resulting in a carbon sequestration of about 900 tonnes of carbon. This is a very small proportion of the carbon released due to human activities (6.5×10^9 tonnes/year), such that it is difficult to see how iron fertilization could scale up to be an effective carbon sequestration method.

Other practical problems using continuous iron fertilization as a carbon sequestration technology include the fact that the macronutrients nitrate, phosphorous and silica would become depleted and would therefore prevent the ongoing growth of phytoplankton. In addition, continuous fertilization would allow mesozooplankton sufficient time to increase in number, leading to increased grazing pressure on the diatoms. This would restrict their proliferation and, therefore, the amount of carbon being exported to deep water.

Modelling studies have predicted that iron fertilization is likely to be highly inefficient. Estimates showed that it would require an impossibly large area to be fertilized each year (equivalent to about twice the Earth's surface!) to have any significant impact as a carbon sequestration technology. Verifying the quantity of carbon sequestered from iron fertilization is also likely to be difficult (if not impossible) because of the large spatial and temporal scales involved.

It is also likely that commercial-scale iron fertilization would be prohibitively expensive because of the cost of the large-scale monitoring programs which would be needed in order to trace and verify the amount of carbon sequestered, as well as to monitor for any negative impacts such as nitrous oxide formation, de-oxygenation or ecological changes.

The Way Forward

Current scientific knowledge strongly indicates that large-scale commercial iron fertilization would not be an effective climate mitigation strategy. Moreover, there are risks of potentially devastating impacts on marine ecology from such an approach and unpredictable consequences on global climate from the release of climate-active gases.

Concerns regarding proposals for commercial ocean fertilisation schemes have been voiced by some for many years, though only recently has the issue become more widely debated. In June 2007, the Scientific Groups to the London Convention and London Protocol (Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter) issued a Statement of Concern, setting out their view that large-scale ocean iron fertilization operations are not justified by current knowledge on both effectiveness in sequestering carbon and potential negative impacts on environment and human health. Similarly, concerns have also been voiced among scientific experts in the field in 2007, to the effect that "*ocean fertilization will be ineffective and potentially deleterious and should not be used as a strategy for offsetting carbon dioxide emissions*".

1. INTRODUCTION

1.1 Phytoplankton

Phytoplankton are microscopic, single-celled, photosynthetic organisms that inhabit the surface waters of the oceans (Chisholm *et al.* 2001). Phytoplankton require sunlight, water and nutrients for growth and are therefore restricted to the photic (or euphotic) zone, a layer (10s-100s metres deep) near the ocean surface where there is sufficient light for photosynthesis to occur. Through the process of photosynthesis, phytoplankton convert the dissolved inorganic carbon in seawater into organic matter (particulate organic carbon). The conversion of inorganic carbon into organic matter is known as primary production (Falkowski 2002). All life on earth is directly and indirectly dependent on primary production. The monitoring of 'chlorophyll a', a photosynthetic pigment in phytoplankton, by satellite, together with other experimental data, has led to the knowledge that roughly half of the primary production on earth is attributable to oceanic phytoplankton, with the balance being due to marine macro algae and terrestrial plants (Behrenfeld *et al.* 2006, Falowski 2002). More than a hundred million tons of carbon in the form of carbon dioxide are fixed into organic material in the upper ocean each day by phytoplankton (Behrenfeld *et al.* 2006).

Phytoplankton are the foundation of the marine food chain (Herring 2007). Their turnover is rapid, with cells dividing every six days on average (though this can be even more rapid under bloom conditions). Some of the daughter cells subsequently die or are eaten by zooplankton , miniature animals that in turn provide food for shrimp, fish and larger carnivores (Falkowski 2002). Behrenfeld *et al.* (2006) note that the entire phytoplankton biomass of the global oceans is consumed every two to six days.

1.2 The Biological Pump

Because phytoplankton utilise carbon dioxide in photosynthesis, their activity results in depletion of dissolved inorganic carbon from the surrounding seawater and the consequent drawdown of carbon dioxide from the atmosphere to rebalance the equilibrium. If they are consumed by other organisms, the organic carbon in the phytoplankton is regenerated into carbon dioxide as these consumer organisms respire (Chisholm *et al.* 2001). In addition, dead phytoplankton cells and faecal material from zooplankton or other organisms (that is, particulate organic carbon or POC) sink and are consumed by microbes that convert them back into inorganic nutrients, including carbon dioxide (Falkowski 2002). This process is know as remineralization. It occurs at shallow or intermediate depths from which the carbon dioxide produced may subsequently be ventilated back to the atmosphere by deep mixing and upwelling (Bakker 2004) over relatively short timescales, or can again be used in photosynthesis (Falkowski 2002).

A proportion of the particulate organic carbon from the phytoplankton escapes the remineralization process and instead sinks into the deeper ocean before it decays, this proportion depends on a large number of ecological and physical (hydrodynamic) factors. When decay releases carbon dioxide below about 200 metres, the carbon dioxide can remain at these depths over longer time-scales because the lower temperatures and higher density of the water prevents it from mixing efficiently with the warmer waters above. Through this process, known as the 'biological pump', phytoplankton can remove carbon dioxide from surface waters and the atmosphere and 'store' it in the deep ocean (Falkowski 2002). In the course of time however, within a few hundred years or so, all nutrients released into the deep ocean again find their way back to surface waters via upwelling and ocean currents. Over timescales of millions of years, however, the biological pump 'leaks' slowly, with a very small proportion (about 0.5%) of the dead phytoplankton cells and faecal matter settling to the seafloor sediments. In turn, a fraction of this carbon becomes incorporated into sedimentary rocks, including in the form of hydrocarbon deposits.

In summary, by affecting the level of carbon dioxide in the atmosphere via the biological pump, phytoplankton undoubtedly have an influence on the global climate. However, the efficiency with which this process effectively 'locks' carbon away in deep waters and sediments over sufficiently long timescales to mitigate against climate change may be very low.

Present global warming is attributed to the accumulation of greenhouse gases, such as carbon dioxide, in the atmosphere largely due to human activity. Global warming would be much faster if it weren’t for the fact that the oceans have absorbed nearly half the anthropogenically produced carbon dioxide (Sabine *et al.*, 2004) produced to date. This is due both to the ‘biological pump’ and the ’solubility pump. The solubility pump is a physical process whereby carbon dioxide dissolves in cold dense surface water in polar regions which subsequently sinks to depths transporting the carbon dioxide into the ocean’s interior (Smith 2006).

In an attempt to reduce atmospheric carbon dioxide and mitigate climate change, various carbon sequestration strategies have been considered – and some researchers and private corporations have turned their attention to the ‘biological pump’. In this regard, it has been speculated that if the oceans were fertilized to increase phytoplankton growth, the rate of carbon exported to the deep sea could also then be increased. Aside from the concerns regarding efficiency and adverse impacts, this would in any case be only a temporary solution because deep ocean carbon dioxide reservoirs are eventually re-exposed to the atmosphere. Nevertheless, it has been argued that temporary storage would buy us time. It has also been proposed that the carbon stored could be sold as credits in the carbon marketplace.

One method proposed by which the oceans could be commercially fertilized to sequester carbon is by the addition of iron. This proposal comes after a number of scientific experiments that have studied the impact of iron on oceanic phytoplankton. The basic idea is that phytoplankton could help to solve global warming and a number of corporations and private entrepreneurs have expressed an interested in commercial large-scale fertilization of the oceans over the last decade (Chisholm *et al.* 2001).

In this report, the reasoning behind scientific investigations into the impact of iron on phytoplankton growth is discussed (section 1.3 below). The overall findings of the scientific studies on iron fertilization are discussed in section 2 (with short summaries of the results of individual scientific studies included in Appendix 1). Section 3 discusses drawbacks and scientifically-based objections to iron fertilization on a commercial scale.

1.3 The Iron Hypothesis

Iron is an essential element for life on Earth. It is a key element in cellular electron transfer processes, nitrate reduction, and the synthesis of chlorophyll (see Bowie *et al.* 2001).
In a third of the world’s oceans, major nutrients for plant growth – especially nitrates and phosphates - are relatively abundant and yet phytoplankton stocks remain constantly lower than would be expected (Boyd 2004, Chisholm *et al.* 2001). These areas have been termed high-nutrient, low chlorophyll (HNLC) regions and include the equatorial Pacific, the sub-Arctic Pacific and the Southern Ocean.

Oceanographers have long been puzzled by the paucity of phytoplankton growth in HNLC regions. As early as 1931, Gran suggested that low iron levels may be limiting phytoplankton growth in the Southern Ocean. Later, laboratory experiments and bottle incubations were used to investigate HNLC waters of the Southern Ocean and showed that phytoplankton increased in response to iron addition (eg. Buma *et al.* 1991, De Baar *et al.* 1990).This lead to the proposal of the “Iron Hypothesis” in a 1990 publication by Martin, which postulated that phytoplankton growth was iron-limited in the Southern Ocean and equatorial Pacific (Martin 1990). Martin noted that iron is supplied to surface waters by upwelling in some regions, but iron is also supplied to surface waters by long-range transport and fallout of iron-rich atmospheric dust originating in terrestrial arid regions. However, in HNLC areas, the amount of iron currently falling on surface waters is not sufficient for other major nutrients to be used up by phytoplankton. To establish historical trends, Martin also considered evidence from ice core records which showed that, when dust inputs were relatively high and iron was readily available, atmospheric carbon dioxide was low and vice versa. In addition, Martin noted there was some evidence that biological productivity rates may have been higher during the last glacial maximum than in previous and present interglacial periods. This information led Martin (1990) to propose as part of his ‘iron hypothesis’, that increases in iron supply from dust during glacial periods would stimulate phytoplankton growth (primary production), which, in turn, would lead to a decrease in atmospheric carbon dioxide levels leading to global climate change (a cooling effect) . Thus, during glacial times, an increase in iron from dust deposition would stimulate the ‘biological pump’, which would deliver more carbon dioxide to the deep sea. More recently, a modelling study suggested that iron had some influence on atmospheric carbon dioxide changes in glacial periods in the Southern

Ocean (Watson *et al.* 2000). Another study lends support to the idea that the delivery of airborne iron to the Southern Ocean stimulates primary production and strengthens the link between increased iron delivery and lower atmospheric carbon dioxide during the ice ages (Cassar *et al.* 2007).

There was a genuine concern that initial experiments supporting the ‘iron hypothesis’ may not mimic the response of whole ecosystems to iron addition since they were not performed in the environment at large. Consequently, it was proposed that the ‘iron hypothesis’ could be tested in HNLC regions by mesoscale iron enrichments of whole ecosystems (Martin *et al.* 1994). Since 1993, a total of 12 such mesoscale iron enrichment studies have been conducted in different HNLC regions around the world (Boyd *et al.* 2007). These experiments were designed to determine whether iron was indeed the limiting nutrient in HNLC regions as Martin had hypothesized. The more recent of these studies had the additional aim of establishing whether iron can influence carbon export (the sinking of dead plankton and faecal matter to the deeper ocean). The experiments were not undertaken to investigate the feasibility of iron fertilization for the purpose of carbon sequestration to combat climate change (see e.g. Chisholm *et al.* 2001). Appendix 1 of this report outlines the findings of the 12 mesoscale iron enrichment studies.

2. SUMMARY OF MESOSCALE IRON ENRICHMENT EXPERIMENTS 1993 - 2005

In total, 12 iron-enrichment studies have been carried out over the last decade in polar, subpolar, and tropical HNLC waters. De Baar *et al.* (2005) reviewed the findings of the first eight of these studies. It is known that wind mixing strongly influences the amount of light phytoplankton receive for growth and in the iron enrichment experiments, the depth of the wind mixed layer varied widely between studies. De Baar *et al.* (2005) found a significant relationship between the depth of the wind mixed layer and phytoplankton biomass, as indicated by chlorophyll a, or, removal of dissolved inorganic carbon. From this it was concluded that light is the ultimate determinant of the phytoplankton biomass response. Thus, the depth of the wind mixed layer in regulating light climate was identified as the major factor controlling photosynthesis in HNLC regions of the ocean. This was not unexpected as light flux is a key controlling factor of photosynthesis in phytoplankton. In looking to identify one over-arching limiting factor for each iron enrichment study carried out, it has been concluded that SOIREE and EisenEx in the Southern Ocean were predominantly light-limited, SEEDS and SERIES were predominantly iron-limited while IronEx-2 and SOFeX-N and –S showed limitation intermediate between light penetration and iron.

The rate of growth of phytoplankton is also known to be governed by temperature and a comparison of results showed that this was apparent in the iron enrichment studies. De Baar *et al.* (2005) also noted that the initially seeded iron patches tended to dilute due to combined wind mixing and shear stress such that initial patch size areas of 50-80 km^2 and 225 km^2 for SOFeX could exceed 2000 km^2 by the end of the experiment. The extent of dilution varied between experiments, since some individual experiments were longer than others, allowing a greater dilution to take place. With regard to the phytoplankton community structure, a review of results showed that, in all of the experiments, there was a striking increase in cell numbers of larger size classes of diatoms and, in general, the community shifted from mostly nanoplankton (<10 µm) to mostly microplankton (>10 µm). It appeared that large and initially rare diatoms benefited from a release in grazing pressure, at least in the early stages of the iron-enriched blooms, because their specialized grazers were not sufficiently numerous to control them as their numbers increased rapidly due to the added iron.

Barber and Hiscock (2006) made an in-depth analysis of different phytoplankton groups in IronExI and IronEx II and detailed their findings on the dynamics and fate of phytoplankton following iron fertilization. Initially, small phytoplankton (picophytoplankton) dominated the phytoplankton community and larger diatoms were rare. Following fertilization, most of the iron is first partitioned to the abundant picophytoplankton community, which increase their photosynthetic efficiency and growth rate. However, the picophytoplankton thereafter become subjected to efficient grazing from microzooplankton and their numbers are checked. In contrast, the initially present low number of diatoms are able to take up the available iron much faster than the picophytoplankton and they increase their growth rate and numbers, eventually accounting for most of the iron taken up. They initially escape heavy grazing pressure from mesozooplankton and, therefore, are able to bloom, monopolizing the available iron. Thereafter, as the iron becomes depleted, ecological theory predicts that picophytoplankton, with a lower requirement for iron, would again displace diatoms from the community (Barber and Hiscock 2006) though this was not explicity followed experimentally.

The mesoscale iron enrichment studies have shown that, as predicted, phytoplankton growth generally decreased the concentrations of nutrients and carbon dioxide in the mixed layer and resulted in the production of particulate organic carbon (Bakker 2004). Monitoring of export of particulate organic carbon to deeper waters, however, showed that export to deep waters was either very low or could not be detected (see appendix 1). In some of the experiments, changes in concentration of the gas dimethyl sulphide (DMS), generated as a byproduct of growth in some algae, were also detected. DMS is a ‘climate-active’ gas that can contribute to reducing the radiative flux to the Earth’s surface, primarily by promoting cloud formation. Variations in its generation highlights the fact that biogenic gases other than carbon dioxide but which nonetheless can exert significant influence on the climate, must also be considered if the cumulative impact of iron enrichment on climate is to be evaluated fully (Turner *et al.* 2004, Boyd *et al.* 2007).

In a recent publication, Boyd *et al.* (2007) brought together findings of all 12 of the iron enrichment studies. It was noted that time-series observations of the enrichment experiments have enabled study of the open-ocean blooms from initiation through to the evolution and decline phases. The studies have confirmed that iron enrichment enhances primary production from polar to tropical waters and that iron supply has a fundamental role in photosynthesis (photosynthetic competence). The experiments have enabled the study of the entire pelagic food web in response to iron enrichment (albeit over a relatively short time frame) and have shown that upon iron enrichment, stocks of all phytoplankton groups initially increased but only the diatoms bloomed by escaping grazing pressure. Thus these experiments caused observable changes in food web dynamics.

At a meeting of some of the scientists involved with iron enrichment studies (SOLAS Synthesis of Mesoscale Iron-Enrichment Studies) it was concluded that experiments had conclusively tested the ‘iron hypothesis’ and solved the puzzle of why productivity of some ocean waters is lower than it could be on the basis of levels of macronutrients present. This had led to a better understanding of the biological functioning of HNLC waters, which can now be represented more accurately in mathematical model simulations (Harvey *et al.* 2006). The meeting also looked at new questions raised by experimental work that must be addressed to help improve understanding of the role of iron supply in ocean productivity and its effects on global climate.

3. DRAWBACKS OF COMMERCIAL IRON FERTILIZATION

3.1 Carbon Sequestration – Inadequate and Impractical

3.1.1 Consideration of Results from Mesoscale Iron Enrichment Studies

To assess whether iron fertilization has potential as an effective carbon sequestration method, it is necessary to measure in field studies the ratio of iron added to the amount of carbon sequestered (in the form of sinking particulate organic carbon) to the deep ocean (Buesseler and Boyd 2003).

In reviewing results of the mesoscale iron enrichment studies, de Baar *et al.* (2005) noted that, in general, the transfer of carbon from dissolved inorganic carbon pools to particulate organic carbon pools *via* photosynthetic fixation was characterized by large inefficiencies. Only 18-26% of primary production accumulated as particulate organic carbon. Results for export of particulate organic carbon to deeper waters showed that export could not be detected or was very low (see appendix X). For example, in SOIREE and SEEDS I, there was no significant increase in carbon export from the iron enriched areas and for EisenEx it was not possible to tell whether carbon was exported. The most direct evidence for export was found in sediment traps of SERIES upon the collapse of the bloom (de Baar *et al.* 2005). In SERIES, IronEx II, SOFeX-N and –S there was an increase in carbon export but it was low. This inefficient export of particulate organic carbon to deeper waters does not favour the use of iron fertilization as a climate change mitigation strategy. Results for EIFEX, SAGE and FeeP have yet to be published.

Taking the results for carbon export in the SOFeX experiment, rough estimates can be made as to how iron fertilization would scale-up for use as a carbon sequestration strategy (Buesseler and Boyd

2003, Buesseler *et al.* 2004). In particular these results could provide information on two key scaling factors which are needed to find out whether iron fertilization could be a successful climate change mitigation strategy - the carbon export efficiency and the size of the ocean area which would need to be involved. Significantly, however, geo-engineering proposals for commercial fertilization of the oceans have not to date used data from mesoscale iron enrichment studies to calculate these parameters. Instead, laboratory culture-based determinations of the ratios of iron added to carbon exported (2×10^{-6} to 7×10^{-6}) have been used to scale up predictions of the impact of iron additions to downward particulate organic carbon flux. These extrapolations have been used, in turn, to support claims of low financial costs for iron fertilization as a potential carbon sequestration strategy ($1-2 per metric tonne of carbon sequestered (Markels and Barber 2000)).

By contrast, data from mesoscale iron enrichment studies of the Southern Ocean (SOIREE, EisenEx and SOFeX) showed, in fact, that evidence of sinking particles carrying particulate organic carbon to the deep ocean was limited (Buesseler and Boyd 2003). Based on the SOFeX experiments, Buesseler and Boyd (2003) have calculated that 1.3 tonnes of elemental iron resulted in a particulate organic carbon flux at 100 metres depth of 2100 tonnes. This is equivalent to a molar ratio of iron added to carbon sequestered of $1.3 \times 10^{-4.}$ This ratio is some two orders of magnitude higher than ratios calculated from laboratory experiments and implies a much lower carbon export efficiency than suggested in the various geo-engineering proposals.

In order to consider the impact of commercial iron fertilization, the patch size also has to be considered. In SOIREE AND SOFeX, the initial iron seeded patch size (200-250 km^2) spread to about 1000 km^2 by the end of observations, Taking these figures of carbon export and patch size, and extrapolating them to represent what impact commercial iron fertilization could have, Buesseler and Boyd (2003) calculated that one would need the equivalent of 1 million SOIREE or SOFeX experiments to achieve a downward particulate organic carbon flux at 100 meters equivalent to 30% of the carbon released annually as a result of human activities (1 million x 2000 tons particulate organic carbon export = 30% of annual carbon input of 6.5 billion tons). This would scale up to an area of 10^9 km^2, which is more than an order of magnitude larger than the entire area of the Southern Ocean (defined, in this case, as waters south of 50 ^{o}S). In conclusion, Buesseler and Boyd (2003) commented that iron fertilization on a commercial basis “may not be a cheap and attractive option if impacts on carbon export and sequestration are as low as observed to date”.

With regard to the low carbon export efficiency in mesoscale experiments, as compared to laboratory cultures, Buesseler and Boyd (2003) noted that this is not surprising because in an oceanic setting, not all the iron is bioavailable, and some is also lost by physical scavenging. In addition, the fraction of carbon leaving the surface waters on sinking particles is naturally low – typically <5 to 25% of total carbon uptake rates – due to efficient ‘recycling’ of carbon by zooplankton and microbes. In a further discussion of figures generated from SOFeX in relation to commercial iron fertilization, it was noted by Buesseler *et al.* (2004) that when remineralization rates were considered, SOFeX resulted in carbon sequestration below 250 metres of about 900 tonnes of carbon. This is a very small number when compared to the rates of carbon released globally due to human activities (6.5×10^9 tonnes/year). Thus it was noted that “it is difficult to see how ocean iron fertilization with such a low carbon sequestered to iron added export efficiency would easily scale up to solve our larger carbon imbalance problems”.

The mesoscale iron enrichment studies to date have also been short in time duration. In general, large diatoms have bloomed in these studies as a consequence of iron enrichment and escape from predation by larger zooplankton. The impact of longer-term iron fertilization is not known. It may give larger zooplankton time to increase, though how this would impact on the bloom signature is not known (Boyd *et al.* 2007). Barber and Hiscock (2006) discuss this point further. They suggest that continuous iron fertilization would not work because, for efficient carbon sequestration, a low abundance of mesozooplankton is necessary to enable diatom biomass to accumulate quicker that mesozooplankton can graze it. Continuous fertilization would allow the mesozooplankton enough time to respond to the increase in primary production and to become more abundant, such that they would increasingly graze and recycle a large proportion of the newly produced diatom biomass in the surface layer. This grazing pressure would prevent the accumulation of diatom biomass, which is necessary for efficient carbon export. In order to favour carbon sequestration, therefore, it would probably be necessary to repeat iron enrichments periodically, wherein picophytoplankton were again allowed to become dominant between fertilization events.

A further problem is the depletion of other macronutrients. Iron enrichment drives the consumption of nitrate, phosphate and silica at a rate faster than the ocean can re-supply these macronutrients. Therefore continuous fertilization would not continue to sequester additional carbon because these macro-nutrients would no longer be in sufficient supply and would, themselves, limit production.

A recently published study reported on a natural phytoplankton bloom over the Kerguelen plateau in the Southern Ocean (Blain *et al.* 2007). It was found that the bloom was sustained by iron and major nutrients supplied to the surface waters from iron-rich deep water below and surrounding waters. In terms of carbon sequestration, the efficiency of the iron fertilization (ratio of carbon export to the amount of iron supplied) was at least 10 times higher than previous estimates from mesoscale iron enrichment experiments. The results of this natural bloom are tightly linked to the mode of iron supply from below which differs from purposeful additions in mesoscale experiments. The study suggested that the natural system was far more sensitive to iron than implied by mesoscale iron addition experiments. However, the authors warn that "we emphasize that the high sequestration efficiency determined in the Kerguelen bloom should not be taken as an indication that controversial geo-engineering carbon dioxide mitigation proposals will be able to obtain high efficiencies". The results of the study did suggest that iron supply from below – as invoked in some paleoclimatic and future climate change scenarios – may have a more significant effect on atmospheric carbon dioxide concentrations than previously thought.

3.1.2 Modelling Studies

The results generated by modelling studies have not generally been favourable towards using oceanic iron fertilization as a climate change mitigation strategy. Sarmiento and Orr (1991) used an ocean general circulation model and found that iron fertilization would have the largest effect on atmospheric carbon dioxide reduction in the Southern Ocean (46-85 ppm reduction in a century). However, the model runs surface nutrients to zero, an extreme situation which is unlikely to be met in practice and ignores other factors that could limit nutrient uptake such as light supply and zooplankton grazing. Modelling also predicted that oceanic oxygen would be reduced significantly with anoxia resulting in the southwestern Indian Ocean. This would have a dramatic effect on ocean biology and chemistry in the region. Overall, it was concluded from the modeling scenarios that results echoed those of previous modeling studies, in that they implied that it is unlikely that an iron fertilization strategy will achieve much in practical application. In addition, iron fertilization would risk dramatic, unpredictable effects on oceanic ecology (Sarmiento and Orr 1991).

In a more recent study, Gnanadesikan *et al.* (2003) used an ocean general circulation model to consider more realistic scenarios involving the fertilization of smaller regions (several thousand square kilometers) for limited periods of time (of the order of 1 month). Various combinations of parameters were considered, including full or partial depletion of macronutrients; fertilization for one month of the year and consideration of the impact of future fertilizations; remineralization near the sea surface or remineralization at the sea bottom. Simulations were carried out for different combinations of these parameters. The model assumed that iron fertilization results in increased particulate organic carbon export, although in reality this has not always been shown in iron fertilization studies. The results and conclusions of this modeling study included the following points:

- Iron fertilization, resulting in depletion of other nutrients, can reduce biological productivity in the long term. For example, if fertilization is effective at causing drawdown of atmospheric carbon dioxide by exporting particulate organic carbon (POC) to great depths, it also exports phosphate to great depths. This means that less phosphate is available for tropical production and, over century timescales, the reduced production and, hence, reduced carbon export could be significant.
- The efficiency of carbon drawdown from the atmosphere resulting from tropical iron fertilization can therefore be very low, commonly less than 10% over 100 years. Furthermore, if remineralization occurs near the sea surface, drawdown efficiencies can be as low as 2% of the POC initially exported when extrapolated over 100 years.
- Modelling also showed that large scale fertilization could potentially remove the nutrient supply from biologically productive areas that support major fisheries. The net impact of macronutrient depletion on export production could be negative. In considering the southeast Pacific, where a significant proportion of the impacts were found in the modelling study, it was noted that this area accounts for almost 20% of global fisheries landings. Assuming that

fisheries landings are directly proportional to export flux, and using a worst case scenario in the model, it was found that the cost to fisheries could be highly significant.

In conclusion, the study noted that the results raised serious questions about the utility of iron fertilization for the reduction of atmospheric carbon dioxide. It revealed that atmospheric carbon dioxide drawdown associated with iron fertilization "is likely to be relatively inefficient, highly dependent on the remineralization profile, and may have disproportionate long-term impacts on export production. Insofar as reducing the supply of nutrients to the surface oceans would be expected to reduce the productivity of the surface ocean, macronutrient depletion with deep remineralization will not be particularly efficient at sequestering atmospheric carbon dioxide and subsequent impacts on fisheries might be large". The study also noted that verifying the quantity of carbon sequestered from iron fertilization is likely to be very difficult (if not impossible) because of the large spatial and temporal scales involved.

Zeebe and Archer (2005) used data on carbon export from the SOFeX iron enrichment experiment in various carbon cycle models to assess the feasibility of iron fertilization as a climate mitigation strategy. Modelling predicted that large-scale iron fertilization was not a feasible strategy to sequester anthropogenic carbon dioxide. For example, for a desired carbon export of 1 Pg C y^{-1}, (annual global carbon dioxide emissions from human activities are about 6.6 Pg C y^{-1}), the required annual fertilization area would be 15 times the total of the HNLC regions, equivalent to about twice Earth's surface - clearly impossible to carry out. And, even if considerable carbon export could be achieved by iron fertilization, the effective carbon sequestration is only about 10-25% of the carbon exported. So, for a desired carbon sequestration of 1 Pg C y^{-1} in the Southern Ocean, an additional export of at least 5-10 Pg C y^{-1} would be required. This would need 1000 to 2000 vessels or more for shipping the iron, and fertilizations at a frequency of 77 to 154 times per year. This is unrealistic and, in practice, the fertilized areas would simply become depleted of other nutrients. The study concluded tha,t based on results from SOFeX and currently available technology, large-scale iron fertilization is not a feasible strategy to sequester anthropogenic carbon dioxide.

3.2 Ecological Impacts

Proponents of ocean fertilization have claimed that iron fertilization would be environmentally benign, or even that it could contribute to 'ecosystem restoration'. This is not consistent with the blunt fact that iron fertilization significantly changes the composition of the phytoplankton community (Chisholm *et al.* 2001). In general terms, in the mesoscale iron fertilization studies, the biomass of smaller phytoplankton initially increased, but then stabilized as a result of grazing pressure whereas diatoms bloomed. As a consequence of changes to the plankton community, correspondingly, marine food webs and biogeochemical cycles would be altered in unintended and unpredictable ways. With significant changes in the plankton community and subsequent unknown effects on other species of the marine food web, large-scale iron fertilization cannot be viewed as environmentally benign, let alone beneficial. A study which serves to illustrate that fundamental changes in plankton communities of this nature, however they are induced, may have a detrimental impact on marine food webs is that of Freeland and Whitney (2000) in the Gulf of Alaska. This study reported that phytoplankton and zooplankton in the surface waters have decreased alongside temperature changes due to climate change and, concurrently, the numbers of salmon have decreased, possibly due to starvation.

As discussed in section 3.1.2 above, iron fertilization results in macronutrients (nitrate, phosphorous, silicate) being used up by phytoplankton (Barber and Hiscock 2006). Herein lies, another probable and detrimental ecological impact on communities down-current from an artificially iron-fertilized area. Reduced nutrient availability in ecosystems would result in reduced productivity and the structure of the marine food web could also be changed as a result. In this regard, it is of great concern that results of modelling by Gnanadesikan *et al.* (2003) implied that commercial iron fertilization could result in non-local impacts on marine biology, i.e. long-term reduction in biological productivity over a much wider ocean area, which could have a significant negative impact on fisheries.

Commercial iron fertilization may have the potential to cause still further ecological damage if it led to harmful algal blooms. Harmful algal blooms can have serious consequences for both marine life and humans (Sellner *et al.* 2003). Off the West Florida coast, harmful algal blooms (red tides) have been linked to iron supplied by wind-blown dust from the Sahara and to localized phosphorous input. It is thought that the iron in the dust leads to blooms of bacteria (*Trichodesmium*) which release nitrogen into the water. In turn, this creates an environment favourable to toxic red algae (*Karenia brevis*), resulting in red tides (NASA 2001, Walsh *et al.* 2006). Fishing, aquaculture and tourism are negatively impacted by such red tides because they can cause, *inter alia*, fish kills and shell-fish poisoning (NASA 2001). There is evidence that increasing desertification and eutrophication around the world is also leading to red tides in other places (Walsh *et al.* 2006). In the light of the risk of harmful algal blooms occurring as one consequence of an increased supply of iron, it would be prudent not to carry out large-scale iron fertilization as a carbon sequestration strategy.

Iron addition, and subsequent increases in phytoplankton growth, carbon export and remineralization, could also act to reduce oxygen levels in subsurface waters. It is possible that commercial long-term or large-scale fertilization programmes could create conditions with "zero oxygen concentrations" (anoxic conditions) at intermediate depths. Low oxygen levels and anoxic conditions would have a negative impact on all aerobic marine organisms.(Bakker 2004).

In support of their case, the proponents of commercial iron fertilization have also argued that iron fertilization would be similar to natural iron deposition from atmospheric dust and from natural upwellings of nutrients from the deep sea. In reality, however, commercial iron fertilization would not mimic nature (Chisholm *et al.* 2007). With regard to mimicking atmospheric dust deposition, although artificial iron addition in the mesoscale enrichment studies was analogous to natural episodic dust events, the total iron supplied in the experiments is much larger than natural dust deposition (Boyd *et al.* 2007) and this would be the case also in commercial iron fertilization operations. Furthermore, artificial addition of iron would require the use of an artificial chelator (such as lignin acid sulphonate) in order to keep the iron in solution, but this is chemically very different to natural atmospheric iron sources (Chisholm *et al.* 2001). The proposition that commercial iron addition would mimic natural upwelling nutrients is also misguided. Phytoplankton species that bloom in response to upwelling are adapted to a turbulent regime and a complex mixture of upwelling nutrients that are part of the natural nutrient regeneration cycle of the oceans (Chisholm *et al.* 2001).

Chisholm *et al.* (2001) noted that the carbon cycle is intimately coupled with those of other elements, some of which have critical roles in climate regulation. Therefore, it is not possible to sequester additional carbon without, in some way, changing coupled biogeochemical cycles.

3.3 Geophysical Concerns

3.3.1 Nitrous Oxide and Methane

Nitrous oxide is produced by the breakdown of inorganic nitrogen when organic matter is remineralized in the ocean's interior (Jin and Gruber 2003). One pathway is linked to the oxidation of ammonium to nitrate and a second pathway appears at low oxygen concentrations in which organic nitrogen is converted to nitrous oxide. Low oxygen levels and anoxic conditions, such as may be induced after large-scale iron fertilization, are likely to favour the production of methane and nitrous oxide. Both of these are far more powerful greenhouse gases than carbon dioxide (respectively 275 and 62 times more potent than carbon dioxide over a 20-year time scale in the ocean). Therefore, it is possible that iron fertilization could lead to increased release of these greenhouse gases, potentially counteracting any benefits of carbon dioxide sequestration by a considerable margin. Using modeling techniques, Jin and Gruber (2003) predicted that long-term iron fertilization could indeed induce nitrous oxide emissions that would offset the radiative benefits of the carbon dioxide drawdown.

In practice, there was evidence from the SOIREE iron enrichment study of a small, but nonetheless significant, nitrous oxide increase at the bottom of the mixed layer (Law and Ling 2001), although methane concentrations did not change (Bakker 2004). In contrast, nitrous oxide accumulation was not detected in EIFEX and may therefore not always be produced by iron fertilization. The authors noted, however, that the methodology employed may simply have failed to detect it. It was suggested that further long-term studies are needed to investigate the link between iron addition, enhancement of nitrous oxide formation and subsequent release of nitrous oxide to the atmosphere (Walter *et al.* 2005). In the meantime, since it is theoretically possible that nitrous oxide and methane may be produced as a consequence of iron fertilization, and the fact that nitrous oxide has already been detected in one mesoscale iron fertilization experiment, it would be prudent to err on the side of caution by not conducting commercial iron fertilization operations.

3.3.2 Dimethylsulphide (DMS) and Other Trace Gases

A question raised in a recent publication in regard to commercial iron fertilization is whether atmospheric trace gases, be they greenhouse gases or gases affecting air quality, would be changed (Lawrence 2002). The possibility of changes in such gases and subsequent unintended climatic or atmospheric change are important factors in the evaluation of ocean fertilization strategies. In this regard, Lawrence (2002) discusses the biogenic production of dimethylsulphide (DMS), and volatile organohalogens such as the methyl halides and carbonyl sulfide, which can occur during blooms of certain phytoplankton assemblages. It was noted that an increase in methyl halides or carbonyl sulfide would enhance stratospheric ozone depletion and therefore lead to intensified ultraviolet levels at the Earth's surface. Liss *et al.* (2005) present results of EisenEx which showed substantial increases in iodomethane (CH_3I) and dibromochloromethane ($CHBr_2Cl$), no change in methyl nitrate (CH_3ONO_2) and a decrease in bromoform concentrations. Since the results were not clear cut, it was suggested that further studies will be needed to predict the net effect of iron fertilization on air chemistry. In considering changes in some halocarbons and an alkyl nitrate during EisenEx, and changes in DMS concentrations in other studies, Bakker (2004) suggested that "changes in the marine source of these gases following iron fertilization could open a Pandora's box with feedbacks on atmospheric chemistry and global climate".

Some phytoplankton produce DMS as a metabolic byproduct, an important precursor for maritime sulfate aerosols and cloud condensation nuclei, which influence cloud properties and climate (Lawrence 2002). Turner *et al.* (2004) and Liss *et al.* (2005) noted that increases in DMS have been common to many iron fertilization studies. Three-fold increases are typical, but can be up to eight-fold. An increase in DMS could, in theory, work to reduce atmospheric temperature by enhancing the formation of reflective clouds, although the magnitude of any potential change is highly uncertain. Although DMS levels increased in many iron fertilization studies (Turner *et al.*, 2004), a reduction in DMS was recorded in SERIES and no change was observed in SEEDS I.

<u>3.4 Financial Cost</u>

Advocates of commercial-scale iron fertilization, often with the primary motive of generating money from carbon credit trading, claim that large scale iron fertilization could be a viable strategy to sequester carbon. However, to utilize iron fertilization as a carbon mitigation strategy would inevitably require the verification of the amount of carbon exported. Tracking the carbon sequestered, as well as any negative impacts such as de-oxygenation or nitrous oxide production, and so demonstrating a clear cause - and - effect of large scale fertilization, would be likely to prove incredibly expensive due to the requirement for detailed but large-scale, regional monitoring programs.

Quite apart from very costly monitoring, other primary costs arising from large-scale iron fertilization are also likely to be very substantial, including mining cost, other material costs and transport costs. As discussed earlier (section 3.1.1), geoengineering proposals for commercial iron fertilization have frequently claimed a low financial cost of $1-2 per metric tonne of carbon sequestered (Markels and Barber 2000). However, these are not based on knowledge from scientific mesoscale iron enrichment studies. Based on the IronExII and SOIREE experiments, Bakker (2004) estimated that continuous iron fertilization of waters south of 31^0 would require 6 x 10^6 tons of iron/year (1 ton = 10^6 g). This equates to about 1% of the global crude steel output of 700 x 10^6 tons iron/year. Iron mining to meet this requirement would strongly raise the economic and energy cost of iron fertilization. Transportation of the iron would also add to anthropogenic emissions of carbon dioxide from the use of fuel. To date, however, there have been no published attempts tp arrive at a full financial cost estimate of the process of iron fertilization, including the cost of the monitoring programs which would be a necessity for any proposals of commercial iron fertilization.

4. Conclusions

From scientific research published to date, it is apparent that iron fertilization would be highly inefficient in terms of carbon sequestration, as well as being highly impractical and costly. Iron fertilization on a commercial scale could be devastating to marine ecosystems including fisheries and, in this regard alone, the risks must be seen as totally unacceptable. Furthermore, commercial iron fertilization could have unpredictable impacts on atmospheric chemistry and global climate through the formation of climate-active gases. With regard to these uncertainties and the potential for adverse and irreversible consequences, it is vital that the precautionary principle be applied when considering any applications to pursue iron fertilization operations.

The precautionary approach is now central to the Convention on the Prevention of Marine Pollution by the Dumping of Wastes or Other Matter, otherwise known as the London Convention (1972). The Convention has a global character, and contributes to the international control and prevention of marine pollution. It now prohibits the dumping of all but a restricted range of waste materials, requires a waste prevention audit before dumping can be considered and sets out conditions under which any permissible dumping operations must be conducted.

Although initially established as the London Dumping Convention, with the primary role of overseeing the issuing of permits for waste dumping at sea (including, at that time, industrial and radioactive wastes), the London Convention has evolved into an instrument for which the main purpose is the prevention of pollution and the protection of the marine environment. Dumping of industrial waste was finally prohibited in 1996, a year which also saw the signing of a new protocol to the London Convention aimed at consolidating the more protective aspects of the Convention, adopted over the years by resolution. This includes the application of the precautionary approach, "whereby appropriate preventative measures are taken when there is reason to believe that wastes or other matter introduced into the marine environment are likely to cause harm even when there is no conclusive evidence to prove a causal relation between inputs and their effects".

The 1996 Protocol, or the London Protocol, entered into force in 2006 and continues to run in parallel with the existing Convention. Both bodies receive scientific advice on existing and emerging issues of pollution prevention from their Scientific Groups, which meet concurrently. At their most recent meeting, in June 2007, the Scientific Groups to the London Convention and London Protocol considered in detail the issue of commercial iron fertilization operations, and took the view that large-scale ocean iron fertilization operations are not justified by current knowledge on both effectiveness in sequestering carbon and potential negative impacts on environment and human health. Specifically, the Scientific Groups' Statement of Concern on large-scale iron fertilization is as follows:

1. Large-scale fertilisation of ocean waters using micro-nutrients such as iron to stimulate phytoplankton growth in order to sequester carbon dioxide is the subject of recent commercial interest. The Scientific Groups of the London Convention and the London Protocol take the view that knowledge about the effectiveness and potential environmental impacts of ocean iron fertilisation currently is insufficient to justify large-scale operations.

2. According to the Intergovernmental Panel on Climate Change (IPCC), iron fertilisation of the oceans may offer a potential strategy for removing carbon dioxide from the atmosphere by stimulating the growth of phytoplankton and thereby sequestering the carbon dioxide in the form of particulate organic carbon. However, the IPCC also stated that ocean fertilisation remains largely speculative, and many environmental side effects have yet to be assessed.

3. The Scientific Groups of the London Convention and London Protocol note with concern the potential for large-scale ocean iron fertilisation to have negative impacts on the marine environment and human health. They therefore recommend that any such operations be evaluated carefully to ensure, among other things, that such operations are not contrary to the aims of the London Convention and London Protocol.

In addition to this Statement of Concern another position statement on large-scale commercial iron fertilization has been issued by SOLAS SSC (Surface Ocean - Lower Atmosphere Study Scientific Steering Committee):

"Large-scale fertilisation of the ocean is being actively promoted by various commercial organisations as a strategy to reduce atmospheric CO_2 levels. However the current scientific evidence indicates that this will not significantly increase carbon transfer into the deep ocean or lower atmospheric CO_2. Furthermore there may be negative impacts of iron fertilization including dissolved oxygen depletion, altered trace gas emissions that affect climate and air quality, changes in biodiversity, and decreased productivity in other oceanic regions. It is then critical and essential that robust and independent scientific verification is undertaken before large-scale fertilisation is considered. Given our present lack of knowledge, the judgement of the SOLAS SSC is that ocean fertilisation will be ineffective and potentially deleterious, and should not be used as a strategy for offsetting CO_2 emissions" (SOLAS SSC 2007).

APPENDIX 1 - Findings of Twelve Mesoscale Iron Enrichment Experiments 1993-2005

The technology to measure ultra-trace concentrations of the inert gas sulphur hexafluoride (SF_6) made it scientifically possible to mark a patch of seawater and track it for long periods of time. This technology, coupled with iron enrichment, made it possible to assess ecosystem level responses to the addition of iron to the oceans (Watson *et al.* 1991, Martin *et al.* 1994).

A number of parameters were used in the mesoscale iron enrichment experiments to assess the biological response (plankton growth and species composition) and the chemical response (response of nutrients, carbon dioxide and exported carbon). Explanation of the terms used are as follows:

- size classes of phytoplankton: in order from smallest to largest - pico-phytoplankton , nano-phytoplankton, micro-phytoplankton

- chlorophyll a: phytoplankton pigment, used to measure total phytoplankton i.e. phytoplankton biomass

- photosynthetic competency (F_v/F_m): the potential photochemical efficiency of photosystem II. An indication of the photo-physiological state of the phytoplankton

- fugacity of carbon dioxide: the partial pressure of carbon dioxide corrected for the slightly non-ideal behaviour of the gas. Used in these experiments to monitor the drawdown of carbon dioxide by phytoplankton growth.

- DMSP and DMS: Dimethylsulphoniopropionate (DMSP) is produced by certain classes of phytoplankton. It degrades to dimethylsulfide (DMS), a climate-active gas that contributes to reduce the radiative flux to the Earth's surface (Levasseur *et al.* 2006).

- Carbon export: the quantity of particulate organic carbon (POC) that sinks to deeper waters. This is measured using sediment traps or the thorium-234 technique.

- The mixed layer: is a term used to describe the layer between the ocean surface and a depth (usually ranging from 25 to 200 metres) where the density is about the same as at the surface.

The findings of the twelve mesoscale iron enrichment experiments, conducted between 1993 and 2005, are discussed in chronological order below

IronEx I

Date: Mid-October 1993.

Location: Equatorial Pacific Ocean, approximately 500 km south of the Galapagos Islands.

Duration: 9 days.

Iron Fertilisation: Prior to iron fertilization, ambient iron concentrations in seawater in the area were of the order of 0.06 nM. Iron was added to surface waters concurrently with a tracer sulphur hexafluoride (SF_6) which enables rapid identification of iron-enriched waters. An area of about 64 km^2 was enriched with iron to yield a concentration of approximately 4nM. (Under experimental conditions, a concentration of 4 nM is sufficient to cause large increases in chlorophyll of phytoplankton and depletion of the available nutrients within 5 to 7 days). As predicted, the added iron and SF_6 tracer were distributed rapidly through the mixed layer (by horizontal eddy diffusion and convective overturn) (Martin *et al.* 1994).

Biological response: There was an increase in phytoplankton biomass (2-fold) estimated from cell number and volumes by microscopic examination. Chlorophyll increased by nearly 3-fold. Primary production was calculated to increase by 3-4 times in all size fractions of phytoplankton. There was an increase in photosynthetic energy conversion in all size classes of phytoplankton inside the fertilized patch. This indicated that at least some of the phytoplankton community were limited by lack of available iron.

The largest contributors to plankton biomass in the fertilized patch were *Synechoccus*, red fluorescing picoplankton. Diatoms were a small fraction of the total plankton biomass (17%) but showed increases similar to other groups (Martin *et al.* 1994).

Chemical response: Measurements of nutrients – nitrate, phosphate and silicate concentrations – within the mixed layer showed no difference inside the fertilised patch compared to outside the patch. (Note that the decrease in nitrate expected for the measured chlorophyll increase would be outside of the limit of detection in this study). Phosphate and silicate showed no change during the course of the experiment inside the fertilized patch.

Within 2 days of the iron release, measurement of carbon dioxide fugacity showed this parameter was significantly lower inside compared with outside the patch indicating drawdown of carbon dioxide inside the fertilized patch.

Particulate dimethylsulphonioproionate (DMSP), integrated throughout the water column, showed a significant increase (50-80%) in the fertilised patch. DMSP is produced by phytoplankton and decays to produce DMS. There were no changes in DMS concentration in surface waters. It was noted that this is not surprising considering the duration of the study compared to the time needed to degrade DMSP to DMS (Martin *et al.* 1994).

Carbon export, measured by thorium-234 technique or sediment trap was not measured in this study.

Study of a Natural Phytoplankton Bloom: In addition to studying iron fertilization, Martin *et al.* (1994) also investigated waters upstream and downstream of the Galapagos to evaluate the potential role of iron in regulating primary production. It has been hypothesised that the high chlorophyll levels found in Galapagos waters are caused by iron derived from the island platform. This study showed that the downstream plume had elevated chlorophyll in association with elevated iron concentrations. This result is consistent with the fore-mentioned hypothesis.

Conclusions: The results of this iron fertilization experiment demonstrated “a direct and unequivocal biological response of the equatorial Pacific ecosystem to added iron. The response observed in the fertilization experiment was similar in magnitude and character to the increased production and chlorophyll found in the Galapagos plume” (Martin *et al.* 1994).

Although the iron-fertilized patch was monitored for 9 days, it is highly likely that the response to the iron was limited to 4-5 days due to the patch becoming subducted beneath a layer of less-dense surface water.

It was noted that the purpose of the iron fertilization experiment was to understand the nature on the controls of primary production and ecosystem function in HNLC waters. It was not intended as preliminary steps to climate manipulation (Martin *et al.* 1994).

IronEx II

Date: May 29 to 15 June, 1995

Location: Equatorial Pacific Ocean, starting at 4^o S, 105^o W

Duration: 18 days.

Note: In IronEx I, the iron-fertilized patch was subducted beneath a layer of less-dense surface water and hence the size of the biological and geochemical response was much smaller than predicted from experimental data. Ironex II was designed to test various hypothesise on why the biogeochemical response in Iron Ex I was small (Coale *et al.* 1996).

Iron fertilization: 225 kg of iron (as acidic iron sulphate) was mixed with the tracer SF_6 and added to surface waters of a 72 km^2 rectangular patch. Two subsequent infusions were made, each of 112 kg of iron on days 3 and 7 of the experiment, to maintain the enhanced concentration of iron in the patch (Coale *et al.* 1996). The target iron concentration was 2 nM – a 40-fold increase from the 0.05 nM ambient concentration (Cavender-Bares *et al.* 1999). The multiple additions of iron over several days were used to simulate a natural iron event. It was noted that iron inputs of the magnitude used in this experiment are not uncommon in certain regions of today's oceans (Coale *et al.* 1996).

Biological Response: Total Chlorophyll a, a proxy for phytoplankton biomass, increased up to day 9 of the experiment. Biomass increased in all phytoplankton groups, but diatoms showed the by far greatest increase in biomass (85x). The bloom was dominated by the pennate diatom *Nitzschia spp*. Smaller phytoplankton also increased in biomass initially suggesting they were stimulated by iron addition but the biomass of microzooplankton (<200 µm) also increased at the same time. Results suggested that grazing by the microzooplankton kept the growth of the smaller phytoplankton in check. Overall, there was a shift in the phytoplanktom community composition from smaller cells (< 10 µm) which comprised 90% of the total initially, to large cells (>10 µm) which rose from 10 to 60% of the total (Cavender- Bares *et al.* 1999, Coale *et al.* 1996).

Results suggested that the smaller phytoplankton (picoplankton) were kept in check by grazing of the microzooplankton. On the other hand, diatoms were not suppressed by grazing of microzooplankton, presumably because they were too large to be grazed by these fast-growing organisms. In addition, the diatoms were too fast-growing to be suppressed by larger zooplankton – mesozooplankton – which have longer generation times with respect to the doubling of the diatoms (Coale *et al*. 1996).

The results of chlorophyll fluorescence indicated that there was an increase in cellular pigment concentration for all phytoplankton groups in response to iron treatment which means that the phytoplankton were iron-limited at the start of the experiment. The pennate diatoms were the only cells identified by the study that bloomed following iron enrichment (Cavender-Bares 1999).

Chemical Response: With regard to nutrients, there was a strong drawdown of nitrate (approximately 5µM) inside the iron-fertilised patch. Results suggested that diatom growth was responsible for most of the nitrate uptake (Coale *et al.* 1996).

The fugacity of carbon dioxide was significantly reduced within the iron-fertilized patch and paralleled the drawdown of nitrate. The iron-enhanced growth of the phytoplankton resulted in a carbon dioxide drawdown of about 90 µatm, which strongly reduced out-gassing of carbon dioxide from the iron-fertilized waters (Coale *et al.* 1996).

Carbon Removal: Particulate organic carbon (POC) and dissolved organic carbon (DOC) increased in the iron-fertilised patch. About 75% of the increase in POC was attributed to increase in living biomass and the rest from the accumulation of detrietal carbon as dead plankton remains.

Conclusions: The seeding of a patch of water in the equatorial Pacific with low concentrations of dissolved iron triggered a massive phytoplankton bloom which consumed large quantities of carbon dioxide and nitrate. The results, in combination with other studies, provide unequivocal support for the 'iron hypothesis' (that iron availability limits phytoplankton growth and biomass in the HNLC regions of the world's oceans) (Coale *et al.* 1996). In addition, the study indicated that phytoplankton community structure changes dramatically when productivity is stimulated by nutrient enrichment (Cavender-Bares *et al.* 1999).

The Southern Ocean Iron RElease Experiment (SOIREE)

Date: February 9th to 22nd 1999

Location: Australasian-Pacific sector of the Southern Ocean, south of the polar front, 61^{o} S 140^{o} E.

Duration: 13 days

Note: IronEx II showed that iron supply controls phytoplankton processes in the HNLC equatorial Pacific Ocean. The largest HNLC area in the world's ocean is the Southern Ocean. Therefore, in the light of findings of the IronEx II experiment in equatorial Pacific waters, a mesoscale iron enrichment experiment in the polar waters of the Southern Ocean – SOIREE – was the next logical step (Boyd and Law 2001).

Iron fertilization: As in IronEx I and II, dissolved iron and SF_6 were added to surface waters. Iron was released over an area of about 50 km^2. Iron concentrations in the water increased to about 3 nM. Subsequent additions were carried out on days 3, 5 and 7 to keep iron levels approximately constant. The patch expanded to cover 200 km^2 by day 13 (Boyd *et al.* 2000, Boyd and Law 2001).

Biological Response: Prior to iron fertilization, the phytoplankton community was dominated by picoplankton and nanoplankton and diatom abundance was low. After iron fertilization, there was a shift in community structure. Picoplankton stocks increased but were subsequently grazed down by micrzooplankton to their initial levels. Of the nanoplankton, haptophytes (<20 µm) increased in abundance. For larger phytoplankton, different species of diatom increased in their abundance and came to dominate the community after day 6. One species of pennate diatom in particular (*Fragilariopis kerguelensis*) increased and dominated the bloom. The chain length of this diatom increased from initial numbers of 6 cells long to 14 cells long by day 12 of the experiment. (Gall *et al.* 2001a). (Note: Natural phytoplankton blooms of *Fragilariopis kerguelensis* have been reported at the polar front in the Atlantic sector (Boyd *et al.* 2000)).

The first indication of a phytoplankton response to iron enrichment was a small increase in photosynthetic competence after 24 hours (Boyd *et al.* 2000). Primary production rates were slower to increase, becoming raised by day 7. Increases in primary production largely due to increases in microplankton (the dominant algae in which were diatoms) (Gall *et al.* 2000b). Chlorophyll a, a proxy for phytoplankton biomass, increased inside the iron fertilized patch but the response was 5 days slower than IronEx II. The slower growth was attributed to cooler water conditions (2.5 ^{o}C) in polar waters (SOIREE) compared to tropical waters (18.5 ^{o}C) (IronEx II) (Gall *et al.* 2001a).

Chemical Response: Iron fertilisation resulted in a drawdown of the macronutrients nitrate, phosphate and silica in ratios that were consistent with the growth of diatoms under iron-replete conditions (Frew *et al.* 2001).

There was a 30-40 µatm lower partial pressure of carbon dioxide inside the fertilized patch (Gall *et al.* 2001b). Thus as the fugacity of carbon dioxide decreased in the iron-fertilized waters they became a sink for atmospheric carbon dioxide. Outside the patch in unfertilized waters after day 4, the fugacity of carbon dioxide in surface waters increased slightly, making these waters a small source of carbon dioxide to the atmosphere (Bakker *et al.* 2001).

Particulate dimethylshlphoniopropionate (DMSP) levels increased inside the patch after day 3. Dissolved dimethyl sulphide (DMS) concentrations increased on day 8 and tripled by day 13 (Boyd *et al.* 2000).

Law and Ling (2001) reported a minor increase in the production of nitrous oxide at the base of the iron-fertilized patch. Nitrous oxide is a powerful greenhouse gas and it was suggested that an benefit in lowering carbon dioxide levels in the atmosphere by iron fertilization in regard to climate change may be negligible due to enhanced nitrous oxide production.

Carbon Removal: Carbon export was monitored by the deficit of total thorium (^{234}Th) in the upper 100 metres of water and measurement of particulate organic carbon (POC) in sediment traps.

Estimates of carbon export using the ^{234}Th technique showed no increase in export. Measurements from sediment traps showed some increases in the export of POC but when controls were considered the results were ambiguous (Boyd *et al.* 2000, Fasham *et al.* 2006).

Conclusions: The SOIREE experiment demonstrated iron addition to surface waters elevated phytoplankton biomass and rates of photosynthesis causing a large drawdown of carbon dioxide and macronutrients, and increased DMS levels. This drawdown was mostly due to proliferation of diatom stocks but the export of carbon was not increased. Overall, the experiment showed that iron controls plankton growth and community composition during the summer in the polar waters of the Southern Ocean but the fate of phytoplanktonic carbon remains unknown (Boyd *et al.* 2000).

EisenEx

Date: 8 to 30 November 2000 (austral spring).

Location: Atlantic sector of the Southern Ocean 48^{o} S 21^{o} E

Duration: 22 days.

Note: The goal of EisenEx was to test the hypothesis that primary productivity in the Southern Ocean is limited by iron availability in the austral spring. EisenEx differed from SOIREE in the season it was performed and was at a different location in the Southern Ocean (Gervais *et al.* 2002).

Iron Fertilization: 780 kg of acidified iron sulphate containing the tracer SF_6 was deployed to enrich an area of about 50 km^2. Subsequent enrichments (of 780 kg) of iron were carried out on day 8 and day 16 of the experiment. Before the start of the experiment, the iron concentration was <0.1 nM. Iron additions theoretically raised backgrounds concentrations to between 2.5 to 3.8 nM (Bakker *et al.* 2005, Gervias *et al.* 2002).

Biological Response: At the start of the experiment the phytoplankton community was dominated by picophytoplankton and nanophytoplankton. Diatoms were species rich (>50 species) but low in number. After iron fertilization the community changed in composition. Measurements of chlorophyll a showed that biomass of pico-, nano- and microplankton started to rise 4 days after iron infusion. Henceforth, picophytoplankton showed no further increase in biomass whereas nano- and micro-phytoplankton (which includes diatoms) increased continuously at almost equal rates until day 16. After this, microphytoplankton showed the strongest increase. By the end of the experiment, diatom biomass had increased five-fold and the dominant diatom species was the pennate diatom *Pseudo-nitzschia lineola* (Assmy *et al.* 2007, Gervais *et al.* 2002). Assmy *et al.* (2007) noted that the species composition of the artificially iron-fertilized phytoplankton blooms experiments in the waters of the Antarctic Circumpolar Current of the Southern Ocean are similar to natural oceanic blooms fertilized by natural sources of iron along oceanic fronts and from melting icebergs discharging their accumulated dust load in surface waters. Iron-fertilization experiments may therefore represent a method to advance the understanding of oceanic phytoplankton ecology.

In waters outside the iron-enriched patch, measurements showed that photosynthetic efficiency (F_v/F_m) was low and there was low daily primary productivity. Inside the iron-enriched patch, photosynthetic efficiency increased. Primary productivity increased from day 2 onwards inside the patch, reached a maximum on day 16 and decreased thereafter. Microplankton became the dominant producer (>50%) inside the patch by the end of the experiment (compared to 10 to 38% outside the patch) (Gervais *et al.* 2002).

Chemical Response: Concentrations of the major nutrients phosphate, nitrate and silicic acid all decreased during the experiment but did not become limiting to phytoplankton growth (Assmy *et al.* 2007, Bakker *et al.* 2005).

Measurements of carbon dioxide fugacity showed there was drawdown of carbon dioxide during EisenEx, the iron- enriched waters becoming a sink for atmospheric carbon dioxide. A storm on days

6 and 7 increased the size of the patch and any carbon dioxide fugacity reduction was lost by the dilution, but on days 8 to 12 carbon dioxide fugacity decreased again (by about 18 µatm below ambient value). Another storm then ensued and lessened carbon dioxide fugacity but after the storm the carbon dioxide fugacity gradually decreased again (reaching 20 µatm after 21 days). Calculations showed the total biological uptake of inorganic carbon across the patch was 1433 tons (where 1 ton = 10^6g). This was similar to SOIREE (1389 ton) probably reflecting the similar size of iron additions (Bakker *et al.* 2005).

Carbon Removal: An increase in carbon export may have occurred during EisenEx but it is not possible to tell how much carbon eventually left the surface ocean (Bakker *et al.* 2005).

Conclusion: The results of EisenEx provide unequivocal evidence that iron supply is the central factor controlling phytoplankton primary productivity in the Southern Ocean (Gervais *et al.* 2002).

The Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS I)

Date: 18 July to 1 August 2001

Location: 48.5^0 N 165^0 E, near the centre Western Subarctic Gyre of the North Pacific

Duration: 14 days

Note: Previous mesoscale iron enrichment experiments in the equatorial Pacific Ocean and Southern Ocean confirmed the iron limitation hypothesis in these regions. The subarctic Pacific was the remaining major HNLC region where an iron enrichment experiment had not been performed. SEEDS I was undertaken to investigate this region (Tsuda *et al.* 2003).

Iron Fertilization: 350 kg of acidified iron sulphate containing the tracer SF_6 was released to enrich an area of about 80 km^2. The single addition of iron initially raised dissolved iron levels to about 2.9 nM after which levels decreased to 0.15 nM by the end of the experiment (Takeda and Tsuda 2005, Tsuda *et al.* 2003).

Biological Response: There was a shift in community structure of phytoplankton from a pico- and nano-phytoplankton dominated community to a micro-phytoplankton dominated community. Biomass of phytoplankton increased, as shown by a rapid and exponential increase in phytoplankton chlorophyll a from day 6 to day 10. Although biomass of pico- and nano-phytoplankton increased 2- and 5-fold respectively, micro-phytoplankton increased 45-fold during the 13 day observation period of the experiment.

The change from a community formed of smaller phytoplankton to one dominated by larger diatoms in SEEDS I is similar to shifts in community witnessed in other mesoscale iron enrichment experiments. However, previous experiments resulted in the stimulation of pennate diatom growth whereas SEEDS I resulted in increased growth of chain-forming centric diatoms with one dominate species in particular, *Chaetoceros debilis*. Prior to the SEEDS I experiment, the dominant diatom in the area was a species of pennate diatom and *C. debilis* was a negligible component. By day 6 of the experiment *C.debilis* came to dominate, eventually accounting for 90% of the micro-sized phytoplankton abundance (Takeda and Tsuda 2005, Tsuda *et al.* 2003).

It was noted that *C. debilis* is known to be a major phytoplankton species in spring bloom conditions in the North Pacific, but the SEEDS I bloom lacked other major species common in natural blooms in the area (Takeda and Tsuda 2005).

During SEEDS I, primary production increased around 5-fold. Photosynthetic efficiency (F_v/F_m) increased after day 3 up until day 9 after which it decreased. This, together with other results, suggested that phytoplankton growth on day 10 onwards became limited by iron and possibly also by light due to self-shading (Takeda and Tsuda 2005, Tsuda *et al.* 2003).

Chemical Response: The phytoplankton bloom of SEEDS I resulted in large decreases in the concentrations of macronutrients, nitrate, phosphate and silicate. There was also a marked drawdown of carbon dioxide indicated by a decrease in carbon dioxide fugacity.

DMS production was reported to be little stimulated in SEEDS I. This correlated with the fact that a pigment of phytoplankton called prymnesiophytes (which are probably responsible for elevated DMS) increased by only 3-fold during SEEDS I.

Carbon Removal: Results of the experiment suggested that most of the particulate organic carbon remained in surface waters throughout the experiment and was not exported to deeper water. For example, there was no increase in particulate organic carbon export observed by the sediment traps and little detected using ^{234}Th as a tracer (Takeda and Tsuda 2005).

Conclusion: SEEDS I demonstrated that iron availability controls phytoplankton abundance in the HNLC waters of the western subarctic Pacific. It also showed that all HNLC waters do not respond identically to an increase in iron supply – in SEEDS I there was a rapid and extensive response of phytoplankton to iron enrichment due to the presence of the fast-growing centric diatom *C. debilis* – the growth rate was 1.8 times higher than pennate diatoms which dominated in IronEx II and SOIREE. This suggested that species composition of phytoplankton at the start of the experiment strongly influences the ecosystem's response to iron addition (Takeda and Tsuda 2005, Tsuda *et al.* 2003).

Southern Ocean Iron Expriment (SOFeX-S and SOFeX-N)

Diatoms require the macronutrient silicic acid for their growth. Although all Southern Ocean surface waters have high concentrations of the macronutrients nitrate and phosphate, which are also required for phytoplankton growth, silicic acid concentrations differ significantly from north to south. Subarctic waters north of the Antarctic Polar Front Zone (APFZ) have low silicic acid concentrations (1 to 5µM) whereas to the south, silicic acid concentrations are high (>60 µM). This difference in silicic acid concentrations suggests that iron addition to surface waters would cause diatoms to bloom in the high silicic acid waters of the south whereas nonsiliceous phytoplankton would more likely bloom in low silicic acid waters of the north.

Previous iron enrichment experiments in the Southern Ocean took place in the Australian sector (SOIREE) and the Atlantic sector (EisenEx). In these areas there are moderate concentrations of silicic acid. Natural phytoplankton blooms in these regions each year deplete the waters of silicic acid. SOIREE and EisenEx did not demonstrate the potential interactions of iron and silicic acid to regulate phytoplankton growth, and hence the carbon cycle, in very low silicic acid waters north of the APFZ or in the high silicic acid waters to the south where no silicic acid depletion occurs. This study, SOFeX, was undertaken in the northern waters (SOFeX-N) and southern waters (SOFeX-S) of the Southern Ocean to address this issue (Coale *et al.* 2004).

Date: Northern patch : 12 January 2002.
Southern patch: 24 January 2002

Location: Northern patch: 56.23^0 S, 172^0 W in the Subantarctic Zone
Southern patch: 66.45^0 S, 171.8^0 W in the Subpolar Region

Duration: 39 days

Iron Enrichment: An acidified iron sulphate solution containing SF_6 tracer was added to areas 15 km x 15 km in the north and the south areas. Multiple iron enrichments were carried out to maintain a level of iron that exceeded saturation for phytoplankton growth. In the northern patch, surface water concentrations of iron were approximately 1.2 nM and in the southern patch 0.7 nM.

Biological Response: In both the north patch and south patch, iron addition caused enhanced growth of the larger sized phytoplankton groups. In the north patch, growth of larger cells (>5 µm) was enhanced whereas the size structure of the phytoplankton community remained unchanged in the south. In the north patch (low silicic acid) there was enhanced growth of flagellated phytoplankton groups (that is, non-siliceous phytoplankton) as well as the diatom *Pseudonitzchia* spp. By day 38 of the experiment, compared with other phytoplankton, diatom biomass showed the greatest change with respect to initial levels although they represented somewhat less than half of the total. The south patch on the other hand was dominated by diatoms both inside the patch and in control regions outside the patch.

Photosynthetic competency (F_v/F_m) increased after iron addition in the north and south patch indicating that the photosynthetic community was relieved from iron limitation. Chlorophyll a concentration in the north and south patch increased by factors of 10 and 20 respectively indicating an increase in biomass. Results of primary production suggested that light limitation attenuated the development of blooms in the north and south patches (Coale *et al.* 2004).

Chemical Response: Iron addition resulted in enhanced rates of nitrate uptake in the north and south areas with clear decreases in the nitrate concentration in surface waters. Silicic acid uptake rates increased in the north and the south patches. Even though the northern patch was low in silicic acid, the maximum rates of primary production were about double those in the south patch. Most of the difference is most likely attributable to higher temperatures in the north patch and "demonstrates that the low silicic acid concentrations do not necessarily limit primary productivity or particulate organic carbon accumulation after iron addition to low silicic acid waters" (Coale *et al.* 2004).

Carbon dioxide fugacity decreased in the north and south patches by about 40 µatm. Total inorganic carbon (TCO_2) concentrations became depleted in the north and south patches as iron increased photosynthetic rates and nitrate consumption (Coale *et al.* 2004).

Carbon Removal: Particulate organic carbon export from the blooms into the deep ocean was measured during the course of the experiments. For the northern patch, an autonomous profiler was "parked" at 100m depth and recorded carbon export flux over more than 50 days. For the southern patch export was monitored using the thorium-234 deficit method. Both methods reported several-fold higher export from iron enriched waters compared to adjacent non-enriched waters (Boyd 2004). However, the magnitude of the particulate organic carbon export was small relative to natural blooms from the region. With this in mind, in regard to proposals for carbon sequestration from commercial iron enrichment, the very small amount of carbon sequestered would not be able to impact on solving global carbon imbalance problems (Buesseler *et al.* 2004). SOFeX and previous mesoscale iron enrichment studies have not demonstrated a large carbon export response to artificial addition of iron (Buesseler *et al.* 2005).

Conclusion: SOFeX demonstrated that iron availability is the fundamental factor limiting primary productivity in both the high and low silicic acid regions of the Southern Ocean during the austral summer. The addition of iron causes the removal of silicic acid from the surface mixed layer due to the increased production of diatoms in both the north and south enrichment sites (Hiscock and Millero 2005). The results of SOFeX also "strongly suggest that the Southern Ocean was more productive and exported more carbon during periods of higher atmospheric iron input, which occurred during the last glacial maximum" (Coale *et al.* 2004).

Subarctic Ecosystem Response to Iron Enrichment (SERIES)

Note: SERIES was undertaken to study both the evolution and termination of an iron-induced diatom bloom in the HNLC waters of the northeast subarctic Pacific. Previously, only one iron enrichment study, IronEx II, had investigated the termination of a bloom.

Date: 9 July to 4 August 2002

Location: Northeast subarctic Pacific, 50km northeast of Ocean Station Papa (50^o N, 145^o W) in the Gulf of Alaska.

Duration: 25 days

Iron Fertilization: Dissolved iron and the tracer SF_6 were added to a $77km^2$ patch and raised iron concentrations in seawater to > 1 nmol/L. A second iron infusion was added on day 6 of the experiment.

Biological Response: Before iron enrichment, the phytoplankton community was dominated by small phytoplankton, specifically *Synechoccus* and haptophytes with diatoms making only a small contribution. Following iron enrichment *Synechoccu*s initially increased until day 4 when it returned to ambient levels while haptophtes increased from days 4 to 11. After day 6 there were exponential increases in diatom stocks (comprised of several species). Diatoms peaked on day 17 and then subsequently declined.

Chlorophyll increased after iron fertilization and primary production also increased (Boyd *et al.* 2005). Photosynthetic competence (F_v/F_m) increased, plateaued and subsequently declined after day 12. The decline reflected iron limitation.

Results indicated that the bloom in SERIES peaked around day 16-17, then terminated, with a rapid decline in phytoplankton stocks thereafter. There was evidence that the bloom terminated due to nutrients becoming limited (iron on day 12 and silicic acid on days 15-16) and possibly also mass sedimentation of phytoplankton. Similarly, for the Iron Ex II bloom, termination was probably triggered by iron and silicic acid depletion although it is thought that microzooplankton herbivory on the dominant diatom was also a factor in the termination of this bloom (Boyd *et al.* 2005).

Chemical Response: DMSP increased in SERIES for several days alongside the nanophytoplankton bloom. As the bloom collapsed due to zooplankton grazing, DMSP also declined back to initial levels and remained low as the large diatoms subsequently bloomed. DMS levels increased inside the patch up to day 6 by 2-fold but then became persistently lower. This result differs to previous iron enrichment experiments (Iron Ex II, SOIREE, EisenEx) where a doubling of DMSP levels led to a subsequent increase in DMS levels by 1.7-6.8 times but not a reduction. This would be expected because DMS is a breakdown product of DMSP. The lowering of DMS levels in SERIES is thought to have been caused by a very high metabolism of DMSP by bacteria and possibly micrograzers. The authors noted that no increase in DMS was recorded in SEEDS I. It was concluded that the results of SERIES confirm the rapid increase in nanoplankton and DMSP reported in other iron enrichment experiments but results on DMS are a clear departure from other studies. Since DMS emissions act to reduce the radiative flux to the Earth's surface, it was noted that a reduction in DMS levels from artificial iron fertilization may not always lead to conditions that could mitigate climate warming (Levasseur *et al.* 2006).

During the period of algal growth, the macronutrients nitrate, silicic acid and phosphate all reduced (Boyd *et al.* 2005). Carbon dioxide fugacity decreased during some stages of the bloom with a total drop of 85 µatm (Wong *et al.* 2006). Particulate organic carbon increased during the development of the bloom alongside chlorophyll increase (Boyd *et al.* 2004).

Carbon Removal: The decline of the bloom was signaled by rapid decrease in particulate organic carbon after day 18. Using sediment traps set at depth, it was found that only 18% of the decrease in particulate organic carbon was sequestered to 50m depth and only 8% to 125m depth. It was calculated that at least 69% of the deficit in particulate organic carbon during the bloom decline was due to bacterial remineralization both within and below the mixed layer. Thus only a small fraction of the particulate organic carbon from the bloom was exported to the deeper ocean. The export to 125m depth (8%) was low compared with naturally occurring blooms (15-30%) (Boyd *et al.* 2004).

Conclusion: Termination of the bloom was not only influenced by iron limitation but also silicic acid availability. In terms of commercial iron enrichment proposals, eventual depletion of silicic acid may negate the impact of repeated iron enrichment on diatom stocks. In addition, SERIES showed the export of carbon from an iron-induced bloom was inefficient and may therefore limit the effectiveness of using iron fertilization for carbon sequestration purposes (Boyd *et al.* 2004).

European Iron Fertilization Experiment (EIFEX)

Date: 21 January – 4 March 2004 (Southern Hemisphere autumn)

Location: 50^{o} S, 2^{0} E in the Southern Ocean (subpolar South Atlantic Ocean).

Duration: 44 days

Iron Enrichment: A relatively stable water mass, an eddy, was fertilized with 6000 kg of iron sulphate over an areas of 150 km^2. Before fertilization, iron concentrations were about 0.08-0.2 nmol/L. After fertilization the iron concentration was approximately 2 nmol/L. A second fertilization was conducted on day 15 because iron levels had fallen to 2-3 times background levels. After the second fertilization, iron concentrations remained significantly elevated above background levels (Hoffmann *et al.* 2006, Walter *et al.* 2005).

Biological Response: The main beneficiaries of the iron fertilization were large diatoms (of size >20µm) which underwent massively enhanced growth. This is comparable to other iron fertilization experiment results described for different HNLC regions. In EIFEX, the increase in larger micro-phytoplankton diatoms did not change the relative group composition of the micro-phytoplankton though because diatoms were already dominant at the start of treatment. Other diatoms, of size fraction >2µm also increased during EIFEX, the smaller of them (2-8 µm) increasing more than the larger fraction (8-20 µm). This indicated that even very small diatoms enhance their growth rates due to iron fertilization. The increase in these diatoms (2-8 µm) changed the community composition of this size fraction from a haptophyte to a diatom-dominated community (Hoffman *et al.* 2006).

It is thought that the reason why larger diatoms tend to have an advantage over other phytoplankton groups under high iron conditions is due to their low surface to volume ratio. However, other diatoms may also be beneficiaries from iron fertilization as well because diatoms have a generally better ability to take up and store iron compared with other phytoplankton groups. Secondly, diatoms are better protected against grazing pressure by their silica frustules compared with other, naked phytoplankton groups.

Chlorophyll a increased after iron fertilization indicating an general increase in biomass of phytoplankton. The increase was of the same magnitude as the two Southern Ocean iron fertilization experiments SOIREE and EisenEx. Of the different size classes of phytoplankton (pico-, nano- and micro-), microphytoplankton showed the strongest biomass increase during EIFEX as determined by chlorophyll a, increasing its relative amount of total chlorophyll a from 12% to 46%. Toward the end of the experiment, a general decline in chlorophyll a (and some other parameters) suggested the demise of the iron-induced bloom (Hoffmann *et al.* 2006).

Chemical Response: Nitrous oxide measurements taken during EIFEX revealed that there were no significant changes in nitrous oxide concentrations. This is in contrast to the SOIREE experiment in which nitrous oxide levels increased. In SOIREE, iron fertilization was performed four times during one week over a smaller area. The increase in nitrous oxide may therefore have been a response to the intensive short-term iron fertilization. In contrast, nitrous oxide sampling did not start until day 16 of EIFEX and it was therefore suggested that a short term increase in nitrous oxide may have been missed during EIFEX. In addition, during EIFEX there was rapid export of fresh organic phytoplankton material to the deep ocean about 23 days after the second iron addition. Such a rapid export may have been too rapid for the nitrifying bacteria in the deep ocean to adapt so that a build of nitrous oxide could not take place. It was suggested that further research is necessary to prove a link between iron enrichment and nitrous oxide formation (Walter *et al.* 2005).

Note that data on carbon dioxide fugacity and carbon export has not yet been published for EIFEX (personnel communication with Linn Hoffmann)

SOLAS Air-Gas Exchange Experiment (SAGE).

Note: SAGE aimed to study the exchange of gases important to climate (carbon dioxide and DMS) in the Southern Ocean in a semi-controlled situation – by stimulating the growth of plankton through iron fertilization over 50 km^2. It was expected that these conditions would provide an enhancement of gas fluxes for several weeks. SAGE also aimed to provide an understanding of the physical, biological and chemical processes governing the interchange of gases to enable predictions to be made on timing and magnitude of future changes in climate (NIWA Science 2007).

Date: March/April 2004

Location: 46.5^{o}S, 172.5^{o}E in the southwest of the Bounty Trough to the southeast of New Zealand (western Pacific sector of the Southern Ocean).

Duration: 15 days

Iron Fertilization: 1.35 tonnes of dissolved iron sulphate with added SF_6 tracer was dispensed over an area of 40 km^2. In total, four iron additions were made over a period of 15 days.

Biological Response: The phytoplankton population response to iron fertilization was unexpectedly slow and limited. Chlorophyll a only doubled in the fertilized patch. This was considered to be a very modest response compared with previous iron fertilization experiments (Harvey *et al.* 2004). The response seemed to have been limited by other factors, possibly light availability, other micronutrients, grazing by zooplankton or dilution of the fertilized patch. At a meeting to discuss the results of the previous 10 iron fertilization experiments, which informed the Collective Findings Synthesis, light availability was identified as critically important, with the SAGE experiment conducted under the lowest light conditions of all the experiments (Law 2006).

Chemical Response: There was little evidence of enhanced carbon dioxide uptake or increased production of DMS and other trace gases (Law 2006).

Conclusion: "Although the SAGE experiment did not generate strong gas gradients, it provided a contrast to other iron fertilization experiments and showed that iron addition alone is not a panacea to promoting phytoplankton stocks and carbon dioxide uptake in iron-limited waters" (Law 2006).

FeeP – a dual release, dual ship experiment to investigate nutrient limitation of biological activity in the north-east Atlantic.

Only one short reference is available to date on FeeP (Rees *et al.* 2005).

Phytoplankton productivity in two-thirds of the global ocean appears to be limited by nutrient availability. Nitrogen is thought to be the most likely candidate but other elements, including iron and phosphorous may well be important. FeeP was the first experiment to investigate the possible interaction of iron and phosphorous in controlling phytoplankton growth in an in situ experiment.

FeeP makes a shift from the other iron fertilization experiments in focusing on Low Chlorophyll Low Nutrient (LCLN) regions rather than HNLC regions. Iron may play a role in LCLN regions via the stimulation of nitrogen fixation where it is required as a component of the genes for diazotrophy. Therefore, an iron-induced increase in nitrogen fixation may fuel increased primary production (as the nitrogen is released and recycled in the non-nitrogen fixing organisms) and so increase carbon fixation and carbon export.

Fertilization: Two 25 km^2 patches of ocean were "seeded", the first with 20 tonnes of phosphate, and the second with phosphate and iron sulphate. SF_6 was used as a tracer.

Biological Response: Results for the phosphate seeded patch showed there was initially little effect on phytoplankton photosynthesis, but bacterial productivity was enhanced by up to three-fold for a short period after the phosphate addition.

Results for the iron and phosphate seeded patch showed there were significant changes in phytoplankton community composition.

Conclusion: There is still work to do on sample analysis but it is apparent that FeeP will reveal hitherto unknown insights into marine nutrient cycling (Rees *et al.* 2005).

APPENDIX 2 - REFERENCES

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