

# Ocean Iron Fertilization

## Enrichment or back to the Iron Age?

An overview of Ocean Iron Fertilization as a potential climate mitigation tool

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## Introduction

The increase in concentration of atmospheric carbon dioxide (CO<sub>2</sub>), together with other greenhouse gases, has been shown to be the leading cause of climate change. Since 1999 the actual rate of increase in CO<sub>2</sub> exceeds even the highest of the so-called SRES emission scenarios of the Intergovernmental Panel on Climate Change (IPCC) (Raupach et al. 2007). To limit climate change, both the Kyoto Protocol and the recent Copenhagen Accord acknowledge the importance for aiming to keep temperature rises below 2°C. This challenge means leveling off atmospheric CO<sub>2</sub> concentration to around 450 ppm. As shown by recent models, we must eventually reduce CO<sub>2</sub> emissions by at least 90% (Weaver et al. 2007, Matthews & Caldeira 2008). Because the deadline of the first "commitment period" of the Kyoto Protocol (1997), which is due to expire at the end of 2012, is approaching fast, it is clear that only limiting greenhouse gas emissions is not enough.

Several mitigation methods have been developed and proposed, such as alternative energy towards fossil fuel burning, reflecting particles in the stratosphere or establishing large-scale plantations. Also several 'geo-engineering options' have been suggested to actively remove CO<sub>2</sub> from the atmosphere. Would there be a cheap and safe way to do this?

One of the 'geo-engineering options' that has received considerable interest by science and media has been the concept of Ocean Iron Fertilization (OIF). To reduce atmospheric CO<sub>2</sub> concentrations dissolved iron is added to enhance growth of phytoplankton in ocean regions where iron is limiting (High Nutrient, Low-Chlorophyll regions). These regions are found in the Southern Ocean, the subarctic Pacific and the equatorial Pacific. By adding iron in these regions, that would otherwise contain very little organic material, growth of phytoplankton is boosted. This causes an increase in photosynthetic uptake of atmospheric CO<sub>2</sub>. The organic material would then sink down to the deep ocean, where carbon storage in the deep ocean seabed should occur.

Since the development of this hypothesis in 1990 (Martin, 1990), a vast amount of research has been done to investigate the potential of OIF as a plausible mitigation strategy. Next to several laboratory culture experiments (Sunda & Hutsman 1995), shipboard studies (Hutchins et al. 2001) and modeling simulations (Aumond & Bopp 2006) the most valuable data has been obtained by several mesoscale OIF experiments. These experiments provide an initial assessment of the difficulties of conducting OIF, the apparent magnitude of its actual carbon storage and the possible harmful side effects.

Although OIF is initially regarded as a relatively low-cost and easy strategy compared to other mitigation measures, research has shown that this is not truly the case. Furthermore, the ethics of interfering with the biochemical cycle of the earth on such a massive scale are extensively debated. Also it is difficult to assess how to work out political frameworks for conducting OIF globally. (Chrisholm & Morel 1991)

In this bachelor thesis my aim is to give the reader a clear overview of the results of the last twenty years of research conducted on OIF, the potential magnitude of carbon storage, the natural implications of OIF and the risk of possible unwanted side effects. Additionally, a comparison of OIF with the costs and risks of other mitigation measures will be presented. I will conclude with an overall evaluation of the feasibility of OIF and its future prospects.

## Chapter 1: The Iron Age in Oceanography

### Iron requirement in phytoplankton

Phytoplankton requires certain essential nutrients for growth. Carbon, nitrogen and phosphorus are essential macronutrients and are needed in a well-defined ratio, the so-called Redfield Ratio (106 C: 16 N: 1 P). For every 106 atoms of carbon that are turned into organic matter, 16 atoms of nitrogen and 1 atom of phosphorus are needed. For certain groups of phytoplankton calcium or silicon are important nutrients, of which they build their cell walls, or shells. Phytoplankton also needs very small amounts of trace metals such as iron, copper, zinc and cobalt. Iron is a vital micronutrient in chlorophyll synthesis (in key-enzymes like ferredoxin) and in nitrate reduction. When taking iron requirement into account, the Redfield Ratio constant may be expanded to "106 C: 16 N: 1 P: 0.001 Fe", expressing that (in iron deficient conditions) each atom of iron can theoretically be sufficient to fix 106,000 atoms of carbon (Sunda & Hutsman, 1995).

### Regions with iron limiting phytoplankton growth

Iron has been regarded to be a limiting factor for phytoplankton growth in certain regions of the ocean for decades. Already in 1931, Gran suggested that if growth of phytoplankton is dependent on a factor that limits the production, that factor would probably be an element which "in its circulation does not follow the nitrates and phosphates accumulating in solution in the deep sea and reaching the surface again by vertical circulation of any kind". He suggested that that element would "irreversibly go out of the circulation in the sea, and could only be renewed from the land" (Gran, 1931). He concluded that growth was probably mostly limited by iron (Fe). Iron is usually delivered to the ocean water masses by dust storms from arid lands or weakly by upwelling of deep waters. Data obtained in that time showed the iron content of seawater to be very low (ranging from 3 to 21 mg Fe per m<sup>3</sup>) (Braarud & Klem, 1931).

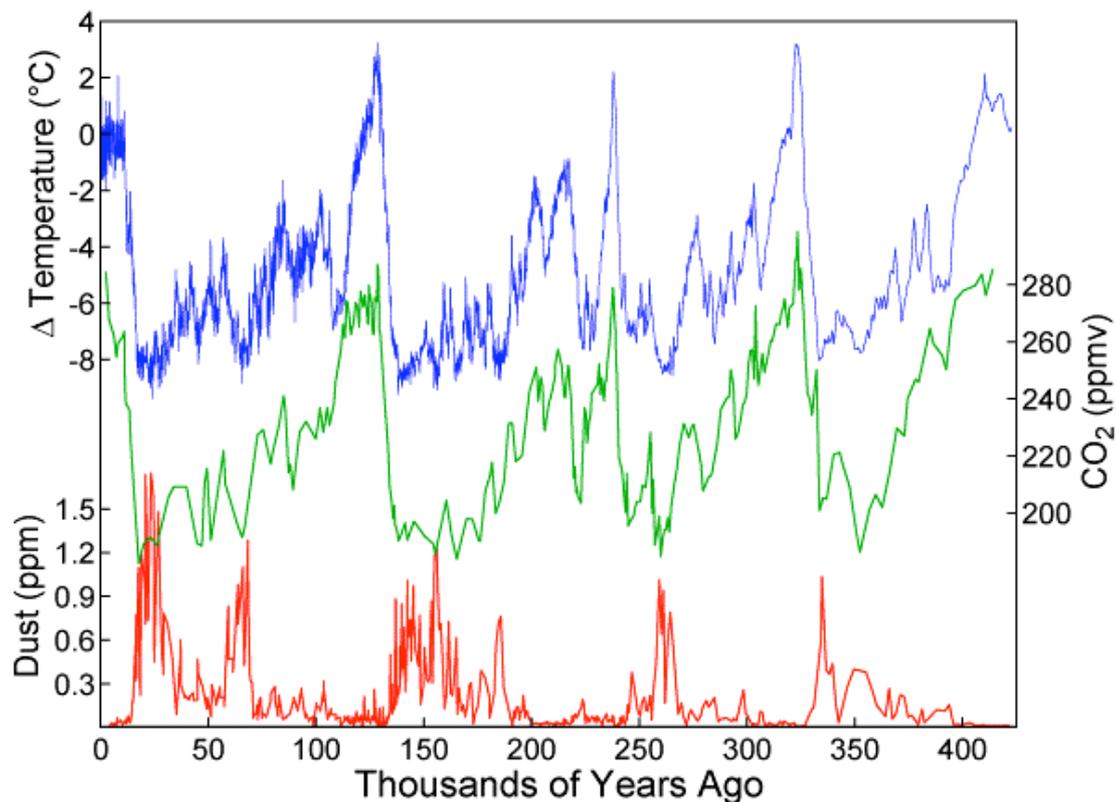
Many years after the hypothesis of Gran in 1931 that iron could be the limiting nutrient in certain regions in the ocean, Martin and Fitzwater (1988) showed that phytoplankton growth was indeed strongly stimulated after iron was added in seawater from the North Pacific, a high-nitrate, low-chlorophyll (HNLC) area. In spite of high macronutrient concentrations (nitrate, phosphate, silicic acid) these areas have low phytoplankton growth. Martin and Fitzwater (1988) suggested, just as Gran in 1931, that Fe would probably also be limiting phytoplankton growth in the Southern Ocean, another HNLC region. One year later this hypothesis was tested successfully, showing a stimulation of chlorophyll a after addition of iron in several water masses of the Southern Ocean (de Baar et al. 1990). In total there are three vast HNLC regions: the Southern Ocean, the subarctic Pacific and the equatorial Pacific. These oceans are lacking a continuous supply of dust storms from arid regions like the Sahara desert. This indicates that in up to 30-40% of the world's oceans iron is the limiting nutrient for phytoplankton growth (Martin and Fitzwater 1988).

Open oceans contain orders of magnitude lower levels of iron than coastal waters. A comparison of developed cell sizes of phytoplankton in experiments with coastal and oceanic phytoplankton clones indicate that cellular iron uptake-rates are similar

among the species when rates are normalized to cell surface area. In open ocean waters with low iron content the physical or chemical limits on iron-uptake force phytoplankton species to decrease in cell size and to reduce growth requirements for cellular iron by 8-fold, growing at a maximal rate on the minimum amount of iron (Sunda & Hutsman, 1995).

### Geological records show relationship natural iron fertilization and climate

The concept of ocean iron fertilization (OIF) was developed in 1990 by the biochemist John Martin. In his observations of the Vostok ice core record he observed an anti-correlation of atmospheric CO<sub>2</sub> concentrations across glacial-interglacial cycles with amounts of iron-containing dust (fig. 1). In the ice core layers of ice corresponding to times when temperatures were high concurred with ice-layers where low concentrations of dust and high CO<sub>2</sub> were found and vice versa. This led Martin to develop his iron hypothesis (Martin 1990), in which he presented the current Southern Ocean's productivity levels ( $7.4 \times 10^{13} \text{ g yr}^{-1}$ ) as being limited by iron shortage. Martin asserted that if iron would not be limiting, phytoplankton growth would be enhanced to a total Southern Ocean new production of  $2\text{--}3 \times 10^{15} \text{ g C yr}^{-1}$ .



**Figure 1** Graph showing the relation of atmospheric CO<sub>2</sub> (green), temperature (blue) and iron-containing dust concentration (red) measured from the Vostok ice core in Antarctica, reported by Petit et al (1999). The anti-correlation of dust and CO<sub>2</sub>/temperature caused the hypothesis that high dust concentrations are linked to cold and dry periods.

## Active Iron Fertilization to sequester carbon

Martin hypothesized that increasing phytoplankton photosynthesis by adding iron could slow or even reverse global warming by sequestering enormous amounts of carbon from the atmosphere to the ocean and even more avorably the ocean seabed. This hypothesis led to the development of OIF rapidly being considered worldwide as a potential climate mitigation tool (Keith & Dowlatabadi 1992). However, there is still a discussion concerning the Vostok ice core about what exact mechanism(s) caused (i) the change of 80 ppmV of atmospheric CO<sub>2</sub> concentrations, (ii) the relative contribution of iron (dust) fertilization to this change (Watson et al. 2000, Toggweiler et al. 2006) and (iii) the correlation in timing between dust flux and atmospheric CO<sub>2</sub> (Watson et al. 2000).

Although the preliminary results of OIF looked promising, the outcome of the first extensive scientific evaluation sponsored by the American Society of Limnology and Oceanography (ASLO) (1991) highlighted the still large scientific uncertainty of OIF as a successful mitigation strategy. It was brought to mind that OIF could possibly result, even if implemented globally, in only a short-term and a relatively small effect on atmospheric CO<sub>2</sub>, and would only delay the rise of atmospheric CO<sub>2</sub> by several years. The ASLO-meeting also advised on further research into OIF effects *in situ* on the regulation of ocean productivity, acidity and the ecosystem, and advised against using OIF as a policy option for climate mitigation.

Before the ASLO-meeting (1991) several small-scale experiments in incubation bottles in the subarctic Pacific (Martin & Fitzwater 1988, Coale 1991) and Southern Oceans (de Baar et al. 1990, Buma et al. 1991, Martin & Gordon 1990) were done. Shortly afterwards an early *in situ* fertilization experiment took place in the equatorial Pacific Ocean (Martin et al. 1994, Watson et al. 1994) and showed a significant stimulation of phytoplankton growth after addition of iron. Especially large diatoms such as *Fragilariopsis kerguelensis*, *Corethron* sp. and *Thalassiothrix* sp. showed a strong increase in abundance in the Southern Ocean (Buma et al. 1991). The results of these experiments showed not only a stimulation of chlorophyll a synthesis and nutrient assimilation, but also that factors greatly affecting growth were light limitation and grazing. Grazing is difficult to observe in bottle-incubated seawater experiments, because of the potential and inevitable exclusion of certain groups of micro- or macrozooplankton (Buma et al. 1991).

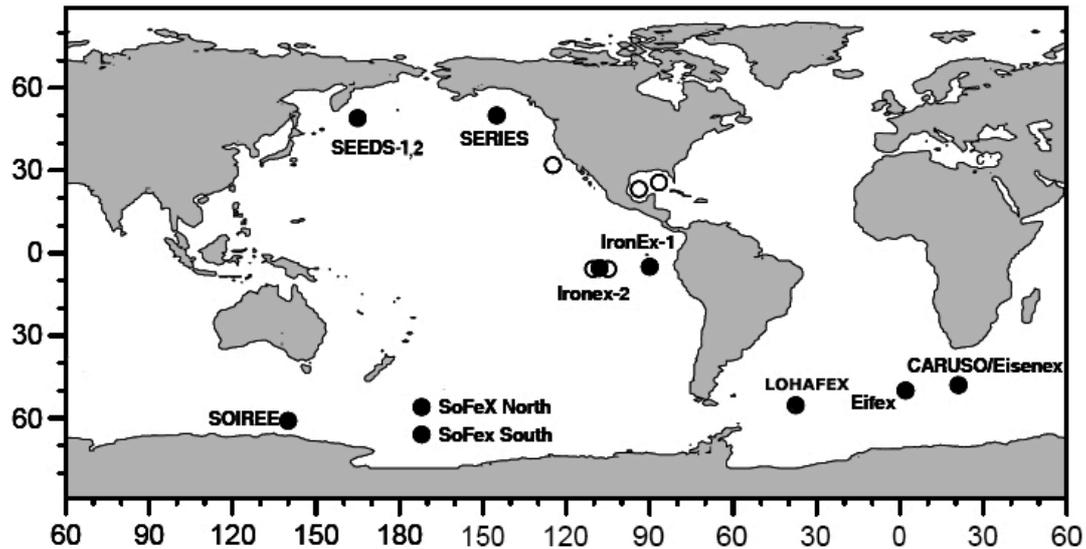
Iron fertilization was also found to be observed naturally in the Southern Ocean. It was shown that the iron-rich Polar Frontal jet (de Baar et al, 1995) causes vast blooms of large diatoms, such as *Fragilariopsis kerguelensis* and *Corethron* sp. (Quéguiner et al, 1997) leading to an eminent drawdown of CO<sub>2</sub> (Bakker et al. 1997).

## Chapter 2: The mesoscale Iron Fertilization Experiments

The most relevant data about OIF was found through several mesoscale OIF experiments that have been conducted from 1993 onwards, in several HNLC regions (table 1). By adding dissolved iron to a mesoscale patch of HNLC water, vast blooms of diatoms and a significant drawdown of CO<sub>2</sub> were hoped to be found. By adding the tracer sulfur hexafluoride (SF<sub>6</sub> tracer) it was possible to mark and track a patch of water for several days (Martin et al., 1994). Particulate organic carbon (POC) export could be measured by the decay of Uranium-238 (<sup>238</sup>U) into the isotope Thorium 234 (<sup>234</sup>Th). Some experiments used isotopically-labeled nitrogen (<sup>15</sup>N) to establish nitrogen uptake. The outcomes of these time-series experiments provide the first step in a quantitative assessment of how the ecosystem in HNLC waters responds to elevated iron concentrations.

No.	Acronym	Region	Year	Source
1	IronEx-1	East equatorial Pacific Ocean	1993	Martin et al. (1994)
2	IronEx-2	East equatorial Pacific Ocean	1995	Coale et al. (1996, 1998) Rue and Bruland (1997)
3	SOIREE (Southern Ocean Iron Release Experiment)	Southern Ocean (Australian sector)	1999	Boyd et al. (2000) and Law et al. (2001)
4	CARUSO/EisenEx	Southern Ocean (Atlantic sector)	2000	Gervais et al. (2002)
5	SEEDS-I (Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study)	Northwest Pacific Ocean	2001	Tsuda et al. (2003)
6	SOFEX-North (Southern Ocean Iron Experiment)	Southern Ocean (Pacific sector)	2002	Coale et al. (2004)
7	SOFEX-South (Southern Ocean Iron Experiment)	Southern Ocean (Pacific sector)	2002	Coale et al. (2004)
8	SERIES (Subarctic Ecosystem Response to Iron Enrichment Study)	Northeast Pacific Ocean	2002	Boyd et al. (2004)
9	SEEDS-II	Western subarctic Pacific	2004	Tsuda A, et al. (2007)
10	EIFEX (European Iron Fertilization Experiment)	Southern Ocean	2004	Hoffmann et al. (2005)
11	LOHAFEX (Indian and German Iron Fertilization Experiment)	Southern Ocean (Southwest Atlantic Sector)	2009	Data not yet published

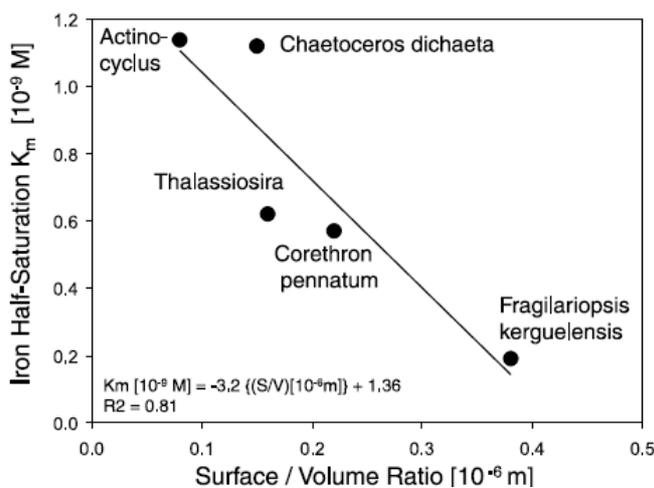
**Table 1** Number, Name, Region, Year and References of eleven major in situ OIF-experiments in High-Nutrient and Low-Chlorophyll (HNLC) waters (de Baar et al., 2005) Several more experiments were conducted but are not discussed here, as they were not in HNLC waters (actually LOHAFEX was in HNLC waters, but very low silica levels) or investigated natural iron fertilization blooms and export rates, like CROZEX (2005). Some unpublished experiments, like SAGE (2004) and FeeP (2004) are left out as well. There have also been several OIF tests conducted by commercial stakeholders (Markels & Barber 2001, Schiermeier 2003) but these were viewed as controversial and resulted in an extensive debate within the scientific community and media (Chisholm et al. 2001, Johnson & Karl, 2002).



**Figure 2** World map showing locations of 11 mesoscale Iron Fertilization experiments. (Map redrawn after de Baar et al. (2005))

The experiments differ a lot amongst each other in seasonal timing and location (fig. 2), ranging from IronEx-1 (1993), the first experiment conducted near the Galapagos Islands, to LOHAFEX, recently (2009) conducted in the Southern Ocean. Drawing a general conclusion of the key results of OIF experiments to different regional and seasonal levels is complex because of differences in experimental designs, modes of iron supply and weather conditions. Nevertheless, several valuable syntheses by multiple authors (de Baar et al. 2005, Boyd et al., 2007) of integrated datasets show remarkable trends focusing on several basic variables (i.e., Chlorophyll a, phytoplankton community response, macronutrients, CO<sub>2</sub> system variables).

### Primary production boost and shift-up in diatom size classes



**Figure 3** Relationship between size and half-saturation value  $K_m$  of Antarctic diatoms, showing bigger cells (low Surface/Volume Ratio) needing higher dissolved iron concentrations. Growth rates from Timmermans et al. (2004) (Graph after de Baar et al. (2005))

In all experiments, the added dissolved iron produced a significant increase in Chlorophyll a and atmospheric carbon uptake. As iron is required for synthesis of the Chlorophyll molecule, the primary response of Fe-depleted phytoplankton is an increase in cellular Chlorophyll a.

The major response of the phytoplankton community was always a striking shift-up towards larger size class diatoms. The normally low iron content forces phytoplankton cells to retain an optimal surface/volume ratio for maximum iron-uptake, which is favored at small cell sizes (Sunda &

Hutsman, 1995). When iron concentrations were increased the community generally made a shift from a nanoplankton (<10 mm) dominated to a microplankton (>10 mm) dominated community. There was an almost general flourish of the intermediate-sized pennate *Pseudo-nitzschia* sp. (clearly dominating in IronEx-2, CARUSO/EisenEx, SOFeX-North and SERIES). Other abundant phytoplankton species were *Fragilariopsis kerguelensis*, *Chaetoceros debilis* and other diatom species.

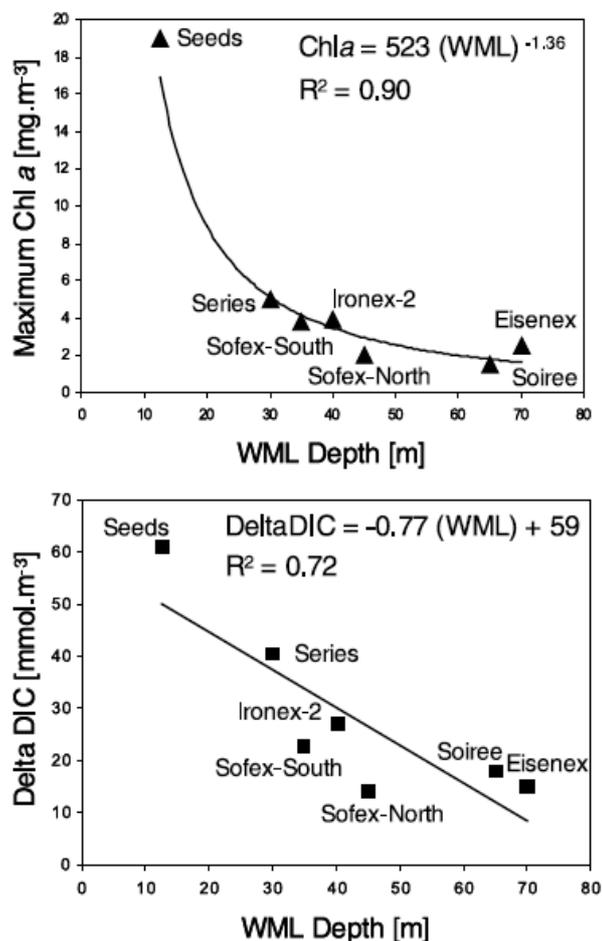
The shift-up in size class was mostly determined by the minimum maintained level of dissolved Fe during the experiments, allowing growth of bigger cells in the phytoplankton community (fig. 3). The “dissolved” iron however had the tendency to continuously transfer from dissolved reduced iron Fe(II) into colloidal iron, which is not directly available for phytoplankton uptake. Shortly after infusion about 75% of the “dissolved” iron consisted of this colloidal iron, which subsequently complicated the actual efficiency of the experiments. For export rates of carbon, the shift-up in size class is favorable, because diatoms sink out of the surface water more rapidly than small cells such as bacteria and are less easy degradable.

### Factors influencing phytoplankton growth

The ultimate determinate of phytoplankton growth found in the experiments was the amount of light available for photosynthesis. Light conditions were a major influence on primary productivity and were most favorable during IronEx-2, SEEDS and SERIES. The photosynthetically available radiation (PAR), dependent on weather conditions and sea surface irradiance, varies from day to day, latitude and season.

A large influence on the light environment was due to depth of the wind-mixed layer (WML), caused by the commonly high wind velocities in the Southern Ocean. The very deep WML, as clearly seen in CARUSO/EisenEx (Bakker et al., 2005) had a strong impact on Chlorophyll a levels and dissolved inorganic carbon (DIC) removal (fig. 4). Moreover, when a phytoplankton bloom develops the maximum extent of available light diminishes because of self-shading.

Ocean circulation modeling by Sarmiento and Orr (1991) showed that only in the Southern Ocean long-



**Figure 4** Inverse significant relationship between maximum observed Chlorophyll a concentrations ( $mg.m^{-3}$ ) and wind-mixed layer (WML) depth (upper graph). A clear effect of WML can be observed. The same is observed for maximum removal of dissolved organic carbon ( $mmol.m^{-3}$ )(lower graph). Data from seven OIF experiments reviewed in de Baar et al (2005), excluding IronEx-1. (graph after de Baar et al. (2005))

term(>100 yr) storage of CO<sub>2</sub> could occur in the deep sea. Other oceans are less suitable as CO<sub>2</sub> would more quickly be returned to the atmosphere by upwellings. However, exactly in the Southern Ocean the local deep WML caused by very strong winds causes the algae to suffer from light limitation (Mitchell et al., 1991)

Other factors influencing the effectiveness of the experiments were temperature (where warmer temperatures, as in the Pacific Ocean, speed up growth and metabolism), lateral patch dilution and the chemistry of Fe in seawater. After the phytoplankton bloom is formed another major influence is grazing by zooplankton (de Baar et al., 2005). Grazing interactions with phytoplankton seem more complex, as the grazing of certain species of phytoplankton is reflected in the growth rate, which is the net realized difference between growth and mortality rates. As a consequence it is difficult to detect what the magnitude of grazing is on the actual restraint of the Fe growth response. However, particulate organic carbon (POC) showed an increase of approximately 25% of the primary production, indicating substantial food web losses of 75%. Zooplankton consists of micro- (<200µm) and macrozooplankton. The HNLC seawater, because of low growth rates by mostly only small phytoplankton cells, has generally low abundances of macrozooplankton, which usually graze on microzooplankton and large phytoplankton species. In the complex succession of phytoplankton after addition of Fe an increase towards large diatoms can be observed. These diatoms appear to be released from heavy grazing pressures, at least in the early stages after iron addition. In these stages the initial zooplankton community seems even to reinforce the selective growth of large cells, by grazing on small cells. However, after a continuous bloom is evolved the specialized grazers could raise levels sufficiently abundant to control and damming the effect of Fe fertilization (Boyd et al., 2007). Heavy grazing pressure, exerted by macrozooplankton, occurs in some upwelling regions (Frost, 1996) where a continuous nutrient supply maintains a high-productivity system.

### **Carbon drawdown fluxes**

In the process of photosynthesis the pool of dissolved organic carbon (DIC) is converted into particulate organic carbon (POC). This creates an undersaturation of CO<sub>2</sub> in the surface layers, which drives an influx of CO<sub>2</sub> from the air into the sea. The POC is being mineralized or settles out into deeper layers, thus exporting carbon into the deep sea, where some of the carbon is taken by currents to be taken up to the surface later by upwellings and some of the carbon is stored by sedimentation. Annually the global rate of natural transfer of CO<sub>2</sub> to the deep ocean is in an estimated scale of 2 Gt C (Hueseman, 2008).

The question of OIF being a successful mitigation strategy obviously is about the actual drawdown and sequestration of carbon. However, export of carbon into deeper waters is difficult to assess and although the obtaining a solid value through comparison of the different experiments is complex because of the variable experimental conditions some concluding results can be drawn. For all OIF experiments the overall C/Fe efficiency of carbon uptake was approximately DIC 5600:1 Fe (de Baar et al., 2005) but different carbon depth-integrated rates (mmol m<sup>-2</sup> d<sup>-1</sup>) were estimated for the different OIF experiments (figure 5). With using <sup>14</sup>C uptake measurements the increase in POC was on average one quarter (26 ± 22%) and approximately half of the primary production was eventually turned into DIC (51 ± 26%). Of this primary production,. But when excluding the exceptionally

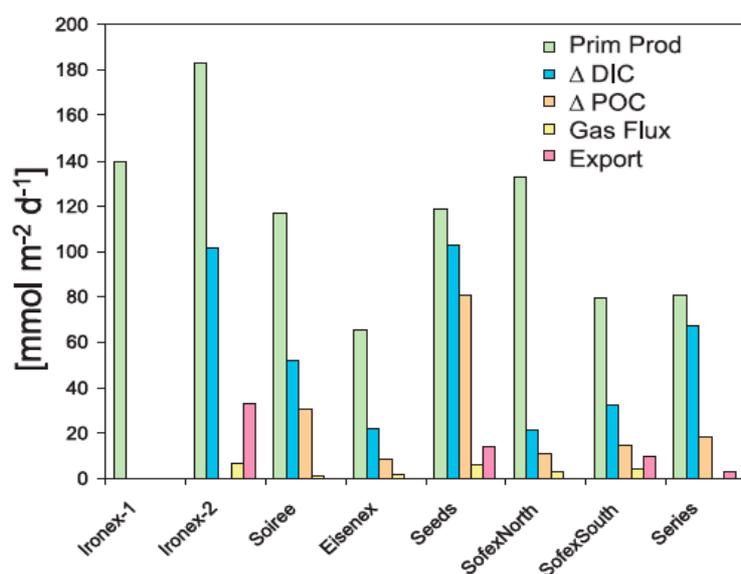
successful OIF experiment SEEDS (with very high efficiency in increase of DIC and POC) from this dataset, it is shown that on average only 18–26% of primary production accumulates as POC. This indicates the large losses due to trophic processes (grazing) or other inefficiencies. Dissolved organic carbon (DOC) can also contribute to export, but reports on DOC fluxes have been sporadic, small and no real trends were found.

The flux of atmospheric CO<sub>2</sub> gas into the ocean surface was shown to be only a small 8% portion of the DIC removal rate and only a 3% of primary production rate. This indicates a slow CO<sub>2</sub> replenishment from the atmosphere to the surface layer compared to the rapid growth (and DIC uptake) caused by the iron enrichment. However, a DIC deficiency was not reached, due to the additional compensation by heterotrophic respiration.

Export fluxes of organic carbon (DOC, POC) into deeper waters varied between experiments and have been assessed by different calculations. Calculated export rates were usually only a small fraction of primary production and they barely exceed the noise of the overall carbon budget. Export rates obtained from SEEDS, EisenEx, SOIREE (constant but short duration), SERIES and SOFeX-South led to a significant estimate of carbon export, but these estimates are only modest rates and comparable to similar estimates for natural export (Buesseler et al., 2004, 2005).

In the early 1990's it had been suggested that only a small amount of added Fe would increase the photosynthetic activity and uptake of CO<sub>2</sub> perhaps to such an extent that a major uptake of CO<sub>2</sub> could be realized. It was speculated that approximately 500000 atoms of C per added Fe atom could be fixed. However, due to inefficiencies caused by e.g. wind-mixed layer the calculated efficiency turned out to be only 2800 to 8000 atoms of C fixed per added atom of Fe (deBaar et al., 2005), 60 to 180 fold lower than the speculated efficiency.

All above-mentioned estimates however are discussing carbon export rates, which seem to suggest the actual carbon storage by sequestration. Model studies however show that particle export is only weakly related to oceanic carbon storage (Gnanadesikan & Marinov, 2008). In deep water layers the increase of carbon particles will probably lead to an increase in mineralization.



**Figure 5** Comparison (in  $\text{mmol.m}^{-2}.\text{d}^{-1}$ ) of depth-integrated primary production (green bars), DIC loss (blue bars), POC abundance (orange bars), sea gas exchange of CO<sub>2</sub> (yellow bars) and export rates to deeper waters (red bars). Further percentages were compared to primary production: DIC loss from 16% in SOFeX-North to 87% in SEEDS (average  $51 \pm 26\%$ ). POC biomass was about one-quarter (average  $26 \pm 21\%$ ). Gas fluxes were small (average  $3 \pm 1.7\%$ ) but difficult to measure. Export rates range from almost nil in SOIREE (Charette & Buesseler, 2000) to 10-27% in IronEx-2. References of experiments can be seen in table 1. (Graph after de Baar et al. (2005))

## Carbon sequestration rates from model studies and geological data

Modeling studies by Buesseler et al. (2008) predict that a global implementation of sustained OIF over a longer timescale (decades) in all the HNLC-regions of the ocean ( $\pm 30\%$  of the world ocean) would sequester at most  $0.5 \text{ Gt C yr}^{-1}$ , corresponding to a reduction of  $0.24 \text{ ppmV}$  atmospheric  $\text{CO}_2 \text{ yr}^{-1}$  (Aumont & Bopp 2006, Cullen & Boyd 2008). Fertilization with a mix of iron and macronutrients of several oligotrophic waters (waters where also macronutrients are limiting,  $\pm 50\%$  of the world ocean), could lead to even higher carbon export rates to the deep sea by stimulating growth of nitrogen fixing phytoplankton (Karl & Letelier, 2008). However, these rates are the potential upper boundary of OIF carbon sequestration and would require a huge effort to implement globally. Moreover, to obtain this rate would mean a global alteration of most of the world's ocean ecosystems and biochemical cycles for a century or more (Cullen & Boyd 2008).

Other than data from experiments and model simulations, geological records like the Vostok ice record (Fig. 1) are a valuable data-source for assessing the scale and speed of change in atmospheric  $\text{CO}_2$  by OIF. This available data-source provides information for a possible outcome of sustained (millennia) large-scale OIF (Boyd, 2008). It has been estimated that perhaps  $30\%$  of the  $80 \text{ ppmV}$  (i.e. up to  $25 \text{ ppmV}$ ) atmospheric  $\text{CO}_2$  drawdown observed in the ice record could be attributed to OIF (Sigman & Boyle 2000). Over a time-scale of roughly  $5000$  to  $10\,000$  yrs a drawdown of approximately  $20 \text{ ppmV}$  drawdown in atmospheric  $\text{CO}_2$  concentrations could be observed (Petit et al. 1999), leading to a C sequestration rate of  $0.01$  to  $0.005 \text{ Gt C yr}^{-1}$ , which is considerably less than the estimations from modeling studies of global OIF (Aumont & Bopp 2006). The underlying reasons for the disparity between the modeling study from Aumont & Bopp (2006) and the Vostok record (Petit et al. 1999) can be found in the differences of how OIF is parameterized in the model study relative to the OIF estimates of the Vostok record. The model was based on settings such as dissolved iron being maintained at  $2 \text{ nM}$  globally and a relatively high efficiency of carbon sequestration. The Vostok ice record provides more robust data and integrates a wide range of oceanic processes over millennia that probably illustrate the combination of direct alterations (e.g. increased production and export) and indirect alterations (e.g. biogenic gas production, foodweb structure change) due to OIF. Additionally, the Aumont & Bopp (2006) model is run under elevated atmospheric  $\text{CO}_2$  concentrations at present, causing higher C sequestration rates. But even a global OIF simulation by Aumont & Bopp (2006) with atmospheric  $\text{CO}_2$  comparable to the geological past resulted in a less than  $10 \text{ ppmV}$   $\text{CO}_2$  drawdown within  $100$  yr. This is still a huge difference with the Vostok sequestration rates. All in all, if OIF is to be viewed as an effective mitigation tool, it is important that a much better understanding of the magnitude and rate of C sequestration has to be obtained.

### Chapter 3: Evaluating the cost of OIF as a climate mitigation tool

Since the early 1990 OIF has originally been considered as a relatively low-cost and easy strategy compared to other mitigation methods (Chisholm & Morel 1991, Keith et al. 2005, Huesemann 2008); original estimates ranged from \$US 2 US ton<sup>-1</sup> C (1 US ton = 0.9072 t) (Markels & Barber 2001) to \$US 5 US ton<sup>-1</sup> C. This was based on assumptions that each ton of dumped iron fixes 30.000 tons of carbon and that 53% of this fixed carbon gets sequestered (based on the early study of Hansell et al. (1997) in the equatorial Pacific Ocean. (P. Lam & S. W. Chisholm unpubl. data)), ultimately suggesting that each US ton of dumped iron can sequester 15 900 US tons of carbon.

However, in the several mesoscale OIF experiments and evidence from natural ocean blooms (Marin et al. 1993, de Baar et al. 2008) it is shown that this assumed sequestration rate by Markels was a clear overestimate and with less actual sequestration the costs per sequestered carbon are much higher. Using the C export measurements (not even C sequestration) of several OIF studies, more realistic (but still uncertain) costs between \$US 30 and \$US 300 t<sup>-1</sup> C are estimated (Boyd, 2008).

Furthermore, with cost estimations based simply on scaling original cost to the C sequestration no costs of deleterious side-effects were taken into account, such as the possibility of a reduction in ocean productivity with an estimated fisheries loss. This could mean a possible commercial loss of up to \$US 150 US ton<sup>-1</sup> C sequestered by OIF (Gnanadesikan et al. 2003). Next to this, the expenses of the second generation of research that will be conducted before OIF could be commercialized (including multiple fertilization vessels or aircrafts, necessary chemicals, monitoring, modeling, employment researchers and evaluators) will also have to be included in the total sum of costs (Watson et al. 2008). Other possible unintentional side-effects (e.g. possible greenhouse-gas production (Law 2008)) would increase costs even more.

All in all, a more realistic assessment of the cost implies that the primary attraction of OIF (the estimated low cost compared to other mitigation strategies) is not applicable.

## Chapter 4: Unwanted side effects

A geo-engineering mitigation tool as OIF could have many potentially unwanted consequences for both humans and the environment, since it means a vast intervention with a responsive ecosystem. Although several negative side effects are known, there is still little knowledge about the possible magnitudes (Denman, 2008).

Most importantly, an increase of organic matter in the upper ocean means an increase in remineralisation, which occurs mostly in the subsurface layer of water 500 meters below the euphotic zone. Remineralisation requires dissolved oxygen at a rate of approximately 1.5:1 (mol O<sub>2</sub>: mol C). Under permanent large-scale iron fertilization this could result in large areas of the subsurface ocean becoming very low in oxygen or even anoxic (Sarmiento & Orr 1991). Not only are those areas practically inhabitable for many higher organisms, also denitrification occurs in these areas, which could result in an increased production of N<sub>2</sub>O, which is the third most abundant long-lived greenhouse gas. The increase in production of this gas by OIF even has the potential to offset the benefits gained from carbon storage by OIF. The magnitude of this effect is however still poorly known (Law 2008).

Another side effect of iron fertilization is an alteration in the structure of the marine food web. With sustained fertilization the composition of phytoplankton changes from a small phytoplankton dominated community to a larger diatom dominated community. (Marchetti et al. 2006) This enhances numbers of larger zooplankton, like copepods, instead of microzooplankton, as observed in SERIES, Tsuda et al. (2006). The shift to diatoms results in a larger uptake of silicic acid relative to nitrate (Boyd et al. 2004), which is a process that cannot continue over a long-term extended fertilization.

Furthermore, iron fertilization could cause a reduction in ocean productivity over a longer time. Due to a reduction of available macronutrients returning to the surface, primary production and so biological export of carbon would reduce on a time-scale of decades to centuries (Gnanadesikan et al. 2003, Aumont & Bopp 2006, Zahariev et al. 2008). This could also lead to a reduction in harvestable marine resources and so economical losses by commercial fisheries.

Another possible side effect of large-scale iron fertilization is an even more rapid increase in ocean acidity, which is already a threat to ocean ecosystems. As more CO<sub>2</sub> is added to the ocean, it dissolves rapidly and reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>) which completely dissociates into bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate ions (CO<sub>3</sub><sup>2-</sup>). This set of reactions adds protons (H<sup>+</sup> ions) to the ocean, causing a decrease of pH and thus an increase in acidity. Large-scale iron fertilization could increase the increasing acidity even more rapidly, as more CO<sub>2</sub> is added into the ocean. With increasing CO<sub>2</sub> content, also the concentration of carbonate ions falls. When carbonate becomes undersaturated versus solid CaCO<sub>3</sub>, biogenic structures made of calcium carbonate are vulnerable to dissolution. This is a problem for many species, primarily for oceanic calcifying organisms, such as coccolithophores, corals, foraminifera, echinoderms, crustaceans and molluscs.

Another side effect is an alteration in the production of the climate-active gas dimethylsulfide (DMS) a gas that stimulates the formation of cloud condensation nuclei (Liss et al. 2005). Emission to the atmosphere of this gas occurs from the oceans as its precursor, dimethylsulfoniopropionate (DMSP) is produced by some species of phytoplankton. However, if there would be an increase or decrease is still not clear, even as the magnitude, because of the short time-span of the OIF

experiments. Several of the experiments saw a short-term increase in DMS concentrations (Boyd et al. 2007), however the SERIES experiment showed a relative decrease in concentrations (Levasseur et al. 2006). In the latter there was a strong domination of diatoms, which produce little DMSP, which implies an apparent displacement of DMSP-producing plankton-species (Steiner & Denman 2008).

A recent study by Trick et al. (2010) shows yet another unwanted possible side effect. Most OIF experiments showed a domination of the toxigenic diatom genus *Pseudonitzschia*. These *Pseudonitzschia* species have the capacity to produce the neurotoxin domoic acid (DA), sometimes generating massive toxic harmful algal blooms (HABs) in coastal waters. Here toxic *Pseudonitzschia* blooms cause an accumulation of DA in animal tissues, causing mortality throughout the foodweb (Goldstein et al. 2008). Initially oceanic *Pseudonitzschia* species were considered non-toxic. However, laboratory cultures (Marchetti et al. 2008) and *in situ* experiments in the Eastern subarctic Pacific have shown that the oceanic *Pseudonitzschia* community is very variable in respect to toxin production and has the physical capability to suddenly change to a DA producing physiology in response to iron addition. Whether enhanced toxicity upon iron enrichment may reach levels sufficient to cause ecosystem damage is still unsure, but under conditions of large-scale continuous iron fertilization it could be that DA levels reach serious toxicity.

All in all there is a wide range of possible negative side effects, some predictable, some probably still not known or realized, bringing unforeseen consequences. Despite the amount of research conducted it is still unsure how the ecosystem responds to large-scale continuous iron fertilization and how quickly marine organisms can adapt to the altered conditions such as a possible enhanced increase in ocean acidity. Another, perhaps less obvious side effect of the consideration of any geo-engineering project may be that it reduces the political pressure and media's attention to reduce emissions.

## Chapter 5: Iron fertilization compared to other mitigation measures

To attain a realistic view on the magnitude of the global effect of OIF of reducing climate change, it is necessary to make also a comparison with other climate mitigation approaches. In a quite recent paper from Huesemann (2008) OIF is compared to several climate mitigation strategies (listed in table 2). These include efficiency improvements of present-day energy supplies (loss of heat, electricity etc.), several ways of carbon sequestration (in the biosphere, earth or in the oceans) that are already applied or still in development and several ways of alternative energy, of which most of them are already globally applied. In this chapter only the geo-engineering options will be covered, each with their own estimated long-term sequestration potential, stage of development, costs and risks/disadvantages.

An approximate 2 000 Gt C is currently stored in the biosphere in plant biomass and soil humus (US DOE 1999). By reforestation and improved agricultural practices this pool of carbon could probably be increased by an approximate 200 Gt C (Scholes & Noble 2001). However, the large disadvantage of this is competition for space.

Geologically, the capacity of carbon storage in the earth is estimated to be 10-100 Gt C in coal seams, hundreds to ten thousand Gt C for saline aquifers and several hundred Gt C in depleted oil and gas fields (Herzog 2001, Bruant et al. 2002). These numbers are tremendously high, but the danger of geologic carbon sequestration is the potential leakage of CO<sub>2</sub> from the reservoirs. Slow CO<sub>2</sub> leakage can cause unwanted alterations in water quality (acidification of groundwater, leakage of nutrients), geochemistry, both causing a decrease in the health of the ecosystem (Bruant et al. 2002). A sudden catastrophic release of large amounts of CO<sub>2</sub> (by reservoir fracturing by earthquakes or pipeline failures) could cause immediate death of both people and animals. Particularly since CO<sub>2</sub> is a dangerous gas because it is difficult to detect (odor-, color- and tasteless). It is also heavier than most gasses and so has the tendency to stay near the ground, spreading like a cover.

Turning for carbon storage to the oceans seems a safer way. The two proposed ways of storing carbon in the oceans are CO<sub>2</sub>-disposal in mid- or deep ocean layers and the addition of macronutrients or bio-essential metals, such as iron, for stimulation of plankton growth. Estimations for injecting CO<sub>2</sub> show a capacity of several thousands Gt C (Herzog 2001). However, large potential and known problems with CO<sub>2</sub> disposal in ocean seawater by this method are the threats of an even more rapid increase in ocean acidification and also pollution with CO<sub>2</sub> impurities such as NO<sub>x</sub>, SO<sub>x</sub>, and several trace metals (US DOE 1999). These effects are a problem for many organisms. For iron fertilization the main setback, besides the negative side-effects, is its very low C sequestration potential (~0.2 Gt C/yr<sup>-1</sup>). This number is almost nothing compared to other carbon sequestration methods, all with potential sequestration rates ranging from 100 to 10000 Gt C.

One less known carbon sequestration method that is often overlooked is enhanced weathering of olivine rock (Schuiling & Krijgsman, 2006). Weathering is the geological process in which minerals are being transformed into other minerals by uptake of CO<sub>2</sub> or H<sub>2</sub>O. Olivine is one of the most common minerals on earth. When weathered, SiO<sub>2</sub> and metal oxides like MgO (and a small amount of Fe<sub>2</sub>O<sub>3</sub>) are being released, of which the Mg binds to CO<sub>2</sub> (forming MgCO<sub>3</sub>). Increased olivine weathering would enhance the enhance this process. The extent of olivine rock weathering is only limited by the area that can be used for this kind of process.

However, it still remains unknown if this technique is feasible (Hartmann & Kempe, 2008) and little research is done.

Although the capacity of CO<sub>2</sub> disposal methods by injecting CO<sub>2</sub> (terrestrial or oceanic) is large, it is also limited. On the contrary, the yearly amount of C sequestration by OIF is not large; but it has no limits and on the long run this could be a better option.

One difficulty with all geo-engineering options however is how to devise political frameworks in which the methods would be conducted.

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

**Table 2** Comparison of different climate change mitigation in terms of their long-term potential, stage of development, relative costs and potential risks. R&D: research and development, C: carbon, tech: technology, med: medium (table from Huesemann (2008))

## Chapter 6: Analysis of Iron fertilization as a climate mitigation tool

OIF was initially considered a relatively low-cost, quick and easy strategy compared to other mitigation measures. Natural and induced iron fertilization studies have showed that in HNLC-regions as the Southern Ocean iron fertilization can lead to a significant increase in primary production and export of carbon from the sea surface to the ocean interior. However, the efficiency of exported atoms of carbon per added atom of Fe appears to only be very modest (de Baar et al., 2008) and any actual sequestration is still difficult to detect. Export of carbon to the ocean interior causes probably only a short-term decrease in atmospheric CO<sub>2</sub> concentrations as currents reach the surface again or the gas dissimilates to the atmosphere.

Fluctuating factors such as weather conditions or initial phytoplankton community composition are of major importance and create very different outcomes. For example, SEEDS-I and II were basically on the same spot, in the same time of year and outcomes from these experiments were very different. This makes it difficult to make predictions how the ecosystem will respond.

Moreover, increased CO<sub>2</sub> concentrations in the ocean interior could cause possible negative side-effects as increased ocean acidification, anoxification or emissions of the potent greenhouse gases nitrous oxide and methane.

As efficiency rates of exported carbon appear to be much lower than initially estimated, also the costs of OIF become much higher. OIF is currently classified as a medium-risk, medium-cost mitigation strategy (Keith et al. 2005, Huesemann 2008). We do better to turn to other more efficient mitigation strategies, which have similar or lower costs and lower risks.

In the last IPCC report (IPCC AR4, 2007) iron fertilization was again dismissed as a viable mitigation measure. All in all, iron fertilization just does not seem to be feasible. And if fertilization with iron is not realistic, fertilization will probably also not work with any other nutrient. As iron is a trace element, phytoplankton needs only very little concentrations to grow. Fertilization with other (regionally) limiting (macro)nutrients would mean an approximate hundred-fold increase of fertilizer. The biggest problem of any fertilization strategy is that most of the particulate organic material is being mineralized before it can reach deep waters.

Even if OIF is probably eventually not being applied on a large scale, the extensive research by OIF experiments has not been for nothing: the results have greatly increased our knowledge of marine ecological and biochemical dynamics and their interrelationships (Boyd, 2007). They have given us a better understanding of the dynamics and factors that play a role in naturally occurring blooms e.g. bloom diversity, magnitude and bloom evolution.

The first generation OIF experiments were typically on a 10 km length-scale, with a duration of weeks. Little information was gained of how longer-term changes in ecosystem structure and function might be. Future prospects of OIF are 100 km length-scale second generation OIF experiments. These would preferably also be observed for a longer time (Watson et al. 2008).

Until now OIF does not seem to be a solution for stabilizing atmospheric CO<sub>2</sub> concentrations. Hopefully, the second generation experiments can shed a new light on this question.

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