

Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment

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[1] Comparison of eight iron experiments shows that maximum Chl *a*, the maximum DIC removal, and the overall DIC/Fe efficiency all scale inversely with depth of the wind mixed layer (WML) defining the light environment. Moreover, lateral patch dilution, sea surface irradiance, temperature, and grazing play additional roles. The Southern Ocean experiments were most influenced by very deep WMLs. In contrast, light conditions were most favorable during SEEDS and SERIES as well as during IronEx-2. The two extreme experiments, EisenEx and SEEDS, can be linked via EisenEx bottle incubations with shallower simulated WML depth. Large diatoms always benefit the most from Fe addition, where a remarkably small group of thriving diatom species is dominated by universal response of *Pseudo-nitzschia* spp. Significant response of these moderate (10–30 μm), medium (30–60 μm), and large (>60 μm) diatoms is consistent with growth physiology determined for single species in natural seawater. The minimum level of “dissolved” Fe (filtrate < 0.2 μm) maintained during an experiment determines the dominant diatom size class. However, this is further complicated by continuous transfer of original truly dissolved reduced Fe(II) into the colloidal pool, which may constitute some 75% of the “dissolved” pool. Depth integration of carbon inventory changes partly compensates the adverse effects of a deep WML due to its greater integration depths, decreasing the

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differences in responses between the eight experiments. About half of depth-integrated overall primary productivity is reflected in a decrease of DIC. The overall C/Fe efficiency of DIC uptake is $\text{DIC/Fe} \sim 5600$ for all eight experiments. The increase of particulate organic carbon is about a quarter of the primary production, suggesting food web losses for the other three quarters. Replenishment of DIC by air/sea exchange tends to be a minor few percent of primary CO_2 fixation but will continue well after observations have stopped. Export of carbon into deeper waters is difficult to assess and is until now firmly proven and quite modest in only two experiments.

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1. Introduction

[2] In August 1987, *Martin and Fitzwater* [1988] demonstrated that phytoplankton Chl *a* growth was strongly stimulated when iron (Fe) was added to bottle-incubated seawater samples from the subarctic North Pacific (Figure 1a). They further suggested that Fe limited phytoplankton growth in the Southern Ocean, another region characterized by chronically high nutrients and low chlorophyll (HNLC). This long-forgotten hypothesis of Fe limitation of the Southern Ocean [Gran, 1931] was tested successfully [de Baar et al., 1990] 1 year later (Figure 1b), with iron addition significantly stimulating larger diatoms such as *Nitzschia fragilaria* (subsequently renamed *Fragilariopsis kerguelensis*), *Corethron* sp. and *Thalassiothrix* sp. [Buma et al., 1991]. With these events, the iron age in oceanography had begun [Coale et al., 1999; de Baar and La Roche, 2003].

[3] Nevertheless in both regions the control experiments also had outgrown the field biomass (Figure 1), hence other factors such as light limitation and grazing were also at play. Another major change resulting just from the incubation, was the marked development of microzooplankton, presumably due to exclusion of macrozooplankton predators from the bottles [Buma et al., 1991]. In austral spring 1992, natural Fe fertilization in the Polar Frontal jet [de Baar et al., 1995] was found to cause an ecosystem shift-up [Lancelot et al., 1993, 2000] with the production of vast blooms of large diatoms, notably *Fragilariopsis kerguelensis* and *Corethron* sp. [Quéguiner et al., 1997; van Leeuwe et al., 1997; Scharek et al., 1997] and concomitant CO_2 drawdown [Bakker et al., 1997]. Meanwhile, experimental mesoscale Fe fertilizations of whole ecosystems were proposed as a direct test of the Fe limitation hypothesis [e.g., Martin, 1992]. The developed sulfurhexafluoride technique (SF_6 [Upstill-Goddard et al., 1991; Ledwell et al., 1993, 1998; Law et al., 1994, 1998]) made it possible to mark and track a patch of water for days to weeks [Martin et al., 1994]. The first in situ Fe fertilization experiment IronEx-1 in 1993 [Martin et al., 1994; Coale et al., 1998] has led to a suite of now nine such experiments (Table 1) in HNLC waters (Figure 2).

[4] Among the wide variety of objectives and observations from these experiments, here only the most striking aspects of the phytoplankton responses, and the impact on carbon dioxide (CO_2) and major nutrients are presented as a modest first step to more elaborate synthesis, integration and generic ecosystem simulation modeling [Hannon et al., 2001; Pasquer et al., 2005]. Other significant findings have been or will be reported elsewhere. The responses of

nanoplankton, such as the haptophytes and associated DMS(P) metabolism, as well the production of several other biogenic trace gases, have been very well described [Lévesque, 2002; Turner et al., 1996, 2004; Chuck et al., 2002; Chuck, 2004; Law and Ling, 2001; Wingenter et al., 2004; Y. Le Clainche et al., Simulation of the ocean DMS pool during SERIES: An inverse modeling approach, submitted to *Journal of Geophysical Research*, 2005]. Several articles also consider Fe-influenced shifts in Redfield stoichiometry (C/N/P/Si) [e.g., de Baar et al., 1997; Takeda, 1998; Frew et al., 2001; Bozec et al., 2005; Timmermans et al., 2004; Twining et al., 2004a; Marchetti and Harrison, 2004; Hiscock and Millero, 2005].

2. Iron Fertilization Experiments in the 1993–2004 Era

[5] In October 1993, some 450 kg Fe (7800 mol) together with SF_6 tracer (0.35 mol) was introduced into about 64 km² surface waters for the IronEx-1 experiment [Martin et al., 1994]. A significant increase of photosynthetic quantum efficiency, Fv/Fm, from 0.3 to 0.6 occurred within 24 hours [Kolber et al., 1994]. An increase in primary productivity from 10–15 mg C m⁻³ d⁻¹ to 48 mg C m⁻³ d⁻¹, an increase of Chl *a* from about 0.24 to 0.65 mg m⁻³, and a modest decrease of fugacity of carbon dioxide, $f\text{CO}_2$, of about 7 10⁻⁶ atm [Watson et al., 1994] were also observed within the first 3 days. No systematic differences were observed for the major nutrients (nitrate, phosphate and silicate) of the fertilized patch compared to out-patch ambient waters. Unfortunately, the patch subsided to about 30–35 m, after 4 days, and not much happened during the remaining 5 days of observations [Watson et al., 1994], apart from some increasing trend of Chl *a* and a decline in Fv/Fm [Kolber et al., 1994]. Obviously, the lower light level at depths exceeding 35 m, was detrimental for further ecological and biogeochemical response, but the dissolved Fe within the patch had also decreased below the shipboard detection limit of about 0.3 nM within 5 days, consistent with the decrease in Fv/Fm. Afterward, by Fe analyses in the home laboratory, the final dissolved Fe within the patch was still above the very low (<0.05 nM) natural dissolved Fe in ambient waters [Gordon et al., 1998].

[6] The follow-up experiment IronEx-2 in May 1995 was a major success, and it still is in the context of the seven subsequent Fe addition experiments (Table 1). One initial Fe infusion (225 kg) together with SF_6 tracer at day 0 (29 May), was followed by two more Fe infusions of 112 kg

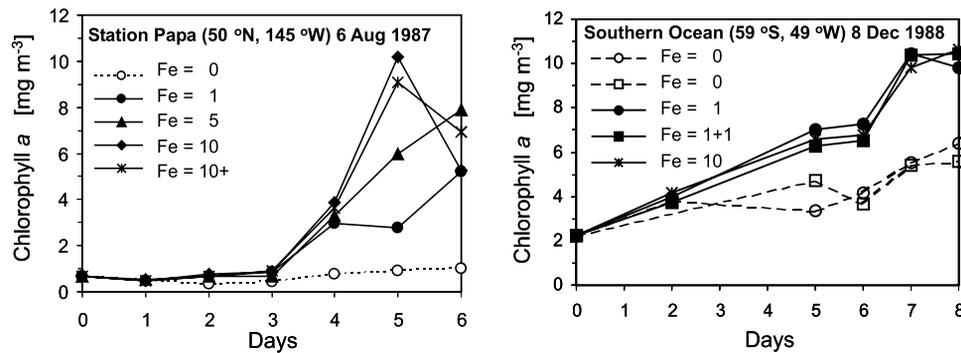


Figure 1. Evidence of Fe-stimulated phytoplankton growth shown as increasing Chl *a* (mg m^{-3}), but the controls also increase, indicating that other factors (light, grazing) are also important. (left) Deck incubations of second experiment starting on 6 August 1987, with seawater collected at Station Papa (50°N , 145°W) by *Martin and Fitzwater* [1988], consistent with results of simultaneous experiments of *Coale* [1991]. (right) Incubations starting on 8 December 1988, under a controlled light cycle, of seawater collected in the Southern Ocean (59°S , 49°W) [*de Baar et al.*, 1990]. See original articles and *de Baar* [1994] and *de Baar and Boyd* [2000] for more such experiments.

each at days 3 and 7 [*Coale et al.*, 1996]. The wind mixed layer (WML) deepened in a suite of small mixing events from 25 m at day 0 to 50 m by day 11. The Fv/Fm increased rapidly from 0.25 to 0.5 [*Behrenfeld et al.*, 1996]. The maximum Chl *a* increased 27-fold from 0.15–0.20 mg m^{-3} to values approaching 4 mg m^{-3} on day 9, and then decreased to 0.3 mg m^{-3} by day 17. This was accompanied by a strong nitrate drawdown of 4 mmol m^{-3} and a maximum decrease of fCO_2 of more than $70 \cdot 10^{-6}$ atm, also at day 9 [*Cooper et al.*, 1996, Table 1]. These dramatic impacts are convincingly illustrated by a day 5 transect across the patch (Figure 3). A strong initial increase of both DMSP and its conversion product DMS in the first 6 days [*Turner et al.*, 1996], followed by a decreasing trend, appears consistent with a similar increase and then decrease in the haptophytes, the nanoplankton-sized major producers of DMSP. All size classes of phytoplankton responded to the added Fe by increasing their cellular photopigment concentration, indicating that they had previously been Fe limited

[*Cavender-Bares et al.*, 1999]. However the smaller pico- and nanoplankton size classes were kept at relatively constant concentrations by heterotrophic grazers, allowing the initially rare and large ($>20 \mu\text{m}$) pennate diatom *Pseudo-nitzschia* (rather than *Nitzschia* sp. as reported) to strongly dominate carbon biomass by the end of the experiment [*Cavender-Bares et al.*, 1999; *Landry et al.*, 2000a, 2000b]. The recently discovered strong organic complexation of dissolved Fe [*Gledhill and van den Berg*, 1994; *van den Berg*, 1995] was also nicely confirmed with two organic ligand classes L_1 and L_2 in the ambient waters, and a striking 400% increase of Fe(III)-binding ligands, largely in the stronger L_1 ligand class, was observed within 48 hours of Patch-1 Fe fertilization [*Rue and Bruland*, 1997]. The ^{234}Th deficiency method provided a first assessment of particulate organic carbon (POC) export increasing from $7 \text{ mmol m}^{-2} \text{ d}^{-1}$ prior to enrichment to $\sim 15 \text{ mmol m}^{-2} \text{ d}^{-1}$ in the day 2–7 period, and values approaching $50 \text{ mmol m}^{-2} \text{ d}^{-1}$ during days 8–14 [*Bidigare et al.*, 1999].

Table 1. Number, Name, Region, Position, Month(s) by Number, and Year of the Nine In Situ Fe Enrichment Experiments in High-Nutrient and Low-Chlorophyll (HNLC) Waters in the 1993–2004 Era^a

No.	Acronym	Region	Latitude, deg	Longitude, deg	Month(s)	Year
1	IronEx-1	east equatorial Pacific Ocean	–05	–090	10, 11	1993
2	IronEx-2	east equatorial Pacific Ocean	–04 to –07	–105 to –111	5, 6	1995
3	SOIREE	Southern Ocean (Australian sector)	–61	140	2	1999
4	CARUSO/EisenEx	Southern Ocean (Atlantic sector)	–48	021	11,12	2000
5	SEEDS	northwest Pacific Ocean	49	165	7	2001
6	SOFEX-North	Southern Ocean (Pacific sector)	–56	–172	1, 2	2002
7	SOFEX-South	Southern Ocean (Pacific sector)	–66	–172	1, 2	2002
8	SERIES	northeast Pacific Ocean	50	–145	7	2002
9	EIFEX	Southern Ocean	–50	002	2, 3	2004
a	GreenSea 1	Gulf of Mexico			1	1998
b	GreenSea 2	Gulf of Mexico			5	1998

^aThe first and last experiments are briefly or are not discussed here due to early subduction (1) or results still being preliminary (9). Two other experiments (a and b (for a three patches of 9 mile², each with chelated Fe, P/Fe = 6.35 and P/Fe = 63.5 additions, for b one patch of 9 mile² with chelated Fe-containing pellets [*Markels and Barber*, 2001])) were not in HNLC waters and are not further discussed here either. See original articles for exact daily positions of drifting patches. Sources are as follows: (1) *Martin et al.* [1994]; (2) *Coale et al.* [1996, 1998] (for exact latitude/longitude, see *Rue and Bruland* [1997]; here only patch 1 of patches 1–3 is discussed; for test site off California, see *Coale et al.* [1998]); (3) *Boyd et al.* [2000] and *Law et al.* [2001]; (4) *Gervais et al.* [2002]; (5) *Tsuda et al.* [2003]; (6) *Coale et al.* [2004]; (7) *Coale et al.* [2004]; (8) *Boyd et al.* [2004a]; (9) *Hoffmann et al.* [2005]; (a, b) *Markels and Barber* [2001]. The recently published 14 articles with many findings of SEEDS [*Tsuda*, 2005] have not been incorporated in this synthesis article.

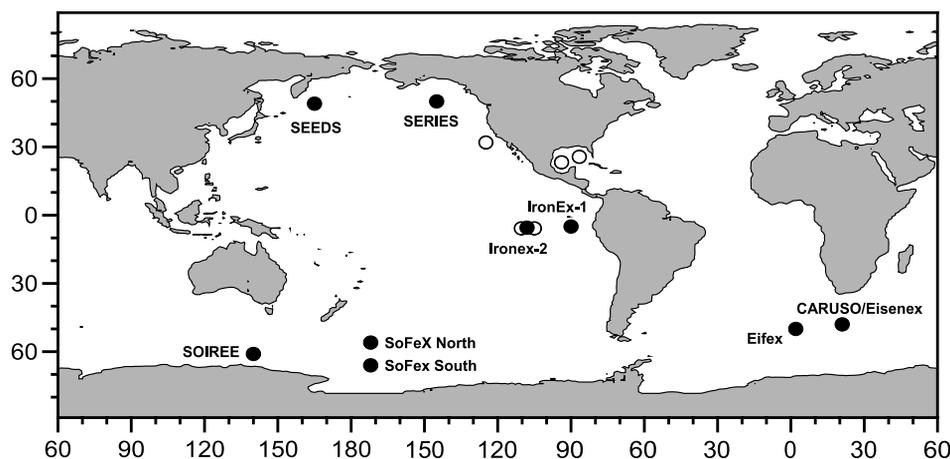


Figure 2. Chart showing the locations (filled circles) of the nine in situ Fe enrichment experiments conducted thus far. Moreover, also indicated are the open circle off California for the IronEx test site [Coale *et al.*, 1998], two open circles for two extra patches during IronEx-2 not further discussed here, and two experiments GreenSea 1 and 2 at unknown positions in the Gulf of Mexico [Markels and Barber, 2001].

[7] The first Southern Ocean Iron Release Experiment (SOIREE) [Boyd *et al.*, 2000] took place at the end of austral summer in February 1999 with four Fe infusions (days 0, 3, 5 and 7) in the Antarctic Ocean proper, i.e., south of the Polar Front where all 3 major nutrients silicate, nitrate and phosphate are present. The depth of the Wind Mixed Layer was on average about 65 m [Boyd and Law, 2001]. Dissolved silicate at the onset was about 10 mmol m^{-3} which is well below winter values. This and the significant abundance of larger diatoms *Fragilariopsis kerguelensis* ($>35 \mu\text{m}$ per cell, $4500 \text{ cells L}^{-1}$), and other diatoms ($\sim 1900 \text{ cells L}^{-1}$) indicated that diatom blooms during the preceding summer had provided an “inoculate” population [Gall *et al.*, 2001a]. Two haptophyte groups, with pigment signatures typical of *Phaeocystis* sp. and coccolithophores, respectively, increased steadily during the first 8–10 days, and then decreased somewhat [Gall *et al.*, 2001a]. This trend was closely correlated with increases of DMSP and its breakdown product DMS at about days 8–9, consistent with cell lysis or grazing, and indeed, the abundance of heterotrophic ciliates grazers increased as well on day 9 [Hall and Safi, 2001].

[8] On day 13, the in-patch was dominated by diatoms [Gall *et al.*, 2001a, Table 2], notably the chain-forming pennate, *Fragilariopsis kerguelensis* ($16,500 \text{ cells L}^{-1}$) which has a heavily silicified architecture as grazing protection [Hamm *et al.*, 2003], and also *Rhizosolenia* sp. ($4800 \text{ cells L}^{-1}$) and *Pseudo-nitzschia* sp. ($1400 \text{ cells L}^{-1}$). The increasing chain length of *Fragilariopsis kerguelensis* (up to 14 cells/chain) indicated favorable growth conditions (chains up to 40 cells/chain were found in sediment traps [Waite and Nodder, 2001]). On the final day 13, primary production was indeed dominated by the $>22 \mu\text{m}$ size class [Gall *et al.*, 2001b] consisting of diatoms. Among these, various very large diatom species were abundant, notably *Thalassiothrix antarctica* ($\sim 0.2 \text{ cells L}^{-1}$), *Asteromphalus flabellatus* ($\sim 300 \mu\text{m}$; $\sim 1 \text{ cell L}^{-1}$), *Trichotoxon reinboldii* (“needles” $> 1 \text{ mm}$ length, and $\sim 2 \text{ cells L}^{-1}$), *Nitzschia cf. sicula* varieties ($\sim 30 \text{ cells L}^{-1}$), *Coscinodiscus* spp. ($\sim 12 \text{ cells L}^{-1}$), *Eucampia antarctica* ($\sim 0.8 \text{ cells L}^{-1}$)

and various *Navicula* spp. ($\sim 3.4 \text{ cells L}^{-1}$) as shown by Waite and Nodder [2001, Figure 1]. These very large diatoms contribute significantly to the overall diatom biomass.

[9] Dissolved nitrate and silicate both decreased by 3 mmol m^{-3} during 13 days [Frew *et al.*, 2001]. Similarly the $f\text{CO}_2$ and DIC in the patch center had decreased by about $35 \cdot 10^{-6} \text{ atm}$ (Figure 4) and 17 mmol m^{-3} , respectively [Bakker *et al.*, 2001]. The area of the fertilized patch increased from 50 to about 250 km^2 by day 13, a fivefold patch dilution constituting a “chemostat effect” where major nutrients are replenished while the trace element Fe and plankton biomass are diluted [Abraham *et al.*, 2000]. The observation of the chlorophyll patch by remote sensing even 40 days after the start of the experiment, also requires to invoke continuation of a chemostat effect [Abraham *et*

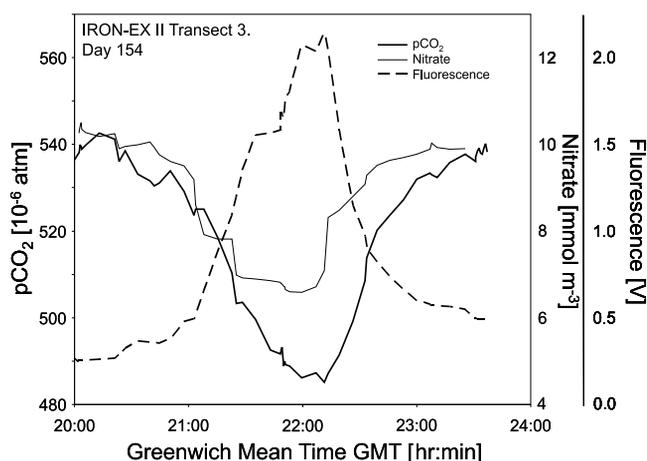


Figure 3. Response to Fe enrichment shown by high fluorescence signal (V) of Chl *a* being mirrored by strong decreases of fugacity of CO_2 (pCO_2 (10^{-6} atm)) and dissolved nitrate (mmol m^{-3}) in surface waters of a transect across the patch during IronEx-2 [Coale *et al.*, 1996; Cooper *et al.*, 1996] (redrawn after Steinberg *et al.* [1998]).

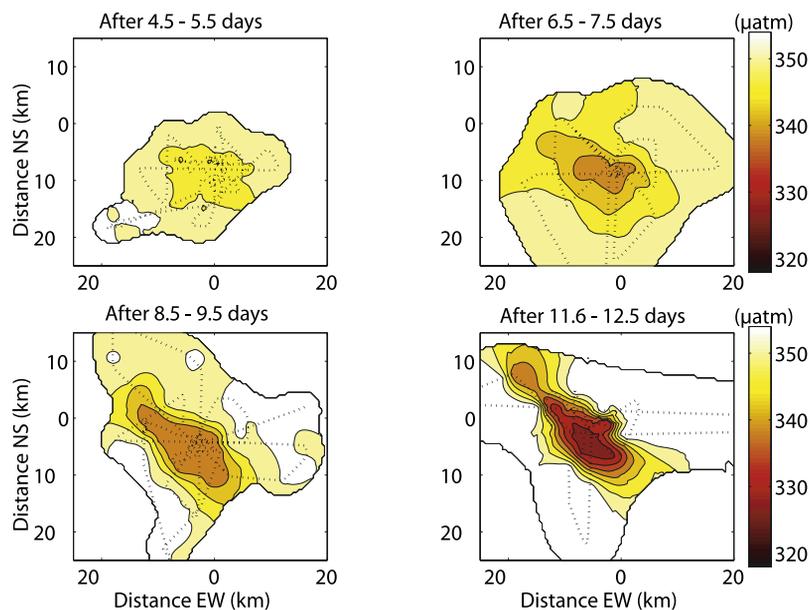
Surface water $f\text{CO}_2$ during SOIREE

Figure 4. Significant decrease of fugacity of CO_2 (10^{-6} atm) during the 12 day evolution of the Southern Ocean Iron Release Experiment (SOIREE) in the Southern Ocean (61°S , 140°W [Bakker *et al.*, 2001]).

al., 2000] and has implications also for self-shading, coagulation and other processes [Boyd and Law, 2001]; yet due to lack of data in the 13–40 day period these cannot be verified. For example somehow retention of Fe during 40 days would presumably be required, somewhat in contrast to some 70% of added Fe being unaccounted for, i.e., lost, within first 13 days of observations [Bowie *et al.*, 2001].

[10] The ^{234}Th : ^{238}U ratio was less than 1 before the experiment, hinting at significant export in the preceding late summer. During the experiment the ^{234}Th : ^{238}U ratio increased similarly at both IN and OUT stations by natural ingrowth of ^{234}Th during conditions of near zero net particle flux [Charette and Buesseler, 2000], consistent with lack of clear IN versus OUT differences in shallow sediment trap fluxes [Nodder and Waite, 2001; Nodder *et al.*, 2001].

[11] Comparison of the significant responses between IronEx-2 in the tropical Pacific and SOIREE in the Southern

Ocean (Figure 5) shows much faster rates of primary production and nitrate removal in IronEx-2 experiment, consistent with the far lower temperature, deeper Wind Mixed Layer (WML) and stronger lateral patch dilution for SOIREE. This lateral patch dilution may also have slowed down the aggregation of particles as a step toward export of larger aggregates in SOIREE relative to IronEx-2 [Boyd *et al.*, 2002].

[12] The Carbondioxide Uptake Southern Ocean (CARUSO)/Eisen(=Iron) Experiment (EisenEx) took place in the austral spring, November 2000, in the core of a cold Antarctic eddy that had spun off the Polar Frontal jet into the sub-Antarctic region. The eddy being Antarctic water had all major nutrients present but was surrounded by sub-Antarctic waters with ample nitrate and phosphate as well, but low in silicate. Three Fe infusions of 780 kg each at days 0, 7–8, and 16 were diluted downward and laterally

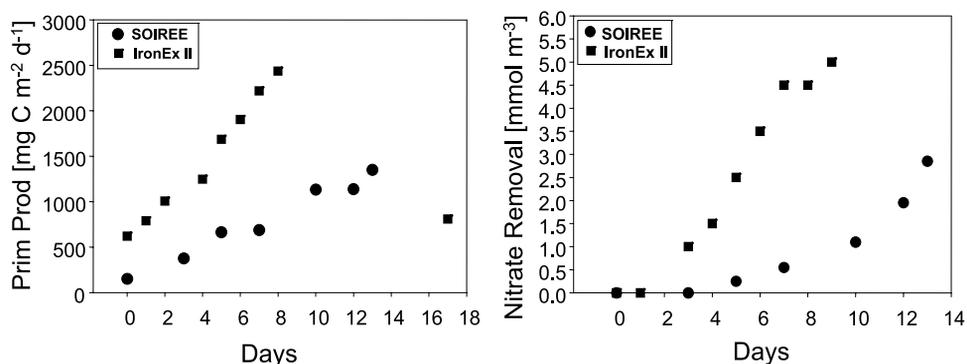


Figure 5. Comparison of IronEx-2 and SOIREE. The faster response in (left) primary production and (right) nitrate removal during IronEx-2 in the equatorial Pacific Ocean is consistent with the lower ambient temperature, lower PAR, deeper wind mixed layer (WML) depth, and severe lateral patch dilution during SOIREE.

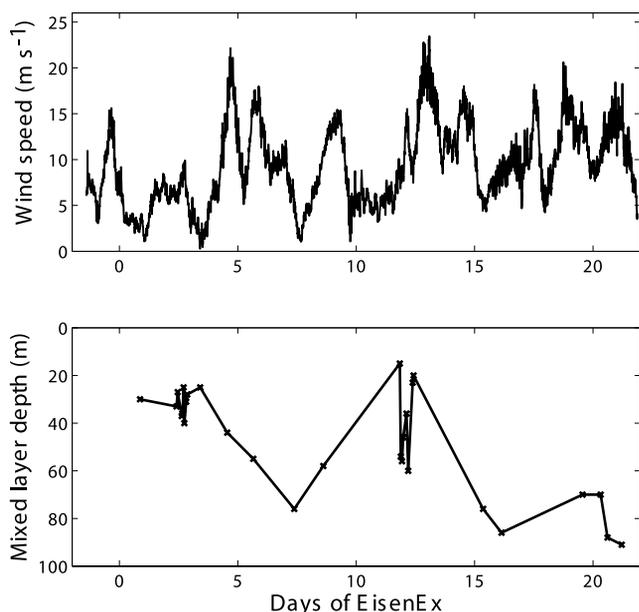


Figure 6. Generally high wind velocities (m s^{-1}) and two storms in the Southern Ocean caused a very deep wind mixed layer (m) during 21 days of the Carbondioxide Uptake Southern Ocean (CARUSO)/Eisen(=Iron) Experiment (EisenEx) [Bakker *et al.*, 2005].

by two major storms (days 5 and 13) and overall strong winds throughout the 23 days of observations [Bakker *et al.*, 2005]. The WML increased from an initial 40–50 m to almost 100 m during the final days 16–22 (Figure 6). Patch size increased concomitantly. Shear stress in the energetic ocean frontal region also played a role in increasing the patch size from 50 km^2 during the first Fe/SF₆ infusion to 950 km^2 in the final survey map. The Fv/Fm responded with a slight but distinct increase within a day [Gervais *et al.*, 2002]. Within 48 hours, Fv/Fm increased from 0.3 to 0.4 and steadily increased to 0.52 by final day 21. An increase in primary production on day 2 preceded increases in Chl *a* on day 4 for all pico-, nano-, and microphytoplankton size classes (pico < 2; 2 < nano < 20; micro > 20 μm). After day 2, the picoplankton Chl *a* remained constant, likely due to a balance between growth and grazing, but the nanoplankton Chl *a* steadily increased, and the initially smallest pool of microplankton Chl *a* (>20 μm) increased exponentially to dominate primary production after day 16 [Gervais *et al.*, 2002]. The first study of diurnal carbohydrate dynamics in an enrichment experiment showed increases of both daytime production and nocturnal consumption of polysaccharides in Fe enriched waters, the polysaccharide production furthermore being light limited [van Oijen *et al.*, 2005]. During the initial phase, the microplankton diatoms were dominated by *Fragilariopsis kerguelensis* with a mean depth-integrated abundance of 5737 cells L^{-1} at $T = 0$ (day 0) of the experiment. This species increased to 22,146 cells L^{-1} inside and 9,389 cells L^{-1} outside the patch by day 21. Chain lengths on the order of 4–30 cells/chain were indicative of favorable growth, with maximum observed lengths of up to 160 cells/chain. During the second phase of the experiment the smaller *Pseudo-nitzschia lineola* became by far the most abundant,

ultimately accounting for 53% of total diatom cells and 25% of total diatom biomass [Assmy, 2004]. A similar marked response was observed for the small centric diatom *Chaetoceros debilis*. Among all diatom species *P. lineola* showed the highest accumulation rate of 0.20 d^{-1} , and even outside the patch was growing at 0.09 d^{-1} [Assmy, 2004]. By the end of the experiment the depth-integrated cell numbers of *Pseudo-nitzschia* had increased 11-fold within the patch ($18.7 \cdot 10^9$ cells m^{-2}) versus the control station ($1.7 \cdot 10^9$ cells m^{-2}). Very large diatoms (e.g., *Rhizosolenia* sp., *Thalassiothrix* sp., *Corethron pennatum*) also responded strongly. Although cell numbers of this very large size class were much lower, in terms of biomass (both organic and opal) they may be quite significant. Twenty days after the first Fe infusion, the maximum changes in the surface waters of the patch relative to the outside patch measurements [Bozec *et al.*, 2005] were -15 mmol m^{-3} for DIC, $-23 \cdot 10^{-6}$ atm for $f\text{CO}_2$, $+0.033$ units for pH, $-1.61 \text{ mmol m}^{-3}$ for nitrate, and $-0.16 \text{ mmol m}^{-3}$ for phosphate (Figure 7). Despite the significant increase in larger diatoms within the patch, the dissolved silicate showed a similar decrease of about 4 mmol m^{-3} for the in-patch and out-patch stations.

[13] The Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS) enjoyed favorable summer weather (July 2001) and a shallow 10 m wind mixed layer during the single infusion of 350 kg Fe and 0.48 M SF₆ into its 8 × 10 km patch size [Tsuda *et al.*, 2003]. The Fv/Fm of the whole community rose from a low initial value of 0.2 to 0.3 on day 4, significantly exceeding the out-patch value. This coincided with the onset of a strong growth phase of the >10 μm size class on day 4 due to a very rapid increase of the chain-forming centric diatom *Chaetoceros debilis*, which initially had occurred in low numbers (~ 400 cells L^{-1} at day 0). This gave rise to a very strong increase in Chl *a* in the >10 μm size class which fully dominated the total Chl *a* pool reaching a record of 19 mg m^{-3} at the final day 13 of observations (Figure 8). The smaller diatom *Pseudo-nitzschia turgidula* [Hasle, 1993] did have higher initial abundance (10,000 cells L^{-1}) but increased slowly and was surpassed by *C. debilis* on day 6 in terms of cell numbers. Similar to the previous IronEx-2 and SOIREE experiments, albeit more trivial at SEEDS, there was an increase and finally a decrease, of the nanoplankton (2–10 μm). On the final day 13 both nitrate and silicate were virtually depleted (Figure 8), consistent with a decrease again in Fv/Fm on days 11 and 13 indicative of nutrient stress (N, Fe or both), and accompanied by record decreases in $f\text{CO}_2$ ($94 \cdot 10^{-6}$ atm) and DIC (61 mmol m^{-3}) [Tsuda *et al.*, 2003].

[14] The Southern Ocean Fe Experiment (SOFeX), in January–February 2002 increased the effort compared with the previous experiments by fertilizing two patches (North and South) at the same time, each patch being larger (225 km^2) than before, with sophisticated multiship logistics of R/V *Revelle*, R/V *Melville* and icebreaker *Polar Star* [Coale *et al.*, 2004].

[15] The SOFeX-North patch with low-silicate (<3 mmol m^{-3}) high-nitrate (20 mmol m^{-3}) sub-Antarctic waters, had two infusions of 631 kg Fe on days 0 and 5 (10–12 and 16 January) and a third 450 kg infusion on day 30 (10 February). The initial WML was 45 m deep increasing to 55 m 1 month later [Coale *et al.*, 2004, Table S1]. Owing to many frontal systems in the region, SOFeX-North expe-

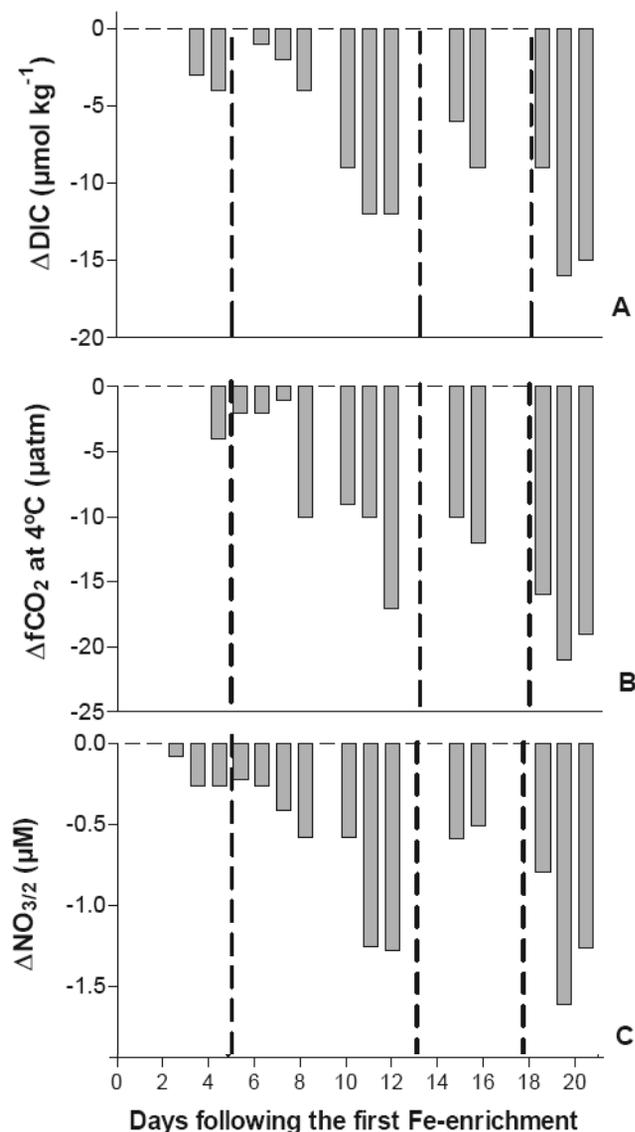


Figure 7. Changes in (a) dissolved inorganic carbon (DIC ($\mu\text{mol kg}^{-1} = 10^{-6} \text{ mol kg}^{-1} \text{ seawater}$)), (b) fugacity of CO_2 (10^{-6} atm), and (c) nitrate + nitrite ($\mu\text{M} = \text{mmol m}^{-3}$) during 21 days of the CARUSO/EisenEx experiment in the Southern Ocean [Bozec et al., 2005]. Dotted lines indicate heavy storm events at days 5, 13, and 17.

rienced more shear stress than CARUSO/EisenEx. It was streaky immediately after the first infusion, and by day 38 the patch had evolved into a 7-km-wide by at least 340-km-long filament. The Fv/Fm increased from the initial 0.2 to 0.5 at the end. The SOFeX-North patch was characterized by an approximately 20-fold increase in Chl *a* (up to 2.6 mg m^{-3}) and a fourfold increase in phytoplankton carbon biomass. In the early stages (first 2 weeks), the increase was almost entirely due to $>5 \mu\text{m}$ nonsiliceous taxa (prymnesiophytes, pelagophytes, dinoflagellates). After a month, however, $>20 \mu\text{m}$ diatoms, strongly dominated by *Pseudo-nitzschia*, had risen from 5 to 38% of total phytoplankton biomass despite low available silicate [Coale et al., 2004; S. Brown and M. Landry, personal communication, 2005]. Physical mixing and dilution processes

entrained dissolved silicate into the patch [Coale et al., 2004; Hiscock and Millero, 2005], akin to the chemostat effect in SOIREE [Abraham et al., 2000]. This prevented the complete removal of silicate, thus allowing for sustained, however Si-limited, diatom production [Brzezinski et al., 2005; Hiscock and Millero, 2005]. The maximum changes in carbonate and nutrient parameters for the North Patch were $-14 \pm 5 \text{ mmol m}^{-3}$ for DIC, $-26 \pm 5 \cdot 10^{-6} \text{ atm}$ for fCO_2 , $-0.09 \pm 0.03 \text{ mmol m}^{-3}$ for phosphate, $-1.1 \pm 0.4 \text{ mmol m}^{-3}$ for silicate, and $-1.4 \pm 0.2 \text{ mmol m}^{-3}$ for nitrate [Hiscock and Millero, 2005].

[16] The SOFeX-South patch in high silicate (60 mmol m^{-3}) and high nitrate (28 mmol m^{-3}) Antarctic waters had four infusions of 315 kg Fe on days 0, 4, 7 and 11 (24 January–5 February), with the depth of the WML remaining constant at 35 m [Coale et al., 2004, Table S2]. The study site was strongly dominated by diatoms (2/3 of phytoplankton C at initial and out-patch “control” stations), notably *Pseudo-nitzschia*, *Chaetoceros*, *Thalassiothrix* and *Fragilariopsis* species and various smaller pennates. The community-wide Fv/Fm increased from 0.25 to 0.65, and overall maximum photosynthetic rates increased from 0.29 to $4.6 \text{ mmol C m}^{-3} \text{ d}^{-1}$ (Figure 9). Total fluorometric Chl *a* increased by about eightfold, from ~ 0.5 on day 0 to 4 mg m^{-3} on day 21. This response comprises a greater than threefold increase in the phytoplankton Chl *a*:C ratio, and slightly greater than a twofold increase in carbon biomass (M. Landry and S. Brown, personal communication, 2005). Cells in the size ranges of $10\text{--}20$ and $20\text{--}100 \mu\text{m}$ showed the highest net rates of change, increasing to about 3 times initial levels, with net rates of change dropping appreciably for $>100 \mu\text{m}$ cells (very large diatoms) and negligible change for $<10 \mu\text{m}$ cells. Thus while the community response was not dramatic, there was a significant shift to intermediate and large-sized cells and more diatoms (increasing from 66 to 80% of phytoplankton carbon biomass) (M. Landry and S. Brown, personal communication,

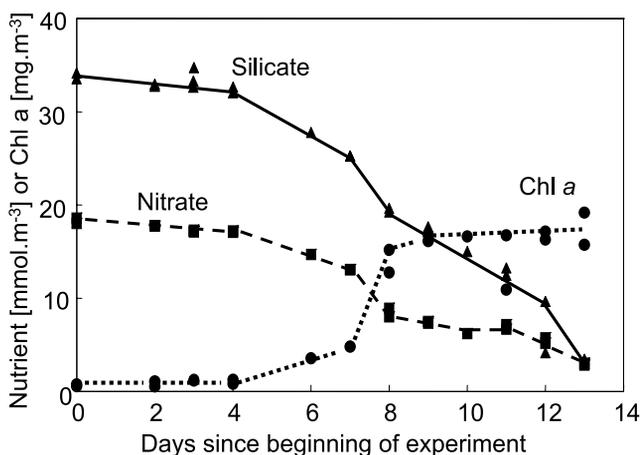


Figure 8. After a single Fe addition, a record increase in Chl *a* (mg m^{-3}) and virtual depletion of nitrate (mmol m^{-3}) and silicate (mmol m^{-3}) due to blooming of fast growing diatom *Chaetoceros debilis* under favorable WML depth conditions of the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS) experiment in the northwest Pacific Ocean [Tsuda et al., 2003].

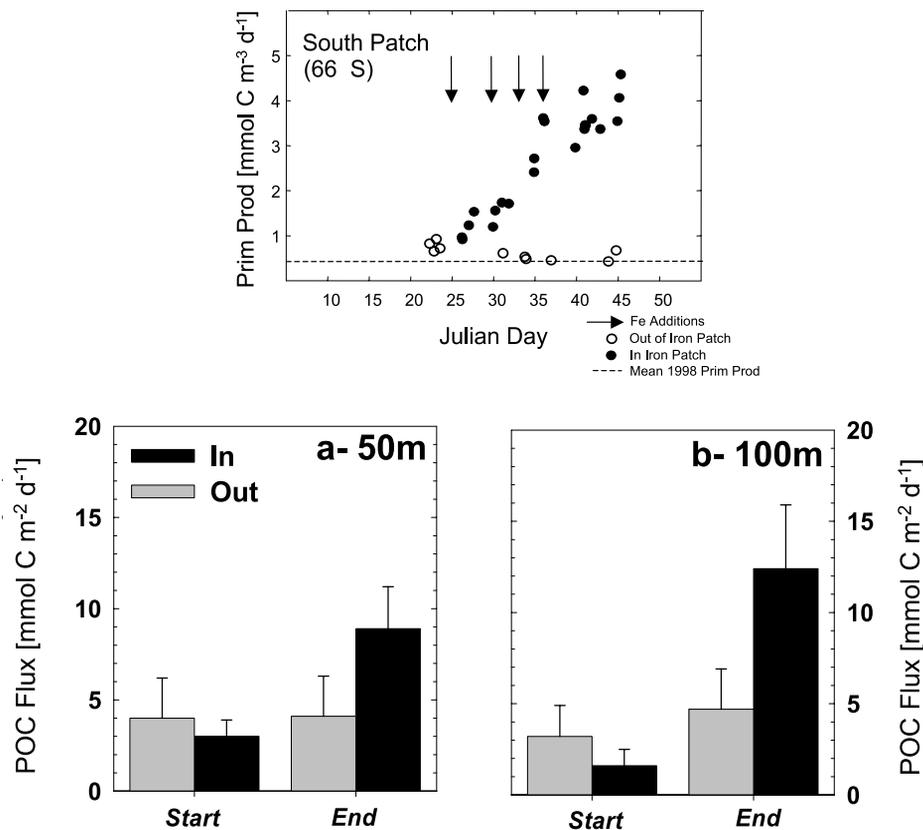


Figure 9. (top) Upon four consecutive Fe fertilizations (arrows on top) of the large 255 km² South patch of Southern Ocean Fe Experiment (SOFeX), dramatic increase (filled dots) of the primary production (mmol C m⁻³ d⁻¹) compared to the out-patch development (open circles) [Coale *et al.*, 2004]. For exact times of fertilizations, see Coale *et al.* [2004, Tables S1 and S2]. (bottom) Significant increase of the particulate organic carbon (POC) export (mmol C m⁻² d⁻¹) across the (a) 50 m and (b) 100 m depth horizons at the end of day 28 of the SOFeX-South patch (in iron, filled, shaded), derived from the ²³⁴Th deficiency method (redrafted after Buesseler *et al.* [2004]).

2005). The maximum changes of carbonate parameters in the South Patch mixed layer were -21 ± 5 mmol m⁻³ for DIC and $-36 \pm 4 \cdot 10^{-6}$ atm for fCO₂ [Hiscock and Millero, 2005]. The maximum changes for nutrients were -0.22 ± 0.03 mmol m⁻³ for phosphate, -3.6 ± 0.2 mmol m⁻³ for silicate, and -4.1 ± 0.2 mmol m⁻³ for nitrate [Hiscock and Millero, 2005]. Changes in the carbonate and nutrient systems of the South Patch were larger than those in the North Patch. In addition, the export of carbon as particles settling into deeper layers was determined to be significant by the ²³⁴Th deficiency technique (Figure 9), but modest with respect to regular estimates in the region [Buesseler *et al.*, 2004, 2005].

[17] During summer of the same year (July 2002), another multiship experiment, the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) was conducted at ocean station “Papa” (50°N, 145°W) where it all had started [Martin and Fitzwater, 1988]. Upon two Fe infusions (days 0 and 6) of the quite favorable fairly shallow 30 m WML depth, the 77 km² patch enlarged to >200 km² by day 13 and to a maximum of about 1000 km² by days 17–18 [Boyd *et al.*, 2004a]. The Fv/Fm increased from an initial value of 0.2 to at most 0.4 by day 11, dropping to about 0.2 by day 19 then decreasing further to well below 0.2 at day 21 [Boyd *et al.*, 2004a, suppl. Figure 1]. The Chl *a* increased

[Harrison *et al.*, 2004] from an initial 0.6 mg m⁻³ to a maximum 5.5 mg m⁻³ on day 17, then dropped sharply to about 1.5 mg m⁻³ by days 23–25 (Figure 10). The parallel increase of diatom biovolume was stronger relative to the low initial values, and the strongest increase (days 10–15) was nicely mirrored by a sharp decrease in dissolved silicate (Figure 10). The most dramatic blooming was by the small pennate diatom, *Pseudo-nitzschia* sp., which increased from an initial 174 cells L⁻¹ to 192,000 cells L⁻¹ at peak days 15–18 [Marchetti and Harrison, 2004]. Similarly the almost 100-fold larger cells of the pennate *Thalassiothrix* increased from 17 to 12,100 cells L⁻¹, thus dominating by some 33% the carbon inventory of all diatoms. Centric diatoms of medium (*Chaetoceros* sp.), large (*Thalassiosira*, *Proboscia*) and very large (*Rhizosolenia*) sizes, together comprised over 60% of the diatom carbon inventory. On about day 16, silicate was depleted, and the bloom declined, leading to increased export flux into sediment traps at 50, 75, 100 and 125 m (Figure 10). This, and the above-mentioned export flux at SOFeX-South, were the first convincing observations of Fe-stimulated export of POC and Si into deeper waters. Over the 25 day experiment, about 14 mmol m⁻³ silicate and 5 mmol m⁻³ nitrate were removed (Figure 10). The fCO₂ showed its maximum decrease of over 70 · 10⁻⁶ atm in the patch centre at day

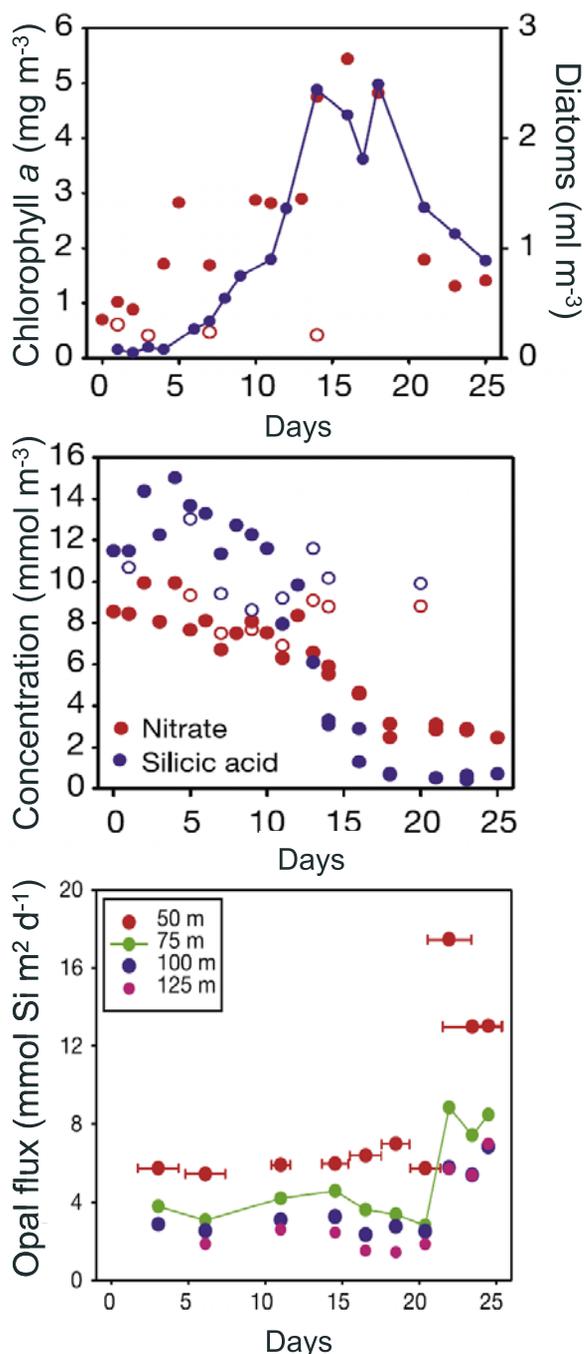


Figure 10. Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) experiment in the northeast Pacific Ocean: (top) the initial strong bloom development of (red) Chl a (mg m^{-3}) and (blue) diatom biovolume (mL m^{-3} seawater) eventually led to (middle) nutrient depletion, causing a decline of the bloom after day 18 (upper panel) as well as a significant increase in settling particles exported into (bottom) deeper waters. Solid symbols are in patch, open symbols are out of patch (graphics after *Boyd et al.* [2004a]).

18 [*Boyd et al.*, 2004a, supplement]. On the same day, DIC had decreased by about 40 mmol m^{-3} , but then it increased again due to the combined effects of bloom decline (respiration) and patch dilution with ambient waters.

[18] Finally the very recent EIFEX experiment (2004) in the Southern Ocean is mentioned but results are not yet available.

3. Light Limitation and Other Physical Forcings

[19] Wind mixing strongly influences the amount of light that phytoplankton receive for growth. When comparing the eight Fe experiments there is a wide range of average depths of the wind mixed layer (Figure 11, black bars), which vary from a shallow 10–15 m for SEEDS to ~ 100 m for CARUSO/EisenEx (Figure 6). The maximum yield of Chl a abundance shows an inverse relationship with WML (Figure 11, green bars).

[20] Excluding IronEx-1, which is anomalous due to early subduction, one finds a striking and significant ($R^2 = 0.90$) inverse relationship between maximum Chl a yield and average WML depth (Figure 12 (top)). Hence having dumped a total of 8795 kg of Fe into HNLC waters and utilizing about 1 year of shiptime, we may conclude that

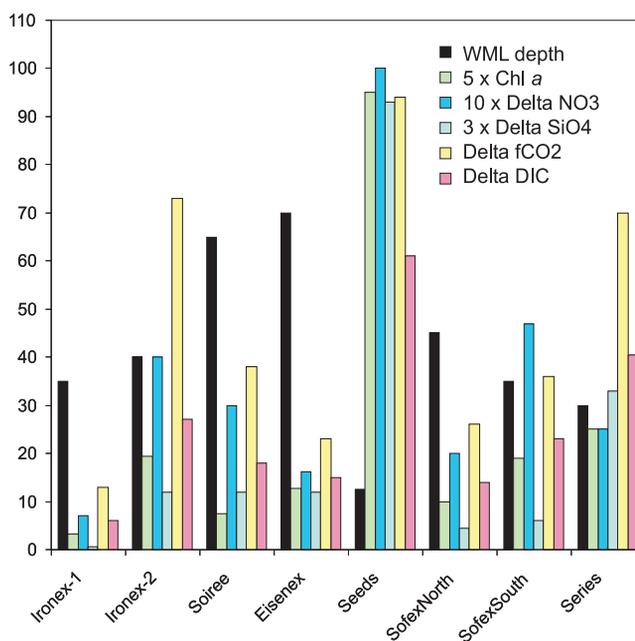


Figure 11. Comparison of WML depth and maximum observed abundance (Chl a) or concentration change in the patch for eight experiments; some variables are scaled such that all fit a common 0–100 vertical axis. WML depths are as reported for each experiment; see source articles for WML definition criteria (e.g., density gradient) of any given experiment. For SOFeX the WML values are after *Coale et al.* [2004, Tables S1 and S2], rather than deviating values in the printed article. Black is WML depth (m), green is fivefold the maximum observed Chl a (mg m^{-3}), dark blue is 10-fold maximum observed nitrate removal (mmol m^{-3}), light blue is threefold maximum observed silicate removal (mmol m^{-3}), yellow is maximum observed decrease in fugacity of CO_2 (10^{-6} atm), and red is maximum observed DIC removal (mmol m^{-3}). Sources are as follows: *Cooper et al.* [1996]; *Bozec et al.* [2005]; *Bakker et al.* [2005]; *Hiscock et al.* [2002]; *Hiscock and Millero* [2005]; *Tsuda et al.* [2003]; *Coale et al.* [2004]; and *Boyd et al.* [2004a].

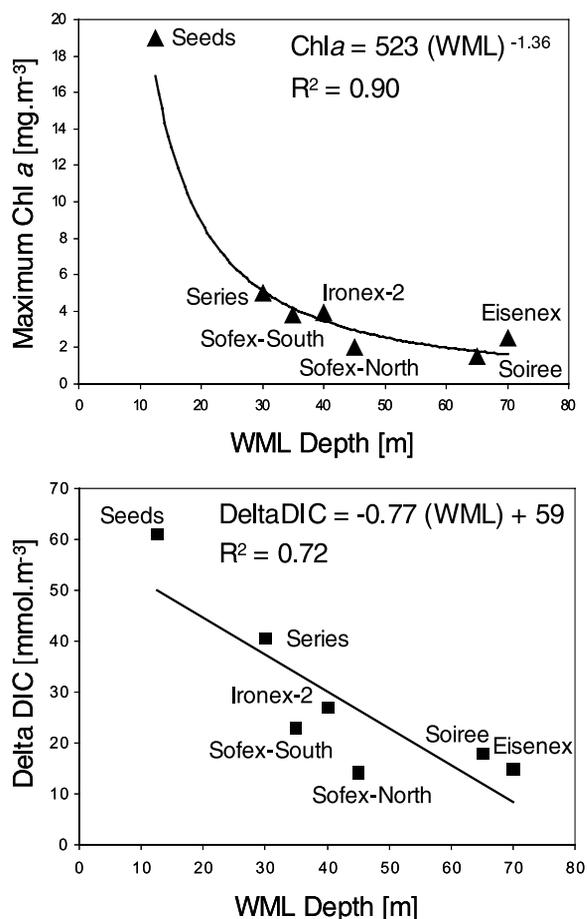


Figure 12. (top) Apparent inverse and significant relationship between the maximum observed Chl *a* abundance (mg m^{-3}) and WML depth (m) for seven experiments. The probability that the fitted curve with an exponent of -1.342 is due to chance alone is low enough ($P = 0.003$, $t = -5.55$, $R^2 = 0.90$, $n = 7$) to reject the hypothesis that WML depth has no effect. Excluded is IronEx-1 for its somewhat anomalous premature end on day 4 due to the subduction of the patch. (bottom) Same for maximum observed removal of DIC (mmol m^{-3}).

light is the ultimate determinate of the phytoplankton biomass response. However, Chl *a* may not be the most suitable variable for biomass. Since iron is required for synthesis of the chlorophyll molecule, and Fe-depleted phytoplankton tend to be short in Chl *a*, one of the first responses to Fe enrichment is an increase in cellular Chl *a* (Figure 13). For example, the mean C:Chl ratio of phytoplankton decreased by factors of 4–5 in the IronEx-2 and CARUSO/EisenEx patches [Landry *et al.*, 2000a; M. J. W. Veldhuis and K. R. Timmermans, Phytoplankton dynamics during the EISENEX in situ iron fertilization experiment in the Southern Ocean: A comparative study of field and bottle incubation measurements, submitted to *Limnology and Oceanography*, 2005] and only slightly less in SOFeX-South (M. Landry, personal communication, 2005). Since Chl *a* yield exaggerates the phytoplankton biomass response to Fe fertilization, a more suitable indicator may be preferable.

[21] Both the maximum nitrate removal and the maximum fCO_2 drawdown (Figure 11, blue and red bars, respectively) also show trends opposite to the WML depth, but the fits ($R^2 = 0.69$ and $R^2 = 0.63$, respectively) are less convincing (Table 2). Perhaps the maximum net removal (photosynthesis/respiration) of DIC, which also shows an inverse trend with WML depth (Figure 11) with a better fit ($R^2 = 0.72$; see Figure 12 (bottom)), is the most suitable overall biomass indicator.

[22] Of course other physical factors are also at play here. First, the amount of incident light at the sea surface, or photosynthetically active radiation (PAR), varies from day to day, by region and by season (Figure 14). Moreover, when a bloom develops, the self-shading by the more abundant phytoplankton diminishes the available light below, and thus the maximum extent of the euphotic zone of positive phytoplankton growth (not shown).

[23] The optimal or maximum rate of growth (μ_{max} after Monod [1942]) is well known to be a function of temperature, where for each 10°C rise in temperature the maximum growth rate doubles [Eppley, 1972; Goldman and Carpenter, 1974]. Given the range in temperatures (Figure 14) one would expect the primary production during IronEx-2 (25°C) to be almost fourfold faster than during SOIREE (2°C), and such trend is apparent indeed (Figure 5).

[24] Similarly, SEEDS (9.5°C) showed growth rates about 50% faster than CARUSO/EisenEx. In fact, during days 4–7 of SEEDS, the major diatom *C. debilis* grew at a net rate of 2.6 doublings/day ($\mu = 1.8 \text{ d}^{-1}$), exceeding the expected maximum of 1.5 doublings/day ($\mu = 1.0 \text{ d}^{-1}$) at 9.5°C [Tsuda *et al.*, 2003].

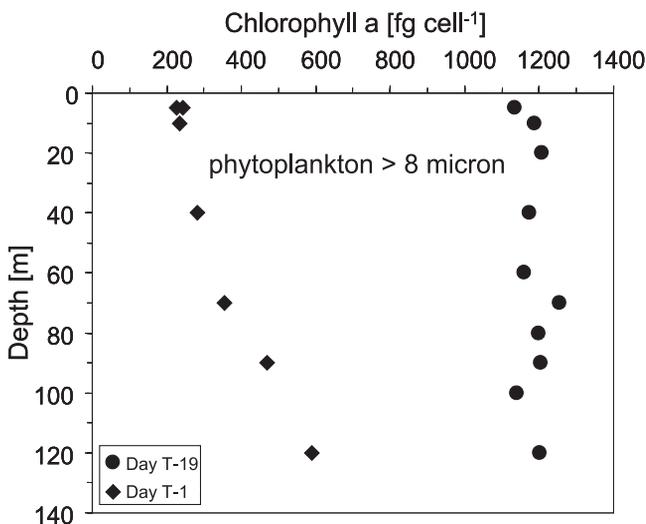


Figure 13. Amount of Chl *a* per cell ($\text{femtogram cell}^{-1}$) increased about fourfold in the most stimulated largest size class ($>8 \mu\text{m}$) eukaryote phytoplankton (i.e., diatoms) during the first 19 days of the CARUSO/EisenEx experiment (data of M. J. W. Veldhuis). Such an increase of cellular Chl *a* was evident already from the C/Chl *a* ratio in one of the first bottle experiments [Coale, 1991, Figure 6] and in IronEx-2 [Cavender-Bares *et al.*, 1999]. In retrospect, this also indicates that Chl *a* exaggerates the phytoplankton biomass response to added Fe (Figures 11 and 12).

Table 2. Apparent Inverse Relationships of Wind Mixed Layer (WML) Depth Versus Observed Maximum Chl *a* and Versus Observed Maximum Removals of Nitrate, Fugacity of CO₂, and Dissolved Inorganic Carbon (DIC) in Seven Experiments^a

Function of WML Depth	Best Fit	R ²	n
Maximum chlorophyl = <i>f</i> (WML)	$y = 523.21 x^{-1.3598}$ (exponential)	0.90	7
Maximum delta nitrate = <i>f</i> (WML)	$y = 82.33 x^{-0.884}$ (exponential)	0.69	7
Maximum delta fCO ₂ = <i>f</i> (WML)	$y = -1.087 x + 97.62$ (linear)	0.63	7
Maximum delta DIC = <i>f</i> (WML)	$y = -0.772 x + 59.04$ (linear)	0.72	7

^aWML depth is in meters. Observed maximum Chl *a* is in mg m⁻³. Fugacity of CO₂ is in 10⁻⁶ atm. Dissolved inorganic carbon is in mmol m⁻³. The probability that the fitted curve of Chl *a* versus WML with an exponent of -1.342 is due to chance alone is low enough ($P = 0.003$, $t = -5.55$, $R^2 = 0.90$, $n = 7$) to reject the hypothesis that WML depth has no effect. Excluded is IronEx-1 due to premature end at day 4 by patch subduction. The better fits for Chl *a* and for DIC are illustrated in Figure 12. The goodness of fit R^2 for $n = 7$ data points is remarkable but certainly not perfect due to several other factors (temperature, photosynthetically active radiation, patch dilution, grazing, and K_m for Fe limitation of predominantly responding phytoplankton species) also playing roles; see text.

[25] Finally, due to combined wind mixing and shear stress, the initial patch tends to dilute, somewhat by mixing with underlying waters, but apparently more by lateral mixing. With most initial patch size areas of about 50–80 km², and 225 km² for SOFeX patches, the final patch area after 13–38 days of observations may well exceed 2000 km² (Figure 15). Obviously the resulting dilution factor will be least at the patch centre and increase toward its edges, and in principle can be assessed from the distribution of SF₆ tracer in time and space, after a correction for SF₆ loss by gas exchange. However, matters are complicated by the need for several Fe infusions, while only the first infusion included the SF₆ tracer. Also, patches can evolve very chaotically (CARUSO/EisenEx, SOFeX-North) defying quantitative description. Here, we simply have taken the ratio of initial patch size and reported final patch size as indicative of lateral patch dilution. This dilution factor varies from 3 and to 19, where obviously the length in days of the experiment plays a role (Figure 15 and its caption).

4. Linking the Peaceful Pacific With the Roaring Forties

[26] Given the wide range in physical conditions (WML depth, PAR, temperature, patch dilution) and biogeochemical responses (Figures 11, 14, and 15), we will take up the challenge of determining coherence between only the two extreme cases: SEEDS with favorable conditions and record responses, and CARUSO/EisenEx.

[27] After completing the 15 hours of the first Fe infusion for CARUSO/EisenEx, seawater samples were immediately collected in both the in-patch and at an out-patch control station. This seawater was placed in a suite of PMMA bottles (transparent for UVB + UVA + visible light) in deck incubators with screening to simulate a 12 ± 4 m light depth [van Oijen and Rijkenberg, 2004], as well as in large 20 L polycarbonate bottles incubated under artificial light on a 12/12 hour day/night cycle at a light level ($3.5 \text{ mol m}^{-2} \text{ d}^{-1}$) corresponding to the 25 m light depth (K. R. Timmermans et al., manuscript in preparation, 2005). The PAR reaching the sea surface as well as the screened deck incubators varied between 12 and 55 $\text{mol m}^{-2} \text{ d}^{-1}$, averaging 30 $\text{mol m}^{-2} \text{ d}^{-1}$.

[28] Four cases can now be compared. The CARUSO/EisenEx in situ in-patch stations reached a maximum nitrate removal of 1.6 mol m^{-3} after 21 days (Figure 7 (bottom)). The in-patch samples of the CARUSO/EisenEx deck incu-

bators were completely depleted of both nitrate and silicate after 12–14 days (Figure 16 (left)), strikingly similar to the SEEDS in situ result after 13 days (Figure 8). In these deck incubators, the same diatoms as found in the field showed healthy net growth rates of $0.4\text{--}0.6 \text{ d}^{-1}$, with significantly (10–15%) higher growth for the Fe-fertilized in-patch bottles, notably for *Pseudo-nitzschia* which eventually was dominant both in these bottles and in the in situ in-patch stations [van Oijen and Rijkenberg, 2004].

[29] Remarkably, only *Fragilariopsis kerguelensis* did not show higher growth rates for the Fe-enriched in-patch bottles versus control out-patch bottles. This is consistent with its failure to eventually dominate the in situ in-patch stations (as opposed to SOREE). Finally, the CARUSO/EisenEx in-patch samples cultured under lower artificial light were somewhat slower, only exhausting nitrate and silicate after 18 days (Figure 16 (right)).

[30] When comparing the physical forcing parameters temperature, WML depth and the patch dilution factor for

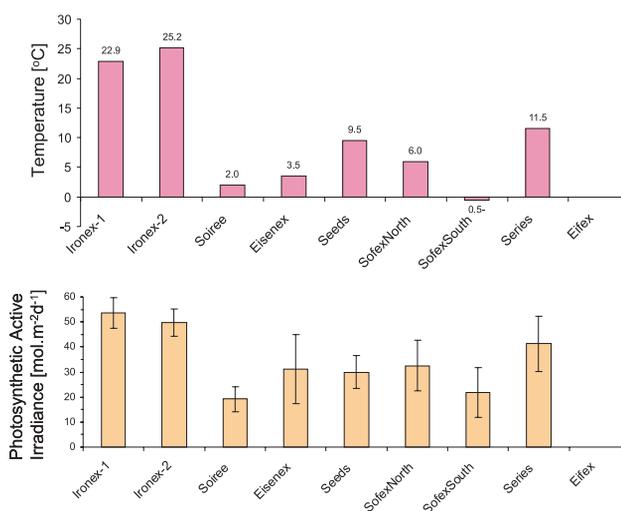


Figure 14. (top) Average temperature (°C) in surface waters. (bottom) Photosynthetic active irradiance (PAR) ($\text{mol m}^{-2} \text{ d}^{-1}$) at the sea surface; average value over the given experiment. Day-to-day variability indicated by error bars (two sigma standard deviation of the daily values for the given experiment) is small in equatorial IronEx-1 and IronEx-2 and large in EisenEx.

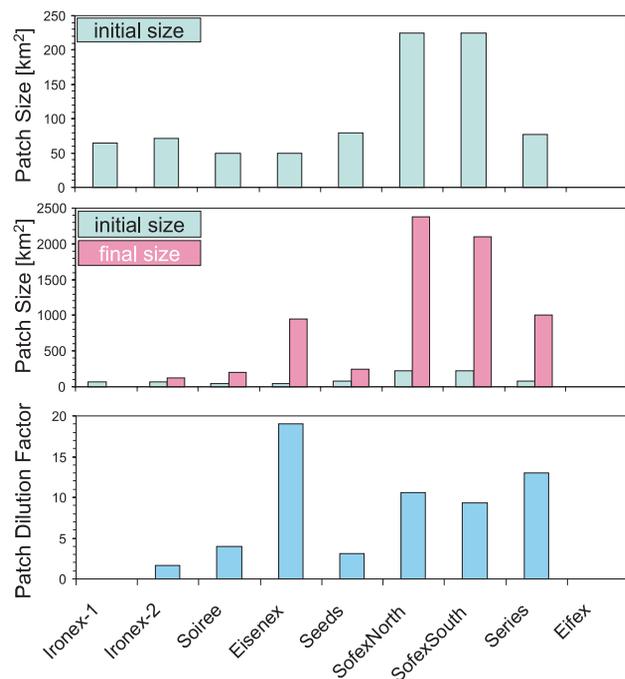


Figure 15. (top) Initial patch area (km²) compared with (middle) final patch area (km²) (note 10-fold larger vertical scale) and (bottom) their derived ratio (final/initial) or patch dilution factor. Patch dilution factor obviously also tends to increase with the length (days) of the observation period: IronEx-2 was 17 days, SOIREE was 13 days, EisenEx was 23 days, SEEDS was 13 days, SOFeX-North was 38 days, SOFeX-South was 20 days, and SERIES was 18 days at bloom optimum and 23 days overall.

the two extreme in situ experiments CARUSO/EisenEx and SEEDS (Figure 17 (top)), one notices that simulated WML depths of the CARUSO/EisenEx bottle treatments are similar to, or slightly deeper, than for SEEDS. Moreover, bottles obviously have a dilution factor of 1 (no dilution), closer to the modest factor of 3 of SEEDS than the large dilution factor of 19 for CARUSO/EisenEx. The resulting daily removal rates of nitrate and silicate (Figure 17 (bottom)) in both bottle treatments nicely bridge the gap between the nutrient removal rates of the two in situ experiments. The fact that both nutrients are also fairly rapidly removed in the control treatments (Figure 16), further confirms the major impact of light relative to Fe deficiency. Even though the differences of PAR as well as temperature between CARUSO/EisenEx and SEEDS (Figure 14) have been ignored here, the strong influence of WML depth, defining the mean light environment, as well as the dilution factor, is very obvious. Admittedly, this is just a very simple approach, only providing a working hypotheses for a more refined validation of day-to-day changes in these four cases by plankton ecosystem modeling [Lancelot et al., 2000; Pasquer et al., 2005], with all physical forcings (WML depth, PAR, dilution factor, temperature) in the model varying daily and acting simultaneously.

5. Large Diatoms

[31] In all of the experiments, added Fe produced a striking shift-up response of cell numbers of larger size classes of diatoms. In general the community biomass shifted from mostly nanoplankton (<10 μm) to mostly microplankton (>10 μm). As noted previously, the intermediate-sized pennate (*Pseudo-*) *Nitzschia* sp. took over in

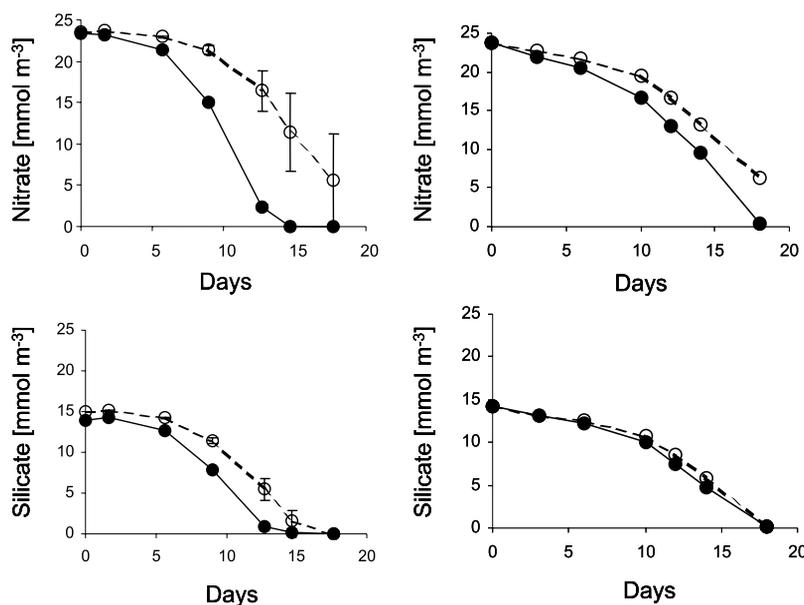


Figure 16. (left) Rapid removal of dissolved nitrate (mmol m⁻³) and silicate (mmol m⁻³) in deck incubations at ~8–16 m simulated light depth of in-patch (filled symbols) and out-patch (open symbols) of 20 L seawater during CARUSO/EisenEx [van Oijen and Rijkenberg, 2004]. (right) Similar but under controlled 12 hour light/12 hour dark cycle with 3.5 mol m⁻² d⁻¹ light level corresponding to a ~25 m simulated light depth during EisenEx (K. R. Timmermans et al., manuscript in preparation, 2005).

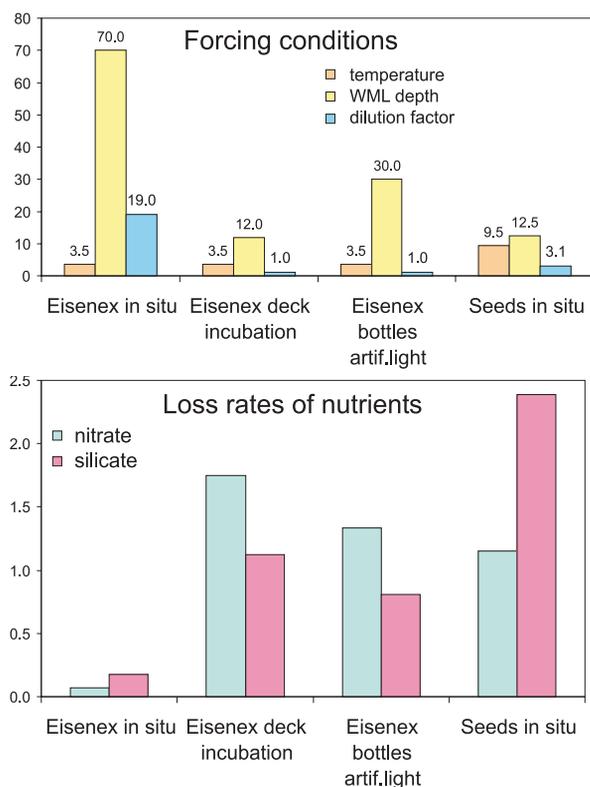


Figure 17. (top) Case study linking EisenEx and SEEDS by comparison of different physical forcings, temperature (°C), WML depth (m), and dilution factor, with (bottom) resulting daily nutrient removal rates ($\text{mmol m}^{-3} \text{d}^{-1}$). Not shown in Figure 17 (top) is the different forcing by incident light PAR averaging $31.1 \text{ mol m}^{-2} \text{d}^{-1}$ during EisenEx and $29.96 \text{ mol m}^{-2} \text{d}^{-1}$ during SEEDS.

IronEx-2 [Landry et al., 2000a]. *Pseudo-nitzschia* species also dominated in CARUSO/EisenEx, SOFeX-North and SERIES. The large chain-forming pennate *Fragilariopsis kerguelensis* was most successful in terms of cell numbers in SOIREE, consistent with its spring bloom development and dominance in the naturally Fe-rich Polar Frontal jet [de Baar et al., 1995, 1997]. Both *Fragilariopsis kerguelensis* and *Pseudo-nitzschia* were numerically dominant in SOFeX-South, also at the control stations. During SEEDS, the centric chain-forming *Chaetoceros debilis* responded very strongly, replacing the smaller pennate *Pseudo-nitzschia turgidula* in both cell abundance and biomass after 6 days. These in situ results are consistent with the major conclusion of a preceding synthesis of all preceding bottle incubation experiments and natural Fe-replete regions which documented a systematic Fe stimulation of the large size class of diatoms [de Baar and Boyd, 2000].

[32] Reports on very large diatoms (0.1–1 mm) have been relatively sporadic. Nevertheless, very large taxa (*Rhizosolenia* sp., *Thalassiothrix*, *Thrichotoxon*, *Asteromphalus*, *Actinocyclus* sp.) with elongate “needles” as well as perfectly discoid forms should not be overlooked. In terms of biomass (organic matter or opal), these “giants” may in some experiments have grown to higher levels than the numerically more abundant (cells m^{-2}) large diatoms.

[33] Timmermans et al. [2001a, 2001b, 2004] have succeeded in maintaining such very fragile (spines, weak chains) diatoms of moderate (10–30 μm), medium (30–60 μm) and large (>60 μm) size classes in cultures of natural (no EDTA disturbances [Gerringa et al., 2000]) Antarctic seawater. From their curves (not shown) of growth rate responses versus added dissolved Fe, the constants K_m for half-saturated growth (= 50% of maximum growth rate) now show a convincing inverse relationship with surface/volume ratio (Figure 18). Since surface/volume ratio is itself inversely related to size, the required ambient Fe concentration to achieve 50% of maximum growth rate clearly increases as a (fairly linear) function of diatom size. Moreover, the required Fe concentrations (0.2–1.2 nM) are above the typical dissolved Fe concentrations of remote oceanic surface waters. In other words, these size classes of moderate (10–30 μm), medium (30–60 μm) and large (>60 μm) diatoms can only bloom upon an extra delivery of dissolved Fe, either by wet dust deposition from above [Jickells and Spokes, 2001], by an Fe-rich oceanic front [de Baar et al., 1995, 1997], by an upwelling/mixing supply event from below [Hoppema et al., 2003], by iron supply from shallow topography [Blain et al., 2001], or by an in situ Fe fertilization experiment.

[34] The observed linear relationship between diatom size and Fe requirement for growth is a major step forward and key to understanding the in situ experiments. When superimposing the above K_m of the large *F. kerguelensis* and very large *Actinocyclus* on the time series of dissolved Fe (<0.2 μm filtrate) in SOIREE, the minimum observed dissolved Fe is more or less adequate to support half-

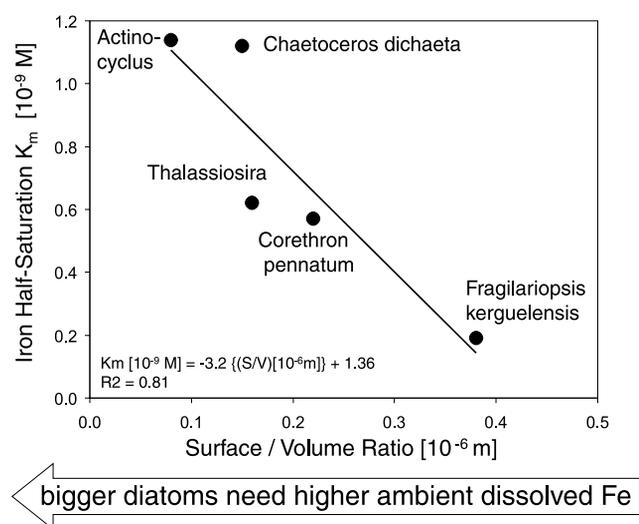


Figure 18. Inverse relationship between surface/volume ratio of medium-sized and large-sized Antarctic diatoms versus the half-saturation value K_m for growth $\mu/\mu_{\text{max}} = [\text{Fe}]/(K_m + [\text{Fe}])$ after Monod [1942]. Shown are large *Fragilariopsis kerguelensis* and larger *Corethron pennatum*, *Thalassiosira*, and very large *Actinocyclus* sp., the latter very similar in perfect discoid shape and 300–400 μm size as *Asteromphalus* sp. [Waite and Nodder, 2001]. Graph plotted after K_m data of dissolved Fe (nM) growth curves (not shown here) in natural Antarctic seawater; see Timmermans et al. [2004] for these growth curves.

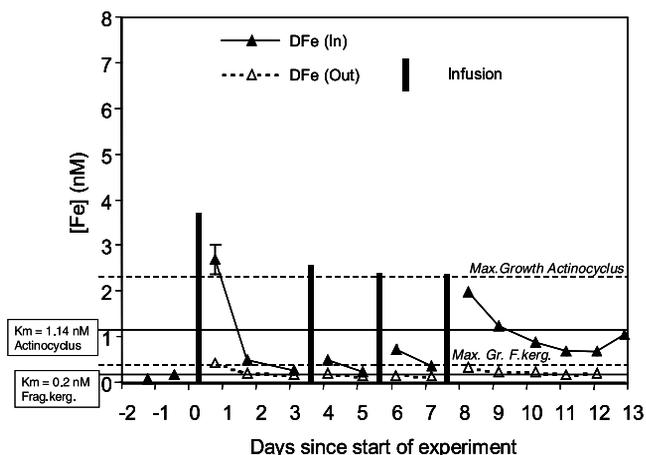


Figure 19. K_m value of dissolved Fe (nM) for 50% of optimal growth rate (lines) and optimum 100%, i.e., double K_m or maximum growth rates (horizontal dotted lines) for large *Fragilariopsis kerguelensis* and very large *Actinocyclus* sp. superimposed on the sawtooth pattern of averaged dissolved Fe observed in the in-patch of SOIREE (filled triangles) as a result of imbalance of rapid Fe losses and four consecutive Fe releases. Open triangles connected with bold dotted line is averaged dissolved Fe at the control (out) station. Graph drawn after *Bowie et al.* [2001] and *Timmermans et al.* [2004].

maximum growth of *F. kerguelensis*, but inadequate for *Actinocyclus* (Figure 19). The double Fe concentrations (dotted lines) for optimal 100% growth are occasionally met for *F. kerguelensis* and rarely, if at all, for *Actinocyclus*. Obviously, if one could maintain a steady and carefully chosen dissolved Fe concentration throughout an experiment, the relationship (Figure 18) might reliably predict the size class of diatom that would dominate in the end (in the absence of loss processes to grazing, sinking, etc.).

[35] Even this, however, has proven to be a major stumbling block of the in situ experiments. The intrinsic instability of the added reduced Fe(II) in oxygenated seawater (discussed below) leads to rapid removal of the Fe enrichment. In an effort to remedy this problem, a lignopolysulfonate ligand had been added during the two experiments (GreenSea 1, 2) in the Gulf of Mexico (Table 1), but its effect cannot be discerned from the brief report [*Markels and Barber*, 2001]. In all other experiments, only dissolved [Fe(II)] was added.

[36] In SOIREE, four successive Fe additions (vertical black bars) were applied in an effort to compensate for the major Fe loss. Despite a rigorous budgeting approach [*Bowie et al.*, 2001], only 30% of the added Fe could be accounted for, the remaining 70% being “lost.” Similar repeat Fe infusions have been done for most other experiments (except IronEx-1 and SEEDS), with Fe budgeting hardly, if at all, being attempted anymore. The overall result tends to be a sawtooth pattern of dissolved Fe concentration inside the patch.

[37] This sawtooth pattern creates a conceptual dilemma in which the K_m values (Figure 18) are only valid at steady state, i.e., constant dissolved Fe, while patch in situ Fe concentrations oscillate markedly. Presumably, during events of high natural input of dissolved Fe, diatoms are

capable of luxury accumulation of Fe within their cells, to be used later when Fe concentration fall below a critical threshold level, e.g., K_m . Perhaps for any given diatom species, a bandwidth of suitable dissolved Fe between, for example, 50% and 100% of optimal growth, defines the range to be maintained in an in situ experiment. Future culture experiments exposing diatoms to oscillating Fe levels may demonstrate such Fe storage capacity and help bridge the conceptual gap between our present understanding of linear steady state relationships (Figure 18) and the more dynamic algorithms that will be needed for the next generation of ecosystem simulation models of in situ experiments [*Lancelot et al.*, 2000; *Hannon et al.*, 2001]. Obviously, this is also desirable for understanding the real ocean where natural dissolved Fe varies over daily timescales in surface waters.

6. Fe Chemistry in Seawater

[38] Until now, the role of Fe has been described using dissolved Fe in filtered seawater ($<0.2 \mu\text{m}$ filtrate) as the common variable. In reality, however, the physical chemistry of Fe in seawater is far more complicated.

[39] During CARUSO/EisenEx, polyethylene hollow-fiber ultrafiltration was used to distinguish another size class, colloids ($200 \text{ kDa} < \text{colloids} < 0.2 \mu\text{m}$), with the ultrafiltrate ($<200 \text{ kDa}$) being called the soluble fraction [*Nishioka et al.*, 2005]. Prior to the first infusion of iron, the dissolved ($<0.2 \mu\text{m}$) iron concentrations in the ambient surface seawater were extremely low ($0.06 \pm 0.015 \text{ nM}$), with colloidal iron being a minor fraction. For the iron addition, the eddy was fertilized with an acidified FeSO_4 solution (i.e., reduced [Fe(II)]) 3 times over a 23 day period [*de Baar*, 2001]. High concentrations of dissolved iron ($2.0 \pm 1.1 \text{ nM}$) were measured in the surface water until 4 days after the first iron infusion (Figure 20). After every iron infusion, when high iron concentrations were observed before storm events, there was a significant correlation between colloidal and dissolved iron:

$$[\text{Colloidal Fe}] = 0.7627[\text{Dissolved Fe}] + 0.0519, R^2 = 0.93.$$

These results indicate that a roughly constant proportion of colloidal versus dissolved iron ($\sim 76\%$) was observed after iron infusion. Thus it appears that most of the added [Fe(II)] was rapidly converted into fine colloids.

[40] The operationally defined division of Fe into three size classes, soluble $<200 \text{ kDa}$, $200 \text{ kDa} < \text{colloids} < 0.2 \mu\text{m}$, and particles $>0.2 \mu\text{m}$, is also reflected in the organic complexation of iron. Organic binding of Fe was investigated only in the soluble and colloid fractions [*Boyé et al.*, 2005]. In the natural seawater before Fe addition, some $91 \pm 3\%$ of the organic Fe-binding ligands was found in the soluble fraction. In contrast, the size distribution of ligands in the mixed layer after Fe release was balanced between soluble ($\sim 55\%$) and colloidal ($\sim 45\%$) ligands. Soluble and colloidal ligands were produced rapidly within the mixed layer after the first and second Fe infusions. Here a dramatic increase of the colloidal ligand concentrations was observed, increasing concentrations by two- to three-fold for soluble, and up to 35-fold for colloidal ligands, relative to their respective out-patch levels.

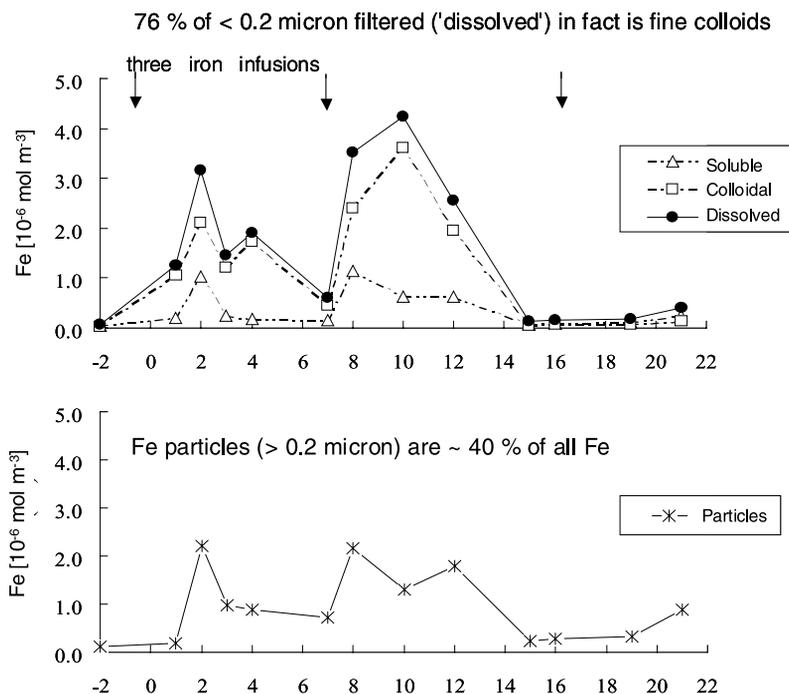


Figure 20. During EisenEx the operationally defined “dissolved” Fe (nM) in seawater (filled dots) in fact consisted of a constant major 76% portion of fine colloids in the >200 kDa size class (open squares). Only the remaining 24% soluble Fe (open triangles) is deemed to be directly available for uptake by phytoplankton [Nishioka *et al.*, 2005]. Photoreduction of some colloids in daytime to Fe(II) (not shown here; see Croot *et al.* [2005]) is partly responsible for maintaining the soluble fraction, where organic complexation in both colloid and soluble fraction also plays a role (not shown here; see Boyé *et al.* [2005]). The rapid formation of colloids and then their conversion into larger (>0.2 micron) particles surely is the major route by which much added Fe is lost, therefore necessitating repeat Fe additions. Otherwise, some of the colloids may dissolve again by photoreduction [Rijkenberg *et al.*, 2005], and some particulate Fe may dissolve again by grazing [Barbeau and Moffett, 2000]. More research is needed to assess how these processes interact and how they may together indirectly supply Fe for uptake by phytoplankton.

[41] Simultaneous measurements of Fe(II) and H_2O_2 showed detectable Fe(II) concentrations for up to 8 days after iron infusion [Croot *et al.*, 2005]. Vertical profiles of Fe(II) showed maxima consistent with the plume of the iron infusion. Parallel H_2O_2 profiles revealed corresponding minima, showing the effect of ongoing oxidation of Fe(II) by H_2O_2 . The H_2O_2 concentrations increased at the depth of the chlorophyll maximum when iron concentrations returned to preinfusion concentrations (<80 pM), possibly due to biological production related to iron reductase activity. During a later surface survey of the iron enriched patch, elevated levels of Fe(II) were found in surface waters presumably from Fe(II) dissolved in the rainwater that was falling at this time. Model results suggest that the reaction between uncomplexed Fe(III) and O_2^- was a significant mechanism helping to maintain high levels of Fe(II) in the water column, and the low temperature of Antarctic seawater slows down the reverse oxidation reaction considerably [Croot *et al.*, 2001]. Finally, photochemical reduction of finely dispersed colloids may act as a source of reduced [Fe(II)] in surface waters [Rijkenberg *et al.*, 2005], thus making Fe available again for plankton uptake.

[42] We are only beginning to understand the chemistry of Fe in seawater. Nevertheless two main lines of thought can already be identified.

[43] First, the artificial ~100-fold increase of overall Fe levels after the addition of dissolved inorganic Fe(II) ions is a major disruption of the natural physical-chemical abundances and reactivity of Fe in seawater. Hence the ensuing plankton responses, while significant, are not necessarily representative of natural enrichment by dry or wet deposition of aeolian dust [Boyé *et al.*, 2005], or from adjacent continental margins or ocean island plateaus. This notion has led to another experiment (FeCYCLE, 2003) where only SF_6 tracer was added just to follow the natural physical chemistry of Fe in seawater [Boyd *et al.*, 2004b] (available at <http://aslo.org/honolulu2004>). Moreover, two parallel programs BICEP and KEOPS were undertaken in austral summer 2004–2005 using natural gradients of dissolved Fe near the ocean islands of Crozet and Kerguelen [Blain *et al.*, 2001; Bucciarelli *et al.*, 2001] as a natural laboratory for unraveling the complex interactions of Fe chemistry and phytoplankton growth.

[44] Second, algal cells can only directly assimilate “truly dissolved” Fe and thus the Fe residing within the

soluble (<200 kDa) size fraction. This soluble fraction consists of reduced [Fe(II)] as well as organically bound [Fe(III)ligand], with evidence for more than one ligand type, and also some inorganic [Fe(III)]. It is not clear which is the preferred form for uptake by algae. If the kinetics of exchange between these three major forms within the soluble pool are faster than the overall uptake rate, algal uptake preferences do not really matter. On the other hand, if one or more of the transformation reactions are slow, it (they) could potentially control growth rates of the algae. Moreover, the colloid size class (>200 kDa) is not directly available for uptake, but may rapidly replenish the soluble pool, as colloids dissolve by photoreduction [Rijkenberg *et al.*, 2005], releasing dissolved [Fe(II)] for algal uptake. Yet, in due course, the [Fe(II)] will also be oxidized again into colloids. The kinetics of exchange between these various Fe pools must be quantified in order to understand how Fe controls the rate of phytoplankton growth. Thus the above consistency between K_m values (Figure 18) from diatom growth curves [Timmermans *et al.*, 2004] and dissolved Fe (<0.2 μm fraction) during an in situ experiment (Figure 19) is an important step forward, but only one step on a long road to unraveling the complexities of iron-phytoplankton interactions.

7. Grazing Impacts

[45] In discussing the potential roles of grazers in Fe-fertilized ecosystems, it is useful to distinguish between two major size classes: the micro- and mesozooplankton. Operationally, the “microzooplankton” includes all consumers <200 μm in size, a size class typically dominated by a diverse assemblage of heterotrophic and mixotrophic protists. Such organisms are the major direct consumers of phytoplankton in the open oceans [Calbet and Landry, 2004], and can grow at rates comparable to or greater than similarly sized phytoplankton. Because of these qualities, meaningful studies of the grazing impacts and population responses of the microzooplankton can be conducted on the days-to-weeks scale of the typical fertilization experiment. The “mesozooplankton,” on the other hand, are larger (>200 μm) animals with longer and more complex life histories, some (in polar and subpolar systems) with generation times of a year or more. Mesozooplankton play central roles in ocean food webs as consumers of large phytoplankton, as trophic intermediates to higher-level consumers (e.g., fish), as fecal pellet producers (thereby accelerating sinking and export flux), and as predators and regulators of the microzooplankton, all of which make them relevant to understanding system level responses to Fe. However, the temporal and spatial scales of experimental studies conducted to date are inadequate to study population and community responses of mesozooplankton to Fe, or to predict their direct and indirect implications for large-scale and long-term Fe fertilization. Because our current understanding of Fe effects on ocean ecosystems does not extend past single-celled organisms, the comments below are meant to apply mainly to this “microbial” portion of plankton communities.

[46] Since Fe concentration strongly affects growth rate and, therefore, the intrinsic competitiveness of phytoplankton taxa and size classes (Figure 18) and since light-related

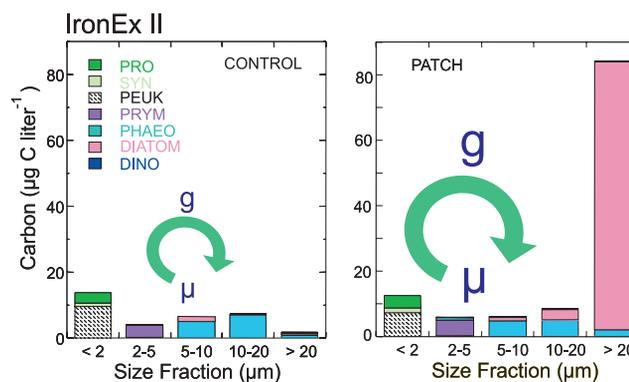


Figure 21. Phytoplankton community size structure in the ambient environment (CONTROL) and the iron-fertilized PATCH during IronEx-2 (May–June 1995). Carbon estimates are based on flow cytometric analyses of picophytoplankton (PRO, *Prochlorococcus*; SYN, *Synechococcus*; PEUK, picoeukaryotic algae) and biovolume-based microscopical assessments of prymnesiophytes (PRYM), *Phaeocystis* (PHAEO), diatoms (DIAT), and dinoflagellates (DINO). Distributions are the means of three sampling dates in ambient waters and 4 days of sampling during the peak of the patch bloom. Inserts indicate that the instantaneous growth rates (μ) of all taxa shift up in response of added Fe, but most size categories are maintained at constant levels by corresponding increases in microzooplankton grazing (g), except for >20 μm diatoms dominated by *Pseudo-nitzschia*. (Modified from Landry *et al.* [2000b].)

variables, like WML depth, appear to control maximum levels of biomass accumulation (Figure 12), grazing interactions would seem, at first glance, to have little influence on phytoplankton responses to Fe addition. However, temporal changes in populations and communities do not simply reflect growth rates or potential, but rather the net realized differences between growth and mortality rates. Consequently, if the goal is to predict the timing and magnitudes of Fe responses at the community and system levels, the mortality “environment” is as important as the growth environment for determining net rates of change. The role of mortality becomes particularly apparent when one considers how initially rare taxa rise to dominance quickly in Fe fertilization experiments. In IronEx-2, for example, the estimated Fe stimulated growth rate for the diatom *Pseudo-nitzschia* was ~ 2 cell doublings d^{-1} ($\mu = 1.4 \text{ d}^{-1}$ [Landry *et al.*, 2000b]) while *Prochlorococcus* growth rate was observed to shift up from 0.7 d^{-1} to 1.1 d^{-1} when Fe was added [Mann and Chisholm, 2000]. If left entirely to the growth rate difference of 0.3 d^{-1} , the initially rare *Pseudo-nitzschia* would need about 8 days of growth (16 generations) to catch up to *Prochlorococcus* for each order-of-magnitude difference between the two in their initial contributions to community biomass. In reality, *Pseudo-nitzschia* was rapidly installed as the bloom dominant within 5 days of the IronEx-2 patch fertilization because *Prochlorococcus* and other small cells were held entirely in check by grazing (Figure 21). For these initially dominant phytoplankton, already growing at relatively high rates under ambient conditions, the adjustments that lead to continued grazing balance at Fe-stimulated rates of growth

can be relatively modest, e.g., a 50% increase in grazer standing stock, or perhaps just slight increases in prey vulnerability due to Fe-enhanced changes in cell size or physiochemical cell surface properties [Monger and Landry, 1990; Monger et al., 1999].

[47] Diatoms do not dominate Fe-stimulated blooms because they physically cannot be eaten by microzooplankton. Within this diverse group, there are clearly organisms with appropriate size, behaviors and apparent preferences for feeding on diatoms [e.g., Gaines and Taylor, 1984; Jacobson and Anderson, 1986]. In IronEx-2, large dinoflagellates and ciliates eventually exerted a heavy grazing toll on *Pseudo-nitzschia* [Landry et al., 2000b], and large protists were also the major grazers in the diatom-dominated waters of SOFeX-South [Coale et al., 2004; M. Landry, personal communication, 2005]. It does appear to be true, however, that initially rare and relatively large diatoms enjoy a release from heavy grazing pressure in at least the early stages of an Fe-stimulated bloom because their specialized grazers are not sufficiently abundant to control them when their growth rates are strongly stimulated by the added Fe. The larger the difference between the growth rates of large rare species in Fe-deficient ambient waters and their maximal growth potential with added Fe, the larger will be their net growth rate advantage in the early bloom. It is also likely the case that regulatory potential by microzooplankton grazers diminishes with increasing cell size of phytoplankton, such that “giant” diatoms, at the extreme, are minimally vulnerable to such losses. Thus grazing pressure would seem to act in a way that systematically reinforces the selective growth advantages of large cells under Fe-replete conditions, accelerating, in fact, the rate at which they can rise relative to other cells to dominate the community response.

8. Carbon Fluxes

[48] Photosynthetic fixation of CO_2 in all experiments depletes the pool of dissolved inorganic carbon (DIC) in seawater by converting it into particulate organic carbon (POC). The DIC loss is paralleled by a decrease of the fugacity of CO_2 in surface waters (Figures 3, 4, 6, and 11), where an undersaturation versus atmospheric CO_2 may develop. For a sufficient rate of gas exchange, this undersaturation may drive an influx of CO_2 from the air into the sea, thus somewhat replenishing the DIC pool. In addition, part of the POC inventory may settle out into deeper layers, thus exporting carbon into the deep sea (Figures 8 and 9).

[49] A detailed comparison of carbon budgets among the eight Fe experiments would be desirable, but the designs, implementations, weather conditions and actual evolutions of these experiments have been quite different. Patch dilution has notably varied greatly (Figure 15) and efforts to quantify this using the SF_6 (and ^3He) tracer(s) have proven quite challenging [Goldson, 2004; Bakker et al., 2005; C. S. Law et al., Patch evolution and the biogeochemical impact of entrainment during an iron fertilization experiment in the subarctic Pacific, submitted to *Deep-Sea Research, Part II*, 2005], if pursued at all. In general, the variability and patch dilution interfere with sampling, for example at any given day of any experiment nobody can guarantee the true core (SF_6 maximum) of the patch was

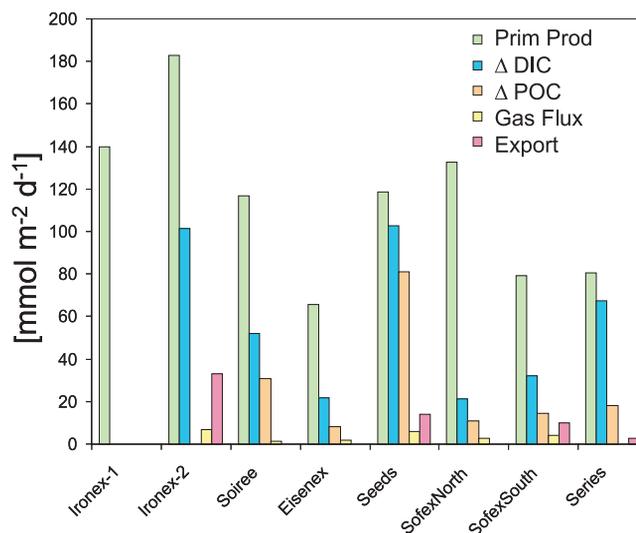


Figure 22. Depth-integrated primary production (green bars ($\text{mmol m}^{-2} \text{d}^{-1}$)) compared with the depth-integrated inventory change terms ($\text{mmol m}^{-2} \text{d}^{-1}$) of DIC loss (blue bars), POC gain (orange bars), replenishment of CO_2 by air/sea gas exchange (yellow bars), and loss by export (red bars) of settling particles into deeper water layers. Primary production values as measured inside the Fe-enriched patches from a recent compilation [Coale, 2004]. Owing to continuing primary production in ambient (out-patch) waters, the primary production enhancement ($\text{PP}_{\text{in-patch}} - \text{PP}_{\text{out-patch}}$) solely due to Fe enrichment would be less (not shown). The decrease of DIC is about half (average is 51%, s.d. 26%) of the primary production, ranging from 16 to 87% in SOFeX-North and SEEDS, respectively. The buildup of POC biomass is about one-quarter (average 26%, s.d. 21%) of primary production, ranging from 8 to 68% in SOFeX-North and SEEDS, respectively. In general, both the air/sea exchange term and the export flux tend to be small or negligible and difficult to quantify during the time course (12–24 days) of the experiments. The CO_2 gas flux into the sea averages at 3% (s.d. 1.7%) of primary production, ranging from 1.2% in SOIREE to 5% in SOFeX-South. Compared to the DIC decrease, the CO_2 gas flux into the sea averages at 8% (s.d. 5%), ranging from 2.7% in SOIREE to 13% in both SOFeX sites. The export estimates range from virtually nil (hence not discernible in graph) for SOIREE [Charette and Buesseler, 2000], to 3% of primary production in SERIES, to 12% in both SEEDS and SOFeX-South, and as high as 10–27% in IronEx-2 (plotted is average 33 of 15 and 50 $\text{mmol m}^{-2} \text{d}^{-1}$; see text [Bidigare et al., 1999]). Export of SEEDS indirectly from budget [Tsuda et al., 2003, supplement]. Sources are as follows: Steinberg et al. [1998]; Bidigare et al. [1999]; Tsuda et al. [2003]; Boyd et al. [2004a]; Coale et al. [2004]; Buesseler et al. [2004]; Coale [2004]; Bozec et al. [2005]; Bakker et al. [2005]; and U. Riebesell et al. (unpublished manuscript, 2003).

sampled. In other words, the response reported is intrinsically a function of sampling strategy and intensity. Also sampling grids differ between variables, the Primary Production assay typically being done at one in-patch station, while some state variables have been mapped extensively.

Finally, the C budgeting efforts for various experiments (sources as in caption Figure 22) have used different approaches. Thus overall, the comparison presented here is somewhat incompatible. Further study may improve this, but full comparability may never be achieved.

[50] Depth-integrated rate estimates ($\text{mmol m}^{-2} \text{d}^{-1}$) for the different Fe fertilization experiments tend to vary less (Figure 22) than previously shown maximum changes per volume seawater (Figure 11). A deep WML is unfavorable for phytoplankton growth, for example, but the effect is partially offset by integrating over a greater depth. Thus the “rankings” of experimental impact shift somewhat between Figures 11 and 22. On this basis, the primary production of IronEx-2 now exceeds that of SEEDS. This is consistent with the twofold higher optimal growth rates of IronEx-2 predicted from temperature differences (Figure 14).

[51] For the experimental data represented in Figure 22, measured DIC drawdown averages half ($51 \pm 26\%$) of primary production rates, from ^{14}C uptake measurements which typically underestimate true gross production by a factor of two or more [e.g., Laws *et al.*, 2000]. In the same data set, the POC increases average one quarter ($26 \pm 22\%$) of primary production. Excluding the unusually high ratios for SEEDS, these POC ratios reduce to 45% of DIC drawdown and 18% of primary production. It is clear from these relationships that only SEEDS demonstrated the kind of response, very high efficiency in moving carbon from DIC to POC pools via photosynthetic fixation, that one might associate with a relatively pure phytoplankton “culture.” More generally, the transfers are characterized by large inefficiencies (only 18–26% of production accumulates as POC), which speaks to the importance of loss processes due to grazing and related trophic processes. Such results are consistent with rate estimates of phytoplankton instantaneous growth and biomass accumulation in the fertilization experiments. For example, in IronEx-2, growth rates of 1.5 to 2 cell doublings d^{-1} (μ of 1.0–1.4 d^{-1}) produced only a net fivefold increase in phytoplankton carbon biomass over the course of a week [Landry *et al.*, 2000a]. Similarly, in the SOFeX-South patch, phytoplankton biomass only doubled despite mean estimated growth rates (μ of 0.2–0.3 d^{-1}) that could have led to a biomass increase of 20-fold or more [Coale *et al.*, 2004; M. Landry, personal communication, 2005]. Because production/biomass accumulation precedes grazer responses, there must also be a substantial time dependency to calculated estimates of the DIC \Rightarrow primary production \Rightarrow POC transfer ratios. For example, phytoplankton POC estimates plateaued for 4–5 days at peak levels in the IronEx-2 patch, during which phytoplankton continued to grow at a high rate while their biomass remained static. Clearly, during such times, in the mid to late stages of bloom response to added Fe, the ratios of DIC and POC changes to time-integrated primary production should decline significantly.

[52] Of the average 70–80% of primary production that does not accumulate as POC in Fe-fertilized patches, some appears as DOC or contributes to export. Reports on DOC changes have been sporadic. In CARUSO/EisenEx over the first 12 days, during which the DIC decreased 12 mmol m^{-3} (Figure 6), the DOC showed a small increasing trend from about 48 to 52 mmol m^{-3} suggesting a net increase on the order of 4 mmol m^{-3} $\sim 30\%$ of the DIC decrease. However

the DOC data were scattered, and over the complete 21 days there was no real trend. In addition, the 4 mmol m^{-3} change is hardly discernible at an about 1 mmol m^{-3} analytical reproducibility.

[53] The CO_2 gas flux into the sea has been calculated for most experiments and is a small $\sim 8\%$ portion of the DIC removal rate, ranging from 2.7% at SOIREE to as much as 13% for both SOFeX sites (Figure 22). The gas flux tends to be about 3% of primary production (Figure 22). The percentage variability between experiments is partly real, partly also due to different calculation approaches and applied gas exchange coefficients [e.g., Wanninkhof, 1992; Wanninkhof and McGillis, 1999]. Nevertheless, the slow replenishment of CO_2 from the air is as expected due to the slow relaxation time of this gas as a result of its equilibration reactions with the seawater, as opposed to nonreactive gases, e.g., O_2 or SF_6 . On the other hand, this also implies that CO_2 supply from the air continues long after the observer ships have left the scene. Hence the overall drawdown of CO_2 from the air likely is more than shown here only for the 12–24 day observation periods of individual experiments. In the end, the DIC deficiency (e.g., Figures 6 and 11) will be largely compensated for from the atmosphere, as well as from net heterotrophic respiration, once the bloom has collapsed. Such a collapse was observed in SERIES, but the CO_2 gas flux results are not yet available. The relative contribution of both terms (gas flux *versus* respiration) will remain the subject of debate until longer observation strategies are implemented in this type of experiment.

[54] Export flux of organic carbon into deeper waters has been assessed by difference from budget calculations. For SEEDS an elegant effort has been reported [Tsuda *et al.*, 2003, supplement]. Similarly for CARUSO/EisenEx (not shown) such an effort has been made (U. Riebesell *et al.*, unpublished manuscript, 2003). However with export being only a small fraction of primary production and the changes in DIC and POC, and given the difficulty in assessing DOC and its changes, calculated export signals hardly exceed the noise of the overall budget, if at all. The export of organic matter remained constant in SOIREE, perhaps due to its short duration and patch dilution [Charette and Buesseler, 2000; Nodder and Waite, 2001]. The most direct evidence for export was observed in sediment traps of SERIES upon collapse of the bloom (Figure 9 (bottom)). However, derivation of an overall export number does require extra information on, e.g., trapping efficiencies [Boyd *et al.*, 2004a]. Finally, for SOFeX-South, the observed ^{234}Th deficiencies have led to an estimate of carbon export which is significant, yet still modest relative to similar estimates for the natural Southern Ocean [Buesseler *et al.*, 2004, 2005].

9. Light Climate Due to Wind Mixed Layer Depth

[55] Nine experiments in the 1993–2004 era have each been successful in following an Fe-enriched water mass and observing a distinct impact, small or large. The combined nine experiments have demonstrated that the depth of the wind mixed layer (WML), in regulating light climate, is the major factor controlling photosynthesis in the high-nutrient

Table 3. Preliminary Overview of Derived DIC/Fe Efficiencies for Several Experiments^a

Acronym	Fe, kg	Fe	DIC Removal	DIC ^b	WML Depth, m	Patch Size, m ²	DIC Loss, moles	DIC/Fe Efficiency, mol/mol
IronEx-1	450	8058 moles	6 10 ⁻³ mol m ⁻³	A	35	64,000,000	13,440,000	1668
IronEx-2	449	8039 moles	27 10 ⁻³ mol m ⁻³	A	40	72,000,000	77,760,000	9672
Ironex-2	449	8039 moles	27 10 ⁻³ mol m ⁻³	A		<i>120,000,000</i>	<i>129,600,000</i>	<i>16,120</i>
SOIREE	1745	31,246 moles	400 t	B	65		33,302,806	1066
SOIREE	1745	31,246 moles	800 t	B			66,605,612	2132
SOIREE	1745	31,246 moles	1389 t	C			115,643,993	3701
EisenEx	2340	41,900 moles	1433 t	C	70		119,307,302	2847
SEEDS		4 10 ⁻⁶ mol m ⁻³	61 10 ⁻³ mol m ⁻³	see text	12.5			15,000
SEEDS	350	6267 moles	1.3 mol m ⁻²	D		80,000,000	104,000,000	16,595
SOFeX-North	1712	30,655 moles	14 10 ⁻³ mol m ⁻³	D	45	225,000,000	126,000,000	4110
SOFeX-South	1260	22,561 moles	23 10 ⁻³ mol m ⁻³	E	35	225,000,000	181,125,000	8028
SOFeX-South	1260	22,561 moles	23 10 ⁻³ mol m ⁻³	E		<i>1,000,000,000</i>	<i>805,000,000</i>	<i>35,680</i>
SERIES	489	41.3 10 ⁻⁶ mol m ⁻²	ΔPP 1.61 mol m ⁻²	F	30			38,983
SERIES	489	41.3 10 ⁻⁶ mol m ⁻²	ΔDIC 1.1 mol m ⁻²	F				26,634
SERIES	489	8756 moles	ΔPOC 1776 t	F			147,864,458	16,887
Σ Antarctic	5345	95,708 moles					416,076,295	4347
Total	8795	157,483 moles					885,140,752	5620

^aThe added Fe (kg) is accurately known (where 1 mole Fe is 55.847 g). Patch dilution hampers the accuracy of the calculation of overall DIC loss. The DIC removal from several sources is processed with various approaches (not necessarily consistent among each other) listed below (A–F) to obtain DIC loss (moles) for each experiment. The total DIC loss (moles) by addition, where alternative estimates (values in italic font) were ignored. The DIC/Fe efficiency scales inversely with WML depth (excluding IronEx-1): DIC/Fe = $-240.3\text{WML} + 18818$ (linear, with $R^2 = 0.73$ for $n = 7$ data points), with SERIES deviating above the line and two SOFeXs deviating below the line. The grand total overall DIC/Fe efficiency is 5620 and about threefold below the optimum 15,000 calculated for SEEDS. The Antarctic summation of SOIREE, EisenEx, and SOFeX-South in high-silicate, high-nitrate Antarctic waters yields an efficiency DIC/Fe = 4347 and hinges largely on the most robust estimates by Bakker et al. [2005]. For the time being, this may serve as the state-of-the-art gross DIC removal estimate for austral spring-summer-early autumn season (October–February), e.g., when assessing the impact of the approximately 10-fold extra atmospheric Fe dust input [Edwards et al., 1998] during the Last Glacial Maximum.

^b(A) Steinberg et al. [1998]; integrated using WML and patch size of Figures 11 and 15 for IronEx-1 initial patch size; for IronEx-2, both initial and final patch size provide lower and upper limit of C/Fe efficiency, respectively. (B) Boyd et al. [2000]; providing an upper limit of 800 t from algal carbon integration over 200 km² patch size and 400 t when assuming algal carbon follows SF₆ distribution. (C) Bakker et al. [2005] estimates for both SOIREE and EisenEx based on covariance analysis with the SF₆ distributions, apparently the most robust DIC removal estimates available now. (D) Tsuda et al. [2003, Figure S1]. (E) Hiscock et al. [2002]; see also text description of SOFeX and Figure 11. Integration over initial patch size is deemed to provide a lower limit estimate of C/Fe. For example, the larger final patch size of 1000 km² as suggested by Buesseler et al. [2004] would increase the DIC/Fe efficiency accordingly to a quite high ratio DIC/Fe = 35,680. (F) Boyd et al. [2004a, Table 2]. The change in particulate organic carbon (ΔPOC) estimate for the entire patch is based on Chl *a* signal from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) ocean color image [Boyd et al., 2004a, 2004b, suppl. Figure 3] multiplied by C/Chl *a* ratio = 80 in patch center at day 18 and WML depth of 25 m. This yields a C/Fe efficiency similar to SEEDS. The ΔDIC estimate and the ΔPP for the iron-mediated increase in net primary production are both for the patch center only and yield quite high C/Fe efficiencies.

low-chlorophyll regions of the ocean. This is not surprising. Light climate with its various parameterizations (e.g., PAR, WML depth, self-shading) has been recognized in every oceanography textbook [e.g., Lalli and Parsons, 1993] as a key control of photosynthesis. Moreover, for some of the Fe enrichment experiments in HNLC regions, light effects have been considered explicitly, such as WML depth and self-shading in SOIREE [Boyd et al., 2000; Gall et al., 2001b], and self-shading in SOFeX [Coale et al., 2004], and the unfavorable WML depth during CARUSO/EisenEx [Bozec et al., 2005]. Nevertheless it is by combination of these experiments (Figure 12; Tables 2 and 3) that the dominant role of WML depth for the worldwide HNLC regions has become more evident. In other words, when challenged to specify just one over-ruling limitation for each individual Fe enrichment experiment, one might conclude from Figure 12 that SOIREE and CARUSO/EisenEx in the Southern Ocean were predominantly light limited, while the SEEDS and SERIES regions were predominantly Fe limited, but IronEx-2 and SOFeX-South and SOFeX-North were intermediate between limitation by light and iron. However, the concept of one overruling limiting factor is fruitless [de Baar, 1994; de Baar and Boyd, 2000]. Instead colimitation by iron and light [Sunda and Huntsman, 1997; van Leeuwe, 1997; Maldonado et al., 1999; Lancelot et al., 2000; van Oijen, 2004] best describes the HNLC regions in 40% of the world oceans. Otherwise, the case for predominantly Fe limitation in SEEDS and SERIES is further underlined by the virtual

complete exhaustion of notably silicate as well as nitrate (Figure 8 and Figure 10 (middle)) after 13 and 18 days respectively, where during SERIES indeed the bloom was observed to collapse in days 19–23 (Figure 10 (top)).

[56] The well-documented climatology of wind velocity and WML depths in the world oceans [Monterey and Levitus, 1997] (available at <http://www.nodc.noaa.gov>) is a major resource when one wishes to understand, predict or simulate what prevents HNLC regions from achieving full biomass growth potential. Notably in the Southern Ocean this is the case [Mitchell et al., 1991; Lancelot et al., 1993, 2000; Hannon et al., 2001; Pasquer et al., 2005]. Here the most favorable conditions are in austral summer months December–January. Indeed SOFeX-South in January 2002 showed a major impact of Fe enrichment. These 2 months being favorable also for many other lines of research and expeditions, it has proven to be very difficult to secure suitable shiptime for Fe experiments in the Southern Ocean. Thus SOIREE had been accommodated during late summer, and CARUSO/EisenEx during early austral spring, when wind and WML conditions were not optimal for light.

10. Efficiency of Moles Carbon Removed per Moles of Iron Added

[57] The key role of light climate also implies that simple stoichiometric arguments for the amount of Fe required for a given level of C, N, P or biogenic Si production by

phytoplankton, as popular during the past 15 years, do not hold in general. This is even more the case because the added [Fe(II)] is rapidly lost via the formation of colloids, and then into larger ($>0.2 \mu\text{m}$) particles. In other words, for any amount of dissolved Fe(II) added, only a minor portion of perhaps about 20% remains soluble and available for direct uptake by phytoplankton. Part of the colloid portion may, or may not, become indirectly available via photoreduction [Rijkenberg *et al.*, 2005], and part of the particulate Fe may, or may not, again become available due to dissolution and remineralization via grazing [Barbeau and Moffett, 2000].

[58] In SEEDS, the most optimal and perhaps also most straightforward experiment, one single Fe infusion, bringing the initial total Fe to about $4 \cdot 10^{-6} \text{ mol m}^{-3}$, led to a maximum DIC removal of $61 \cdot 10^{-3} \text{ mol m}^{-3}$ (Table 3). Accordingly, each Fe atom removed 15,000 carbon atoms as DIC or CO_2 . Where in general the DIC removal was found to be about half of the primary productivity (Figure 22), in SEEDS it was 88% such that one expects a ratio $\text{C/Fe} = \sim 17,250$ for diatom growth in SEEDS. The cellular Fe content of plankton has long been a vexing question, but the first direct measurements of Fe quotas of individual plankton cells have recently been made by Twining *et al.* [2004b] detecting Fe in single cells by synchrotron X-ray radiation (Table 3). Within the Fe-enriched patch of SOFeX-South, the reported ratio $\text{C/Fe} = \sim 25,000$ [Twining *et al.*, 2004b] is remarkably consistent with above expected $\sim 17,250$ in SEEDS. The $\text{C/Fe} = \sim 25,000$ is substantially less than initial suggestions of oceanic phytoplankton cellular Fe requirements as high as 500,000 on the basis of the Fe' paradigm in EDTA-manipulated laboratory cultures [Sunda *et al.*, 1991]. The ratio $\text{C/Fe} = \sim 33,000$ previously calculated from excess (i.e., biogenic) particulate Fe in the deep North Pacific [Martin *et al.*, 1989] would agree more closely, but may be fortuitous as deep biogenic particles are not necessarily comparable with the Fe/C of primary production. The ratio C/Fe derived from dissolved Fe versus nitrate ($\text{C/Fe} = \sim 483,000$) or versus O_2 ($\text{C/Fe} = \sim 384,000$) in the nutricline of the North Pacific [Martin *et al.*, 1989; Martin, 1992] (discussed by de Baar and de Jong [2001, p. 164]) is much higher, but again not necessarily comparable with newly synthesized phytoplankton cells.

[59] In fact, the DIC/Fe ratio of 15,000 of SEEDS is a maximum value, occurring during the early build up of the bloom with more to be returned to DIC by heterotrophic respiration during the decline phase. For the sake of argument, the general POC buildup is about half of DIC removal (the other half is recycled by respiration), but higher at 79% for SEEDS such that the maximum POC/Fe efficiency of in situ Fe enrichment would be on the order of $\text{C/Fe} = 11,800$, potentially an upper limit for drawdown of CO_2 from the atmosphere. In fact, the thus far observed net export flux is only a few percent (Figure 22), this in keeping with a typical f ratio in the order of 1–10% of primary production for ocean plankton blooms. The primary production in general being about twice the DIC removal but 115% for SEEDS, this implies 1.15–11.5% of DIC removal will eventually be exported. Thus the ultimate efficiency of CO_2 removal from surface waters would be more on the order of 150–

1500 C atom for each Fe added. For all other conditions with a deeper WML, notably in the Southern Ocean, and in all other experiments (Figure 11), the DIC/Fe efficiency would be less than the upper limit $\text{C/Fe} = 11,800$, here derived from SEEDS.

[60] The major uncertainty in such overall DIC/Fe efficiency estimate is due to the patch dilution somehow to be taken into account when converting from maximum DIC loss (mol m^{-3}) to overall DIC removal (moles) for the overall experiment. Here the above estimate for SEEDS is relatively robust as its patch dilution factor was only threefold. Table 3 provides an account of overall DIC/Fe efficiencies which indeed tend to be less than the above derived optimum $\text{DIC/Fe} = 15,000$ ratio, but all suffering greater or lesser uncertainty due to patch dilution. Nevertheless, the derived C/Fe efficiencies, being either better or worse, also tend to scale inversely with WML depth (Table 3, caption).

11. Iron Fertilization During the Last Glacial Maximum and Anthropocene

[61] The implications of above DIC/Fe ratio values for the last deglaciation (17,000–11,000 y BP) as well as for intentional Fe fertilization of the modern ocean have been reported elsewhere (H. J. W. De Baar *et al.*, Iron makes big diatoms blooming, but cannot change carbon dioxide and climate, submitted to *Science*, 2005, hereinafter referred to as de Baar *et al.*, submitted manuscript, 2005). Briefly, during the Last Glacial Maximum (LGM) the Fe dust input into the Antarctic region was 11-fold the modern dust flux [Edwards *et al.*, 1998]. Sometime after this dust flux terminated, the atmospheric CO_2 has risen initially with $80 \cdot 10^{-6} \text{ atm}$ and eventually with $90 \cdot 10^{-6} \text{ atm}$ to the preindustrial value of $280 \cdot 10^{-6} \text{ atm}$ [Petit *et al.*, 1999; Watson *et al.*, 2000]. Taking the Antarctic summation of SOIREE, EisenEx and SOFeX-South in high-silicate high-nitrate Antarctic waters yields an efficiency $\text{DIC/Fe} = 4347$ (Table 3), which by assuming 20% export, yields an export efficiency $\text{C/Fe} = 870$. This combined with a factor 10 in Fe dust flux, 30% wet deposition of which 14% dissolves, and a 3 month austral summer growth season, yields an Fe fertilization effect which can account for only 0.5% of the observed rise of atmospheric CO_2 . Taking a more favorable export ratio $\text{C/Fe} = 3257$ after Buesseler *et al.* [2004], the Fe effect would be higher, but still only 2 % of the observed rate of atmospheric CO_2 increase. When also taking a more favorable overall mean $\sim 32\%$ dust dissolution (operational defined range is 9–89% [Edwards and Sedwick, 2001]) instead of above 30% of which 14% dissolves, the Fe effect might be as high as $\sim 15\%$ of the observed CO_2 rise.

[62] Similarly extrapolation to the current anthropogenic fossil fuel CO_2 emission rate of about $6.6 \text{ Petagram C yr}^{-1}$ ($0.55 \cdot 10^{15} \text{ mol C yr}^{-1}$) would lead to a required Fe fertilization of $0.63 \cdot 10^{12} \text{ mol Fe yr}^{-1}$ or $35 \cdot 10^9 \text{ kg Fe yr}^{-1}$, i.e., 35 million tons Fe yr^{-1} (de Baar *et al.*, submitted manuscript, 2005). This is 40-fold more Fe than originally hypothesized (430,000 tons Fe to remove 3 PgC yr^{-1} [Martin, 1990]). Extrapolation of the most favorable C export of $\text{C/Fe} = 3257$ for only SOFeX-South in austral summer [Buesseler *et al.*, 2004] would yield a lower required

Fe fertilization of $0.17 \cdot 10^{12} \text{ mol yr}^{-1}$ or $9.4 \cdot 10^9 \text{ kg yr}^{-1}$. This is 9.4 million tons Fe yr^{-1} .

12. Artefacts

[63] One major reason for in situ enrichment experiments was to independently verify bottle incubations, notably with respect to perceived artefacts of the latter. One such artefact, the control bottles also outgrowing the field biomass (Figure 1) due to more favorable light climate in deck incubators, has now been confirmed. Indeed, while Fe addition is effective when light is optimal (Figures 11 and 17), added Fe has little effect when light conditions are unfavorable.

[64] The in situ experiments have their own artefacts as well [Boyd *et al.*, 2002]. Most notably, the 100-fold higher Fe is a strong perturbation of Fe chemistry, the effects of which on phytoplankton growth have yet to be understood. Moreover, the rapid formation of Fe colloids is reason for some caution when interpreting coagulation of particles and export fluxes with approaches and concepts developed in the unperturbed natural ocean. Briefly, freshly formed Fe colloids are adhesive and reactive and may not necessarily be inert versus coagulation of biogenic debris and scavenging processes of trace elements and isotopes. In fact, Fe colloid formation is a standard method worldwide for purifying natural fresh waters in the production of drinking water. Obviously the applied levels are much higher, but some effectiveness at the typical 3–5 nM concentrations of in situ experiments is not necessarily ruled out.

[65] Another physical phenomenon to be considered is patch dilution (Figure 15), which gives rise to the chemostat effect [Abraham *et al.*, 2000]. Patch dilution can be overcome, in principle, by fertilizing very large patches vis-à-vis the expected shear stress and wind forcing, such that the core of the patch will be unaltered and dilution only a boundary effect. On the other hand, the patch sizes used thus far, 80 or 225 km², are perhaps of similar order as natural wet deposition mesoscale events (combined rain/dust storms) or natural upwelling events, bringing in extra Fe from either above or below. In other words, patch dilution is, on the one hand, an artefact for understanding details of Fe responses in a controlled reproducible manner, yet, on the other hand, perhaps quite realistic in the natural ocean.

13. Perspectives

[66] Experimental oceanography has now been proven a powerful and exciting approach for unraveling the drivers and inner mechanisms of plankton ecosystems. This preliminary synthesis next needs more rigorous verification by application of a generic plankton ecosystem simulation model to most or all of the 8–9 experiments. This is crucial also for the design of the next generation of experiments, some by tinkering with innovative techniques for delivering the extra Fe more naturally and effectively, others by relying on natural Fe supply and gradients instead. Moreover one would like to be able to follow an experimental water body over longer time periods of several months. Finally new techniques are desirable to quantify more reliably and routinely the exchanges of CO₂, DMS and other biogenic

gases with the atmosphere, as well the thus far difficult to quantify biogenic export to the deep ocean.

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