The SOLAS Air-Sea Gas Exchange Experiment (SAGE) 2004.

Mike J. Harvey[1], Cliff S. Law[1], Murray J. Smith[1], Julie A. Hall[2], Edward R. Abraham[1,A], Craig L. Stevens[1], Mark G. Hadfield[1], David T. Ho[3,B], Brian Ward[4,C], Stephen D. Archer[5], Jill M. Cainey[6], Kim I. Currie[7], Dawn Devries[8], Michael J. Ellwood[2,D], Peter Hill[1], Graham B. Jones[9], Dave Katz[10#], Jorma Kuparinen[11], Burns Macaskill[2#], William Main[1#], Andrew Marriner[1], John McGregor[1], Craig McNeil[10], Peter J. Minnett[12], Scott D. Nodder[1], Jill Peloquin[13], Stuart Pickmere[2], Matthew H. Pinkerton[1], Karl A. Safi[2], Rona Thompson[1#], Matthew Walkington[1], Simon W. Wright[14], Lori A. Ziolkowski[15#]

[1]*National Institute of Water and Atmospheric Research (NIWA), P.O. Box 14-901, Kilbirnie, Wellington, New Zealand*
[2]*National Institute of Water and Atmospheric Research (NIWA), P.O. Box 11-115, Hamilton, New Zealand*
[3]*Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W Palisades, NY 7 10964, U.S.A.*
[4]*Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543-1050, U.S.A.*
[5]*Plymouth Marine Laboratory, Prospect Place, West Hoe, Plymouth, PL1 3DH, U.K.*
6 Cape Grim B.A.P.S., Bureau of Meteorology, PO Box 346, Smithton, Tasmania 7330 Australia
[7]*National Institute of Water and Atmospheric Research (NIWA),Centre for Chemical and Physical Oceanography, Department of Chemistry, University of Otago, Dunedin, New Zealand*
[8]*University of Colorado Denver, P.O. Box 173364, Denver, Colorado 80217-3364, U.S.A.*
[9]*Centre for Climate Change Studies, School of Environmental Science and Management, Southern Cross University, Lismore, NSW 2480, AUSTRALIA*
[10]*Graduate School of Oceanography, University of Rhode Island, South Ferry Road, Narragansett, RI 02882 USA*
[11]*Department of Biological and Environmental Sciences, P.O. Box 65, FI-00014 University of Helsinki, Finland*
[12]*Meteorology & Physical Oceanography, Rosenstiel School of Marine & Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149-109, USA*
[13]*Virginia Institute of Marine Science, College of William and Mary, P.O. Box 1346, Gloucester Point, VA 23062. U.S.A.*
[14]*Australian Antarctic Division, Channel Highway, Kingston, Tasmania 7050, Australia*
[15]*Department of Oceanography, Dalhousie University, Halifax, NS B3H 4J1, Canada*
[#]No longer affiliated with organisation
Current Affiliation:
[A]DragonFly, Wellington, New Zealand.
[B]Department of Oceanography, University of Hawaii, 1000 Pope Road, MSB 517, Honolulu, HI 96822, USA
[C]School of Physics & Environmental Change Institute, National University of Ireland, University Road, Galway, Ireland
[D]Department of Earth and Marine Sciences, Australian National University, Canberra, Australia

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Abstract

The SOLAS air-sea gas exchange experiment (SAGE) was a multiple-objective study investigating gas-transfer processes and the influence of iron fertilisation on biologically driven gas exchange in high-nitrate low-silicic acid low-chlorophyll (HNLSiLC) Sub-Antarctic waters characteristic of the expansive Subpolar Zone of the southern oceans. This paper provides a general introduction and summary of the main experimental findings. The release site was selected from a pre-voyage desktop study of environmental parameters to be in the south-west Bounty Trough (46.5°S 172.5°E) to the south-east of New Zealand and the experiment conducted between mid-March and mid-April 2004. In common with other mesoscale iron addition experiments (FeAX's), SAGE was designed as a Lagrangian study quantifying key biological and physical drivers influencing the air-sea gas exchange processes of CO_2, DMS and other biogenic gases associated with an iron-induced phytoplankton bloom. A dual tracer SF_6/^{3}He release enabled quantification of both the lateral evolution of a labelled volume (patch) of ocean and the air-sea tracer exchange at the 10's of km's scale, in conjunction with the iron fertilisation. Estimates from the dual-tracer experiment found a quadratic dependency of the gas exchange coefficient on windspeed that is widely applicable and describes air-sea gas exchange in strong wind regimes. Within the patch, local and micrometeorological gas exchange process studies (100 m scale) and physical variables such as near-surface turbulence, temperature microstructure at the interface, wave properties, and wind speed were quantified to further assist the development of gas exchange models for high-wind environments.

There was a significant increase in the photosynthetic competence (F_v/F_m) of resident phytoplankton within the first day following iron addition, but in contrast to other FeAX's, rates of net primary production and column-integrated chlorophyll *a* concentrations had only doubled relative to the unfertilised surrounding waters by the end of the experiment. After 15 days and four iron additions totalling 1.1 tonne Fe^{2+}, this was a very modest response compared to the other mesoscale iron enrichment experiments. An investigation of the factors limiting bloom development considered co-limitation by light and other nutrients, the phytoplankton seed-stock and grazing regulation. Whilst incident light levels and the initial Si:N ratio were the lowest recorded in all FeAX's to date, there was only a small seed-stock of diatoms (less than 1% of biomass) and the main response to iron addition was by the picophytoplankton. A high rate of dilution of the fertilised patch relative to phytoplankton growth rate, the greater than expected depth of the surface mixed layer and microzooplankton grazing were all considered as factors that prevented significant biomass accumulation. In line with the limited response, the enhanced biological draw-down of pCO_2 was small and masked by a general increase in pCO_2 due to mixing with higher pCO_2 waters. The DMS precursor DMSP was kept in check through grazing activity and in contrast to most FeAX's dissolved dimethylsulfide (DMS) concentration declined through the experiment. SAGE is an important low-end member in the range of responses to iron addition in FeAX's. In the context of iron fertilisation as a geoengineering tool for atmospheric CO_2 removal, SAGE has clearly demonstrated that a significant proportion of the low iron ocean may not produce a phytoplankton bloom in response to iron addition.

Introduction

Of the ~8 Pg yr^{-1} of carbon emitted to the atmosphere through fossil fuel combustion (Canadell et al., 2007), there is a net annual uptake of ~5 PgC yr^{-1} split roughly equally between terrestrial and ocean sinks. Within the latitude band from 40° to 60°S there exists a strong sink region associated with photosynthetic (biological) carbon uptake, and Takahashi *et al*. (2009) have identified the southern hemisphere oceans (south of 14°S to Antarctica) as providing the largest oceanic sink region for CO_2. Increased observation has helped to refine this estimate. Takahashi *et al*. (2002) previously identified a disproportionate influence of the southern oceans (between 50 and 62°S), which occupy 10% of the global ocean yet account for 20% of the global CO_2 uptake, although the more recent estimates by Takahashi *et al.* (2009) with a 3x larger database do not support such a large influence. This net uptake of CO_2 reflects the balance between the biological drawdown during summer and significant emission in winter.

There is uncertainty in the mean ocean uptake of CO_2, and its inter-annual variability, due in part to windspeed dependence of the gas exchange coefficient *k* (Carr et al., 2002; Olsen et al., 2005). There are a number of wind-based parameterisations of *k* derived from observation: Liss and Melivat (1986) found a linear-spline relationship to wind; Wanninkhof (1992) and Nightingale *et al.* (2000) a quadratic relationship; Wanninkhof *et al*. (2004) either quadratic or cubic and Wanninkhof and McGillis (1999) a cubic relationship. Clearly estimates from these different parameterisations will diverge with increase in windspeed and so the uncertainly in *k* will be larger at higher windspeed. The requirement to further constrain the processes determining gas-exchange is especially relevant to the subantarctic waters where zonally averaged windspeeds increase poleward through the mid-latitude 40° to 60°S storm belt (Sura, 2003). Processes associated with strong winds, such as bubble-mediated exchange (D'Asaro and McNeil, 2008; Woolf, 1997), will not be adequately accounted for in parameterisations developed at lower windspeed. In addition to the wind influence on the magnitude of surface air-sea exchange processes, concern has arisen from model analyses that suggest the CO_2 sink strength in this region could in fact decline due to the poleward displacement and intensification of westerly winds that drive increased upwelling of carbon rich waters from the ocean interior (Le Quéré et al., 2007). The certainty of this finding is still the subject of debate, in part because the model predictions are poorly constrained by observation (Law et al., 2008). Model results presented by Zickfeld (2008) found that as atmospheric CO_2 continues to rise through the 21st century, the efficiency of the southern ocean sink will tend to increase.

This paper provides a general introduction and summary of the main experimental findings of the SOLAS Air-Sea Gas Exchange Experiment (SAGE). Accompanying papers in this volume provide more details of the results of SAGE conducted in sub-Antarctic waters of the south-west Bounty Trough (46.5°S 172.5°E) between mid-March and mid-April 2004. The experiment used the $^3He/SF_6$ dual tracer method which has been successfully used in the open ocean to provide a patch-scale (10-100 km) air-sea gas exchange estimate in a diffusive ocean mixed-layer (Nightingale et al., 2000; Wanninkhof, 1993; Wanninkhof et al., 1997; Wanninkhof et al., 2004). Whilst most of the existing dual tracer gas exchange data from ocean experiments are from shallower water bodies such as the North Sea, Georges Bank, or the Florida Shelf, these studies have confirmed that the uncertainty in the parameterization of gas exchange coefficient *k* increases as a function of wind speed, and so refinement of the parameterisation is particularly important in regions such as the subantarctic waters which are subject to high wind speeds. For SAGE, the dual-tracer release was complemented by micrometeorological-scale gas exchange determination and measurement of the dominant physical processes known to affect gas exchange, including wind speed, near surface turbulence, the micro-structure of temperature and salinity, and wave characteristics.

From early planning stages, SAGE was devised as a combined gas-exchange process and mesoscale iron fertilisation experiment. The initial aim was to produce a purposefully stimulated and tracer labelled phytoplankton bloom, and provide a laboratory in the natural environment for study of enhanced biogeochemical fluxes and associated air-sea gas exchange, particularly of CO_2 and DMS driven by the biological activity. The southern oceans are the largest High Nutrient Low Chlorophyll (HNLC) area of ocean where productivity is limited by levels of the micro-nutrient iron. Previous experience with iron fertilisation has shown that significant enhancement of algal biomass and primary production can occur (e.g. Boyd et al., 2000; Trull et al., 2001). The results of a review of eight mesoscale fertilisations (de Baar et al., 2005) has since confirmed that maximum biological signal typically scales inversely with the depth of the wind-mixed layer, mediated through the relationship between underwater light climate and phytoplankton photosynthesis.

The HNLC condition as applied to sub-Antarctic waters is more precisely described as (HNLSiLC) or "low-silicic acid HNLC" (Dugdale and Wilkerson, 1998). This condition is found over much of the southern hemisphere oceans in the Sub-Antarctic zone south of 45°S down to the Antarctic Polar frontal zone (Brzezinski et al., 2005). This HNLSiLC ocean area south of 45°S is approximately twice that of HNLC polar waters south of 60°S. Following addition of iron to the low Si waters, it is highly likely that silicic acid will rapidly limit the development of diatoms (Coale et al., 2004). Prior to SAGE, there was interest in examining the response to iron over a longer duration into the bloom decline phase, as done with the European Iron Fertilisation Experiment EIFEX (Bathmann, 2005), with the aim of quantifying carbon sedimentation fluxes. Following the SAGE experiment, there has been further synthesis of the results from 12 mesoscale iron addition experiments including SAGE (Boyd et al., 2007) and heightened interest in the prospects of ocean (iron) fertilisation as a (bio)geoengineering solution to atmospheric CO_2 build-up (Lenton and Vaughan, 2009). However, the need for caution has been clearly identified due to the relatively low efficiency as a carbon sink (Boyd et al., 2004), the difficulty in confirming the degree of permanence of CO_2 removal from the atmosphere and the large uncertainty around unplanned consequences and other environmental impacts without further biogeochemical research (Buesseler and Boyd, 2003; Buesseler et al., 2008).

The progression in iron fertilisation experimentation from incubation study (Martin et al., 1990), to open-ocean equatorial HNLC (Coale et al., 1996), to the Southern Ocean HNLC (Boyd et al., 2000), and more recently to longer-term tracking (Coale et al., 2004), and natural fertilisation study (Blain et al., 2001; Pollard et al., 2009), has been mirrored to an extent by advances in gas exchange studies. Early wind tunnel experiments (Liss, 1983) have been followed by shelf–sea tracer experiments (Nightingale et al, 2000; Wanninkhof et al, 1997) to open ocean process studies (Fairall et al., 2000; Feely et al., 2004; Ward et al., 2004), More recently, attention turned to the higher windspeed regime of the southern oceans (Wanninkhof et al., 2004) where there has been little in-situ study, given the logistic challenges of this work. In extending the observational work at the time, there is no doubt that the combined broad goals of mesoscale iron fertilisation and gas-exchange process study under episodic high-wind conditions, as proposed by SAGE, were ambitious.

Experimental goals and site selection

SAGE had three main experimental goals to determine the drivers and controls of ocean-atmosphere gas exchange through quantification of:

- *biological production and utilisation of climatic relevant gases (in particular CO_2 and DMS) in the surface ocean in association with a phytoplankton bloom through measurement of environment and ecosystem variables, dissolved and atmospheric gas concentrations;*
- *physical control of gas exchange across the interfaces of the surface mixed layer through the dual tracer method at the patch scale (Ho et al., 2006), ship-borne micrometeorological flux measurement, with a combination of in-situ measurement of boundary layer exchange and remote sensing of the air-sea interface for sea surface temperature and wave properties;*

- *production of aerosols resulting from interaction of biological and physical processes, (in particular, study of the oxidation products of DMS) through measurement of the atmospheric mixing ratios of DMS, SO_2 and condensation nuclei properties.*

There were five criteria that guided the site selection:

1. a relatively quiescent and homogeneous region allowing tracer labelled patch tracking for up to a month.
2. a 30 to 80 m mixed layer depth to limit dilution of SF_6 and iron
3. a range of atmospheric wind speeds to allow study of gas exchange coefficient—wind speed relationship
4. Non-limiting macro-nutrient availability and phytoplankton in HNLC waters receptive to iron fertilisation
5. low variability and shear in currents on the patch scale for maintenance of a coherent patch.

Sites for SAGE were identified in a pre-experiment desktop study (Hadfield, 2010) at three potential locations. Site 1 at the NIWA Southern Biophysical time series mooring (S. Bio Mooring in Figure 1) 46° 40'S, 178° 30'E, was rejected as possibly too dynamic, as was found with the FeCycle experiment conducted at this location (Boyd et al., 2005). The second site on the Central Campbell Plateau, approximately 169.5°E, 50.5°S, is relatively quiescent but has consistently low phytoplankton stocks based on remote-sensing data. The third and chosen site was around the South-western Bounty Trough, at approximately 47° 0'S, 172° 0'E shown as the red dot in Figure 2. In this region of Sub-Antarctic waters, the mean flow is towards the northwest, adjacent to the Southland Current and has lower current variability than the SBM site. In common with the SBM site, the SAGE site has a naturally occurring late summer (February) chlorophyll maximum (Figure 3) which in 2004 peaked at around 0.5 mg m^{-3} satellite-derived chlorophyll *a*. Examination of remote sensing data (SST, SSH and ocean colour) immediately prior to the voyage lead to the decision to move the site slightly east to avoid entrainment into the Southland current. Following the pre-release survey, the first iron infusion was made at 46° 44’S 172° 32’E (Law et al., 2010).

In the following summary it is apparent that not all the site selection criteria were met, particularly those related to “quiescence” and low current speed and sheer, and the consequences of this are discussed.

Initial conditions and iron addition

Table 1 gives the initial upper ocean conditions at the time of the first infusion, made just east of the cyclonic eddy centred at 47°S 172°E (Figure 4) which was a persistent feature during SAGE. In Figure 5 the cruise track is overlaid on a geostrophic current plot. More detail on the infusion pattern and subsequent evolution of the labelled patch are presented by Law *et al.* (2010).

For the iron addition, a solution was prepared in two plastic 7500 litre tanks that were initially half–filled with seawater and acidified to ~pH 2 by the addition of 25 litres of hydrochloric acid. A total of 1.35 tonnes of $FeSO_4.7H_2O$ (containing 274 kg Fe2+) were used in each infusion. The aim was to raise the initial dissolved iron concentration to 2nM over a 6x6 km patch with a 50 m mixed layer depth. The dual tracer solution was prepared in two steel 4000 litre containers of seawater by saturation with SF_6 and ^3He. A headspace of ~5 L was continuously flushed with SF_6 and circulated through the water via a diffusion hose by pump, until the water was saturated. ^3He saturation was undertaken just prior to release, with ~10 litres of ^3He dissolved for 20 minutes of headspace recirculation (Law et al., 2010).

Details of the infusions are shown in Table 2 below. The iron and SF_6 solution were pumped out at a depth of ~12-15m from a pipe attached to a towed fish at a distance of ~20m behind the vessel. As sea-water was pumped out of the tracer tanks the volume was replaced by water filling a meteorological balloon by gravity feed from the top of the tank; this flexible cap minimised diffusive loss of ^3He and SF_6 that would have occurred if a headspace had been allowed to develop. The 1st infusion on the 25 March covered 6 x 6 km and was executed within a Lagrangian framework with an expanding hexagonal release track (with track spacing of 0.7 km), referenced to a drogued drifter buoy at the nominal patch centre. The need to reinfuse was dictated by the decline in SF_6 towards background concentrations. The 2nd infusion on 31 March of iron, SF_6 and ^3He took place when the patch was distributed as a long filament running NNW-SSE, and so was adapted to an along filament release track of ~12 x 3 km using the nocturnal underway Fv/Fm signal as reference for patch location. The 3rd infusion on 3 April was iron only, and was released using the underway surface SF_6 signal. The 4th and final infusion, of SF_6 and iron, on 6 April was released using the underway Fv/Fm signal as reference because the dissolved SF_6 signal was low at this stage. All re-infusions were successfully placed within the boundaries of the existing patch (Law et al., 2010).

Patch evolution and response to addition

The accompanying papers in this volume expand on a number of key aspects of the SAGE experiment. Unlike other experiments, there was no evidence for macro-nutrient depletion during the experiment (Figure 6a) and there is a trend of nutrients increasing around days 5-8 when the fertilised area was affected by an interflow/intrusion of a water body at the west boundary (Law et al., 2010). Whilst initial post-fertilisation dissolved iron levels were generally greater than 1 nM (Table 2), values did decline rapidly although levels were generally kept above 0.1-0.2 nM within the fertilised patch (Figure 6b). There was a rapid initial response to iron addition detected as an increase in photosynthetic competence (F_v/F_m) measured by fast repetition rate fluorometry (Figure 6d). The increase is consistent with observations in other iron experiments (Boyd et al., 2000). A difference in F_v/F_m of ~0.04 between IN and OUT of the patch was maintained throughout the experiment based on the threshold of 10 fM SF_6 as demarcation of the patch boundary (Law et al., 2010). After the second infusion, this IN-OUT Fv/Fm difference was maintained against an increasing trend in F_v/F_m outside the patch.

Kuparinen et al. (2010) identified that bacterioplankton growth rates were in general low with no significant enhancement in the patch, but with the greatest increase towards the end of the experiment. Phytoplankton stocks and primary productivity were slow to respond in spite of the partial relief of iron stress with a small increase in surface chlorophyll *a* until Day 3 (Figure 6 c and e). Details are discussed by Peloquin *et al.* (2010b). Whilst a clear in-patch enhancement in biomass and primary productivity appeared to exist around days 4-5, the elevated IN concentrations declined the following day and there was then little difference between IN and OUT patch values through to day 12 although the background values were slowly increasing. From day 13 onwards, the in-patch chlorophyll *a* and IN-OUT difference began once again to increase. The final enhancement (IN-OUT) at the end of the experiment (day 16) was an approximate doubling of both surface (Figure 6 c and e) and column integrated (~40 mg m^{-2} OUT, ~80 mg m^{-2} IN) chlorophyll *a* and primary productivity (~0.4 gC $m^{-2}d^{-1}$ OUT, ~0.8 gC $m^{-2}d^{-1}$ IN) (Peloquin et al., 2010b). In the accompanying volume we consider the component factors that are thought to have led to this modest response (Law et al., 2010; Peloquin et al., 2010b).

Limiting factors

Physical factors limiting and causing the rapid shift in chlorophyll concentrations around days 5-6 were investigated. Figure 7 shows a summary of u_{10} wind statistics discussed in detail by Smith *et al.* (2010). With the northward passage of a storm along the east coast of New Zealand on day 3, there was an accompanying maximum in the recorded u_{10} windspeed of >20 m s^{-1}. The strong wind produced a deepening of the surface wind-mixed layer. Comparison of the predicted conditions with those encountered by Hadfield (2010) identified that the actual mixed-layer depth during SAGE was significantly greater than that predicted by climatological values. Stevens *et al.* (2010) describe detailed physical measurements of the ocean mixed-layer and environmental influences governing the mixed-layer depth and include a new method for mixed-layer depth estimation. It was a few days after this storm around days 5-8 that an interflow/intrusion produced a high rate of lateral dilution as the patch was drifting north-east (Law et al., 2010). Chlorophyll concentrations did not increase further until after the final infusion of iron, coincident with a decrease in windspeed and rate of patch advection as well as improved meteorological conditions with higher incident light levels (*e.g.* on days 9, 10, 12 in Figure 8). Law *et al*. (2010) found that there were only two periods when the phytoplankton growth rate exceeded the minimum dilution rate (0.125 d^{-1}) on D3-6 and D10-14, and these correspond to periods when IN station chlorophyll exceeded that at the OUT station (Fig. 6c).

The pivotal role of light in limiting the development of diatom blooms in subantarctic waters towards the equinox has been discussed by others (Boyd et al., 1999; van Oijen et al., 2004). SAGE was conducted at a time and location that experienced the lowest range of theoretical clear-sky photosynthetically active radiation (PAR) for any of the FeAX's (Figure 9). In the figure we also show the likely range of surface PAR (allowing for cloud attenuation) using the SeaWIFS PAR product described by Frouin (2003) for 8-day composite data of a 7 x 7 tile of 9-km tile of pixels over the duration of each experiment. In these data, SAGE and SOIREE have equal lowest median incident surface PAR. SOIREE was conducted in high silicic acid polar waters (61°S) and there is a persistent trend of increasing fractional cloudiness poleward from 30° to 60° (Mokhov and Schlesinger, 1994). In-situ measured PAR data are available for both SOIREE and SAGE and there is good agreement with the median of the in-situ and SeaWIFS estimates The measured range for SOIREE was relatively large between 13 – 40 (average 21.4) mol m^2 d^{-1} and a significant bloom followed the alleviation of iron stress (Boyd and Abraham, 2001). In SAGE, the range of PAR of 16 – 32 (average 19.7) mol m^2 d^{-1} was similar yet there was a much smaller biological response. Peloquin *et al.* (2010a) consider in more detail macro- and micro-nutrients, light, seed-stocks and relative rates of phytoplankton growth against grazing by micro- and meso-zooplankton and influence of dilution of the patch. Peloquin *et al.* (2010a) suggest that received irradiance was not the major limiting factor affecting the biological response of SAGE in the HNLSiLC waters although the phytoplankton assemblage may have been on the cusp of light limitation.

The potential for macro-nutrient co-limitation was also assessed (Law et al., 2010). The mixed-layer deepening & intrusion resulted in an increase in mixed-layer macronutrient concentrations until D10, with the result that concentrations were higher at end than the beginning, unlike any other FeAX's. No significant floristic shifts occurred during the experiment and, with a very low (~1%) initial diatom seed-stock in waters and the lowest initial silicic acid to nitrate (Table 1) ratio of any of the iron addition experiments (Boyd et al., 2007), there was little likelihood of a diatom bloom following the fertilisation. In the absence of suitable conditions for diatom growth, the main biological response came from a modest increase in picophytoplankton biomass but without an increase in particulate organic carbon (POC). Growth was thought to have been kept in check by the resident microzooplankton grazers with the increase in POC being recycled through the microbial food web. In the patch, growth generally exceeded biomass except during the middle of the experiment (D5-7) with high grazing on eukaryotic picoplankton during the first 7 days (Peloquin et al., 2010a). Law *et al*. (2010) found that the mean net algal growth:dilution rate of 1.13 (0.4-2.2) is the lowest reported for a FeAx, underpinning the importance of dilution in SAGE. However the dilution rate decreased for Day 10-14 and growth exceeded grazing for the total picophytoplankton and picoprokaryotes from D11.6 until the end of the experiment (D15). We conclude, therefore that a combination of biological (grazing) and physical (dilution rate) factors were important in limiting biomass accumulation in the treated patch.

Consistent with the limited biological response, the change in biologically influenced climate relevant gases (CO_2 and DMS) was small (Figure 6f). Any enhanced biological draw-down of pCO_2 was masked by a general increase in pCO_2 in the patch and mixing with higher pCO_2 waters to the west (Currie et al., 2010) during the period of intrusion. In the final phase of the patch occupation, the median or mean in-patch CO_2 fugacity never dropped more than 1 μatm below the OUT patch value. The cycling of sulfur components is discussed by Archer *et al*. (2010). Any enhancement in production of dimethylsulfoniopropionate (DMSP) appears to have been kept in check through grazing activity and, in contrast to most other iron fertilisation experiments, the dissolved dimethylsulfide (DMS) concentration actually declined over the course of the experiment.

Comparisons and concluding remarks

The ocean physics component of SAGE investigated processes important for gas exchange estimation at strong windspeeds where the commonly used windspeed-based parameterisations diverge. The SAGE dual-tracer gas exchange experiment was successful in obtaining measurements under the highest average windspeed conditions (up to $16\ m\ s^{-1}$) sampled to date, as described in Ho *et al.* (2006) and in Smith *et al.*, (2010). From re-examination of previous dual-tracer experiments along with the SAGE measurements, Ho *et al.* (2006) found that a quadratic relationship $k = 0.266\ u_{10}^2\ (600/Sc)^{0.5}$ accurately described gas transfer for SAGE and previous dual-tracer datasets for the entire windspeed range. Here k is gas transfer velocity, u_{10} is the windspeed 10 metres above the surface estimated from QuikSCAT satellite derived winds, and Sc the Schmidt number used for normalisation with 600 being the Schmidt number for CO_2 in freshwater at 20°C. In contrast, the Liss and Merlivat (1986) relationship significantly underestimated and the Wanninkhof and McGillis (1999) cubic relationship significantly overestimated exchange. Ho *et al*. (2006) suggest that their function is applicable to the entire global ocean including both the coastal and open ocean environments. Smith *et al*. (2010) examine the influence of uncertainty and error in windspeed (*u*) measurement on the gas-transfer velocity (*k*) windspeed relationship, and considered the sea-state properties that can be used for refining estimates for strong winds e.g. when bubble mediated transfer can be significant. Minnett *et al*. (2010) made skin temperature measurements at higher windspeeds during SAGE than previously reported and suggest that skin temperature is a more relevant temperature for input to gas exchange estimation that bulk ocean temperature. The impact of skin versus bulk temperature on gas exchange estimation is further examined by Currie et al. (2010).

Following the synthesis of de Baar *et al.* (2005) we compare the outcome of SAGE with other iron addition experiments (FeAX's). Figure 10 shows the trend of increasing $\Delta f CO_2$, i.e. the difference between IN and OUT patch CO_2 fugacity, with increasing surface chlorophyll *a* biomass. The SEEDS experiment (Tsuda et al., 2003) produced a very large draw-down through a centric diatom bloom that developed in a very shallow surface mixed layer; by comparison SAGE had a negligible impact in a deep mixed layer. Figure 11 shows SAGE and SEEDS at the extremes of the range of response in chlorophyll concentrations in relation to the range of mixed layer depths encountered in mesoscale iron addition experiments.

It is instructive to compare the biological responses in SAGE with the SEEDS II experiment which was published after the de Baar et al. (2005) synthesis. SEEDS II was conducted in a more diffusive ocean with a deeper mixed-layer depth and windier atmosphere resulting in a much smaller response compared to the first SEEDS (Tsumune et al., 2009). In both SAGE and SEEDS II, picoplankton are an important component of the total assemblage. In SEEDS II the picoplankton biomass (sized as 0.2 or 0.7 to 2.0 µm) of 0.17 mg m^{-3} initially accounts for ~a quarter of the surface Chl-*a*. The picoplankton biomass increased substantially (1.1 mg m^{-3}); at Day 10 and accounts for an increased proportion (40%) of the surface Chl-*a* (Kudo et al., 2009). The trend continues in the decline phase with picoplankton accounting for 65% of the surface Chl-*a* after 25 days. In SAGE, the initial picoplankton Chl-*a* amount and proportion is substantially larger than in SEEDS II (0.47 mg m^{-3} and ~70%) (Peloquin et al., 2010b) and whilst the Chl-*a* reaches 0.9 mg m^{-3} by Day 15, the dominant proportion around 65-70% remains almost unchanged. Under the ecumenical iron hypothesis (Cullen, 1995; Morel et al., 1991) it is proposed that small cells with high surface to volume ratio are less sensitive to iron limitation and likely to be more sensitive to grazing controls. The results from SAGE do not contradict this hypothesis where picoplankton biomass increased when grazing pressure is reduced (Peloquin et al., 2010b). In both experiments, diatoms did not bloom. Initially in SEEDS II diatoms were the second most abundant of larger plankton

(Suzuki et al., 2009), and as the assemblage evolved, there tended to be a dominance of grazing resistant species (Tsuda et al., 2009). However, Tsuda *et al*. (2007) reported an exponential increase in copepod mesozooplankton, with copepod grazing representing a major factor that prevented the formation of a diatom bloom. By contrast (Peloquin et al., 2010b) found that diatoms comprised less than 1% of the initial biomass of SAGE and there was no evidence of increase through the experiment. Whilst at first sight, this finding appears to contradict the ecumenical iron hypothesis with the expectation of floristic shifts following iron fertilisation, allowing diatoms that are less grazing dependent to bloom, it does agree with the broader principle behind the hypothesis which suggests that no single factor will regulate bloom development.

The biological response of SAGE was unexpected, representing a minimum end member amongst the FeAX's conducted to date (Boyd et al., 2007), and has provided an excellent framework for the study of multiple factors limiting primary productivity (Peloquin et al., 2010a). The findings support and extend the analysis of de Baar *et al*. (2005) in the relationship between response to iron addition and depth of the wind-mixed layer. Peloquin et al (2010a; 2010b) suggest the system was only on the verge of light limitation and important limiting factors included an active zooplankton grazing community and the diluting effects of strong horizontal and vertical mixing. Furthermore, a diatom bloom in a HNLSiLC region was unlikely because of the small (1%) initial diatom biomass and the low Si:N nutrient status, especially later in the growing season following the seasonal drawdown of macro-nutrients.

SAGE has demonstrated that iron fertilisation will not produce a response in all HNLC regions at all times. In addition to the small response, conditions favoured the dominance of picophytoplankton < 2 μm (Peloquin et al., 2010b) which might suggest that any iron-mediated gain of carbon is most likely to stay in the mixed-layer and be remineralised rather than sink and be sequestered in the deep ocean. This leads us to suggest that seasonal effects, HNLC sub-type (*e.g*. HNLSiLC) as well as ecosystem factors all need to be considered in large-scale global models of iron fertilisation and in projected estimates of the ocean carbon sink resulting from any large-scale ocean fertilisation (Browman and Boyd, 2009).

In planning this work, the SOLAS programme provided the case for integration of physical and biological process studies to develop understanding of biologically driven air-sea gas exchange. In conducting the broad-ranging SAGE experiment in the challenging environment of the southern oceans, logistical capabilities were close to the limit of what is achievable with a single vessel. For future multidisciplinary studies of this type, there are clear benefits in the development of experimental design with multiple platforms, as has since been demonstrated with some of the longer duration FeAX's.

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Figure legends

Figure 1: Bathymetry map to the south-east of New Zealand in the vicinity of the SAGE experiment. Depth (meters) is indicated by the colour bar.

Figure 2: SeaWiFS chlorophyll *a* composite Mar – Apr 2004. SAGE site is shown as a red dot.

Figure 3: Timeline of SeaWiFS chlorophyll *a* for SAGE site, extracted from 8 day composite standard mapped images. Statistics are for a tile of up to 48 pixels (approx 50 x 50 km) centred on 46.5°S 172.5°E. The vertical arrow marks the time of the SAGE experiment.

Figure 4: Sea surface height plot for 24 March 2004 from AVISO delayed-time, reference, merged, Mapped Sea Level Anomalies (MSLA_DT_REF) from sea level anomaly data set at 0.25° × 0.25° derived from satellite altimeters on TOPEX/Poseidon and ERS satellites www.aviso.oceanobs.com and NRL Coastal Ocean Model Sea Surface Height Mean. Release site is centred on the white dot. Anomaly (m) is indicated by the colour bar.

Figure 5: Geostrophic current velocity calculated from SSH for 3 April 2004, data source as in Figure 4 (Hadfield, 2010). The yellow line shows the entire voyage track which progressed in an anti-clockwise direction. Current barbs show direction, filled contours show speed (m s^{-1}): 0–0.05 white, 0.05–0.10 light grey, 0.10–0.20 darker grey, 0.20–0.30 blue, 0.30–0.40 navy.

Figure 6: Evolution of the SAGE fertilised patch. Variables in the left column were measured from daily CTD casts, where Day 0 is the night 25/26 March (19:00 25-Mar-2004 for continuous data). The vertical arrows show the mid-times of the four iron infusions. Variables in the right column are from continuous underway seawater sampling where samples are assigned as IN patch from SF_6 tracer levels above 10 fM and are otherwise regarded as OUT patch (a) Surface (top 10 m) nitrate and silicate concentrations IN and OUT of the patch. (b) Median surface (2 m) dissolved iron measured from towed torpedo trace iron sampler. The vertical bars extend between minimum and maximum values. (c) Total euphotic zone chlorophyll-a by trapezoidal integration to the 0.5 % light level as mean and standard error as calculated by Peloquin et al. (2010b). (d) Photosynthetic competence F_v/F_m measured at night. Vertical bars show the mean and standard deviation for each night-time. (e) Total euphotic zone primary productivity by trapezoidal integration to the 0.5 % light level as mean and standard error as calculated by Peloquin et al. (2010b). (f) Median fugacity of CO2. The vertical bars extend between minimum and maximum values.

Figure 7: Median, maximum and minimum daily u_{10} windspeed calculated from vessel anemometer and corrected for flow distortion according to Popinet *et al.* (2004). The dashed bar to the left shows a horizontal mark at the median and extends from the 5th to the 99th percentile of ship windspeed observations presented by Hadfield (2010).

Figure 8: Measured and theoretical maximum clear sky daily incident photosynthetically active radiation calculated with an atmospheric transmission coefficient of 0.86 and top of the atmosphere PAR of 2500 µmol m^{-2} s^{-1}. Inverted triangles are 8-day composite surface PAR from SeaWIFS for 1°x1° box including the SAGE site presented by Hadfield (2010).

Figure 9: Comparison of light availability in iron addition experiments. The black bars show the range of theoretical maximum clear sky daily incident PAR calculated with an atmospheric transmission coefficient of 0.86 and top of the atmosphere PAR of flux of 2500 µmol m^{-2} s^{-1}. The box plots show the range, quartiles and median of surface PAR (allowing for cloudiness) based on 8-day composite SeaWIFS PAR estimate (Frouin et al., 2003) for a 7 x 7 tile of pixels at 9-km resolution over the duration of each experiment.

Figure 10: A comparison of the maximum IN:OUT patch difference in fCO_2 versus the maximum surface chlorophyll for a number of FeAX's. Data sources are from Boyd et al. (2007) including supplemental tables. In addition SEEDSII data are from (Tsumune et al., 2009) and KEOPS data from a study of natural iron fertilisation on the Kerguelen Plateau (Blain et al., 2007).

Figure 11: The enhancement in surface chlorophyll *a* ranked in approximate order of reducing mixed-layer depth for 10 FeAX's (note IronEx-1 did not evolve due to patch subduction after 4 days). Adapted from de Baar et al (2005), with inclusion of data from SEEDS II and SAGE (Boyd et al., 2007 Suppl. tables).

Tables

Variable ± stdev	**Initial condition**
SST (°C)	11.5 ± 0.05
Salinity	34.316 ± 0.003
Background dissolved Fe (nM)	0.09 ± 0.005
Surface NO_3 range (µM)	7.6 – 10.3
Surface SiO_4 range (µM)	0.83 - 0.97
Dissolved reactive phosphorus (µM)	0.62 – 0.85
Fv/Fm	0.27 ± 0.02
Primary Productivity ($mmolCm^{-3}d^{-1}$)	0.53 ± 0.02
Biology	Picophytoplankton dominated
3 hour prior wind (ms^{-1})	10.7 ± 1.1
“Mixed-layer depth” (m)	~60
Surface chlorophyll *a* (mg m^{-3})	0.64 ± 0.05
Integrated chlorophyll *a* (mg m^{-2})	44.4 ± 1.5
pCO_2 (µatm)	327.3 ± 2.0

Table 1: Summary of initial conditions at the SAGE first release site 46° 44’S 172° 32’E with seawater sampled from ships scientific supply (5 m depth)

Infusion	**Date (NZST)**	**Tracer added**	**Fe added** kg (Fe)	**Flow rate** $L\ h^{-1}$	**Ship speed** kts	**Post infusion Fe** nM
1	25/03/04 1500 – 2330	SF_6 & ^3He	265	Fe 925 Lh^{-1} SF_6 & ^3He 475 Lh^{-1}	4.25	3.03
2	31/03/04 0000 – 0600	SF_6 & ^3He	265	Fe 1370 Lh^{-1} SF_6 & ^3He 690 Lh^{-1}	5.5	1.59
3	03/04/04 1230 – 1830		265	Fe 1200 Lh^{-1}	7-8	0.55
4	06/04/04 2220 - 0330	SF_6	265	Fe 1200 Lh^{-1} SF_6 500 Lh^{-1}	5-6	1.01

Table 2: SAGE infusion details

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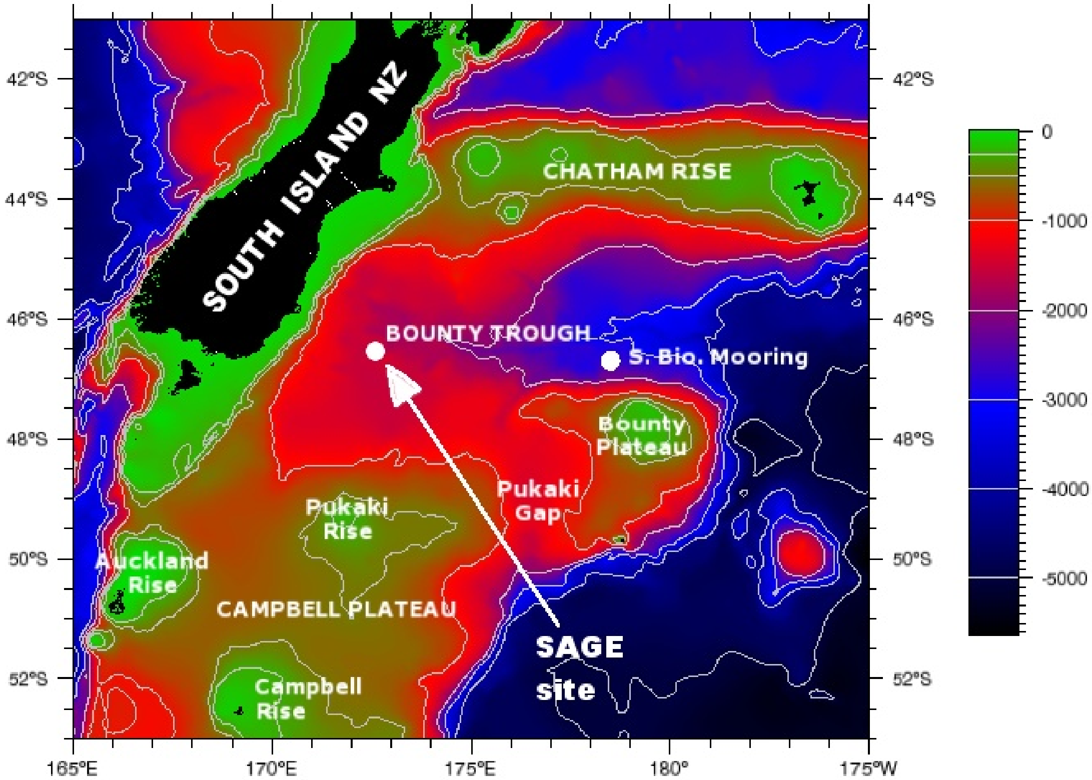

Figure 1: Bathymetry map to the south-east of New Zealand in the vicinity of the SAGE experiment. Depth (meters) is indicated by the colour bar.

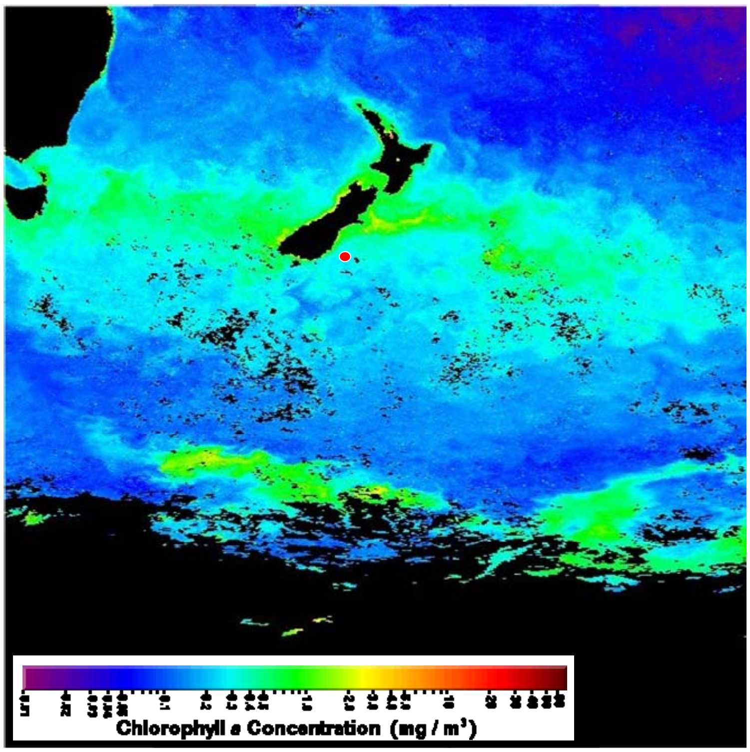

Figure 2: SeaWiFS chlorophyll-a composite Mar – Apr 2004 SAGE site is shown as a red dot.

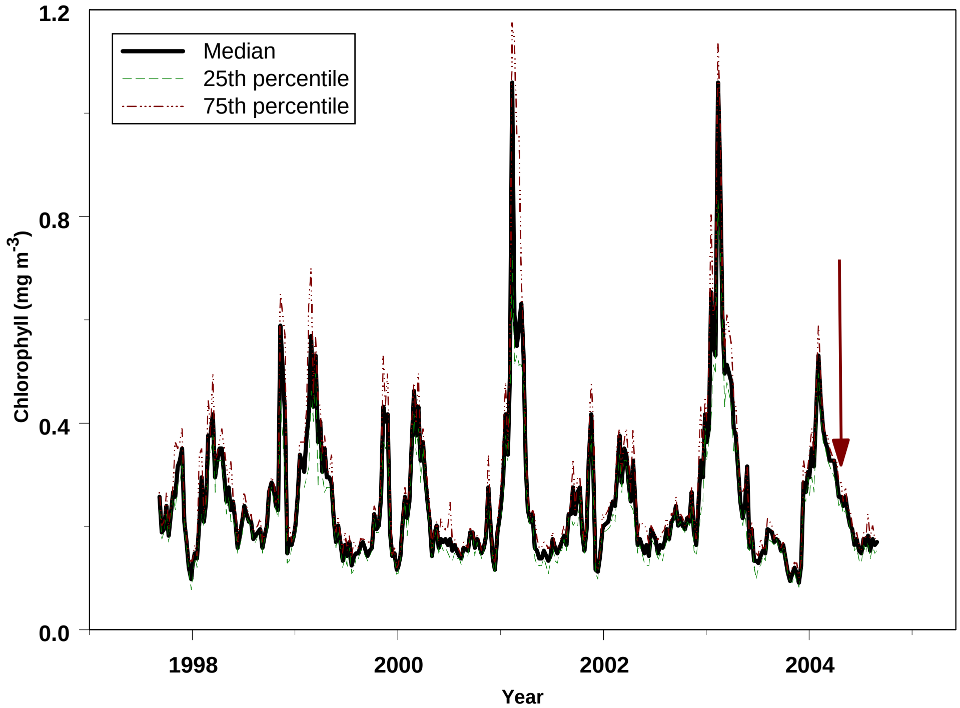

Figure 3: Timeline of SeaWiFS chlorophyll-a for SAGE site, extracted from 8 day composite standard mapped images. Statistics are for a tile of up to 48 pixels (approx 50 x 50 km) centred on 46.5°S 172.5°E. The vertical arrow marks the time of the SAGE experiment.

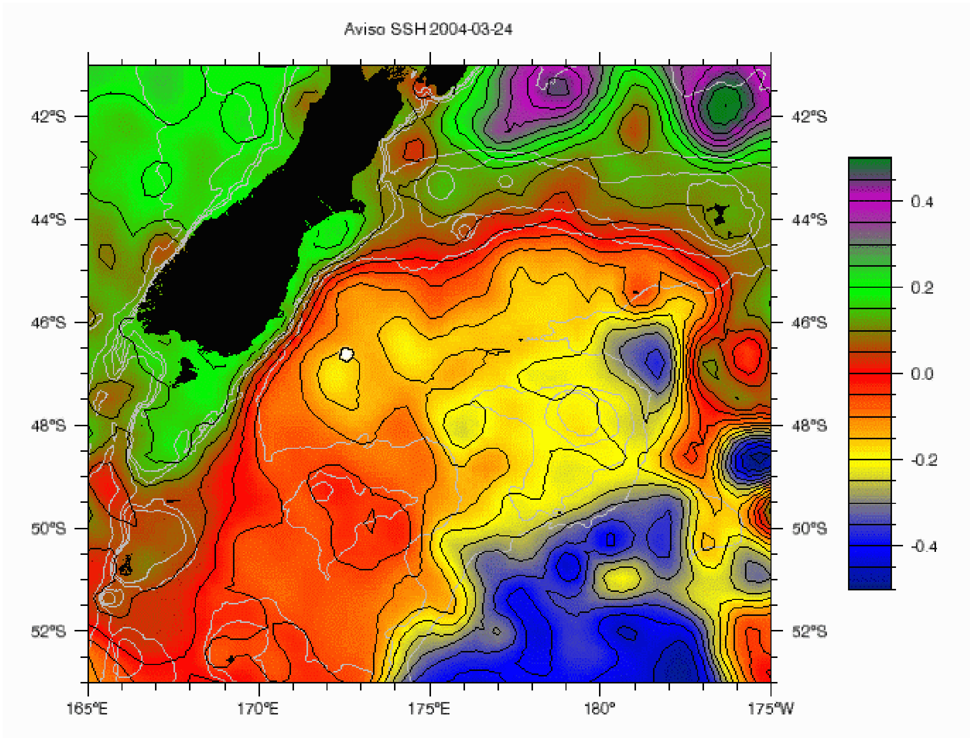

Figure 4: Sea surface height plot for 24 March 2004 from AVISO delayed-time, reference, merged, Mapped Sea Level Anomalies (MSLA_DT_REF) from sea level anomaly data set at 0.25° × 0.25° derived from satellite altimeters on TOPEX/Poseidon and ERS satellites www.aviso.oceanobs.com and NRL Coastal Ocean Model Sea Surface Height Mean. Release site is centred on the white dot. Anomaly (m) is indicated by the colour bar.

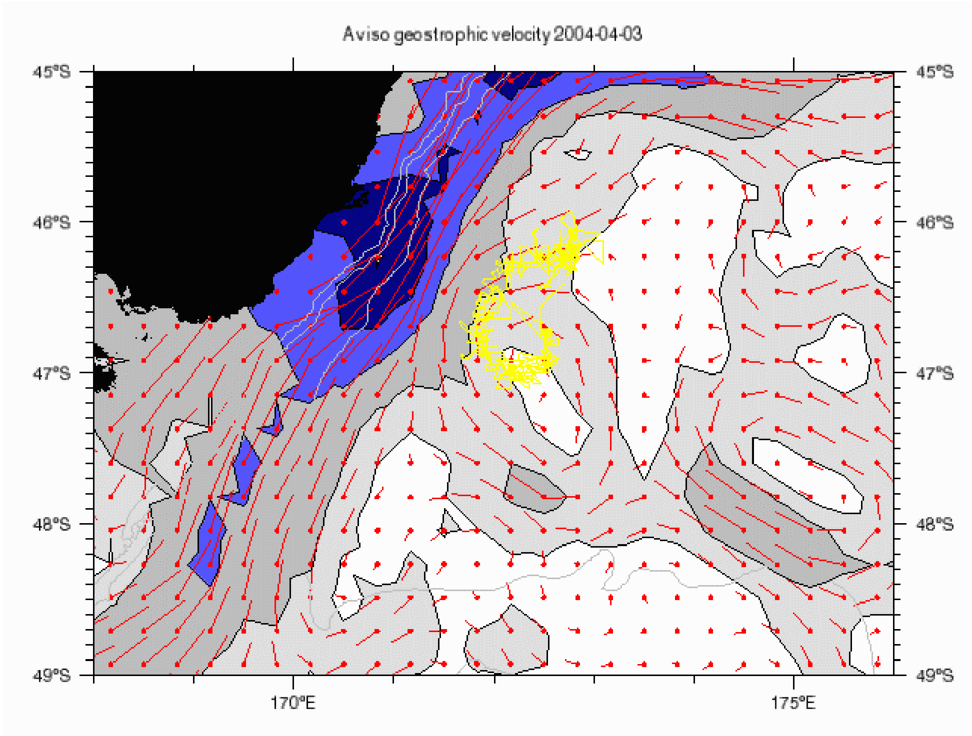

Figure 5: Geostrophic current velocity calculated from SSH for 3 April 2004, data source as in Figure 4 (Hadfield, 2010). The yellow line shows the entire voyage track which progressed in an anti-clockwise direction. Current barbs show direction, filled contours show speed (m s^{-1}): 0–0.05 white, 0.05–0.10 light grey, 0.10–0.20 darker grey, 0.20–0.30 blue, 0.30–0.40 navy.

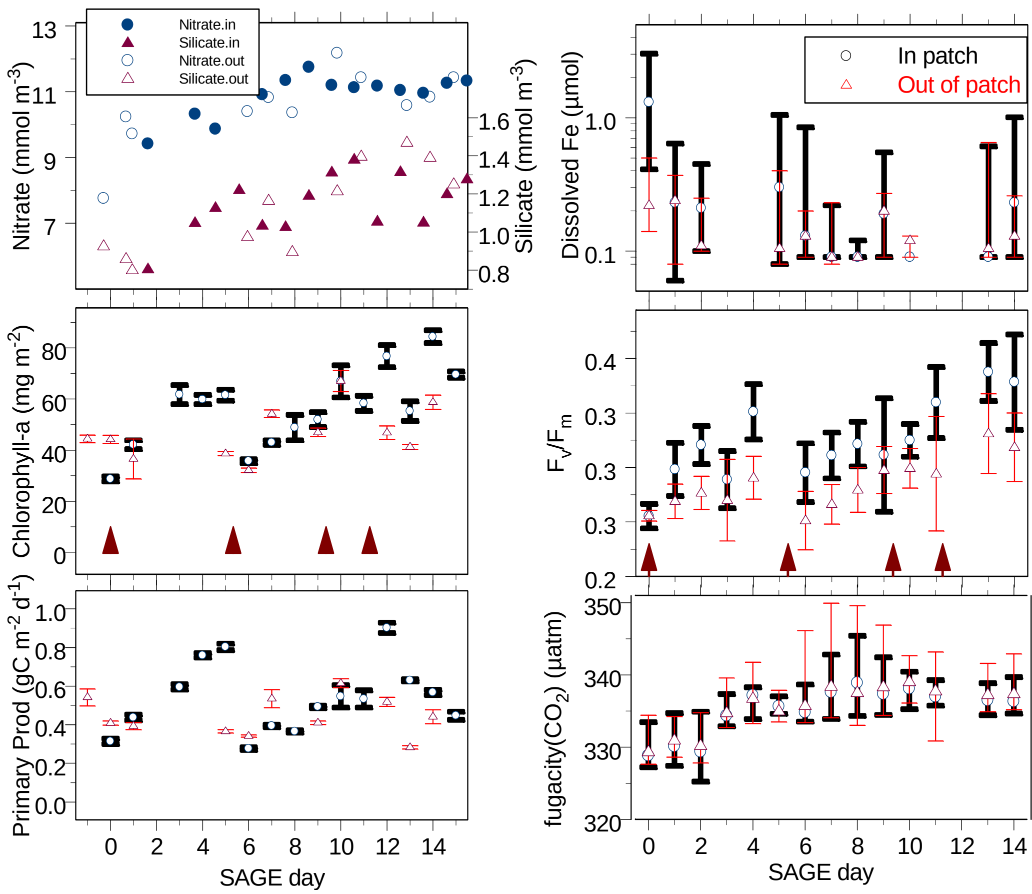

Figure 6: Evolution of the SAGE fertilised patch. Variables in the left column were measured from daily CTD casts, where Day 0 is the night 25/26 March (19:00 25-Mar-2004 for continuous data). The vertical arrows show the mid-times of the four iron infusions. Variables in the right column are from continuous underway seawater sampling where samples are assigned as in patch from SF_6 tracer levels above 10 fM and are otherwise regarded as OUT patch (a) Surface (top 10 m) nitrate and silicate concentrations IN and OUT of the patch. (b) Median surface (2 m) dissolved iron measured from towed torpedo trace iron sampler. The vertical bars extend between minimum and maximum values. (c) Total euphotic zone chlorophyll-*a* by trapezoidal integration to the 0.5 % light level as mean and standard error as calculated by Peloquin et al. (2010). (d) Photosynthetic competence F_v/F_m measured at night. Vertical bars show the mean and standard deviation for each night-time. (e) Total euphotic zone primary productivity by trapezoidal integration to the 0.5 % light level as mean and standard error as calculated by Peloquin et al. (2010). (f) Median fugacity of CO_2. The vertical bars extend between minimum and maximum values.

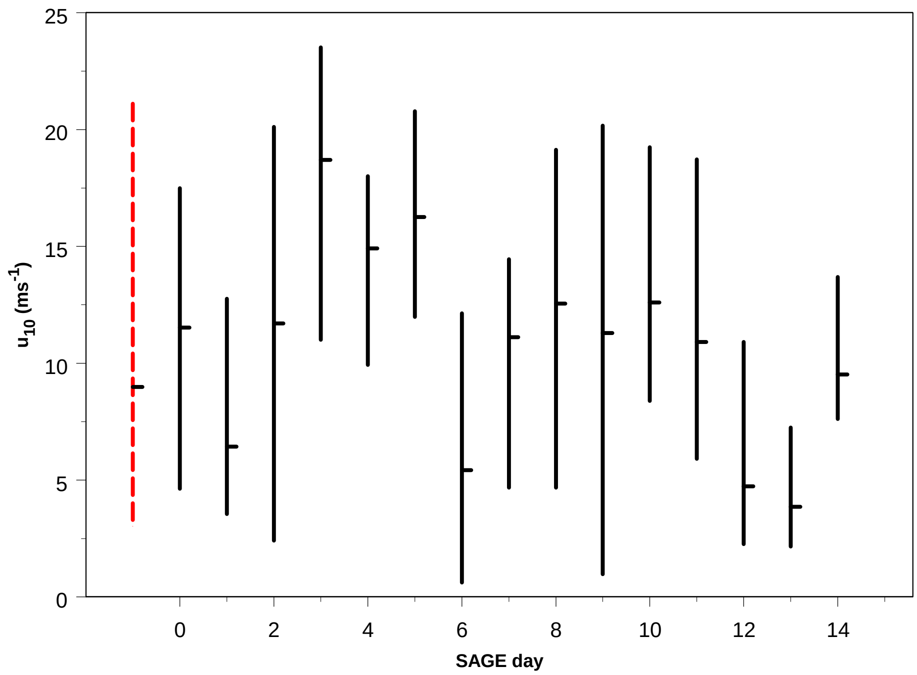

Figure 7: Median, maximum and minimum daily u_{10} windspeed calculated from vessel anemometer and corrected for flow distortion according to Popinet et al. (2004). The dashed bar to the left shows a horizontal mark at the median and extends from the 5th to the 99th percentile of ship windspeed observations presented by Hadfield (2010)

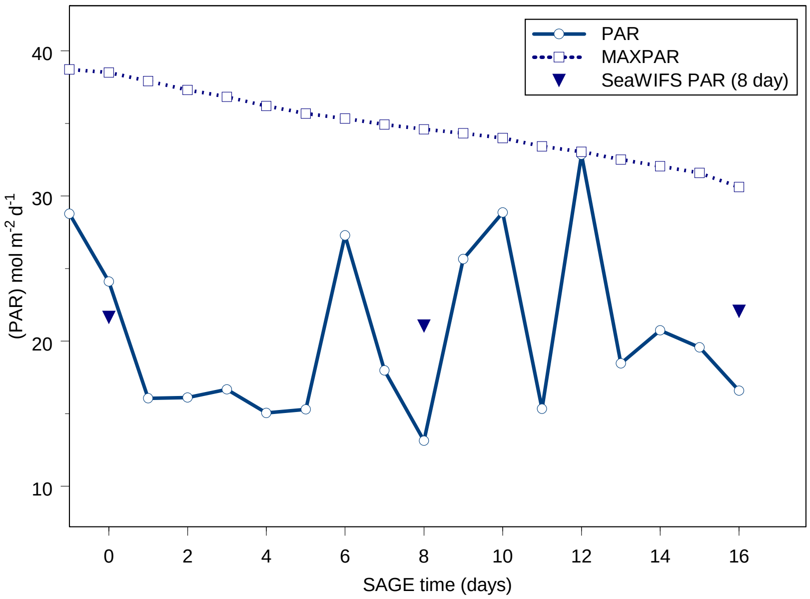

Figure 8: Measured and theoretical maximum clear sky daily incident photosynthetically active radiation calculated with an atmospheric transmission coefficient of 0.86 and top of the atmosphere PAR of 2500 µmol m^{-2} s^{-1}. Inverted triangles are 8-day composite surface PAR from SeaWIFS for 1°x1° box including the SAGE site presented by Hadfield (2010).

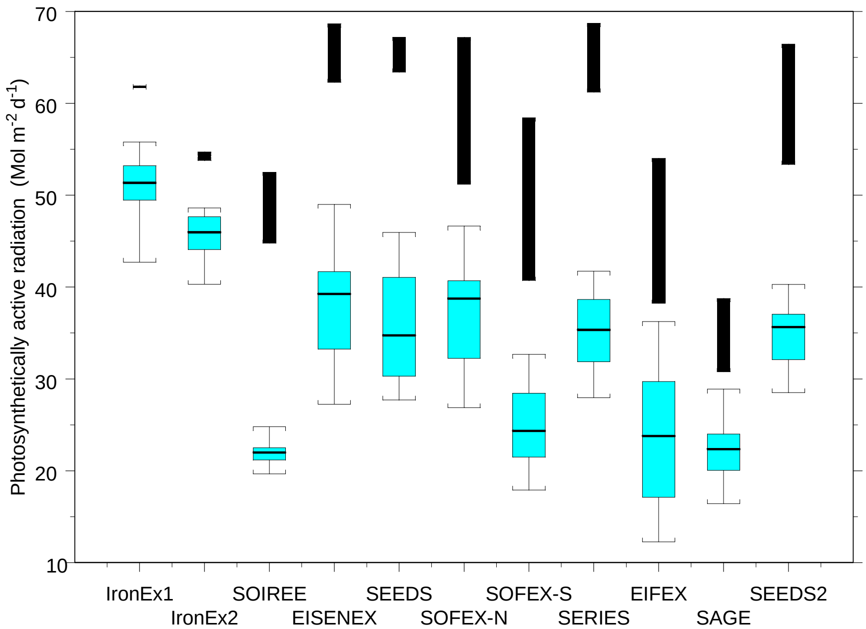

Figure 9: Comparison of iron addition experiments. The black bars show the range of theoretical maximum clear sky daily incident PAR calculated with an atmospheric transmission coefficient of 0.86 and top of the atmosphere PAR of flux of 2500 µmol m^{-2} s^{-1}. The blue box plots show the range, quartiles and median of surface PAR (allowing for cloudiness) based on 8-day composite SeaWIFS PAR (Frouin *et al.*, 2003) estimate for a 7 x 7 tile of pixels at 9-km resolution over the duration of each experiment.

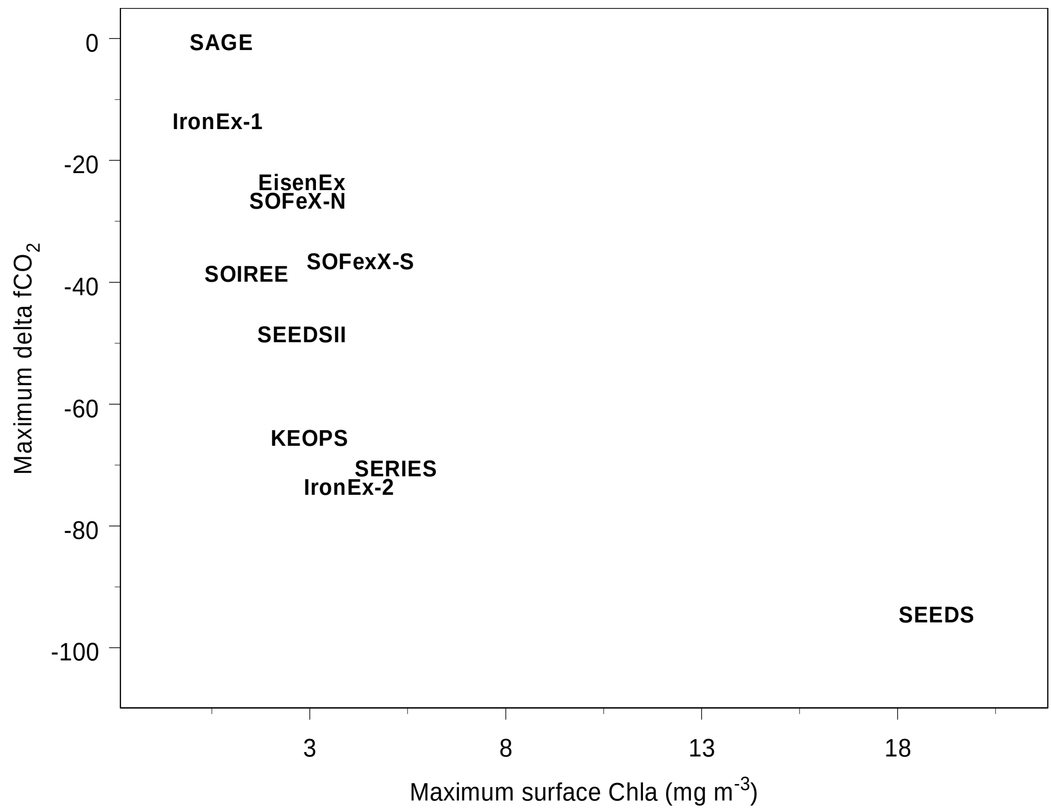

Figure 10: A comparison of the maximum in:out patch difference in fCO_2 versus the maximum surface chlorophyll for a number of FeAX's. Data sources are common with (Boyd et al., 2007) including supplemental tables. In addition SEEDS-II data were presented by (Tsumune et al., 2009); KEOPS are data from a study of natural iron fertilisation on the Kerguelen Plateau ((Blain et al., 2007).

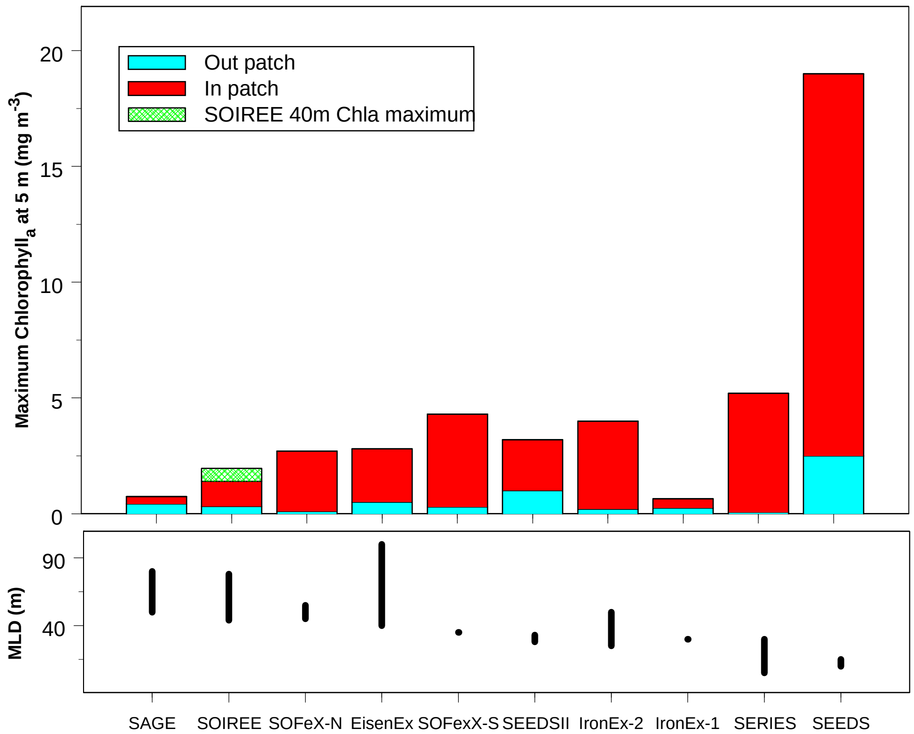

Figure 12: The enhancement in surface chlorophyll-*a* ranked in approximate order of reducing mixed-layer depth for 10 FeAX's (note IronEx-1 did not evolve due to subduction after 4 days).). Adapted from de Baar et al (2004), with inclusion of data from SEEDS II and SAGE (Boyd *et al.*, 2007 Suppl. tables)