SOIREE - Southern Ocean Iron Release Experiment
February 1999
Preliminary Voyage Report
March 1 1999

Vessel
RV *Tangaroa*

Dates
30 days (31 Jan - 1 March 1999)
Sailed from and returned to Wellington

Aim To maintain a coherent patch of iron-enriched seawater for the duration of SOIREE and to interpret any iron-mediated effects on the patch by conducting measurements and performing experiments during this period.

Participants

Philip Boyd	NIWA Scientific Leader,Active fluorescence/Fe stress markers/Si uptake
E. Abraham	NIWA CTD calibration/site selection/navigation co-ordination
K. Downing	NIWA CTD/ Electronics/Nu-Shuttle/ADCP
R. Murdoch	NIWA Voyage leader/Nu-Shuttle/CTD
S. Pickmere	NIWA underway nutrients/nutrient vertical profiling
C. Law	PML SF6, biogases
G. Jameson.	PML SF6, buoy system
M. Liddicoat	PML SF6
R. Ling	PML biogases, pCO2, (SF6)
A.Watson	UEA TCO2, pCO2 (SF6)
M. Gall	NIWA PI expts/prim prod//phyto-HPLC* samples
M. Maldonado	McGill/Canada Algal and bacterial Fe uptake
R. Strepek	UBC/Canada Fe/PAR interactions
S. Turner	UEA DMS
M. Harvey	NIWA DMS
K. Tanneberger	UEA TCO2
D. Bakker	UEA pCO2
P. Croot	NIOZ/Holland Fe speciation (CSV)
A. Bowie	PML/UK Realtime mapping of DFe (FI-CL)
R. Frew	Otago/NZ D and PFe - vertical profiles / mapping
J. Hall	NIWA microbial processes/event logging
K. Safi	NIWA microzoo grazing
J. Zeldis	NIWA meso- and macro-zoo grazing
A. Waite	UWA/Australia drifting traps/POC/PON
T. Trull	Tasmania DOC/particle pumping/drifting traps
M. Charette	WHOI Thorium/particle pumping/drifting traps

Many thanks to the bridge, deck, galley and engine room (also all those back in Greta Point and overseas) who helped make this such a successful venture.

Voyage Narrative

31 January 1999
After several days of fraught preparations and many questions - put the iron in the hold or not?, would the stirrer units hold out?… we set sail at 1830 h with all gear somehow miraculously lashed down. We said farewell to Wellington and met pounding seas and 60 knots SW winds long before any of us wanted to. Little sleep was had that night, but it was a relief to be at sea.

1 February
We awoke off Kaikoura having made 70 n miles overnight, having made sluggish progress. We had not anticipated losing weather contingency time so early in the trip. As the seas abated d safety drills were run and we fought our way into and out off the survival suits. By evening the vessel was passing Banks Peninsula in fine weather, and the party was thinking about catching up on sleep.'

2 February
A fine morning off Omaru with dolphins. We had a short instrument test station. Matt's pump ran fine but there not enough power for Tom's pump. The ship's DAS went down temporarily, but email is now working.

3 February
We sailed S of the Snares, our last land for 3 weeks or so, and onwards south out of the roaring forties and on towards the furious fifties. The glass is high and seas presently calm. The crew roped the scaffolding in, and we started to 'firm up' the water budgets for the CTD casts. At the first 'gang of six' meeting we decided to perform a re-run of the Astrolab section from 59S to 61 S (XBT's and 1000 m CTD's) in order to identify the positions of the major oceanographic features. This would be followed by a E to W section to 142W (ie crossing the SR3 line).

4 February
Creeping into the fifties and we awake to beam seas and 40 knot winds. Winds and seas abated in the afternoon but we seem to be in a 'low' factory. Tom's pump finally up and running on UPS! The gang of six met again to revise plans for the pre-release survey; we now plan to drop buoys and traps after an initial 24 h larger scale feature survey and see what they do. We may also use the Shuttle to map the fine scale. The meetings are charged with healthy differences in opinion which should shake things down effectively. A daunting task but the data sets from Tom and Steve Rintoul offer exceptional help.

5 February
Weather fine and we are making 13 knots to the SW. The inevitable low lies somewhere to the west. Peter Croot still unwell, but we are keeping an eye on him. Another physics meeting saw the gang of six move closer to finalising our pre-release survey.

6 February
Now S of 57S, and W of 150E. The glass is down and the swell is up, but the vessel is riding these big beam seas well and we are making 10 knots. Nutrients at 57 40S and 147 E are 30, 16 and ca. 2 uM for nitrate, silicate and phosphate. No sign of any

icebergs.

7 February
Big seas and 45 knots of wind, but they are gradually moderating. We are working our way down the XBT line (Astrolab section) with NW following seas. A problem with 'loose chips' in the XBT programme! But Rob and Ed sorted it out. Silicate levels increased from 6 to 13 uM as we approached the 'No-name front'. Low chlorophyll levels and low values of photosynthetic competence were recorded. Silicate levels increased to > 30 uM as we went further south - and thus close to the 'no-name front'.

8 February
A S Ocean millpond - seas calm as we commence running west towards 142E (ie W of SR3 line). Other issues we must resolve for site selection are homogeneity and 'light' water. We are seeing a strong pycnocline which is pleasing, but have to resolve the 'shear versus silicate' dilemma. If we go to a high silicate region (ie > 12 uM which is the Ks for species just N of the Polar Front in this region) this will be closer to the No-name front where shear will be higher. Can we risk doing this, or is it preferable to find a lower shear/silicate region and hope that the diatoms are not silicate limited? We decide to steam N along 142 W and look for a lower shear region (using ADCP) but with silicate levels of greater than 10 uM.

9 February
At 2 am we drop the buoy and 1 free-drifting trap. Is this the place? Wind is up, and we commenced loading the iron - 25 bags per tank and a chain gang of people. The acid was safely dispensed. Biggest worry is the dust from the iron bags getting into peoples eyes. The time zero station was aborted as the CTD required retermination. Instead, we commenced the release at 7 PM. The buoy - drogued at 30 m - was drifting at 0.8 knots, and the trap was moving W to E at about half of this speed. Turned the non-toxic seawater supply off until the end of the release period. There were a few problems with the connections between the rope to the depressor and the hosing, but duct tape can to the rescue once again.

10 February (t=1)
The release went well and Ed was pleased with his hexagonal pattern - the last iron being added as we rounded the final leg of the hexagon. Its too late to stop now. Mapping after the release revealed that the buoy was ca. 7 nm SE of the patch i.e. in the direction of the prevailing winds. Were is the drogue? Cliff pleased with the SF6 levels - as high as he has seen in any experiment. The patch has a length scale of ca. 6 n miles, with DFe levels ranging from 0.3 - 5 nM. We commence our first 'in' patch station. Later we recovered buoy #1 without any drogue, and deployed buoy #2. But we soon lost the buoy radio signal (from #2) and the patch for some time! Cliff eventually picked up the patch, by which time the wind was gusting 60 knots.

11 February (t=2)
We are in 8-10 m seas with the wind still blowing 45 knots, and the patch some 9 n miles away. We attempt to download ADCP data in an attempt to predict the patch movement, then 'get out of jail' and find the patch - after the seas moderate - to the NE of its original position. Weather now improving rapidly and seas going down. The forecast looks promising. The mixed layer depth has deepened to 70 m - a bit of

a concern. Mapping overnight then trap recovery.

12 February (t=3)
The trap was successfully recovered and we also bumped into buoy #2 which was on the edge of the patch. Today we will have the first back to back 'in' and 'out' stations. The stations took longer (by 2 h) than budgeted - the main problem is that of repositioning the vessel within the patch - particularly after the longer casts.

13 February (t=4)
Calms seas but mapping revealed that some patchiness in the SF6 labelled waters. A hint of a nudge of a wink that Fv/Fm may be increasing within the patch relative to outside of the patch. As Fe levels had declined to ca 0.3 nM we reinfused - with Fe only. Mapping revealed that the patch seems to be stretching along the W-E axis. Winds up to 30-40 knots in the early evening.

14 February (t=5)
A day of bright lights -the sun came out - maybe a SEAWIFS image today ? No cards but Fv/Fm was ca. 0.45 within the patch and 0.25 without it. DFe levels are again getting low so a reinfusion again perhaps tomorrow. Day 5 of the experiment - did any of us really think that we would get this far into the experiment?

15 February (t=6)
We carried out our second reinfusion at the 'building site' of tanks. John Zeldis is a natural. It took place under calm conditions and went well. Everyone is well into the swing of the 'in' and 'out' stations, so much so that these infusion days come as a welcome catch up day to conclude incubations etc. The infusion was followed by a short 'out' station and then Tom, Anya and Matt deployed 2 traps in the patch.

16 February (t=7)
We towed the shuttle overnight, still no sign of it undulating, so it was flown level (around 25 m). DFe levels are back up to ca. 1 nM and both traps are in the patch - great news. There is also evidence of the patch taking off - those reliable 'at sea' indicators such as longer filtering times, and even some colour on the filters. Another day of 'in' and 'out' stations interspersed with waste disposal 'station' well away from the patch. CTD problem - noisy traces - was resolved today by Ken. There was corrosion on one of the pins in the pump. We had a short meeting to discuss what measurements are still required in order to make a conclusive and successful experiment.

17 February (t=8)
The weather gods continue to smile on us. Iron levels around 0.3 nM so another reinfusion day today - using the BHP iron. The tanks resemble large cappuccino's as they foam and froth. Cliff did an extensive mapping/survey overnight in order to close off the patch boundaries. We observed a sharp cut-off to the east (ie. downstream of the patch). In contrast there was a tail/smeared signal to the west - the region through which the patch had previously passed. We carried out a short 'in' station towards the end of the day, then flew the shuttle and mapped the patch overnight.

18 February (t=9)
After Cliff's mapping we proceeded to do an out station. We are starting to discern differences between transmissivity levels within and without the patch - but have not

really talked about it as we are pre-occupied with sampling and stations. Also, ironically, one problem with the calm weather is the development of transient thermal structure (upper 15 m) which is preventing the added Fe from mixing throughout the water column, and potentially confounding interpretation of the experimental result. Marks chlorophyll's are showing that the initial increase in biomass was by the 0.2-2 micron fraction. Stu and Dorothee are seeing decreases in silicate and pCO_2 in the patch. We then did an in station and recovered the 2 traps - both of which had drifted out of the W side of the patch on day 3 of their collecting period. One trap got snagged on a s/b acoustic pod for a short time. But both were recovered successfully. An additional trap was deployed in the patch.

19 February (t=10)

Roger and Peter were picking up krill and zooplankton targets on the sounder overnight. Today the winds increased - at last - and eroded the shallow structure (mixing it down to ca. 50 m). Iron levels remain ca. 1 nM so no infusion today. Instead we performed another set of in/out stations. The trap had rapidly moved out of the patch and to the south - looks ominous. It was recovered just before midnight - trap and buoy had parted company. No shuttle tow tonight due to weather.

20 February (t=11)

The seas moderated overnight and we carried out a further in/out set of stations; DFe levels - puzzingly - remained around yesterdays level of 1 nM so there was no need to perform a reinfusion. Have we 'saturated' the upper ocean with Fe? Two traps were deployed in the patch and a Minke whale showed up to help fill the trap cups. There is now a three layer system, with transient structure at 20 and 45 m, and the 'mixed' layer at ca. 70 m. After the in station, we performed a short out station and deployed the 'out' trap 10 n miles NE of the patch. The main engine was then turned off for some maintenance - well away from the patch. The shuttle was flown at ca. 30 m depth over night during the mapping of the patch.

21 February (t=12)

Yet again we have calm conditions, and the three layered system remains. Both 'in' traps are within the patch which seems to be stretching to the NW/SE. Again no Fe reinfusion as levels of 0.6 nM were observed. Also the 3 layer system would cause problems in getting the Fe to depth. The main growth of biomass - based on transmissivity - appears to be at depth! We carried out a highly resolved vertical profile today for nutrients and biogenic gases in the patch. A planned deep Kevlar cast for trace metal samples was cancelled due to lack of time. The last day of the experiment is tomorrow.

22 February (t=13), T

The last day and a very tight schedule as we try to grab the last set of samples. Several people have expressed strong interest in staying for another week…but alas. After our final in station, we carried out a highly resolved CTD section - in lieu of a fully functional shuttle - with casts to 200m every 1.5 n miles outside the patch and 0.75 n miles within the patch. The first survey leg (SW to NE) cut through the thin tail of the patch (ca. 3 n miles across). We broke off from the survey to recover the 2 in patch traps - the visibility was getting poor in the early evening - which were both successfully recovered (apart from a mishap with some of the control tubes and the block). The second survey was through the main part of the patch (some 10-12 n miles) and the transmissivity section showed an increase in biomass from the 0- 60 m

over this area. Plots such as these make the penny drop - we start to realise just what we have achieved during SOIREE. We finished the experiment with the 'bad karma' cast - the deep go-flo cast which was done under marginal conditions and resulted in 1 lost go-flo, and an out of action HIAB and A frame. A sign to quit while we are ahead perhaps.

23 February
On our way home around 0700 h this morning. We will run the underway systems out of the patch and tow the shuttle. Some of the underway instruments will be run back to Wellington in order to collect data for the Ocean-Atmosphere programme. A day to conclude incubations from 22 February or catch up on sleep.

24 February
The weather came up again as we entered the furious fifties and blew over 60 knots. Difficult to filter or play cards with the ship rolling around. Despite this we made 11 knots to the NE. If we make good time on the way back Tangaroa tours may take us home by the west coast via Milford Sound.

25 February
The last samples from the deckboard experiments are taken off - before the water temperatures begin to rise. Today we wrote up a joint press release and a short information page to be sent out to colleagues and friends.

26 February
We are making good progress NE and doing 13 knots at times. Todays science meeting ran for over 2 hours - despite a hot stuffy room and rolling seas - there is a tangible air of excitement as we discuss data, and trends, and ponder some of the more puzzling aspects of SOIREE

27 February
The landfall. We are treated to clear skies and the peaks of Fiordland. In the evening we run up into Milford Sound and have Mitre peak Towering 1700 m above us. Cameras galore and a relaxed mood on the foredeck where many group pictures were taken. We then had our SOIREE and I had to re-check my scientific participants list - we appear to have more women scientists on board that I had realised.

28 February
A quiet day on board the vessel after last nights festivities. Everyone seems to be wearing their own clothes once again. In contrast to yesterday's glorious landfall it is grey and overcast - no alpine vistas today. We start to pack up our equipment.

1 March
Arrive in Wellington and tie up at Miramar.

Individual Voyage Reports

Physics - CTD and underway data

Edward Abraham, Rob Murdoch, Ken Downing (NIWA)

Underway data was collected throughout the voyage from a CTD, Fluorometer and FRRF. These instruments were put in chilly-bins which were continually flushed with water from the ships sea-water system. Data was logged to the ships Data Acquisition System (DAS), which also logged information on the ship (position, speed, winch wire-out lengths, etc.); meteorological data (wind speed & direction, humidity, air temperature etc.); SF6 data and buoy positions. Data was also continually recorded from a hull mounted ADCP which gave good data on the currents within the top 200m of the water column. This data was used to estimate the movement of the patch, and will be used to correct the patch mapping for the water movement during the mapping periods. The ADCP velocities showed intertial oscillations, with a radius of ~ 2nm and a period of ~14 hr, superimposed on a steady eastward drift. In addition to velocities, the ADCP records acoustic back scatter which may give information on meso-zooplankton densities and behaviour. The underway data was at times complimented by CTD/F and FRRF data collected from the undulator towed at a fixed depth within the mixed layer.

During the transit south XBT and CTD data was collected to determine the position of the ocean fronts in the region of the planned release site. The fronts were found to be close to their mean positions and the survey confirmed the release site as a relatively quiescent region, between the southern branch of the polar front and the no-name front. Satellite altimetry also suggested that the planned site was a region of low geostrophic velocity. CTD data was collected throughout the cruise at within patch and out of patch stations. The CTD package included a beam transmissiometer, fluorometer and PAR sensor.

Gear problems:
The undulator was re-wired to communicate data in real-time using the deck unit from the aqualink CTD. The aquapack in the undulator worked well throughout the cruise however the undulator failed to undulate and so had to be towed at fixed depth.

There was initially a problem with the CTD rosette mis-firing, and the quality of the CTD data deteriorated early in the cruise. This problem was traced to a corroded underwater connector. The underwater unit was swapped with a backup system and after that the CTD worked well for the remainder of the cruise. The PAR sensor was plagued by a faulty connector and so often gave unreliable data, PAR data will be available from the FRRF.

A Turner designs fluorometer was also used to collect underway fluorescence, however it appeared to give unreliable data.

Nutrient Analysis

S.E. Pickmere
NIWA Hamilton

A Technicon AAII autoanalyser was used to measure Dissolved reactive phosphorus (DRP), Dissolved reactive silicate (DRSi), and Nitrate (Nitrate + Nitrite) both in 'underway' and discrete modes during the voyage. During underway analysis water drawn from the ship's supply was passed continuously through a perspex filtration block (3um cellulose acetate filter) and a filtered sample fed to the autoanalyser. During underway measurement periodical calibration checks were made to quantitate the analysis. Quantitative primary standards were prepared from vacuum dried Analar grade chemicals and diluted for analytical use using clean artificial seawater which was also used as the autoanalyser baseline solution. Both DRP and DRSi were determined following of the molybdate complex by organic acid to form a blue complex. Nitrate was determined following quantitative reduction to nitrite by Cadmium metal. The nitrite was then measured as an azo dye following diazotization with sulfanilamide and subsequent coupling with N-1-naphthylethylenediamine dihydrochloride

SF6 Tracer Component

Cliff Law, Malcolm Liddicoat, Greg Jameson, Roger Ling
Plymouth Marine Laboratory, Centre for Coastal and Marine Sciences, Plymouth, Devon, UK.

The inert gas, sulphur hexafluoride (SF6) was used as a label for the fertilised patch of water and a surrogate for the Fe. Near real-time mapping of the SF6 provided a framework and sampling strategy for the experiment within which the impact of the added Fe could be assessed.

a) **Preparation and release**
The SF6 solution (~0.32 mmol/l) was prepared during the outward transit leg by saturating 2 x 4000 litre tanks of seawater with pure SF6. Saturation was monitored by TCD-GC (Thermal Conductivity Detector-Gas Chromatography) and was complete by 36 hours, with approximately 200g SF6 dissolved in each tank. One tank was used for the initial infusion which, contrary to expectations, provided a sufficient signal for the entire 13-day survey period. Immediately prior to release a metereological balloon was inserted into the head of Tank A and attached to an external header tank with a surface seawater supply. During the release the met balloon was filled from the header tank, and took up the residual space within the tank, so reducing SF6 loss into the headspace. After three initial attempts during which problems with the iron release line and the depressor were sorted out, the release began at 2200 on 10/2/99. The SF6 solution was pumped out at a rate of 300 litres/hour, mixed with the FeSO4 solution and released into the surface waters of the target site at a depth of 10-15m for a period of 12 hours. The release was co-ordinated within a Lagrangian framework to account for surface water advection. A WOCE-type surface drifting buoy attached to a holey-sock drogue centred at 30m and fitted with GPS and ARGOS was used as the centre-point. The buoy position was updated

at 10 minute intervals by uhf link. The release track was based upon an expanding hexagon around the centre point with track spacings at 600m intervals at a ship speed of 2-3 knots. The release was highly successful and resulted in the production of a coherent patch on the order of 50 km2. This was despite the deviation of the drifter buoy to the south two-thirds of the way through the release, as a result of drogue loss.

b) **Lateral evolution of the SF6 patch**

Water from the ships surface supply was pumped directly into the continuous SF6 mapping system, and dissolved SF6 was stripped from solution, trapped cryogenically, separated chromatographically from oxygen, and quantified by ECD-GC (Electron-Capture Detector-Gas Chromatography). A measurement was obtained every 195 seconds and time- and position-stamped by GPS, with continuous update of a graphical representation of the patch and ships position. Although this output was not in a Lagrangian frame, this allowed visualisation of the approximate patch position and dimensions and so facilitated optimisation of the ships' track to sample both fertilised and control waters. The period of mapping was less than originally envisaged due to the stability and relatively slow transit of the patch, and varied between 9 and 12 hours a day. The speed of the ship during mapping varied between 7.5 and 12 knots, with a resulting resolution of 0.4-0.65 miles. Mapping of the patch began at 2320 (GMT) on 09/02/99, immediately after release. Initial SF6 concentrations in the patch were maximal at ~600 fmol/l (1 fmol = 1 x 10-15 mol), but declined as the tracer dispersed in the mixed layer to ~400 fmol/l (250 times background concentrations) at the end of the mapping period. Concentrations remained relatively high, despite winds of 50 knots in the initial period after release. Although it is difficult to gauge the patch dimensions accurately before Lagrangian correction, some observations can be made regarding patch evolution. In the first 36 hours the patch approximately doubled in size to occupy an area of ~100 km2, after which it remained relatively constant for 3-4 days. Some minor smearing of the tracer was observed to the W and S of the patch concurrent with an elevated FRRF signal between Days 4 and 7. From Days 8-9 the patch developed a tail along its transit axis running NW-SE. Development of this feature may have been associated with variability in mixed layer vertical structure and cessation of oscillations within the patch track. The main body of the patch remained at dimensions of ~5 x 6 miles, with the tail lengthening towards the end of the experiment. The final transect during the CTD survey showed the patch to be >13 moles long along the NE-SW axis before mapping ended at 1255 (GMT) on 22/2/99. The continuous SF6 system was in operation for 20-22 hours a day for the two week period of the experiment during which >5500 measurements were obtained. The system performed well considering the high throughput, although resolution of the background SF6 signal was hindered by a co-eluting contaminant peak of unidentified origin. We would like to thank the Captain and the officers for their assistance and cooperation during the mapping.

Further use of the drifter buoys was severely limited. The body of the first drifter buoy was damaged during recovery. No GPS information was received during the deployment of the 2nd drifter buoy, although ARGOS positions were obtained and it was recovered. The buoy had sustained considerable damage to the GPS receiver, antennae and body and was not used further. The first buoy was re-deployed following repair but GPS and ARGOS positions were only obtained for the first two hours, and the buoy was not recovered. The first re-infusion of Fe was achieved by combined use of Drifter Buoy 2 and the SF6 mapping system, with the two

subsequent releases relying on the latter and the ADCP drift. Both methods were successful and the Fe re-infusions were always within the SF6 patch.

c) **Vertical evolution of the patch**

At the end of each mapping period an 'IN' station was identified in the SF6 maximum. The ship was maintained in the maximum by re-adjustment of position between casts if slippage was identified by the SF6 continuous system. Vertical profiles were obtained on 45 Casts (28 IN station, 6 OUT station, 11 CTD survey). At each IN station SF6 samples were collected on Casts 1, 3 (Biogas) and 4, with an additional High Resolution Cast at Station T1167. SF6 was generally uniformly distributed in the mixed layer and declined sharply at the pycnocline to background levels (~1.6 fmol/l). Mixed layer concentrations decreased uniformly with time from 350-400 fmol/l at the first IN station to 60 fmol/l on the last as a result of dispersion and atmospheric loss. Some indication of structure was observed in the mixed layer on T1158 and T1162 with elevated SF6 concentrations below 30m due to stratification. Mixed layer concentration at the final IN station was ~60 fmol/l (36 x background). The rate of transfer of SF6 across the isopycnals with time during patch evolution will be used to estimate Kz, the vertical diffusion, which will then be applied to nutrients and other dissolved species to estimate vertical fluxes. Atmospheric SF6 samples were also obtained at selected stations. The discrete SF6 analysis also suffered from the unidentified interferent noted above.

Nitrous oxide and Methane

Roger Ling, Cliff Law, Greg Jameson

Dissolved N2O and CH4 were sampled on the Biogas casts at 11 IN stations and 5 OUT stations. The time frame of the survey period was probably too short for the microbial source processes to respond to increased particulate carbon supply, and no significant change in the distribution of either gas was observed at the IN or OUT stations. Dissolved surface water and atmospheric levels were sampled continuously in transit from the survey site back to Wellington at 20 minute intervals.

Measurements of the inorganic carbon system

Dorothee Bakker, Kim Tanneberger and Andy Watson

Sampling of discrete DIC and pCO_2

The content of dissolved inorganic carbon (DIC) and the partial pressure of CO_2 (pCO_2) were determined for the seventeen CTD-'gases'-casts both inside (IN) and outside (OUT) the patch throughout the experiment. Typically four or five bottles were closed in the mixed layer, two in the pycnocline and three or four between the pycnocline and 170 m depth. DIC and pCO_2 were also determined for the high resolution pycnocline cast inside the patch on 21 February. Up to four duplicate DIC-samples were taken from the online water intake at 8 m depth during the daily mapping of the patch. The online water intake was sampled for DIC at the CTD-stations of the sections on 22 February.

Analysis of DIC

Glass bottles for DIC sampling had a volume of 250 ml. The bottles were kept in a cold water bath before analysis to prevent bubble formation by warming. For analysis a 21 ml subsample was acidified with 8.5% phosphoric acid and bubbled through with nitrogen. The evading gaseous CO_2 was captured in an ethanol-amine solution with a colour-indicator. A coulometer photometrically backtitrated the solution. Three replicate analyses were carried out on each sample. A Dickson seawater DIC-standard (DOE, 1994) was analysed for each coulometric cell.

Analysis of discrete pCO_2

Discrete pCO_2 was sampled in 500 ml glass bottles. The bottles were put into a waterbath with a temperature of 8° to 16°C 20 to 60 min before the analysis. Two samples were analyzed in parallel with a system similar to that of Wanninkhof and Thoning (1993). During analysis a 40 ml headspace was created in each bottle with a calibration gas of 500 µmol mol^{-1} of CO_2. The CO_2-content of the headspace was equilibrated with the pCO_2 of the water for 20 minutes before the mixing ratio of CO_2 in the headspace was determined by a LICOR LI-6262. Duplicate samples for pCO_2 were regularly taken from the online water intake to check the accuracy and precision of the analysis.

Results from discrete measurements: drawdown of DIC in the patch

Figures 1 to 4 show some of our results. Initial analysis shows a gradual decrease of DIC in the mixed layer on the IN-stations amounting to 15 µmol kg^{-1} between 10 and 22 February (Figure 1). On the OUT-stations DIC in the mixed layer did not have an apparent trend (Figure 2).

On 22 February surface-water DIC was lower by 10 µmol kg^{-1} in the tail of the patch than in waters outside the patch during the SW to NE transect (Figure 3). During the SE to NW section DIC decreased by 17 µmol kg^{-1} on entering the patch. (Figure 4). Values in the tail were similar to those observed in the previous section.

Figure 5 shows discrete pCO2, reduced to 13 degrees celsius, for stations from 1159 onwards. “Out” stations are plotted as asterisks while “in” stations are circles. For these later stations, the separation between “in” and “out” is clearly apparent in the discrete pCO2 samples.

Use of pCO2 and TCO2 measured simultaneously on the various stations will enable us to calculate the alkalinity of the samples to determine whether there was any change in this quantity; this has yet to be done however.

Underway pCO2 analyses

Measurements were made of pCO2 equilibrated with surface seawater, and atmospheric CO2, from the second day of the voyage to the second to last day (1-28th February). The instrument, based around a licor 6262 analyser, took readings every four minutes. Typically, surface pCO2 was measured for about 80% of the four-minute intervals, the rest being air measurements made from an air line with an intake above the bridge, or gas standards. A “showerhead” type of equilibrator was used for the outward leg and the iron experiment, which has a short response time for

equilibration of CO2 partial pressure (Robertson et al., 1993). Measurements were made without drying the air or equilibrator gas, and the licor analyser's measurement of water vapour was used to correct them to X_{CO2} in dry air. Equilibrator pCO_2s were then calculated assuming 100% humidity.

The equilibrator was mounted in the "fish factory", and fed from the incoming non-toxic supply by a flow of ~10 litres per minute running through thermally insulated tubing to minimise temperature rise. The flow into the equilibrator itself was ~1 -2 litres per minute, the remainder being run to waste. A platinum resistance thermometer measured the temperature of the equilibrator, and after merging with the DAS data the measured pCO2 was corrected to the seawater temperature, assuming an increase in pCO2 of 4.23% per degree centigrade. There was an offset between the two sensors logged by the DAS for seawater temperature. After comparing the values with that given by the profiling CTD when it was at the surface, we took the mean of these two values as the best estimate of the seawater temperature.

The precision of the measurements is approximately 0.4 ppm for atmospheric X_{CO2}. For seawater pCO2, based on examination of the record over periods when the ship was drifting with the water we estimate precision to be about 0.5 ppm. Absolute accuracy is dependent on the standards, for which we currently have only values accurate to 1%, or about 3.5 ppm. These will be calibrated to higher accuracy when the instrument has returned to the UK.

Results from underway pCO2 system:

Figure 6 shows sea-surface pCO2 for the whole of the period of the experiment, plotted against time. Initially, during the release and surveys up to day 5, little rapid change was seen in the record, indicating no strong spatial gradients in the water. Subsequently, as a difference between the "in patch" and "out of patch" condition developed, rapid changes began to be observed. The upper envelope of these changes represents the "out of patch" condition while the lower envelope is the maximum "in patch". Longer periods where the record is constant represent stations, while surveys show up as rapid switches in conditions. The in-patch-to-out-of-patch difference grew throughout the remainder of the time, though not at a constant rate,; it stalled during days 18-20 on the graph (i.e. Feb 17-19, 7-9 days from release). It was continuing to increase strongly at the end of the experiment.

It is notable also, that the "out of patch" condition is not constant. There are temporal changes occurring over periods of a few days, but no trend in the "out" condition over the experiment as a whole. The atmospheric value is 360 ppm, so the "out" condition is slightly above the atmosphere and the water is a weak source of CO2 to the atmosphere, while the patch develops into a fairly strong sink. At the time that we left the patch, the drawdown in patch relative to out of patch was about 40uatm.

References

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DMS measurements

Two DMS measurement systems were operated during the voyage, one by Sue Turner, UEA and a second by Mike Harvey, NIWA. Concentration measurements were made of particulate DMSP, the DMS precursor synthesized by plankton by Sue Turner, dissolved DMS in surface waters and in depth profiles to 100 m by both Sue Turner and Mike Harvey and atmospheric DMS by Mike Harvey from a 1/2" FEP air sampling line run from the top of the crow's nest.

Dimethyl sulphide (DMS) and dimethylsulphoniopropionate (DMSP) Production
Suzanne Turner
(School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ)

A study was made of the effects of iron enrichment on the production of DMS and its precursor, DMSP, in surface seawater. DMSP synthesis by phytoplankton is variable; high cellular levels are found amongst prymnesiophytes and dinoflagellates, whereas diatoms are generally low producers.
Samples were analysed for DMS and DMSP from eleven In-station CTD casts (C3) and five Out-stations, from surface to 110m. DMSP samples were also taken from a number of casts (C4) in tandem with samples for HPLC accessory pigments and phytoplankton speciation and enumeration. Samples were also taken from the ship's pumped water supply during transects across the patch while mapping and during reinfusions in order to quantify lateral variability with time. DMS analyses were made using purge-and-trap extraction followed by gas chromatography and flame photometric detection. DMSP was collected on AP25 depth filters, which were placed in bottles or vials containing sodium hydroxide solution (>pH 13). After 8 hours the DMSP is completely hydrolysed to DMS which was analysed as above.
Preliminary data analysis suggests that DMSPp levels within the patch started to increase within the 2 days following commencement of iron deployment. Levels continued to increase, during the next 7 days or so, after which losses were observed. The series of Out-stations showed some changes with time, but this may have been due to spatial variability as well as temporal fluctuations. A small increase in surface water DMS concentration was observed fairly early in the experiment which was probably caused by the significant reduction in windspeeds which caused a shift in the balance of production and sea-to-air evasion. Significant increases in DMS were not seen until the later part of the experiment, around the time when DMSP levels were starting to decrease.
This was an extremely successful cruise and I would like to thank everybody on board for their help and support in my work, for CTD rosette driving and handling and not least, a big thank you to everyone who helped create and track the first Antarctic iron enriched experimental patch.

DMS and Atmospheric Measurements
Mike Harvey (NIWA Wellington)

A new automated preconcentration system was designed and built at NIWA in 1998 specifically for this Southern Ocean voyage. The new system proved very reliable and operated continuously through the voyage. Sample preconcentration is on Tenax

TA at -12¦C with flush off in Nitrogen carrier at 160¦C. Regular calibrations were done using dynamic dilution of permeation tube standards with a "Dynacalibrator" unit. Standards of DMSP from the UEA were converted to DMS and run through the system as a cross calibration.

1a/ **Airborne DMS**
Two 1.5 litre air samples were taken with the automated preconcentrator every hour during the voyage except during periods when water samples were being analyzed.

1b/ **Dissolved DMS**
Dissolved DMS was measured by Helium sparging 30 mL (20 mL in concentrated samples) of filtered seawater samples collected from CTD gas casts. 17 gas casts were measured at 8 depths to 100 m (11 at "in" stations, the remainder at "out" stations.

2/ **Condensation nuclei**
A continuous record of condensation nuclei (CN) was collected using TSI model 3010 CN monitor to measure the concentration of airborne particles greater than 10 nm. Diesel engines produce very large quantities of CN and this measurement was used in real time to detected episodes when the gas sampling lines were contaminated by engine exhaust and vent air from the ship. Gas grab samples were collected during unpolluted episodes. Unpolluted baseline concentrations of around 80 cm-3 were measured compared with >10000 cm-3 during polluted periods.

3/ **Surface Ozone**
A continuous record of in-situ ozone was made using a Thermo-Environmental Instruments UV-photometric ozone analyser. There was a brief period of downtime mid-voyage when service was required to the internal pump and the data-logger malfunctioned. Immediately before the voyage, this instrument was run alongside NIWA's long term measurement instrument at Baring Head and was found to have a slow response to short term fluctuations but similar long term average. These surface ozone values will be used as input to boundary-layer DMS photo-oxidation modeling.

4/ **Aerosol and sulfur dioxide**
A filter sampler was mounted on the port side guard rail just forward of the bridge. Two airlines were run back to vacuum pumps in the transformer room below the wheelhouse. 11 samples were collected, mostly during the transect into and away from the SOIREE site from Wellington. The typical collection period was 24 hours. There were occasions when bad weather prevented changing of filters. It also proved impossible to collect samples uncontaminated by exhaust soot at the SOIREE site because of the circular path followed by the ship. Future work of this type will need to have automated pump switching dependent on ship heading and wind vector. Two collection systems were operated. One collected aerosol in two size fractions (> 1 ¦m diameter on 8 um Nuclepore filters and < 1 um on 1 um Fluoropore filters); the other system had a pre-impactor to remove coarse aerosol and collected <1 ¦m on 1 ¦m Fluoropore filters and SO2 on impregnated filters (using a 1% potassium carbonate adsorbent solution)

5/ **Gas grab samples**
NIWA glass flasks

24 pressurized (24 psig) dry air samples were collected in 1.5 L glass flasks for subsequent high precision concentration and 13C/12C isotope ratio measurement of CO2 in the NIWA gas lab.. Six of the samples were collected on the southbound leg at approximately 3 degree latitude intervals. The remainder were collected on the northbound leg at approximately 2 degree latitude intervals.

University of York, Ontario BRC/Rasmussen cans
27 pressurized (30 psig) ambient air samples were collected for Alex Thompson, York University - 6 on the southward transect at 3 degree latitude intervals, 9 at the SOIREE site and 12 on the northward transect at 2 degree latitude intervals. These samples will be analyzed at York, Ontario for measurement of 13C/12C in a range of volatile organic gases in clean air.

SOIREE Cruise Report û Trace Metal Group

Andrew Bowie (University of Plymouth & PML, UK)
Peter Croot (Netherlands Institute of Sea Research NIOZ, The Netherlands)
Russell Frew (University of Otago, Dunedin, New Zealand)

During the cruise we had the following three objectives: (1) Undertake continuous sampling of the infused patch for dissolved/total iron (2) Obtain samples from vertical profiles, using Go-Flo bottles, to examine the partitioning between dissolved and particulate iron within the water column, both inside and outside the patch. (3) Undertake measurements to determine iron speciation within the water column.
Go-Flo casts were taken both inside and outside the patch during the course of the experiment. Typically, water samples were obtained from four standard depths (20, 40, 60 and 80 m) throughout the water column at each station. Deeper samples (> 80 m) were obtained at some stations to examine the concentration of iron below the mixed layer. Both filtered (0.2 um) and unfiltered samples were collected. These samples will be analysed for Fe and other trace metals (Zn, Cd, Mn, Cu) back in the clean laboratory at the University of Otago.

The speciation of iron was measured using competitive ligand exchange cathodic stripping voltammetry (CLE CSV) on samples from 40 m depth from stations both inside and outside the patch. This technique determines the total concentration of iron binding ligands present in the sample and their relative binding strengths. From the data generated an estimation of the inorganic iron concentration, Fe`, can also be made, this value can be used to approximate the amount of iron that may be available for uptake by the phytoplankton.

Underway Fe Mapping
(*Andrew R. Bowie*, UoP / PML, UK)

Objectives
(i) To map the ambient concentration and investigate surface water changes in Fe2+, dissolved (diss-Fe, <0.2mm) and total dissolvable (TD-Fe) iron during the experiment
(ii) To study the vertical distribution of Fe INside and OUTside the fertilised

patch via laboratory based analysis of sub-samples taken from daily Go-Flo casts
(iii) To perform an intercalibration exercise between FI-CL (AB) and solvent extraction GFAAS (RF) technologies from identical samples taken from Go-Flo casts
(iv) To study the surface water distribution of Fe and other trace metals along a latitudinal transect of the west coast of New Zealand

Analytical and Sampling Methodologies
Shipboard determinations were performed using a semi-automated flow injection chemiluminescence (FI-CL) analyser. The technique enabled real-time analysis of Fe2+, diss-Fe and TD-Fe fractions at the sub-nanomolar concentration level. The system is based on the oxidation of luminol, which is catalysed by Fe2+ ions, emitting blue light. A reduction step was performed to determine the Fe(II+III) fraction and in-line matrix elimination / sample preconcentration was achieved using a 8-hydroxyquinoline micro-column. Surface samples were taken from a torpedo-style fish deployed at 1-2 m and pumped directly into container designed for trace metal work. Vertical profiling samples were collected from 5L and 30L trace metal Go-Flo sampling bottles deployed on Kevlar rope.

Preliminary Results
The FI-CL system performed with only minor problems throughout the one-month cruise period. A minimum of 50 samples were analysed during each mapping period for Fe2+, diss-Fe and / or TD-Fe fractions. Ambient surface water diss-Fe levels (0.08 nM) were raised to ca. 2 nM on the first infusion, to 1 nM during infusions 2 and 3 and to 2nM on infusion 4. Rapid loss of diss-Fe INside the patch to near ambient levels was noted after the first 3 infusions; this was due to the conversion of the added iron sulphate heptahydrate to colloidal and particulate phases. However, >1 nM diss-Fe persisted INside the patch for the 5 days following the 4th infusion. Furthermore, significant concentrations of Fe2+ species existed INside the patch on days 12 and 13 of the experiment. Maximum surface water TD-Fe levels (>5 nM) were measured on day 8, following the 4th infusion.

Algal and bacterial iron acquisition

Maite Maldonado

Phytoplankton up-regulate their Fe transport system under Fe-limitation. Thus, Fe uptake rates of Fe-limited phytoplankton communities are faster than those of Fe-sufficient ones. One of my objectives was to compare Fe-limited phytoplankton Fe uptake kinetics (outside the patch) with those of Fe-sufficient phytoplankton (inside the patch). Particularly, I expect to see a progressive down regulation of the Fe uptake systems of phytoplankton inside the patch as they became less Fe-limited. For these experiments I collected seawater with 30 L Go-Flow at 20 m and measured short-term (24 hours) size-fractionated Fe uptake rates (0.2, 2 and 20 um) at 5 different Fe concentrations.
The recent discovery that 99.9% of dissolved Fe in seawater is bound to strong organic ligands has raised new questions concerning Fe nutrition of phytoplankton in the sea. Until recently, only inorganic Fe species were thought to be available to phytoplankton for uptake. Bacteria, on the other hand, rely exclusively on organic Fe. In these cruise I examined how bacteria and phytoplankton compete for organically

bound Fe when Fe is added at low concentrations. Experiments were performed as previously described except that Fe was added bound to the strong organic ligands, desferal B or E.
A series of experiments were performed in collaboration with Julie Hall and John Zeldis in order to investigate the rates of Fe regeneration by micrograzers and copepods, respectively, as they grazed upon bacteria or phytoplankton (see their reports for more info).
Two deckboard incubation experiments were performed with Robert Strzepek and Phil Boyd to examine Fe-light interactions in phytoplankton and Fe-Zn-Si requirements of phytoplankton (see Robert's and Phil's reports for details).

Algal Iron and light limitation

Robert Strzepek

My primary goals on this cruise were to examine the following questions: 1) how does iron addition affect the photoacclimatory capability of the phytoplankton assemblage and, 2) are photosynthetic iron requirements affected by growth at different irradiances? Samples were collected from surface waters (5m) and the deep chlorophyll maxima (~60m) both inside (7 occasions) and outside (2 occasions) of the iron patch. Two size fractions were studied: 2-20 μm and 20-200 μm. Samples for cytochrome *f* and P700 (proxies for the cytochrome b_6f complex and photosystem I, respectively) were collected for later analysis. Photosynthesis versus irradiance (O_2 evolution method) and photosystem II oxygen flash yield measurements were conducted on living cell concentrates. In conjunction, these later measurements can be used to calculate the rate of electron transfer ($1/\tau$) through the photosynthetic electron transport chain. More generally, measuring PSII, PSI and Cyt b_6f provide an estimate of the photosynthetic iron requirement of the phytoplankton assemblage. The following samples were also taken to normalize the data: total and size- fractionated Chl *a* (2-20 and 20-200 μm), CHN, and cell counts (total and size-fractionated). Seawater samples were also prepared from both inside and outside of the patch at two depths for future cell culturing attempts.

Two deckboard experiments were conducted in collaboration with Maite Maldonado and Philip Boyd. In the first, Fe-light interactions were further studied by inoculating water samples from the 'in' station on t7 with either high or low concentrations of iron and growing them at 3 different irradiances. In the second deckboard experiment, water samples (same station and depth as the Fe-light experiment) were amended with: Si, Zn, Zn and Si, Fe, or Fe and Si (see Phillip Boyd's report for additional details).

Phytoplankton Processes

Mark Gall and Philip Boyd

We were interested in Fe-mediated shifts in phytoplankton physiology, productivity and community structure during SOIREE. The following measurements were conducted during the voyage:

i) **Community photosynthetic competence**

The photochemical efficiency of PSII (F_v/F_m) has proved to be a sensitive indicator of micronutrient stress. Measurements of F_v/F_m were made underway using the FRRF (every 60 seconds, mean of 10 readings) throughout the voyage. These data were logged in the DAS. Other biophysical data (such as σ) can be calculated from these data. On 3 occasions another FRRF was concurrently 'flown' at ca. 30 m depth using the shuttle during mapping of the patch. F_v/F_m was also measured on dark-adapted (10 minutes) discrete samples (community and size fractionated samples) from 5-6 depths over the upper ocean. Vertical profiles of F_v/F_m were obtained daily using the FRRF at the in and out stations. The instrument was also used in benchtop mode to measure F_v/F_m in subsamples from the deck-board experiments.

ii) **Size-fractionated chlorophyll a and primary production**
The partitioning of algal biomass (chlorophyll a) and production (24 h simulated in situ ^{14}C uptake) within 4 size fractions (0.2-2, 2-5, 5-20, > 20 microns) was estimated daily at 6 depths over the upper water column both in and out of the patch.

iii) **P:I characteristics**
Community photosynthesis:irradiance characteristics were measured (^{14}C) daily during 4 h P:I incubations using samples from ca. 10, 40 and 70 m both within and without the patch.

iv) **Vertical biophysical parameters**
In addition to F_v/F_m other biophysical parameters were measured (such as σ) or can be derived (such as P_f) over the upper water column (0-150 m) both inside and outside the patch.

v) **Incident irradiance measurements**
Five minute averaged PAR data were obtained throughout the voyage using a Licor logger.

vi) **Vertical irradiance casts**
Profiles of water column irradiance were obtained daily inside and outside the patch using a either a Licor sensor or the sensor attached to the FRRF.

vii) **Algal Silicate uptake**
Community silicate uptake was estimated using the incorporation of ^{32}Si from samples inside and outside the patch. Uptake was also measured on a subset of samples from the Fe/Si/Zn deckboard experiment.

viii) **Fe vs PAR deckboard experiments**
2 Fe vs PAR experiments were run. The first from day 0-day 13 provides a comparison of the effects of Fe fertilisation under in situ vs in vitro conditions. Three treatments provided a range of 'mixed layer conditions' - 35m, 60 m and 90 m. In the second experiment (run in conjunction with Maite Maldonado and Robert Strzepek), a similar range of mean light conditions were used, but additional measurements were made every 2 days (14C, 55Fe…)

ix) **Fe, Si, Zn deckboard experiments**
An in vitro experiment in levels of Fe, Zn, Si, Si+Zn, Fe+Si were perturbed was run for 6 days and subsampled 3 times. This and the second FePAR incubation were run for a period after we departed the patch, and therefore also provide some information on how algal biomass levels changed after day 13.

x) **Phytoplankton samples**
Lugols samples were taken each day within the patch at 6 depths over the upper ocean. Occasional samples were also taken from vertical casts outside of the patch and from deckboard experiments. These samples will complement those epifluorescence microscope slides prepared by Julie Hall and Karl Safi.

xi) **HPLC pigment samples**
Pigment samples were taken daily at three depths within and without the patch.

x) **Algal iron stress**
Cell concentrates for flavodoxin, ferredoxin and single cell flavodoxin immunofluorescence were taken daily from the upper water column inside the patch. Occasional samples were taken outside of the patch and within the DCM.

xii) **Underway chlorophyll a**
A Chelsea and a Turner designs fluorometers recorded chlorophyll a concentrations underway throughout the voyage. These instruments were calibrated using discrete samples.

Microbial Food Webs

Julie Hall and Karl Safi (NIWA)

Changes to the structure and dynamics of the microbial food web were investigated durig SOIREE. Samples were collected at 9 stations within the patch and 5 stations outside the patch for later analysis of bacterial, picophytoplankton, nanoflagellate and ciliate biomass while measurements of bacterial production at these stations was conducted on board. The grazing of the microzooplankton population on bacteria was measured using 0.5 um fluoresecently labelled beads and the dilution method was used to measure microzooplankton grazing on three size fractions of the phytoplankton population. These measurements were conducted on 8 stations within the patch and 4 stations outside the patch. Due to the nature of this work no results were available before the end of the voyage.

Mesozooplankton

John Zeldis (NIWA)

These studies determine whether there were changes at the SOIREE site in mesozooplankton community composition, biomass, grazing rates and diet, in response to Fe infusions. During the voyage period the mesozooplankton community was dominated by copepods, so the grazing and diet studies used only copepods, whereas the biomass studies covered the entire community.

Biomass samples were taken at every in and out station, using nested 200 and 64 μm mesh nets fitted with real-time acoustic depth and time-depth-flow recording. Quasi-vertical tows were made through the mixed layer during daylight hours, except for one made at night to check for diurnal effects on mixed layer mesozooplankton composition and biomass. Important outcomes will be mesozooplankton community/biomass changes in the mixed layer through time, perhaps reflecting arrested vertical migration in response to Fe-induced microplankton prey increases, or increased abundance of reproductive stages of copepods (eggs, nauplii) in response to increased food supply.

Grazing experiments were made by incubating two size fractions of copepods (< and > 1000 μm) with ambient (20 m depth) prey concentrations in 2 L bottles and assessing clearance rate of chl-a (2-20 and >20 μm) and Lugol's-preserved microplankton after 24 h. Experiments were made every second day until 19 Feb., and

daily thereafter. The objects were to assess the capability of the mesozooplankton community to crop phytoplankton biomass and daily primary production, and to investigate whether grazing response changed inside the patch as microplankton biomass increased, relative to outside the patch.

Diet was investigated by filtering size fractions of mesozooplankton (200-500, 500-1000 and > 1000 μm) soon after capture (<0.5 h) to collect gut pigments. Samples were taken each 2 or 3 days from 16 Feb., at in and out stations. Gut pigment signatures will be assayed using HPLC, and compared with those of animals kept in filtered seawater for 24 h to void their guts. The object will be to determine if increases in microplankton after Fe infusion were reflected in mesozooplankton gut fullness, and to determine which fractions of the microplankton community were grazed by mesozooplankton.

Experiments were made in collaboration with Maite Maldonado on the incorporation and regeneration of algal-derived Fe by mesozooplankton. Phytoplankton >2 μm were incubated with ^{55} Fe concentrations which created deficient, sufficient and replete Fe complements in the cells, and then they were fed to 2 treatments of copepods (from in and out stations) for 24 h. The harvested copepods will be assayed for radiolabelled Fe uptake and carbon content, accounting for the grazing rate and gut passage time. Filtrate of the medium (0.2 μm) was taken to assay dissolved Fe^{++} regeneration by the copepods back into the water. The objectives will be to determine if copepods exhibit Fe deficiency which is alleviated by grazing on Fe replete cells, and to determine the efficiency of regeneration of dissolved Fe, the bioavailable form of Fe for bacteria and phytoplankton.

Particulates

Anya Waite, Matt Charette, Tom Trull, and Scott Nodder

Samples were taken to estimate particle concentrations and particle export throughout the SOIREE experiment. In addition, experiments on settling rates and flocculation processes were carried out.

Particle concentrations:

Particulate organic carbon (POC) and particulate silica (PSi) samples were taken at stations within and outside of the patch. Six-point profiles were collected at typically 5, 20, 40, 60, 70 and 110m depths. For POC measurements, 2 L of seawater was filtered onto 25-mm precombusted Whatman GF/F filters (0.7 ¦m) and stored frozen for analysis at NIWA. For PSi ~1 L of seawater was filtered onto 47-mm polycarbonate membrane filters (0.2 ¦m) and stored frozen in centrifuge tubes for analysis at NIWA. Dissolved organic carbon samples were taken at most of the POC/PSi stations. These samples were filtered through 25mm GFFs, and acidified with phosphoric acid for analysis at the Antarctic CRC.

Particle compositions:

A hose pump was also used to obtain large volume 4 point vertical profiles (10,30,70,100m) and ~6 in and out stations for 13C, 15N, and biomarker lipid analyses. Comparison of the particulate 13C to 13C in DIC (sampled in the high resolution cast and in early and late in and out stations) may provide an estimate of

growth rate (from the Laws et al, 1995) CO2 supply and demand model for carbon isotopic fractionation during phytoplankton growth. Comparison of the particulate 15N to nitrate 15N (samples taken by Russel Frew) will allow an estimate of the role of ammonia in phytoplankton nitrogen uptake. The biomarker analyses in combination with the size fractionated samples (described below) will provide some constraints on carbon source organisms.

Phytoplankton Sinking Rates
Phytoplankton sinking rates were measured on phytoplankton populations at all stations inside and outside the patch, at 5m ("surface" or SFC) and either 70 m or 40 m ("chlorophyll maximum" or CMX) using the SETCOL homogeneous sample method. At each station measurements were made with 1) chlorophyll and 2) cell number as a biomass index at both depths. In addition, separate measurements were made on unconcentrated whole water samples and on samples enriched in the >20 ¦m size fraction. Sinking rates of nutrient addition incubation experiment end points (See experiments of Maldonado, Strzepek and Boyd) were also made.

Flocculation measurements
Three times during the field experiment (t=0, t=5 SFC and t=11 CMX) Natural populations were placed in an artificial shear chamber (5 s-1) and the aggregation response was documented on high-resolution video over 1 h.

Particle export:
Sediment traps were deployed at days t0-t2 (1 string, 100 and 300, depth) outside the patch; days t6-t8 (2 strings, 100, and 100 and 300m) inside the patch, and days t11-t13 (3 strings, 100 and 300m on each) 2 inside and 1 outside the patch. Samples were obtained for 234Th analysis from all the 100m traps, and for POC,PSi, pigments, and particle microscopy in gel filled traps for all the depths and deployments. These samples will allow POC, PSi, and pigment export estimates to be calculated as well as providing information on the nature of the material exported from the gel studies, C/N measurements, and 13C and 15N measurements.

Particle export will also be estimated from 234-Th deficit (in comparison to secular equilibrium generation rates from its parent 238U) samples collected using an in situ battery-operated pump deployed on the CTD/Rosette frame. Large-volume (400 L) integrated samples (0-100 m) of 234-Th in two particulate fractions (>70 ¦m and 1-70 ¦m) and the dissolved form (<1 ¦m) were obtained. The deficit of 234-Th will be combinded with measurements of the POC/234-Th ratio on sinking particles (defined here as the >70-¦m fraction) to calculate the downward flux of POC. In addition, measurements of the 234-Th flux to the sediment traps will be compared to the water column-derived fluxes to evaluate the reliability of the traps. We will also compare intrinsic phytoplankton flux rates based on sinking rate measurements with Th-based flux estimates from pump analyses.

Using the hose pump, on four occasions (twice inside and outside the patch) large-volume (> 200 L) size-fractionated samples were collected for 234-Th, POC, and stable carbon isotopic analyses. Filter pore-sizes of 200 um, 70 um, 20 um, 5 um, and 1 um were chosen based on other size-fractionation experiments being conducted on-board, namely those relating to the phytoplankton community structure. This data will be used to examine what drives changes in the POC/234-Th ratio, our link between

234-Th and POC export. This pump was also used to obtain 5 discrete depth samples (5, 30, 70, 100 and 200m) to examine the vertical structure of the 234Th deficit.

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