SOLAS Air-Sea Gas Experiment (SAGE) RESEARCH VOYAGE REPORT 17 March to 15 April 2004 Mike Harvey



| NAME OF VOYAGE: | SOLAS/SAGE |
|-----------------------------|---|
| MODILICE. | Surface-Ocean Lower-Atmosphere Studies Air-Sea Gas Experiment |
| WIUDILISE: | wednesday 17 March 2004 |
| RETURN: | Thursday 15 April 2004 |
| VOYAGE DURATION: | 27 days |
| STUDY AREA: | South-East of New Zealand in the vicinity of the S.W. Bounty Trough 48°S, 173E |
| VESSEL: | R.V. Tangaroa (VTD0410) |
| PERSONNEL (NIWA staff | unless indicated): 30 Scientists |
| Voyage leader | Mike Harvey |
| Safety officers: | Bill Main (Deckboard) |
| | Andrew Marriner (Chemicals) |
| Home base science contacts: | Mark Hadfield (m.hadfield@niwa.co.nz) |
| | Matt Pinkerton $(m pinkerton@niwa co pz)$ |
| | Malissa Bowen (m bowen@niwa.co.nz) |
| | Menssa Bowen (<u>III.bowen@inwa.co.iiz</u>) |

Funding:

SAGE was primarily funded through the New Zealand Foundation for Research, Science and Technology (FRST) programs (C01X0204) "Drivers and Mitigation of Global Change" (C01X0223), and "Ocean Ecosystems: Their Contribution to NZ Marine Productivity," with specific collaborator research grants from the U.S. National Science Foundation, the N.Z. International Science and Technology (ISAT) fund (Archer and Ziolkowski), and the many collaborator institutions who provided support.

Participants (All NIWA unless indicated)

| GROUP | NAME AND AFFILIATION | MEASUREMENT |
|-------------------|---|---|
| Gas transfer co- | Murray Smith | REA, Eddy fluxes (Wind stress, |
| ordinator (6) | m.smith@niwa.co.nz | heat, DMS, H_2O) |
| | Kim Currie | pCO ₂ |
| | k.currie@niwa.co.nz | |
| Voyage leader | Mike Harvey | REA/DMS |
| | m.harvey@niwa.co.nz | CN, Aerosol |
| | Dave Katz, Uni of Rhode Island | pN_2/pO_2 surface mapping, |
| | drkatz@gso.uri.edu | Winkler titrations |
| | Burns Macaskill | pH, total alkalinity |
| | b.macaskill@niwa.co.nz | |
| | Rona Thompson | Atmospheric CO_2/O_2 |
| | r.thompson@niwa.co.nz | 1 |
| | | |
| Tracer /dissolved | Cliff Law | SF ₆ bio-gases, vertical |
| gases co- | <u>c.law@niwa.co.nz</u> | profiling sampling/CTD |
| ordinator (5) | | |
| | Edward Abraham | Upper ocean physics, CTD, |
| | e.abraham@niwa.co.nz | ADCP, DAS , SF_6 , FRRF |
| Electronics | Peter Hill | SF ₆ , CTD (electronics support) |
| | p.hill@niwa.co.nz | |
| | David Ho, LDEO, Columbia | ³ He & Ne vertical profiles in |
| | david@ldeo.columbia.edu | water |
| | | O ₂ /Ar sample collection |
| Chemical safety | Andrew Marriner | SF_6 and N_2O , general GC |
| | a.mariner@niwa.co.nz | support |
| | | |
| Surface physics | Craig Stevens | Upper ocean physics, TRAMP |
| co-ordinator (4) | <u>c.stevens@niwa.co.nz</u> | Temperature µstructure, Vector |
| | John McGregor | Radar sea state and wave- |
| | j.mcgregor@niwa.co.nz | breaking |
| | Peter Minnett, RSMAS | Radiometric skin temperature, |
| | pminnett@rsmas.miami.edu | SST, radiosonde flights |
| | Brian Ward, WHOI | Radiometers, SkinDeep |
| | <u>bward@whoi.edu</u> | (autonomous high-res |
| | | temperature and salinity) |
| | | |
| Biology/DMS co- | Julie Hall | Microbial, flow cytometry, |
| ordinator (7) | <u>J.hall@niwa.co.nz</u> | Bacteria and micro- and meso- |
| | | grazers, Size frac Chia |
| | Stephen Archer, PML, UK | DMS(P)/ecosystem |
| | <u>stda@mail.pml.ac.uk</u> | Interactions, bacterial Sulfur |
| | Granam Jones, Southorn Cross Uni Australia | DMS/DMSP/DMSO, HPLC |
| | gionas as a du au | pigments |
| | Jorma Kunarinan (sabhatiaal) | Flow automatry uzoa bastaria |
| | joina Kuparinen, (saubaucai) | (stocks/productivity) |
| | J.Kuparmen@mwa.co.nz | (Stocks/productivity) |
| | JIII Feloquin, VIIVIS | fractionated Chl a |
| | <u>sty</u> B iolemone | Hacuonated Uni-a |
| | Stu Fickmere | inuurents |
| | s.pickmere@mwa.co.nz | |

| | Karl Safi | Heterotrophic grazing, taxon, |
|--------------------|--------------------------------|------------------------------------|
| | <u>k.safi@niwa.co.nz</u> | phytoplankton samples DMSP |
| | | production/utilisation |
| | | |
| Phytoplankton | Michael Ellwood | Fe speciation, other metals |
| processes/iron (2) | m.ellwood@niwa.co.nz | algal iron stress, dissolved iron, |
| (Philip Boyd) | | sedimentation total ligands |
| | Doug Mackie | Fe: dissolved and algal + |
| | dmackie@alkali.otago.ac.nz | atmospheric iron |
| | | |
| Photochemistry | Lori Ziolkowski, Dalhousie | CO, CDOM |
| (1) (Cliff Law) | University, Canada | |
| | lori.ziolkowski@dal.ca | |
| Atmos Chem(2) | Jill Cainey, CGBAPS, Australia | SO2, UCN |
| (Mike Harvey) | j.cainey@bom.gov.au | |
| | Dawn DeVries, Univ of Colorado | Berner aerosol + assisting |
| | ddevries@carbon.cudenver.edu | sulfur gas and aerosol |
| | | |
| Export (2) | Scott Nodder | Export Sediment traps, - marine |
| | s.nodder@niwa.co.nz | particulates & Chl a, mooring |
| | | turnaround) |
| Scientific Safety | Bill Main | Mooring turnaround, iron |
| Officer | w.main@niwa.co.nz | release deck operations |
| | | · · · · |
| СТД | Matt Walkington | CTD |
| operations(1) | m.walkington@niwa.co.nz | |

Background:

A separate science plan ("SOLAS-ANZ Dual Tracer Gas Exchange Experiment") has been produced for this voyage and contains details of the rationale, voyage objective and scientific methods. A brief summary is given here:

Phytoplankton blooms, either natural or stimulated, provide effective natural laboratories in which to study the pronounced biogeochemical fluxes and gradients associated with their evolution and decline. These phytoplankton-mediated signals are mainly expressed in the ocean, but also result in enhanced fluxes of carbon dioxide (CO₂), dimethylsulfide (DMS) and other biogenic gases across the air-sea interface. The Southern Ocean is a net sink region for atmospheric CO₂, yet uncertainties remain in the strength of this sink because few measurements of the efficiency of ocean-atmosphere gas exchange have been made under turbulent windy open-ocean conditions.

During SAGE, in a similar fashion to SOIREE in 1999, we proposed to stimulate a phytoplankton bloom through addition of iron fertiliser to iron-limited Sub-Antarctic waters. The fertilisation was marked with the addition of two inert dissolved gas tracers, sulfur hexafluoride (SF₆) and Helium-3 (³He), creating a lagrangian patch/dual-tracer study with the tracer SF₆ providing a control volume, vertical and lateral diffusion rates and estimates of air-sea gas exchange in association with ³He. The enhanced gas fluxes associated with the bloom should provide optimal conditions for measuring the rate of gas exchange and the key physical processes governing the exchange. These processes include near-surface turbulence (typically generated by breaking waves), temperature microstructure, stratification, wave field, wave breaking and wind speed. In conjunction with these patch scale and surface physics measurements, the micrometeorological relaxed eddy accumulation technique (REA) was deployed to make direct atmospheric measurements of gas fluxes. A combination of gas concentration measurement and REA flux potentially

allows the efficiency of gas exchange to be calculated at the local scale. These local scale measurements can be compared with exchange rates derived from the dual tracer technique for the larger labelled patch.

Experimental goals

Determine drivers and controls of ocean-atmosphere gas exchange quantifying:

- biological production and utilisation of climatic relevant gases in particular CO₂ and DMS) in the surface ocean
- physical control of exchange across the interfaces of the surface mixed layer
- production of aerosols resulting from interaction of biological and physical processes

Objectives:

This experiment combined seven main research objectives considering:

- 1. quantification of gas transfer fluxes and velocities for a variety of gases
- 2. physical processes affecting gas transfer
- 3. ecosystem interactions controlling dissolved DMS concentration and CO₂ removal
- 4. the impact of iron availability upon phytoplankton productivity and its influence upon dissolved gas concentration
- 5. the impact of photochemistry in the surface ocean on dissolved gas concentration and air-sea exchange
- 6. the fate of DMS in the atmosphere and aerosol condensation nuclei production from chemical transformation in the atmospheric boundary-layer.
- 7. Role of aggregation in the timing and magnitude of export processes

Additional objectives were the:

- 1. servicing of NIWA biophysical moorings: 41°11.28'S 178°28.62'E Northern Biophysical Mooring (NBM) and approximately 46°38.202'S 178°33.486'E Southern Biophysical Mooring (SBM)
- 2. final release of 2 Carioca Buoys at SBM

BACKGROUND TO SCIENTIFIC METHODS

See Science Plan

Voyage Timetable

| DATE | Day No | Summory | Commonte |
|-------------------------|-----------|---|--|
| DATE Mon 15 March 04 | 110 | Summary | Craw Changeover dev |
| | - | Science meeting Grets Pt am Commence | Shin maintenance Day |
| | | loading from noon with loading main deck | Ship manitenance Day, |
| Tue 16-March-04 | | thru hatch | Load gear down hatch (pm) |
| Wed 17-March-04 | | Loading day 1 | |
| Thu 18-March-04 | | Loading day 2 | |
| Fri 19-March-04 | | Loading day 3 | Hand load iron to container |
| | | 13:00 Transit to SAGE site - SW Bounty | |
| Sat 20-March-04 | | Trough (~35hrs) | |
| | | Pre-release Survey Day 1 | XBT and CTD transect south on 173°E |
| | | 13:00: commence pre-release survey at 45° | TCD/GC failure for dual tracer monitoring: |
| | | 45.05'S 173 E: to SW Bounty | consider options |
| Sun 21-March-04 | | | Initial general science meeting |
| | | Heading W at 48°S to Dunedin to collect back- | |
| Mon 22 March 04 | | n and a transect on way in for | |
| | - | 08:00 arrive Port Chalmers | |
| | | 15:00 depart Port Chalmers | |
| | | Run Munida transect line (pCO_2) then | Collect 2 TCD/GC's for pre-release tracer |
| | | continue pre-release survey heading south to | monitoring and confirm operation before |
| Tue 23-March-04 | | 47°S 173°E | departure |
| | | Pre-release Survey Day 2 | |
| | | 09:40 CTD followed by smaller scale CTD | |
| | | survey | |
| Wed 24 March 04 | | 20:00 1st deploy Carloca 22:00 Start Balaasa | |
| weu 24-March-04 | | 08:41: Carioca release | 19:00 Experiment Time Zero |
| | | 11.00. Pre-release CTD's | RELEASE 1 |
| | | 14:37: Select release centre, deploy drifter | |
| | | 15:05 Start Iron/SF6/3He release | |
| Thu 25-March-04 | 0 | 23:35 End Release 1 | |
| | | | Commence daily routine Map/In/Out |
| Fri 26-March-04 | 1 | | stations |
| Sat 27-March-04 | 2 | | Deploy Sediment traps 1 & 2 |
| Com 29 Manah 04 | 2 | | Activities curtailed 04:00 for about 24 |
| Sun 28-March-04 | 3 | Hove too for a period | nours due to strong winds |
| Mon 29-March-04 | и | | Extra time devoted in alternoon to patch |
| | | 18:50 pre reinfusion CTD's | Recover sediment trans 1&2 |
| Tue 30-March-04 | 5 | 23:55 Start Iron/SF6/3He release | RELEASE 2: |
| Wed 31-March-04 | 6 | 05:57 End release 2 | Patch overlain on high Fy/Fm |
| Thu 1-April-04 | 7 | | Mid-vovage science meeting |
| Fri 2-April-04 | 8 | | |
| | | 12:30 Start Fe only | RELEASE 3 |
| Sat 3-April-04 | 9 | 18:30 Finish Fe only | |
| Sun 4-April-04 | 10 | Iron depth profile | |
| Mon 5-April-04 | 11 | | |
| Tue 6-April-04 | 12 | 22:24 Start Fe and SF6 | RELEASE 4 |
| Wed 7-April-04 | 13 | | |
| Thu 8-April-04 | 14 | | |
| Fri 9- April-04 | 15 | | I ast full day in patch |
| | | 04:47 Final CTD's in patch | |
| | | 07:00 End Of SAGE | |
| | | 08:45 Intercomparison pCO ₂ near Carioca | Carioca not sighted |
| | | location | Č . |
| Sat 10-April-04 | 16 | Transit to SBM (22 hrs) | |
| | | SBM Mooring recovery prevented by strong | Good Friday: Waiting for abatement of |
| Sun 11-April-04 | | wind | winds at SBM site |

| Mon 12 April 04 | 05:00 Transit to Chatham Rise (24 hours) | Easter Monday |
|--|---|---|
| 06:00 Chatham Rise Gas station 43° 30'S 178° | | |
| | 00'E 11:00 "Cas station" CTD | |
| Tue 13-April-04 | 16:00 Transit to NBM (~6 hrs) | |
| Wed 14-April-04 | Pre-dawn CTD at NBM Evening depart for WGTN (16.5 hrs) | Day spent in search of response from NBM pm: Science wrap-up meeting |
| Thu 15-April-04 | 09:00 Arrive Aotea Wharf | Demob Day 1 |
| Fri 16-April-04 | Finish DeMobilisation | Demob Day 2 |

VOYAGE ACTIVITIES

1. Pre-voyage site selection

Prior to SAGE, a desktop survey was undertaken by Mark Hadfield and colleagues in order to identify the most promising site for this work. The site selection criteria were:

- 1. A relatively quiescent and homogeneous region allowing tracer labelled patch tracking for up to a month.
- 2. Ideally a 30 to 80 m mixed layer depth for optimal preservation of SF_6 and dilution of iron.
- 3. A range of atmospheric windspeeds to allow study of gas exchange coefficient—windspeed relationship
- 4. HNLC waters receptive to bloom development by iron fertilisation & non-limiting macro-nutrients, thus an area where gas fluxes (CO_2 and DMS) would be enhanced by the artificially stimulated bloom
- 5. Variability in currents on the patch scale is undesirable because it will distort the patch and make it hard to track. High current speeds will move the patch rapidly and may also make it hard to track.

Initial work identified 3 areas:

- 1. Southern Biophysical Mooring: 46° 40'S, 178° 30'E, later rejected as possibly too dynamic, based in part on the experiences of the FeCycle experiment;
- 2. Central Campbell Plateau, approximately 169.5° E, 50.5° S not affected by summer blooms but less well understood biologically;
- Southwestern Bounty Trough, at approximately 48° S, 172° E. In this region the mean flow is probably towards northwest, in inflow to Southland Current but thought to be somewhat less turbulent than SBM site. The area is known to be affected by late summer (February) blooms as is the SBM site.

Considering proximity to the Southland current and remote sensing data (SST, SSH, ocean colour) immediately prior to the voyage lead to the recommendation to move slightly east to 48°S 173°E.

2. Voyage site selection survey:

commenced on 21 March with a 24 hour CTD/XBT transect line run south



Figure 1: Bathymetry map to the south-east of New Zealand in the vicinity of the SAGE experiment.

on 173°E from 46 to 48°S. Along with XBT and CTD, underway seawater sampling, nutrients and ADCP measurement of current velocity and shear was undertaken. Macro-nutrient levels in the proposed area were

adequate at around 0.8-1umol/l for silicate, 0.8umol/l DRP and 10umol/l nitrate. A finer scale survey was completed on 24 March homed in 46° 40'S 172° 30'E as the preferred release point.

3. Iron fertilisation, labelled patch tracking, advection and diffusion of patch

Work plan

This group was responsible for the iron fertilisation tracer labelling and mapping the 10 km length-scale fertilised SF_6 patch. Vertical profiling and mapping of SF_6 will be used to provide estimates of vertical and horizontal diffusivity. Accompanying the mapping, were continuous underway measurements of T,S, nutrients fluorescence, FRRF, ADCP currents. Vertical information on SF_6 was provided from discrete gas samples collected from CTD hydro casts which also included collection of samples for subsequent 3-Helium analysis by mass spectrometry at LDEO, New York.

Cliff Law, Peter Hill, David Ho, Andrew Marriner, Ed Abraham, Bill Main

<u>**Pre-release preparation – Iron: (Bill Main) –**</u> Two 7500 litre tanks were initially half–filled with seawater and acidified to ~pH 2 by the addition of 25 litres of Hydrochloric acid. A total of 54 x 25 kg bags of FeSO4.7H2O (1.35 tonnes of salt containing 274 kg Fe2+) were used per 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 iron salt was added by filling a hopper that was lifted by crane winch to the tank inlet. The tanks were then filled completely with seawater and sealed. Caking of the iron sulphate in the bags as they had been previously inadvertently exposed to moisture hampered initial preparation; bags were subsequently selected that had been less exposed reducing the mixing process to a couple of hours per tank. The new NIWA mixing/release system built for the voyage performed very well and the smooth mixing and release operations were a credit to the efforts of Bill Main, Greg Foothead and the Tangaroa crew.

Pre-release preparation – SF₆ and Helium saturation: (Cliff Law/David Ho/Andrew Marriner) –Two 4000 litre containers of seawater were injected with SF₆ and ³He en route to the study site, and released into the surface mixed layer. A headspace of ~ 5 L was continuously flushed with SF₆ and circulated through the water via a diffusion hose by pump, until the water was saturated. Monitoring SF₆ saturation was complicated during transit by lack of a working analytical detector; the NIWA Thermal Conductivity Detector Gas Chromatograph (TCD-GC) was exposed to rain during mobilization and, although initially appearing to be functional, deteriorated after departure from Wellington. An alternative strategy of determining SF₆ saturation by dilution of tank water and analysis by ECD (Electron Capture Detector) during this period was then used. However, the requirement of determining the tank concentration of both SF₆ and ³He to give confidence in the dual-tracer experiment led to a decision to berth in Port Chalmers where we collected and tested two more TCD-GCs and confirmed that SF₆ saturation in both tanks was 100%. ³He saturation of Tank 1 was undertaken just prior to the first release, with ~ 10 litres of ³He dissolved in 20 minutes of headspace recirculation. A second dual-tracer infusion was performed once we were confident that all the initial injection of Helium had been lost to the atmosphere. For the second dual tracer infusion, 5 litres of ³He were dissolved in Tank 2. TCD-GC analysis again confirmed that SF₆ and ³He saturation were successful. For the 3rd tracer re-infusion only SF₆ was added on 06/04/04; this was achieved by saturating a further 4000 litres of water whilst the ship was en route to and from the OUT station, with saturation achieved in 3 hours.

Release: (Ed Abraham/Bill Main/Cliff Law) – Details of the infusions are shown in the table below. The iron and SF₆ 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 Tangaroa. As saturated 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 prevented diffusive loss of ³He and SF₆ that would have occurred if a headspace had been allowed to develop. The 1st infusion on the 25/03/04 covered 6 x 6 km and was executed within a Lagrangian framework that incorporated an expanding hexagonal release track (track spacings of 0.7 km), and referenced a drogued drifter buoy as the nominal patch centre. The 2nd infusion of iron, SF₆ and ³He took place when the patch was distributed as a long filament running NNW-SSE, and so was adapted to a compressed "lawnmower" release track of ~12 x 3 km using the underway Fv/Fm signal as reference for patch location. The 3rd infusion, of SF₆ and iron, on 06/04/04 was released using a butterfly track with

the underway Fv/Fm signal as reference because the dissolved SF_6 signal was low at this stage. All reinfusions were successfully placed within the boundaries of the existing patch.

| | Date | Start | End | Materials | Flow rate | Ship speed |
|----------|----------|-------|-------|----------------------|--------------------------------|------------|
| | | time | time | | | |
| Infusion | 25/03/04 | 1500 | 2330 | Fe, SF_6 & | Fe 925 Lh ⁻¹ | 4.25 knots |
| 1 | | | | ³ He | $SF_6 \& {}^{3}He 475 Lh^{-1}$ | |
| Infusion | 31/03/04 | 0000 | ~0600 | Fe, SF_6 & | Fe 1370 Lh ⁻¹ | 5.5 knots |
| 2 | | | | ³ He | $SF_6 \& {}^{3}He 690 Lh^{-1}$ | |
| Infusion | 03/04/04 | 1230 | 1830 | Fe | Fe 1200 Lh ⁻¹ | 7-8 knots |
| 3 | | | | | | |
| Infusion | 06/04/04 | 2220 | | Fe & SF ₆ | Fe 1200 Lh ⁻¹ | 5-6 knots |
| 4 | | | | | SF_6 500 Lh ⁻¹ | |

Table 1: Infusion details.

Patch mapping: (Ed Abraham/Cliff Law) – Mapping of the patch began 3 hours after the end of Infusion 1. Surface water from 5 m depth was continuously analysed, with the SF₆ stripped, cryogenically trapped and detected by Electron Capture Detector (ECD). The semi-autonomous analytical system provided a SF₆ measurement every 3 minutes with near-real time realization of each data-point in a concentration dot-plot on Lat-Long coordinates (Figure 2). This output incorporated ship track, drifter buoy position and ADCP drift for location and reference and facilitated navigation around the patch. Patch mapping at night was also assisted by using underway photosynthetic efficiency (Fv/Fm) which increased within one to two days of release and remained elevated above background levels. The patch was distributed on a relatively narrow isotherm (~11.4-11.9°C), and this was also used to assist location between Days 8-10, during daytime when Fv/Fm could not be used (due to light saturation effects).

The initial tracer release site was located ~10 miles east of an eddy centre and the patch evolution was subsequently dominated by transport and dilution along an eddy streamline (Figure3). Initially the patch was relatively straightforward to follow with a clearly defined centre, but stretching of the patch accelerated on the 28-29/04 coincident with 50 knot winds. During this period the ship was hove too and mapping was suspended for 24 hours. Following the high winds the patch had evolved into a long filament >30 miles long and only 1 mile wide in places, and was situated to the west of the eddy centre. SF₆ concentrations had decreased by >70% as a result of dilution and air-sea exchange. By 1/04/04 the patch was apparent as two "nodes" separated by a narrow isthmus of SF₆. However the evolution subsequently changed around 3/04/04 with translation of the patch around the eddy slowing as it reached a point due north of the eddy centre. This coincided with a period of stability until the end of the experiment during which movement and dilution of the patch were relatively low compared to the earlier dynamic phase.

The ship was usually mapping between 2100 and 0730 each day, SF_6 and dissolved iron mapping were coordinated (Michael Ellwood) on most nights. Mapping was usually suspended for zooplankton net sampling for a period of half an hour each night at the patch centre. Following mapping a suitable position for the IN station was selected at 07:30 each morning. The mapping system was subsequently used to monitor drift of the ship whilst on the IN station, with relocation between deck board activities when required. This was most important when the patch was stretched out into a narrow filament, although ship drift and movement of the patch combined to frustrate effective IN station profiling on the 30/4. The evolution of the SF₆ patch should prove interesting in examining the role of dispersion at the sea surface, particularly as the patch experienced two different regimes of mixing, with initial rapid dilution and filamentation followed by a cessation in spreading and transport.

The SF₆ mapping system worked exceptionally well throughout the voyage, running for periods of between 9 and 24 hours a day, with the longest period of 40 hours. The system performed over 4500 analyses in 16 days of mapping, with a total downtime of <30 minutes to replace a sheared collar on a valve. Analytical reproducibility between traps did not vary by more than 2%, and the system response altered by <2.2% between the start and end of the experiment.



Figure 2: Screen shot from the first mapping of the patch. The large circles show measured SF6 concentrations, with the warmer colours indicating high concentrations. The small circles show the trajectory of the drifter buoy, and the yellow track is the integrated drift from the ADCP.



<u>SF₆ profiles: (Cliff Law/Peter Hill/David Ho)</u> – the vertical SF₆ distribution was monitored by collection and analysis of water samples from CTD hydro casts. Analysis was undertaken on a similar system to that of the SF₆ mapping, that analysed a larger volume (380 ml) and incorporated a vacuum-sparge stage for rapid extraction. SF₆ profile measurements were required for

1. dual tracer estimates of transfer velocity

- 2. estimates of vertical diffusion (Kz) across the seasonal pycnocline, and smaller transient density discontinuities that waxed and waned throughout the voyage and
- 3. as a "reference label" for all other parameters to confirm whether samples had experienced iron addition on all CTDs.

Samples were analysed from the "Gas" and "Biology" casts at the IN station in the morning, the "Biology" cast at the OUT station in the afternoon and the "Tracer" cast at night. Prior to the 2nd infusion a series of CTD transects were run across the patch on the 30/03/04 to examine variability in structure and tracer distribution in the patch. OUT stations were generally 8-10 nautical miles from the IN station; one OUT station on the 05/04/04 was on the edge of the SF6 patch and had to be discarded.

 SF_6 concentration was initially ~400 fmol L⁻¹ but declined following the 50-knot winds on the 28/04 to ~40 fmol L⁻¹. Re-infusion of SF_6 took place twice, as levels had fallen to within the 15x background concentration. Vertical penetration of the SF_6 was initially pegged at 40 m by a minor density gradient, but extended down to 75 m following the strong winds on 28-29/3/04 (see Figure; preliminary data); however there was no evidence of subduction. Following re-infusion the SF_6 was again held at ~40-50 m before mixing down to 60-65 m.



Figure 4: SF6 vertical profiles

The SF₆ discrete system analysed samples from 56 CTD Hydro casts with a total of ~750 measurements. The system performed well with minimal down time, that was only required for changing a constricted water inlet tube and repositioning the sparge tower collar following cleaning. Analysis of duplicate samples gave a reproducibility of ~0.4-0.5% at tracer levels and ~3% at background levels below the pycnocline, with an analytical sensitivity of better than 0.05 fmol L⁻¹. A background vertical hydro cast was collected and sampled for SF₆ at the Northern Mooring site to examine the potential for using SF₆ as a transient tracer of water mass chronology.

<u>SF₆ emission measurements: (Cliff Law)</u> – immediately after the initial infusion, REA samples were collected downwind of the patch and analysed for SF₆ to examine whether air-sea SF₆ emissions could be determined directly. In addition measurements of near–surface SF₆ gradients and SF₆ emission into a floating chamber were made from the Naiad on two occasions.

4. Iron chemistry

Work Plan

The iron module was responsible for mapping patch dissolved iron, iron speciation, ligands and particulate iron. A key role was keeping track of iron availability in the early stages of the experiment following

fertilisation in order to provide information for planning possible re-infusions. Iron mapping was conducted at night at the same time as SF_6 mapping with the fish deployed whilst steaming. The plan was to map every second night to monitor patch evolution. For determining whether iron reinfusion is required, a sample was collected every day from the centre of the patch, during or just after completion of the SF_6 mapping.

In addition to oceanographic measurements, aerosol sample collection was planned for the transit legs to quantify atmospheric iron input. A high-volume sampler was installed with an inlet on the bow micrometeorology tower.

Michael Ellwood, D'ugh Mackie

Methods and Activities

Dissolved iron concentrations determined during the site survey were low with concentrations at about 0.11 nmol L⁻¹ between 46°45′S and 47°03′S along 173°00′E.

After the first dual tracer and iron release (12pm 25/3/04 to 1am 26/3/04) surface dissolved iron concentrations within the patch were elevated with values ranging between 0.14 nmol L⁻¹ to 3.03 nmol L⁻¹ and an average dissolved iron concentration of $1.27 \pm 0.82 \text{ nmol } \text{L}^{-1}$. Over the following days the dissolved iron concentration declined to an average value of $0.20 \pm 0.09 \text{ nmol } \text{L}^{-1}$. On the 31^{st} of March the patch was reinfused with iron. The maximum dissolved iron concentration after 8 hours infusion was $1.59 \text{ nmol } \text{L}^{-1}$. Over the coming days the dissolved iron concentration declined to a mean level of $0.1 \text{ nmol } \text{L}^{-1}$ by the 2/4/04. A third infusion of iron occurred on the 3/4/04. This infusion only raised dissolved iron concentrations to a maximum of $0.55 \text{ nmol } \text{L}^{-1}$. Finally, a forth infusion of iron was carried out on the 7/4/04. By the 9/4/04 dissolved iron concentrations had decayed from a high of $1.01 \text{ nmol } \text{L}^{-1}$ to $0.32 \text{ nmol } \text{L}^{-1}$ just prior to leaving the patch site.

A depth profile for dissolved and particulate iron was carried out on the 4/4/04 following the third iron infusion. Dissolved iron concentrations ranged between 0.09 nmol L⁻¹ and 0.41 nmol/L while particulate iron concentrations ranged between 0.61 nmol L⁻¹ and 3.57 nmol L⁻¹. On average, between 85 % and 97 % of iron infused into the patch was associated in the particulate phase.



Figure 5: Dissolved iron concentrations (all data) plotted against time since first release ended. Arrows indicate infusions of iron.



Figure 6: Dissolved iron concentrations plotted against latitude and longitude. Arrows indicate infusion of iron.

5. Major Nutrients

Work Plan:

Major nutrients (N, P and Si) were quantified as part of the initial site selection in order to identify optimum watermass and avoid potential nutrient limitation. The time course of nutrient concentration was followed during the evolution of the patch.

Methods and Activities:

Dissolved nutrients were run throughout the voyage using an Astoria Pacific segmented flow analyser. Nitrate (nitrate + nitrite), dissolved reactive phosphorus (DRP) ammonia and silicate analyses were run both in underway mode using the ship's scientific supply and for the discrete profile samples.

During the initial prospecting for the patch, underway surface nutrients were fairly consistently around the 0.8-1umol/l for silicate, 0.8umol/l DRP and 10umol/l nitrate levels. During the course of the experiment these either remained the same or increased with deeper mixed layer development (weather), and possible entrainment from adjacent current water masses. At the end of the patch experiment silicate had increased to 1.2 umol/l, nitrate to 11umol/l and DRP to 0.9umol/l. Given these available nutrients there should not have been limitation from the N & P during the experiment.

Several nitrite profiles were measured and maximum nitrite levels of up to 1umol/l were found at the pycnocline.

Nutrient measures were also recorded for a number of biological time course experiments involving light, or trace iron and cobalt additions.

Underway measurement was continued during the biophysical moorings transect run between the Southern and Northern biophysical mooring, this time with a 9 hour break on top of the Chatham Rise for atmospheric experiments.

6. Daily routine:

Following the release of iron and tracers to create a labelled patch of water, a daily routine was established. Some of the daily activities, in particular the use of the RHIB workboat were dependent on sea-state and weather, generally limited to winds below 20-25 kts. Typically, the patch was mapped overnight for SF_6 (10-12 h required at 8-10 knots, underway seawater sampling). The remaining 12-14 h each day was spent sampling ocean and atmosphere in and out of the SF_6 labelled waters. The usual schedule involved 2 CTD casts at an "IN" patch station in the morning, one for biology (biology cast), one for dissolved gases (gas cast), repeated in afternoon "OUT" patch CTD stations. In the early part of the experiment a second "IN" station gas cast around midnight was done to provide better temporal resolution for the helium tracer. Below is a typical full-day schedule. Not all activities were done on days, all CTD's and over-side deployments were given a unique station identifier, a list of the actual CTD drops and deployments is recorded in the voyage meta-data record "SAGE_station_meta.xls". Ships grey water/sewage was only dumped outside of the patch and given the relatively high grey water production rate and smallish holding tanks, a dump was usually required every 16 to 20 hours.

| Table 2: Example | e full daily plan |
|------------------|-------------------|
|------------------|-------------------|

| Time | Activity | Hours | In/Out |
|------------|--|-------|--------|
| 19:00 | Mapping including fish sampling for (Iron) | 10-12 | |
| 21:00 | Dump ship waste | | |
| including: | | | |
| 22:00 | CTD Gas tracer cast | | In |
| 22:30 | Zooplankton nets | | In |
| | | | |
| 07.30 | CTD Gas | | In |
| 08:00 | SCAMP | 0.3 | In |
| 08:20 | Reposition | | |
| 08.30 | CTD Biology | | In |
| 09:00 | Deploy RHIB/Naiad (Autonomous profilers) | | |
| 10:45 | Deploy microspa | | |
| 11:00 | Deploy RHIB/Naiad (Gas flux chambers and atmosphere) | | |
| 11.30 | P-UV | | In |
| 12.00 | Zooplankton nets | | In |
| 13.00 | Microspa retrieve | | |
| 13:30 | Leave for Out station | 1 | |
| 14:30 | Deploy RHIB/Naiad (profilers) | | |
| 15:00 | Radiosonde launch | | |
| 16.00 | CTD Biology | | Out |
| 16:30 | Recover RHIB | | |
| 17:30 | CTD Gas | | Out |
| 18:00 | Pump tanks | | |

7. Voyage narrative

For brief and occasional periods, the cruise leader sat down and wrote notes. The best narrative however was provided to the outside world daily via email in the form of a web-log of text and images that was posted at SAGE web sites at NIWA and Wood Hole Oceanographic Institution. Each day a group or person gave their own perspective of SAGE. Brian Ward and Murray Smith collated and edited material for email transmission for publication at:

http://www.whoi.edu/science/AOPE/dept/research_highlight/SAGE/intro.html http://www.niwa.co.nz/rc/atmos/sage/log

19/3/4: 3 days of mobilising including the frustrations of drizzle and transport between Aotea Wharf and Greta Point look is like it will turn to 4 days as last minute fittings and engineering problems are fixed. The crew work quickly through the hard labour of hand-loading of the iron sacks on deck. 20/3/4: Set sail after lunch into perfect weather.

21/3/4: Fair weather on route to first waypoint for site selection. Cliff and Bill get underway with tank preparations. The complex plumbing and wiring exercise is coming together, extension cords are used to solve circuit overload and power distribution problems. However problems include failure of GC/TCD so unable to see He for tracer preparation. The question is do we do it blind or try to get another instrument? The initial survey is going well. Nutrients increase as we head south up to 10 nM NO₃ 1 nM SiO₄, 0.8 PO₄

22/3/4: 06:00 Heading west at 48S with a bit more swell. Decide to head to Dunedin to pick up another TCD instrument for tracer tank monitoring. The course is set for Port Chalmers whilst taking the opportunity to run Munida transect line in and out.

23/3/4: 08:00 docking at Port Chalmers – Met by Malcolm Reid, Bill Currie and Philip Boyd: 2 GC's. Head out again at 15:30 running Munida transect line then heading south overnight to 47°S 173°E with rain and wind and deteriorating weather. The ship encounters some big rolls leading to further GC/TCD equipment damage.

24/3/04: Blowing 30 to 40 kt SW with squalls and sleet. Decide to do a CTD at 09:30 as a shakedown as part of survey, a deep mixed layer is indicated at 70 m. Maximum resources are put to getting the 3^{rd} TCD up and running before infusion. Winds had eased by evening to around 30 kts and TCD looking good. Plans are made for a "small" 6 x 6 km patch over 8 hours tomorrow afternoon.

25/3/04: A very productive 24 hours, with pre-release CTD, the spot is picked and fertilisation done in the afternoon, completed just before midnight.

26/3/04: Yesterday there was much relief to see the successful first patch infusion. The pumping operation was smooth and faultless due to Bill's careful planning and design. A good patch has been laid down and we now have a focus for our activities as we develop the daily sampling strategies. Sampling today generally went very well. The swell had dropped and Craig and Brian were able to experience life in the RHIB. For tomorrow, wind is forecast to get up in the afternoon and may limit activities.

27/3/04: The day dawns grey as usual. A good overnight mapping session shows the patch at 4 by 15 km and stretching out. Fe levels around 0.6 nM, Fv/Fm around 0.35 so patch development looking good.

Problems on the air sampling side include not enough sample time of good winds on foredeck. Radiosonde balloon launches attempted in the afternoon with 2 launch failures in fairly breezy conditions. The first dips down from the ship and skims the water and does not get away. The second hits the a-frame and looses a battery. Wind conditions are simply too strong.

28/3/04: Overnight mapping goes well through to about 04:00 when the wind gets too strong to continue. Patch looks good still for SF₆, iron levels are dropping, we will need reinfuse soon. The day dawns grey as usual but now blowing 45 knots and hove too for a while. What can be done under these conditions to get the all important dual-tracer measurement, it must be a priority as soon a conditions allow?

29/3/2004: Day dawns grey as usual. Extra time is put to mapping and the patch was located overnight stretched out NW to SE having previously been lying NE to SE. It's fairly thin. Questions include: Do we reinfuse on the centre of this where the biology has picked up? What are Chl-a levels? Do we risk compromising the dual tracer experiment by reinfusing SF₆ on top? Distribution over a fairly narrow temperature helps with mapping and predicting the patch.

30/3//2004: Day dawns grey as usual but the weather is showing signs of improving. The barometer is rising. Overnight Ed found the patch had slewed round to a NW/SE axis. We are spinning round an eddy. Fv/Fm signal is strong. The patch is quite long and narrow, perhaps 2 by 10 n. miles. SF₆ levels are really low, indicating it would be fine to do another dual tracer over the top. Ed's thoughts are to infuse over the top of the biological patch using Fv/Fm at night. Today we do an in station then head off to recover the traps that have drifted a few miles to the south. The recovery goes very smoothly. We than head back to the patch with a plan to survey a few transects from north to south across it looking to see if there is any signs of structure in the upper ocean or tracer lurking in the depths. Everything checks out and we decide to go infusing at night with Fe, SF₆ and ³He.

31/3/2004: Infusion 2 starts at midnight and finishes around 05:30 (5.5 hours) Stayed up on watch with Bill and Jill. We stand off for a couple of hours then go back to an in station. Problems at the in station are encountered due to the materials not yet having mixed in well. I'm not sure if the day dawned grey as I went to bed once the infusion had finished but the weather had died down considerably -15 to 10kt into the morning and smoother seas. I get up around noon to clear skies and light winds. The RHIB had been out for a couple of deployments and we head off to do an out station before getting back to mapping tonight to see what our patch looks like.

1/4/2004: Quite a light wind day but still mostly dull allowing some boat deployments. We managed further testing of the REA, not seeing big differences in up/down gas and not sure why. Somehow the cat got out of the bag Barry had baked a glorious cake.

2/4/2004: Light winds again this morning but forecast of wind coming up. We should make the most of it this morning and mix some more iron up in the afternoon for a 3^{rd} infusion. However the science is

interesting and iron doesn't get mixed until the afternoon although is quick to. Winds come up around midnight into 3rd April around 35 to 40 kts. A few gear problems today on the air/dms side which will need to get fixed and the sonic misbehaves in the evening, resetting itself after a glitch. Has it been damaged by the constant pounding?

3/4/2004: A bit of a wind blow overnight but then a very nice day turns up with light winds and sunshine. There was even an evening RHIB deployment for Brian and Craig. Spent the morning fixing gear then work with Murray on tedlar bag sampling for gas fluxes.

4/4/2004: Michael runs an iron depth profile.

5/4/2004: Julie leads the biology team through teasing out why the bloom has failed to develop. It's an interesting story with experiments looking at mixed layer depth / light limitation story, Cobalt limitation, grazing pressure. A phase of experiments are planned. Murray & I plan gas flux experiments to look at gradient to near surface. Is the flux too small to measure?

6/4/2004: SF₆ is becoming critically low, We decide to run a final SF₆ and iron infusion overnight.

7/4/2004: Productivity in the patch is increasing as is chlorophyll. The weather is brighter and perhaps will be more settled for a few days looking at the chart. Today was the second day of RHIB deployment for gas gradients of DMS in tedlar bags. We see the hint of a flux measurable between RHIB and Tangaroa for concurrent bag DMS in the atmosphere is up slightly, no suggestion this is from our patch.

8/4/2004: The penultimate full day in the patch. Many people feeling very tired at this stage. However, the air is incredibly clean, particle concentrations are as low as we have seen them, DMSa is very low, and the wind is up on yesterday preventing RHIB deployment. Cliff has interesting N₂O production at depth linked coincident with nitrite, Burns hints at increased DIC at depth.

9/4/2004: Final patch day, we need more water to take away for biology experiments, chlorophyll seems to be holding up but not taking off.

10/4/2004: Last CTD early in the patch then we run with the wind out west to the SBM.

11/4/2004: Conditions look bad on arrival at SBM site. We have too all day in 40+ kt winds waiting to see if the weather improves, squalls are moving rapidly through with hail.

12/4/2004: no signs of improvement in the wind or with the forecast for a few days. Time is short. Heading north in the early morning. No sign of the weather abating at the SBM for a few days so we have to leave and head north. The pressure rising as we steam and seas slowly improve. However some big rolls causing gear damage with gear that breaks loose.

13/4/2004: Arrive early at the Chatham Rise "Gas station" and nose up to a CTD point giving 1-2 hours into the wind at 1.5 kt then down wind to repeat. Biology is active, seabirds are active, wind nice and steady, pCO2 down at 330 µatm, and DMS up. Unfortunately my GC failed in the strong winds yesterday so we decided to run some bag samples on Steve's GC for REA flux.

14/4/2004: Calm day at NBM site. The big pack-up has started. A frustrating day is spent on the hydrophone with no response. The day is spent scouting around looking for response and a RHIB goes out in excellent conditions but by afternoon tea time we have to depart for Wellington.

15/4/2004: heading in to Aotea, docking around 09:00 followed by a day of lifting and shifting.

16/4/2—4: much gear is quickly cleared from down below but it is impossible to clear everything before refuelling and the crew changeover at lunch. In the afternoon we quickly shift the remaining heavy gear from wagon wheels to MAERI.

8. Biological responses and DMS

Work plan:

The basic suite of biological measurements in the water column included: chlorophyll a , size fractionated chlorophyll (0.2-2, <20, Total), HPLC samples, bacteria –microzooplankton –(flagellates & ciliates), mesozooplankton – phytoplankton biomass. Daily primary production was estimated from simulated in-situ measurements. Along with the nutrients, accompanying column measurement of DMS(P) were made.

This group investigated the role of the ecosystem in governing the production of dissolved DMS. In addition to the suite of biological measurements, on-board experiments looked at the biological productivity as well as utilisation of DMSP and DMS.

Production DMSPp was measured using dilution grazing experiments. The role of microzooplankton and mesozooplankton grazing was investigated. Bacterial production will be measured using tritiated thymidine. Experiments were conducted to estimate bacterial turnover of DMSP/DMS.

Julie Hall, Stephen Archer, Jorma Kuparinen, Jill Peloquin, Karl Safi, Stu Pickmere, Graham Jones

Methods and Activities:

8.1 Biological responses

The biological team made a wide range of measurements on the cruise from individuals cell metabolism measurements to the grazing of the mesozooplankton on phytoplankton and protozoans. The work of the team was a combination of measuring biomass, productivity and grazing of the various components of the food web and the conducting of experiments to gain a more detailed knowledge of the response of the food web to the Fe addition and the consequent production of sulphur gases.

Plankton response to iron: The biological response to the Fe addition was not what was expected from previous experience, as there was no large increase in chlorophyll a or phytoplankton numbers although by the time we were leaving the patch the chlorophyll a levels had doubled. (Figure 7) and flow cytometry counts of cell numbers indicated that phytoplankton cell numbers in the patch had approximately doubled during the period of the experiment. Although the increase in phytoplankton biomass was smaller than we had expected there was a physiological response of the phytoplankton to the addition of Fe within 48 hours, with F_v/F_m (by Fast Repetition Rate Fluorometer FRRF) increasing from 0.25 to 0.35, within the patch. After that initial increase F_v/F_m plateaued, with little increase until after the final iron infusion, when it rose to a maximum of 0.45 on days 14 and 15.



Figure 7: The on-board "approximate" chlorophyll a ($\mu g/L$) concentration for the last 10 days of patch occupation (Peloquin). Chlorophyll steadily increased over the time of the patch occupation and roughly doubled over the experiment.

The response of the patch was also monitored with a pulse-amplitude modulated (PAM) fluorometer. Although the PAM and the FRRF can both measure the quantum efficiency of photochemistry, PAM works with a different light protocol. It does the saturation pulse method, where it allows one saturating light source to rapidly close all the light reaction centres. By working on a relatively longer time scale (seconds) compared to the FRRF, it results in a slightly higher yield value. Comprehensive studies have been done to define and constrain the difference with the conclusion that one can expect the PAM to be about 10% higher. For PAM, profiles were done on nearly every IN and OUT station at the 66%, 40% and 5 % light level. Yields quickly responded and stayed elevated throughout the patch occupation. The maximum in efficiency was seen on the last day (0.63). Out stations ranged from ca. 0.3-0.4.

The response of the phytoplankton to the Fe addition was monitored in a variety of ways. Primary productivity was measured for every, In (17) and Out (10) station. "In" primary productivity was measured by incubating water samples with radio-labelled (¹⁴C) carbon. The quantity of radio-labelled carbon organically fixed by phytoplankton is counted and related back to total fixed carbon. Incubations were done at 6 isolumes; 100, 66, 40, 15, 5 and 0.5 % of surface irradiance. The samples were incubated for 24 hours at ambient temperature. When the incubations were completed they were size fractioned for carbon production in the > 20 μ m, < 20 - > 2 μ m, and < 2 μ m size fractions. Daily integrated primary production through the euphotic zone will be calculated from the collected samples which will be analysed at NIWA, Hamilton.

Zooplankton Grazing experiments: a number of types were designed to monitor the impact of the Fe additions on the food web in the patch and the production of DMS by phytoplankton. The primary grazers on the phytoplankton population are the microzooplankton. Microzooplankton grazing was measured at 15 in patch stations and 6 out of patch stations using the dilution grazing method. In brief, microzooplankton grazing is measured over 24 hours in on deck incubations. These experiments are prepared by collecting water off the CTD (filtering at 200 µm) and then mixing this water with 0.2 µm filtered water taken from the same CTD at ratios of 100%, 70%, 40% and 10%. Grazing and growth are then assessed over the 24 hour period. Our measurements include size-fractionated chlorophyll a (200 µm, 20 µm, 2µm), total phytoplankton counts, picoplankton counts (eukaryotic and prokaryotic), autotrophic and heterotrophic flagellate counts, microzooplankton, DMSp, and nutrients. Each of these were measured at the beginning and the end of the incubations. Preliminary results from DMSp indicate that the experiments were successful and we observed increased growth and grazing occurring within the patch. The results suggest that grazing may have been an important constraint on the development of the phytoplankton population over the period of this experiment. To assess the grazing impacts on the bacterial population small beads (0.5um) were used to mimic bacterial sized particles. These experiments were conducted at stations in and outside the patch in conjunction with the dilution grazing experiments.

The grazing of the mesozooplankton population on the phytoplankton and protozoan population was measured on five occasions inside the patch throughout the experiment with biomass of the mesozooplankton being measured on 12 occasions: 6 during the daylight period and 6 at night. The grazing experiments were conducted with animals collected at night and held for 24 hours. Three size fractions of animal were assessed: >1000um, 500 to 1000um and 200 to 500 um. The grazing rates on both phytoplankton and protozoan populations were measured after 12 and 24 hours.

Bacterial response: the response of the bacterial population to the addition of Fe was followed by the measurement of bacterial numbers and productivity. Bacterial numbers were measured with the flow cytometry. Bacterial productivity was measured with the tritiated thymidine incorporation technique from all stations in and outside the patch. Water samples of 1-7 ml from 5-8 depths from the mixed layer and below the pycnocline were incubated at surface water temperature with (²H)thymidine for 1-2 hours. Incubations were stopped with additions of trichloric acid (TCA) and bacteria were collected and treated by centrifugation for measurements of radioactivity at NIWA Hamilton after the voyage. Saturation level experiments for the thymidine incorporation technique were conducted four times during the cruise, two from patch stations and two from outside the patch to check if the applied additions of thymidine saturated uptake. Also four conversion factor experiments were conducted similarly for the patch and outside the patch stations to enable conversion of thymidine incorporation rates to carbon production.

For the conversion factor experiments, predator free seawater cultures from surface waters (5-12m depths) were incubated over five days and subsampled daily for cell counts and cell sizing and for thymidine incorporation. Two of these conversion factor experiments were conducted in 20 L bottles to allow additional measurements of bacterial oxygen demand (BOD-bacteria) and particulate organic carbon (POC). The BOD and POC values are used to calculate bacterial carbon transfer efficiency, the efficiency of bacterial growth in the patch and outside the patch waters.

<u>Understanding the slow rate of response</u>: the slow response of the phytoplankton population to the addition of Fe into the patch was the subject of a number of experiments. These included the response of the phytoplankton and bacterial populations to micro and macro-nutrients. The thymidine incorporation technique and flow cytometric observations of bacterial cell numbers were applied in these experiments.

Two incubation experiments were conducted to investigate the plankton communities response to the addition of other trace elements over and above that of iron. These experiments involved collecting 'raw' seawater, adding various trace elements and incubating for a set time period. Periodically these treatments were sub-sampled and various growth parameters determined. Based on the results from the first experiment, a second experiment was designed and implemented.

Two experiments were also conducted to investigate the role of light in limiting the accumulation of biomass in the patch by conducting a series of two on-deck incubations. Samples were collected in the patch and placed in the 100, 66, 40, 15, 5, and 0.5 % light incubators. The experiment was subsampled at 2 and 4 days to determine if the system had the potential for biomass accumulation. Measurements were made of cell numbers, chlorophyll concentration, Fv/Fm, species composition, and phytoplankton absorption. A

comparison will be made of the daily light experienced by the phytoplankton in the tanks to the ambient water column conditions to determine when or if light was limiting. The results from the flow cytometer suggest that at the higher light levels, biomass was accumulating. These are initial results and further data analysis is planned.

<u>Additional sampling</u>: In addition samples were also collected on several occasions for collaborators who will analyse samples for viral numbers and bacterial species composition. One hundred and sixty eight pigment samples were collected from in and out of the patch, from all CTD profiles. These will be analysed by Dr Simon Wright (Australian Antarctic Division) to ascertain the phytoplankton assemblages in the study area.

8.2 DMS and DMSP in the water column (Steve Archer, Karl Safi.)

Aims:

Dimethyl by biological transformation sulphide (DMS) is generated processes from dimethylsulphoniopropionate (DMSP), synthesised in varying amounts by a variety of phytoplankton species. Recently, several independently developed ecosystem models of DMS(P) cycling have illustrated that in order to effectively predict the temporal and spatial dynamics of DMS concentration and hence, sea to air flux, it is vital to: 1. understand why and how DMSP production varies in relation to primary production; and 2. the role that microzooplankton play in transforming phytoplankton DMSP to the dissolved phase either as DMS or DMSP. Yet both aspects remain poorly constrained in the natural environment.

Our specific objective was to quantify DMSP production rates, the rates of turnover by microzooplankton of that DMSP and the yields of dissolved DMS and DMSP during the progression and decline (if reached) of a phytoplankton bloom. With this information, in conjunction with measurements of net change in DMS and particulate and dissolved DMSP concentrations afforded by the lagrangian experiment, we hoped to develop a budget of DMS(P) cycling and flux in relation to bloom development and iron availability in the Southern Ocean.

Methods and Activities:

DMS and DMSP concentrations: Seawater samples collected at discrete depths were filtered through GF/F filters using a syringe pump at a standard flow rate of 5 ml min⁻¹. In the process, the filtrate was injected directly into a purge chamber and purged with nitrogen, the volatiles being trapped over liquid nitrogen for quantification of DMS. Filters were transferred to sealed vials and DMSP hydrolysed to DMS in 0.5 M NaOH. Similarly, the purged filtrate was retained for hydrolysis of dissolved DMSP to DMS. DMS was quantified on a Varian 3800 gas chromatograph with PFPD detector.

DMSPp production and consumption rates: A dilution approach was used to quantify the specific production rate of DMSP by phytoplankton and the rate that DMSP was consumed by grazers. The dilution series generated a gradient of grazing pressure. Subsamples were filtered for DMSPp quantification at the beginning and end (T24) of incubations allowing an instantaneous production rate to be calculated for varying levels of dilution/grazing pressure (see Figure below).

The table below details the nature, timing and depth of samples used and the timing of experiments.

| Table 3. | DMSP/dilution | orazino | experiments |
|----------|------------------|---------|-------------|
| Table 5. | DIVISI / unution | grazing | experiments |

| Date | CTD in | Depths | CTD out | Depths | Dilution | Dilution |
|--------|--------|-------------------|---------|----------------|----------|----------|
| | | | | | in | out |
| 24-Mar | | | Х | 3,7,15,30,50,9 | | #1 |
| | | | | 0 | | |
| 25-Mar | Х | 3,7,90 | | | #2 | |
| 26-Mar | 538 | 3,7,15,30,50,90 | 544 | 3,7,15,30,50,9 | #3 | #4 |
| | | | | 0 | | |
| 27-Mar | 555 | 3,7,15,30,50,90 | | | #5 | #6 |
| 28-Mar | | | | | | |
| 29-Mar | Х | 10,15,30,50,60 | | | #7 | |
| | | (90) | | | | |
| 30-Mar | 575 | 10,15,30,50,60,90 | | | #8 | |
| 31-Mar | 588 | 4,10,22.38,60,90 | 599 | 4,10,22.38,60 | #9 | |
| 01-Apr | 607 | 5,11,22,55,90 | 615 | 55,90 | | |
| 02-Apr | 625 | 3,12,28,48,90 | 629 | 3,12,28,48,90 | #13 | |
| 03-Apr | 639 | 5,12,26,54,90 | | | #14 | |
| 04-Apr | 651 | 5,12,27,50,90 | | | #15 | |
| 05-Apr | 665 | 5,12,27,50,90 | | | #17 | |
| 06-Apr | 679 | 5,14,36,50,90 | | | #18 | |
| 07-Apr | 691 | 5,14,36,50,90 | 700 | 5,14,36,50,90 | | |
| 08-Apr | 710 | 5,12,32,50,90 | 719 | 5,12,32,50,90 | #21 | |
| 09-Apr | 724 | 5,12,28,48,90 | 730 | 5,12,28,48,90 | | #22 |
| 10-Apr | 736 | 5,12,28,48,90 | | | | |
| 11-Apr | | | | | | |
| 12-Apr | | | | | | |
| 13-Apr | | | | | | |

Preliminary results:

DMS, dissolved DMSP (DMSPd) and particulate DMSP (DMSPp) concentrations: DMS and DMSPd concentrations in the region of the experiment were relatively low with near surface concentrations in the

region of the experiment ranging from 0.51 to 0.95 nM DMS and 3.8 to 6.8 nM DMSPd. On the other hand, DMSPp concentrations were unexpectedly high, showing a range of from 30 to 54 nM in the near surface waters.

During the experiment DMS showed little variation at the surface or integrated through the mixed layer (Figure 8). The changes that did occur reflect the high wind events that occurred with presumably greater sea to air flux and possibly more significantly,



Figure 8: DMS concentration in near surface waters

increased mixing, decreasing DMS concentrations. DMSPd and DMSPp concentrations have not yet been analysed for the duration of the experiment, but initial indications are that little significant change occurred and in and out stations remained similar.

DMSPp production and consumption: Of the 16 experiments from which DMSP analyses were carried out, we have analysed 4, 3 from early stages of the experiment and 1 from mid-way through.



Figure 9: Dilution plots from day 1 (circles) and day 8 (triangles) of the lagrangian experiment.

All 4 experiments produced results, giving significant (P<0.05) values for gross production of DMSPp and the rate of consumption of DMSP by microzooplankton. Figure 9 illustrates the results of two dilution experiments. The results demonstrate the close coupling between DMSP production and consumption rates, interestingly they suggest that initial, relatively low rates of production had substantially increased by day 8 but continued to be almost matched by consumption rates. If this trend is real then it may explain the lack of an increase in DMSPp standing stocks in the patch during the experiment. It also suggests that the microbial loop is utilising a large fraction of the DMS(P), diverting it from DMS production and hence, preventing a build up in concentration in the surface waters.

Bacterial turnover of DMS/DMSPd: An inhibitor approach was used to attempt to quantify the bacterial consumption rates of DMS. Dimethyl disulfide was used as a competitive inhibitor of DMS. However, results from the 5 experiments were variable and provide little indication of the rates involved. This is in part a consequence of the low DMS concentrations experienced and the relatively small input allocated to this aspect of the work. A radioisotope approach would have been more likely to succeed but we were unable prior to the cruise, to produce DMSP of a high enough specific activity to use in tracer experiments.

9. Dissolved gases and responses to fertilisation:

Work Plan:

This module investigated the potential drawdown of CO_2 in response to fertilisation and the production of biogenic gases (O_2 , DMS and N_2O) within the fertilised patch. In order to define the inorganic carbonate system, a combination of pCO_2 , pH and alkalinity measurements were made. A significant component of the work is done whilst underway, spatially mapping surface seawater using on-line samples collected from the scientific seawater supply. The dissolved gas concentrations are an important component of the data used by the gas exchange module. For some species, depth profiles were also determined from discrete

samples collected from CTD hydro casts. Atmospheric signals (not specifically patch related) were followed through the measurement of CO_2 and O_2 .

Kim Currie, Burns Macaskill, Graham Jones, Cliff Law, Andrew Marriner, Dave Katz, Rona Thompson

Methods and Activities:

Carbonate chemistry (Kim Currie and Burns Macaskill)

The carbonate chemistry lab was set up in the temperature controlled room off the fish factory.

Underway pCO_2 and pH were measured on surface water throughout the cruise. Alkalinity and pH were measured on samples taken at depths through and beyond the fully-mixed layer on CTD casts inside and outside the patch. This allowed total inorganic carbon to be calculated, so that we had the two important parameters pCO_2 and C_T .

 pCO_2 was measured by infrared analysis of the carbon dioxide in a gas stream equilibrated with the seawater. The system worked well, with only a few hours down time for maintenance. Periodically, measurements of atmospheric CO_2 were also made to compare with the more comprehensive measurements made by the atmospheric CO_2 system operated by Rona Thompson.

pH measurements were made on surface water with an automated semi-continuous system, a result being logged every 10 minutes. Measurement employed the spectrophotometric technique, in this case using thymol blue as indicator. Water samples from CTD casts were taken over the depth range 10m-125m both inside and outside the patch and pH was measured with a manual variant of the underway system. Alkalinity was determined by potentiometric titration in a closed cell.

Initial results indicate that there was no change in the carbonate chemistry of the patch due to iron addition. Furthermore, the waters bounding the patch appeared to have temperature and carbonate characteristics that differed from those within the patch. The data will therefore need careful interpretation to tease out the various factors affecting the chemistry.

Water was taken from the scientific supply; this worked reasonably well, although there were occasionally issues with air-entrapment in the line, particularly during periods when the vessel was heading into high seas. It is important to maintain a high flow rate through the scientific seawater supply, dumping excess water. This ensures the residence time, and the warming of the sampled water is as low as possible, and also minimises the prospect of water degassing when drawn-off at various points.

Carioca Drifter Buoys (Kim Currie with Merlivat and Etcheto, LODYC, Paris):

Two Carioca buoys supplied by LODYC, Paris were deployed during the voyage. The pre-voyage plan was to deploy buoys in the patch initially to provide improved spatial coverage of pCO_2 measurement and to perform an intercalibration with the on-board underway pCO_2 system.

The first drouged buoy was released at 08:41 on 25 March (station U518: 46° 40.05'S 172° 28.00'E) in the morning before the first infusion of iron and tracer. This buoy quickly drifted away from the labelled patch. Infrequent position fixes (approximately 12 hourly) were received by email from Argos data received by LODYC. On-board assistance with positioning was provided by a direction finder (goniometer) although this never successfully identified a signature from the Carioca. Given the windy conditions, the difficulty in safely recovering the buoy and the time needed to search, a decision was made not to attempt to recover the buoy during the SAGE experiment.

At the end of SAGE, the ship headed to the projected region of the first Carioca and slowed for about 1 hour to gather further in-situ intercomparison data from the on-board pCO_2 system. Look-out from the bridge also failed to locate this buoy The second Carioca buoy was prepared for release at the Southern Biophysical Mooring site (46° 38.202'S 178° 33.486'E). Storm conditions encountered at that site prevented recovery of the biophysical mooring, and it was not possible to safely deploy the Carioca buoy at the site. However, the buoy was released close to the site as the vessel was steaming north en-route to the Chatham Rise at 08:45 on 12 April. At this stage the vessel was steaming north and relatively stable whilst running

with the wind. This second buoy was safely and successfully released over the stern roller (station U737a 46° 21.91'S 177° 39.69'E).

Dissolved oxygen and gas tension device measurements (Dave Katz)

The total pressure of dissolved air using a Gas Tension Device (GTD) and oxygen measurements using the Aanderraa Optode were determined for the ships scientific seawater supply. High values of oxygen concentrations that would be produced by a coherent fertilized bloom were not observed, but we did see surprisingly high values of gas tension associated with high wind speed events, up to nearly 1200 mbars. It is still to be determined as to whether these high values may result from bubbles being entrained by the seawater inlet of the Tangaroa. If it does turn out that these high values are the result of a sampling problem from the ship (i.e. air being brought into the seawater inlet and pumped into the high pressure line) we should be able to recover data from before and after high wind speed events to determine the amount of gas injected into the ocean and its subsequent relaxation back to equilibrium values with the atmosphere. Information on shipboard plumbing layout design will be used to help determine whether we may be sampling a bubbly fluid.

Also performed during the cruise were a number of Winkler titrations for calibrating the dissolved oxygen (DO) probe on the CTD rosette and the Optode on the underway GTD package. Samples were taken from the CTD daily for calibration at 5m and 2 separate profiles were also performed from the CTD in conjunction with oxygen isotope sampling. Oxygen isotopes will provide information on primary productivity in the patch and also argon levels will be determined for comparison with assumptions made in the calculation of dissolved nitrogen. Many of the oxygen isotope samples were taken from the underway line of the Tangaroa while inside the fertilized patch. These samples will be analyzed by Michael Bender's group in Princeton. In conjunction with Jorma Kuparinen biological oxygen demand (BOD) samples were analyzed with the Winkler Titration system. Results from these experiments produced very low levels of oxygen consumption in both the unfertilized and fertilized patches of the ocean.

Dissolved DMS (Graham Jones, Mike Harvey, John McGregor)

Dissolved DMS was measured throughout the voyage on the ships underway surface seawater system. Every 14 minutes a seawater sample was collected and transferred to a purge chamber where the DMS was purged with oxygen-free nitrogen onto a Tenax trap at low temperature. After about 10-12 minutes DMS was thermally desorbed into a Varian 3400 GC with a pulse flame photometric detector. The sampling, purging, desorption and gas chromatography was fully automated using a LabVIEW control system.

Throughout the voyage the system performed well, with about 7 calibrations being performed with permeation tube gas standards generated from a dynacalibrator. An intercalibration exercise was done with Steve Archer's system on one CTD cast. Measurements agreed to within 0.1-0.2 nM DMS. Despite the overall robustness of the system some modifications to the filtration system are envisaged for future surveys, in order to reduce contamination problems resulting from plankton breakthrough in the continuous filtered seawater stream. Some 2000 analyses of dissolved DMS have been made, and a valuable data set obtained.

In and out of patch measurements, and transects from Dunedin to the area of study and to the southern and northern biophysical moorings have been carried out. The surface DMS data will be quality audited, and comparisons between "in patch" and out of patch" made. In the unaudited data so far there appears to be regions where elevated DMS levels occurred. However, further analysis is necessary.

The following studies of the data will be carried out:

- (1) In and out of patch comparisons of dissolved DMS, with DMS in CTD profiles.
- (2) Calculations of DMS flux from the transects, and in and out of the patch.
- (3) Comparison of 20 surface samples for pigments, DMSP, and DMS in the patch.

(4) Assessment of whether there is a significant diurnal variation of dissolved DMS, and its relationship to zooplankton grazing.

(5) Comparison of DMS flux values determined by various piston velocity parameterisation techniques, with the REA and atmospheric monitoring of DMS. An overseas student from the Institute for Marine Chemistry and Biology at the Carl von Ossietzky University, Oldenburg in Germany will be assisting with these studies.

Nitrous oxide (Cliff Law and Andrew Marriner)

Water samples for dissolved nitrous oxide were collected from the surface to 125 m on 26 CTD hydro casts at IN and OUT stations, with analysis of a total of ~400 samples. Analysis was by headspace equilibrium in 100 ml syringes and duplicate samples showed good reproducibility. The surface mixed layer was generally in equilibrium with the atmosphere, with a N₂O maximum apparent in the pycnocline, and N₂O supersaturation in waters to 125 m (see Figure 10; preliminary data). The N₂O maximum in the pycnocline undoubtedly originates from release of N₂O as a by-product during microbial nitrification. Interpretation of this dataset was augmented by collection of 65 samples for N₂O isotopes, for analysis by Brian Popps' group at the University of Hawaii. Samples were also analysed from selected casts for nitrite, another intermediate of nitrification, which showed good correlation with the N₂O maximum in the pycnocline. Water samples for N₂O and N₂O isotopes were also collected to 3000m at the Northern Mooring Site, to augment the dataset collected in November 2003.



Figure 10: Example of N2O vertical profile.

Atmospheric Oxygen and Carbon Dioxide (Rona Thompson)

Atmospheric O_2 and CO_2 were measured continuously from 24 March to 14 April during the SAGE voyage. Data was recorded at 2-minute intervals with a precision of 7 per meg (per meg unit explained below) for O_2 and 0.5 ppm for CO_2 for a 10-minute average.

Air was pumped from the crow's nest and sampled below deck using a Non-Dispersive Infrared (NDIR) CO_2 analyser (LICOR 6252) and a fuel cell to measure O_2 . The fuel cell measurement is based on the redox of reaction of O_2 with a lead electrode, which produces a current that is proportional to the O_2 partial pressure in air. SAGE was the second time this system has been used at sea and proved successful with no serious equipment malfunction. The only problem encountered was the ambient pressure fluctuation, which affected the measurements of CO_2 and O_2 . The ambient pressure induced instrument drift could be eliminated over timescales of an hour by the frequent measurement of a standard gas but fluctuations over shorter timescales contributed to background noise.

During the 3 weeks of measurements, atmospheric CO_2 was found to be higher than the Southern Hemisphere background of about 373 ppmv and very variable, ranging from 373.5 ppmv to 380 ppmv. O_2 was equally variable and ranged from -260 to -330 per meg. The per meg unit represents changes in the O_2/N_2 ratio (assuming N₂ is constant) on a relative scale. In this scale 4.8 per meg is equivalent to

1 ppmv(ie. 1 µmole of O_2 per mole of dry air). The O_2 signal was anti-correlated with the CO_2 signal and the mole ratio of O_2 : CO_2 was about -1.2 ($R^2=0.7$). The O_2 : CO_2 ratio varied during the experiment but was mostly around -1.2 and the strength of correlation also varied. A weak correlation between CO_2 concentration and wind speed was detected on some days ($R^2=0.3$) and also with sea surface temperature ($R^2=0.3$). However, no change in the O_2 or CO_2 concentrations was observed from the fertilization of the patch.

Further investigation will look at the association of atmospheric O_2 and CO_2 with dissolved O_2 and CO_2 concentrations and at regional differences, comparing the Chatham Rise to the fertilized patch. The effect of the movement of air masses on O_2 and CO_2 will also be looked at using back trajectories.

10. Aquatic Photochemistry

Work plan:

This module looked at the photochemical production of carbon monoxide (CO) in surface waters with a combination of in-situ chamber and incubation techniques. Measurements of light absorption by dissolved organic matter and UV_R profiles in the water column were obtained, along with water column sampling for Coloured Dissolved Organic Matter (CDOM) and CO.

Cliff Law, Lori Ziolkowski

Methods and Activities:

<u>Carbon monoxide (Cliff Law)</u> was measured in near-surface gradients at 5 depths in the upper 1.5 m using a High Resolution Vertical Profiling unit deployed on four occasions from the Naiad (RHIB). Two of these profiles showed a CO gradient with a minima at the surface, whilst two profiles displayed increasing CO from the surface to 1.5 m. Direct CO emissions were measured on two occasions using a floating flux chamber deployed from the Naiad. Significant fluxes were observed but the reproducibility of duplicate samples was not acceptable. One water column CO profile to 35 m was obtained on the 9/04/04; water from 10 m on this cast was used in an incubation to determine CO oxidation rate.

Photochemistry during SAGE voyage (Lori Ziolkowski): a primary objective of the photochemistry group was to establish the apparent quantum yield (AQY) spectrum for CO in the SAGE region of the Southern Ocean. To date there are less than a dozen published CO AQY spectra, while there are about 20 more CO AQY spectra (Ziolkowski et al) in preparation for publication. Most of these spectra have focused on the east coast of N. America or coastal NW England. Other objectives during this voyage were to measure the CO AQY in the waters near the microlayer, which have been thought to contain higher levels of chromophoric dissolved organic matter (CDOM), - the precursor to photochemically produced CO - and to determine if Fe has an effect on the CO photoproduction rate. We then hoped we could use irradiance data (both at the surface and in the water) to calculate the photoproduction of CO in the water column.

Apparent Quantum Yield Spectra: Samples for AQY spectra were taken from the upper mixed layer (typically 10 m) and 0.2 um filtered directly off of the CTD rosette. Samples were then transferred to irradiation cells, 10cm quartz spectrophotometer cells (14 samples and one dark). The irradiation cells were inserted into a temperature-controlled block under a number of different light treatments (using long-band pass Schott filters) in the solar simulator (1.5 kW lamp, made by Heraeus, Germany). After irradiating the samples for 6 to 8 hours, the amount of CO in the cells was then extracted into a headspace and measured using a Reduction Gas Analyzer (RGA-2, Trace Analytical, Florida).

Early experiments during this cruise showed that the AQY spectrum in this region of the ocean is of the same magnitude as other oligotrophic regions (e.g.: Sargasso Sea). Although the spectrum was in the same order of magnitude, the spectrum had a different slope. Preliminary calculations show that the efficiency of CO photoproduction is higher at longer wavelengths (into the visible wavelength) in sub-Antarctic waters, than seen in previous measurements (Gulf of Maine and Sargasso Sea). The suggestion is that the AQY spectrum for CO photoproduction in the Southern Ocean is more efficient at longer wavelengths than the oligotrophic waters of the Atlantic. Post-cruise data processing will further investigate this matter.

Another finding of early experiments during this cruise, was that samples left for a number for hours after the end of an irradiation before being analyzed for CO photoproduction seemed to exhibit a steeper slope than samples analyzed immediately after the end of an irradiation. This lead us to believe that there may be a loss process involved. Possible loss processes could be microbial consumption of CO or out gassing of the CO from the irradiation cells. To investigate the possibility of microbial consumption, two irradiations were made on the same sample where both samples were treated with MgCl₂ (to kill any biology) and one set of samples were analyzed as soon as the irradiation was over, while the other sample was left to sit for a number of hours before analysis. These two experiments had the same result, the steepest slopes indicated that all samples had to be analyzed directly after the end of the irradiation.

In moderate weather near surface samples were collected off of the RHIB. The CDOM in the microlayer is thought to be higher than the CDOM in the water column, and thus be more photoreactive. The first microlayer experiment had an AQY spectrum that was higher, or more efficient, than mixed layer samples. However, in preliminary calculations, subsequent near surface samples (two more samples) did not have as high of an AQY spectrum as the first irradiation.

The final objective during this cruise was to investigate the effect of Fe concentrations on the photoreactivity of CO. Previous studies have found Fe (in micromolar concentrations) to catalyze CDOM photochemical reaction in riverine and coastal waters. To date, there haven't been any conclusive results of Fe on CO photoproduction in the open ocean. Samples taken after the Fe-injections (as high as 2 nM) in the ocean did not exhibit a difference in rate of CO photoproduction. *In-vitro* enhancement of iron at higher levels with micromolar iron concentration was also tested. This experiment is to be completed in duplicate and the first sample showed a higher AQY spectrum, thus higher efficiency due to the Fe concentration.

<u>Ancillary Photochemical Data</u>: Samples were taken off of the CTD rosette from a number of depths on a number of casts, at both in and out stations for CDOM. The CDOM was measured on board using a spectrophotometer. Quantifying open ocean absorption spectrum of CDOM is challenging even in the lab, never mind at sea, as there is not a lot of CDOM in open ocean waters!

Throughout the cruise, when the weather permitted, PUV (Profiling UltraViolet, Biospherical, California) were measured, and recorded in the station log. The PUV is a free falling light meter, measuring the downwelling irradiance at 4 wavelengths in the UV as well as PAR. These data will be examined to see if the UV was attenuated at the in-patch stations versus the out-stations. It should be noted that this instrument has not been calibrated since 1998, and thus the data collected on this cruise may need to be corrected with a new calibration. Mounted above the bridge there was another light meter, measuring the incident light on 5 wavelengths in the visible every 10 seconds throughout each day. These data will be coupled with some modelled irradiance data (STARR Model).

In further analyses, the AQY data will be coupled with the irradiance data to calculate the CO produced in the water column and to compare the response (AQY * irradiance) of CO in these latitudes in the Southern Ocean, with the Northern Hemisphere. A motivation for this is examination of the effect of the ozone depletion on the CO photoproduction.

11. Ocean-atmosphere gas exchange

Work Plan:

Patch scale measurements of air-sea gas exchange were made using the dual-tracer technique with SF_6 and 3 He. In addition to these kilometre scale measurements, the team used continuous underway point sampling of dissolved and atmospheric CO₂, and DMS to estimate air-sea exchange fluxes. For DMS, the flux into the atmosphere was investigated with direct flux measurement using the relaxed eddy accumulation technique with a sonic anemometer mounted on-top of the foredeck mast. The REA technique partitions gas samples into the concentrations associated with updraft and downdraft eddies in air arriving at the mast and in combination with the sea-water concentration, allows the gas exchange coefficient to be calculated. For CO₂, a combination of pCO₂ and atmospheric measurements will be made to allow exchange coefficient estimates of CO₂ fluxes.

Murray Smith, David Ho, Mike Harvey, Kim Currie, Rona Thompson, Cliff Law, Andrew Marriner

Methods and Activities:

³He Analysis for dual tracer estimates of gas exchange: (David Ho) - 208 ³He samples (36 with volume ca. 20 mL; the rest with volume about 40 mL) were drawn from 31 CTD hydro casts to be used in conjunction with SF₆ to calculate the gas-transfer velocity and to determine the extent of horizontal and vertical mixing. The samples are stored in copper tubes closed tightly at both ends by means of stainless steel pinch-off clamps. The ³He measurements will be performed at Lamont-Doherty Earth Observatory of Columbia University's Noble Gas Laboratory. ³He and other gases will be extracted from the copper tubes and transferred to glass ampoules containing activated charcoal using a vacuum extraction system [Ludin et al., 1998]. The extracted gases are flame-sealed and stored in glass ampoule with low helium permeability. The ⁴He concentration and the ³He/⁴He ratio are measured on a dedicated VG-5400 He isotope mass spectrometer. Prior to introduction into the mass spectrometer, He will be separated from all other gases by a series of cold traps. ⁴He will be measured using a Faraday Cup and ³He will be measured using a channeltron. Neon is measured in parallel on a quadrupole mass spectrometer [Ludin et al., 1998]. Precision is expected to be about 0.5 % in ³He for samples with very high ³He excesses (100% < ³He < 1000%), and 0.2 to 0.5 % for samples with lower ³He excesses (-1.7% < 3He < 100%). Precision of the ⁴He and Ne measurements is expected to be about 0.2 to 0.5, and 0.5 to 1 %, respectively.

Calculations and Interpretation - Excess 3 He concentrations in the mixed layer, 3 He_{exc}, will be calculated from the measured 3 He/ 4 He ratio, R_{s} , and 4 He concentration, 4 He_s, as follows:

³He_{exc}=⁴He_s($R_s - R_a$)+⁴He_{eq} · R_a (1-**a**)

where ${}^{4}\text{He}_{eq}$ is the atmospheric equilibrium concentration of ${}^{4}\text{He}$ [Weiss, 1971], R_{a} is the atmospheric ${}^{3}\text{He}$ / ${}^{4}\text{He}$ ratio [1.386 x 10-6, Clarke et al., 1976], and α is the solubility isotope effect [0.983, Benson and D. Krause, 1980].

References:

Benson, B.B., and J. D. Krause, Isotopic fractionation of helium during solution: a probe for the liquid state, *J. Solution Chem.*, **9** 895-909, 1980.

Clarke, W.B., W.B. Jenkins, and Z. Top, Determination of tritium by mass spectrometric measurement of 3He, Int. J. Appl. Radiat. Isotopes, 27 217-225, 1976.

Ludin, A., R. Weppernig, G. Bönisch, and P. Schlosser, *Mass spectrometric measurement of helium isotopes* and tritium in water samples, pp. 42, Lamont-Doherty Earth Observatory, Palisades, NY, 1998.

Weiss, R.F., Solubility of Helium and Neon in water and seawater, J. Chem. Eng. Data, 16 235-241, 1971.

Benson, B.B., and J. D. Krause, Isotopic fractionation of helium during solution: a probe for the liquid state, *J. Solution Chem.*, **9** 895-909, 1980.

Clarke, W.B., W.B. Jenkins, and Z. Top, Determination of tritium by mass spectrometric measurement of 3He, *Int. J. Appl. Radiat. Isotopes*, **27** 217-225, 1976.

Ludin, A., R. Weppernig, G. Bönisch, and P. Schlosser, *Mass spectrometric measurement of helium isotopes and tritium in water samples*, pp. 42, Lamont-Doherty Earth Observatory, Palisades, NY, 1998.

Weiss, R.F., Solubility of Helium and Neon in water and seawater, J. Chem. Eng. Data, 16 235-241, 1971.

<u>Micro(meteorological) measurements:</u> were mainly made from a 6 m high mast on the foredeck. A Gill sonic anemometer mounted on the top of the mast provided turbulent velocities and temperature. Data were routed back to the atmospheric chemistry container on the Forecastle Deck. Sonic velocities were corrected for ship motion with data supplied from the POSMV via an Ethernet link in order to provide true U,V,W wind components for input to the valve switching control software of the relaxed eddy accumulation (REA) gas flux system. The sonic wind system was operated quasi-continuously throughout the voyage and will be analysed to produce time series of wind stress and sensible heat flux, when air was not disturbed by the ship. On 3/4/04 the Gill sonic temperature developed an offset. An second (ATI) sonic was mounted on the mast towards the end of the voyage when conditions permitted, to cross-compare with the Gill turbulent temperature measurements. Dual gas intakes REA were also mounted at the masthead, immediately behind the sonic head with a pair of miniature solenoid valves (Clippard Instrument Labs Inc., Ohio) controlling two air-intakes, one for up,- one for down-draft gas samples.

Other meteorological equipment mounted on the mast included: vane and anemometer (Vector Instruments W200P and A101M), temperature, relative humidity (Vaisala 50Y). A PAR sensor was mounted separately with gimballed Eppley long and short sensors radiation wave (Peter Minnett) on a crossarm above the port railing. Data were supplied at 10 sec intervals via ethernet to the ship DAS, and recorded as 10 minute averages on the local Campbell logger. This provided a continuous record throughout the voyage. This wind data was uncorrected for ship heading in order to provide a relative wind direction at the mast which was used to control sector sampling for the Berner impactor and hi-volume aerosol pump. If this wind data is used for other purposes, due account must be made for the severe wind flow distortion which occurs when the wind direction is beyond 45° of the bow, and for the ship speed.

The Tangaroa automatic weather station (AWS) also provided wind speed and direction (corrected for ship velocity), temperature, humidity, dew point, and pressure. This was transmitted at 30 s intervals to the DAS.



Figure 11: Foredeck mast set-up

Ship Motion: data on ship motion

(pitch, roll, heading, together with 3 components of acceleration and velocity) were recorded from the Tangaroa's POS MV 320. In addition to the real-time corrections for orientation and motion made in the REA system.

<u>ADCP</u>: ocean currents were recorded throughout the voyage to a depth of 320m at 4m resolution depth bins. The data will be post-corrected for ship motion using the POSMV data. Detailed data were recorded continuously throughout the voyage on the ADCP computer A sample of the ADCP data was also recorded on the DAS.

Relaxed eddy accumulation (REA) (Murray Smith & Mike Harvey): measurements of DMS for flux determination were made from the 24 March onwards. The configuration involved a pair of ultra-clean (all PTFE/Stainless steel) trace gas sampling pumps (KNF model UN05/12VDC) supplying segregated (up and down draft) air at a nominal 300 mL min⁻¹ to the atmospheric chemistry container lab through two lengths of 60 m 1/8" O.D. FEP tubing. The pump box (Mark 3) ran continuously and reliably during the voyage and suffered none of the pump failure and overheating problems of the Mark 2 design which has smaller (KNF NMP830) pumps. The up- and down-draft sample gas was sub-sampled simultaneously at 90 mL min⁻¹ onto two Tenax traps in an automated pre-concentrator with flow meter controlled vacuum pumps. Samples were preconcentrated over 20 or 30 minutes and analysed by thermal desorption onto HP-5890 GC/FPD with 1 ppm SF₆ detector doping and (3 metre x 1/8" teflon lined stainless packed with Carbopack B 60/80/1.5%XE-60/1% H₃PO₄ (Supelco)). Care was taken to keep the masthead and long sample lines clean and dry and, especially after spells of rough weather, the lines were flushed out with de-ionised water followed by 5 to 10 minutes of purging with dry compressed air.

The DMSa GC ran with good sensitivity from start up through to early midday on 12 April when massive column contamination appears to have occurred in rough weather. At the time it was thought that with excessive rolling, some liquid (possibly including seawater) passed through the freeze-out traps and got onto the column. Recovery looked possible through bake-out but was exceedingly slow (days) so a decision was made to remove the GC column and insert a newly packed replacement which itself proved to need several days of conditioning. In the remaining 2 days, sensitivity was below that required for flux measurement. The HP system was left in air sampling mode and as an alternative several discrete tedlar bag measurements for flux determination were performed on Varian 3800 with external pump and flow meter by Steve Archer. Aside from this major problem at the end, one coolant control solenoid valve failed and was replaced and one pump diaphragm failed and was replaced with minimal downtime.

Preliminary analyses showed the DMSa concentration was of the order of 100 pptv. The paired mixing ratio fluctuated significantly between consecutive pairs but the between pair difference was much less and generally below the noise limit for integration. This suggested that the flux to the atmosphere was below detection limit or that there were problems with the REA system. Careful post-voyage analysis is required. In particular, segregation was clearly sensitive to the orientation of the ship relative to the wind, and on short-term variations of orientation which alters the air flow over the bow which then meant a restabilisation time was required for the REA partitioning algorithm . It proved difficult to orient the ship optimally for air sampling (wind straight on the bow $\pm 30^{\circ}$) whilst on CTD station without excessive drift off station. The preferred wind orientation during CTD operations was wind to aft starboard quarter and this is unsuitable for providing undisturbed airflow to the foremast.

Following the observation of negligible up- down-draft difference and the determination of seawater DMSd concentrations around 0.5 to 1 mM, various alternative strategies of flux measurement were attempted in order to diagnose the situation and/or better define the lower limit of flux that could be determined.

The alternatives included:

1/ discrete sampling into tedlar bags on the foredeck – thus bypassing the long FEP lines;

2/using the flux-profile approach with 2 inlets on the foredeck mast, one at deck rail height, one at mast-top height, either through the long FEP lines or into tedlar bags;

3/using the flux-profile approach with three inlet heights, 2 as above and one at 1 m asl sampling upwind of the ship from the Naiad RHIB, sampling into tedlar bags.

In addition to DMS determination, a small number of REA segregated tedlar bag samples were analysed by an enclosed open path IRGA for water vapour to provide latent heat fluxes; these will be compared with bulk estimates. Initial comparisons are quite favourable.

Profile Measurements: During periods when profile measurements were made, sampling from the mast was conditioned according to a window of ship heave, in order to maintain a constant height above sea level. In addition to the 2 heights on the foremast, tedlar bag samples were obtained at 1 metre above sea-level from the Naiad on April 6,7,8,14. As expected, the near surface samples exhibited consistently higher mixing ratios of DMS than the two heights on the foremast and these measurements will be valuable in defining the lower limit for flux quantification.

12. Surface Physics

Work Plan:

This group measured the state of the sea-surface interface to examine the role of waves, skin temperature and near surface ocean stability in governing gas exchange. Measurements included radiometer and radar measurements from sea-surface viewing instrumentation on the vessel and over side and from Naiad RHIB deployments of microturbulence profilers. On suitable days, the physics deployments were combined with floating flux chamber measurements for gases. The table below gives an instrumentation summary.

Table 4: Surface physics instruments.

| Instrument | Owner | IS | GIVES |
|------------|----------------|-------------------------------------|--------------------|
| Skindeep | Brian W. | autonomous T profiler with | microT |
| | | Iridium beacon – 24 hr | |
| | | deployments | |
| SCAMP | Craig S. | T microstructure from RHIB | turbulence |
| | | (workboat) profiles to 50m | |
| TRAMP | Craig S. | T/Shear profiler sim to | turbulence |
| | | SKINDEEP w/- GPS/VHF beacon | |
| SparBuoy | Murray S. | Floating mini-spar, deployed over | Velocity/wave |
| | | Tangaroa side for 2 hours. | |
| Beacons | Edward A/Craig | VHF/GPS beacons with drogues | Lagrangian |
| | S. | | |
| ADCP | Edward A. | inboard operation, integrated with | currents |
| | | DAS/SF6 etc | |
| M-AERI | Peter M. | Port railing in front of bridge | Real-time skin SST |
| radiometer | | throughout voyage. 10 min | |
| | | update to (network) PC | |
| S-band | John McGregor | stbd railing just below bridge. Op. | surface VV/HH |
| Radar | | from bridge, mainly during CTDs | |

Craig Stevens, John McGregor, Peter Minnett, Brian Ward

Methods and Activities:

Downward Profiling Temperature Microstructure (SCAMP) (Craig Stevens):

Temperature microstructure profiles were recorded using a SCAMP profiler recording temperature and conductivity every 1-5mm in the water column down to between 60 and 100 m depending on conditions.

This will enable the following:

medium-quality estimate of vertical diffusivity/energy dissipation

good quality estimate of Thorpe lengthscales (eddy scale) between about 12m and the base of the profile – and hence an estimate of the actual "mixed layer"

high resolution temperature structure

indication of perturbations in profile near water surface for validation of Gerris (CFD) modelling of flow distortion under a vessel.

Note: Because of ship motion and drift (waves >5m on occasion) the profile speed is faster and more variable than a typical application of this device. Processing for Kt and epsilon will require tight quality control. I am much more confident of overturn lengthscales.



Figure 12: example of SCAMP profile: left panel shows temperature from SCAMP and CTD, second panel shows temperature gradient microstructure, third panel shows profiler drop speed and right-hand panel shows Thorpe lengthscale. The Thorpe scale shows perhaps eddies of 30m near the surface dropping steadily with depth.

Table 5: SCAMP profiles were recorded in between most gas/biology CTD pairs at the following times.

| Date Time-NZST | Station |
|----------------|---------|
| 04mar26 10:07 | U535 |
| 04mar26 1055 | U537 |
| 04mar26 1300 | U539 |
| 04mar27 0947 | U556 |
| 04mar30 1914 | U582 |
| 04mar31 1750 | U599 |
| 04apr01 0853 | U608 |
| 04apr01 1605 | U616 |
| 04apr02 0814 | U624 |
| 04apr02 1621 | U630 |
| 04apr03 0815 | U637 |
| 04apr04 0824 | U650 |
| 04apr04 1517 | U654 |
| 04apr05 0749 | U664 |
| 04apr05 1616 | U669 |
| 04apr06 0804 | U678 |
| 04apr07 1122 | U692 |
| 04apr07 1613 | U701 |
| 04apr08 0800 | U709 |
| 04apr09 0810 | U724 |
| 04apr09 1727 | U731 |
| 04apr10 0454 | U735 |

from workboat

from workboat

Improvements: Better drag "brush"

Workboat SCAMP Deployments

The Naiad RHIB workboat was used for a number of normal scamp deployments. In addition the workboat was utilised for a number of other tasks described elsewhere including SkinDeep & Tramp profiling and high resolution gas sampling.

In addition to these and the over-the-side SCAMP profiles there were 5 shallow (30m) casts from the workboat to look at vessel-induced mixing. This took place on the evening of the 7 April during station U704.

The topic of water flow disturbance by the vessel and the implications for sampling is one we plan to follow up on.

Improvements: Conduct experiment during warming period when there is more signal to distort.

MicroSPAR (Craig Stevens/Murray Smith)

This NIWA-built Lagrangian drifter is in development. It contained:

- 1. GPS/VHF locator beacon
- 2. 2x Seamon temperature loggers (nominal 1 and 4.5m depths).
- 3. Dobie Tattletale logger recording Xbow 3xaccelerometer and pressure.

The data provide a measure of the wave heights as well as near-surface stratification. Ultimately it will also contain a Vector Velocimeter but this voyage involved development of deployment techniques and evaluation for protective guards.

Each deployment generated 2 thermistor files and a number of tattletale files (10 minute files every 15 minutes at 16 Hz).



Figure 13: Scamp profile showing temperature and temperature gradient profiles...the strong signal at around 9.5 m is very unusual and probably indicative of underflow...draught of Tangaroa ~6m. Almost all over the side profiles exhibited similar structure. Certainly the profiles from the workboat did not have such structure.

| Table 6: 3 | 5 MicroSPAR | deployments |
|------------|-------------|-------------|
|------------|-------------|-------------|

| # | Date | time | Station |
|-------------|-------------------|--------------------|---------|
| 1 | 23marnot deployed | | |
| | at sea | | |
| 2 | 31mar04 | 1141-1338 | U591 |
| upper therm | 2T1254.dat | | |
| lower therm | 2T1255.dat | | |
| tattletale | FD01237.acc- | | |
| | FD011515.acc | | |
| 3 | 03apr04 | 1839-2023 | U642 |
| upper therm | 3T1254.dat | | |
| lower therm | 3T1255.dat | | |
| tattletale | FD031625.acc- | | |
| | FD032030.acc | | |
| 4 | 05apr04 | 2156-1441 (07apr) | U672 |
| upper therm | 4T1254.dat | | |
| lower therm | 4T1255.dat | | |
| tattletale | FD051242.acc- | | |
| | FD071515.acc | | |
| 5 | 08apr04 | 0929- 1420 (9 Apr) | U711 |
| upper therm | 5T1254.dat | · • • / | |
| lower therm | 5T1255.dat | | |
| tattletale | FD080850.acc- | | |
| | FD091445.acc | | |

Improvements: Buoyancy foam in remaining cavity Guard for Vector Guard for aerial Better mount for DOBIE Better download for DOBIE



Figure 14: µSpar being recovered showing the instrument locations.

Figure 15: data from μ Spar over nearly a 2 day period.

Top panel: temperatures

Bottom panel: standard deviation of pressure and vertical accelerometer. Both are in raw volts units as calibrations are yet to be included.



Beacon (Craig Stevens/Ed Abraham)

T...

Table 7: BIGEYE GPS/VHF drifter (beacons) were deployed to aid in tracking the patch.

| rnes: | | | | |
|------------|------|----------------|----------|------|
| NIWA03 | | solas_03b.txt | | |
| NIWA15 | | solas_15recove | r.txt | |
| NIWA20 | | solas_20b.txt | | |
| NIWA04 | | solas_04b.txt | | |
| | | | | |
| Deployment | | | | |
| History: | | | | |
| NIWA20 | U519 | deploy | 25mar04 | 0849 |
| NIWA15 | U525 | deploy | 25mar04 | 1437 |
| NIWA20 | U548 | retrieved | 27 mar04 | 0020 |
| NIWA20 | U551 | deploy | 27mar04 | 0223 |
| NIWA03 | U586 | deploy | 30mar04 | 2350 |
| NIWA03 | U631 | retrieve | 02apr04 | 1943 |
| NIWA03 | U638 | deploy | 03apr04 | 0944 |
| NIWA03 | U737 | recover | 10apr04 | 0318 |
| | | | | |

These data were recorded in various files on board Tangaroa however the best quality comes from the ondrifter loggers. 03, 15 & 20 were drogued at 20m with a 4m sail. NIWA03 a veteran of FeCycle did the job...it had some water inside on recovery as well as losing its aerial upon recovery.

NIWA15 was not recovered (possibly was run over during injection) so no post-file exists. We do have the VHF received data and these have been compiled into a single file.

NIWA20 data are very erratic – it has a different buoyancy to earlier versions so for its initial deployment it lay on its side. This was corrected but its data quality is low and will require removal of poor quality fixes.

NIWA04 data comes from the µspar beacon and so has different drift characteristics as well as being only deployed for short periods.

Drogue transmitted timestamps are NSDLST so times in GPS NMEA strings must be brought back one hour.



Figure 16: Drogue tracks for 3 drifters plus segments of μ Spar deployment (04).

TRAMP (Craig Stevens)

The first sea-trials of the TRAMP microstructure profiler were conducted. Effort was concentrated on getting the SUCA engine working satisfactorily consequently there were only a few successful data-taking deployments.

It resolves temperature and shear from 8 m to the surface. When working properly it resolves around 45 profiles an hour.

| Table 8: TRAMP deployments | |
|----------------------------|------------------------------|
| ddmmyy hhmmss | |
| 310304 075439 | GOOD FILE thru chance !!! #1 |
| 060404 115302 | no diving |
| 070404 150041 | partial diving |
| 080404 085042 | good file |

The files are with a directory for each deployment under a directory for each day. Each deployment contains 16 data files data.CXX in binary with a parameters.txt setup file.



Figure 17: Clear indications of wave-effects on the tether line are shown in TRAMP profiles and will need to be addressed in future deployments.

Improvements: Noise Tether Extra sensors Power up/down

SkinDeEP (Brian Ward)

The Skin Depth Experimental Profiler (SkinDeEP) is an autonomous, self--contained, hydrodynamic instrument capable of making repeated, high--resolution profiles within the ocean's upper decameter. Autonomous profiling operation is accomplished through SkinDeEP's ability to change its density: positive buoyancy is achieved by pumping air from inside the body of the profiler into an external, neoprene, inflatable sleeve; the instrument sinks when the sleeve is deflated by returning the air to the interior. The sensors are mounted some distance from the top endcap and data are recorded only during the ascending phase of the profile so as to minimize disruption of a naturally occurring scalar structure by the presence of the instrument. The sensors deployed on SkinDeEP during the SAGE cruise were as follows: Temperature: measured with a fast-responding FP07 thermistor

Conductivity: measured with 2 sensors to provide accurate low spatial resolution conductivity, and a high-resolution low accuracy sensor

Fluorescence/turbidity: measured with a FT2-D fluorometer/ turbidity sensor Irradiance: measured with a ED-50 3-channel sensor (470, 555, and 683 nm)

SkinDeEP was attached to an Iridium/GPS float, which provided its position onboard via the Iridium network. SkinDeEP was deployed during SAGE on two occasions, but recovered only after the first deployment. During its second deployment, which lasted for three days, the float was recovered, but the line to which SkinDeEP was attached had been cut. The profiler was lost.

Data availability from SkinDeEP are for the following times:

Mar30 11:17 UTC to Mar31 15:00.

A total of approximately 250 profiles were acquired during this deployment.



Figure 18: SkinDeEP being deployed from the WorkBoat.

Skin temperature (Peter Minnett)

Many of the processes associated with the air-sea exchange of gases, heat and momentum are directly responsive to temperature, on both sides of the air-sea interface as well as at the interface itself. The solubilities of gases in sea water are temperature dependent, and the relevant temperature governing the exchange processes is the so-called skin temperature of the ocean. This can best be measured radiometrically. The objectives of the University of Miami project in SAGE are to study the behaviour of the ocean skin layer and its response to wind and flux forcing, and to determine its effect on gas transfer. This is a collaborative project with Brian Ward (WHOI) and Craig Stevens (NIWA), who measured subsurface properties in the upper several meters of the ocean, and Murray Smith (NIWA) who determined



Figure 19. The MAERI mounted on the R/V Tangaroa

ocean-atmosphere turbulent fluxes, and John McGregor (NIWA), who, with Murray Smith, is detecting ocean whitecapping events using a RADAR mounted on the starboard side of the ship.

Instruments on the Tangaroa: The skin temperature of the ocean was measured radiometrically by a Marine-Atmospheric Emitted Radiance Interferometer (M-AERI) that was mounted ahead of the bridge on the port side (Figure 19). The M-AERI is a Fourier transform infrared interferometric spectroradiometer that measures spectra in the infrared (? ~3 to ~18 μ m) with a resolution of ~0.5 cm⁻¹. It uses two infrared detectors cooled to 78 K by a Stirling cycle cooler to reduce the noise equivalent temperature difference to levels well below 0.1 K. The radiometric calibration of the M-AERI is done continuously using two internal black-body

cavities, each with an effective emissivity of >0.998. The mirror scan sequence includes measurements of the reference cavities before and after each set of spectra from the ocean and atmosphere. The absolute accuracy of the M-AERI calibration is monitored by episodic use in the laboratory of a NIST-certified water-bath black-body calibration target and residual errors in the M-AERI spectral brightness temperature

measurements at temperatures typical of the ocean surface and lower troposphere are typically <0.03K. The interferometer integrates measurements over a pre-selected time interval, usually a few tens of seconds, to obtain a satisfactory signal to noise ratio, and a typical cycle of measurements including two view angles to the atmosphere, one to the ocean, and calibration measurements, takes about ten minutes. The absolute accuracy of the spectral measurements (when expressed as a brightness temperature) is 20-30 mK. The measured spectra are processed in real-time to generate measurements of the skin SST and air temperature at the height of the instrument to accuracies much better than 0.1K.

The M-AERI operated continuously, but puts itself in a "safe" mode during rainfall or when spray is detected at the aperture of the instrument. This is to keep the gold-plated mirror dry and free of salt crystals resulting from sea spray reaching the mirror, as such contamination causes a degradation in the radiometric performance of the M-AERI. During these periods no measurements are taken. For much of the cruise the rainfall was not prolonged, so the data gaps are quite short. A few other periods when the spray from the bow threatened to reach the instrument, or when prolonged rainfall was expected, the M-AERI was covered by a tarpaulin to protect the mirror surface. This is the major cause of gaps in the data record.

Hard-Hat Float: subsurface, bulk temperature measurements were taken with a precision thermometer mounted in a surface float made from a foam-filled hard hat (Figure 20). The thermometer is at a nominal depth of 5cm and the float has been deployed at most stations (Table 9). The thermometer is sampled every second, and 20-s averages are logged (N in Table 9).



Figure 20. The Hard–Hat float of the port bow of the R/V Tangaroa, when seen from above.

| Start time | e UTC | Start p | osition | End time | e UTC | End p | osition | Temp- | N |
|------------|----------|---------|---------|------------|----------|---------|---------|---------|-----|
| | | | | | | | | erature | |
| Date* | Time | Lat | Lon | Date* | Time | Lat | Lon | Mean | |
| | | °N | °E | | | °N | °E | °C | |
| 03-23-2004 | 21:49:23 | -46.996 | 173.003 | 03-23-2004 | 22:20:41 | -46.987 | 173.013 | 11.132 | 91 |
| 03-23-2004 | 23:26:47 | -46.997 | 173.005 | 03-23-2004 | 23:59:50 | -46.991 | 173.014 | 11.218 | 96 |
| 03-24-2004 | 20:53:29 | -46.666 | 172.470 | 03-24-2004 | 22:08:58 | -46.660 | 172.495 | 11.546 | 218 |
| 03-24-2004 | 23:01:37 | -46.667 | 172.470 | 03-24-2004 | 23:29:48 | -46.665 | 172.480 | 11.508 | 82 |
| 03-24-2004 | 23:41:25 | -46.668 | 172.467 | 03-25-2004 | 00:11:00 | -46.665 | 172.478 | 11.448 | 86 |
| 03-25-2004 | 21:12:36 | -46.825 | 172.517 | 03-26-2004 | 01:46:01 | -46.885 | 172.563 | 11.549 | 787 |
| 03-26-2004 | 02:31:43 | -46.895 | 172.564 | 03-26-2004 | 02:42:50 | -46.898 | 172.566 | 11.338 | 33 |
| 03-26-2004 | 05:49:54 | -46.895 | 172.302 | 03-26-2004 | 07:54:47 | -46.905 | 172.323 | 11.645 | 360 |
| 03-26-2004 | 20:14:41 | -46.938 | 172.498 | 03-27-2004 | 00:28:16 | -46.939 | 172.567 | 11.389 | 730 |
| 03-27-2004 | 03:00:27 | -46.978 | 172.499 | 03-27-2004 | 04:07:35 | -46.967 | 172.537 | 11.401 | 194 |
| 03-27-2004 | 06:19:31 | -46.954 | 172.240 | 03-27-2004 | 07:57:37 | -46.933 | 172.275 | 11.599 | 283 |
| 03-28-2004 | 22:10:44 | -46.978 | 172.159 | 03-28-2004 | 22:15:15 | -46.978 | 172.160 | 10.992 | 14 |
| 03-28-2004 | 23:07:13 | -46.974 | 172.152 | 03-28-2004 | 23:29:08 | -46.974 | 172.160 | 11.116 | 64 |
| 03-29-2004 | 00:40:51 | -46.987 | 172.141 | 03-29-2004 | 00:59:38 | -46.983 | 172.145 | 11.114 | 55 |
| 03-29-2004 | 01:47:11 | -46.970 | 172.157 | 03-29-2004 | 02:22:40 | -46.959 | 172.168 | 11.072 | 103 |
| 03-29-2004 | 21:12:26 | -47.001 | 172.134 | 03-29-2004 | 21:19:03 | -46.999 | 172.123 | 10.852 | 20 |
| 03-29-2004 | 22:03:46 | -46.997 | 172.141 | 03-29-2004 | 22:18:45 | -46.994 | 172.144 | 10.843 | 43 |
| 03-30-2004 | 02:01:30 | -47.089 | 172.352 | 03-30-2004 | 02:30:02 | -47.080 | 172.352 | 10.901 | 83 |
| 03-30-2004 | 21:16:37 | -46.878 | 171.908 | 03-30-2004 | 21:46:11 | -46.873 | 171.905 | 10.891 | 86 |
| 03-30-2004 | 22:11:59 | -46.882 | 171.922 | 03-30-2004 | 23:45:34 | -46.870 | 171.911 | 11.050 | 270 |
| 03-31-2004 | 00:22:04 | -46.877 | 171.904 | 03-31-2004 | 01:11:07 | -46.870 | 171.898 | 10.950 | 142 |
| 03-31-2004 | 05:55:16 | -46.823 | 172.014 | 03-31-2004 | 07:06:14 | -46.829 | 171.995 | 11.238 | 205 |
| 03-31-2004 | 20:19:51 | -46.771 | 171.850 | 03-31-2004 | 21:39:09 | -46.767 | 171.856 | 10.889 | 229 |
| 04-01-2004 | 20:18:19 | -46.521 | 171.906 | 04-01-2004 | 20:48:35 | -46.523 | 171.904 | 10.313 | 88 |
| 04-01-2004 | 21:29:23 | -46.526 | 171.924 | 04-02-2004 | 00:18:26 | -46.488 | 171.958 | 10.917 | 487 |
| 04-03-2004 | 20:22:02 | -46.230 | 172.413 | 04-03-2004 | 21:06:34 | -46.226 | 172.432 | 10.657 | 129 |
| 04-03-2004 | 21:39:29 | -46.250 | 172.426 | 04-03-2004 | 21:54:26 | -46.249 | 172.433 | 10.673 | 44 |
| 04-03-2004 | 23:32:28 | -46.250 | 172.442 | 04-04-2004 | 00:04:29 | -46.244 | 172.463 | 10.703 | 93 |
| 04-04-2004 | 03:08:36 | -46.072 | 172.386 | 04-04-2004 | 04:41:29 | -46.047 | 172.435 | 10.294 | 535 |
| 04-04-2004 | 20:17:45 | -46.253 | 172.611 | 04-04-2004 | 22:01:25 | -46.254 | 172.661 | 10.663 | 299 |
| 04-04-2004 | 22:32:10 | -46.252 | 172.610 | 04-05-2004 | 01:47:40 | -46.220 | 172.709 | 10.679 | 563 |
| 04-05-2004 | 04:10:49 | -46.429 | 172.515 | 04-05-2004 | 06:03:31 | -46.422 | 172.561 | 10.659 | 325 |
| 04-05-2004 | 20:03:32 | -46.248 | 172.677 | 04-05-2004 | 21:52:25 | -46.233 | 172.683 | 10.569 | 314 |
| 04-06-2004 | 01:50:39 | -46.062 | 172.773 | 04-06-2004 | 02:16:24 | -46.064 | 172.773 | 10.753 | 75 |
| 04-06-2004 | 03:13:08 | -46.060 | 172.769 | 04-06-2004 | 03:54:53 | -46.054 | 172.774 | 10.801 | 121 |
| 04-06-2004 | 21:01:51 | -46.235 | 172.696 | 04-06-2004 | 22:25:41 | -46.228 | 172.709 | 10.554 | 242 |
| 04-06-2004 | 22:50:30 | -46.236 | 172.693 | 04-07-2004 | 02:06:21 | -46.212 | 172.710 | 10.596 | 564 |
| 04-07-2004 | 03:44:45 | -46.215 | 172.712 | 04-07-2004 | 06:03:54 | -46.218 | 172.714 | 10.652 | 401 |
| 04-07-2004 | 09:30:37 | -46.223 | 172.716 | 04-07-2004 | 10:29:04 | -46.224 | 172.717 | 10.564 | 169 |
| 04-07-2004 | 19:56:16 | -46.222 | 172.772 | 04-07-2004 | 23:42:02 | -46.206 | 172.858 | 10.533 | 650 |
| 04-08-2004 | 10:39:46 | -46.206 | 172.782 | 04-08-2004 | 11:20:28 | -46.201 | 172.800 | 10.447 | 118 |
| 04-08-2004 | 20:15:33 | -46.173 | 172.821 | 04-08-2004 | 20:58:20 | -46.163 | 172.835 | 10.472 | 124 |
| 04-08-2004 | 21:35:36 | -46.195 | 172.798 | 04-08-2004 | 22:28:28 | -46.181 | 172.813 | 10.495 | 153 |
| 04-08-2004 | 22:58:50 | -46.198 | 172.785 | 04-08-2004 | 23:58:19 | -46.200 | 172.806 | 10.471 | 97 |
| 04-08-2004 | 03:34:39 | -46.073 | 172.765 | 04-08-2004 | 04:37:59 | -46.067 | 172.787 | 10.659 | 183 |
| 04-09-2004 | 00:19:18 | -46.177 | 172.802 | 04-09-2004 | 01:00:21 | -46.165 | 172.817 | 10.485 | 119 |
| 04-09-2004 | 04:40:40 | -46.062 | 172.778 | 04-09-2004 | 06:20:31 | -46.034 | 172.801 | 10.462 | 288 |
| 04-12-2004 | 20:50:07 | -43.486 | 178.036 | 04-12-2004 | 23:33:37 | -43.489 | 178.006 | 12.093 | 471 |
| 04-13-2004 | 00:35:19 | -43.491 | 178.018 | 04-13-2004 | 03:02:49 | -43.516 | 177.944 | 12.162 | 421 |

Table 9: Deployments of Hard-Hat Float during SAGE

* Dates are given as month-day-year

Radiosondes: profiles of atmospheric temperature, humidity, wind speed and direction were measured using Vaisala RS80-GPS radiosondes carried aloft by helium balloons. A list of radiosonde launches is given in Table 10. The data are transmitted from the sonde to a shipboard receiver and these are stored at 2-s intervals by computer. This sampling gives good height resolution in the atmospheric boundary layer, which is under the direct influence of the fluxes through the sea surface. The radiosondes were generally launched to coincide with the overpasses of the NASA *Aqua* earth observation satellite, as the atmospheric

profiles derived from the radiosondes can be used to validate satellite retrievals of atmospheric temperature and humidity distributions.

| Date | Time | Latitude | Longitude | Hmax | Pmin | N | Sonde code |
|-------------|-------|----------|-----------|-------|--------|------|------------|
| | | | | | | | number |
| UTC | UTC | °N | °E | km | hPa | | |
| 01-Apr-2004 | 06:11 | -46.91 | 171.74 | 23.31 | 33.00 | 3596 | 012103809 |
| 01-Apr-2004 | 22:23 | -46.53 | 171.93 | 19.52 | 59.70 | 3453 | 841501511 |
| 03-Apr-2004 | 02:05 | -46.31 | 172.12 | 25.80 | 22.40 | 3596 | 841501513 |
| 04-Apr-2004 | 03:41 | -46.23 | 172.40 | 26.18 | 20.90 | 3574 | 841501514 |
| 06-Apr-2004 | 01:43 | -46.06 | 172.77 | 13.59 | 145.90 | 3598 | 012103810 |
| 07-Apr-2004 | 02:05 | -46.20 | 172.75 | 19.70 | 56.80 | 3598 | 011502908 |
| 08-Apr-2004 | 01:54 | -46.22 | 172.77 | 21.30 | 44.50 | 3041 | 012103707 |
| 09-Apr-2004 | 02:51 | -46.07 | 173.06 | 23.72 | 30.40 | 3598 | 012103814 |
| 13-Apr-2004 | 02:50 | -43.53 | 177.96 | 23.07 | 33.30 | 3598 | 012103808 |

Table 20: Radiosonde launches made from the R/V Tangaroa during the SAGE voyage

Incident radiation: The radiation budget at the sea surface is important in determining the forcing of the thermal structure in the upper ocean, and of the surface skin layer. Broad-band radiometers were mounted on gimbals on a mast fixed to the foredeck railing and the output was recorded every minute throughout the cruise. Two radiometers were used – Eppley Laboratory Precision Spectral Pyranometer (PSP) responsive to solar radiation in the wavelength range of 0.285 to 2.8 μ m and Eppley Laboratory Precision Infrared radiometer (PIR) measuring infrared radiation in the 3.5 to 50 μ m wavelength interval. The radiometers were gimballed to remove the effects of mean tilts of the sensors caused by the ship's attitude (Figure 21).

All Sky Camera: an all-sky camera system was mounted on the above the bridge of the Tangaroa. This is a colour video security camera mounted above a hemispheric mirror. The output is recorded by a time-lapse recorded every 17 s. The resulting images will be analyzed after the cruise to determine the cloud amount and could type present through the daytime part of each day. This information, in addition to its own intrinsic value, has applications in the study of the surface radiative heat fluxes and the response of the skin effect to external forcing.



Figure 21. The gimbaled Eppley radiometers on foredeck port rail.

Preliminary temperature results

Skin effect: the oceanic skin temperature is generally a few tenths of a degree cooler than the subsurface sea temperature (the bulk temperature), but measurements of the magnitude of the cool skin temperature and its behaviour in response to forcing by wind and heat flux have been limited in the past to winds of $\sim 15 \text{ ms}^{-1}$ and less. Furthermore, the data sets that exist have generally been taken under conditions that are favourable to the generation of a diurnal thermocline, leading to a warmer surface layer, and the analysis of radiometric skin temperature measurements, with respect to bulk temperature gradients. Consequently analyses have been restricted to night-time data, with the assumption that the daytime behaviour of the skin layer would be the same. The high wind conditions encountered during this cruise and the generally low levels of insolation, combined with the sheltered position of the M-AERI, have provided the first opportunity to study the skin layer during the day and under higher winds. Figure 22 shows the skin temperature, as determined by the difference between the M-AERI radiometric skin temperature determination and the Hard-Hat float

subsurface temperature at a depth of ~5cm, as a function of wind speed and time of day. The solid line is a fit derived from nighttime measurements (Donlon, C.J., P.J. Minnett, C. Gentemann, T.J. Nightingale, I.J. Barton, B. Ward, and J. Murray. Towards improved validation of satellite sea surface skin temperature measurements for climate research. Journal of Climate, 15, 353-369, 2002). The daytime measurements from this cruise do indeed correspond with the night-time fit. They also extend the winds speed range of such measurements beyond the $\sim 15 \text{ms}^{-1}$ limit of previous measurements.

Air-seatemperaturedifference:thethetemperaturedifferencebetweenthesea-surfaceandtheoverlyingatmospherenotonlydetermines



Figure 22. Measurements of the wind-speed dependence of the oceanic thermal skin layer.

the sensible heat flux between the two fluids, which is generally rather small, but also the stability of the atmospheric boundary layer, and this influences the exchange of gases, heat and momentum between the ocean and atmosphere. Conventional measurements of the air-sea temperature difference, taken with two thermometers – one in the air and the other below the sea-surface – are prone to large errors caused by the calibration uncertainties of each thermometer. Furthermore, the air-temperature measurements are also susceptible to contamination during sunny days by direct solar heating of the thermometer, or by heat island

effects of the ship. These are particularly pronounced in measurements in the tropics, where archives of conventional measurements show a change in sign of the air-sea temperature difference each afternoon. The radiometric measurements of the M-AERI are not subject to either of these sources of uncertainty and provide a much more accurate determination of the air-sea temperature difference. In the tropics the M-AERI measurements have revealed a distribution of air-sea temperature differences that appears to be common to many There are very few regions and seasons. instances of measurements where the air is warmer than the sea surface, and these appear to be confined to coastal regions where the air is of continental origin. The measurements from this cruise have a different distribution, in which there are many cases of the air being warmer than the sea (Figure 23). These are associated with the passage of atmospheric fronts embedded in the storm systems of these latitudes. This implies that there are differences in air-sea fluxes to be expected in areas dominated by storm tracks, compared to



Figure 23. Histogram of air-sea temperature differences measured radiometrically by the M-AERI during the SAGE cruise.

tropical regions, that extend beyond the obvious differences in wind speed.

Radar Wave Measurement (John McGregor)

NIWA's ocean remote sensing radar operated successfully throughout the voyage, recording data on ocean surface properties of relevance to air-sea gas exchange. The specific quantities of interest were whitecap/breaking and ocean waveheight spectra. From these, wave properties such as whitecap percentage (when ship orientation enabled upwind operation of the radar), significant waveheight and period are derived.

The radar measured surface velocities and backscattered power along a beam out to 300m at 2.5m intervals, with a time resolution of 0.5 sec Simultaneous transmission of two electromagnetic wave polarizations allows breaking wave echoes to be distinguished from those from unbroken water. Wave heights ranged from 1m to 6m with swell periods typically around 10secs.

Raw data recorded by the radar consists of digitised receiver output. First level processing of this raw data produces rangeresolved Doppler spectra of sea surface echoes. Second level processing calculates moments of these Doppler spectra. During the voyage all radar data was



Figure 24: Wave image from the radar. The upper panel shows backscattered power from the sea surface. The lower panel shows sea surface velocity. The slanting lines are ocean waves moving towards the ship.

processed through to second level and archived on CD-ROM with a second backup copy on DVD. A total of approximately 18 GB of raw, 1st and 2nd level data was obtained. A selection of second level data was processed through to yield ocean waveheight information. Processing of the remainder of the data through to final form will be performed on shore in due course.

Due to the sheer volume of data produced by the radar, it is impractical to run the radar continuously, and so radar operation was targeted to coincide with other experiments (in particular the REA/air sampling and subsurface profiling instruments) and interesting sea conditions. Radar data will be used in conjunction with data from these surface physics experiments. Due to the wide range of conditions this will be an excellent dataset which should contribute to a better understanding of surface physics.

13. Atmospheric Chemistry

Work Plan:

This group will examine the atmospheric gas and aerosol products resulting from DMS oxidation. SO₂ is a key intermediate in the atmospheric oxidation of DMS. It is a challenge to measure at low level and to do so we used an HPLC fluorescence technique. Size resolved aerosol chemistry will be measured by collecting samples on Tedlar film using a Berner impactor with four stages of size segregation: 4-10 um, 1.1-4 um, 0.55-1.1 and less than 0.55 μ m with subsequent analysis by IC. Particle sizing will be done on occasion using a ASASP-100X laser optical sampler, which bins particles into 15 channels between 0.1 and 3 μ m diameter, used to give an estimate of the concentration of mechanically generated sea salt aerosol. Condensation nuclei (>10 nm) and ultrafine nuclei (>3 nm) will be measured using TSI 3010 and 3025A nuclei counters, used to give an indication of any events of new aerosol particle formation.

Mike Harvey, Jill Cainey, Dawn Devries

Methods and Activities:

<u>Sulfur Dioxide (Jill Cainey)</u>: Sulfur dioxide was measured using an HPLC technique (Low-level atmospheric sulfur dioxide measurement using HPLC/fluorescence detection, Saltzman, ES; Yvon, SA; Matrai, PA, *Journal of Atmospheric Chemistry*, 17(1), 73-90, 1993).

A series of measurements were made inside and out of the patch. Post-patch, the instrument was run for 14 hours, commencing pre-dawn, on the Chatham Rise "Gas Station" around 43°30'S, 178°30'E.

Data at this stage are preliminary but indicate that background levels of sulfur dioxide in this region of the Southern Ocean are between 3-15 pptv, $(17 \pm 11 \text{ pptv})$, with a detection limit of 4 pptv), consistent with measurements made at Cape Grim and Baring Head in clean on-shore winds.

Due to contamination from the ship's exhaust, it may not be possible to pick out any naturally occurring elevations of sulfur dioxide, but with a combination of CN data and wind direction data, it may be possible to make an assessment. However given that atmospheric DMS levels were low for the duration of the cruise, it is unlikely that there were any naturally occurring spikes of sulfur dioxide.

The only problem with making these measurements was the location of the inlet, which was prone to contamination from the ship's exhaust (but that would have been likely in most locations on the Tangaroa) and due to the proximity of the inlet to the surface ocean, sampling was limited to periods when waves were not breaking close to or over the container laboratory on the forecastle deck.

TSI 3025 ultrafine and TSI 3010 condensation nuclei (Mike Harvey, Jill Cainey, John Gras): ran continuously between 23 March and 15 April, logging particle counts at 30 second intervals to a PC based logger through 2 serial ports, programmed in Pascal running MS-DOS! There were 2 periods amounting to about 1.5 days when the logger was inadvertently not run Air was sampled through a purged $\frac{1}{2}$ inch dekoron tube with a coarse (sea salt) particle impactor on the inlet which was above the roof of the crow's nest, nominally 25 m asl at the same location as the O_2/CO_2 inlet. Of the two instruments, the ultrafine condensation particle counter TSI 3025A specification is for 50% detection at 3 nm, 90% detection at 5 nm compared with the TSI 3010 specification of 50% detection at 10 nm. Figure 25 shows the time line of concentration for the two instruments. The main features of this time series are that both instruments follow each other closely, the median UCN concentration is 258 cm⁻³, the median CN is 239 cm⁻³. Clean air values are clearly discernable as a baseline ranging from about 100 to 3000 cm⁻³, similarly spikes of polluted air sourced from the vessel fantail diesel engine exhaust are also clearly visible. In clean air, the difference between UCN and CN was in the range 0 to 15% of UCN for most of the voyage although there were one or two short episodes where the proportion of UCN was higher, indicative of recent particle nucleation. The background to these episodes will be investigated further.



Figure 25: UCN/CN particle concentration time series.

ASASP-100x particle spectrometer (Mike Harvey): A bracket for the ASASP was fabricated to mount the instrument off an existing mast on the port side rail of the Monkey Island. Cabling was run through the access tube into the bridge science area. During the transit to the experimental site and especially during periods of rough weather the probe was not operated for fear of contaminating the optical system with excessive sea salt. When the probe was "un-capped" for operation at the site it was found to be nonfunctional with only spurious counts appearing in some particle channels. It was suspected that excessive vibration and shaking during the rough transit had upset the optical alignment. Given the overall priorities and resources available on SAGE, a prior decision had been made that field servicing was not an option and no further work was done with the ASASP. This was the first deployment of ASASP on Tangaroa. If we discover with servicing that damage or misalignment has occurred, we recommend that for any future deployments, that a shock-proof mounting be developed or that the instrument is run on a bench-top mode.

Berner Impactor size resolved particle chemistry (Dawn Devries): four stages of a 7-stage Berner impactor were used to collect aerosols (using tedlar films and a final Millipore filter) and separate them into size bins. The cut-offs for these size bins, assuming 80% relative humidity, are $<0.5 \,\mu\text{m}$, 0.5-1.1 μm , 1.1-4 μm , and 4-10 μm . Particles larger than 10 μm were eliminated from the samples by collecting them with silicon grease at the inlet and on a subsequently discarded silicon spray coated tedlar film on the top stage.

During sampling, the Berner was encased on the foredeck mast with a ¹/₂" copper tubing inlet approximately 11 m above sea level and a pump and mass flow controller (30 slpm) situated in the winch house. Samples were collected during the day as well as at night, as conditions allowed, in order to cover diurnal variability.

In order to minimize stack contamination, a sector control defined by $>3 \text{ ms}^{-1}$ wind speed and 50-310° relative wind direction (with the bow at 180°) was set up and used for the majority of sampling. This, in addition to a minimum sample time of 6 hours based on the low productivity conditions, meant that some

samples had to be continued over 2-3 days in order to get enough sample time, precluding the ability to get a night sample.

Chemical analysis on the films and filters will be done at NIWA using ion chromatography. This analysis will include the determination of Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ SO₄²⁻, and MSA and should be complete in June.

Additionally, periodic hi-volume aerosol samples were collected and will also be analyzed back at NIWA. Over the duration of the cruise, about 15 Berner samples and about 7 hi-volume samples were collected.



Figure 26: Berner on bench for unloading

14. Ocean particulates, export processes and biophysical moorings

Work Plan:

Floating sediment trap deployments were planned, both in (5 deployments) and out (3 deployments) of the patch. Measurement from the traps will be used to determine the time-scales of aggregation and export processes and linkages to temporal changes in physical, chemical and biological processes within a bloom. The size, composition and flux magnitude of exported organic matter will be calculated with chemical fluxes of (POC, PP, PN, PSi) in and out of the SF₆-defined patch including profiles from CTD casts.

At the end of the voyage, routine servicing of the two NIWA biophysical moorings was planned, firstly the southern mooring at approximately 46°38.202'S 178°33.486'E followed by the northern mooring at 41°11.28'S 178°28.62'E.

Scott Nodder, Bill Main

Methods and Activities:

Seawater samples were taken from 10 litre carboys that drained duplicate Niskin bottles from the same depths on each "Biology" IN and OUT cast (i.e., twice a day, 5-6 depths, ranging from 90 m to 2 m water depths). Samples were filtered for particulate organic carbon and nitrogen (POC/PN, filtered onto precombusted 25 mm GFF filters, rinsed with 0.1 N H_2SO_4 and 0.2 µm filtered seawater, frozen), particulate phosphorus and nitrogen (PPPN, pre-combusted GFF filters, soaked overnight in 10% HCl acid and rinsed in deionised distilled water, frozen), chlorophyll *a* (GFF filters, placed in liquid nitrogen) and particulate biogenic silica (0.8 µm polycarbonate filters, frozen). Nutrient samples were also collected using the filtrate from POC/PN filtrations. In addition nutrient samples were filtered on each "Gas" IN cast and occasional OUT cast at selected depths across the pycnocline (Cliff Law).

Settling column (SETCOL) experiments to determine the sinking rate of phytoplankton were undertaken 7 times inside the patch and 3 times outside. Only one SETCOL was available for use in these experiments due to breakages (fixed onboard by Bill Main) and flawed designs for the remaining 4 SETCOLs that were provided. Ascent and sinking rates for the phytoplankton community (as estimated using flow cytometry (run onboard by Julie Hall) and chlorophyll a - 100 ml filtered onto 0.2 µm polycarbonate filters, frozen in liquid nitrogen) and individual species (Lugol's iodine preserved samples) will be determined. Jill Peloquin

also measured Fv/Fm ratios on each of the fractions collected from the SETCOLS (top, middle and bottom) using PAM (pulsed amplitude modulation) to determine relative photo-efficiencies of the resident phytoplankton populations in ascending, suspended and sinking modes.

Two free-floating sediment trap deployments to sample sinking particle populations were undertaken with traps sets at depths of 80 and 300 m with the top trap set 30 m below the mixed-layer at 40-50 m. Traps were back-filled with a NaCl-enriched basal brine (115 g NaCl and 20 g borax in 20 litres of filtered 0.2 μ m seawater). The traps were deployed for ~3 days, but drifted to the SW out of the patch as the patch became strung out on 28-29 March under strong 50 knot wind conditions. During this high wind event the mixed-layer deepened to 75-80 m and trap recoveries were undertaken in less than ideal conditions, probably compromising the collected samples. Trap samples were processed for later analyses of POC/PN, PPPN, total mass/biogenic silica and pigments, including chlorophyll *a* and phaeophorbides. Total mass/biogenic silica samples were poisoned to a 5% formalin solution to be filtered back in the laboratory. Zooplankton samples (>200 µm) from each trap cylinder were also collected and poisoned with formalin (5%).

Two particle camera deployments were undertaken with poor results due to battery failure and problems with flash synchronization. More developmental work is required.

Recovery and redeployment of the Southern Biophysical Mooring was not possible due to persistent high wind and seas from arrival at the site in the early hours of 11 April where the ship remained until 05:00 on 12 April when conditions and forecast showed no sign of improvement. Recovery of the Northern Biophysical Mooring was not attempted because of a poor fix and lack of signal from the mooring release system in spite of repeated attempts to contact both on the vessel and from the work boat.

OPERATIONAL MATTERS

Science Operations management

With the complexity of the voyage, weather dependency and frequently changing concerns, on-board science planning was managed through a planning team meeting every few days as required. This group comprised: Mike Harvey, Ed Abraham, Julie Hall, David Ho, Cliff Law, Murray Smith, Craig Stevens, Brian Ward.

A provisional plan for the 24 hours ahead was generally developed between 19:00 and 21:00 by the cruise leader. Round the clock operations and communications with the bridge re deployments and navigation at any given time were the responsibility of a single lead scientist. During a normal day, responsibilities passed from Julie Hall (day-time deployments 07:00 to 19:00) to Cliff Law (evening mapping 19:00 to 00:00) to Edward Abraham (overnight mapping 00:00 to 07:00) with hand-over. This management, once established worked well and allowed the voyage leader to maintain an overview as well as some science time.

CTD Operation (Matt Walkington)

CTD-related instrumentation consisted of:

- a Seabird Electronics (SBE) 911plus CTD with:
 - SBE-5 pumped SBE-3 temperature, SBE-4 conductivity and SBE-43 dissolved oxygen sensors.
 - SBE-5 pumped secondary SBE-3 temperature and SBE-4 conductivity sensors.
 - Seapoint Sensors, Inc. SCF chlorophyll fluorometer.
 - 25-cm Wetlabs C-star transmissometer.
 - Biosherical Instruments Inc. photosynthetically active radiation (PAR) sensor, model QSP200L4S.
 - Datasonics sonar altimeter, model PSA-900D.
 - a SBE 32 24x10-litre Carousel water sampler.
- Ocean Test Equipment Standard BES external-spring Niskin-type water-sampling bottles.
- Salinity sample bottles.

•

• CTD winch with 10-km 10.5-mm single-core seacable.

<u>Performance</u>: With the exception of issues noted below, the CTD-related instrumentation apparently functioned to specification and was operated essentially according to accepted practices for the duration of the voyage. A total of 85 one-cast CTD stations were completed, labelled u3502 to u3743.

<u>PAR Sensor</u>: The initial CTD PAR sensor experienced an intermittent fault that manifested as a time variable offset, both cast to cast and, less evidently, within casts. It was eventually replaced with a formally identical spare unit for station u3719 cast 1 and subsequent casts.

Secondary Conductivity Sensor: The initial secondary conductivity sensor eventually developed a clear fault (during station u3740 cast 1). It was replaced with a formally identical spare unit for station u3740 cast 1 and subsequent casts. The development of this fault was perhaps somewhat progressive, as possibly indicated by slight shifts in the primary-secondary conductivity difference on casts before station u3740 cast 1.

Problems, observations, recommendations

Mobilisation/Demobilisation: there was an enormous amount of equipment and containers to load. The sequence was considered carefully in advance. Mobilisation took a half to one day longer than anticipated. In part this was due to the extra transport time through town being based at Aotea Wharf, in part drizzle on two days slowed progress. Engineering issues arose in plumbing the tanks in-situ, not helped by the late delivery of the fertiliser pumps from overseas. All these engineering issues were worked through as swiftly and efficiently as possible. An extra flat deck truck with a crane was hired and essential during mobilisation. On demobilising, the off-loading by deck crane was rapid but a bottleneck developed during fuelling when the crane could not be used which slowed down the off-loading and meant that a second flat deck truck could not be used effectively. Not having the conflict with fuelling and having more than one crane operator to allow continuous crane operations would have sped up the off-loading by perhaps half a day.

IT/DAS operation: The DAS set-up was demanding with the addition of a large number of additional instruments both inputting and outputting data. Time in port was fully utilised by Chris Edsall to set the system up. However, the resulting configuration proved to be somewhat unstable with fairly frequent crashes once everything was up and running. Although there were science staff on board with DAS knowledge, they were also very busy with other duties and were not able to devote time to working on the problem in liaison with Chris Edsall in Wellington. With the level of problem, a decision was made to be vigilant and reboot as required. In practise, general down time and data loss was small apart from perhaps two main periods when a hard reset had been performed. It was easy for personnel to do the hard reset yet not recommended for recovery in the DAS manual and this could have resulted in corruption of the database files back to 00 UT from the time of the reset. Once realised, a sign was posted on the machine. Given the importance of DAS to the success of the mission, it is recommended that in future voyages of this level of complexity that there is a dedicated IT person on board to manage the DAS/IT facility.

The major effort by IT ahead of the voyage by Chris Edsall, Geoff Blair and Bob Walker was greatly appreciated. Considerable effort was required to set up additional networking to container laboratories and in the set up of many client lap-tops and the email system.

Mains power distribution: The potential for power distribution problems was recognised ahead of SAGE and considerable work was put in by Peter Hill and the engineers in planning ahead of the voyage. The main problem encountered was power overload in one or two areas and this was generally fixed quickly and efficiently by running flexible extension leads from circuit outlets with additional capacity. There was one power overload incident in the dark room area that required an unavoidable rapid shut down of a number of circuits. Thanks to Alan Harvey and Fred de Jager for swiftly dealing with these power problems. Power distribution will need to be reviewed for future high-demand voyages.

Potable water/ grey water: with a full ship, water production had to be increased by the engineers to meet demand and this was successful along with requests to conserve water. In addition, a high production of grey water meant that tank emptying had to be scheduled in at around 16 hour intervals.

Deionised water: planning work, spares and work before sailing was required to ensure good quality deionised water which was essential to the voyage.

Health and Safety concerns: with the wide range of activities, crowded work spaces and rough conditions, all activities were carried out safely. Personal protective equipment was used for handling the iron sand, a major concern here was avoiding the possibility eye contamination from wind-blown dust. The major safety issue was work in exposed positions in moderate seas. The policy had to be reinforced particularly for work on the foredeck of working in pairs, wearing flotation jackets and clip-on harness for changing foremast samples, along with alerting the bridge. A second safety issue was a new fridge that broke loose in the darkroom in rough seas and damaged science equipment in that area. If a person had been present, there could have been serious consequences.

Simultaneous micrometeorological and CTD station work: proved difficult in practice. When on station with CTD, wind was generally from the aft starboard quarter for safe operation and minimal drift. Optimally for micrometeorological work, the wind should be in the forward $\sim 60^{\circ}$ sector for minimal air-flow disturbance. It was not appreciated before the voyage that in general, it was not possible to satisfy both requirements and so dedicated periods of air sampling with bow in the wind were required.

Primary production measurements: with the high workload on the biological team, it was noted that measurement and work load seemed to be more easily manageable with the adopted protocol that did not involve a pre-dawn CTD cast for the primary production work.

Additional SAGE documents

- 1. Science proposal document: SOLAS-ANZ_Dual_tracerV1_9.pdf
- 2. Voyage logistics planner: VDT0410_TangaroaVoyPlan.doc
- 3. Web log summary: SAGE_weblog.pdf
- 4. Station meta data information on measurements: SAGE_station_meta.xls
- 5. Atmospheric meta data: SAGE_Air+underway_meta.xls
- 6. this report: VDT0410_SAGE_VoyageReport.pdf

7. Password protected ftp site for data distribution is available at <u>ftp.niwa.co.nz</u> through the web link: <u>http://www.niwa.co.nz/rc/atmos/sage/data</u>

ACKNOWLEDGEMENTS

SAGE was one of the most ambitious undertakings attempted by NIWA and RV Tangaroa. It was regarded as moderate to high risk in terms of achieving objectives. Significant advances in science often come with attendant high risk. Given the preliminary findings reported here, SAGE was highly successful, produced a number of unexpected results and will extend our knowledge of gas exchange in the strong wind regime of the Southern Ocean. The successful completion of an extremely busy field programme with many deployments under conditions that were at times rough was only made possible by the major efforts of many individuals as well as a strong team approach. I wish to thank all for the support and hard work that made this project possible.

The whole science team wish to thank the entire crew of R.V. Tangaroa and personnel at NIWA Vessels for the high quality of the service onboard and the constant willingness to help. The smooth running of the vessel was maintained with the efficient professional attitudes and assistance of Captain Roger Goodison, First Mate Alexander Morris and Second Mate Yoshi Suzuki on the bridge. A focus on getting the science done was maintained against the backdrop of a frequently changing daily schedule dictated by conditions. Assistance of Chief Engineer Allan Harvey and Second Engineer Fred de Jager was invaluable given the variety and number of laboratories, electrical loadings and new science equipment deployed on this voyage. With in excess of 300 oceanographic stations as well as numerous deck-board activities, the efforts of the deck crews under Bosun Peter Healy and Leading Hand Tony Reiri were exemplary with a focus on safe operations in a cluttered environment. Meals prepared by Barry McBrearty, Yvonne French, and service by Sharon Henderson were superb.

The success of SAGE also owes a great deal to the assistance provided by NIWA Vessels at the planning stage and to the Vessels Workshop for their engineering work with design and build of a number of critical components. A special mention must be given to Greg Foothead who oversaw this engineering effort and put in many hours from planning right through to the final departure. Thanks to Bob Walker, Chris Edsall and Geoff Blair for providing IT and DAS support. Thanks to the shore-based Dunedin support team for assistance with equipment repairs at Port Chalmers.

There were many others, not named, who helped in many ways to get the show on the road (and back off again). Thanks to you all. Finally, Steve Archer made a comment which captures the comments I received from all the overseas science collaborators: "*Not many of the research ships I've been on would have continued to work safely in some of the weather we experienced on the trip.*"

Appendix 1

Collaborating organisations

| 8_8 | |
|---|--|
| National Institute of Water and | E.Abraham, S.Bury, P.Boyd, K.Currie, |
| Atmospheric Research, (NIWA), | M.Ellwood, J.Hall, M.Hadfield, M.Harvey, |
| New Zealand : | P.Hill, C.Law, B.Macaskill, W.Main, |
| | A.Marriner, J.McGregor, S.Nodder, S. Pickmere, |
| | K.Safi, M.Smith, C.Stevens, R.Thompson, |
| | M.Walkington <u>i.xxxx@niwa.co.nz</u> |
| University of Otago | Doug Mackie dmackie@alkali.otago.ac.nz |
| AUSTRALIA | |
| Australian Government Analytical | Hilton Swan <u>Hilton.swan@agal.gov.au</u> |
| Laboratories (AGAL) | |
| Bureau of Meteorology | Jill Cainey j.cainey@bom.gov.au |
| CSIRO Atmospheric Research | John Gras John.Gras@csiro.au |
| Southern Cross University | Graham Jones gjones@scu.edu.au |
| INTERNATIONAL | |
| Dalhousie University, Canada | Lori Ziolkowski lori.ziolkowski@dal.ca |
| University of Helsinki, Finland | Jorma Kuparinen (sabbatical) |
| | j.kuparinen@niwa.co.nz |
| Laboratoire D'Océanographie Dynamique | Liliane Merlivat |
| et de Climatologie (LODYC), France | Liliane.Merlivat@lodyc.jussieu.fr |
| | Jacqueline Etcheto |
| | Jacqueline.Etcheto@lodyc.jussieu.fr |
| Lamont Doherty Earth Observatory, USA | David Ho david@ldeo.columbia.edu |
| Plymouth Marine Laboratory, UK | Steve Archer stda@mail.pml.ac.uk |
| Princeton University | Michael Bender <u>bender@Princeton.edu</u> |
| | Matt Reuer mreuer@Princeton.EDU |
| RSMAS, University of Miami, USA | Peter Minnett pminnett@rsmas.miami.edu |
| University of Colorado at Denver, USA | Herman Sievering |
| | hsieveri@carbon.cudenver.edu |
| | Dawn Devries ddevries@carbon.cudenver.edu |
| University of Rhode Island, USA | Craig McNeil mcneil@gso.uri.edu |
| | David Katz drkatz@gso.uri.edu |
| University of Hawaii, USA | Brian Popp popp@hawaii.edu |
| Virginia Institute of Marine Science, USA | Jill Peloquin jillp@vims.edu |
| Woods Hole Oceanographic Institute, USA | Brian Ward <u>bward@whoi.edu</u> |

Electronic copies sent to: Shipboard scientific & technical staff (as above) All SAGE science staff Peter Gerring, Dave Lowe, Matt Pinkerton (NIWA) NIWA Publicity (Geoff Baird) NIWA GIS/Voyage Archive (Kevin MacKay) NIWA GIS/Voyage Archive (Kevin MacKay) NIWA IT (Bob Walker, Chris Edsall) Vessel Management (John Hadfield, Greg Foothead, Clive Glover, Fred Smits) Regional Manager (Andrew Laing) Research Director (Rob Murdoch) Neil Andrew (GM Marine) Murray Poulter (GM Atmosphere)

Hard copies sent to Master (2) (NIWA Vessel Management) Bosun (2) (NIWA Vessel Management)