



Regional Operations Centre Canadian Coast Guard – Pacific

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PACIFIC REGION CCG VESSEL -POST CRUISE REPORT

NAME OF SHIP/PLATFORM: John P Tully

DATE: **FROM:** 27 June 2002 **TO:** 28 July 2002

SCIENCE CRUISE NUMBER: 2002-16 **SHIP'S PATROL NUMBER:** **02-05**

CHIEF SCIENTIST[S]: Marie Robert, Philip Boyd

AREAS OF OPERATION: NE Pacific, Gulf of Alaska, Line P, Station P

INTRODUCTION/

PROGRAM BACKGROUND: The monitoring Line P program is one of the longest time-series of oceanographic data in the north-east Pacific Ocean. It provides a good indication of how the ocean is changing.

CRUISE OBJECTIVE/OBJECTIVES: Survey water properties along Line P, enrich a patch of ocean with iron near Station Papa (50N, 145W) and observe biological changes for a period of 18 days.

Conduct a mesoscale iron enrichment experiment at a site to the NE of P26 (Ocean Station Papa). The rationale for this experiment was to follow the changes in phytoplankton growth rate and related biogeochemical properties of the iron-limited resident cells.

DAYS ALLOCATED: 31

DAYS OF OPERATION: 31

DAYS LOST DUE TO WEATHER: None

RESULTS:

Site selection for iron enrichment was based upon the location of waters with low density (to minimise any potential subduction of the labelled iron-enriched waters), uniform physical characteristics (in particular to the NE of the site, the predominant direction of the drogued drifter buoys we deployed), and matching the HNLC condition (iron-stressed cells, high macronutrients and low chlorophyll). The waters in the immediate vicinity of station Papa did not meet all of these criteria (salty, colder waters, low degree of uniformity in the physical properties). There was also evidence of two eddy-like features (one to the SW and one to the NE of P26 that we had to take into consideration in our site selection i.e. avoid. A 64 km² area was enriched with iron (ambient concentrations were raised to 4 nM) and the patch was tracked using the concurrent release of an inert tracer sulfur hexafluoride. The Tully was one of three ships participating in this international study – the others being the Mexican research vessel El Puma (chartered by Canadian scientists) that arrived in the vicinity of our site on July 9 and remained after our departure (until July 28). A Japanese research vessel the Kaiyomaru arrived late on the 23rd July and will remain at this study site until August 4. The events during the Tully's 14 day occupation of this labeled enriched patch of ocean are summarized below. The initial addition of iron and a subsequent re-infusion (July 16th) resulted in a ten-fold increase in chlorophyll concentrations (0.3 to > 3 mg m⁻³), and concomitant decreases in the plant nutrient nitrate, and a drawdown of pCO₂.

RADIOISOTOPE USE: Decommission lab and report use to IOS RSO (Radioisotope Use & Wipe test forms attached)

A copy of the wipe test results was given to the first officer on board the Tully at the end of the cruise.

PROBLEMS |SCIENTIFIC GEAR



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AND OPERATIONS]:

One of our sediment trap drifters was lost. It got trapped in the propeller during recovery following a manoeuvring error. Captain Webb wrote a report regarding the incident.

The GPS signal coming from the bridge to the lab had been modified again and many of our instruments were not working properly because of this.

We had been asked to take some plankton samples for another science group at IOS. None of the gear was ready to use when we received it on the ship.

SUCCESSSES [SCIENTIFIC]:

The Line P survey was really successful. All the stations were completed as planned. The iron injection experiment was also a success.

PROBLEMS [SHIP'S EQUIPMENT/ OPERATIONS/PLATFORM SUITABILITY]:

The settings of the LAN system on the Tully need to be documented. Both main uses for it, which are data transfer from one computer to another, and transfer of email to local computers in order to reduce the traffic to the bridge as well as for convenience, could not be performed properly because all the computers were not set properly. Either a member of the ship's crew should know the system, or else the science crew will have to bring a computer/electronics person. Also, ALL cabins should have an access box to the LAN system. The water loop system in the lab is presently controlled by flow. It would have been much more appropriate and useful to have a pressure control instead of a flow control.

SUCCESSSES [SHIP]:

Despite having some very occasional problems, the loop system in the main scientific lab still provided us with all the water we needed to conduct our experiment.

For this one cruise we needed an extra bunk in the Chief Scientist's Cabin, A. This arrangement worked quite well. Hopefully it will never have to be used again, but thanks to Coast Guard and the Tully crew for accommodating us with this request. Thanks also for the "three musketeers" who happily shared the cabin.

DELAYS [OTHER THAN WEATHER]: none.

SAFETY CONCERNS:

HAZARDOUS OCCURRENCES:

A minor incident happened with radioactive materials. See Appendix A for details.

EVENT LOG:

	<u>DATE</u>	<u>OPERATIONS</u>
Entire patrol:	27 June	Start loading the Tully
	29 June	Depart Pat Bay around 1630.
	30 June	Start Line P work.
	7 July	Complete Line P work and start CTD survey for Fe experiment
	9 July	Injection of SF6 and iron
	17 July	Second injection of iron
	23 July	Depart injection site
	27 July	Arrive in Pat Bay
	28 July	Finish offloading, end of patrol.



Summary of events during iron enrichment

Iron injection experiment:

DATE JULY	REGION	SURVEY	CTD'S	SED TRAPS	BUOYS	Fe/SF6 additions
5	P35 to eddy	Mapping				
6	Eddy to p26	Mapping				
7	NW, NE, SE of p26	Mapping/site Selection				
8	NE of p26	Mapping			2 buoys#*	4 nM Fe
9	NE of p26	SF6 #1				
10	NE of p26	SF6 #2	I1, O1	Deploy O	Deploy buoy O	
11	NE of p26	SF6 #3	I2, 3, O2	Deploy I		
12	NE of p26	SF6 #4	I4, 5, O3		Redeploy buoy O	
13	NE of p26	SF6 #5	I6, 7, O4			
14	NE of p26	SF6 #6	I8, 9, O5	Recover I		
15	NE of p26	SF6 #7	I10, 11, O6	Recover O&		
16	NE of p26	SF6 #8	I12		Deploy* I	1 nM Fe
17	NE of p26	SF6 #9	I13, 14, O7			
18	NE of p26	SF6 #10	I15, 16, O8			
19	NE of p26	SF6 #11	I17, O9			
20	NE of p26	SF6 #12	I18, 19, O10	Deploy I		
21	NE of p26	SF6 #13	I20, 21, O11	Recover I, Deploy O		
22	NE of p26	SF6 #14	I22, 23, O12		Deploy* I	
23	NE of P26		I24, O13	Recover O, Deploy I	Recover* I	

* denotes Clearview 15 min uplink GPS; # radar transponder buoy, I denotes IN cast, O is OUT cast; & denotes failed recovery

SUMMARY/FINAL COMMENTS:

I very strongly recommend that science purchases its own GPS receiver. Once again, the GPS signal coming from the bridge to the lab was modified, and many of our instruments were therefore not working properly. In some cases the problems might not have been caused by the poor GPS signal, although it is the most likely explanation. In any case, a good GPS signal would have helped to trouble-shoot the problems. There were many repercussions created by the problem with the GPS signal:

- Numerous packs of paper wasted to print each data point from the SF6 instrument
- Many hours spent entering each data point manually in a spreadsheet, each data point having to be compared and matched (manually again) against the ship track in order to have all the useful information. Manual data entry is always a potential cause for errors.
- Loss of useful information from the thermosalinograph because the clock cannot keep the proper time
- Major loss of time figuring out the thermosalinograph data because of that internal clock problem
- Extra time needed to process the CTD data because the latitude and longitude of each cast will need to be entered manually, the GPS string not being decoded by the deck unit
- Potential loss of information during manual entry of latitude, longitude, and time in the logbook while performing a CTD/Rosette cast.



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All these inconveniences were extremely costly in time, during a cruise which was already very busy. The price of an independent GPS receiver is covered many times in the cost due to overtime work because of these inconveniences.

This was a very busy cruise, and I thank everyone who helped the spirit on board the ship to stay high, or at least calm. Most people were under lots of stress but dealt with things very well. Unfortunately some people were feeling so over-worked that they could not provide the little extra effort that would have made other people's lives easier. I believe that the stress level could have been lower if all the instruments had been working better before we left, and mainly if the right staff had been chosen to be part of this cruise. Some key people were needed on board who were not here, whereas some people here could only provide a limited help. If such a project happens again, better care should be taken in the choice of participating staff.

Special thanks to the crew of the John P Tully for their help throughout the entire cruise.

Marie Robert

See Appendix B for individual reports/results.



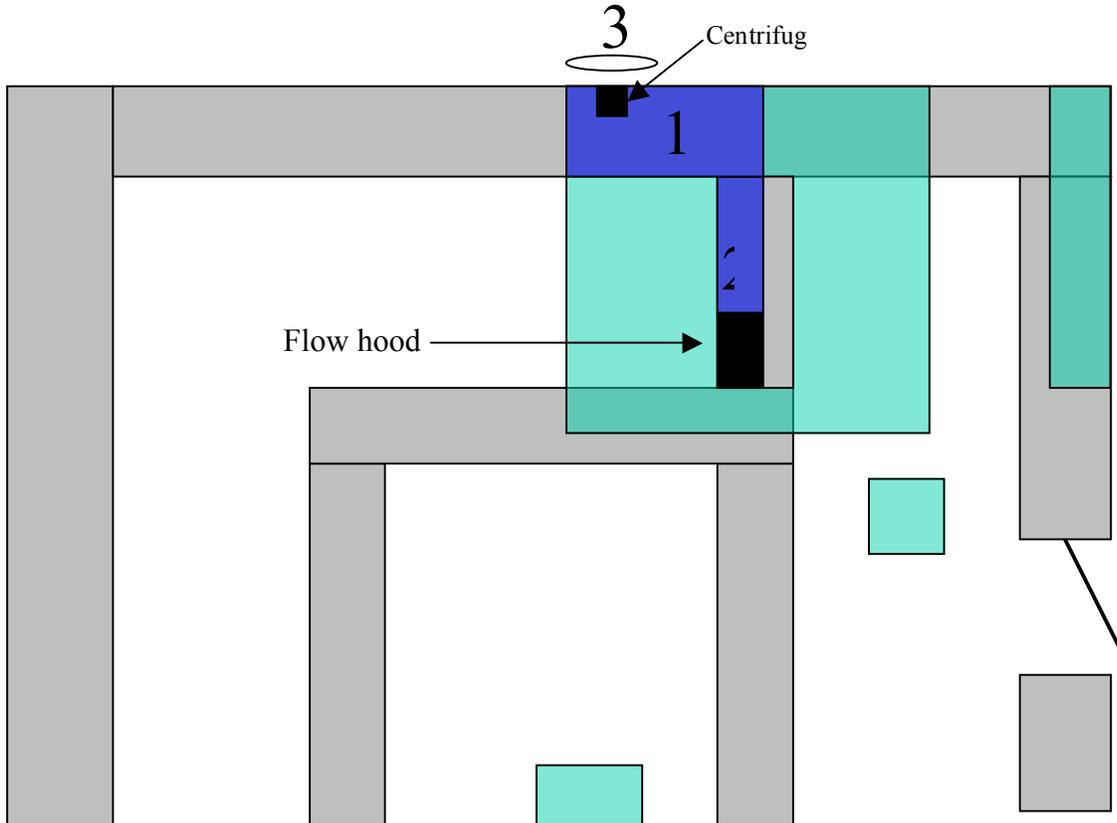
APPENDIX A

Centrifuge accident

At around 22h30 on Monday July 22nd the rotor a small benchtop centrifuge failed, causing plastic debris to spread over an area of ca. 2 m² (see drawing). The instrument was being used under normal conditions and was supervised by the user (Carol Adly) at the time of the accident. Neither the user nor the other scientists working in adjacent areas were injured. People were asked to move away and the affected area was immediately sealed off.

The centrifuge contained 12 sealed vials, each containing 1 ml of a mixture of 5% trichloroacetic acid (TCA) and < 0.2 uCi tritiated leucine (³H). All vials and debris were promptly recovered during a systematic search, ten were intact and two ruptured as a result of the initial shock. The two ruptured vials were recovered within the designated radiolabel work area and the remaining contents were emptied in the liquid waste container. The resulting spill is estimated at no more than 1.0 ml of 5% TCA containing < 0.2 uCi of ³H, which does not represent a significant health hazard for the people present in the main lab at the time. All spill paper in the affected area was removed and disposed of as solid waste. Wipe tests (100 cm²) were conducted over potentially affected area (see drawing). A sweep was performed with the portable radiation meter and levels were found to be indistinguishable from background radiation. The radiolabel work area was cleaned and new spill paper was installed.

-  Radiolabel work area
-  Area where plastic debris were





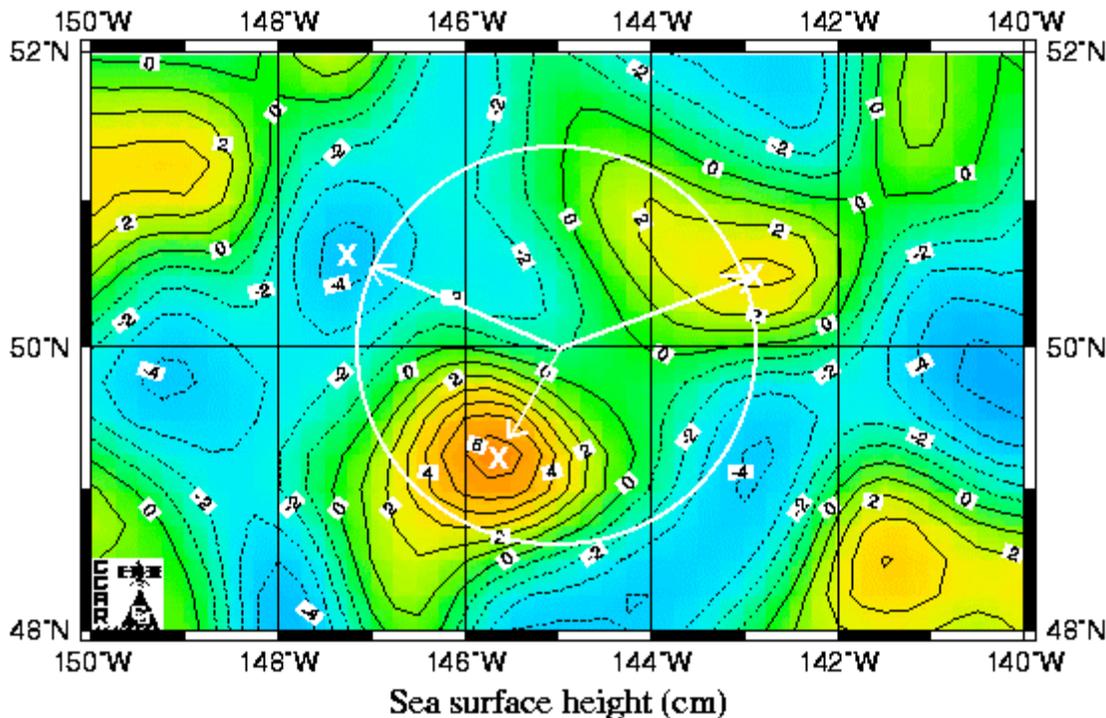
APPENDIX B

Results

OVERVIEW – PHIL BOYD

Following the completion of the Line P transect sampling we conducted a mesoscale iron enrichment experiment at a site to the NE of P26 (ocean station Papa). The rationale for this experiment was to follow the changes in phytoplankton growth rate and related biogeochemical properties of the iron-limited resident cells. Site selection was based upon the location of waters with low density (to minimise any potential subduction of the labelled iron-enriched waters), uniform physical characteristics (in particular to the NE of the site, the predominant direction of the drogued drifter buoys we deployed), and matching the HNLC condition (iron-stressed cells, high macronutrients and low chlorophyll). The waters in the immediate vicinity of station Papa did not meet all of these criteria (salty, colder waters, low degree of uniformity in the physical properties). There was also evidence of two eddy-like features (see below, one to the SW and one to the NE of P26 that we had to take into consideration in our site selection i.e. avoid.

TOPEX/ERS-2 Analysis Jul 1 2002



Satellite altimetry data showing 2 eddy-like features to the SW and NE of P26 (50N 145W, data courtesy of Bill Crawford, IOS). The white circle, centered at Station Papa, has a radius of about 150 km.



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Summary of events

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* denotes Clearview 15 min uplink GPS; # radar transponder buoy, I denotes IN cast, O is OUT cast; & denotes failed recovery

The initial addition of iron and a subsequent reinfusion (July 16th) resulted in a ten-fold increase in chlorophyll concentrations (0.3 to > 3 mg m⁻³), and concomitant decreases in the plant nutrient nitrate, and a drawdown of pCO₂.



CRUISE SUB REPORT SUMMARY

2002-16

LINE P AND SERIES

Keith Johnson and Nes Sutherland

LINE P

An abbreviated sampling program was utilised to allow for maximum time for the SERIES iron injection experiment. The normal sampling program for DIC, alkalinity and C13 was accomplished at the major stations. For iron and DOC P04 was skipped and P12, P16, and P20 were reduced to Go-flow sampling to 200 meters rather than the usual 1000 meters. Pumping at these stations was also eliminated to save time. For station P26 pumping to 40 meters and go-flos to 600 were completed as this could also be used as a control for the iron enhancement experiment. There were some problems with borrowed Go-flos from Japan both mechanically and in cleanliness, which had to be rectified. Approximately 34 depths including duplicates were sampled and 96 samples collected for iron for either reactive, dissolved, or <0.03u (onboard analysis) and total dissolved and total for shore analysis were collected. For organic carbon we collected filtered DOC (0.2u using Opticap) and TOC (unfiltered) samples from all Go-flo and pump samples. For inorganic carbon (DIC and alkalinity) 110 depths were sampled as well as a calibration cast and many duplicates. For C13 samples were collected at station P only (sampled in duplicate).

SERIES Iron enrichment study

The sampling program for iron, trace metals, ligands and organic carbon was modified due to the shallow mixed layer. Rather than sample to 200 meters which would require at least 2 to 3 hours the sampling was limited to pumping only, to 40 meters, as the mixed layer was 30 meters. The in station was normally sampled twice per day late morning and early evening. The morning station was limited to one depth (10 meters) which was sampled for all parameters (iron –reactive, dissolved, <0.03, total dissolved and total; ligands for Dr. Powell and Dr. Takeda; trace metals for Dr. Sohrin, iron solubility for Dr. Kuma; biological response for Dr. Boyd and DOC/TOC for Dr. Wong. Dr. Trick also collected samples for chlorophyll etc. from the bypass line. The late afternoon or early evening sampling was usually a 4-depth profile (10, 20, 30 and 40 meters). On occasion 6 or 8 metres were also sampled and a surface using the Zodiac when time permitted. Over the two-week period approximately 100 depths were sampled for iron analysis. Some of the initial values for reactive or unfiltered iron were in the 4 nM range while dissolved was as high as 2.5 nM. Values declined very quickly over the first few days when the iron was contained in the top 10 meters due to a weak thermal layer and very calm weather. Winds and rough seas mixed the iron down uniformly to 30 meters on the 13th to 14th with reactive iron close to 1 nM on the 13th and dissolved close to 0.5 nM down to 30 meters on the 14th. A second smaller injection on the 16th brought levels up to as high as 2 nM for reactive (20 m) and 0.6 to 0.7 nM for dissolved in the 3 to 10 meter depths on the 17th. By the 20th this had been reduced to less the 0.7 nM for reactive and down to 0.2 nM for dissolved and by the 22nd were very close to background.



The SF6 tracer component

Cliff Law, Mike Arychuk, Val Forsland, Marie Robert, Rousilin Chichkin, Tim Soutar

SF6/Iron release (0105-1845 9/07/02)

Approximately 8000 litres of seawater were sparged with pure SF6 gas during the Line P survey. The sparging was halted at intervals whilst on station for the Line P casts, during which time SF6 in the air in both lab and on deck became elevated. SF6 saturation of the seawater was monitored at two hour intervals by headspace analysis of the water using TCD-GC. From comparison with SF6 levels obtained during the February trial, the saturation appeared to be complete after 36 hours, and the headspace in the tanks was displaced with water and the tanks sealed.

Extensive surveying over a two day period identified the most promising site for the release. A Clearsat drifter buoy was deployed at the nominal centre and its transport monitored for a 12-hour period to determine that the drift rates was acceptable. The Clearsat drifter buoy gave GPS position updates at 15 minute intervals and provided the Lagrangian reference for the release, with the release track corrected for the drifter buoy movement. A Radar transponder on a drifter buoy was also deployed in close proximity to the Clearsat buoy as a back-up. The release track was an expanding square covering 4.75 x 4.74 nmiles, with a distance between transects legs of 0.4 nmiles. The release was achieved using the *Tullys* EcPIN Search and Rescue package which has the capability to set search track patterns and update their centre point at regular intervals. The total ships track length during the 17.7 hour release was ~80 nmiles, at a speed of ~ 4 knots. The SF6 and iron solutions were mixed and pumped over the side at rates of 5 and 20 litres/min to a depth of ~7m as maintained by attachment of the outlet to a Hi-Fin fish.

SF6 mapping (9-23/7/02)

The ship remained outside the patch for the following 4 hours (2245) to allow the SF6 to mix vertically into the surface mixed layer. The patch was located at 2345 where high levels of SF6 were encountered; this initially decreased towards the patch centre indicating that the SF6 had not mixed in laterally. The SF6 became uniformly dispersed during the mapping and the Clearsat buoy remained at the patch centre (50 10.55N 144 46.04W at 0615 10/07/02). Sampling of surface waters for Ligands was coordinated with the SF6 during the first survey.

For the remaining 13 days the daily program consisted of mapping for 12 hours starting from 2000-2300 to 0930-1100, with the mapping coordinated by reference to the Clearsat buoy current position, the recent buoy drift over the previous 12 hours, the previous SF6 centre position and the corrected Lagrangian SF6 distribution from the previous nights mapping. As the experiment progressed and the biological response became apparent this was also augmented by underway surface pCO2 and fluorescence. The *El Puma* was given the position at the patch edge at ~0730 each morning and then the patch centre coordinates at ~0900, so that they could do an IN station cast whilst the *Tully* completed mapping. The *Tully* would then follow with an IN station. The mapping system was generally started up again in late afternoon to relocate the patch centre for the 2nd IN station. The rate of drift of the patch was generally low (~0.15-0.4 nmiles/h) which aided the mapping, although early on (around Day 3-4) the patch began to elongate along a N-S axis which required a shift in mapping strategy with the "propellor-style" mapping survey replaced by a sawtooth track in a N-S orientation. This "Xmas-tree" track was quite successful in constraining the patch, and the N and S boundaries were often closed even when the patch was 16 miles long and 5 miles wide. Mapping of the patch only became difficult on two nights when increased windspeeds combined with an increased easterly transport of the Clearsat drifter buoy. Pumping of surface water samples for iron sampling was occasionally coordinated with the SF6 mapping.



Iron Re-infusion (144516/7/02 - 0800 17/7/02)

An expanding rectangle was used for re-infusion of the iron, as the patch was elongated along the N-S axis. The re-infusion covered 7.3 by 3.7 nmiles, with a release track of ~ 85 nmiles and ship speed of 4 knots, with 0.54 nmiles between transects in a N-S direction and 0.27 nmiles in an E-W direction. Once again the release was coordinated with reference to, and began from, the position of the Clearsat drifter buoy. Iron was added, at a rate of 13 l/min, with the SF6 mapping system used to monitor the release; when SF6 decreased below a pre-determined concentration the pumps were turned off to prevent iron being injected outside the tracer patch. The re-infusion was briefly stopped and re-started due to concerns over the Hi-Fin.

The IOS SF6 mapping analytical system (sparge-cryogenic trap with ECD-GC analysis) worked well and reliably with few problems throughout the experiment, and the patch could still be distinguished when SF6 levels had fallen to less than 10 time background levels on the final mapping survey. Initial contamination was dealt with by optimisation of the valve program. The only problems were the lack of a water watcher, which meant that the system had to be constantly monitored to prevent flooding, and the mapping package which did not plot the SF6 concentration consistently and did not work at all for the final three nights mapping. Both of these faults put excess pressure on the operators and data handlers, and it is a testament to their efforts and tenacity that the mapping was so successful. We also thank the officers and crew for their tremendous help and assistance with the mapping, and being so accomodating in letting us take the reins of the ship.

Vertical dispersion of the SF6

Mike Arychuk, Cliff Law

Twenty-three vertical profiles were obtained of dissolved SF6, including one background (OUT station) cast. In addition transferred water samples from *El Puma* and spot samples from 10m at some of the OUT stations were also analysed, with a total of 270 analysis. The OUT station profile indicated SF6 concentrations on the order of 1.1-1.4 fmol/l in agreement with equilibrium with the atmosphere. At the IN stations the SF6 was initially restricted to the upper 15m due by relatively minor stratification within the surface "mixed" layer, but after increased windspeeds on Day 5 had mixed down to ~25m. The vertical profiles indicate cross-isopycnal transfer of SF6 with a high resolution cast on 22/7 nicely constraining the decline of the SF6 in the pycnocline. The data look promising for assessing the rate of vertical diffusion across the pycnocline and so the vertical nutrient exchange. The IOS discrete SF6 analysis system worked well with good sensitivity and reproducibility, with some problems experienced with trap heating. Cryogenic trapping was achieved using liquid nitrogen for the final two days when the liquid CO2 ran out.

Trace gases

Cliff Law

Dissolved nitrous oxide (N2O) profiles (5-75m) were obtained on 22 IN casts, 8 OUT casts and 2 pre-release casts using static headspace equilibrium and analysis by ECD-GC. Air measurements were also made for flux calculation. The dissolved vertical profile was largely dictated by temperature and solubility, although there was evidence of an increase in N2O concentration in the pycnocline at the IN stations during the latter part of the experiment. Coincident measurements of nitrite and ammonium (Janet Barwell-Clarke) and bacterial production (Carol Adley) were made on selected IN and OUT station casts to aid the interpretation of this data.



Dissolved methane (CH₄) measurements were made on the same water samples but are not expected to yield valuable data due to the reduced sensitivity of the FID detector following shipment from the UK to NZ.

Dissolved carbon monoxide (CO) was measured by headspace equilibrium and Reduction Detector analysis on 4 vertical profiles at the start of the experiment and in the atmosphere on several occasions. The relative rates of photolytic production and microbial consumption of CO at both the IN and OUT stations were determined in 11 deckboard incubations using UV-transparent tubes in ambient light and in black bags at ambient surface temperature. During the deck incubations ambient UV was recorded using separate UV-A and UV-B sensors and samples collected for chromophoric dissolved organic matter (CDOM) (transferred to *El Puma* for analysis by Lori Ziolkowski) and dissolved organic carbon (Nes Sutherland). One set of CO samples were transferred to the *Tully* from a solar simulator incubation on the *El Puma* (Lori Ziolkowski); however subsequent problems with filters in the solar simulator unit prevented more samples.

Thanks to Doug Anderson, Tim Soutar and the *Tully* crew for CTD and rosette operations.

SERIES Cruise Report

Jean-Eric Tremblay, Graham Peers and Carol Adly
(McGill University, Price)

During the series cruise, McGill's team (Price) investigated the effect of iron fertilization on bacterial dynamics, the uptake of iron and carbon by different size groups of planktonic organisms (bacteria, phytoplankton), the elemental composition of phytoplankton and oxidative stress indicators. The vast majority of samples were stored and preserved for future analysis on shore. Preliminary results obtained by chlorophyll-*a* extraction indicate that total phytoplankton biomass increased by one order of magnitude during the first two weeks of the experiment. The biomass of the > 20 µm size fraction (mostly diatoms) increased by a factor of 50, showing that the experiment was successful in stimulating the production of the large phytoplankton that generally contribute most to the vertical export of carbon.

The uptake of iron and carbon was determined simultaneously by dual labeling with ⁵⁵Fe and ¹⁴C. In order to investigate uptake kinetics and the partitioning of different sources, the iron was provided in trace and saturating concentrations and bound to either EDTA or DFB. Duplicate samples were incubated on deck for 8 hours under simulated *in-situ* light conditions. Post-incubation size fractions were obtained by cascade filtrations onto 20, 5, 1 and 0.2 µm filters. Matching chlorophyll-*a* concentrations were determined by standard fluorometric techniques.

Changes in the elemental composition of phytoplankton (POC, PON, BSi, POP) during the bloom were monitored using large-volume filtrations. Owing to the large quantity of material needed for these analyses, samples were first concentrated by sequential, tangential flow filtration onto 20, 5 and 0.4 µm membranes (volumes ranging from 20 to 70 liters). The concentrates were filtered onto pre-combusted GF/F filters (POC, PON, POP) and 0.4 µm polycarbonate filters (BSi) and stored frozen for future analysis.



The bacterial response to iron enrichment was followed both during the bloom and in a series of shipboard incubations containing Fe and/or DOC. Production was measured by the rate of leucine incorporation and samples were preserved for analysis of biomass. Changes in bacterial carbon metabolism were monitored by isolating the bacterial size fraction onto 0.45 μm filters for future enzymatic analysis. Growth efficiency was estimated by incubating bacteria with ^{14}C -labelled phytoplankton extract and following the fate of carbon (CO_2 vs. biomass production). These experiments will address the importance of iron in determining whether bacteria act as a 'link' (returning DOC to higher trophic levels) or a 'sink' (respiring DOC as CO_2) for carbon.

The importance of other micronutrient metals (Mn, Cu and Zn) for phytoplankton production was assessed in deckboard incubations. No other metal appeared to stimulate phytoplankton biomass as measured by changes in chlorophyll-a over the period of 2 weeks. To assess whether or not there was any physiological response to the other metals, short term ^{14}C incubations were performed.

Phytoplankton oxidative stress parameters were monitored throughout the fertilization and during the initial site selection. Large phytoplankton were collected on 5 μm filters for later measurement of oxidative stress enzymes such as catalase and superoxide dismutase (both Fe-containing). Plankton were also collected on GF/C filters for analysis of oxidative damage products. Reactive oxygen species generation rates were measured in collaboration with Charlie Trick. Generation of superoxide will be normalized to short term ^{14}C incubations to determine relative oxidative stress in and out of the patch.