# Voyage report TAN1109 June 6 to June 30 2011



Trace metal rosette coming inboard brim full of low metal waters.



Western portion of GP13 section from Brisbane to South of Tahiti; Sections from the CLIVAR P06 line in 2002/3.

# Goals

a) Carry out leg two (S of New Caledonia to S of Tahiti) of the GEOTRACES GP13 zonal section (Brisbane to Lima, <u>http://www.ldeo.columbia.edu/res/pi/geotraces/</u>) by vertically sampling dissolved and particulate trace elements every degree of longitude along 32.5 S from 172W to 150W (in situ pumps and TM rosette and TM fish).

b) Conduct conventional physical, chemical and biological sampling to provide an underpinning oceanographic description of this section (CTD rosette and TM fish).

c) Further enhance our understanding of the biogeochemical drivers of oligotrophic subtropical waters N of New Zealand by building on observations from prior studies (COST, NCycle and PINTS) (CTD rosette, TM fish sampling to set up perturbation experiments).

d) Explore the stoichiometry of the major and minor elements in both the particulate and dissolved phases

| Participants      |                          |
|-------------------|--------------------------|
| NIWA              |                          |
| 1 Philip Boyd     | Voyage Leader NIWA/Otago |
| 2 Els Maas        | NIWA                     |
| 3 Greg Olsen&     | NIWA                     |
| 4 Cara Mackle     | NIWA                     |
| 5 Scott Nodder    | NIWA                     |
| 6 Peter Gerring   | NIWA                     |
| 7 Neill Barr      | NIWA                     |
| 8 Matt Walkington | NIWA                     |
| 9 Andrew Marriner | NIWA                     |
| 10 Karl Safi#     | NIWA                     |
| 11 Debbie Hulston | NIWA                     |
| 12 Cliff Law      | NIWA                     |

#### Other Institutions

| 13 Michael Ellwood       | Australian National University (ANU) |
|--------------------------|--------------------------------------|
| 14 Scott Meyrick         | ANU                                  |
| 15 Malcolm Woodward      | Plymouth Marine Lab, UK              |
| 16 David Drapeau         | Bigelow Marine Lab, USA              |
| 17 Sylvia Sander         | Univ. of Otago                       |
| 18 Sruki Thalayappil     | Univ. of Otago                       |
| 19 Melanie Ringold-Gault | Univ. of Otago                       |
| 20 Tina Sommerfield      | Univ. of Otago                       |
| 21 Linn Hoffman          | Univ. of Otago                       |
| 22 Jill Sohm             | Univ. S. California, USA             |
| 23 Amandine Sabadel      | Univ. of Otago                       |
| 24 Zac Powell            | Univ. Of Otago                       |

&Chemical safety officer # Deck safety officer

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#### Narrative

We commenced loading the vessel on Sunday 5<sup>th</sup> June and completed loading on Monday 6<sup>th</sup>. Sailing was delayed by 12 h until 0700 h on Tuesday 7<sup>th</sup> due to a dental emergency and engine troubles. We departed Wingyard Wharf at 0715 h on 7<sup>th</sup> June and headed for our first sampling station near to the Brothers undersea volcano (179E 32S) and successfully sampled the plume at > 1000 m depth using the conventional CTD rosette. We then proceeded on to 180, 35S where samples were collected for Ocean Acidification experiments and for incubations with N fixers. We then steamed for 36 h to pick up the GP13 west to east transect at 172W, and thus had three 'overlap' stations with the previous Australina leg of GP13. At 170W we carried out our first mega station and then proceeded eastwards, carrying out 5 h standard stations (TM rosette to 1500 m; CTD rosette hydro cast to 1500 m and a bio cast to 200 m. As we transited eastwards we had to adjust the timing of the longer 18 h mega and super stations, as in some instances theweather was marginal for deep casts or deep pumps. Around halfway through our section we lost the Mclane pumps (6 of them in > 5000 m of water). The TM team were able to sample large volumes of water at 30, 100 and 300 m and prepare particulate samples. We reached GT23 at the eastern end of the transect (150W, 32.5S, 900 nm S of Tahiti) on Wednesday 22 June and then sailed for home. Our return home included ongoing aerosol and underway sea water sampling. Towards the end of the voyage we altered course to med-vac the Chief Engineer on the Chatham Islands. We docked at 0730 h on Friday 1 July in Wellington.

### Individual reports

## Philip Boyd

## (Phytoplankton active fluorescence; aerosol dust sampling)

On all bio-casts, samples were taken and dark acclimated for 1 h then run through a Chelsea Instruments FRRF to measure Fv/Fm (phytoplankton photosynthetic competence) and other biophysical parameters such as s (cross-sectional area of photosystem II). These measurements were also made on a detailed profile fo the DCM at 150W, and on all time points of the Ocean Acidification and dust dissolution experiments (see report of Law and Marriner). In general the cells were in poor physiological shape (Fv/Fm ca. 0.1, but higher values were consistently observed in the DCM (up to 0.45).

Aerosol sampling using a Lear-Siegler Hi-Vol sampler (48 m3/h) was carried out daily on the monkey island. Sector control was set to ensure no contaminated air from the ships stacks were sampled. Sampling time was usually of 24-30 h duration and 9 samples (including two blanks) were taken a long the GP13 transect. The filters will be analaysed for both trce metals and the major anions.

#### Voyage report - Jill Sohm

At all stations, phosphate turnover (demand) was determined in the mixed layer. Particulate phosphorus samples were also taken in order to determine PO4 affinity, and thus P stress. Els and Debbie also determined phosphatase and glucosidase activity in the same samples I determined P turnover. At the large stations, P uptake kinetics were determined. P turnover was also determined in the

CO2 experiments, as well as one Fe/dust addition experiment. Samples were also taken at all stations for determining the composition of the *Synechococcus* community, and at a few stations to try and culture *Synechococcus*.

In general I will be measuring phosphorus cycling in surface waters, looking at DIP turnover and uptake kinetics using 33P. These assays can provide a proxy for P stress of the microbial community. In support of these measurements I will also be measuring particulate P in surface waters. The DIP turnover measurements will be carried out in the CO2 perturbation experiments as well. In support of some of my other research interests in cyanobacteria, I will also be making microscope slides to look for evidence of extracellular polysaccharide production in some phenotypes of *Crocosphaera* and collecting samples to archive for the future investigation of the distribution of different clades of *Synechococcus* using qPCR.

# Karl Safi

# Microzooplankton abundance, biomass and grazing Aims:

- To measure the distribution, abundance and biomass of microzooplankton (including ciliates and nanoflagellates) along the West-East transect line in surface epipelagic waters.
- To measure the grazing pressure of microzooplankton populations on phytoplankton and assess their role in trophic linkages in surface waters
- To compare the standard "dilution experiment grazing methodology" with a new C<sup>14</sup> carbon dilution method.
- Where possible to assess distribution biomass and abundance in deeper mesopelagic and bathypelagic waters

# Sampling/experiments achieved

We successfully collected microzooplankton samples (including ciliates, 110 samples and nanoflagellates, 109 samples). Microzooplankton were collected at 5 depths at all stations (0 - 100 m). Nanoflagellates were collected at 9 depths at super and mega stations (surface and ~5500m) and 5 depths at standard stations (surface -1500m). We missed four standard profiles (intermittently) for flagellate counts due to a lack of preservative and analysis costs.

Microzooplankton grazing was measured intermittently 13 times along the transect using the dilution grazing method. Experiments were conducted at ~15 m to represent mixed layer grazing. The dilution microzooplankton grazing method, in brief, is conducted by measuring microzooplankton grazing over 24 hours in on deck incubations. These experiments were prepared by collecting water off the CTD (filtering at 200  $\mu$ m) and then mixing this water with 0.2  $\mu$ m 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 included size-fractionated chlorophyll *a* (200  $\mu$ m, 20  $\mu$ m, 2 $\mu$ m), picoplankton counts (eukaryotic and prokaryotic), autotrophic and heterotrophic

flagellate counts, microzooplankton, and nutrients. Each of these are measured at the beginning and the end of the incubations. We also conducted 5 additional dilution experiments which we run in parallel to standard dilution experiments to compare <sup>14</sup>C based dilution- experiment with our standard methodology. The <sup>14</sup>C based dilution methods followed those described by Nicholas Welschmeyer.

Nutrients were measured on board while all other processing of samples i.e. picophytoplankton, chlorophyll *a* (200  $\mu$ m, 20  $\mu$ m, 2 $\mu$ m), autotrophic and heterotrophic flagellate counts, and microzooplankton counts will be completed on our return (~1130 samples; 696 Chlorophyll a, 312 picophytoplankton, 26 microzooplankton and 26 flagellate samples, 70 C<sup>14</sup> samples).

# NUTRIENTS Cruise Report RV Tangaroa TAN1109 June 2011. Malcolm Woodward and Amandine Sabadel\* PLYMOUTH MARINE LABORATORY, UK (\* University of Otago, Dunedin)

### **OBJECTIVES:**

To investigate the spatial and temporal variations of the micromolar nutrient species; Nitrate, Nitrite, Silicate, and Phosphate during the research voyage in the Southern Pacific Ocean as a component of the New Zealand Geotraces programme along part of the Geotraces GP13 zonal section along 32 degrees 30 minutes South, from 172 West to 150 West. We also deployed innovative analytical techniques for detecting nanomolar nutrient concentrations of Ammonium, Phosphate, Nitrate and Nitrite in the surface oligotrophic nutrient deplete waters encountered for most of this voyage. Nutrient analysis and sampling was carried out according to GO-Ship protocols wherever possible, and the micromolar samples were run alongside certified International Nutrient reference materials from KANSO, Japan, this study also being part of a global programme (IOC-ICES) to improve nutrient analysis data quality world-wide. Samples were also analysed for on-deck experiments carried out for Dust and Iron additions and also for regulated Ocean Acidification experiments. Numerous samples were also analysed for nanomolar nitrate, nitrite and phosphate, taken during the first leg of this voyage carried out by the Australian Ship the Southern Surveyor.

#### SAMPLING and ANALYTICAL METHODOLOGY:

The micro-molar analyser used was the PML 4 channel (nitrate, nitrite, phosphate, silicate) Bran and Luebbe AAIII segmented flow, colorimetric, autoanalyser, using classical proven analytical techniques.

Nanomolar ammonium was analysed using a method based on the gas diffusion of ammonia across a Teflon membrane due to a differential pH gradient, and there then followed its reaction with a fluorescent reagent and the subsequent detection by a Jasco high precision fluorimeter.

Nanomolar nitrate, nitrite and phosphate were detected using colorimetric methodologies as with the standard segmented flow analyser, but using 2 metre Liquid waveguides capillary cells as the detector flow cells.

Water samples were taken from either a 24 x 10 litre stainless steel CTD/Rosette system (SeaBird), or an automatically fired trace metal free CTD, 12 bottle system, on a trace metal free rosette system. These samples were processed within the trace metal free sampling laboratory container .The CTD bottles were sub sampled from the CTD bottles into acid clean, 'aged', 60 mls HDPE (nalgene) sample bottles and analysis for the nutrient samples was in most cases complete within 2-3 hours of sampling. Clean handling techniques were employed to avoid any contamination of the samples, particularly for the ammonium samples. Gloves used were Dura-Touch, and all people sampling prior to the nutrients from the CTD wore these gloves to avoid any contamination. Samples were not decanted and kept tightly closed until just before analysis for the ammonium, this to avoid any contamination from external sources. No water column water samples were frozen or stored, except for minimal periods.

# CTD SAMPLES ANALYSED by AAIII Micromolar, and Nanomolar analysers.

Details of all samples analysed can be found in the cruise 'event' log available separately.

# **CRUISE RESULTS and SUMMARY**

The 5-channel autoanalyser worked very well throughout the cruise as did the nanoamnmonium analyser. The liquid waveguide had problems in that the waveguides were damaged during the flights to New Zealand and despite repairs the nitrate channel was almost a constant problem during the cruise to get good results. The nanomolar nutrient results from the Australian leg of the voyage were unreliable and apparently contaminated, either by the sample tubes or by the freezing process, which is never to be recommended for nutrients, however in this case there was no option but to try. Due to the large sample work load it was not possible to process any sample results during the voyage and these will be done on return to the UK.

# THANKS:

To the RV Tangaroa, her officers, crew, and catering team for making it all possible. Thanks to Phil Boyd and Cliff Law for giving me the invitation and opportunity to participate in this voyage and thanks to the New Zealand International Traveller Grant that supported transportation and consumables.

Also thanks to Director and Science Team at PML for contributing the staff time of EMSW, and to University of Otago for allowing AS to join the voyage, and make an invaluable contribution to the nutrient team output.

Malcolm Woodward and Amandine Sabadel. 25th June 2011

Cliff Law & Andrew Marriner

- 1. Water column
- a) Surface mixed layer Nitrogen fixation profiles

2.4 Litre water samples collected in duplicate from 15, 30, 50, 75 & 100m at 19 stations & incubated with  $^{15}$ N-N<sub>2</sub> for 24 hours followed by filtering. Total 323 N fixation samples collected.

- b) N<sub>2</sub>O concentration & isotopes
  240ml water samples collected in duplicate at 15 depths at 4 mega/super stations on the CTD Hydro casts for Nayeem Muhammed
- c) O<sub>2</sub> concentration & isotopes
  120ml water samples collected at 15 depths at 4 mega/super stations on the CTD
  Hydro casts for Nayeem Muhammed
- d) Water isotopes

5ml samples collected at all depths at 16 stations on the CTD Hydro casts for Nayeem Muhammed.

- e) Underway Nitrous oxide and methane
  Surface water and atmospheric N<sub>2</sub>O & CH<sub>4</sub> were measured at 6- minute intervals, from 150W (23/6/2011) to Outer Cook Strait (30/6/2011), using a semi-autonomous system comprising an air-water equilibrator & Gas Chromatograph.
- 2. Incubations (Cliff Law, Linn Hoffman, Karl Safi, Andrew Marriner)

a) Ocean acidification incubations

Water was sampled from ~25m using a trace metal clean weighted line and teflon pump at three stations into 9 x 23-Litre cubitainers. Triplicates samples were run for the Control (ambient conditions) & two treatments, High CO2 (pH ~7.8) & Greenhouse (pH ~7.8 &  $+3^{\circ}$ C). pH was adjusted using pure CO2 and permeable tubing with continuous pH monitoring of all treatments using a Labview controlled sequential sampler linked to a spectrophotometer with colourimetric measurement using Thymol Blue. The target pH was generally reached after 12-18 hours, after which a number of parameters (see Table below) were sampled at T0, Day 2 and Day 4 or 5.

|                         | OA1       | OA2        |
|-------------------------|-----------|------------|
| Cubitainers filled      |           |            |
| Station No on event log | 4         | 45         |
| Date                    | 8/06/2011 | 16/06/2011 |
| Start Time              | 2015      | 0045       |
| Lat                     | 35.00S    | 32 30.958  |
|                         |           | 162        |
| Long                    | 180.00W   | 59.63W     |

| Depth:        |              | ~25m      |            |            | ~25m       |            |          |
|---------------|--------------|-----------|------------|------------|------------|------------|----------|
| Sampling      | For          | TO        | D2         | D5         | TO         | D2         | D4       |
| Date          |              | 9/06/2011 | 11/06/2011 | 14/06/2011 | 16/06/2011 | 18/06/2011 | 20/06/20 |
| Start Time    |              | 1230      | 1600       | 1740       | 1600       | 1430       | 1430     |
| Parameter     |              |           |            |            |            |            |          |
| Fe & ligands  | Linn         | X         | Х          | Х          | Х          | Х          | Х        |
| DIC           | Linn         | Х         | Х          | Х          | Х          | Х          | Х        |
| Nanonutrients | Malcolm      | X         | Х          | Х          | Х          | Х          | Х        |
| Fv/Fm         | Phil         | X         | Х          | Х          | Х          | Х          | Х        |
| Flow Cytom    | Els/Debbie   | X         | Х          | Х          | Х          | Х          | Х        |
| BP            | Els/Debbie   | X         | Х          | Х          | Х          | Х          | Х        |
| DNA           | Els/Debbie   | Х         | Х          | Х          | Х          | Х          | Х        |
| Enzymes       | Els/Debbie   | Х         | Х          | Х          | Х          | Х          | Х        |
| P uptake      | Jill         | X         | Х          | Х          | Х          | Х          | Х        |
| Synnec        |              |           |            |            |            |            |          |
| diversity     | Jill         | X         |            | Х          | Х          |            | Х        |
| nifh RNA &    |              |           |            |            |            |            |          |
| DNA           | Tina         | Х         |            | Х          | Х          |            | Х        |
| N fixation    | Cliff/Andrew | Х         | Х          | Х          | Х          | Х          | Х        |
| Carbonate,    |              |           |            |            |            |            |          |
| BSi           | Dave         | X         | Х          |            | Х          | Х          |          |
| TEP           | Karl         | X         |            | Х          | Х          |            | Х        |
| Lugols        | Karl         | Х         |            | Х          | Х          |            | Х        |

# b) Iron and dust incubations

Water was sampled from ~25m using a trace metal clean weighted line and teflon pump at two stations into 15 x 2.4-Litre bottles. Triplicates samples were run for the Control (ambient conditions) & treatments including + FeCL<sub>2</sub>, Australian dust (Brisbane & Red), Volcanic Ash (Japan), EPS & Protoporphyrin. Control & treatments were sampled as detailed below.

|                         | ID1        | ID2        |
|-------------------------|------------|------------|
| Station No on event log | 30         | 93         |
| Date                    | 13/06/2011 | 21/06/2011 |
| Start Time              | 1625       | 1650       |
| Lat                     | 32 30.085  | 32 26.40S  |
| Long                    | 166 59.90  | 152 00.52  |
| Depth:                  | ~25M       | ~25m       |
| Sampling For            |            |            |
| Date                    | 16/06/2011 | 24/06/2011 |
| Start Time              | 1230       | 920        |

## Parameter

| Fe & ligands  | Linn         | X (15/06/2011 1120) | Х |
|---------------|--------------|---------------------|---|
| Nanonutrients | Malcolm      | Х                   | Х |
| Fv/Fm         | Phil         | Х                   | Х |
| Flow Cytom    | Els/Debbie   | Х                   | Х |
| BP            | Els/Debbie   | Х                   | Х |
| Enzymes       | Els/Debbie   | Х                   | Х |
| P uptake      | Jill         |                     | Х |
| N fixation    | Cliff/Andrew | X                   | Х |

All went well and there were no significant problems with the sampling or incubations. Many thanks to those who helped out with the pumping and incubations, particularly Scott & Pete, Fred & Alan, Sylvia & Michael.

## Trace metals group

A dust sampling program and an integrated transect were carried out between the 7<sup>th</sup> and 30<sup>th</sup> of June 2011 in the southwest Pacific Basin as part of the GEOTRACES campaign. The aim of the program was to characterise trace metal and nutrient distributions along a latitudinal transect between 172 W, 32.5 S and 150 W, 32.5 S. A stop was also made at the Brothers under-sea Volcano (179.03 W, 34.52 S) along the Kermadec Arc in an attempt to retrieve samples from the hydrothermal plume.

The Ocean is vitally important to the regulation of the earth's climate and plays a particularly important role in regulating the concentration of atmospheric carbon dioxide. An important component of the system involves the biogeochemical cycling of trace metals. Previous studies have already highlighted the importance of iron as a key micronutrient for marine productivity, however little is known on the importance of other trace metals such as copper, zinc and cadmium. As well as ascertaining the distribution of trace metals, the group will also characterise the distribution of trace metal isotopes and determine the factors affecting their fractionation.

The Otago group includes Sylvia Sanders, Melanie Ringold-Gault, Zach Powell and Sruthi Thalayappil. They will be responsible for determining trace metal speciation in each of the samples. Sruthi Thalayappil conducted bio-remineralisation and dust dissolution experiments en-route and intends to ascertain the dissolution kinetics for iron minerals.

The Otago group will collaborate with Michael Ellwood, Claire Thompson and Scott Meyerink of ANU. Michael Ellwood will be responsible for the isotopic analysis of trace metals including iron and zinc. Claire Thompson will determine the cycling of copper in the global ocean through the analysis of copper isotopes. She will also determine copper speciation and ligand distribution. Scott Meyerink assisted with the sample collection during the New Zealand Leg.

Zach Powell will be analysing plume samples for trace metal speciation. He intends to characterize the source(s), function and importance of ligands produced in hydrothermal vents. The intention will be to ascertain the effects of hydrothermally produced ligands on the biogeochemical cycling of trace metals in the global oceans.

Melanie Ringold-Gault will establish depth and surface distributions of cadmium isotopes and compare these with samples taken during a sub-Antarctic cruise. She intends to look at any potential biological factors that could affect the fractionation and distribution of cadmium isotopes in the ocean.

Over 1000 samples were collected during the Australian and New Zealand Voyages. Samples were obtained using a Trace metal Rosette (Fig 1), fitted with 12 Trace metal clean Nisken bottles. Trace metal clean procedures were strictly adhered to during all stages of the sampling process. This included collecting the bottles from the rosette and mounting them onto a frame inside a clean lab and filtering samples into bottles (cleaned prior to the voyage).

Filtering was done using a  $0.2 \mu M$  polycarbonate filter cartridge. This was done to remove any particulates, or living organisms that could potentially have any adverse effects on the samples. Trace metal and isotopic samples were then double bagged and placed in fish bins, while ligand samples were frozen at -20°C in the ships freezer.



Figure 1: Trace metal Rosette and Nisken Bottle. It is important to note that trace metal clean procedures were followed during all stages of the sampling process.

With the loss of the Mclaine Pumps; the trace

metals team did a series of 30, 100 and 300 meter casts in an attempt to sample for particulates. Approximately 30-40 litres were sampled from each depth using pressurized filtration and quartz fiber membrane filters. All filters were retained and stored at -20°C in the ships freezer.

The samples collected during both Australian and New Zealand voyages should do much in furthering the general understanding of trace metal cycling in the marine environment.

Microbial Processes

Els Maas and Debbie Hulston, NIWA

Samples for microbial analysis were taken at all stations. At the standard stations samples from 15, 50, 100, 300 and 1500m were analysed for bacterial exo-enzymes on board and were incubated with tritiated leucine for bacterial production estimation. In addition

500ml was filtered for subsequent RNA extraction and 4-5L for DNA extraction. Samples for flow cytometer analysis were also collected which will be analysed for bacterial, phytoplankton and picophytoplankton numbers. At the super and mega station the following additional depths 2000, 3000, 4000 and bottom depth were sampled for all the microbial parameters. The 15m samples at all stations were plated on Marine Agar for culturable bacterial number estimation and CAS agar for siderophore producing bacteria. The ocean acidification and dust experiments were sampled for flow cytometer analysis (bacterial, picophytoplankton and phytoplankton numbers), bacterial exo-enzymes, bacterial production (both leucine and thymidine for ocean acidification, leucine only for the dust experiment) and RNA/DNA analysis. The particle bioreminerlisation experiment was sampled daily for bacterial exo-enzymes, microbial community structure (day 0 and 4), bacterial numbers (day 0 and 4) and was plated on CAS and Marine Agar on days 0 and 4.

Bacterial exo-enzymes (phosphatase, protease and  $\beta$ -glucosidase) were analysed on board using a fluorescent plate reader. Protease activity was found throughout the water column at most standard stations at low levels (Figure 1).



**Figure 1:** Protease activity (nmoles  $l^{-1} hr^{-1}$ ) at the standard stations

At the mega and super stations protease activity was low at the western stations (GT3 & GT8) in the deep water compared to the eastern stations (GT9 and GT23) (Figure 2). At these two stations high protease activity was measured down the water column to the bottom (Figure 2).



**Figure 2:** Protease activity (nmoles  $l^{-1} hr^{-1}$ ) at the mega and super stations

 $\beta$ -glucosidase activity was not dtecetd down the water at any depth at the western station of the transect. At Stations GT16, GT20, and GT21 low  $\beta$ -glucosidase activity was detected at 1500 and 300m (Figure 3). No  $\beta$ -glucosidase was detected in the water column at the mega and super stations in the deep samples.



**Figure 3:**  $\beta$ -glucosidase activity (nmoles l<sup>-1</sup> hr<sup>-1</sup>) at the standard stations

Phosphatase activity at the standard stations was low between stations GT2-GT19 and was only found at 300 and 1500m (Figure 4).

Phosphatase (nmoles/l/hr)



**Figure 4:** Phosphatase activity (nmoles  $l^{-1} hr^{-1}$ ) at the standard stations.

Phosphatase activity increased in the water column from GT20 onwards and was detected in 15m and below (Figure 5).



Figure 5: Phosphatase activity (nmoles  $l^{-1} hr^{-1}$ ) at the standard stations GT19 – GT23

Phosphatase activity at the mega and super stations was detected below 300m and was very high  $(73.23 \pm 15.97 \text{ nmoles } \text{l}^{-1} \text{ hr}^{-1})$  at GT15 in the bottom water (Figure 6).

Phosphatase GT19-GT23



**Figure 6:** Phosphatase activity (nmoles  $l^{-1} hr^{-1}$ ) at the mega and super stations

# **MIT Sampling**

Samples for Chisholm lab MIT, were collected at all stations from GT2 onwards, for flow cytometer analysis, qPCR and were preserved in glycerol at 5 depths at the standard stations and 8 depths at the mega and super stations.

David Drapeau, Research Associate Bigelow Laboratory for Ocean Sciences

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# **Cruise Objectives:**

1. Collection of CTD and underway (approximately samples day<sup>-1</sup>) samples for analysis of particulate organic carbon (POC), particulate inorganic carbon (PIC), coccolith enumeration and biogenic silica concentration (BSi). The purpose of these samples was to provide an assessment of the inorganic and organic particle concentrations in surface water, provide indices of community composition, and analytical means to calibrate satellite PIC algorithms.

2. Operation of an along-track flow-through system from the ship's non-toxic seawater system to characterize the fine-scale hydrographic and bio-optical variability of the various water masses for satellite development of the NASA PIC algorithm.

3.Water-leaving radiance measurements in the visible and near infra red taken from the ship's meteorological platform, for characterizing the particulate content of the seawater and to provide sea-truth data for NASA's MODIS-Terra and Aqua satellite-based radiance measurements.

### **UW** sampling

Discrete underway samples were collected from the ship's clean, uncontaminated seawater system in the Middle Lab 2-4 times per day. Samples for POC, PIC, BSi, and coccolith enumeration were obtained along with chlorophyll samples taken for fluorometer calibration (UW chlorophylls taken by Cara Mackle and Greg Olsen, NIWA). PIC samples were collected on 0.4  $\mu$ m polycarbonate filters, rinsed with potassium tetraborate buffer and stored in metal free centrifuge tubes. These will be analyzed by ICPOES for particulate calcium. Coccolith and cell counts are collected on Millipore HA (nitrocellulose) filters, rinsed with potassium tetraborate buffer, frozen at 20°C, dried, then mounted onto slides using Norland Optical Adhesive. They will later be enumerated by birefringence microscopy. Biogenic silica (BSi) samples were filtered onto 0.4  $\mu$ m polycarbonate filters, dried in clean centrifuge tubes, and will be analyzed following the protocol of *Brzezinski* and Nelson (1989). POC samples were filtered onto pre-combusted glass fiber filters, dried, will later be fumed with concentrated HCL to remove inorganic carbon. They will be analyzed for CHN ashore at the University of Maine's Darling Marine Center.

## **CTD** sampling

8 depths from the surface to 200m including the DCM were sampled at each station from either the 1500m 'Standard' or 200m 'Bio' Cast. These will be analyzed for POC, PIC, BSi, and coccolith enumeration as described above.

### Flow-through bio-optical system

This system operates semi-continuously with water from the ships non-toxic sea water supply flowing at a rate of 5 liters per minute. Every 5-7 minutes temperature and salinity are measured (with a SeaBird sensor), chlorophyll fluorescence (WETLabs Wet Star), total backscattering at 532nm (bb<sub>tot</sub>; WETLabs ECO-VSF), acidified backscattering (bb<sub>acid</sub>; backscattering of the seawater suspension after the pH has been lowered to dissolve calcite and aragonite), and acid labile backscattering (bb'; the difference between the bb<sub>tot</sub> and bb<sub>acid</sub>). A WETLabs ac-9 is used to measure absorption and attenuation at 9 visible wavelengths (412, 440, 488, 510, 555, 630, 650, 676, and 715 nm) (every 4 minutes) and absorption and attenuation at the same wavelengths after the water was routed through a serially-mounted 1  $\mu$ m poresize, then 0.2 $\mu$ m poresize filter (during the intervening 4 minute segments). The system is calibrated initially with 0.2 $\mu$ m filtered MQ water, and subsequently cleaned and calibrated once a week. Also, 0.2 $\mu$ m filtered seawater can be easily circulated daily to help track instrument drift and/or fouling.

#### **Above-Water Radiance Measurements**

In order to check the PIC algorithm performance, free of atmospheric error, total upwelling radiance, downwelling sky radiance and total downwelling irradiance were measured from the bow of the *Tangaroa* using a Satlantic SeaWiFS Aircraft Simulator (MicroSAS). The same wavelengths are measured with the MicroSAS as used in the 2-band and 3-band PIC algorithms (except the IR bands which are not needed for the implementation of the ship-derived, three-band algorithm because there is negligible atmospheric correction when measurements are made from ship).

The system consists of a down-looking ocean radiance sensor and an up-looking sky-viewing radiance sensor, both mounted on the platform. The water-viewing radiance detector was set to view the ocean surface at  $40^{\circ}$  from nadir and the sky-viewing radiance sensor was set to view the sky  $40^{\circ}$  from zenith (used in the correction for Fresnel reflectance) as recommended by Mueller et al. (2003b). The downwelling irradiance sensor was mounted far enough forward and aloft so as to minimize any shading from the ship's superstructure. Data from these sensors will be used to calculate spectral normalized water-leaving radiance (after filtering out white-caps and high pitch/roll anomalies) for comparison to the satellite estimates of normalized water-leaving radiance.

Sensors were rinsed regularly with Milli-Q water in order to remove salt deposits and any dust. The water radiance sensor was able to view over an azimuth range of  $\sim 180^{\circ}$ across the ship's heading with no contamination from the ship's deck or wake. The direction of the sensor was adjusted constantly to view the water  $120^{\circ}$  from the sun's azimuth, to minimize sun glint. This was done using a computer-based system that calculated the sun's azimuth angle relative to the ship's heading and position continuously using the ship's gyro-compass and GPS and controlling a stepper motor to adjust the orientation of the sensors accordingly. Protocols for operation and calibration were performed according to Mueller (Mueller et al. 2003a; Mueller et al. 2003b; Mueller et al. 2003c). Data were collected between about 2000 and 0200 GMT when the sun was above 20° elevation. Post-cruise, the 16Hz data will be filtered to remove as much residual white cap and glint as possible (we accept the lowest 5% of the data). Calibrations with 10% reflectance plaque were performed during the cruise in order to assess the status of the radiometric calibrations. A factory calibration of the radiometers was performed before the cruise.

### **Ocean Acidification Experiments**

I was also given the opportunity to participate in experiments conducted by Cliff Law and Linn Hoffman. From their manipulations of  $pCO_2$  and temperature I was able to sample for PIC, BSi and coccolith concentration.

### **Sampling Metrics**

Flow through optics and above water radiance measurements: 22 days UW Samples: 30

CTD casts: 22 OA experiment samples:

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I collected water from the Biocast at 15 m, 30 m, 50 m, 100 m and the DCM. At stations GT1-GT6, I filtered 1 L and 2 L water onto 0.2  $\mu$ m filters for RNA and DNA extractions, respectively. At GT7, I collected 2 L water from 15 m and the DCM and filtered onto 0.2  $\mu$ m filters, for DNA extraction. From the remaining stations (GT8-GT23), I collected a total of 4 L onto 0.2  $\mu$ m filters, 2L for RNA extract and 2 L for DNA extraction. These filters will be used to determine the population of nitrogen-fixing bacteria, using qPCR to amplify the *nifH* genes. Depending on the yield of nucleic acids we will examine cyanobacterial diversity and gene expression.

# Report on McLane water pump and trace metal-clean CTD rosette deployments for particles and biogeochemical studies

Scott Nodder, Peter Gerring (NIWA) Melanie Gault-Ringold, Linn Hoffmann (University of Otago)

Summary

Six in situ, high-volume McLane pumps were deployed at four sites on the New Zealand-GEOTRACES transect from 173°W to 150°W longitude along latitude 32.5°S, including a trial deployment in the vicinity of the Brothers volcano plume (NIWA voyage TAN1109 station #3). Four primary depths were targeted at the GEOTRACES stations: 30, 100, 300 and 1000 m, using polycarbonate and QMA filters for trace metal and biogeochemical analyses (POC, PN, PP, pigments). Only one station at GT3 (station #17 and #20) was sampled at all depths with all filters, including additional samples depths of 200 and 500 m. Other station sampling at GT8 (station #37; 30, 100, 200 m sample depths only) was curtailed due to adverse sea and weather conditions. All samples were processed under clean lab conditions and stored frozen (-20°C). At GT15 (station #64), however, all the pumps, wire and MicroCat instruments were lost when the wire parted.

Additional trace metal particle samples were collected subsequently using the trace metal CTD rosette, targeting 30, 100 and 300 m, and filtering 30-40 litres in-line using pressurised filtration (~20 psi). All QMA filters were retained and stored frozen (-20°C), although several filters appeared to be holed during the filtration process (1-2 hours).

## A. McLane water pump samplers

The plan for determining trace metal particle concentrations on the New Zealand leg of GEOTRACES-SW Pacific sampling transect was to sample at the Super and Megastations (i.e., every 5° of longitude) from 173°W to 150°W longitude along latitude 32.5°S. The standard sample depths were 30, 100, 300 and 1000 m. Four McLane large volume water pumps were transferred from the RV *Southern Surveyor* in port at Wynyard Wharf, Auckland, to RV *Tangaroa* on 5 June, having been used on the previous Australian leg from Brisbane to 173°W. Two of these four pumps (designated C and D) were provided by University of Tasmania/ACE CRC (Dr Andy Bowie) and the other two were NIWA's pumps (A and B). Two new pumps (E and F) were delivered to the vessel in Auckland via Mainfreight. These pumps were found to have metal fittings (baffles and frits), which would compromise the planned trace metal work, so these were removed and plastic frits transferred from other pumps to minimise circulation in the filtration head.

The pumps were deployed on 2 km of marked, 6 mm-diameter, plastic jacketed wire, loaded onto the top-mounted scientific winch on the starboard side of the Shelter Deck onboard RV *Tangaroa*. A 177 kg anchor was provided as a ballast weight, but was later found to be too heavy and was replaced with 60 kg of large fishing chain. Seabird MicroCats (SBE37) were attached to the upper and lower pumps on each cast to verify actual sampling depths and to measure seawater temperature and conductivity through the water column during recovery. Unlike previous voyages (e.g., TAN0811 FeCycle II/Spring bloom), no priming of the pumps was conducted based on recent experiences on the PINTS voyage (M. Ellwood, pers. comm.). Generally, it took about ½ to ¾ hour to prepare the filters for the six pumps and about ½ hour to set-up and program the pumps for deployment using Crosscut terminal emulation software. It took two people about 1 to 1½ hours to subsample the filters after recovery in the clean lab. At the same time, one or two people could pump the excess water off the filters, download the data and reverse pump with deionised water to rinse the pumps.

QMA and 0.2  $\mu$ m polycarbonate (PC) 142 mm-diameter filters were provided by Andy Bowie and Michael Ellwood (ANU, Canberra), respectively. Sample preparation (e.g., loading and sub-sampling of filters), and storage of pump filtration fittings were both undertaken in a laminar flow hood in the clean containerised tent "constructed" in the port-side CT lab. Polycarbonate filters were soaked in 5% HCl acid and stored in Milli-Q water overnight before being loaded onto the filter holder using plastic forceps. Standard sample depths of 30, 100, 300 and 1000 m were identified as critical for the GEOTRACES protocols (and to match the sample depths on the previous Australian leg), with additional sample depths of 200 and 500 m.

After recovery, excess water was pumped off the filters (except for the first 2 pump stations). Filtration heads were bagged and then removed from each pump and transported inside a fish bin to the clean lab. PC filters were folded and placed in trace metal-cleaned vials for analysis at ANU (Michael Ellwood). QMA filters were sub-sampled using a 16 mm cutter to derive 6 sub-samples for trace metal and POCPN analyses (6x4 cell wells, Andy Bowie). A 40 mm cutter for 1 sub-sample for trace metals (trace metal-cleaned vial, Michael Ellwood) and up to nine 25 mm cutters for POCPN/isotopes, PPPN and/or HPLC pigments (approximately 3 replicates each per depth, 3x2 cell wells, Scott Nodder). All samples were frozen at  $-20^{\circ}$ C. In addition, whole PC filters were collected for specific remineralisation experiments conducted onboard the vessel (1 set of 0.2 µm filtered samples from 30, 100 and 300 m water depths at GT8; Sylvia Sanders, University of Otago). These whole filters were placed in trace metal-clean bottles.

The first deployment of four of the McLane pumps (Pump station #1) was conducted on 8 June in the vicinity of the Brothers volcano plume, with all four pumps placed at ~1500 m, with polycarbonate (3 pumps) and QMA (1 pump) filters. This deployment was compromised by timing issues that had the pumps starting to pump at about 500 m water depth before they reached their target depth, and also perhaps resulting in the QMA filter (pump E) rupturing. There was also evidence of wash-out from the PC filter in pump F.

The next deployment was at GT3 (Pump station #2, 11 June) with PC filters and 55  $\mu$ m nylon backing filters, and pumps deployed at 30, 100, 200, 300, 500 and 1000 m. Pump D at 1000 m stopped pumping after only 2 minutes ("low voltage >20 Vb") and Pump F at 500 m kept pumping even while on deck due to an input error for the pump duration (10000 minutes instead of 60 minutes).

The pumps were then prepared for the next deployment (Pump station #3, 12 June) at the same location GT3 and water depths, but with QMA filters, except at 500 m water depth, which was not sampled so that a second pump (Pump E) could be placed at 1000 m with a PC filter (i.e., pumps E and F were both placed at 1000 m). These filters were backed by 200  $\mu$ m nylon backing filters and 55  $\mu$ m nylon pre-filters were also fitted on the overlying frit to exclude zooplankton. Pumps A and B had evidence of air bubbles on one side of the filter, while the filter in pump F had ripped, so little or no material was retained on the filter.

At the next pump station (GT8, Pump station #5, 14 June), QMA and PC filters (with backing and pre-filters) were prepared on alternating pumps deployed at 30, 100 and 200 m, with the PC filters used for remineralisation experiments. The deployment was carried out under very heavy rain and moderately strong (25 knot) southerly winds. Pump A had evidence of an air bubble on the QMA filter and pump C stopped prematurely due to "minimum flow" being reached (4 litres/minute). The bottom 3 depths at GT8 could not be sampled due to the cancellation of over-the-side activities because of higher wind conditions at the end of the station (>30 knots). Nonetheless, pumps were set-up with new filters and all batteries were replaced.

Plans for deploying the McLane pumps at GT13 were curtailed due to adverse wind conditions, and the deployment postponed until GT15 on 18 June (Pump station #5). The same pumps as prepared for GT8 (deep depths) were deployed at 30, 100 and 200 m, with alternating pumps with QMA and PC filters, respectively. Timing issues due to the vessel not being on station and then being unable to hold station were encountered, so that the pumps had to be re-programmed to start at a later time. Upon returning to the work-deck to recover the pumps, it was found that the wire had parted and all 6 pumps and the two MicroCats had been lost.

Upon inspection of the failed end of the wire, it was found that there was a slight knick in the plastic coating and some dark grey surface discolouration of the upper surface of the wire at and away from the breaking point (over about 6 cm of wire). The inner strands of the wire at the breaking point appeared to be free of rust. During the deployment, sea conditions were moderate with 1-2 m swell and an 18 knot SW wind, although occasional swells of up to 4 m were observed by the bridge officers. The wide-mouthed blocks used for the pump deployments may not have been of sufficient diameter (10 cm) for this application. There was also evidence that uncovered bulldog grips on the upper end of the wire on the last layer of wire on the winch may have caused damage to the plastic coating and the wire itself. In conclusion, it appears that a combination of shock loading and weakening of the wire's integrity at the damaged knick point contributed to the final failure of the wire and subsequent loss of all six pumps, 2 km of jacketed wire, 60 kg fishing gear chain, and 2 SBE37 MicroCats. Luckily, no one was on the working deck at the time of the wire breakage and injury was avoided.

A summary of all the pump deployments and sample processing during TAN1109 is provided in Table B1.

Table B1. Summary of all pump deployments and sample processing during TAN1109.

|        |         | PU | Pum  | Schedul  |                |                | Volu                  | Time  | Filtratio | Filter | Subsamples   | SAMPLE NOTES          |
|--------|---------|----|------|----------|----------------|----------------|-----------------------|-------|-----------|--------|--------------|-----------------------|
|        | Statio  | MP | р    | e start  |                |                | me                    | for   | n rate    | types  |              |                       |
| Pump   | n #     | ID | dept | (Date &  | Start          | Start          | filtere               | pumpi | (l/min)   | (PC/Q  |              |                       |
| Statio | (bridg  |    | h    | Time)    | Latitu         | Longitu        | <b>d</b> ( <b>l</b> ) | ng    |           | MA)    |              |                       |
| n #    | e log)  |    | (m)  | NZST     | <b>de</b> (°S) | <b>de</b> (°W) |                       | (min) |           |        |              |                       |
|        | Brothe  |    |      |          |                |                |                       |       |           |        |              |                       |
|        | rs      |    |      |          |                |                |                       |       |           |        |              |                       |
|        | volcan  |    |      |          |                |                |                       |       |           |        |              |                       |
|        | 0       |    |      | 8/06/201 | 34             | 179            |                       |       |           | PC 0.2 |              |                       |
| 1      | plume   | Α  | 1480 | 1 13:15  | 52.49          | 07.25          | 140.7                 | 60.0  | 2.34      | μm     | MikeE - TM   | Brothers volcano      |
|        |         |    |      |          |                |                |                       |       |           |        |              | Pumps started         |
|        | Staitio |    |      |          |                |                |                       |       |           | PC 0.2 |              | working ~500 m        |
|        | n #3    | В  | 1490 |          |                |                | 169.2                 | 60.0  | 2.82      | μm     | SylviaS - TM | water depth           |
|        |         |    |      |          |                |                |                       |       |           |        | NO SAMPLE    | Pumps "On" until      |
|        |         |    |      |          |                |                |                       |       |           |        | - filter     | target depth of 1500  |
|        |         | E  | 1495 |          |                |                | 171.8                 | 60.0  | 2.86      | QMA    | ruptured     | m @ 13:30             |
|        |         |    |      |          |                |                |                       |       |           | PC 0.2 | ElsM -       |                       |
|        |         | F  | 1500 |          |                |                | 167.3                 | 60.0  | 2.79      | μm     | bacteria     |                       |
|        |         |    |      | 11/06/20 | 32             | 170            |                       |       |           | PC 0.2 | ME - whole   |                       |
| 2      | GT3     | Α  | 30   | 11 23:45 | 29.91          | 00.05          | 144.2                 | 42.8  | 3.37      | μm     | filter       |                       |
|        | Station |    |      |          |                |                |                       |       |           | PC 0.2 | ME - whole   |                       |
|        | #17     | В  | 100  |          |                |                | 169.79                | 60.0  | 2.83      | μm     | filter       |                       |
|        |         |    |      |          |                |                |                       |       |           | PC 0.2 | ME - whole   |                       |
|        |         | E  | 200  |          |                |                | 134.62                | 60.0  | 2.24      | μm     | filter       |                       |
|        |         |    |      |          |                |                |                       |       |           | PC 0.2 | ME - whole   |                       |
|        |         | С  | 300  |          |                |                | 195.05                | 60.0  | 3.25      | μm     | filter       |                       |
|        |         |    |      |          |                |                |                       |       |           |        |              | Pump kept pumping     |
|        |         |    |      |          |                |                |                       |       |           |        |              | on deck & through     |
|        |         |    |      |          |                |                |                       |       |           |        |              | water column;         |
|        |         |    |      |          |                |                |                       |       |           | PC 0.2 | ME - whole   | stopped on deck by    |
|        |         | F  | 500  |          |                |                | 295.26                | 129.2 | 2.29      | μm     | filter       | disconnecting battery |

|        |         |    |              |          |                |         |                       |       |           |        | ME - no        | Pump failed - "Low   |
|--------|---------|----|--------------|----------|----------------|---------|-----------------------|-------|-----------|--------|----------------|----------------------|
|        |         |    |              |          |                |         |                       |       |           | PC 0.2 | material on    | battery, no material |
|        |         | D  | 1000         |          |                |         | 6.1                   | 1.9   | 3.30      | μm     | filter         | on filter            |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        |         |    |              | 12/06/20 | 32             | 169     |                       |       |           |        | ME 1x47mm,     | Air bubble on 1 side |
| 3      | GT3     | Α  | 30           | 11 11:00 | 29.58          | 59.91   | 213.76                | 60.0  | 3.56      | QMA    | SN 9x25mm      | of filter            |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        | Station |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     | Air bubble on 1 side |
|        | #20     | В  | 100          |          |                |         | 223.43                | 60.0  | 3.72      | QMA    | SN 9x25mm      | of filter            |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        |         |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     |                      |
|        |         | D  | 200          |          |                |         | 411.82                | 60.0  | 6.86      | QMA    | SN 9x25mm      |                      |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        |         |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     |                      |
|        |         | С  | 300          |          |                |         | 411.82                | 60.0  | 6.86      | QMA    | SN 9x25mm      |                      |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        |         |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     |                      |
|        |         | Е  | 995          |          |                |         | 114.67                | 60.0  | 1.91      | QMA    | SN 9x25mm      |                      |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        |         |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     |                      |
|        |         | F  | 1000         |          |                |         | 171.79                | 60.0  | 2.86      | QMA    | SN 9x25mm      | Filter ruptured      |
|        |         | PU | Pum          | Schedul  |                |         | Volu                  | Time  | Filtratio | Filter | Subsamples     | SAMPLE NOTES         |
|        | Statio  | MP | р            | e start  |                |         | me                    | for   | n rate    | types  |                |                      |
| Pump   | n #     | ID | dept         | (Date &  | Start          | Start   | filtere               | pumpi | (l/min)   | (PC/Q  |                |                      |
| Statio | (bridg  |    | h            | Time)    | Latitu         | Longitu | <b>d</b> ( <b>l</b> ) | ng    |           | MA)    |                |                      |
| n #    | e log)  |    | ( <b>m</b> ) | NZST     | <b>de</b> (°S) | de (°W) |                       | (min) |           |        |                |                      |
|        |         |    |              |          |                |         |                       |       |           |        | ME/SS          |                      |
|        |         |    |              |          |                |         |                       |       |           |        | remineralisati |                      |
|        |         |    |              | 14/06/20 | 32             | 164     |                       |       |           | PC 0.2 | on expts -     | Sample partially     |
| 4      | GT8     | Α  | 30           | 11 14:15 | 29.76          | 59.01   | 141.32                | 60.0  | 2.35      | μm     | whole filter   | washed off?          |
|        |         |    |              |          |                |         |                       |       |           |        | AB 6x16mm,     |                      |
|        | Station |    |              |          |                |         |                       |       |           |        | ME 1x47mm,     | Air bubble on 1 side |
|        | #37     | В  | 30           |          |                |         | 221.36                | 60.0  | 3.69      | QMA    | SN 6x25mm      | of filter            |
|        |         |    |              |          |                |         |                       |       |           | PC 0.2 | ME/SS          |                      |
|        |         | E  | 100          |          |                |         | 113.31                | 60.0  | 1.89      | μm     | remineralisati |                      |

|   |         |   |     |          |       |       |        |      |      |        | on expts -     |                      |
|---|---------|---|-----|----------|-------|-------|--------|------|------|--------|----------------|----------------------|
|   |         |   |     |          |       |       |        |      |      |        | whole filter   |                      |
|   |         |   |     |          |       |       |        |      |      |        | AB 6x16mm,     |                      |
|   |         |   |     |          |       |       |        |      |      |        | ME 1x47mm,     |                      |
|   |         | F | 100 |          |       |       | 171.79 | 60.0 | 2.86 | QMA    | SN 9x25mm      |                      |
|   |         |   |     |          |       |       |        |      |      |        | ME/SS          |                      |
|   |         |   |     |          |       |       |        |      |      |        | remineralisati |                      |
|   |         |   |     |          |       |       |        |      |      | PC 0.2 | on expts -     |                      |
|   |         | С | 200 |          |       |       | 72.31  | 21.8 | 3.32 | μm     | whole filter   | "Min flow reached"   |
|   |         |   |     |          |       |       |        |      |      |        | AB 6x16mm,     |                      |
|   |         |   |     |          |       |       |        |      |      |        | ME 1x47mm,     |                      |
|   |         | D | 200 |          |       |       | 411.82 | 60.0 | 6.86 | QMA    | SN 9x25mm      |                      |
|   |         |   |     | 18/06/20 | 32    | 157   |        |      |      | PC 0.2 |                | ALL pumps lost due   |
| 5 | GT15    | А | 30  | 11 6:15  | 30.20 | 59.97 |        |      |      | μm     |                | to wire failure      |
|   | Station |   |     |          |       |       |        |      |      |        |                |                      |
|   | #64     | В | 30  |          |       |       |        |      |      | QMA    |                | No samples collected |
|   |         |   |     |          |       |       |        |      |      | PC 0.2 |                |                      |
|   |         | Е | 100 |          |       |       |        |      |      | μm     |                |                      |
|   |         | F | 100 |          |       |       |        |      |      | QMA    |                |                      |
|   |         |   |     |          |       |       |        |      |      | PC 0.2 |                |                      |
|   |         | С | 200 |          |       |       |        |      |      | μm     |                |                      |
|   |         | D | 200 |          |       |       |        |      |      | QMA    |                |                      |

# B. Trace metal-clean CTD rosette deployments and pressure filtering

Once the McLane pumps had been lost, an alternative method for collecting trace metal (TM) particles was required. Therefore, the decision was made to undertake a separate deployment of the trace metal-clean CTD rosette at selected stations, sampling at 3 core water depths: 30, 100 and 300 m, firing 3 or 4 10 litre bottles at each depth to obtain a suitable volume to derive enough material to measure trace metal concentrations on the filtered particles. All Niskin bottles from each depth were taken from the rosette and drained into three separate 50 litre carboys inside the ANU trace metal-clean containerised laboratory. The underway trace metal-clean pressure system was reconfigured to filter from the 50 litre carboy via an in-line 47 mm-diameter filter holder. Filters were cut from the large 142 mm-diameter QMA filters using a clean lid from a 40 ml sample vial. Due to the patchy nature of the coverage on the filter, the entire filter for each depth was folded, put into a trace metal-clean vial and frozen (-20°C).

The first TM CTD rosette deployment for trace metal particles was at GT17 on 19 June, with four bottles fired at 300 m (#1, 2, 3 and 5; no #4 available) and 100 m (#6, 7, 8 and 9, although #9 did not close) and three bottles at 30 m (#10, 11 and 12). Each set of bottles from each depth was drained into separate 50 litre carboys and then filtered. Filtrations took about 2 hours with the compressor running at 1.5-1.6 kg/cm<sup>3</sup> (~20 psi). The GT17-30 m filter had very patchy coverage (30 litres filtered) and the GT17-100 m filter (30 litres) had all the particles concentrated in the middle and the filter may have also been holed. The GT17-300 m filter (40 litres) had more even coverage, but there was an apparent air bubble on one side of the filter holder.

The second attempt at obtaining TM particles was at GT20 on 21 June. Filtering took 1-1½ hours. GT20-30 m had reasonably even coverage (30 litres filtered), compared to the filters from 100 m and 300 m, both of which appear to have been holed (40 litres each).

The final TM particles cast was at GT22 on 22 June, with filtering taking  $1\frac{1}{2}$  -2 hours. Sample GT22-30 m had 30 litres passed through the filter (Niskin bottles 9, 10 and 12; bottle 11 unavailable), as did the filter from 100 m. Four bottles were fired and filtered from 300 m, although the filter appears to have holed.

A summary of all the TM CTD rosette particle deployments and sample processing during TAN1109 is provided in Table B2.

## C. Underway C and N stable isotope filtrations

Sixty-nine (69) individual filtrations were undertaken for C and N stable isotope analyses (plus %C and %N) to contribute to an EEZ-wide study on the distribution of such isotopes and to provide additional data for the development of a POC-remote sensing algorithm for the NZ region. Samples were collected in duplicate or triplicate, representing 28 sample sites on the transect from  $173^{\circ}$  W to  $150^{\circ}$  W and on the transits down to the Chatham Islands and then from there towards Wellington.

Water samples were collected directly into a 10 litre carboy from the underway system in the Middle lab from the downstream end of the underway instrument suite. Duplicate or triplicate sub-samples of between 3-5 litres were filtered through pre-combusted GFF filters, attached to an in-line vacuum system. Samples were rinsed with 4 ml 0.1 N  $H_2SO_4$  and 0.2 µm filtered seawater, and then frozen (-20°C).

|           |            | Start    | Start    | Start     | Sample       |        | Volume   |       |
|-----------|------------|----------|----------|-----------|--------------|--------|----------|-------|
|           | Date       | Time     | Latitude | Longitude | depth        | Sample | filtered |       |
| Station # | (DDMMYYYY) | (NZST)   | (°S)     | (°W)      | ( <b>m</b> ) | ID     | (litres) | San   |
|           |            |          |          |           |              |        |          | Ver   |
| GT17      |            |          |          |           |              | GT17-  |          | on 4  |
| particles | 19/06/2011 | 11:42:00 | 32 30.04 | 156 00.69 | 30           | 30     | 30       | 1 x   |
|           |            |          |          |           |              |        |          | Ver   |
|           |            |          |          |           |              |        |          | on 4  |
|           |            |          |          |           |              | GT17-  |          | pos   |
|           |            |          |          |           | 100          | 100    | 30       | x fr  |
|           |            |          |          |           |              |        |          | Goo   |
|           |            |          |          |           |              | GT17-  |          | bub   |
|           |            |          |          |           | 300          | 300    | 40       | filte |
|           |            |          |          |           |              |        |          |       |
|           |            |          |          |           |              |        |          | Goo   |
| GT20      |            |          |          |           |              | GT20-  |          | 47n   |
| particles | 21/06/2011 | 04:33:00 | 32 29.70 | 152 59.86 | 30           | 30     | 30       | froz  |
|           |            |          |          |           |              |        |          | Pate  |
|           |            |          |          |           |              |        |          | mm    |
|           |            |          |          |           |              |        |          | pos   |
|           |            |          |          |           |              | GT20-  |          | outs  |
|           |            |          |          |           | 100          | 100    | 40       | x fr  |
|           |            |          |          |           | • • • •      | GT20-  | 10       |       |
|           |            |          |          |           | 300          | 300    | 40       | Hol   |
|           |            |          |          |           |              |        |          |       |
|           |            |          |          |           |              |        |          | Goo   |
| GTTAA     |            |          |          |           |              | GTAA   |          | 47n   |
| G122      | 22/06/2011 | 04.05.00 | 22 20 52 | 151.00.00 | 20           | GT22-  | 20       | pos   |
| particles | 22/06/2011 | 04:25:00 | 32 29.52 | 151 00.03 | 30           | 30     | 30       | x fr  |
|           |            |          |          |           |              | GTTAA  |          | Goo   |
|           |            |          |          |           | 100          | G122-  | 20       | mm    |
|           |            |          |          |           | 100          | 100    | - 30     | froz  |
|           |            |          |          |           | 200          | G122-  | 10       | Pos   |
|           |            |          |          |           | 300          | 500    | 40       | x fr  |
|           |            |          |          |           |              |        |          | 1     |

Table B2. Summary of all TM CTD rosette particle deployments and sample processing during TAN1109.

Niwa Ocean CTD Facility Event 3174 Report (Version 2.0a)

## Matt Walkington and Neill Barr

# 30 June 2011

NIWA Ocean CTD Facility (NOCF) Event 3174 (TAN1109, NZ Geotraces) occupied 25 stations, named u7001 to u7025. There was one four-cast station (u7025), five three-cast stations (u7005, u7010, u7017, u7021, u7023), sixteen two-cast stations and three single cast stations (u7001, u7002, u7008). All data acquisition and data processing followed NOCF protocols. Performance of all instrumentation was within nominal limits.

Data acquisition instrumentation combined a Seabird Electronics Inc. (SBE) 911plus CTD and a 24 x 10-litre SBE 32 Carousel water sampler. The CTD sensor configuration consisted of primary temperature (SBE 3plus), primary conductivity (SBE 4), and primary dissolved-oyxgen (SBE 43), ducted horizontally and pumped by a SBE 5T pump; secondary temperature (SBE 3plus), secondary conductivity (SBE 4), and secondary dissolved-oyxgen (SBE 43), ducted horizontally and pumped by a second SBE 5T pump; pressure (Digiquartz); fluorescence (Seapoint SCF); transmissivity (Wetlabs C-Star 25-cm Red); solar photosynthetically active radiation (PAR) (Biospherical Instruments QCP-2300L-HP); and sonar altitude (Tritech PA500/6K8). The exact instrument and sensor configuration, including sensor type, serial number and calibration coefficients, for any station u70nn cast 1, filename u70nna1, were specified in the corresponding .con file: ctd3162\raw\u70nn\u70nna1.con. The water sampler carried 24 10-litre external-spring Niskin-type bottles (Ocean Test Equipment Standard 10 BES). Data acquisition software was SBE Seasave-Win32 Version 5.39c.

All raw and processed data for the event were stored in directories under the top-level directory ctd3174. The time series of raw sensor outputs for any station u70nn cast 1, filename u70nna1, was stored in the corresponding .dat file: ctd3162\raw\u70nn\u70nna1.dat. Other files created by the data acquisition software (a .con file, a .hdr file and a .bl file) were also stored in the same directory (ctd3162\raw\u70nn\). The NOCF level2 processed data were stored in the directory ctd3174/level2. Various visualisations of these data, together with the data themselves, were stored in the directory ctd3174/level2\_with\_plots.

Figures 1 and 2 show, respectively, potential temperature-salinity and potential temperature-dissolved oxygen plots for the entire level2 dataset.





# Figure 3

Figures 3, 4 and 5 shows a temperature, salinity and dissolved oxygen sections for stations u7003 to u7025. Figure 6 shows the station positions.







Figure 5



Figure 6



# Figure 7

Figures 7, 8 and 9 show, respectively, the differences between the primary and secondary temperature, salinity and dissolved-oxygen as a function of time. There are two vertical axis variables for each plot: the median (blue) and standard deviation

(red) of the primary-secondary difference in temperature, salinity or dissolvedoxygen, respectively. The median and standard deviation are for all pressures.











# Figure 10

There were a total of 1200 water-sampler bottle fires. CTD sensor measurements at bottle fire were stored in the file ctd3174\level2\3174b.bot.xls.

A total of 269 dissolved-oxygen samples were drawn and measured aboard ship according to NOCF protocols.

A total of 240 salinity samples were drawn according to NOCF protocols and returned for shore-based measurement.

Acknowledgments