# Atlantic Meridional Transect



# **AMT12 Cruise Report**

RRS James Clark Ross 12 May – 17 June 2003

# Principal Scientist: Tim Jickells (UEA)

















University of Southampton

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# **Cruise Principal Scientist**

# T. Jickells

Laboratory for Global Marine and Atmospheric Chemistry School of Environmental Sciences University of East Anglia

> UEA Cruise Report Series No. 8 July 2003





#### Contents

Acknowledgements	1
Cruise Participants	2
Introduction to AMT	4
Cruise Diary	6
Cruise Reports	17
<ul> <li>Micro and Nano Nutrients</li> <li>DON, DOP, Phospholipids and Particulate N Studies</li> <li>Carbon System Measurements</li> <li>Partial Pressure of CO2</li> <li>Iron and Trace Metal Studies</li> <li>Gross Production, Net Community Production     <ul> <li>and Dark Community Respiration</li> <li>Basin Scale Variability of CDOM and Photo Reactivity</li> <li>DMS/DMSP Analysis</li> <li>Nitrous Oxide and Methane Concentrations</li> <li>Measurement of Autotrophic Community Structure and     <ul> <li>Primary Production</li> <li>Measurement of New and Regenerated Phytoplankton Production</li> <li>Dinitrogen Fixation</li> <li>Plankton Size Spectra</li> <li>Carbon and Nitrogen Export</li> <li>Sample Collection for <sup>230</sup>Th and <sup>231</sup>Pa Analysis</li> <li>Bio-optics</li> <li>Remote Sensing Data</li> <li>Atmospheric Sampling</li> <li>POL GRACE Bottom Pressure Recorder Recoveries</li> </ul> </li> </ul></li></ul>	18 22 26 32 35 38 42 43 44 49 51 55 57 60 62 63 67 69
and ARGO Float Deployment Technical Report on Equipment Deployed on AMT12	70 72
Appendix	77

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### **Cruise Participants**



Scientific Party of AMT12

#### **Science Party**

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University of East Anglia, School of Environmental Sciences, Norwich NR4 7TJ Tom Bell Tim Jickells

#### Ship's Officers and Crew

Master
Chief Officer
Second Officer
Third Officer
Radio Officer
Chief Engineer
Second Engineer
Third Engineer
Fourth Engineer
Deck Engineer
Electrician
Pursor
Bosun
Bosun's Mate
Seaman
Motorman
Motorman
Chief Cook
Second Cook
Senior Steward
Steward
Steward
Steward

### **Introduction to AMT**

The AMT programme undertakes biological, chemical and physical oceanographic research during the annual return passage of the RRS James Clark Ross from the UK to the Falkland Islands in September and from the Falklands to the UK in May, a distance of almost 13,500 km.

Twelve research cruises have already taken place, providing the most coherent set of repeated biogeochemical observations made over ocean basin scales, and a 5 year time series of data of bacterial, phytoplankton, and zooplankton community structure and activity. This data has been published in over 70 peer reviewed publications and has contributed to over 20 doctoral theses. Between 2002 and 2005, six further research cruises are planned which will sample further into the centre of the North and South Atlantic Ocean and also along the north west coast of Africa where upwelled nutrient rich water is known to provide a significant source of climatically important gases.

The new AMT programme (2002-2006) involves 45 investigators, researchers and students from 6 partner UK institutions (Universities of Newcastle, Plymouth, Liverpool, Southampton and East Anglia, together with Southampton Oceanography Centre and Plymouth Marine Laboratory) as well as other national and international collaborations. The programme is funded as an NERC Consortium grant in 2002. This cruise represents the first cruise of the new AMT programme.

The AMT aims to quantify the nature and causes of ecological and biogeochemical variability in the planktonic ecosystems of the tropical and temperate Atlantic Ocean, and the effects of this variability on the biological C pump and on air-sea exchange of radiatively active gases and aerosols. The data collected will be distributed for use in the development of models to describe the interactions between the global climate system and ocean biogeochemistry. In addition the programme will provide training for postgraduate students in state-of-the-art sampling strategies, data analysis, new technologies and interdisciplinary teamwork for oceanographic research.

More information on the AMT programme can be found at http://www.pml.ac.uk/amt

All data from the cruise will be stored at the British Oceanographic Data Centre (BODC) in accordance with the AMT data policy.

Figure 1 Satellite Image of Ocean Colour at the Start of the AMT 12 with Cruise Track Overlain



# **Cruise Diary**

Note times here are local ship times, GMT conversions included in text.

#### 10 May

First component of science party arrive JCR 11.30 local (add 4 to get GMT) Mobilisation commences

Second component of science party arrive (travelling via Chile) 19.00 local Safety Brief 20.00

#### 11 May

Mobilisation continues including repairs to CTD damaged on previous cruise, successfully completed and system functioned well throughout the cruise.

#### 12 May

Mobilisation and tie down continues, massive effort allows cruise to sail at 14.00. Boat drills in outer harbour and leave for cruise at 18.30. Science meeting

#### 13 May

Weather sunny, sea state good winds fairly light

CTD 1 (test deployment) standard rig\* 10.00 at 50°09.9'S 55°13.9'W a few leaking bottles but otherwise successful. Free Fall Optical Profiler (FFOP) also successfully deployed. CTD 2 (test deployment) Ti rig\* 15.00 at 49°51.9'S 52°19.4'W + net sampling Both successful

Evening science meeting to plan detailed sampling strategy.

#### Clocks move on 1 hour

Noon Position  $50^{\circ}03.6$ 'S  $52^{\circ}$  54.9'W Course made good  $62^{\circ}$  average speed 12.7k wind NNW force 5 sea moderate

#### 14 May

Overcast wind strengthening sea state deteriorating through the day CTD 3 5am local (now +3 to get GMT) main CTD at 48°38.10'S 48° 43.9'W + Nets CTD 4 11am Ti CTD + Optics Rig and FFOP 12 am Sound Velocity Profile. Note sea surface temperatures are changing by more than 5 degrees, presumably in an eddy field or frontal region.

Noon Position 48°1.4'S 47°28..6'W Course Made Good 62° average speed 12k wind NNW 6 sea rough

Deck access closed from 16.00

#### 15 May

Arrive POL mooring 1 site  $04.00 - 46^{\circ}46.24^{\circ}S 43^{\circ}26.39^{\circ}W$  – release command sent but inconclusive subsequent response from instrument. After various retries recovery attempt abandoned at 08.00. Argo float deployed and then steam for POL2 site. Side on swell continuing throughout giving very difficult motion some minor damage in the labs. Stop twice briefly and come head to sea to collect gear from back decks for lab work and to stabilise gas cylinders, otherwise deck access remains closed.

Noon position 46°18.5'S 42°47.6'W Course made good 65° average speed 11.7k wind NW7/8 sea rough

#### 16 May

Wind and sea abating, sunshine during the day and even a sampled early morning rain. Arrive POL2 site 44°25.197'S 40°22.185'W 04.00.

CTD 5 04.30 to 300m standard rig and nets

Mooring successfully recovered 08.30, no Argo float deployed due to malfunction Steam for POL3

CTD 6 11.00 6 44°15.0', 41°02.9W CTD (Ti frame) to 1000m and optics rig deployed, FFOP deployment abandoned.

Noon position 44°15.0'S 41°02.9W Course made good 289° average speed 11.8k Wind SxW 4 sea moderate

#### 17 May

Weather continues to improve, air and sea temperature both now about 12°C. First aerosol samples retrieved 03.30.

04.00 arrive POL3 43°11.9'S 46°18.1'W mooring released.

CTD 7 04.30 to 300m standard rig and nets. There is now a very strong thermocline at about 80m.

Mooring recovered approximately 08.00, Argo float released.

CTD 8 08.15 to 1000m for Th (and other samples).

08.30 – 12.45 Reconfigure for SAP sampling, deploy SAPS pump for 90 mins and recover.

During this and subsequent CTD, several deployments of the optics rig.

13.00-14.00 CTD 9 Ti rig to 300m.

Leave station and steam on predetermined AMT track.

Noon position 43°12.5'S 45°19.5W (note this represents drift on station and movement to recover mooring but we view this as a single site). Wind WSW 5 sea moderate/rough.

#### 18 May

Weather continues to improve and water temperature jumps about 4°C in an hour in the early morning, but only a few black browed albatrosses and cape pigeons are with us now. Wind coming from behind so no aerosol sampling.

04.30 CTD 10 to 300m standard rig and nets at 41°03.0'S, 42°10.0W. Continuing strong thermocline at about 80m.

Steam north on AMT line.

11.00 CTD 11 to 1000m, optics and FFOP deployed at 40°11.5S, 40°58.1W

All working well sampling is now in a routine, and much but not all laboratory measurements are now underway, still some equipment problems but these are being addressed.

Noon position 40°10.7N, 40°57.7W, Course made good 47°. Average speed 13.7k, wind SxW 5 sea moderate.

#### 19 May

Weather good waters up at about 17°C while air temperature range from 12-15°C through the day. The sea are getting lighter and lighter but the wind remains stubbornly behind us and strong enough to prevent atmospheric sampling. Dawn is getting earlier so we have to move sampling earlier particularly since we will now begin major <sup>14</sup>C effort and this is very light sensitive.

04.00 CTD 12 to 300m standard rig and nets at 37°37.2'S, 37 22.9'W. Thermal structure is changing with warmer water deeper but still a strong thermocline at about 80m.

Steam north on AMT line 11.00 CTD 13 to 1000m Ti rig, optics and FFOP at 37°02.9'S, 36°37.1'W. Noon position 36°55.5'S, 36°27.7'W, Course made good 047°. Average speed 13.6k, wind SW 4 sea slight. 16.00 Fire drill.

#### 20 May

#### Clocks go on 1 hour, GMT now +2hr

#### Warmer and calmer.

05.00 CTD 14 to 300m plus nets at 34°46.8S, 33°34.8W. Surface waters approaching 20° C with strong thermocline at 80m and deep chlorohphyll maximum at similar depth. Steam north on AMT line

11.00 CTD 15 to 1000m Ti rig, optics FFOP and surface water sample for iron using patent Statham bucket at 34°19.9S, 32°59.7W.

Noon position 34°03.6S, 32°37.9W, course made good 047°. Average speed 11.5k, wind SW2 sea slight.

By 14.00 wind has subsided enough to allow atmospheric sampling to resume.

#### 21 May

Continuing to warm and seas calm down, wind drops overnight almost completely, water strongly stratified with strong chlorophyll maximum at base of mixed layer about 100m.

04.30 CTD 16 to 300m standard rig at 31°49.1'S, 29°42.8'W plus nets. There is a problem with the CTD software which requires a complete reboot and delays things but we get going. 06.40 SAPS to 150m – we are now using an auxillary winch to support bottles during their attachement to the wire and this improves things a lot.

09.55 CTD 17 to 1000m for Th. Planned He/tritium sampling can't be done and one bottle isn't fired. Further net sampling.

11.05 CTD 18 to 300m Ti frame.

Various optics casts throughout the station. Final station position 31° 47.2'S, 28° 4.5'W. Argo buoy deployed. Leave station about 11.40.

Wind has moved northerly and there is slight white capping, atmospheric sampling recommences.

Noon position 31° 45.3'S, 29° 40.3'W, course made good 047°. Average speed 11.5k, wind N2 sea slight.

#### 22 May

Wind strengthens and goes a little NNW over night some swell,

04.30 CTD 19 to 300m at 29°25'S 26°46'W standard rig + nets and then an Argo buoy, all in about 45 minutes.

Steam,

Agree to move station to 10.45 from 11.00 due to ship crossing our path

10.45 CTD 20 preceded by FFOP which slows things up a bit but we are going to have trouble with MVP over and using FFOP. CTD to 1000m on Ti frame and optics rig also deployed. Recovery of CTD about 11.45. Sound velocity profiler deployed. Upon recovery last Argo buoy released.

Moving Vessel Profiler (MVP) deployed – initial deployment and recovery to install messengers stops, then full deployment. Leave station about 13.15. Allowing for SVP our station time approximately 2.15hr.

Atmospheric sampling recommenced at 13.40, interrupted as wind comes a bit abeam back on about 19.00.

Noon position (and CTD 20) 28°47.5S, 28°59.2W, course made good 047° average speed 12.8k, wind NW5 sea moderate.

MVP does not regularly profile to full depth and signal rather erratic, recovered about 17.00 to investigate and bridle found to be bent, not clear why. Telephone call to manufacturers and then pictures and data file sent to them for advice.

We alter course about 19.30 to the northerly leg of the AMT transect.

19.30 Presentation to the crew on AMT, seems to go quite well, quite a good turnout and a fifteen minute presentation is followed by about 30 minutes discussion and questions.

#### 23 May

Winds remain light and at least apparently on the bow allowing atmospheric sampling, weather warm and humid, there are some rain showers around, manage to sample from one early morning and remain on watch throughout the day. Water mass structure remains the same, water warming to 24°C with strong thermocline about 100m and deep chlorophyll maximum just below it.

04.30 CTD 21 standard rig to 300m + nets at 26°03.3'S 25°00.4'W Steam on

11.00 CTD 22 Ti rig to 1000m + FFOP and optics rig at 24°52.7S 24°59.9W

Noon position 24°52.7S 24°59.9W, course made good 0.00°, average speed 12.9k, wind SW (260) force 2-3 sea slight.

#### 24 May

Winds and seas continue light and good for aerosol sampling but no sign of rain. Flying fish are fairly common but seabirds a rarity.

04.30 CTD 23 standard rig to 300m + nets at 21°37.7S 25°00.0W.

steam on

11.00 CTD 24 titanium rig to 3500m + optics and FFOP at 20°29.7S 24°59.6W. This is our first and last deep station aimed particularly at sampling for dissolved iron but a number of people are taking the opportunity to sample deep water.

Upon recovery we prepare for MVP redeployment. After checks it is run through one cycle at full speed to check its function and recovered for brief inspection. This appears satisfactory so it is redeployed operationally. Fluoresence sensor is not working but all others functions are working.

Leave station at 14.45 towing MVP at full speed and recommence aerosol sampling. Noon position 20°29.7S 24°59.6W, course made good 000, average speed 12.6k, wind NE force 3 sea slight.

#### 25 May

Winds and seas light, good atmospheric sampling, rain early morning, but sample too small to use.

MVP works well until midnight, then fails and left towed until recovery 4.15.

CTD mainframe has lost connection so early morning CTD abandoned. Jeff and Mark get both CTD and MVP repaired by mid morning.

11.00 CTD 25 titanium rig to 1000m + optics, FFOP at 16°35.7'S 24°59.7W. Then MVP redeployed and atmospheric sampling recommenced.

Noon position 16°35.7'S 24°59.7W, course made good 000, average speed 11.7k, wind ENE force 4, sea slight to moderate.

Science meeting 16.30 to discuss various matters and organise shifts for the MVP.

MVP runs well until about 19.30 (including fluorescence where sensitivity has been increased) generating some interesting data on variability in chlorophyll maximum depths but then breaks down. All auto recovery options fails and manual override is used with the instrument finally on board about 23.00.

#### 26 May

Wind strengthens a bit and conditions continue to be very good for atmospheric sampling. 04.30 CTD 26 standard rig to 300m + nets at 13°55.5S, 24°59.9W

05.10 optics

06.07 nets

06.22 CTD 27 standard rig to 1000m

07.30 SAP deployment begins

10.00 Sap recovery

10.00 Optics deployed and FFOP

10.20 CTD 28 Ti rig to 300m

11.05 leave station and recommence atmospheric sampling.

Noon position 13°44.9'S, 24°59.8'W, course made good 000, average speed 12.1k, wind ENE force 4 sea moderate.

#### 27 May

Wind has moved to SE, apparent wind is on starboard beam and marginal for atmospheric sampling.

04.30 CTD 29 standard rig to 300m + nets at 10°35.8'S, 24°59.8'W

steam

11.00 CTD 30 Ti rig to 1000m + optics and FFOP at 9°30.6', 25°00'W.

Noon position 9°30.8'S, 25°00'W, course made good 000, average speed 11.6k, wind SE force 3 slight.

15.00 tours for scientific party of the engine rooms.

#### 28 May

Wind still SE but lighter. It's warm and sultry and possibly hazy, suggesting dust aloft. 04.00 CTD 31 standard rig to 300m + nets at 6°27.1'S, 24°59.9'W. Water and air temperature up to 27°C, chlorophyll seems a bit higher at the surface and the subsurface maximum is shallow at about 80m

Steam north. Atmospheric sampling recommenced with interruption for next station.

11.00 CTD 32 Ti rig to 1000m +optics including double cast with FFOP to take advantage of clear skies at 5°19.2'S, 25°00.0'W.

Noon position 5°19.2'S, 25°00.0'W, course made good 000, average speed 11.9k wind SSE 3 sea slight.

#### 29 May

Wind remains light SE, weather hot and sultry, atmospheric samplers indicate there is increased particulate loading.

04.00 commence station CTD33 standard rig to 300m + nets at 2°14.2'S, 24°59.9'W 05.00 optics

05.30 CTD 34 standard rig with FRRF removed to 1000m + additional nets

07.00 Commence SAP deployments

10.00 CTD 35 Ti rig to 300m + optics and FFOP

total station time about 6 hr 45 min.

During station, a school of tuna pass chasing flying fish with birds above. Chlorophyll maximum now at about 75m and waters appear much more productive. Atmospheric samplers indicate more terrestrial aerosol.

Noon position 01°57.4'S, 25°00.0'W, course made good 000°, average speed 11.8k, wind SE2/3 sea slight.

#### 30 May

Wind now southerly and about 10k, very marginal for sampling, very hot and sultry, atmospheric samplers again indicate a lot of aerosol.

04.00 CTD 36 standard rig to 300m +nets at 1°05.2'N 26°38.7'W. Chlorophyll maximum and thermocline again shallow at about 80m, squid and lots of flying fish around, strong currents with some wire angle problems.

Steam north

11.00 CTD 37 Ti rig to 1000m + optics and FFOP at 2°12.6'N, 26°18.2'W. Strong currents again and shallower chlorophyll maximum, quite low oxygen concentrations below the mixed layer.

Noon position 02°13.6'N, 26°19.9'W, course made good 329°, average speed 12.6k, wind S 3 sea slight.

15.00 Neptune visits and crossing the line ceremony follows. At the same time the wind swings from S to N approximately in a minute or so and torrential rains starts, this must be the ITCZ. Very heavy rainfall continues for about 3 hours, providing excellent samples but does not prevent the ceremony continuing.

#### 31 May

Wind NW 10k with continuing slight drizzle through the night and sky is almost completely cloud covered.

04.00 CTD 38 standard rig to 300m + nets at 4°53.7'N 27°53.5'W

Chlorophyll maximum still at about 75m, low salinities in surface waters and strong currents. Steam NW

11.00 CTD 39 Ti rig to 1000m +optics and FFOP at 5°55.2'N, 28°28.9'W. Continuing strong currents and shallow chlorophyll maxima. In surface water bucket samples *Trichodesmium* are evident in large numbers for the first time and some *ad hoc* experiments are initiated. Noon position 5°55.2'N, 28°28.9'W, course made good 329°, average speed 11.9k, wind NNE 3 sea slight.

#### 1 June

Wind NE, warm and sunny with clouds. Overnight aerosol samples indicate considerable amounts of dust.

04.00 CTD 40 standard rig to 300m + nets at 8°31.9'N, 30°03.5'W

Chlorophyll maximum still at around 70m but currents less strong. Steam NE.

11.00 CTD 41 Ti rig to 1000m +optics and FFOP at 9°33.8'N, 30°40.6'W. *Trichodesmium* again present but less abundant apparently.

Noon position 9°35.00'N, 30°41.2'W, course made good 329°, average speed 11.8k, wind NE4 sea moderate.

#### 2 June

Wind continues NE with clouds and occasional very light showers. Aerosols still suggest dust.

04.00 CTD 42 standard rig to 300m + nets at 12°14.1N, 32°17.2W

preceded by surface sample in metal free sampler.

06.00 CTD 43 standard rig to 1000m + nets, several problems with communications with the CTD.

07.00 Optics

08.00 Saps deployed

Further testing of CTD before next deployment suggest re-termination is necessary. This is carried out followed by a load test

10.30 Optics

14.00 CTD 44 Ti rig to 300m, successful.

Noon position 12°14.1N, 32°17.1W, course made good 329°, average speed 11.7k, wind NE 3, sea slight.

#### 3 June

Winds continue NE with clouds and occasional very light showers. Aerosol suggests little dust.

04.00 CTD 45 standard rig to 300m at  $14^{\circ}25.2$ 'N  $33^{\circ}36.4$ 'W + nets, preceded by surface sampling with metal free sampler.

There are some continuing problems with the CTD but we have enough information to describe station depths and address the problem after the cast when it is tentatively traced to some damaged connecting cables, Deep chlorophyll maximum moved down to 100m. Steam NW.

11.00 CTD 46 Ti rig to 1000m + optics and FFOP at 15°26.9'N 34°13.8'W chlorophyll maximum now down at 110m and waters are very clear and blue, we are clearly into the northern gyre now.

Noon position 15°26.9'N 34°13.8'W, course made good 329°, average speed 11.7k, wind NE 4 sea moderate.

#### 4 June

Wind moves ENE and strengthens a little. The wind is just forward of the beam allowing aerosol sampling. Sunny with a few clouds, air and water temperatures falling slightly. 04.00 CTD 47 standard rig to 300m + nets and preceded by surface sampling with metal free sampler at 18°02.2'N, 35°49.8'W. There are some more electrical problems with the CTD, we successfully locate the chlorophyll maximum and collect samples but the up cast continuous data is very noisy. Chlorophyll maxima now down at about 125m on a salinity and temperature gradient. There is also a shallow 20m seasonal mixed layer of lower salinity. Extensive bucket sampling takes place on station for large volume biological experiments. Steam NW.

11.00 CTD 48 Ti rig to 1000m + optics and FFOP at 19°03.3'N, 36°27.5'W. Noon position 19°03.3'N, 36°27.5'W, course made good 329°, average speed 11.7k, wind ENE force 4 sea moderate.

#### 5 June

Winds about NE and force 3-4 going to 5/6 under the occasional squalls that bring a little rain.

04.00 CTD 49 standard rig to 300m + nets and preceded by clean surface sampling at 21°24.8'N, 35°48.1'W. Chlorophyll maximum still at 125m, no surface mixed layer really evident. CTD works well so it looks like yesterdays repairs have fixed the problems. Steam NE.

11.00 CTD 50 Ti rig to 1000m + optics and FFOP at 22°13.9'N, 34°54.0'W then sound velocity profile.

Noon position 22°13.9'N, 34°54.0'W course made good 046°, average speed 11.8k, wind NE force 3 sea slight.

#### 6 June

winds continue NE and fairly light, clear skies.

Long station at 24°19.7'N, 33°34.4'W

04.00 CTD 51 standard rig to 300m plus nets and preceded by clean surface sampling.

Chlorophyll maximum now at 150m, water is very clear and blue.

06.00 CTD 52 standard rig to 1000m (primarily for Th work) + nets.

07.00 Deployment of SAPS and optics cast

10.00 CTD 53 Ti rig to 300m + optics and FFOP.

Noon position 24°28.6'N, 32°24.4'W, course made good 046°, average speed 11.8k, wind NE force 3, sea slight.

#### 7 June

#### Note clocks advanced one hour, GMT is now +1 hr on local times here

Winds continue NE clear skies with occasional light showers.

04.00 CTD 54 standard rig to 300m plus nets and preceded by clean surface water sampling at 26°27.6'N, 30°09.7'W. Chlorophyll maximum at about 150m depth Steam NE

11.00 CTD 55 Ti rig to 1000m + optics and FFOP at 27°12.7'N, 29°18.0'W.

Noon position 27°13.2'N, 28°17.5'W, course made good 046°, average speed 11.7k, wind NE force 4, sea slight.

Evening barbeque on the aft deck.

#### 8 June

Winds continue NE die down during the day, several quite heavy showers overnight, 04.00 CTD 56 standard rig to 300m plus nets and preceded by clean surface water sampling at 29°23.3'N, 26°47.1W. Chlorophyll maximum shallows slightly to 100-125m. Steam NE.

11.00 CTD 57 Ti rig to 1000m + optics and FFOP at 30°17.5'N, 25°43.3'W. Noon position 30°17.6'N, 25°43.0'W, course made good 046°, average speed 12.1k, wind ENE force 2, sea slight.

#### 9 June

Wind dies right down overnight and moves to more westerly direction by morning. 04.00 CTD 58 standard rig to 300m plus nets and preceded by clean surface water sampling at 32°40.9'N, 22°52.0'W.

Steam NE.

11.00 CTD 59 Ti rig to 1000m + optics (2 casts with FFOP since clear skies should improve chances of a fit to satellite overpasses) at 33°27.5N 21°42.9W.

Noon position 33°37.4'N, 21°43.0'W, course made good 046°, average speed 12.4k, wind WSW force 4, sea moderate.

#### 10 June

Wind remains in a westerly direction with a long swell side on.

04.00 CTD 60 standard rig to 300m plus nets and preceded by clean surface sampling.

05.30 CTD 61 standard rig (without FRRF) to 1000m plus nets.

07.30 SAPS deployed with 90 minute pumping time.

08.00 A series of short optics casts to try out some modifications to sensors.

09.45 SAPS recovered

10.15 CTD 62 Ti rig to 300m and optics cast.

All sampling at 36°41.6'N, 20°49.2W

Noon position 36°57.7'N, 20°46.6'W, course made good 007°, average speed 12.4k, Wind W force 3 sea slight.

#### 11 June

Wind and swell persist but are not slowing progress or preventing water or air sampling. 04.00 CTD 63 standard rig to 300m plus nets and preceded by clean surface sampling at 40°13, 6'N, 20°14.3'W.

#### Steam

11.00 CTD 64 Ti rig to 1000m plus optics and FFOP. Cast extended to allow crew to check on spooling of hydrowire at 41°29.5'N, 20°01.2'W.

Noon position 41°29.5'N, 20°01.2'W, course made good 007°, average speed 12.4k, wind force 2 NNW, sea slight.

#### 12 June

#### NOTE CLOCKS ADVANCED 1 HOUR, LOCAL TIME NOW GMT

Wind dies down over night, though still some swell

04.00 CTD 65. Standard rig 300m + nets and followed by clean surface water sampling at 44°37.9N, 19°27.3W.

Steam

11.00 CTD 66 Ti rig to 1000m plus optics and FFOP. This followed by sound velocity profile cast at 45°39.0N 18°31.8W.

Noon position 45°39.0N 18°31.8W, course made good 065°, average speed 12.4k, wind S force 2, sea slight.

#### 13 June

Winds generally light and easterly

04.00 CTD 67 Standard rig 300m + nets and preceded by clean surface water sampling at 47°05.5'N 13°56.3W.

Steam

06.30 Deploy magnetometer and sound velocity profiler in preparation for swath bathymetry survey,

08.50 Commence swath bathymetry survey

Cease survey for station

10.55 CTD 68 Ti rig to 1000m plus optics and FFOP at 47°40.9'N 12°40.8W,

Noon position 47°40.9'N 12°40.8W, course variable for survey, average speed 13.2k, wind E force 3 sea slight.

Continue swath bathymetry survey

#### 14 June

Winds die right down Swath bathemetry survey finishes approximately 09.00 Ship resumes cruise track. 11.00 CTD 69 Ti rig to 1000m plus optics and several FFOP casts because clear skies offer excellent opportunities for matching satellite observations.

Noon position 47°58.2'N 11°51.9'W, course variable during steering drill, average speed 13.8k, winds variable force 1.

In the evening an excellent end of cruise dinner

#### 15 June

#### Clocks advance one hour to GMT+1, i.e. BST

10.00 Science meeting to discuss preliminary results form the cruise which went well 12.00 Group photograph

Noon position 49°25.9N 04°47.5W, course made good 073°, average speed 12.8k, wind N force 3, sea slight

Then packing continuing on June 16 prior to docking Grimsby June 17

\* Two CTD rigs were used. Standard rig is a fully instrumented (oxygen, salinity, temperature, fluorescence, transmissometer, ADCP and FRRF, the latter removed if sampling below 300m) stainless steel frame carrying 20l niskin type bottles. Ti rig is similarly instrumented without FRRF but made of titanium and designed for trace metal sampling. This rig is carrying 10l niskin bottles modified to avoid metal contamination.

Figure 2General Pattern of Temperature, Salinity, Calculated Density and<br/>Fluoresence in the Upper 300 m of the Water Column along the AMT12<br/>Transect (Processed by L. Mintrop)



Figures were made using the CTD profile data and show the general distribution of temperature, salinity and fluorescence in the upper 300m of the meridional transect. In addition, potential density at 0 bar (sigma-theta) was calculated.

General features visible from the plots are the elevated temperature and salinity values in the two subtropical gyres, the equatorial upwelling, with the centre slightly shifted northwards, showing two peaks.

# **Cruise Reports from Individual Participants or Groups**

### Micro and Nano Nutrients

### Malcolm Woodward and Katie Chamberlain

Plymouth Marine Laboratory

#### Objectives

To study the spatial and temporal variations of the micro nutrients Nitrate, Nitrite, Phosphate, Silicate and Ammonium, through the contrasting oceanic regions along the cruise track between The Falklands Islands and the UK.

AMT-12 is the first in the new series of Atlantic Meridional Transect cruises, funded as a NERC consortium project, and is building on the successes and format developed by Plymouth Marine Laboratory in pioneering the first eleven of these type of cruises.

The track for this first cruise is to transect through both the North and South Atlantic gyre systems and with the aim of understanding the physical and chemical structures that make up these ocean systems.

The analytical systems used were a Bran and Luebbe AAIII classical colorimetric nutrient autoanalyser.

Where the ambient nutrient concentrations were below the detection limits of the colorimetric systems, we used a nanomolar Ammonium analysis system, and for nitrate, nitrite and phosphate a new nanomolar analysis system using Liquid Waveguide technology coupled with colorimetric analysis.

#### Methodology

The main nutrient analyser was a 5 channel Bran and Luebbe AAIII, segmented flow autoanalyser. This is a new machine purchased for the AMT programme. This was its first deployment and a number of problems were found with the system, not least was the weakness and problems of the controlling computer software which did not allow us to make any post-processing of the data due to a computer bug. Other times the system aborted itself during a run causing much loss of time. However much experience was gained about the system which we hope will be more trouble free in the future AMT cruises.

The analytical chemical methodologies were based on the following:

Nitrate, (Brewer and Riley, 1965); Nitrite, (Grasshoff, 1976); Phosphate (Kirkwood, 1989); Silicate (Kirkwood, 1989), and Ammonium (Mantoura and Woodward, 1983). All summarised in Woodward (1994).

The nanomolar Ammonium system is an adaptation from Jones, 1991 which uses a fluorescent analysis technique following ammonia gas diffusion out of the samples, passing across a hydrophobic teflon membrane, due to pH differential chemistry.

Sadly this system only operated for the first couple of weeks of the cruise in the southern gyre, and even this data was difficult to obtain. Finally the fluorometer broke-down with a similar problem that was supposedly 'fixed' prior to the cruise back at the manufacturers. This cruise was also the first deployment of a new three-channel nanomolar analyser for nitrate, nitrite and phosphate, combining the sensitive segmented flow colorimetric analytical techniques with a Liquid Waveguide Capillary Cell (LWCC). The nitrate and nitrite channels worked extremely well but problems with the phosphate waveguide rendered that channel very unreliable.

Water samples were taken from the 24 x 20 litre CTD/Rosette system (SeaBird), these were sub sampled into acid clean 60 mls HDPE (nalgene) sample bottles and analysis for the nutrient samples was in every case complete within 3 hours of sampling. Clean handling

techniques were employed to avoid any contamination of the samples, particularly by ammonium. No samples were stored.

#### **CTD Samples Analysed**

There were 2 different daily operations for the CTD samplings.

There was always the pre-dawn sampling carried out as a biogeochemistry cast as well as providing the water for the primary production and nitrogen uptake in-situ determinations. During the later part of the morning there was also a CTD drop with the trace-metal free CTD system. This was again used as a biogeochemistry cast for nutrient and other sampling. Every third or fourth day when we occupied SAP stations there was a deep CTD cast to 1000m for tritium sampling and this was again analysed for nutrients.

There was also one deep CTD down to 3400 metres in the southern gyre region.

The maximum sampling depth was normally 300 metres, with one of the daily CTD's being sent to 1000 metres to obtain a profile of the main physical parameters.

СТД	DATE	PROVISIONAL BOTTLE DEPTHS
AMT:12-01	13.5.03	All bottles fired at 500m
AMT: 12-02	13.5.03	All to 500m
AMT: 12-03	14.5.03	7, 25, 50, 70, 85, 120, 150, 185, 200, 250, 300
AMT: 12-04	14.5.03	8, 27, 52, 72, 87, 102, 123, 188, 204, 254, 306, 354
AMT: 12-05	16.5.03	8, 26, 52, 72, 86, 122, 154, 187, 254, 304
AMT: 12-06	16.5.03	1, 10, 25, 50, 75, 100, 125, 150, 175, 200, 250, 300
AMT: 12-07	17.5.03	5, 9, 15, 27, 53, 67, 79, 99, 155, 225, 307
AMT: 12-08	17.5.03	3, 13, 28, 53, 84, 104, 129, 154, 205, 507, 1017
AMT: 12-09	17.5.03	1, 10, 25, 50, 75, 100, 125, 150, 175, 200, 250, 300
AMT: 12-10	18.5.03	5, 10, 18, 30, 45, 60, 85, 100, 205, 255, 305
AMT: 12-11	18.5.03	1, 10, 25, 50, 75, 100, 125, 150, 175, 200, 250, 300
AMT: 12-12	19.5.03	3, 7, 13, 24, 40, 55, 66, 83, 110, 200, 300
AMT: 12-13	19.5.03	1, 10, 25, 50, 75, 100, 125, 150, 175, 200, 250, 300
AMT: 12-14	20.5.03	3, 9, 18, 34, 72, 85, 92, 112, 202, 250, 302
AMT: 12-15	20.5.03	1, 10, 25, 50, 75, 100, 125, 150, 175, 200, 250, 300
AMT: 12-16	21.5.03	5, 11, 20, 37, 85, 95, 110, 129, 150, 250, 300
AMT: 12-17	21.5.03	3, 10, 25, 50, 81, 98, 98, 151, 2000, 501, 1005
AMT: 12-19	22.5.03	8, 13, 23, 40, 101, 117, 126, 142, 202, 251, 302
AMT: 12-20	22.5.03	3, 11, 26, 59, 78, 92, 127, 152, 176, 202, 253, 300
AMT: 12-21	23.5.03	6, 13, 23, 41, 91, 101, 121, 138, 200, 251, 301
AMT: 12-22	23.5.03	3, 11, 26, 51, 79, 106, 127, 152, 177, 202, 253, 304
AMT: 12-23	24.5.03	10, 22, 34, 60, 121, 141, 161, 200, 240, 281, 301
AMT: 12-24	24.5.03	13, 53, 124, 153, 204, 255, 306, 406, 506, 709, 912, 1114,
		1318, 1522, 1725, 1929, 2133, 2338, 2544, 2748, 2954, 3158,
		3363, 3369
AMT: 12-25	25.5.03	2, 12, 26, 52, 76, 91, 130, 151, 178, 203, 252, 304
AMT: 12-26	26.5.03	7, 18, 32, 57, 121, 131, 141, 202, 222, 252, 303
AMT: 12-27	26.5.03	3, 12, 27, 51, 81, 102, 112, 152, 202, 504, 1011
AMT: 12-28	26.5.03	2, 9, 25, 51, 75, 100, 126, 151, 176, 201, 251, 303
AMT: 12-29	27.5.03	8, 17, 28, 49, 80, 101, 108, 141, 174, 202, 303

#### Table 1Nutrient Samples Analysed

$\Delta MT \cdot 12_{-30}$	27 5 03	3 11 26 51 89 101 126 152 176 202 252 303
AMT: 12-30	27.5.03	6 11 20 35 60 78 102 129 159 202 303
AMT: 12-31	28.5.03	2 10 25 51 75 85 126 152 177 202 252 302
AMT: 12-33	29 5 03	5 10 20 34 48 67 91 119 141 201 302
AMT: 12-34	29.5.03	3 11 26 51 65 81 101 151 202 504 1011
AMT: 12-35	29.5.03	2 9 24 50 55 99 124 151 176 201 251 302
AMT: 12-36	30.5.03	6, 12, 21, 38, 56, 68, 71, 101, 132, 202, 303
AMT: 12-37	30.5.03	2, 10, 24, 49, 64, 101, 125, 151, 176, 201, 251, 301
AMT: 12-38	31.5.03	6, 11, 20, 34, 61, 78, 101, 121, 151, 202, 302
AMT: 12-39	31.5.03	2, 11, 26, 50, 66, 101, 125, 151, 176, 202, 251, 302
AMT: 12-40	1.6.03	3, 8, 15, 27, 45, 57, 80, 98, 120, 201, 302
AMT: 12-41	1.6.03	2, 11, 26, 51, 59, 101, 126, 151, 176, 201, 252, 302
AMT: 12-42	2.6.03	8, 14, 28, 49, 65, 75, 98, 120, 201, 302
AMT: 12-43	2.6.03	2, 10, 25, 50, 57, 65, 100, 151, 202, 504, 1010
AMT: 12-44	2.6.03	2, 10-, 25, 50, 70, 100, 126, 151, 176, 202, 252, 303
AMT: 12-45	3.6.03	7, 13, 24, 42, 90, 101, 120, 151, 201, 252, 303
AMT: 12-46	3.6.03	3, 11, 26, 51, 77, 102, 115, 177, 202, 253, 303
AMT: 12-47	4.6.03	8, 13, 25, 42, 91, 101, 111, 151, 201, 232, 303
AMT: 12-48	4.6.03	3, 11, 26, 51, 76, 101, 124, 151, 176, 201, 251, 302
AMT: 12-49	5.6.03	9, 20, 31, 54, 102, 116, 133, 183, 203, 253, 304
AMT: 12-50	5.6.03	3, 11, 26, 50, 76, 101, 126, 151, 177, 202, 251, 303
AMT: 12-51	6.6.03	8, 19, 36, 62, 122, 124, 162, 192, 223, 253, 303
AMT: 12-52	6.6.03	4, 12, 28, 53, 83, 103, 132, 154, 204, 507, 1012
AMT: 12-53	6.6.03	3, 11, 26, 51, 76, 101, 127, 152, 177, 203, 263, 303
AMT: 12-54	7.6.03	8, 22, 37, 68, 135, 149, 153, 228, 292, 304
AMT: 12-55	7.6.03	2, 13, 28, 53, 78, 103, 121, 131, 178, 204, 253, 303
AMT: 12-56	8.6.03	7, 18, 33, 59, 121, 136, 162, 202, 101, 252, 303
AMT: 12-57	8.6.03	3, 11, 26, 52, 77, 105, 127, 152, 177, 203, 252, 304
AMT: 12-58	9.6.03	9, 21, 37, 64, 103, 128, 137, 168, 221, 203, 304
AMT: 12-59	9.6.03	3, 11, 26, 51, 77, 96, 127, 151, 176, 202, 253, 303
AMT: 12-60	10.6.03	5, 10, 20, 36, 70, 83, 102, 122, 141, 203, 303
AMT: 12-61	10.6.03	3, 12, 27, 51, 67, 82, 102, 153, 203, 506, 1015
AMT: 12-62	10.6.03	3, 11, 26, 58, 64, 101, 126, 152, 177, 202, 253, 304
AMT: 12-63	11.6.03	4, 6, 11, 21, 29, 45, 60, 66, 102, 203, 303
AMT: 12-64	11.6.03	2, 18, 23, 49, 77, 102, 127, 153, 176, 204, 254, 305
AMT: 12-65	12.6.03	3, 7, 12, 14, 28, 46, 48, 61, 102, 203, 303
AMT: 12-66	12.6.03	3, 9, 28, 48, 77, 101, 126, 152, 178, 202, 251, 303
AMT: 12-67	13.6.03	5, 7, 9, 17, 20, 30, 37, 57, 102, 204, 305
AMT: 12-68	13.6.03	2, 4, 23, 36, 77, 102, 126, 153, 178, 203, 253, 305
AMT: 12-69	14.6.03	12, 21, 35, 52, 77, 103, 128, 153, 179, 204, 254, 305, 366, 426,
		488, 548, 609, 670, 731, 792, 853, 914, 964, 1016

#### **Underway Sampling**

Daily sampling was carried out from the surface (7m) non-toxic sea-water supply and the majority of samples were analysed for nutrients, DMS, Chlorophyll and pCO2. Samples were taken on a mostly a daily basis starting from the 21<sup>st</sup> of May, at initially 1600, and then at 1500.

#### **Other Analyses**

Samples for nitrate and phosphate were analysed before and after UK irradiation to gain a value for the concentrations of DON and DOP. This work was carried out in collaboration with Catriona Hodge from Liverpool University.

Daily analysis for surface nitrate concentrations on the nanomolar waveguide system was carried from a surface water bucket sample taken at the same time as the CTD sampling, this was in collaboration with the SOC. Also from these studies there were a number of the <sup>15</sup>N spikes that were regularly tested during the cruise.

In the northern hemisphere there were a number of nutrient addition experiments carried out and samples were analysed for these to ensure the 'spikes' of nutrients added to the experimental bottles was as calculated.

#### **Prelimary Results**

The thermocline region was in most stations at about 100 to 150 metres, however rather than the expected oligotrophic situation and as previously experienced the chlorophyll maximum was normally as the depth of the thermocline region, and it was at this maximum that the nutricline was observed.

With the excellent performance of the nanomolar nitrate and nitrite systems the fine scale structure of the depth profiles can be accurately observed, allowing now the real possibility to accurately look at the nitrogen budgets.

Surface nitrate was between 0.5 and 2 nanomoles per litre, with the increase at the nutricline at over 2 orders of magnitude in a depth increase of less than 3 metres. These figures are in good agreement to those previously found but are probably more accurate than those previously due to a greater sensitivity of this waveguide system to that of the old chemiluminescence technique used on previous AMTs.

Nitrite profiles always showed the nitrite maximum associated with the chlorophyll maximum, and has now been observed with a very fine scale structure. When obtained, the ammonia concentrations were around 30 to 50 nanomoles in the surface and deeper waters and at a few stations an ammonia maximum was observed, up to 300 nanomoles, for the sample depths just above the nitrite maximum. Ammonium is produced due to the 'sloppy-feeding' of zooplankton on phytoplankton, and the nitrite is produced as an intermediate product of nitrification, the conversion of ammonium to nitrite, by nitrifying bacteria.

# DON, DOP, Phospholipids and Particulate N isotopic studies

# **Catriona Hodge**

Marine Chemistry Laboratories, Liverpool University

#### Introduction

Traditionally, the nutrient-poor subtropical gyres were thought to be 'ocean deserts', i.e. to have very little productive activity. However, approximately 50% of primary production occurs in these regions, with an export of  $\sim 2 \text{ mol C m}^{-2} \text{ yr}^{-1}$  to the deeper ocean (Emerson et al., 1997), which is thought to be up to 70% of the total global export (Karl et al., 1997). This raises the question of the source of the nutrients that would be necessary to sustain this production - there are various input mechanisms; lateral contribution from upwelling regions via Ekman transfer, atmospheric nitrogen fixation, as well as dust events and small-scale upwelling through eddy action. I will be attempting to a) clarify the nutrient sources through nitrogen isotope analysis (the fractionation values are indicative of the source composition), and b) characterise the composition of the organic nitrogen and phosphorus species to some extent.

#### Objectives

The aim of this cruise was to collect samples for analysis back in the laboratory at Liverpool University. The samples to be collected included;

- 1. filters from the second early morning CTD (every 4 days) both GF/F and also hydrophobic filters, to attempt some form of molecular DOP characterisation.
- 2. filters from the daily late morning CTD GF/F, for phospholipid or  $\delta^{15}$ N natural abundance measurements, as well as a filtered water sample from the chlorophyll maximum for THAA (total hydrolysable amino acid) determinations, and filtered samples for UV oxidation and further analysis on the autoanalyser for DON/DOP concentrations aboard the ship.

As there seemed to be more water allocated to me than I had realised, after discussion with Nick Millward and Stuart Painter (N fixation and N uptake rates respectively), we agreed that I should collect filters from 6 depths on the daily early morning CTD, to coincide with the depths which they were sampling, for  $\delta^{15}$ N natural abundance work – this should provide a comprehensive comparison with their work.

In addition to the CTD work, I filtered the underway water supply to gain a more continuous schematic of the transect, for either phospholipid (to infer viable biomass) or  $\delta^{15}$ N natural abundance analysis. I also used SAPS (stand alone pumping systems) in order to filter large volumes of water *in situ* – these were deployed every 4<sup>th</sup> day along with the second early morning CTD, and I had one each at 50, 100 and 150m depths, which pumped water continuously through a filter for an hour and a half.

#### Sampling

I collected;

Daily pre-dawn CTD – filtered 2 L from six depths – surface, 55%, 33%, 14%, 1% and 0.1% light levels, using autoclaved 47mm GF/F filters, for  $\delta^{15}$ N natural abundance isotope work. 4<sup>th</sup>-day early-morning CTD – collected 2 L from 7 depths – surface, 25, 50, 100, 150, 200 and 1000 m, and after filtering through 47mm GF/F filters, the filtrate was run through 47mm hydrophobic filters – this is in the hope that the less polar dissolved organic phosphorus

species would be retained for analysis of the molecular DOP component. The GF/F filters will also be analysed for  $\delta^{15}$ N isotopes.

Daily late-morning CTD – collected 2 L from 4 depths – surface, 50, 100 and 150 m. I syringe filtered (through 25mm GF/F) ~ 80 ml of each depth into quartz tubes (2 x 40 ml), which were the UV digested for 2 hours, and subsequently analysed for DOP and DON concentrations on the autoanalyser. I also syringe filtered ~ 7-10 ml of the water from the chlorophyll maximum into autoclaved vials for THAA analysis. The rest of the water from each depth was filtered through 47mm GF/F for phospholipid analysis, or for pre- and post-dawn comparative work on  $\delta^{15}$ N natural abundance isotopes.

Underway supply – using a large volume filtration unit with nitrogen gas as the pressure source (as it would not react with any organic material), I filtered (through 142mm GF/F) 40 L at a time. After trying both 20 and 60 L filtrations, this was deemed the optimal volume – there were not enough filters for 20 L each time, and not enough gas for 60 L. The times and locations were noted. These again could be analysed for phospholipids or  $\delta^{15}$ N. SAPS – every 4 days these were deployed – I had one each at 50, 100 and 150 m depths. Large volumes of water were pumped and the filters (293mm GF/F) retained. The deepest one, at 150 m, didn't seem to pump as much although it had the least concentration of particulates to clog the filter, so it was thought to have problems with the actual pump, as the battery was fully charged. As this SAP was below the chlorophyll maximum, I decided that it would be best to keep it at that level instead of swapping any around, so as to at least maintain a good profile at 50 and 100 m. However, after this occurred twice, the pump seemed to recover and the SAP at 100m instead seemed to have problems. All samples – filters and filtrates – were frozen at -20°C until analysis.

#### Methods

The  $\delta^{15}$ N of any nitrogen pool can be controlled by the  $\delta^{15}$ N of the source substrate or by isotopic fractionation during its uptake, subsequent internal processes, and loss (Fogel & Cifuentes, 1993). During growth, algae preferentially utilise <sup>14</sup>N instead of <sup>15</sup>N, due to the relative ease of bond formation, producing <sup>15</sup>N-depleted particulate material. However, in nutrient-limited regions, all of the available nitrogen is sequestered, and so the isotopic composition of the substrate becomes reflected within the organism. Therefore as production in oligotrophic regions essentially utilises all of the bioavailable nutrients, the isotope ratio of nitrogen would reflect the source composition, rather than fractionation effects during preferential assimilation (Minagawa & Wada, 1986). Nitrogen isotope analysis via isotope ratio/mass spectrometry (IRMS) should isolate the sources of nitrogen in the subtropical gyres through fractionation values.

Phospholipids are fundamental components of living organisms, which degrade rapidly following cell death. Therefore measuring phospholipids can be a useful tool in determining viable microbial biomass and community structure (Fang & Barcelona, 1998), which is then useful in evaluating primary production and bacterial trophic interactions and alterations (Findlay et al., 1989; Guckert et al., 1985). Investigation of the phospholipid and fatty acid content of the particulate material using a modified Bligh and Dyer extraction procedure followed by gas chromatography/mass spectrometry (GCMS) will indicate the viable biomass of the area, which can then be extrapolated to calculate requirements of nutrients, and the processes able to provide the necessary sustenance for the biota. High-performance liquid chromatography/mass spectrometry (LCMS) can be used to identify the structure of the intact phospholipid profile; the analysis of phospholipid fatty acids can be used for chemotaxonomical classification and also to identify specific genera, i.e. cyanobacteria and phytoplankton (Kehrmeyer et al., 1996; Rütters et al., 2002), for example the d-enantiomers

of amino acids are abundant in bacterial cell walls (Bronk, 2002), therefore indicative of the bacterial component.

Nitrogen is one of the major nutrients required by every living organism, and accounts for nearly 10% of the dry weight of most marine microbial cells (Karl et al., 2002). Organic forms of nitrogen include amino acids – both free and combined, urea (~5% DON), creatine, nucleic acids, amines, and humic and fulvic substances, although these only contribute to a small percentage of the microbial and planktonic growth supported by organic nitrogen. The majority of organic nitrogen exists as a mixture of substances resistant to degradation, particularly in the deep ocean (McCarthy et al., 1997), and have not yet been classified. Phosphorus can exist in combination with a variety of organic derivatives, including purines, pyrimidines, sugars and lipids, and consists mainly of monomeric and polymeric phosphate esters (C-O-P bonded compounds) and organic condensed phosphates. Among the esterlinked DOP compounds, both phosphomonoesters and phosphodiesters are present (Karl & Björkman, 2002). DOP (dissolved organic phosphorus), also referred to as SNP (soluble nonreactive phosphorus), can exceed the preferred substrate of orthophosphate by 1-2 orders of magnitude in oligotrophic environments. SNP, however, is largely uncharacterised. The DON and DOP analyses on the filtrates should help constrain the organic and inorganic speciation to some degree. Hopefully in the long-term this will lead to a better understanding of nutrient cycles in these regions and the physical processes occurring to affect the biological production.

The direction of this project is designed to create a better understanding of dissolved organic speciation; the characterisation of the nitrogen and phosphorus pools should aid further comprehension of the complex cycles they are involved in, as well as the source mechanisms and biological processes which constrain them. This has many consequential implications; as the phosphorus and nitrogen cycles can affect the carbon, oxygen and sulphur cycles, the understanding of fluxes into and out of the ocean are imperative in the comprehension of gross marine productivity.

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### **Carbon System Measurements**

# Ludger Mintrop

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#### Background

The oceanic carbonate system forms the biggest pool of (accessible) carbon in the global carbon cycle. Therefore it governs the distribution of carbon in the system. The perturbation in the small reservoir atmosphere created by human activity (mainly burning of fossil fuels) will eventually almost vanish in the big pool oceans. However, the establishment of this new equilibrium state will be hampered by the slow kinetics of the system. For the exchange between the ocean and atmosphere reservoirs, only a small pool, the surface boundary layer, is available. Complete mixing of the whole system, provided by surface currents and vertical transport (deep water formation and upwelling) will require a few hundred to thousand years; therefore an intermediate increase of atmospheric  $CO_2$  concentrations is inevitable. This will lead, and already has lead to a more or less dramatic change in climate.

The processes controlling the marine carbon cycle and air-sea exchange may be affected by a changing climate to different degrees. The direct exchange at the surface is influenced by e.g. wind velocity, storm events, precipitation and temperature increase in the surface layer; processes that might also affect the pattern of the general oceanic circulation. The response of the biological pump to a changing climate is another factor difficult to predict, a number of secondary effects of climate change are discussed. In order to include the response of all important processes in numerical models, that eventually will predict the future climatic development, it is crucial to find the adequate parameterisation for all these processes. The AMT cruise samples the surface layer of the Atlantic Ocean from approx.  $45^{\circ}$ S to  $45^{\circ}$ N, investigating numerous processes involved in biological productivity and air sea exchange, in order to address the above mentioned questions. These studies include the determination of the oceanic CO<sub>2</sub> system in the upper ocean layer.

Apart from the (semi -) continuous registration of surface  $CO_2$  partial pressure (p $CO_2$ ) the parameters alkalinity (AT) and total dissolved inorganic carbon (CT) are measured in surface samples and CTD samples. These two parameters allow for the calculation of all other inorganic carbon species in the water samples.

In addition, samples were also collected for Dr. A. Dickson of Scripps Institute of Oceanography, USA to make parallel measurements of alkalinity and TCO<sub>2</sub>.

#### Methods

Dissolved inorganic carbon (CT): DIC was measured using the SOMMA (Single Operator Multiparameter Metabolic Analyzer) system (URI, Rhode Island, USA). The principle of the measurement is to strip the total dissolved inorganic carbon as  $CO_2$  from a sample after acidification, using  $CO_2$  free nitrogen as carrier gas. The liberated  $CO_2$  is absorbed in an organic solution containing ethanolamine and forms an organic acid. The solution also contains a pH-indicator, which turns from blue to colourless when acidified. Using a platinum cathode and a silver anode, OH<sup>-</sup> ions are created electrolytically, that neutralize the acid. The current required for this reaction is recorded. The endpoint is determined photometrically by titrating back to the transmission value of the blue color before  $CO_2$  extraction started. The current gives a direct measure of the  $CO_2$  titrated and the CT of the sample.

#### Total alkalinity (AT):

Apart from some historical developments and few spectrophotometric approaches, today alkalinity is determined mostly by titration of seawater with a strong acid, following the potential of a proton sensitive electrode. The titration curve shows two inflection points, characterizing the protonation of carbonate and bicarbonate, respectively. The acid consumption up to the second point is equal to the titration alkalinity. From this value, the carbonate alkalinity, which is wanted for the adequate description of the marine carbonate system, needs to be calculated by subtracting the contributions to the titration alkalinity from other ions present in seawater. These concentrations are either determined separately or can be derived from salinity and pH of the sample.

On this cruise, the VINDTA (Versatile INstrument for the Determination of Titration Alkalinity, Marianda, Kiel Germany) was used. The VINDTA version 3C is a fully automated system, which only requires the change of sample bottles and keyboard entry of information for the individual sample by the operator. It is an open cell titration system, with sample delivery by thermostated calibrated pipette. Sample handling and titration is done by program control. Results are calculated using a non linear curve fitting approach, fitting a calculated curve to the data points and making use of the best fit coefficients for alkalinity calculation.

#### Accuracy:

CT measurements: The charge (current times titration time) transferred to the solution by the coulometric titration in theory is a direct measure of the amount of carbon (e.g. in µmoles) in the sample. With the precisely known amount of sample, this directly should give the concentration of CT. However, in practise, there is some variability in the counts/concentration relation as there also is a variable background (blank), all varying with the make-up of the coulometric cell from day to day. It is therefore necessary to calibrate the actual cell by either gas calibration or a liquid standard. The gas calibration was not possible with the system used here; therefore the instrument was calibrated daily with two samples of certified reference material (CRM). These are seawater standards with precisely known CT (and AT) concentration and salinity and are available from Dr. A. Dickson (Scripps Institution for Oceanography, La Jolla, USA). The certified value for the CRM (batch 59) is 2007.10  $\pm$  0.36 µmol/kg. Figure 1 shows, how the standard deviation for the measurements of CRMs (batch 59 was used) improves after calibration from  $\pm$  1.42 µmol/kg to  $\pm$  0.40 µmol/kg, reaching about the same range as the standard deviation of the certified value.





AT measurements: The variables that set the accuracy of the potentiometric alkalinity determination are the pipette volume, the acid concentration, and the density of the acid, as well as the accuracy of the mathematical calculation procedure (non-linear curve fitting). Another factor is the quality (and stability) of the electrode, which is hard to determine. The volume of the pipette can be calibrated pre-cruise gravimetrically. The acid has been made up prior to the cruise using ampoules and following instructions to make up exactly 0.1 molar solutions, but checking this factor with the required precision (e.g. 0.5‰) is difficult. Pre-cruise determined volume and factor may also vary due to changing draining characteristics of the pipette or evaporation/condensation processes affecting the acid in the bottle. Therefore, the method is also calibrated using the CRMs.

To calibrate towards the certified value, both the pipette volume and acid factor can be adjusted accordingly. However, values far from the real value affect the curve fitting procedure, since the latter involves calculation of the concentration of a number of species, and therefore is sensitive to both, the volume and the  $H^+$  concentration.

By calibrating with the CRM, the accuracy of the measurement should therefore be comparable to the values certified for the CRMs (batch 59), which is  $2220.98 \pm 0.58$  µmol/kg. A post-cruise recalibration of the pipette is planned, which may improve the quality of the fit, although will hardly change numbers significantly.

#### Precision

Precision (reproducibility) of the analytical method depends on the actual circumstances, under which a method is carried out. Is has to be determined therefore for a specific situation. The precision for the measurements on the cruise with rather unfavourable conditions was therefore determined by running 9 samples of the same batch of surface seawater (collected from the lab seawater supply line), treating these exactly the same way as the samples were handled. Table 1 shows the results:

sample #	CT [µmol/kg]	AT [µmol/kg]
1	2071.00	2345.18
2	2069.83	2345.15
3	2069.92	2345.37
4	2069.10	2345.01
5	2070.08	2346.46
6	2070.79	2346.02
7	2070.52	2346.71
8	2068.82	2346.41
9	2070.98	2345.12
average	2070.12	2345.71
std. deviation	± 0.789	± 0.680

#### Table 2Reproducibility Check for CT and AT

Therefore, the precision of the methods on this cruise is determined as  $\pm 0.8 \ \mu mol/kg$  for CT and  $\pm 0.7 \ \mu mol/kg$  for AT.

#### **Data Quality, Other Parameters**

Both methods need the density of the sample to calculate concentrations in  $\mu$ mol/kg. This is done using the salinity of the sample. For accuracy in the order of the precision of the methods, accuracy of the salinity of the sample of  $\pm$  0.01 is necessary. This is normally achieved without problems with the CTD sensors and no recalculation is required with corrected salinity values. However, on CTD station 45 problems arose with the CTD sensor. The salinity data from this station proved not usable.

It was tried to use the normalized alkalinity, which proved to be rather constant, to estimate the salinities of the samples from this station using the data from neighbouring stations. Since alkalinity itself depends on the salinity used for calculation, this had to be an iterative process. Table 2 lists the recommended salinities for the samples from CTD 45 resulting from this approach. The accuracy of this estimate, as deduced from the variability of normalized AT between stations, is about  $\pm 0.08$ .

#### Table 3Salinities Estimated from Alkalinity Values for CTD 45

Niskin bottle	pressure [dbar]	Salinity
1	8	36.48
6	13	36.50
7	24	36.50
10	42	36.60
13	90	36.80
14	101	36.79
18	121	36.42
21	151	36.29
22	201	36.01
23	253	35.68
24	303	35.59

For the calculation of carbon alkalinity from total alkalinity, the phosphate and silicate alkalinity has to be known. This can be done using the separately determined nutrient concentrations. However, the contribution is low, for phosphate about equal to the phosphate concentration (i.e. 0-3  $\mu$ mol/kg for open ocean waters), a factor of 10 lower for silicate. Nutrient data were not yet available during this cruise and therefore not included in the calculations. Since they were apparently quite low throughout the transect, no significant contribution will be expected.

#### **Data Problems**

A number of profiles show erratic values of AT and/or CT, which may be real, but could also be bad measurements. Another possibility would be the CTD bottle closed at wrong depth or a leaking CTD bottle, exchanging water during haul. These problems are often hard to detect, mostly if several investigators report unexpected values for a certain sample.

CT and AT were measured from the same sample bottle, therefore the potentiometric CT (CT <sub>pot</sub>) could be used as a tool to detect analytical problems. The potentiometric CT

determination is inferior to the coulometric measurement (CT <sub>coul</sub>), especially with this analytic instrumentation using an open cell for titration and no further protection of the sample from  $CO_2$  loss or gain between the CT measurement and the AT measurement (i.e. open bottle).

However, although absolute values of CT  $_{pot}$  are unreliable, the depth profile in general looks very similar to CT  $_{coul}$ , but has a variable offset. The indications of the comparison of profiles for the 3 parameters alkalinity, CT  $_{pot}$  and CT  $_{coul}$  are as follows:

- Case 1: Value for AT and CT <sub>pot</sub> are away from the smooth profile: problem with potentiometric titration for AT and CT <sub>pot</sub>
- Case 2: Value for AT looks ok, but CT <sub>pot</sub> and CT <sub>coul</sub> are off: sample lost (or gained) CO<sub>2</sub> to/from the environment
- Case 3: All 3 values off: Problem with the CTD, wrong depth or leaking bottle?
- Case 4: CT <sub>pot</sub> and CT <sub>coul</sub> look ok, but AT is off: Problem with the calculation of AT (curve-fitting)

The profiles from all stations were scanned for these features, table 3 lists the results:

CTD	Bottle	Pressure		C	ase		Action
Station	#	[dbar]	1	2	3 4	4	
5	21	154	Х		?		AT flagged bad, check other data
5	24	304			Х		check other data
10	23	256	Х				check AT calculation
12	18	67	Х				AT flagged bad
14	24	305			Х		check other data
16	24	303			Х		check other data
26	24	303			Х		check other data
29	24	303			Х		check other data
36	21	132				Х	AT flagged bad
42	10	50				Х	AT flagged bad
49	23	253			Х		check other data
54	23	254				X	AT flagged questionable
63	24	304		Х			CT flagged questionable
65	18	48			?		check other data

 Table 4
 List of Questionable Results from the CTD Station

Results for other parameters from this sample should therefore be checked to possibly identify sampling problems.

#### **Post Cruise Processing**

CT data were calibrated with CRMs, so they can be considered final. AT data were also calibrated with the CRMs, however, the calculation method is dependent on an realistically estimated ratio of acid factor and pipette calibration, since the same calibration factor can also be obtained with various combinations of these two parameters, but the quality of the curve fit will be different. Therefore a re-calibration of the pipette and recalculation of the acid factor will be done in the land laboratory. However, changes that would exceed the mean standard deviation of the method are not likely. Re-processing of the data will however become necessary, if major adjustments to the CTD bottle data will be made post-cruise.

# Partial Pressure of CO<sub>2</sub> (pCO<sub>2</sub>)

# Chris Lowe

Plymouth Marine Laboratory

The pCO<sub>2</sub> system was fully operational from 17:30 UT on May  $14^{th}$  until 09:45 UT on June  $10^{th}$  when it was turned off due to the low pCO<sub>2</sub> calibration gas standard running out.

#### **Removal of Data Taken While on Station**

Due to probability of contamination of the marine air supply from the ships funnel while on station records where the GPS position between consecutive records of the same group (eg marine air(i) – marine air(ii)) was identical were removed. Standards were not edited in this manner since they are not affected by contamination of the marine air supply.

#### **Flow Rates**

Due to a requirement to clear the dead space within gas tubes prior to each reading any samples where the flow rate was measured at below 25 cycles was removed.

#### **GPS** Positions

Positions have been decimalised from the degrees minutes and seconds format of the raw data. North and South have been replaced with positive and negative values respectively.

#### **Gas Standards**

A total of four standards were used; two at a time, one high and one low so as to calibrate for instrument drift. The following log gives details of when these were used, this information is also provided in the dataset.

Standard 1

Std value (ppM)	Day(SDN),Time(UT),notes
383	133 12:30 ON
	134 17:30,Equilbrator plumbed in
	135 14:29 Zero flow, pressure increase, flow returned
	141 16:19 empty
0	142 11:35 ON
	146 15:04 Standards swapped (OFF)
999	146 15:04 ON
	CALIBRATION EXERCISE RUN
	146 18:38 ON

Standard 2

Std value (ppM)	Day(SDN),Time(UT),notes
999	133 12:30 ON
	134 17:30,Equilbrator plumbed in
	146 09:15 Zero flow, pressure increase, flow returned
	146 15:04 standards swapped (OFF)
0	146 15:04 ON
	CALIBRATION EXERCISE RUN
Unknown (483?)	146 18:38 ON
	161 09:46 OFF


Figure 4Uncorrected pCO2 - AMT 12Relative Partial Pressure of CO2 in Water and Air

Figure 5 Graphical Representation of Areas of CO<sub>2</sub> Draw Down on the AMT 12 Cruise Track



Lon

## **Iron and Trace Metal Studies**

## Peter J. Statham and Florence Nedelec

Southampton Oceanography Centre

#### Background

Iron has been demonstrated to be an essential nutrient element for phytoplankton in marine systems and this is particularly important in high nutrient low chlorophyll (HNLC) areas where the element can limit primary production. However, the accurate determination of iron at picomolar concentrations in seawater is a difficult analytical task and the amount of reliable information on this element in ocean waters is very limited. The AMT transect through the north and south Atlantic Oceans provides an excellent opportunity to sample different oceanic provinces, and significantly add to our knowledge of the distribution of iron in this oceanic region. It is intended that these samples will be analysed for several trace metals as well as Fe. An additional major advantage to doing the Fe and trace metal work on this cruise is the large ancillary database to be produced on biology, input processes, and light in the system that can be used to help interpret the Fe and trace metal data.

#### **Sample Collection**

Each day typically twelve samples were collected from the upper 300m of the water column at about 1100h using a purpose built clean sampling system. This system consists of 24 10L OTE water-sampling bottles that have been adapted to minimise metallic components and potential contamination. The bottles are deployed on a titanium rosette-CTD system with the instruments all being housed in titanium cases. There are no zinc sacrificial electrodes on the frame, which have caused considerable problems with contamination for this element when such electrodes have been used. Bottles were fired in duplicate at each depth (that included the chlorophyll and oxygen maxima) to provide adequate water for all samples required. After arrival on deck the 12 bottles containing the trace metal samples were carried to a clean container laboratory. This container laboratory has been substantially modified for trace metal work, and has a small anteroom and a main working space. The walls are coved and lined with plastic, and exposed metallic components have been minimised through choice of materials and appropriate coatings. The air supply is air conditioned and primary filtered, and there is a laminar flow hood for critical handling steps. The OTE bottles containing samples were held on a rack in the container, an external frame was used to clamp top and bottom valves shut, and the bottle was pressurised with filtered nitrogen to 0.5-0.9 atmospheres. Samples were directly passed through filters (normally 0.4 µm pore size acid cleaned polycarbonate membranes) held in all Teflon inline filter holders into acid cleaned lowdensity polyethylene storage bottles. Samples were acidified with 1 ml of quartz-distilled hydrochloric acid per litre to stabilise the contained dissolved metals.

In addition to the standard CTD seawater collection, some other samples were collected:

- a) In the central South Atlantic oligotrophic gyre a deep 24 bottle cast to 3.5km was done (CTD 28). A recent compilation of oceanic profiles of Fe (Ed Boyle, MIT, personal comm.) shows that there is no reliable information on Fe in the southern Atlantic, and this profile has the potential to fill this gap.
- b) Recent research has indicated that a substantial fraction of the Fe in seawater can be present as colloidal phases. To test this for the environment studied here, and also to investigate the impact of biology on the presence of Fe colloids, two filtrations were done on selected samples; i.e. through 0.4 µm and then a separate filtration through 0.1 µm

filters. The intention is to investigate the distribution of colloids with respect to biological activity and biomass in the water column.

- c) In order to give improved horizontal data resolution, surface water samples for Fe analysis were collected before the pre-dawn CTD from the equator northwards. Samples were collected using a device constructed on the ship that consisted of a weighted plastic tube holding a sample bottle that was deployed by a plastic line over the starboard aft quarter into clean water away from the direct influence of the ship. Samples were taken as the ship was coming onto the predawn station. Data from this sampler will be used in combination with data from the Ti rosette system.
- d) Samples were collected from the 20L bottles on the stainless steel rosette system at a few stations to allow comparison of data with samples from similar depths using the Ti rosette in order to assess any potential contamination from the stainless system.

Sampling system	Number of CTDs or	Number of samples
	sampling events	collected
Titanium rosette (0.4 micron	36	401
filtered)		
Titanium rosette (0.1 micron	7	86
filtered) –colloids		
Surface samples	16	16
Stainless steel rosette	4	12
Total number of events/samples	63	515

#### Table 5Number of Samples Collected for Fe and Other Trace Metal Analyses

#### Shipboard Iron Analyser System

The cruise was also used as an opportunity to test a new Fe analyser system built at the SOC, that is based on the system of Bowie et al. (Bowie, A. R., E. P. Achterberg, et al. (1998). "Determination of sub-nanomolar levels of iron in seawater using flow injection with chemiluminescence detection" Analytica Chimica Acta 361(3): 189-200). The system uses a pre-concentration column to remove Fe (II) from the sample, and this collected metal is determined by chemiluminescence using a buffered luminol solution. Significant improvements to the system were made, including the optimization of pH, increasing the sensitivity to sub-nanomolar concentrations, overcoming problems with back pressure in the system, gaining extensive experience with the control software and data processing, and tracking contamination of the MQ water on board with an organic that interfered and gave a huge background signal (not present in sub-boiling distilled water). Despite these advances, the precision of the measurements was poor and although an extensive series of experiments was done to identify and resolve this problem, no definitive cause could be identified. However, it was possible to measure the total iron in selected samples by carrying many replicate analyses, and averaging. The estimates obtained by this approach gave a deep (300m) Fe concentration of about 0.8 nM that decreased in concentration towards the surface. These data are consistent with other recent data for iron in this region, and suggest that the instrument has the potential to measure oceanic Fe and that the samples are not substantially contaminated.

The remaining problems with the analyser will be resolved in the SOC laboratory.

#### **Comments on the Shipboard Equipment and Technical Support**

#### New Clean Container laboratory

Overall this provides an excellent facility for the clean handling of samples for trace element analysis, and the staff at UKHORS is to be commended for the design and commissioning of this facility. The air conditioning worked well and coped with environments ranging from the Southern hemisphere winter to the Tropics. On this first use, a few minor issues were noted (see below), that will be reported back to UKHORS by Richie Phipps. Specific issues:

- a. One of the windows leaked around its edges, and allowed water to penetrate the interior. This nearly led to a major problem as the leak was directly over an analytical instrument in the container. Fortunately all the critical components were raised from the surface and the pool of seawater only destroyed some minor replaceable components. A drainage gutter was fabricated and protected the instrument for the rest of the cruise.
- b. A converter to allow attachment of the three phase supply to different sized sockets should always be in the container, and there should be a single phase cable also supplied
- c. The radio officer was unable to connect the JCR comms to the cable and socket supplied with the container. The suggestion was that the cable may be too long, with associated signal loss. A phone and fire alarm was patched in to the container using separate cables. Ideally the comms should be transparent to at least all the UK research ships to be used.
- d. Currently there is no way to insert cables through the external and internal walls to the main working area. It would be useful to have e.g. 40 mm diameter ports through both skins to allow ingress of cables and tubes. This will be an essential feature for the coming D272 other cruises where the alongside clean fish system will be used and the water take off point will be in the clean container. Such ports will also provide flexibility for other future applications.

#### **Titanium CTD and Modified OTE Water Sampling Bottles**

The CTD system worked extremely well with no major problems during the cruise. It is hoped and expected that the iron CTD cable and attachment to the CTD package will not present a major contamination problem. However, use of a plastic kevlar conducting cable is to be much preferred and should be used with this package as it comes available, and thus further enhance the facility.

The water bottles proved to be highly reliable, with only 2 misfires during all the Ti CTD casts. The clamps (used to hold top and bottom valves of the bottles closed during pressure filtration) worked very well; a minor modification which kept the upper plate attached to the rods with cable ties, eased use of the system. The modifications to the bottles to remove/coat all metallic components seemed highly effective. The only problem noted was some slight corrosion of the stainless crimps used to join lanyards and related nylon lines, and attention will be given to this back at the SOC. Jeff Benson is to be highly commended for his efforts in putting this high quality system together so effectively.

#### **Technical Support**

All the UKORS and BAS ship staff were extremely helpful throughout the cruise; Richie Phipps (help with workshop items) Mark Preston, Doug (deck engineer) and Jeff Benson are particularly thanked for their efforts.

## **Gross Production, Net Community Production and Dark Community Respiration**

## Nicola Gist and Carol Robinson

Plymouth Marine Laboratory

#### Objectives

- To determine the depth and latitudinal distribution of the balance of gross production (P) and respiration (R) and to relate this to community structure and nutrient supply (hypothesis 1).
- To examine the balance of gross production and respiration within the Northern gyre, and to relate any changes in the P:R ratio to the transport of organic nutrients into the gyre (hypothesis 5).
- To compare the P:R ratio in the Northern and Southern Atlantic gyres and relate this to atmospheric and hydrographic derived nutrient supply and to community structure (hypothesis 3).
- To measure dissolved oxygen concentration in order to calibrate the oxygen sensors on the CTDs.

#### Methods

Measurements of dissolved oxygen were made using an automated Winkler titration system with a photometric endpoint (Williams and Jenkinson, 1982). Oxygen saturation was calculated from the equations for the solubility of oxygen in seawater of Benson and Krause (1984).

Gross production (GP), net community production (NCP) and dark community respiration (DCR) were determined from *in vitro* changes in dissolved oxygen. Water was collected directly into opaque polypropylene aspirators from depths equivalent to 55%, 33%, 14%, 1% and 0.1% of surface irradiance. The water was siphoned into 125ml borosilicate glass bottles and up to six zero time replicates were fixed immediately. Two further sets of replicates were incubated for 24 hours in surface water cooled deck incubators or in temperature controlled water baths at *in situ* temperatures. One set was incubated in the dark, the other set in light of equivalent irradiance to that found at the *in situ* depth. This was controlled using polycarbonate screens incorporating neutral density acrylic of differing transmission (Joint *et al.*, 1993; Watts and Owens, 1999; Maranon *et al.*, 2000; Donald *et al.*, 2001). During hours of darkness, the incubators were covered with opaque screens to prevent interference from the ship's deck lights.

Dissolved oxygen was measured for calibration of the Seabird Electronics (SBE) sensors on the CTDs (O<sub>2</sub> sensor numbers: 43B-0363 (stainless steel CTD) and 43B-0013 (Titanium CTD)) using water collected directly from 2-8 Niskin bottles by use of silicon tubing.

#### **Preliminary Results**

The metabolic balance of the oceans is investigated by measuring P and R and there is currently a debate as to whether the worlds' oceans are net autotrophic or heterotrophic, which would have serious implications for global climate (Duarte and Agusti, 1998; Williams, 1998). Measurements on AMT 6 showed that P<R (ie net heterotrophic) over 48% of the transect, but the carbon required for the observed respiration could not be accounted for (Robinson *et al.*, 2002). Work carried out on AMT 11 showed that in the southern

Atlantic gyre,  $R \sim P$ , but that the north eastern edge of the northern gyre, which shares the same chlorophyll concentration, community structure and primary production is net heterotrophic.

P:R ratios are calculated from GP and DCR, both measured in this work at various depths throughout the euphotic layer. P:R values will therefore be calculated for each depth and integrated across the water column. Most samples were taken from depths corresponding to 55%, 33%, 14% and 1% irradiance, but a limited number were taken from the 0.1% depth. In addition, water collected from the 55% was occasionally incubated at both the 55% and 97% light intensity. Incubations were not routinely carried out at each extremity since photo-inhibition can occur in the shallower incubations and rates were not always measurable at the 0.1% depth.

We hope to derive representative P:R ratios for provinces traversed by the AMT 12 transect, characterised by community structure and nutrient supply. Concurrent measurements of community size spectra have been carried out (E. San Martin, A. Poulton, M. Zubkov) and we hope to test the hypothesis that the P:R ratio can be predicted from the slope of the plankton size spectra.

It was hoped to compare the balance between production and respiration in the two gyres and relate observations to other measurements taken concurrently. However, results from the initial section of the transect (south of the equator) were restricted by poor precision, which gave errors of comparable magnitude to the measured rates. This was probably caused by errors in the calibration of the bottles used and it is hoped that it will be possible to re-work and re-claim the early data on completion of the cruise when the bottles will be re-calibrated. Successful measurements have been made within the Northern gyre, however, and our GP/DCR values come from further into the gyre than in any previously published work. We hope to relate P:R ratios from within the gyre to indicators of the transport of organic nutrients into the region.

The majority of the data work-up will be carried out after the cruise has finished and we can establish which data can be re-claimed and what must be rejected. However, some figures are attached as examples of the work that has been carried out. We expect to be able to deposit all  $O_2$ , GP, NCP and DCR data at BODC by 1<sup>st</sup> September 2003.

Calibration  $O_2$  samples for both CTDs have been collected. The complete calibration procedure will be undertaken at BODC, however, figure 5 shows some preliminary data. Figure 6 is a latitudinal plot showing the trophic status of the sampling points at the 55% light depth on the cruise track.

#### **Samples Collected**

Stainless steel CTD + 24 x 20l rosette. Depth profile of GP/DCR samples were collected daily (n=29) *In situ* oxygen for the calibration of the CTD oxygen sensor: Samples from 8 depths collected on 30 occasions.

Samples collected on 3 occasions from 2 depths on the deep (thorium) cast.

#### Titanium CTD + 24 x 10l rosette

*In situ* oxygen for the calibration of the CTD oxygen sensor Samples collected on 8 occasions from up to 10 depths

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Figure 6Preliminary Calibration Data for the Stainless Steel CTD Oxygen Sensor.<br/>The Complete Calibration Procedure will take Place at BODC

Figure 7 Latitudinal Plot Showing the Variation in Trophic Status of the Sampling Points at the 55% Light Depth on the Cruise Track



## **Basin Scale Variability of CDOM and Photoreactivity**

## Jenna Robinson

University of Newcastle

#### Objectives

- To measure the absorbance and concentration of Cromophoric Dissolved Organic Matter throughout Atlantic Ocean Provinces using an Ultrapath UV-Visible Spectrometer.
- To measure the Photo reactivity of Chromophoric Dissolved Organic Matter through on Deck incubations.
- To measure the consumption of Oxygen during Photo degradation of CDOM, and to compare this to the consumption of Oxygen during respiration.

#### Results

CTD	Photo reactivity	CDOM	CTD	Photo reactivity	CDOM
13			41		3 depths
14			42		
15		2 depths	43	1 depth	
16	1 depth		44		
17			45	1 depth	
18		2 depths	46		
19	1 depth		47	1 depth	
20		2 depths	48		
21	1 depth		49	1 depth	
22		2 depths	50		
23	1 depth		51	1 depth	
24		2 depths	52		
25			53		
26	1 depth		54	1 depth	
27			55		
28		2 depths	56	1 depth	
29	1 depth		57		
30		2 depths	58	1 depth	
31	1 depth		59		
32		2 depths	60	1 depth	
33	1 depth		61		
34			62		
35		2 depths	63	1 depth	
36	1 depth		64		
37			65		
38	1 depth		66		
39			67	1 depth	
40	1 depth		68		

#### Table 6CDOM Samples Collected

The results from the analysis of the photo reactivity experiments and the measurement of CDOM absorbance will be carried out at Newcastle University before AMT 13.

## **DMS/DMSP** Analysis

## Tom Bell

## School of Environmental Sciences, University of East Anglia

#### Introduction

During AMT-12 I have been analysing seawater samples for dimethylsulphide (DMS) and its precursor, dimethylsulphoniopropionate (DMSP) in both the particulate and dissolved form. DMS is volatile and considered climatically significant as it impacts cloud formation and hence the climate, at least on a local scale. DMSP is produced by phytoplankton and its conversion to DMS is both intra and extra cellular. These processes are complicated, involving a myriad of factors. My work on AMT-12 comes under hypothesis 8 (see below) but can be linked with every other hypothesis in some way or another. *Hypothesis 8: pCO2 and trace gas exchange are a function of phytoplankton community structure and biomass and significantly influence aerosol formation over the remote oceans* 

#### **Sampling Methodology and Times**

I analysed both DMS and DMSP using a system termed 'Purge and Trap'. This essentially involves bubbling and inert gas through the water sample to purge out the gaseous DMS, and then trapping it onto an adsorbant surface (Tenax) at a low temperature. Having concentrated all the DMS onto the trap, I then inject it onto my gas chromatograph (GC) column by heating the trap. The GC provides me with a measurement of how much DMS was in the volume of seawater purged and, using my own calibration curve, I am able to calculate a concentration. For DMSP, the process is exactly the same, but with an initial preparation step. This simply involves adding concentrated sodium hydroxide (NaOH) to the sample (or filter paper if analysing for particulate DMSP) which cleaves DMSP into DMS plus acrylic acid. The resulting DMS is then purged in the same manner as before. Along the AMT-12 cruise track, I sampled every pre-dawn CTD cast (approx. 0400hrs local time), generally at least 6 depths - the light depths plus the chlorophyll maximum. I also sampled the late morning CTD cast (approx. 1100hrs local time), but only the surface bottle, and took an underway sample from the underway supply at around 1500hrs (local time).

#### **Data and Analysis Aims**

At present, all my data is still in its "raw" form and has not been converted into concentrations. This will take place once I get back to the UK, after which my aims are to:

- 1) Quantify the DMS flux from/to the surface ocean/lower atmosphere. Using the ammonia (NH<sub>3</sub>) flux (using data collected by M. Woodward and T. Jickells), any potential linkages between the reduced nitrogen and sulphur biogeochemical cycles can be identified.
- 2) Analyse the DMS/DMSP data in relation to spatial scale <u>and</u> all other data that potentially affects DMS/DMSP production.

## Nitrous Oxide and Methane Concentrations in the Atlantic Ocean and Stable Isotopic Signatures

## **Grant Forster**

University of Newcastle upon Tyne

#### Aims and Objectives

- To generate vertical profiles of nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) saturations for the Atlantic Ocean on the AMT-12 cruise track. This will utilise single-phase equilibration gas chromatography (Upstill-Goddard *et al*, 1996)).
- To generate vertical profiles of the stable isotopic signature of nitrous oxide (<sup>15</sup>N/<sup>14</sup>N, <sup>18</sup>O/<sup>16</sup>O) using isotopic ratio mass spectrometry (IRMS) to identify the source of the oceanic nitrous oxide.

#### Introduction

A recent synthesis of available data and modelling results reveals an increase in the average global surface temperature of ~  $0.6^{\circ}$ C since the late 19<sup>th</sup> century (IPPC, 2001). Hence concern is growing with regards to the increasing atmospheric burdens of a number of radioactively active trace gases. Nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are of particular interest because they both absorb infrared radiation more intensively than carbon dioxide (Lashof and Ahuja, 1990), together accounting for ~ 18% of enhanced radiative forcing (Hansen *et al*, 1989; Lashof and Ahuja, 1990). CO<sub>2</sub> (57%) and CFC's (25%) account for the remainder (Hansen *et al*, 1989).

In 1998, globally averaged atmospheric mixing ratios of CH<sub>4</sub> and N<sub>2</sub>O were 1,730 ppbv (Dlugokencky *et al*, 1998) and 314 ppbv (IPPC, 2001), respectively. This corresponds to total burdens of 4,850 TgCH<sub>4</sub> and 1510 TgN (IPPC, 2001). However, these burdens are increasing by 0.25-0.31 % yr<sup>-1</sup> for N<sub>2</sub>O (Prinn *et al*, 1990) and 0.3 % yr<sup>-1</sup> for CH<sub>4</sub> (Steele *et al*, 1992; Dlugokencky *et al*, 1994). Data from Pearman and Fraser (1988) show annual increases in methane concentrations of ~0.6 % yr<sup>-1</sup> during the eighties, thus the data from Steele *et al* (1992) and from Dlugokencky *et al*, (1998) show a dramatic decrease in the growth rate of methane emissions for the period 1984 to 1996. This imbalance suggests global source-sink imbalances that deserve much needed investigation.

CH<sub>4</sub> in the ocean is a source of atmospheric CH<sub>4</sub>, thus it is essential to quantify this air-sea exchange if the global CH<sub>4</sub> budget is to be resolved. It has been estimated that this source could contribute as little as  $0.4 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ , approximately 0.1% of natural flux based on measurements from open ocean surface waters (Bates *et al*, 1996). However, larger estimates assign an oceanic source strengths as 2% and 2.5 % of natural source strength corresponding to  $10 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$  and  $15 \text{ Tg}(\text{CH}_4)\text{yr}^{-1}$ , respectively (Fung *et al*, 1991; Lelieveld *et al*, 1998). Bange *et al* (1994) estimated a total marine flux of  $15 \text{ Tg}\text{CH}_4\text{yr}^{-1}$ , this included estuarine and coastal shelf contribution to the marine methane source and supports other estimations (e.g. Brooks *et al*, 1981; Scranton and McShane, 1991; Scranton et al, 1993) suggesting estuarine and coastal sources are a major contributing factor to the marine CH<sub>4</sub> flux. Bange *et al* (1994) calculated 75% of all oceanic CH<sub>4</sub> is from coastal origin, an area that accounts for ~16% of the world's ocean surface.

Deep water, coastal waters and ocean upwellings are all considered to be oceanic sources of N<sub>2</sub>O to the atmosphere (Cohen and Gordon, 1979; Law and Owens, 1990; Naqvi and Norhona, 1991; Owens et al, 1991; Nevison et al, 1995; Bange et al, 1996abc; Bange et al, 1999; Patra et al, 1999; Dore and Karl, 1996; Dore et al, 1998; Morell et al, 2001). As a result of the large spatial and temporal variability of the N<sub>2</sub>O fluxes from the oceans (e.g. areas of intense flux such as north west Indian Ocean) and a lack of spatial and temporal coverage of the study areas, it still remains hard to assign a total oceanic source and estimates remain uncertain (Houghton et al, 1995). According to the IPCC (2001) assessment the major source of N<sub>2</sub>O to the atmosphere is from soils, in particular agricultural soils. Unlike CH<sub>4</sub>, the ocean is considered a large source of N<sub>2</sub>O to the atmosphere. The total net source of N<sub>2</sub>O to the atmosphere from the oceans has been estimated ranging from approximately 17% to approximately 24% (Cline et al, 1987; Butler et al, 1989; Mosier et al, 1998; Olivier et al, 1998 Kroeze et al, 1999) of the total source strength. A model by Kroeze et al (1998) predicts greater than a 2-fold increase in N<sub>2</sub>O production form continental shelves, estuaries, and rivers from 1990 to 2050, this could have strong implication on radiative forcing. The  ${}^{15}N/{}^{14}N$  and the  ${}^{18}O/{}^{16}O$  ratio of N<sub>2</sub>O produced in the oceans can hold important information with regards to the geochemical cycle of N<sub>2</sub>O (Yoshida and Matsuo, 1983) because it can provide information on whether nitrification or denitrification is the dominant N<sub>2</sub>O production mechanism. Importantly the isotopic signature from major terrestrial sources is significantly lighter than that of tropospheric N<sub>2</sub>O. Although isotopic fractionation occurs during the destruction of N<sub>2</sub>O in the atmosphere, this cannot account for the high  $\delta^{15}N$  of atmospheric N<sub>2</sub>O. Observed atmospheric  $\delta^{15}$ N-N<sub>2</sub>O values have been explained by invoking an isotopically heavy source from the oceans (Kim and Craig, 1993; Prasad, 1994). A large marine source of isotopically heavy N<sub>2</sub>O is plausible considering that deep water N<sub>2</sub>O is characterised by high  $\delta^{15}$ N (Kim and Craig. 1990) and the impacts of regions such as the Arabian Sea and the eastern tropical North Pacific where low oxygen and suboxic waters may be major sources of N<sub>2</sub>O to the atmosphere (Law and Owens, 1990; Naqvi and Norhona, 1991; Codispoti et al, 1992). In recent years the formation of the isotopically 'heavy' N<sub>2</sub>O has been attributed to nitrification, denitrification, and a denitrification-nitrification couple.

#### **Data and Samples Collected**

Data has been collected at various stations along the AMT-12 transect. These range from 9-11 depth measurements for N<sub>2</sub>O and CH<sub>4</sub>. For depths and station please see Table I. This data was analysed same day using Single-Phase Equilibration Gas Chromatography (Upstill-Goddard *et al*, 1996) on board RRS James Clark Ross. The final data is yet to be calculated. Also samples have been collected for <sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O analysis. These sample have been collected and stored and will be analysed using Isotopic Ratio Mass Spectrometry (IRMS) at the university of Newcastle upon Tyne.

STATION	METHANE SATURATIONS	NITROUS OXIDE SATURATIONS	ISOTOPES
AMT12_05	10 DEPTHS	10 DEPTHS	
AMT12_07	10 DEPTHS	10 DEPTHS	8 DEPTHS
AMT12_10	9 DEPTHS	9 DEPTHS	8 DEPTHS
AMT12_12	11 DEPTHS	11 DEPTHS	9 DEPTHS
AMT12_14	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12-16	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12-19	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_21	9 DEPTHS	9 DEPTHS	10 DEPTHS
AMT12_23	10 DEPTHS	10 DEPTHS	
AMT12_26	10 DEPTHS	10 DEPTHS	
AMT12_29	10 DEPTHS	10 DEPTHS	
AMT12_33	10 DEPTHS	10 DEPTHS	
AMT12_36	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_38	9 DEPTHS	9 DEPTHS	10 DEPTHS
AMT12_40	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_42	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_45	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_47	10 DEPTHS	10 DEPTHS	10 DEPTHS
AMT12_49	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_51	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_54	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_56	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_58	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_60	8 DEPTHS	8 DEPTHS	8 DEPTHS
AMT12_63	9 DEPTHS	9 DEPTHS	9 DEPTHS
AMT12_65	8 DEPTHS	8 DEPTHS	8 DEPTHS
AMT12_67	9 DEPTHS	9 DEPTHS	9 DEPTHS

#### Table 7Methane and Nitrous Oxide Samples Collected

#### **Observed trends**

-Nitrous oxide- data still to be calculated. However, a trend is still available from the uncalculated data. This trend is near saturation water in the southern gyre. Stations AMT12\_23 to AMT12\_49 show a dramatic increase in nitrous oxide saturation below approximately 130 m. Stations AMT12\_51 to AMT12\_67 shows similar results to the southern gyre. However, accurate data are still to be calculated from chromatograms. -Methane- Data to be calculated.

-Isotopes ( $\delta^{15}$ N-N<sub>2</sub>O,  $\delta^{18}$ O-N<sub>2</sub>O)- To be analysed.

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## Measurements of Autotrophic Community Structure and Primary Production

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#### **Objective**(s);

- 1. To provide an understanding of the autotrophic community structure on a basin-scale with reference to spatial and temporal changes.
- 2. To collect samples for measurements of particulate and dissolved organic carbon and nitrogen.

Table 8Autotrophic Community Structure and Primary Production Samples<br/>Collected

Concerta				
Measurement	No.	No.	Analysis method(s)	Person(s)
	Stations	samples		Responsible
Chlorophyll	60	491	Welschmeyer (1994)	ML, AH, AP
Pigments	60	670	Barlow et al., (1997)	SR
Primary Production	19	80	Maranon et al., (2002)	AP
Particle Absorption	30	335	Tarran et al., (1995)	AP
DON / DOP	15	180	JGOFS, (1997)	SR, RS
POC / PON	30	491	Sharp (1974)	SR
Phytoplankton species	30	600 <sup>[1]</sup>	Hasle, (1975);	SR / AP
(Microscope)			Poulton, (2002)	
Phytoplankton Species (SEM)	30	106	Andruleit (1996);	AP
			Cortes et al., (2001)	
Phytoplankton Species (AFC)	37	583	Zubkov et al., (1998)	SR, MVZ

Note: [1] – Around 400 samples were collected for the microzooplankton group at PML (Elaine Fileman, Paul Hampton).

#### Cruise Summary and plans for future analysis;

The majority of the chlorophyll samples were analysed onboard (AH, ML) with a small number of samples being returned to SOC (frozen, -80 deg C) for analysis and re-calibration of the laboratory TD-700 fluorometer. These samples will be analysed within the first month of return to SOC by AP. Due to continuing problems with the new Thermofinigan HPLC system (comms problem with integrator, mysterious autosampler error message) despite regular contact with technical staff in the UK, no samples were analysed on board: all samples, and replicates, were stored at -80 deg C and will be returned to SOC in liquid-N for analysis within 8 weeks (measurements should be available to the rest of the AMT community within 6 months). Carbon-fixation measurements of primary production were analysed on board with data using the TriCarb 2900C Liquid Scintillation Counter onboard the JCR, with further data processing taking place on return to SOC. Samples for particle absorption (and measurements of phycobilliproteins pigments) will be analysed by Dave Suggett (University of Essex), with storage in liquid-N until analysis. DON/DOP and POC/N samples will be returned to SOC for later analysis in conjunction with Richard Sanders (RS), probably inbetween AMT13 and AMT14. Microscope samples are preserved in 2% acidic Lugols solution and 4% phosphate-buffered Formalin with SR leading the enumeration of Lugols samples for diatoms and dinoflagellates and AP analysing the Formalin samples for

coccolithophore species. Samples for coccolithophore species analysis by Scanning Electron Microscope (SEM) will be returned to SOC and analysed in conjunction with the new coccolithophore PhD student. Unfortunately, due to a lack of suitable filtering equipment no samples for partilcuate inorganic carbon were collected: this is to be remedied by the construction of a deadecated filtering rig suitable for this analysis. Following instructions from Mike Zubkov (MZ), SR collected over 500 samples for later analysis of bacterial diversity and picoplankton community structure.

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## Measurements of New and Regenerated Phytoplankton Production Based on the Incorporation of <sup>15</sup>N and <sup>13</sup>C Stable Isotopes

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#### Introduction

Previous AMT cruises have demonstrated that the subtropical gyres of the North and South Atlantic are characterised by low phytoplankton biomass (often < 0.2µg l-1 chl-a) associated with a deep chlorophyll maxima at 100-125 m ( $\sim$ 1% light depth). Small cells ( $\sim$ 2-5µm) characterise a community often dominated by prochlorophytes (*Prochlorococcus*), cyanophytes (Synechocococcus) and a diverse assemblage of picoeukaryotes (mostly flagellates) which are low-light adapted with appropriate spectrally sensitive pigments. The equatorial upwelling region is characterised by a shallowing of the chlorophyll maximum layer, an increasing biomass and the frequent presence of the nitrogen fixing cvanophyte, Trichodesmium. Control of the community structure is governed by the persistent hydrographic stability of these gyres which results in very low nanomolar concentrations of all nutrients above a strong thermocline and nutricline. Existence in the deep chlorophyll maximum by many of these phytoplankton species is a trade-off between optimising the limited nutrient flux here while trying to harvest sufficient light at low photon flux. Previous studies have examined both phytoplankton community structure and associated light harvesting pigments, but very little is known about the carbon or nitrogen budgets of the oligotrophic sub-tropical gyres of the North and South Atlantic. The goal of AMT-12 and subsequent cruises is to undertake a more process orientated approach to quantifying the carbon and nitrogen budgets, to measure export production and to assess ocean-atmosphere gaseous exchanges.

Unravelling the nitrogen budget of the subtropical gyres is a particularly interesting although complex problem to solve. Nitrogen inputs from the atmosphere in the form of NO<sub>3</sub> and NH<sub>4</sub> associated with rainfall may be quite significant. Dinitrogen fixation (by Trichodesmium for example) provides another atmospheric input of N. From below, diffusivity across the thermocline will introduce small quantities of NO<sub>3</sub>. However, nitrate assimilation has a strong dependency for Fe, as does N fixation, so potential Fe limitation, or its relief through aeolian dust inputs, becomes an important consideration. Furthermore, nitrate assimilation has a high light dependency because of the increased energy required to drive intracellular nitrate reduction. Within the biological community itself, the conservation of nitrogen through the tight coupling of NH<sub>4</sub> regeneration and its uptake by phytoplankton is known conceptually, but not yet measured. Adding to this complexity, we are beginning to get some glimpses of nitrification rates, and rather surprisingly, some evidence for de-nitrification in near surface (300m-surface) waters. Some evidence of net heterotrophy, based on the balance between oxygen production and consumption, begs the question of where a source of organic carbon could be derived from to support this observation. Lateral inputs of DOC (& DON), possibly from productive ocean margins, may be one such source. We cannot therefore ignore the potential for DON assimilation by some phytoplankton groups at least, particularly the cyanobacteria.

Conventionally, nitrate assimilation ( $\rho NO_3$ ) relative to total N assimilation ( $\rho NO_3 + \rho NH_4 + \rho urea [+\rho DON]$ ) by phytoplankton using <sup>15</sup>N tracers provides a useful index, the f-ratio, which indicates what proportion of phytoplankton growth is dependent upon NO<sub>3</sub>

assimilation - i.e. "new" net production. Under long-term equilibrium conditions, the f-ratio provides a measure of export production available to consumers or for sedimentation and therefore provides a valuable tool for indirectly estimating vertical carbon flux. For productive temperate or coastal upwelling waters at least, the upward flux of NO<sub>3</sub> is the most important source of "new" nitrogen. But it is clear that in the sub-tropical gyres, we must modify the more classical f-ratio approach to include atmospheric inputs of both NO<sub>3</sub>, NH<sub>4</sub> and N<sub>2</sub>, all of which are "new" inputs to be accounted for.

It is also becoming apparent that Redfield stoichiometry for C:N uptake can no longer be unequivocally taken as 6.6:1 so that dual-labelled tracer studies become an essential component of <sup>15</sup>N tracer work if carbon fluxes are to be inferred. Furthermore, size-fractionated <sup>15</sup>N tracer studies can provide considerable insight into the structure and functioning of planktonic communities.

#### Methods

**Nitrogen and carbon uptake measurements**: Nitrogen and carbon ( $^{15}$ N &  $^{13}$ C) uptake experiments were carried out for each of the daily dawn (~ 4am) CTD stations. Water was incubated in the simulated *in situ* on deck incubator tubes covered with blue filter screens (Lee) to provide appropriate shading at the 97% (surface), 55%, 33%, 14% 1% and 0.1% light depths. The temperature of surface incubator bottles (97-14% light depths) was maintained by pumping surface (7m) sea water through the tubes. For the 1% and 0.1% depths, the temperature was maintained at ambient for that depth (usually ~ 5°C lower than surface) by using re-circulating chillers.

For each nutrient (NO<sub>3</sub>, NH<sub>4</sub>, urea), 2.0L sample water was measured into a 2.0L polycarbonate bottle(s) and inoculated separately with Na<sup>15</sup>NO<sub>3</sub> (98 atom%), CO(<sup>15</sup>NH<sub>2</sub>)<sub>2</sub> (99.1 atom%) and <sup>15</sup>NH<sub>4</sub>Cl (98 atom%) to a projected final concentration of ~10% of the ambient nutrient concentration wherever possible. However, because of the low nano-molar ambient nutrient concentrations, additions were quite frequently above 10% of ambient and at times 100-150% of ambient concentrations. This necessity is driven by detection limitations of subsequent Mass Spectrometer measurements of <sup>15</sup>N incorporation.

Recognising that additions of nutrient "spikes" were frequently in excess of ambient concentrations in the oligotrophic sub-tropical gyres and that additions are likely to stimulate phytoplankton growth, we ran experiments to examine uptake rates in response to increasing nutrient additions for all three nutrients. It is hoped that from this, we can calculate phytoplankton growth rates at appropriate ambient nutrient concentrations.

To measure C:N uptake ratios and carbon fixation as a measure of primary production, NaH<sup>13</sup>CO<sub>3</sub> was added to all bottles (to ~5% of the ambient DIC concentration). Dark <sup>15</sup>NO<sub>3</sub> and <sup>13</sup>C experiments were also carried out to correct for respiration and dark <sup>15</sup>N uptake. For size-fractionated experiments, the same protocols were followed except that incubation volumes were 6.0L and at the end of the experiment, the samples were fractionated into 3 x 2.0l total, <20µm and <2.0µm fractions. Each separate fraction was then filtered onto pre-ashed (450°C for 6 hours) Whatman 25mm GF/F filters which were frozen at -80°C for later determination of particulate 15N and 13C enrichment (uptake) by mass spectrometry.

**Ammonium regeneration rates:** Ammonium regeneration rate experiments were conducted for many of the CTD stations, particularly those in the southern gyre when there was some prospect of the NH4 analyser operating properly (see below) as this measurement is critical for the calculation of regeneration rates.

**Nutrients**: Ambient nitrate concentrations were determined daily by Malcolm Woodward (PML) using a Skalar Autoanalyser. Samples for urea determinations were frozen and will subsequently be analysed manually using the methods of Grasshoff *et al.* (1983) scaled down to 5ml samples (Probyn 1987). Unfortunately, the nano-molar NH<sub>4</sub> analyser malfunctioned

throughout the cruise so that for ambient  $NH_4$  determinations, samples were also frozen for later analyses – a procedure we recognise to be far from ideal.

**Chlorophyll determinations:** At each station and for every depth, including all underway samples, chlorophyll determinations (Welschmeyer) were undertaken in addition to those routinely taken with the 4am & 11am CTD casts. Samples corresponding to the depths of the 15N & 13C uptake experiments were filtered onto 25mm Whatman GF/F filters. Pigment was extracted overnight in a fridge with 90% acetone and read on a Turner Fluorometer calibrated with chlorophyll standards (Sigma).

#### **Station Listing**

Date	CTD Station	Incubation Type
14 <sup>th</sup> May	CTD 3	Standard
16 <sup>th</sup> May	CTD 5	Standard + $NH_4$ Reg.
17 <sup>th</sup> May	CTD 7	Standard + $NH_4$ Reg.
18 <sup>th</sup> May	CTD 10	Standard + $NH_4$ Reg.
19 <sup>th</sup> May	CTD 12	Standard + $NH_4$ Reg.
20 <sup>th</sup> May	CTD 14	Standard + $NH_4$ Reg.
22 <sup>nd</sup> May	CTD 19	Standard + $NH_4$ Reg. + SF
23 <sup>rd</sup> May	CTD 21	Standard + surface SF
24 <sup>th</sup> May	CTD 23	Standard
26 <sup>th</sup> May	CTD 26	Standard + surface SF
27 <sup>th</sup> May	CTD 29	Standard + $NH_4$ Reg.
28 <sup>th</sup> May	CTD 31	Nutrient conc. response
29 <sup>th</sup> May	CTD 33	Standard + $NH_4$ Reg.
30 <sup>th</sup> May	CTD 36 (Equator)	SF @ 1% light depth
1 <sup>st</sup> June	CTD 40	Standard + surface SF
2 <sup>nd</sup> June	CTD 42	Standard
3 <sup>rd</sup> June	CTD 45	Nutrient conc. response
4 <sup>th</sup> June	CTD 47	Standard
5 <sup>th</sup> June	CTD 49	Nutrient conc. response
6 <sup>th</sup> June	CTD 51	Standard
7 <sup>th</sup> June	CTD 53	Nutrient conc. response
9 <sup>th</sup> June	CTD 58	Surface $SF + NH_4$ Reg.
10 <sup>th</sup> June	CTD 60	Standard
11 <sup>th</sup> June	CTD 63	Standard
12 <sup>th</sup> June	CTD 65	Standard
13 <sup>th</sup> June	CTD 67	Standard

#### Table 9 <sup>15</sup>N Uptake Experiment Stations

<u>Legend</u>: A "Standard" experiment denotes dual labelled ( $^{15}N + ^{13}C$ ) at 6 light depths. "NH<sub>4</sub> Reg." represents an NH<sub>4</sub> regeneration experiment at each light depth. These were later

curtailed because the nano-molar NH<sub>4</sub> nutrient analyser was not functioning which made these experiments less likely to yield reliable results. "SF" denotes a size-fractionated experiment; also curtailed because of water budget restrictions. "Nutrient conc. response" experiments (NO<sub>3</sub>, NH<sub>4</sub> & urea) were designed to examine the changing uptake response with respect to increasing nutrient additions.

#### Results

There was no on-board Mass Spectrometer so that analyses of our samples will need to be carried out at SOC. We anticipate that data will start to become available by

August/September 2003 and that the full data set will be available to the AMT community by the end of 2003.

#### Conclusion

While the <sup>15</sup>N uptake data set produced on AMT 12 is has the potential to be uniquely significant, it will be greatly enhanced by assimilating all the natural abundance <sup>15</sup>N and other N cycling (& related) data produced on the ship into a coherent N budget for the North and South Atlantic subtropical gyres. It is to be hoped that this will indeed be done and that we encourage modellers to help us understand the unique biological features of the sub-tropical gyres which may make phytoplankton key regulators of biogeochemical processes in these regions, previously thought to be relatively inert deserts.

#### Acknowledgements

We would like to thank Malcolm Woodward for undertaking nutrient analyses for us. Very many thanks are due also to Ms. Anna Hickman who shouldered the major responsibility of filtering over 4 tonnes of sea-water to provide us with chlorophyll, HPLC, POC/N and particle absorbance data. For myself, (MIL) I would like to thank the AMT Steering Committee for all their hard work in bringing the cruise to the starting line and to Tim Jickells, Carol Robinson and Alex Poulton for getting us to the finishing line in Grimsby in good shape!

## **Dinitrogen Fixation in the Atlantic Ocean**

## Nick Millward

Plymouth Marine Laboratory

#### Objectives

- To develop an acetylene reduction gas chromatographic method for use with marine oligotophic water samples as an indirect measure of dinitrogen fixation
- To further develop the <sup>15</sup>N stable isotope method for atmospheric dinitrogen fixation.
- To make preliminary measurements of dinitrogen fixation, by means of the acetylene reduction technique.
- To make preliminary measurements of dinitrogen fixation, by means of the <sup>15</sup>N stable isotope incorporation technique.
- To develop protocols for both the <sup>15</sup>N and acetylene reduction techniques in a research vessel environment.

#### Methods

**Acetylene reduction:** Dinitrogen fixation was measured indirectly by means of the acetylene reduction technique. This technique is based upon the biodegradation of acetylene to ethylene, by means of the triple bond in the acetylene being broken by the nitrogenase enzyme. This enzyme is only present in organisms that possess the ability to fix atmospheric dinitrogen, and it therefore a reliable measure of the dinitrogen fixing natural biota Water was collected each morning from the pre-dawn CTD from 5 depth equivalent to (1%, 14%, 33%, 55% and 96%) of surface irradiance. The samples were incubated in 250ml gas tight bottles for 12hrs in on-deck incubators, with the appropriate light filters. The required light depths were calculated from PAR data from the previous day's data. The samples were removed after incubation and stored in a dark box, the headspace of the bottles was then equilibrated and analysed by gas chromatography (flame ionisation detection). Futher to the set objectives, myself, Dr T Jickells and Dr A Poulton carried out a nutrient addition experiment. This consisted of the addition of NH<sub>4</sub>, NO<sub>3</sub>, P, Fe and a mixture of all of these, to a number of bottles. These were then incubated for 6 and 12hrs, then analysed <sup>15</sup>N stable isotope Technique:

This technique is a direct measure of the uptake of <sup>15</sup>N by the dinitrogen fixing organisms. <sup>15</sup>N was introduced as a gas into the cubitainers and any uptake of <sup>15</sup>N labelled nitrogen, therefore must be as a result of atmospheric/dinitrogen fixation.

Water was collected each morning from the pre-dawn CTD from 2 depth equivalent to 1% and 55% of surface irradiance. This was then transferred in to 8 gas tight cubitainers, 4 for each depth.

To each set of cubitainers the following inoculations were carried out

Cubitainers No	light level	Addition	incubation time
1,5	1% and 55%	15N	0 hr
2,6	1% and 55%	14N (Air)	0 hr
3,7	1% and 55%	15N	24hr
4,8	1% and 55%	14N (Air)	24hr

These were incubated for the appropriate time in on deck incubators with the appropriate light filters, removed and filtered on to glass fibre filters (GFFs), placed in to small petri dishes, sealed and frozen at -20°C.

#### **Preliminary results**

One of my objectives was to optimise the acetylene reduction technique, as can be seen below the optimal incubation time is 12hr and volume of acetylene is 50ml (20% v/v)



#### Figure 8 Incubation Timing and Substrate Concentration Optimisation

Data from CTDs 21-40 acetylene reduction experiments were shown to have no significant differences between or within depths. This however may have been due to an experimental error. Early work on fresh water cyano-bacteria has shown that the optimal volume of acetylene needed was 10ml. This was therefore used as a starting point for the first number of CTDs.

A timing and concentration experiment was done after CTD 40 and the subsequent data showed some significant differences in nitrogen fixation between depths.

The data from the nutrient addition experiment revealed some very interesting correlations between nitrate, ammonium and iron, further work on these additions is needed before any conclusions can be make.

All data will be deposited at BODC by September 2005.

## **Planktonic Size Spectra**

## Elena San Martin

Plymouth Marine Laboratory

The main aim of this component of AMT12 was to determine the plankton size spectra along the transect and carry out zooplankton feeding experiments. I hope to ascertain whether there is a latitudinal variation in size spectra and, hence, quantify the export of carbon to the atmosphere and deep ocean. This should help resolve whether planktonic size spectra can be used as a predictive tool in large-scale oceanic regions.

#### Objectives

- To determine phytoplankton and microzooplankton size spectra.
- To obtain depth integrated mesozooplankton size spectra from vertical net hauls.
- To produce "complete plankton size spectra" for each station by compiling both of the above data sets.
- To obtain size fractionated zooplankton biomass.
- To conduct mesozooplankton feeding experiments and observe any latitudinal pattern in grazing activity of a mixed zooplankton population over a mixed prey (phytoplankton and microzooplankton) population.
- Observe the occurrence of large phytoplankton in 50 µm net samples in collaboration with Professor Patrick Holligan and Dr Alex Poulton.
- Prepare heterotrophic microzooplankton slides from each light depth for further microscopic analysis by Elaine Fileman and Paul Hampton.

#### Methods

Vertical 200 and 50  $\mu$ m bongo net hauls were towed up at 30 m min<sup>-1</sup> from both 200 and 50 m depths at each pre-dawn station. Each 50  $\mu$ m sample was fixed in both Lugol's iodine and formalin for later microscopic examination. Time allowing, size fractionated zooplankton biomass sub-samples (> 1000  $\mu$ m; > 500  $\mu$ m; > 200  $\mu$ m) were taken from the 200  $\mu$ m net samples and frozen for later analysis. The rest of the sample was fixed in formalin for later examination.

Phytoplankton and microzooplankton samples were collected from the pre-dawn CTD cast at every depth and fixed in both Lugol's iodine and formalin. FlowCam, which is an instrument that instantaneously counts and sizes particles in the 10  $\mu$ m – 2 mm range, will be used to count and size all of the preserved plankton samples.

The CTD samples taken from the 5 light depths were fixed in gluteraldehyde to yield 0.5% final concentration. Fixed samples can be stored for up to 24 hours in a refrigerator before processing. Hence, epifluorescence staining was conducted as soon as possible after sampling.

The zooplankton feeding experiments were conducted every four days. The mesozooplankton and prey were collected from net hauls and CTD casts after the pre-dawn cast at approximately 0600 hours. Zooplankton samples for the feeding experiments were collected from 100 to 0 m vertical plankton net hauls made with a 200  $\mu$ m mesh net towed at 10 m min<sup>-1</sup>. The experimental water containing the mixed prey for grazing assessment was collected from the CTD at the depth of the chl *a* maximum. 24-hour incubations, involving experimental and control bottles were set up in an on-deck incubator with a screen simulating 1% surface irradiance. Microzooplankton samples from the initial bottle (t=0) were fixed in

Lugol's iodine and formalin and chlorophyll *a* quantification by fluorometry was carried out using GF/F and >5  $\mu$ m filters. Mesozooplankton initial aliquots were filtered onto GF/C glass filters and dried for assessment of biomass (dry weight) and some were fixed in a small bottle with formalin for later taxonomic assessment and sizing. After 24 hours the animals from the experimental bottles were collected and fixed with formalin for later examination. Samples from each bottle were taken for microzooplankton and chlorophyll *a* analysis.

СТЪ	Data	Phytoplankton	Epifluorescence	Experimental Water
	Date	& Microzooplankton	Staining	for Feeding Experiment
3	14/05/03	11 depths	5 depths	
5	16/05/03	9 depths		
7	17/05/03	10 depths		
10	18/05/03	11 depths		
12	19/05/03	11 depths	5 depths	
14	20/05/03	11 depths	5 depths	
16	21/05/03	11 depths		
17				Chl max
19	22/05/03	11 depths		
21	23/05/03	11 depths	5 depths	
23	24/05/03	11 depths	5 depths	
26	26/05/03	11 depths		
27				Chl max
29	27/05/03	11 depths		
31	28/05/03	11 depths		
33	29/05/03	11 depths		
34				Chl max
36	30/05/03	11 depths		
38	31/05/03	11 depths		
40	01/06/03	11 depths	5 depths	
42	02/06/03	10 depths	5 depths	
43				Chl max
45	03/06/03	11 depths	5 depths	
47	04/06/03	11 depths	5 depths	
49	05/06/03	11 depths	5 depths	
51	06/06/03	11 depths	5 depths	
52				Chl max
54	07/06/03	10 depths	5 depths	
56	08/06/03	11 depths	5 depths	
58	09/06/03	11 depths	5 depths	
60	10/06/03	10 depths	3 depths	
61				Chl max
63	11/06/03	11 depths	5 depths	
65	12/06/03	11 depths	5 depths	
67	13/06/03	11 depths		

#### Table 10 Samples Collected for Plankton Size Spectra

Data	Bongo Nets- 200 & 50 µm		Single Net- 200 µm	Size fractionated	
Date	200 m	50 m	100 m	Zooplankton Biomass	
14/05/03	Y	Y		Y	
16/05/03	Y	Y		Y	
17/05/03	Y	Y		Y	
18/05/03	Y	Y			
19/05/03	Y	Y		Y	
20/05/03	Y	Y		Y	
21/05/03	Y	Y			
			Y		
22/05/03	Y	Y			
23/05/03	Y	Y		Y	
24/05/03	Y	Y		Y	
26/05/03	Y	Y			
			Y		
27/05/03	Y	Y		Y	
28/05/03	Y	Y			
29/05/03	Y	Y			
			Y		
30/05/03	Y	Y		Y	
31/05/03	Y	Y		Y	
01/06/03	Y	Y		Y	
02/06/03	Y	Y		Y	
			Y		
03/06/03	Y	Y		Y	
04/06/03	Y	Y		Y	
05/06/03	Y	Y		Y	
06/06/03	Y	Y		Y	
			Y		
07/06/03	Y	Y		Y	
08/06/03	Y	Y		Y	
09/06/03	Y	Y			
10/06/03	Y	Y			
			Y		
11/06/03	Y	Y		Y	
12/06/03	Y	Y		Y	
13/06/03	Y	Y			

#### **Preliminary Results**

There are no results to discuss at present as all analysis is performed back in the laboratory. The only qualitative observation that can be made was that there was a significant difference in the amount of plankton found in the nets in the different oceanic regions. There were fewer and generally smaller animals in the oligotrophic regions compared to a more abundant and apparent diverse sample in mesotrophic and eutrophic waters. The size fractionated zooplankton biomass samples and chlorophyll quantification will be analysed at Plymouth Marine Laboratory. The phytoplankton and microzooplankton samples from the CTD, as well as the 200  $\mu$ m zooplankton net samples will be sized and counted using FlowCam at AZTI in late Autumn 2003. Microscopy on the heterotrophic flagellate slides will be conducted by Elaine Fileman and Paul Hampton in Plymouth Marine Laboratory. The 50  $\mu$ m net samples will be investigated for the presence of large phytoplankton at Southampton Oceanography Centre.

# Carbon and Nitrogen Export Estimated from <sup>234</sup>Th/<sup>238</sup>U Disequilibria

## **Sandy Thomalla**

University of Cape Town

Biological activity in surface waters drives the oceanic particle cycle, which in turn controls the scavenging of trace metals and sedimentation to the sea floor. Carbon fixation and carbon export is central to understanding oceanic productivity, and its long term effect on atmospheric CO<sub>2</sub> concentration. The particle- reactive radioisotope <sup>234</sup>Th (half life 24.1 days) is often in disequilibrium with its parent nuclide <sup>238</sup>U in surface ocean waters. This occurs because <sup>234</sup>Th but not <sup>238</sup>U partitions strongly onto particle surfaces and its removal on the sinking flux of material leads to radioactive disequilibrium. Consequently <sup>234</sup>Th/<sup>238</sup>U disequilibrium is potentially a powerful tool to study the downward flux of carbon in the ocean via sinking particles.

Knowledge of the integrated disequilibrium in the water column combined with a steady-state assumption and with the decay constant of <sup>234</sup>Th yields an estimate for the flux of <sup>234</sup>Th from the surface ocean caused by settling particles. To calculate the POC flux from the surface ocean, the ratio of POC to <sup>234</sup>Th on sinking particles is multiplied by the estimated <sup>234</sup>Th flux. For budget calculations of <sup>234</sup>Th, it is essential to consider all processes that control <sup>234</sup>Th activity in a given volume of water. For dissolved <sup>234</sup>Th these are <sup>238</sup>U decay (i.e. <sup>234</sup>Th production), radioactive decay of <sup>234</sup>Th and loss of <sup>234</sup>Th to the particulate <sup>234</sup>Th pool. For particulate <sup>234</sup>Th the controlling processes are input from the dissolved pool, radioactive decay and loss through particles settling out of the given volume of water.

#### Methods

Samples for thorium analysis were collected from a designated CTD cast that took place every 4 days (see Table1 for station positions). Twenty litre water samples were collected through the water column at depths of 25m, 50m, 100m, 150m, 200m, 500m and a duplicate sample at 1000m. A 20 litre surface sample was collected from the uncontaminated surface sea water supply. The sampling distribution is concentrated in the surface 250m where a significant export of thorium on settling particles is expected to result in radioactive disequilibrium between thorium and uranium. The sample at 1000m represents radioactive equilibrium between <sup>234</sup>Th and <sup>238</sup>U.

Total uranium is calculated from salinity and does not have to be measured separately. Particulate <sup>234</sup>Th is measured by filtering the 20litre sample through 142mm 0.4 $\mu$ m polycarbonate filters. These filters are folded in a reproducible way, wrapped in mylar foil and counted directly in a beta counter using appropriate corrections for self-absorption of radiation due to the filter and for detector efficiencies <100%, and corrections for <sup>234</sup>Th decay and <sup>234</sup>Th in growth from <sup>238</sup>U decay since sampling.

Dissolved thorium is measured by adding potassium permanganate (KMnO<sub>6</sub>), manganese dichloride (MnCl<sub>2</sub>), and concentrated ammonia (NH<sub>3</sub>) to the already filtered water sample. Dissolved <sup>234</sup>Th is precipitated from the filtered water as MnO<sub>2</sub> precipitate within 8 hours. This precipitate is filtered onto 142mm 0.8µm polycarbonate filters which are then processed in an analogous way as filters for particulate <sup>234</sup>Th.

<sup>234</sup>Th decays via beta decay to <sup>234</sup>Pa. <sup>234</sup>Pa has higher energy betas than <sup>234</sup>Th. It has a short half life of 1.2 minutes and therefore always in radioactive equilibrium with <sup>234</sup>Th. Hence, what actually is measured by the beta counter is <sup>234</sup>Pa decaying via beta decay to <sup>234</sup>U. The replicate sample taken at 1000m helps assess the precision of the sampling process. Ideally this is done by taking a number of samples from the same depth and processing them in the same way. This was attempted using the first test CTD with multiple samples at 500m. However due to a combination of problems involving the filtration system and inexperience in all the stages of the sampling technique, it is possible that this precision test will not be entirely satisfactory. It would be beneficial to carry out the precision test again possibly on the next AMT cruise, once again making use of the first test CTD. Accuracy may be assessed by comparing the determined activity of total <sup>234</sup>Th with the <sup>238</sup>U activity at depth (i.e. 500 or 1000m).

Detector drift (which usually is negligible) is monitored by repeated measurements of a standard sample having a known amount of <sup>238</sup>U in equilibrium with <sup>234</sup>Th.

At each of the thorium depths, a 4litre sample was filtered onto GFF filters for particulate organic carbon (POC) and particulate organic nitrogen (PON). Filters were placed into plastic petri dishes and frozen at  $-20^{\circ}$ C in a dark room for future analysis at the Southampton Oceanography Centre.

The large particulate thorium fraction >50 $\mu$ m was sampled in two ways. The first involved the deployment of an in-situ SAPS pump at the bottom of the export layer (~100m). A 293mm 50 $\mu$ m nylon mesh was inserted into the filter holder of the SAPS pump which was set to pump for one and a half hours. During this time an average of 2300 litres of water was pumped through the mesh giving a pumping rate of 25litres per minute. Ideally a gentler pump rate of around 6litres per minute would be preferred to ensure that the large particles are not destroyed. However the pump rate of the SAPS pump cannot be adjusted. This might create a problem in that it is very difficult to determine whether the larger particles are being destroyed or not. Once the SAPS pumps are back on board the 50 $\mu$ m mesh is removed and rinsed with filtered sea water.

As it is unlikely that the SAPS pump will be available on AMT13, an alternative approach for collecting the large settling particles is being tested. This approach uses a  $50\mu$ m zooplankton net which is raised through the water column from a depth of 100m. In order to eliminate the zooplankton or swimmers from the sample a  $220\mu$ m screen is placed in front of the sample holder at the base of the net.

Both the SAPS and Net samples are split using a Fulsam sample splitter.  $6/8^{ths}$  of the sample is filtered onto 142mm 0.4 $\mu$ m polycarbonate filters which are then processed and counted in the beta counter.  $1/8^{th}$  of the sample is filtered onto GFF filters for POC and PON analysis and stored in the -20 degree freezer. The remaining  $1/8^{th}$  of the sample is placed in Lugols solution for future analysis to classify the main constituents of the large particles settling out of the water column.

## Sample Collection for <sup>230</sup>Th and <sup>231</sup>Pa Analysis

### **Sandy Thomala for Gideon Henderson** Geology Department Oxford University

There are two scientific questions which <sup>230</sup>Th and <sup>231</sup>Pa measurements on AMT12 might help address:

- interannual variability in thermocline ventilation
- influence of productivity and ecosystem style on Pa and Th concentrations and fractionation (with an eye to improve Pa/Th as a proxy for past reconstruction of productivity)

Both of these goals will be much easier to realise as part of a full programme such as AMT and in particular in context of the <sup>234</sup>Th measurements. For this reason the water samples collected for <sup>230</sup>Th and <sup>231</sup>Pa analysis coincided with the depths sampled for <sup>234</sup>Th analysis.

#### Methods

Six of the seven Thorium stations were sampled for <sup>230</sup>Th and <sup>231</sup>Pa (see Table.1). At each station a 20litre sample was filtered directly from the surface Niskin bottle onto a 142mm polycarbonate filter, the filtered water was stored in a 20litre cubitainer. At three of the stations 20litres of water from the uncontaminated sea surface water supply were also filtered. This filtration will be compared to that taken from the surface Niskin bottle to determine the contamination level of the sea surface water supply and subsequently whether or not this supply will be able to be sampled on future AMT cruises thereby freeing up a CTD bottle and allowing larger volumes of water to be filtered.

A 20litre (unfiltered) sample was collected in a cubitainer from 25m as the near surface samples are the most difficult to measure having the lowest <sup>230</sup>Th signal. Five 10litre cubitainer samples were collected from 50m, 100m, 200m, 500m and 1000m. All samples (including the filtered samples) were acidified with 37% hydrochloric acid (HCl) at 7ml per litre and stored.

CTD	Latitude	Longitude	Sampled
1 (test)	50 09.97 S	53 13.98 W	<sup>234</sup> Th
8	43 12.50 S	45 19.25 W	<sup>234</sup> Th, POC, PON
17	37 47.12 S	29 42.57 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON
27	13 55.57 S	24 59.85 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON
34	02 14.16 S	24 59.94 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON
42	12 14.06 N	32 17.18 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON
52	24 19.72 N	32 34.43 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON
61	36 44.15 N	20 48.84 W	<sup>234</sup> Th, <sup>230</sup> Th/ <sup>231</sup> Pa, POC, PON

#### Table 11Thorium Station Positions

## **Bio-Optics**

## Gerald Moore and Chris Lowe

Plymouth Marine Laboratory

One of the objectives of the AMT is the interpretation of optical remote sensing at the basin scale. Key to this interpretation of global data are the bio-optical models used for the interpretation of satellite remotely sensed observations of ocean colour. Traditionally, algorithms have been developed from empirical relationships between optical measurements (reflectance) and in water constituents, primarily chlorophyll concentration.

The primary objective of the bio-optics measurements on AMT 12 has been to develop models that enable the determination of the all the biologically active constituents of the water column. Simply the reflectance, allowing for the effects of pure water, is a non-linear ratio of the backscatter to absorbance, where the absorbers, pigments DOC and detrital material (non photosynthetic particles), and the backscatters are detrital material and phytoplankton.

Of the absorbing pigments Chlorophyll a (Chla) is only one of a large number of phytoplankton pigments, including chlorophylls b and c, carotenoids and phycobilliproteins (PBs). Chlorophyll-a is normally less than 50% of the total pigment biomass, and can be only 30% in oligotrophic areas; it has a limited impact on the spectrum of absorbed light with bands at 440nm and 670nm. The carotenoids absorb in a broad band 400-550 and the PBs, 550-600 nm, and dominate is surface oligotrophic waters.

Full bio-optical models, which relate the water absorption spectrum to all the constituents of the water column to their Inherent Optical Properties (IOPs) of absorption and backscatter, have been developed than can derive CDOM, carotenoids and detrital and potential province classification.

These models together with simple atmospheric models enable the determination of the spectral column scalar light field that is the primary driving input to productivity. Inversion of inherent optical properties into the packaged absorption of photosynthetically active pigments, photoprotectant pigments and gelbstoff (ODOM) enables the determination of the photosynthetically useful photon flux.

The characteristic absorption spectra of the different phytoplankton pigments give potential information as to the photo-adaptive state of the phytoplankton assemblage.

These models have largely been developed on extant data from previous AMTs. The experience of these AMTs has pointed out gaps in knowledge of primary bio-optical variables and problems in instrumentation. With this experience the bio-optical sampling and instrumentation was specified for AMT12.

#### Instrumentation

- Satlantic free falling optical profiler that measured the optical properties of the upper euphotic zone. The profiler measured the wavelengths corresponding to the MERIS sensor on ENVISAT (412,443,490,510,560,620, 665 and 685nm). The sensor had matching surface sensors for normalization to incident light. The free fall profiler and its surface sensors were routinely calibrated with the SeaWiFS Quality Monitor (SQM), which after post calibration at PML will give a radiometric accuracy of better than 1%.
- 2) Wetlabs ac/9 absorption and attenuation meter. This is a multiband spectro-photometer that measures at 9 wavelengths (412, 440, 488, 510, 532, 555, 650, 676 & 715nm). It is coupled to a SBE 19+ CTD. The CTD data is used to correct the ac/9 data for the effects in the changes in the optical properties of pure water with temperature and salinity. The

system has flow cells to ensure proper operation of the instruments and to correct for any time lags in sampling. It is also capable of measuring chlorophyll absorption and 676 nm as a biomass indicator.

Additionally at 5 stations the instruments was used with a 0.2 micron supercap filter that enabled the determination of CDOM below a depth of 10m.

- 3) Wetlabs VSF. This is a backscatter meter that measures scattering at three discrete angles (100, 125 and 150 degrees) and at three wavelengths (440,530 and 650nm). The measurement of the change in angular scattering is key to relating water reflectance at the different sun and view angles that are found in ocean colour observations. This is the first time that such measurements have been made on an AMT.
- Phycoerythrin and phycocyanin fluorometers. These have been developed in association with Chelsea Instruments and are modified minitracker fluorometers.
- The specifications were developed from a bench instrument that was used on AMT4.
  5) Fast repetition rate fluorometer (FRRF). This can measure the absorption cross-section of photosystem II, the quantum yield and the rate of photosynthetic electron transport. During the cruise the instrument was calibrated with a number of blanks from both 0.2 micron filtered seawater and the JCR pure water system.
- 6) UV and Near UV / Visible spectrometers. Two Trios spectrophotometers were deployed on the rig after the equatorial stations. They were used on alternative days to determine the optimal wavelengths for determining UV flux.
- 7) Underway Transmissometer. A CI 660nm transmissomter was coupled to the underway system and logged by the ships system. This provides a simple measure of bio-optical variability between stations that is not affected by photochemical quenching.

#### **Instrument Performance and Preliminary Results**

In general the optical instrumentation, with the exception of the free-fall, was working at or near its performance limits in the gyre waters.

Apart from one telemetry failure, the freefall (rocket) performed faultlessly throughout the cruise.

The ac9 and vsf performed well with only minor corruption of files, which will be corrected on return to PML. The clear blue water showed a reference problem with the VSF, which was corrected after discussion with the manufactures. It is hoped that a full dataset of these measurements will be available, after correction for temperature and salinity effects. On five stations the ac/9 was fitted with a 0.2 micron supercap filter with the top inlet removed. Although there was some cavitation on the pump on depths less than 10 - 15 m the system was capable of producing CDOM profiles. Below is an example from one of the last oligotrophic stations (CTD 61, 36N, 24W). The CDOM absorption is measured in one cast and the phytoplankton absorption is calculated by subtracting the CDOM data from not filtered data in a subsequent cast. The data is not salinity and temperature or blank corrected, but looks promising.



#### Figure 9 CDOM Profile CTD 61

The FRRF proved the most problematic instrument. Two instruments were available – serial numbers 460042 and 460043. SN 460042 did not provide any dark chamber data, and despite consultation with Chelsea Instruments it was not possible to resolve this problem. As a result the instrument was deployed on the pre-dawn casts. The fault was eventually traced to an error in the calibration file supplied with the instrument. SN 460043 showed more problems. The instrument has a fault that caused it to return to its internal monitor and loose all calibration data, which resulted in the need to completely reprogram the instrument also produced corrupt data for several tropical casts. The cause of this was identified as an error in the internal calibration routine of the instrument. After much experimentation it was found that the instrument was affect by bright sunlight when starting it on deck. Starting the instrument with the cap on cured this problem, although the procedure was difficult since the instrument is started with a magnet. It is strongly recommended that this instrument is returned to the manufacturer to resolve this problem.

The PAR (sn 460059) produced higher than reasonable PAR levels and Kd's. The PAR sensors on both FRRFs will be calibrated over the next month and the new files configuration made available to BODC.

In the oligotrophic waters both instruments were at the limit of their sensitivity. Blanks were run using 0.2 micron (Gelman Supercap 50) filtered non toxic water, and the ships pure water (see below). These blanks were of a similar order of magnitude to the surface values returned by the instruments. Below is provisional blank corrected surface data from 10m depth at 19°N, 36°W.



#### Figure 10 Provisional Blank Corrected Data at 19°N 36°W

This corrected data shows a significant difference in Fo and Fm, a change in Fv/Fm that is related to the quantum yield of photosynthesis. The change in the dark chamber results could imply that the potential for production in surface waters is higher than expected, and close to the maximal Fv/Fm of 0.65. As present there is no standard procedure for blank correction of the FRRF and this needs further investigation before producing the final FRRF dataset. The pure water system on the ship was much less optically pure than 0.2 micron filtered seawater. The calibration of the ac/9 showed significant offsets and variable from filtered seawater blanks. This was not the case with the previous pure water, where a time series of calibrations of the ac/9 was taken on AMT10. The FRRF blanks were variable with the values for the pure water sometimes being similar to filtered seawater; however there did not seem to be a pattern in this. It is recommended that some checks are made on the system before AMT 13.

#### **Data Availability**

- 1) Satlantic free falling optical profiler: The data will be available after normalization for the SQM calibrations. An integrated PAR Kd and profile will be generated. At present there is some doubt as to how BODC will store the spectral data. It will be available locally from PML.
- 2) Wetlabs ac/9 absorption and attenuation meter. The data requires checking for blanks and salinity / temperature correction. It is anticipated that this will be finished by Sept 2003
- 3) Wetlabs VSF. An integrated depth resolved spectral backscatter will be available by Sep 2003.
- 4) Phycoerythrin and phycocyanin fluorometers. These are experimental, and require further testing with standards. Raw data is available any time from PML. The timescale of final validation is uncertain. Data is potentially available for all the optics cast.
- 5) Fast repetition rate fluorometer (FRRF). The data with the standard CI (corrected) calibration. As soon as a blanks procedure and processing is developed then the data will be updated.
- 6) UV and Near UV / Visible spectrometers. At present these are experimental and work is in progress with the calibration of the spectrometers. It is hoped to provide underwater UV flux, and attenuation by the end of 2003. This should be available at BODC. If spectral data is required then this should be available from PML.
- 7) Underway Transmissometer. Raw counts are available at present, final calibration will be made available to BODC, and this will be a standard merged product.

## **Remote Sensing Data**

## Gerald Moore and Chris Lowe

Plymouth Marine Laboratory

#### Cruise availability

During the cruise remotely sensed data was sent from Plymouth Marine Laboratory to the JCR. On average the images were about 150k bytes each. This is over the warning limit for the BAS mail system, and resulted in an initial delay in reception. These problems were easily overcome on discussion with the Radio Officer and a mail rule was set up that allowed the images to be delivered rapidly, without swamping the BAS official e-mail classification. On future cruise the RO should be given warning of this prior to the departure of the cruise to facilitate

The following types of image were supplied:

- 1) Composite SeaWiFS images of chlorophyll.
- 2) Microwave sea-surface temperature images.
- 3) AVHRR temperature images.
- 4) SeaWiFS LAC images (small local areas)
- 5) TOPEX Composite images SSH image.

Of the images the composite chlorophyll images were the most useful allowing determination of changes in province along the track. This data was augmented by the microwave SST data which was especially useful over the ITCZ where this is the only source of remotely sensed data. The SeaWiFS LAC coverage did not provide much help, since the AMT stations were fixed and could not be changed at such short notice. The TOPEX imagery provides a useful background to the dynamics of the area, but the update rate is such that one good image pre cruise is sufficient.

One of the problems with using the images was the ability to use simple image analysis package. After mutual negotiation with PML the ENVI package was used. Some success was achieved in adjusting the contrast of the images and determining the position of changes in productivity. The ENVI package is however expensive.

In the light of this experience some recommendations for future AMTs can be made:

- 1) Composites showing broad features on the scale of 100nm are more useful than fine scale images.
- 2) A simple image package is required that allows stretching, zooming and interactive picking of image data points is essential.
- 3) Climatologies should be prepared prior to the AMT if there is a lack of other data these provide an essential backup.
- 4) The RO should be informed about the image traffic to expedite transfer.

#### Availability of images post cruise

At present SeaWiFS is still operational, but will be succeeded by MERIS and MODIS. The basic composites from SeaWiFS are released three weeks after acquisition, and efforts will be made to get these on the PML web. Ideally a composite that matches the station timings should be made, but this takes some time.

For subsequent AMTs arrangements should be made for MODIS data. There is a MERIS AO request to make data available for the AMT, and this will be renewed in the next month. Additional optics merit awards:

#### Acknowledgements

Thanks to the crew for getting the rig over safely and back again, Mike for getting the images in on a regular basis, the bridge for getting to rocket astern in some difficult conditions, Jeff Benson for starting the FRRF each morning and letting me have an extra hours sleep and Pete Lens for integrating the free fall and transmissometer box into the BAS system.

## **Atmospheric Sampling**

## Tim Jickells

University of East Anglia

The atmospheric sampling campaign aims to determine atmospheric deposition fluxes of key nutrients (N,P and Fe) along the AMT track and to use this information to assess the importance of atmospheric nutrient supply and its contribution to the nutrient limitation of primary productivity. In addition to determining fluxes, our work aims to identify the sources of these nutrients using air-parcel back trajectories and inter-element and isotopic relationships. In addition sampling aims to help determine the role of marine emissions in regulating atmospheric chemistry, particularly in terms of the formation of aerosol S and N compounds. This objective is shared with groups measuring trace gas emissions.

Atmospheric sampling was conducted on the JCR's monkey island when wind conditions permitted, i.e. apparent wind direction was forward of the monkey island ensuring no contamination form the ship's stacks. Samplers were in general turned off while on station unless the bridge were confident of remaining head to wind throughout all manoeuvring. Sampling throughout passage allowed 16-20 hours sampling per day.

Three high volume aerosol samplers (approximately  $1m^3/min$ ) were deployed. One was for major ions and used conventional Whatman 41 filter substrates. One for trace metals and used conventional Whatman 41 filters after rigorous acid pre-cleaning. A third system provided by U. Liverpool (M. Preston) was for trace organic analysis and used pre-ashed glass fibre filters. One filter system malfunctioned during the cruise and subsequently trace metal and organic samples were collected on alternate days. Filters were changed in a laminar flow cabinet and subsequently frozen. On most occasions, cascade impactors were used for major ion and trace metals sampling to allow discrimination between aerosol particles <1 $\mu$ m>, samples for organic analysis were not size segregated.

One low volume air sampling system (approximately 50l/min) was also operational connected to a filter pack system for the analysis of ammonia gas concentrations. Filters were changed in a glove box with air filtered to remove ammonia and filters frozen. Finally two rain samplers for major ions and trace metals analysis were deployed to sample when the opportunity presented itself. Samplers were processed where practical in a laminar flow cabinet and subsequently frozen.

All subsequent analysis will take place at home laboratories. In the case of ammonia analyses we will need to determine if the system has the sensitivity to measure ambient concentrations over blanks. In the case of the high volume systems, it was clear that samples collected close to the equator were influence by desert dust, though the quantification of this dust source awaits subsequent analysis.

A log of samples collected is in the appendix.

Note JCR standard meteorological system was logging throughout the cruise.
### **POL GRACE Bottom Pressure Recorder Recoveries and Argo Float Deployments**

### **Geoff Hargreaves**

Proudman Oceanographic Laboratory

#### Background

Three Bottom Pressure Recorders (BPRs) from the Proudman Oceanographic Laboratory (POL) were deployed in May 2002, during cruise JR74 on RRS James Clark Ross. These BPRs were deployed in the deep ocean at depths of between approximately 5100m and 5500m, centred on the Zapiola Ridge in the South Atlantic Ocean. The BPRs form part of POL's GRACE Evaluation Experiment which is aimed at validating the data received from the GRACE satellites. GRACE is a gravity mission consisting of a pair of satellites orbiting the earth connected by a microwave link capable of measuring their separation to a precision of 1/100<sup>th</sup> of a millimetre. As a mass on the earth's surface attracts first one satellite and then the other, the gravitational field can then be mapped. The information collected by the GRACE satellites can be used by oceanographers and is equivalent to measuring bottom pressure. To verify the models, in-situ data is needed in an area where a significant gravity signal is expected.

#### **Bottom Pressure Recorder**

The Bottom Pressure Recorder mooring is a lander which freefalls to the seabed and is held by a ballast weight. In this case, the ballast weight is a tripod arrangement that also forms the deployment frame. The BPR records the frequency outputs of the sensors measuring pressure and temperature, and then integrates these signals over a fifteen minute sampling interval. The BPR is recovered by sending an acoustic signal to the release mechanism. This activates the release process by passing current through a burn wire until it has 'burned' away entirely. The BPR, now released from the ballast weight, becomes positively buoyant and ascends to the surface where it is recovered. The entire logging and release system is housed inside a single 17" glass sphere.



#### Recoveries

A recovery attempt was made at the GRACE1 position (Lat 46° 46.24'S, Lon 043° 26.89'W) but was unsuccessful. The BPR at GRACE2 position (Lat 44° 25.197'S, Lon 040° 22.185'W) was successfully recovered and the following day the BPR at GRACE3 position (Lat 43° 11.90'S, Lon 045° 18.10'W) was also retrieved.

#### **Argo Floats**

Eight Argo floats were due to be deployed on behalf of the Argo community. Three floats were configured for the Southern Ocean and the remaining five configured for the South Atlantic. The three Southern Ocean floats were to be deployed at the three GRACE mooring positions. Float No 863 was deployed at GRACE1 position on 15/5/03, float No 864 was

deployed at GRACE3 position on 17/5/03. Float No 865 should have been deployed at GRACE2 position, but it could not be started.

The South Atlantic floats were deployed at positions: Float No 860 at position Lat  $34^{\circ}$  46.700'S, Lon  $033^{\circ}$  34.883'W on 20/5/03Float No 895 at position Lat  $34^{\circ}$  03.650'S Lon  $032^{\circ}$  37.956'W on 20/5/03Float No 902 at position Lat  $31^{\circ}$  47.206'S, Lon  $029^{\circ}$  42.529'W on 21/5/03Float No 894 at position Lat  $29^{\circ}$  31.495'S, Lon  $026^{\circ}$  53.293'W on 22/5/03Float No 893 at position Lat  $28^{\circ}$  47.692'S, Lon  $025^{\circ}$  59.212'W on 22/5/03

Some of the South Atlantic floats were difficult to start, however a strong magnet was borrowed from Jeff Benson, and this proved to be successful. The Argo floats should have been shipped with magnets and instruction manuals, but only one transmission detector was shipped. There should also have been magnets and instructions onboard the ship from a previous deployment, but these could not be located. The Southern Ocean floats were started using a magnet from an acoustic release. This worked for two of the units but it didn't manage to start the third unit. It is possible that float No 865 didn't start because the magnet used was not powerful enough to activate it.

A recommendation to the Argo community for future deployments is to ensure that magnets, manuals and detectors are shipped in every case containing an Argo float. These items can then be returned, if requested, after the deployments.

# **Technical Report on Equipment Deployed on AMT** 12

### J. Benson

UKORS Southampton Oceanography Centre

### **CTD Operations**

1) A total of 69 CTD casts were undertaken on the cruise. The shallow (300 metre) stainless steel frame cast configuration was as follows, consisting of 28 casts:

Sea-Bird 9/11 *plus* CTD system 24 by 20L Ocean Test Equipment External Spring water samplers Sea-Bird 43 Oxygen sensor Chelsea MKIII Aquatracka Fluorometer Chelsea MKII Alphatracka 25cm path Transmissometer RD Instruments Workhorse 300 KHz Lowered ADCP (downward-looking configuration) RD Instruments Workhorse 300 KHz Lowered ADCP (upward-looking configuration) OED LADCP pressure case battery pack Chelsea FRRF/battery pack/pressure sensor

The pressure sensor is located 15cm from the bottom of the water samplers, and 132 cm from the top of the water samplers. Deep cast configuration was the same with the exception of the removal of the Chelsea FRRF assembly, for 9 casts.

2) The Sea-Bird CTD configuration was as follows:

SBE 9 plus Underwater unit s/n 09P-24680-0636

Frequency 0—SBE 3P Temperature sensor s/n 03P-2919 (primary)

Frequency 1—SBE 4C Conductivity sensor s/n 03P-2637 (primary)

Frequency 2—Digiquartz temperature compensated pressure sensor s/n 83008

Frequency 3—SBE 3P Temperature sensor s/n 03P-2758 (secondary)

Frequency 4—SBE 4C Conductivity sensor s/n 03P-2407 (secondary)

SBE 5T submersible pump s/n 05T-3090

SBE 5T submersible pump s/n 05T-3088

SBE 32 Carousel 24 position pylon s/n 32-31240-0423

SBE 11 *plus* deck unit s/n 11P-24680-0588

3) The auxiliary A/D output channels were configured as below:

V2---SBE 43 Oxygen s/n 43B-0363

V3--- Chelsea MKIII Aquatracka Fluorometer s/n 088242

V4--- Chelsea MKII Alphatracka 25cm path Transmissometer s/n 161-2642-03

4) The additional self-logging instruments were configured as follows:

Chelsea FRRF s/n 182042

Druck pressure sensor s/n 1265910 with PDM cable s/n 001 RDI Workhorse 300 KHz Lowered ADCP (downward-looking configuration) s/n 1855 RDI Workhorse 300 KHz Lowered ADCP (upward-looking configuration) s/n 1881 OED LADCP pressure case battery pack s/n 1935-B-L

5) The titanium (trace metal-free) frame cast configuration was as follows, consisting of 32 casts:

Sea-Bird 9/11 *plus* CTD system 24 by 10L Trace Metal-Free Ocean Test Equipment External Spring water samplers Sea-Bird 43 Oxygen sensor Chelsea MKIII Aquatracka Fluorometer Chelsea MKII Alphatracka 25cm path Transmissometer

The pressure sensor is located 30cm from the bottom of the water samplers, and 119 cm from the top of the water samplers.

6) The Sea-Bird CTD configuration was as follows:

SBE 9 *plus* Underwater unit s/n 09P-24680-0637 Frequency 0—SBE 3P Temperature sensor s/n 03P-2728 (primary) Frequency 1—SBE 4C Conductivity sensor s/n 03P-2164 (primary) Frequency 2—Digiquartz temperature compensated pressure sensor s/n 79501 Frequency 3—SBE 3P Temperature sensor s/n 03P-2729 (secondary) Frequency 4—SBE 4C Conductivity sensor s/n 03P-2165 (secondary) SBE 5T submersible pump s/n 05T-3086 SBE 5T submersible pump s/n 05T-3085 SBE 32 Carousel 24 position pylon s/n 32-24680-0346

SBE 11 *plus* deck unit s/n 11P-15759-0458 (BAS)

7) The auxiliary A/D output channels were configured as below:

V0---SBE 43 Oxygen s/n 43B-0013

V2--- Chelsea MKIII Aquatracka Fluorometer s/n 88-2360-108

V4--- Chelsea MKII Alphatracka 25cm path Transmissometer s/n 161-2642-002

For cast number 02 only, the A/D channels used were V0, V4 and V5. The subsequent change to V0, V2 and V4 resulted from corroded connector pins and cables that occurred on JR80; replacement cables for the original configuration were not available.

#### **CTD Miscellaneous**

1) As the Chelsea transmissometer specification maximum temperature operating range is 25°C, once in air and/or water temperatures above this limit, the transmissometers suffered from hysteresis. This affects both the down and up cast, and varies in severity from cast to cast, dependent upon pressure as well as heating on deck and in the water. Transmissometer deck readings were taken throughout the cruise, prior to each cast. The casts affected were from number 27 through 36.

2) Leaking connectors/corroding pins on the stainless steel CTD system, again from damage sustained on the previous cruise, caused noise and loss of pumps on both primary and secondary temperature/conductivity sensors. Casts affected were numbers 40, 42, 43, 45 and 47.

#### SAPS

1) The Challenger Oceanic Stand Alone Pumps were deployed for 7 casts, and configured as follows:

MK3, Type B s/n 003-03, filter type MK3, Type B s/n 003-04, filter type MK3, Type B s/n 003-05, filter type MK3, Type B s/n 003-06, filter type

Typical sampling depths were 50m, 100m (x2) and 150m, with a one-hour delay prior to beginning sampling, and pumping for a further 1.5 hours. Stand Alone Pump s/n 003-06 did not pump an expected volume of water for casts 4 and 5; the battery voltage and charging rate, as well as the timer and power PCB were inspected and proved to be operating normally. The pump bearings and housing were then inspected and found to be operating normally as well. Stand Alone Pump s/n 003-04 did not pump an expected volume of water for casts 6 and 7; again the above inspections were carried out. On s/n 003-06, the PVC union connection to the filter was found to be difficult to secure tightly, and is suspected as causing low volume pumping. Serial number 03-004 was found to have worn housing bearings, and these will be replaced ashore.

#### **Moving Vessel Profiler**

1) A total number of 44 profiles were conducted during the cruise. The sensor configuration was as below:

MVP300-1700 s/n 10014, with MSFFF: AML Micro Sensor CTD s/n 7027 WETLabs Flash Lamp Fluorometer s/n FLF-362D Sea-Bird/YSI 23-01Y Dissolved Oxygen sensor s/n 23-0960 Satlantic OCR 507-ICSW Irradiance sensor s/n 0104 Satlantic OCR 507-R10W Irradiance sensor s/n 0055 PML Tilt and Roll sensor

A report on the observations and impressions of the performance of the MVP is attached.

#### Miscellaneous

 Salinometer - An Autosal 8400B (BAS) salinometer was used on this cruise to process 171 CTD water bottle samples and 13 TSG underway samples. No problems with the salinometer or its performance was noted. The salinometer was located in the Prep Laboratory and operated at 24C bath temperature and 21C to 24C ambient lab temperature. All samples were processed according to WOCE standards and protocols.

#### **Moving Vessel Profiler: General Description**

 Deployment/Recovery and Operations on AMT12JR90 - As a rule, most profiles were done once the ship departed station, during daylight into evening hours, in calm sea conditions (Force 1 or 2), lasting 3 to 6 hours, at maximum ship speed. We completed three separate tows, consisting of 13, 25 and 16 profiles. If tows are at the "maximum" speed of the James Clark Ross of 12 knots, then total depth of the profile is limited to 300 metres; deeper depths of up to 1700 metres can be reached by slowing the ship down to 1 knot, with various depths in between depending upon vessel speed. The Auto Deployment works well, in that profiles can be done on a timed basis, freeing up personnel to do other tasks. We used the Auto mode for 15 to 20 minute intervals between profiles. The Multi Sensor Free Fall Fish itself is easy to handle physically, and the winch is not particularly sensitive nor difficult to operate by inexperienced personnel. In reasonable sea states, (Force 3 to 5), deployments should be able to proceed with the vessel moving ahead at 3 plus knots. The timing of the Auto Deploy profiles can be arranged around the schedule, weather conditions, cruise track and personnel available very easily. The faster the vessel speed, the more cable the winch pays out on the downcast, and coupled with the deeper cast profiles, the longer it takes to complete a full up/down profile. For example, at 10 knots attempting a 300 metre cast, approximately 650 metres of cable is paid out at 7 to 9 metres per second; hauling in at 1.5 metres per second on average means that the entire profile lasts 15 minutes. The downcast data only was recorded to minimise data logging. If only one profile is required every 10 nautical miles, then the Auto Deploy can be set to profile once per hour, and personnel can be performing other duties. The MSFFF is towed at a pre-determined depth at the surface in between casts, usually at 2 to 6 metres in calm sea states. (The surface MSFFF depth is set by the location of the Docking Messenger prior to deployment in profiling mode.) The Auto Deploy feature will not begin until the operator has confirmed the correct Log File at the end of the set time period between profiles, thus the operator has to check on the system prior to each cast, or the MSFFF will simply tow along at the surface. Recovery has been done in calm sea states at 4 to 5 knots ahead without problems, as the MSFFF is very hydrodynamic and does not "plow" the water surface with the subsequent drag that other undulating profilers have.

- 2) Personnel required As noted above, much depends upon the frequency of deployments once the MSFFF is in the water. In calm weather, two people can easily get the MSFFF into the water and/or back onboard, one for the winch and one to handle the MSFFF. In rougher sea states, an additional two people to help with tag lines would be advisable; one OED person can successfully deploy the instrument with help from the scientific party and/or deck crew. An additional OED technician would be recommended for heavy use, and BAS personnel can assist with the daily and weekly maintenance and checks of the winch system, otherwise the operator can check the hydraulic oil reservoir, cooling water flow, temperature, leakage, etc. whilst the MSFFF is profiling. Periodic checks of the cable for wear, fouling and damage, paying especial attention to the messengers and limit switches, is a normal part of any profiling schedule, and can be done whilst the MSFFF is in any part of the deployment/recovery cycle; being "glued" to the MVP Controller monitor is not necessary. The various fasteners, cable termination, towing bridle and shackle should be inspected upon each recovery for wear, vibration induced loosening and damage. We recommend that during profiling, a minimum of one person be designated to handle the Auto Deployments, and monitor the physical state of the system; whenever the MSFFF is in the water it is not a walk away and leave it alone instrument.
- 3) Software The manufacturer supplied software is very friendly, although some knowledge of Labview is helpful. The Configuration files are simple and straightforward to set up for any deployment criteria, and the Manual Control program for diagnostics is quite useful also. Technical and software support is easily and promptly obtained via email and satellite telephone, and assistance for troubleshooting is readily available. Direct logging of raw data to the vessel's computer system has been trouble free, and the software produces printable graphs at the end of each profile. Post-processing software has been successfully used with Surfer to obtain contour plots of various parameters over depth and distance covered in nautical miles.

- 4) Spares and miscellaneous items A remote display for the winch controls on deck is an item that would be helpful on larger vessels where the distance from the lab and Controller to the winch can be considerable. Also, Remote Control for the winch system is an option likely to be pursued in the next year. Lastly, we did not have sufficient spare Brake Coils on board; one spare was found to be faulty. Two pre-tested spares will be included on all future cruises. The new sensor additions performed well; more analysis of the Satlantic light sensors post-cruise is needed, but the Tilt and Roll instrument was very useful and instrumental in trouble-shooting the problems with the first tow.
- 5) Observations and problems Unfortunately, the system is still in the shakedown stage, as several problems came to light during the three tows. One item is the loss of communication to the MSFFF and/or Controller, which occurred frequently enough during the first tow to have to reterminate the seacable. Upon further inspection, it was discovered that the Impulse cable splice that joins the Kevlar EM cable to the MSFFF has an open circuit. This could have been caused by incorrectly routing the cable splice into the MSFFF, or vibration/strumming of the tow cable during the time period when the MSFFF was too close to the surface. The second tow had to be aborted because of a combination of operator inexperience and the failure of the Cable Reset function to accurately keep the amount of cable displayed. We determined to not use the Reset button in between casts on subsequent tows. The third tow failure resulted from loss of TT8 Communications, which in itself was caused by the breakdown of the Brake Solenoid Coil. This coil has had to be replaced three times in three cruises, and BOT are investigating whether this is because of design flaws (i.e. overloading the circuits with current) or manufacturer's defects. The MSFFF had to be recovered using the Emergency Manual Control system, which was found to be dangerous (involved personal extremities inside winch system whilst power was on), and cumbersome (BOT supplied controls are not sufficiently robust enough to power hydraulics under pressure, and will be replaced with easier to use SOC system). In addition, the first deployment resulted in the MSFFF being towed too close to the surface after the messengers were attached, (the ship's maximum speed was underestimated), which caused the bridle to be bent as the MSFFF spun/flipped over in the ship's wake. For the JCR, it is recommended to set the towing depth messenger at 65 metres from the winch drum.

#### Appendix Summary of samples collected

•		-		•			
Day tir	ne (GMT)	lat	lon	SST	sal	СТ	AT
21/05/03	18:02	-31.191	-28.964	21.01	35.818	2045.3	2370.0
22/05/03	18:01	-28.344	-25.550	23.00	36.012	2040.2	2364.1
23/05/03	18:04	-24.062	-25.001	25.28	36.781	2070.1	2416.6
24/05/03	18:06	-20.106	-25.000	26.53	37.045	2089.6	2430.2
25/05/03	18:02	-15.884	-25.001	26.45	37.060	2087.9	2434.5
26/05/03	18:00	-12.978	-24.999	26.87	36.865	2071.2	2426.8
27/05/03	17:04	-8.927	-25.002	27.94	36.443	2043.7	2391.0
28/05/03	18:02	-4.578	-25.001	28.24	35.597	1995.7	2334.4
29/05/03	17:00	-1.359	-25.000	26.90	36.286	2053.9	2378.5
30/05/03	16:32	2.692	-26.590	28.72	35.071	1953.3	2297.8
31/05/03	17:12	6.407	-28.792	28.21	35.128	1954.0	2299.0
01/06/03	17:05	10.879	-30.990	26.94	36.254	2024.8	2373.8
03/06/03	17:00	15.927	-34.530	24.80	36.700	2060.0	2406.1
04/06/03	17:04	19.574	-36.793	24.69	36.976	2075.7	2421.4
05/06/03	17:00	22.592	-34.508	24.40	37.488	2102.6	2452.1
06/06/03	17:00	24.884	-31.955	23.94	37.323	2101.8	2441.6
07/06/03	16:05	27.629	-28.828	22.53	37.072	2102.6	2423.1
08/06/03	16:00	30.752	-25.176	22.86	37.048	2109.9	2421.6
09/06/03	16:04	34.096	-21.235	21.28	36.624	2103.3	2399.2
10/06/03	16:00	37.570	-20.676	20.51	36.139	2085.0	2374.3
11/06/03	16:04	42.039	-19.916	17.07	35.704	2074.4	2347.9
12/06/03	15:00	45.880	-17.837	15.87	35.603	2072.1	2346.9
13/06/03	15:00	48.139	-12.024	14.96	35.550	2060.7	2338.8

#### Underway sampling- one sample collected at approximately 16.00 local

CT TCO<sub>2</sub>, AT Alkalinity  $\mu mol~kg^{\text{-l}},$  additional samples for nutrients and chlorophyll collected in parallel

## **Underway Continuous Seawater System Management During AMT12**

13 May 2003	0815	1315	1	2	Mid	Water On	Sail Stanley GMT-4 Filter 5mm
14	0821	1121	2	2	Mid	Filter Changeover and Clean	Clocks Changed GMT-3
15	0820	1120	1	2	Mid	Filter Changeover and Clean	
16	0821	1121	2	2	Mid	Filter Changeover and Clean	
17	0830	1130	1	2	Mid	Filter Changeover and Clean	
18	0818	1118	2	2	Mid	Filter Changeover and Clean	
19	0818	1118	1	2	Mid	Filter Changeover and Clean	
19	0831	1131	1	1	Mid	Pump Change Over	PM routine
19	0834	1134	1	2	Mid	Pump Change Over	PM routine
19	1156	1456	1	1	Mid	Pump Change Over	PM routine
20	0818	1018	2	1	Mid	Filter Changeover and Clean	Clocks Changed GMT -2
21	0812	1012	1	1	Mid	Filter Changeover and Clean	
22	0820	1020	2	1	Down	Filter Changeover and Clean	
22	0850	1050	2	1	Down/Mid/Down	Probe Mechanism Exercised	
23	0818	1018	1	2	Down	Filter Changeover and Clean	
24	0820	1018	2	1	Down	Filter Changeover and Clean	
24	1050	1250	2	2	Down	Pump Change Over	Requested By M Woodward
25	0805	1005	1	2	Down	Filter Changeover and Clean	
26	0818	1018	2	2	Down	Filter Changeover and Clean	
26	0826	1026	2	1	Down	Pump Change Over	
26	0828	1028	2	1	Down/Mid/Down	Probe Mechanism Exercised	
27	0822	1022	1	1	Down	Filter Changeover and Clean	
28	0818	1018	2	1	Down	Filter Changeover and Clean	

29	0818	1028	1	1	Down	Filter Changeover and Clean	
30	0818	1018	2	1	Down	Filter Changeover and Clean	
30	0819	1019	2	2	Down	Pump Change Over	
31	0816	1016	1	2	Down	Filter Changeover and Clean	
1 June 2003	0820	1020	2	2	Down	Filter Changeover and Clean	
2	0814	1014	1	2	Down	Filter Changeover and Clean	
2	0821	1021	1	2	Down /Mid/Down	Probe Mechanism Exercised	
3	0814	1014	2	2	Down	Filter Changeover and Clean	
4	0812	1012	1	2	Down	Filter Changeover and Clean	
5	0814	1014	2	2	Down	Filter Changeover and Clean	
6	0814	1014	1	2	Down	Filter Changeover and Clean	
7	0816	0916	1	2	Down	Filter Changeover and Clean	Clocks Changed GMT -1
8	0810	0910	1	2	Down	Filter Changeover and Clean	
9	0812	0912	2	2	Down	Filter Changeover and Clean	
9	0814	0914	2	1	Down	Pump Change over	
9	0816	0916	2	1	Mid	Probe Position Change	Increase in ship's speed
10	0814	0914	1	1	Mid	Filter Changeover and Clean	
11	0844	0944	2	1	Mid	Filter Changeover and Clean	
12	0814	0814	1	1	Mid	Filter Changeover and Clean	Clocks Changed GMT
13	0815	0815	2	1	Mid	Filter Changeover and Clean	
14	0816	0816	1	1	Mid	Filter Changeover and Clean	
15	0810	0710	2	1	Mid	Filter Changeover and Clean	Clocks Changed GMT+1 Filter 1mm
16	0810	0710	-	-	Up	Water Off	
17							Arrive Grimsby
	I		1	L		l	l

## **Atmospheric Samples Collected**

1		•			MidPoint Position.		
Date 2003	Major Ion	Metals	Organics	Ammonia	degrees	Comments	Rain Sampled
14-17/05	х		х		45S	clean	х
20-21/5	х	х	хх	х	32S	clean	
21-22/5	х	х	х	х	30S	clean	
22-23/5	х	х	х	х	27S	clean	
23-24/5	х	х	х	х	24S	faint brown/black	
24-25/5	х	х	х	х	19S	clean	
25-26/5	х	х	х	х	15S	faint brown/black	
26-27/5	х	х	х	х	11S	clean	
27-28/5						no sample	
28-29/5		х	х	х	4S	brown/grey	
29-30/5	х		х	х	1S	brown/grey	
30-31/5	х	х		х	3N	brown	х
31/5-1/6	х		х	х	6N	very brown	
1-2June	х	х		х	8N	very brown	
2-3June	х		х	х	13N	clean	
3-4June	х	х		х	17N	pale	
4-5June	х		х	х	20N	brown/grey	
5-6June	х	х		х	23N	brown	
6-7June	х		х	х	25N	pale brown	
7-8June	х	х		х	28N	brown	
8-9June	х		х	х	31N	brown	
9-10June	х	х		Х	34N	grey brown	
10-11 June	X		х		38N	clean	
11-12 June	X	х			43N	clean	
12-13 June	x		х		47N	clean	х

### **Optics Samples**

~	Sumpies									
	Ctation	Data			(	CTD-	Optics-	Trios-	Ontine AC Ontine F	E Commont
	Station			5DN	г 400	RKF	FKKF	туре		
		13-May-C	13	14:11	133					
	2CTD02	13-May-0	13	19:06	133	40004			ОК	CTD - Test Only
	3CTD03	14-May-0	3	08:15	134	460042	2	-		
	4 C I D 04	14-May-0	3	14:02	134		460043	5	ok	1
	5 C I D 05	16-May-C	3	07:50	136	460042	2			
				44.05	400		1000.10	J		Unsafe to deploy FF / FRRF Data
	6CTD06	16-May-0	3	14:05	136	40004	460042			1 Corrupt
	7CTD07	17-May-0	3	07:35	137	460042	2	-		
	8CID08	17-May-0	3	11:22	137		460042	-	ok	6
	9C1D09	17-May-0	3	16:17	137		460042	2	ok	
	10CTD10	18-May-0	3	07:41	138	460042	2			-
	11 CTD11	18-May-0	3	14:00	138		460042	-	data?	3
	12CTD12	19-May-0	3	07:00	139	460042	2			
	13CTD13	19-May-0	3	13:59	139		460042		ok	
	14 CTD14	20-May-0	3	07:11	140	460042	2			
	15 CTD15	20-May-0	3	13:02	140		460043	8	data?	3
	16 CTD16	21-May-0	3	06:32	141	460042	2			
	17 CTD17	21-May-0	3	11:51	141		460043	8	ok	3
	18 CTD18	21-May-0	3	13:06	141				ok	
	19CTD19	22-May-0	3	06:34	142	460042	2			
	20 CTD20	22-May-0	3	12:53	142		460043	3	ok	3 corrupt file on optics
	21 CTD21	23-May-0	3	06:39	143	460042	2			
	22 CTD22	23-May-0	3	13:04	143		460043	3	data?	3 AC9 Failed To process
	23 CTD23	24-May-0	3	06:36	144	460042	2	-		
	24 CTD24	24-May-0	3	13:06	144				data?	3 AC9 Failed To process
	25 CTD25	25-May-0	3	13:02	145		460043	3	ok	3 FRRF - Currupt Data
	26 CTD26	26-May-0	3	06:35	146	460042	2 460043	3n/a		
	27 CTD27	26-May-0	3	08:22	146		460043	svis	ok	3

28 CTD28	26-May-03	12:21	146				
29 CTD29	27-May-03	06:36	147	460042			
30 CTD30	27-May-03	13:00	147		460043 vis	ok	3
31 CTD31	28-May-03	06:13	148	460042			
32 CTD32	28-May-03	13:01	148		460043		4
33 CTD33	29-May-03	06:04	149	460042	460043 n/a		
34 CTD34	29-May-03	07:42	149		460043 vis	ok	
35 CTD35	29-May-03	12:03	149		460043 vis	ok	3 FRRF Partial Downcast (184m)
36 CTD36	30-May-03	06:12	150	460042_			
37 CTD37	30-May-03	12:58	150		460043 vis	ok	3 FRRF Data Corrupt
38 CTD38	31-May-03	06:07	151	460042			
39 CTD39	31-May-03	13:02	151		460043 uv	ok	1
40 CTD40	01-Jun-03	06:07	152	460042			
41 CTD41	01-Jun-03	13:00	152		460043 vis	ok	
42 CTD42	02-Jun-03	06:04	153	460042			2
43 CTD43	02-Jun-03	08:23	153		460043 uv	ok	
44 CTD44	02-Jun-03	16:00	153		460043 uv	ok	3
45 CTD45	03-Jun-03	06:04	154	460042			
46 CTD46	03-Jun-03	13:04	154		460043 vis	ok	3
47 CTD47	04-Jun-03	06:03	155	460042			
48 CTD48	04-Jun-03	13:01	155		460043 vis	ok	3
49 CTD49	05-Jun-03	06:05	156	460042			
50 CTD50	05-Jun-03	13:01	156		460043 vis	ok	3
51 CTD51	06-Jun-03	06:06	157	460042			
52 CTD52	06-Jun-03	07:53	157		460043 uv	ok	
53 CTD53	06-Jun-03	12:15	157		460043 uv	ok	2 Free Fall failure - LU03 Sensor
54 CTD54	07-Jun-03	05:32	158	460042			
55 CTD55	07-Jun-03	11:58	158		460043 uv	ok	3
56 CTD56	08-Jun-03	05:04	159	460042			Free Fall re-terminated
57 CTD57	08-Jun-03	12:00	159		460043 uv	ok	3

AMT 12 Cruise Report

58 CTD58	09-Jun-03	05:03	160	460042			
59 CTD59	09-Jun-03	11:59	160		460043 vis	ok	4
60 CTD60	10-Jun-03	05:05	161	460042			
61 CTD61	10-Jun-03	06:46	161		460043 uv	ok	
62 CTD62	10-Jun-03	11:14	161		460043 uv	ok+CDOM	2 Optics Casts m,n - 0.2micron ac9 test
63 CTD63	11-Jun-03	05:03	162	460042			
							Optics Cast - m is 0.2 micron - seabird is not valid for m cast. Casts not split in
64 CTD64	11-Jun-03	11:59	162		460043 vis	ok+CDOM	3FRRF.
65 CTD65	12-Jun-03		163	460042			
66 CTD66	12-Jun-03	11:02	163		460043 uv	ok+CDOM	2 Optics Casts - m - 0.2 micron
67 CTD67	13-Jun-03	04:04	164	460042			
68 CTD68	13-Jun-03		164		460043 vis	ok+CDOM	2
69 CTD69	14-Jun-03		165		460043 uv	ok+CDOM	4