

**UK-SOLAS Cruise Report
RRS Discovery D325
13th Nov - 18th Dec 2007.**

INSPIRE

**Investigation of
Near-Surface
Production
of Iodocarbons –
Rates and Exchange.**



RRS Discovery D325 Cruise Report

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Investigation of Near-Surface Production of Iodocarbons – Rates and Exchange

13th November to 18th December 2007.

Principal Scientist: Gill Malin

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**A collaborative project between
the University of East Anglia and Plymouth Marine
Laboratory, funded by the U.K. Natural
Environment Research Council as part of the Surface
Ocean Lower Atmosphere Study (SOLAS)
programme.**



**Plymouth
Marine Laboratory**



Front cover photograph by Claire Hughes:
Discovery from rigid inflatable boat during the INSPIRE D325 research cruise.

Document Data Sheet

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<p>ABSTRACT The Discovery D325 research cruise sailed to and from Santa Cruz in the Canary Islands to the area around the Cape Verde Islands and was funded by the NERC U.K. Surface Ocean Lower Atmosphere programme (SOLAS). The INSPIRE project is a collaboration between the University of East Anglia and the Plymouth Marine Laboratory that focuses on the marine production, consumption and sea-to-air emissions of volatile iodocarbons in seawater. The overall aim is to improve understanding of the factors controlling iodocarbon production and consumption processes. The main objectives of INSPIRE are to:</p> <ol style="list-style-type: none"> 1) Identify the dominant biological, chemical, physical and photochemical iodocarbon production and loss processes in tropical Atlantic waters of varying productivity around Cape Verde. 2) Explore how the key processes may be related to variables that can be simulated by an ecosystem model or derived from earth observation. 3) Compare iodocarbon sea-air fluxes calculated using bulk seawater values to those that consider near-surface profiles, and assess how both relate to atmospheric concentrations. 4) Use a model to simulate temporal iodocarbon sea-air fluxes and compare these with time-series data from the atmospheric monitoring conducted at Cape Verde observatory. <p>The cruise focused primarily on objectives 1 and 3, and the data will be used for objectives 2 and 4. Sampling and incubation experiments were done at 6 sites chosen on the basis of near real-time satellite images of surface chlorophyll concentration such that 2 sites were of approximately, low, medium and high chlorophyll/productivity. Each site was occupied for a 4-day period and where weather/sea conditions allowed a drifter and drogue was deployed and followed to enable semi-lagrangian sampling. A range of sampling methodologies were used including: CTDs and sample bottle rosette (stainless steel and titanium frames), stand alone pumps (SAPS), optics rig, trace metal clean sampling FISH, aerosol collector and denuder tubes. When weather conditions permitted a rigid inflatable boat was launched for near-surface sampling and a near-surface sample profiler was deployed. The report details of the sampling undertaken, sample analysis and incubation experiments conducted and samples stored for post-cruise studies and analysis.</p>	
<p>KEYWORDS IODOCARBONS, CH₃I, CH₂I₂, CH₂ClI, C₂H₅I, CH₂BrI, CHCl₂I, CH₂ClI₂, 1 and 2-iodopropane, HALOCARBONS, NORTH ATLANTIC, CANARY ISLANDS, CAPE VERDE ISLANDS, CANARY CURRENT, GAS CHROMATOGRAPH, MASS SELECTIVE DETECTOR, GC-MS, ELECTRON CAPTURE DETECTOR, GC-ECD, ANALYTICAL FLOW CYTOMETER, CTD, TOWED FISH, AFC, DRIFTER, NEAR-SURFACE SAMPLE PROFILER, MICROLAYER, MICROLAYER, RIGID INFLATABLE BOAT, RIB, FRRF SYSTEM, AEROSOL SAMPLER, DENUDER TUBES, OPTICS, UV, PAR, FRRF, PRIMARY PRODUCTION, NITROGEN FIXATION, HETEROTROPHIC ACTIVITY, SPECIES DIVERSITY, GRAZING MORTALITY, VIRAL MORTALITY, VIRUSES, AGGREGATES, BIOLOGICAL OXIDATION, ISOTOPE ADDITIONS, PHOTOCHEMISTRY, NUTRIENTS, NANOMOLAR NUTRIENTS, HPLC PIGMENTS, PHYTOPLANKTON, BACTERIA, PRIMARY PRODUCTION, BACTERIAL PRODUCTION, VIRUSES, NITROGEN CYCLING, NITROGEN FIXATION, TRACE METAL BIOASSAY, AEROSOLS, OZONE, IODATE, IODIDE, SALINITY, SEA SURFACE TEMPERATURE, SATELLITE IMAGES.</p>	
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<p>COPIES OF THIS REPORT ARE AVAILABLE (ONLINE) FROM</p> <ol style="list-style-type: none"> 1) British Oceanographic Data Centre, website http://www.bodc.ac.uk/, e-mail: enquiries@bodc.ac.uk. 2) The Natural Environment Research Council www.nerc.ac.uk/funding/thematics/solas/. 3) Via the homepage of the Principal Investigator Gill Malin http://www.uea.ac.uk/~e061/ 4) To request a copy on CD contact: Gill Malin, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ. UK. Email: G.malin@uea.ac.uk. Phone: +44 (0) 1603 592531. 	

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1. Background.

The INSPIRE: **Investigation of Near-Surface Production of Iodocarbons – Rates and Exchange** project is collaboration between the University of East Anglia (UEA) and the Plymouth Marine Laboratory (PML). We were funded through the Natural Environment Research Council (NERC) UK-SOLAS programme (Surface Ocean Lower Atmosphere Study <http://www.nerc.ac.uk/research/programmes/solas/>) which is studying interactions between the atmosphere and oceans, focusing on chemical exchanges that affect marine productivity, atmospheric composition, and climate.

Our focus is the flux of iodine from the oceans to the atmosphere. This is a vital biogeochemical exchange in the Earth System because seawater is considered to be the source of most of the iodine in the active geochemical cycle. Marine iodine emissions also influence air composition because they cause ~13% of the total daily loss of ozone, they may play a part in climate regulation via the production of new particle and cloud-condensation nuclei (CCN) in the marine boundary layer, and iodine is also critical for human health. Beyond sea spray, iodocarbons and molecular iodine (I₂) are the suggested vectors for sea-to-air iodine transfer. The term ‘iodocarbons’ includes a range of trace gases that are produced and cycled in the surface ocean. It includes compounds that contain iodine and mixed halogenated compounds e.g. CH₃I, CH₂I₂, CH₂ClI, C₂H₅I, CH₂BrI, CHCl₂I, CH₂ClI₂. Over recent years our knowledge of the distribution and diversity of the iodocarbons in the sea has increased, but as yet we do not fully understand the production and consumption processes involved in controlling iodocarbon concentrations in the pelagic environment. The remit for the INSPIRE ‘**Investigation of the Near Surface Production of Iodocarbons: Rates and Exchanges**’ project was to improve overall understanding of these iodocarbon production and consumption processes. We also plan to develop an ecosystem model to simulate iodocarbon production. This would allow us to predict how much iodine is transferred from the oceans to the atmosphere. It will also help us to better understand how the iodine biogeochemical cycle operates and how it might alter with future climate change.

2. Aim and objectives.

The overall aim of the project is to understand the mechanisms controlling the cycling of iodocarbons in the surface oceans in order to be able to predict sea-air emissions of these compounds via remotely sensed products and modelling.

The underlying idea for the INSPIRE project is that iodocarbon concentrations in seawater represent a balance between production and loss processes, see Figure 2.1. Therefore we planned to use a combination of data from field campaigns, together with data from supporting laboratory, earth observation and modelling studies to achieve the following objectives:

- 1) Identify the dominant biological, chemical, physical and photochemical iodocarbon production and loss processes in tropical Atlantic waters of varying productivity around Cape Verde.

- 2) Explore how the key processes may be related to variables that can be simulated by an ecosystem model or derived from earth observation.
- 3) Compare iodocarbon sea-air fluxes calculated using bulk seawater values to those that consider near-surface profiles, and assess how both relate to atmospheric concentrations.
- 4) Use a model to simulate temporal iodocarbon sea-air fluxes and compare these with time-series data from the atmospheric monitoring conducted at Cape Verde observatory.

The INSPIRE D325 research cruise focused primarily on objectives 1 and 3, and the data obtained will also be used for objectives 2 and 4.

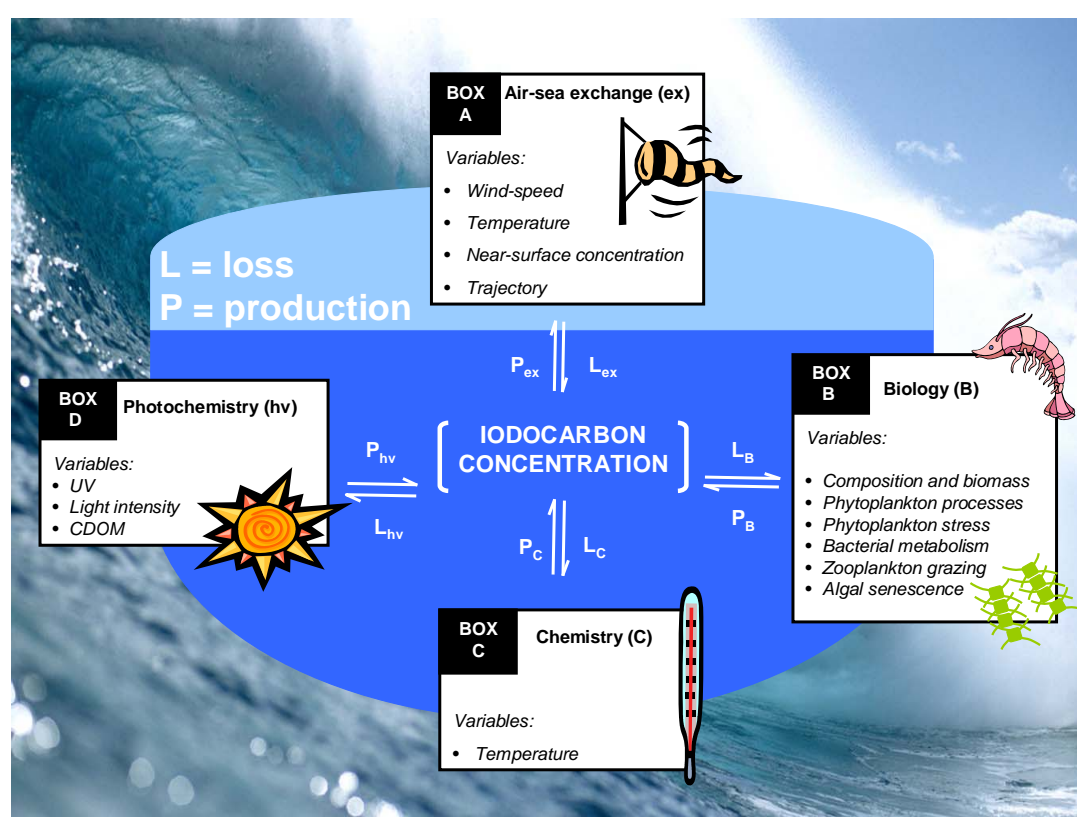


Figure 2.1. The 4 major categories and underlying component processes considered to be involved in controlling surface ocean iodocarbon concentrations.

3. Approach.

Originally we had planned for Claire Hughes and Manuela Martino (UEA) to conduct preliminary research for the INSPIRE project on another SOLAS research cruise working in the same region in January-February 2007 (Cruise D314, Principal Scientist: Eric Achterberg, University of Southampton). Unfortunately, following mobilisation of equipment and personnel onboard Discovery in Glasgow, the cruise was cancelled due to problems with the ship's engines. This meant that we were not able to base our plans for D325 upon data acquired at sea in the same area. However,

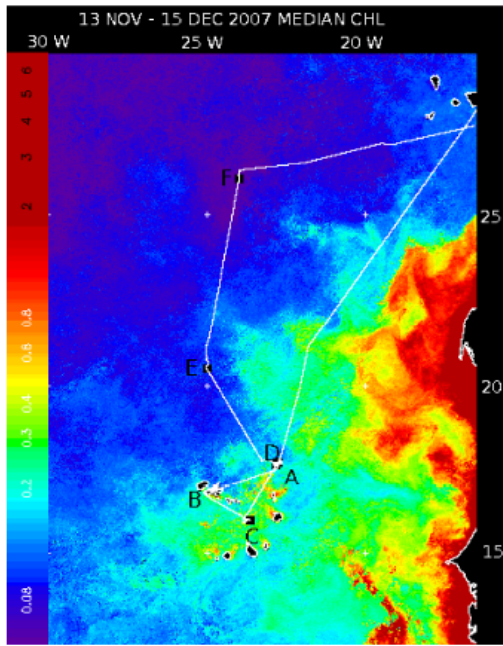
on an earlier research cruise that passed through the region, Adele Chuck (UEA) had observed large super saturations of iodomethane (methyl iodide, CH₃I) and estimated a mean sea-to-air flux of 20 nmol m⁻² d⁻¹. This data suggested that this is a strong iodocarbon source region, despite the area being predominantly oligotrophic.

As mentioned above, the shipboard field campaign was planned for the Cape Verde region in the tropical North Atlantic Ocean. The primary reason for choosing this area was that the tropics are highly significant for ozone production and loss processes. The Cape Verde region is also an area of high dust input which delivers nutrients to the seawater and enhances marine primary production. The site is also downwind of the Mauritanian upwelling. A major advantage was the possibility for linking the data we acquired at sea with data from the SOLAS Cape Verde Atmospheric Observatory. This air monitoring station is located on the island of SaoVicente (16° 51'49 N, 24° 52'02 W) where the prevailing trade winds blow directly off the ocean thereby enabling the analysis of clean marine air.

D325 Scientists from the University of East Anglia, Plymouth Marine Laboratory and the Universities of York and Plymouth (see section 5.1) joined the RRS Discovery in Santa Cruz, Tenerife, Canary Islands. Three days were spent securing and setting up equipment onboard and we set out to sea on 13th November heading towards the Cape Verde Islands region.

A key element of the INSPIRE shipboard research was to identify the dominant biological, chemical, physical and photochemical iodocarbon production and loss processes in tropical Atlantic waters of varying productivity. Hence, a wide range of water column sampling and incubation studies were done at 6 sites. These were chosen on the basis of near real-time satellite images of surface chlorophyll concentration such that 2 each were of approximately, low, medium and high productivity (see section 7.1). Figure 3.1 shows the cruise track and sampling sites superimposed on a composite MODIS satellite image for the whole cruise period. Each of the 6 sites was occupied for at least 4 days. The original intention had been to do an initial mapping of iodocarbon concentrations and associated surface hydrography prior to each 4-day at each site, but the time available did not allow this for every site

Within the 4-day sampling periods it was necessary to have a different sampling schedule for each day to accommodate the variety of seawater sampling instruments and methods, as well as experimental needs of the different groups and/or individuals. An example of the schedule for one of the sites is shown in Table 3.1. All sites except site B included a diel series of CTDs to collect water for the analysis of iodocarbons. Where the water and weather conditions allowed a drifter was deployed to enable sampling within the same water patch. A variety of water sampling instruments were used including: CTD and sample bottle rosette (stainless steel and titanium frames), stand alone pumps, optics rig, trace metal clean sampling FISH. When the sea state/weather conditions allowed a rigid inflatable boat was launched for near-surface sampling and a near-surface sample profiler instrument was deployed. See Figure 3.2. As far as possible the ship was held in head-to-wind position and this facilitated aerosol and denuder tube sampling for iodine species.



SITE	Chl a / productivity
A: 17deg45'N/22deg45'W	Medium
B: 16deg55'N/24deg45'W	High
C: 16degN/23deg40'W	High
D: 17deg40'N/22deg50'W	Medium
E: 20deg30'N/25degW	Low
F: 26degN/24deg'W	Low

Figure 3.1. Cruise track and sampling sites superimposed on a colour-stretched composite MODIS satellite image for the whole INSPIRE research cruise period. The colour scale represents the concentration of chlorophyll mg m^{-3} .

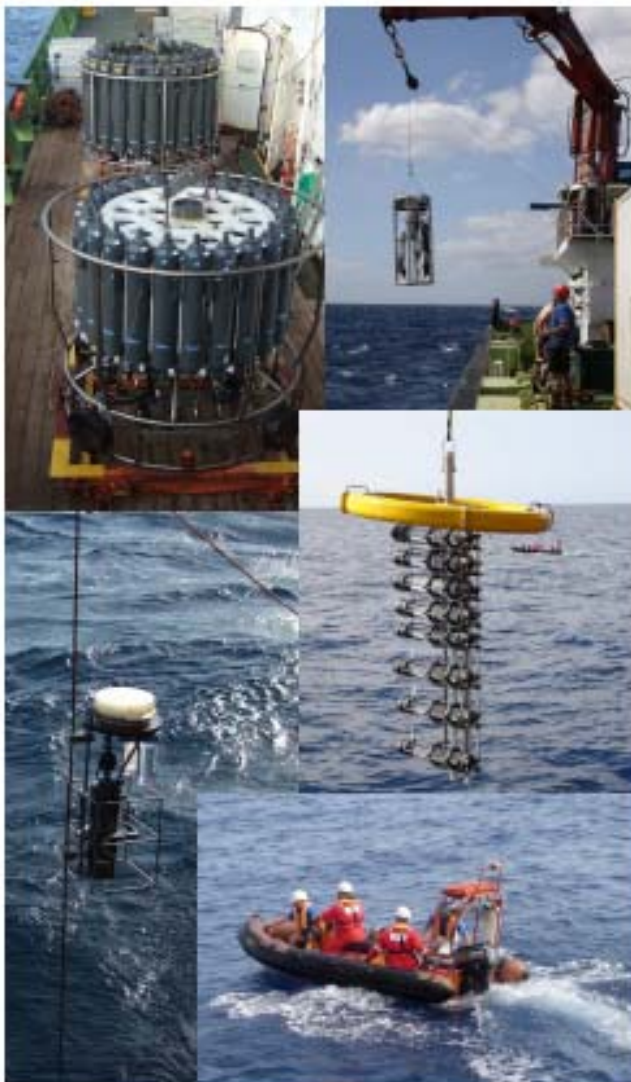


Figure 3.2. Main sampling instruments deployed during the INSPIRE cruise. From top left, clockwise: CTD, OPTICS, NSS, RIB, SAPS. See table 3.1 for explanation of abbreviations.



Figure 3.3. The wide range of on-deck seawater flow-through incubators used for the various sample incubation experiments during the INSPIRE cruise.

Table 3.1. An example site schedule.

Abbreviations: FISH (TMS): trace metal clean sampling fish; CTD (STS): ‘standard’ stainless steel unit for general sampling fitted with Seabird CTDs, a rosette of sampling bottles and associated equipment; CTD (TIT): as for STS but with a titanium unit for trace metal sampling (note the TIT was used for some standard sampling when the STS was under repair); OPTICS: optics rig comprising see ac-9 and flow cells, Fast Repetition Rate Fluorometer, UV sensor and Seabird CTD. (See section 7.10 for full details); SAPS: Stand-alone Pumps; NSS: near-surface sampler; RIB: rigid inflatable boat.

Time	SITE C Day 1 Wed 28/11/07	SITE C Day 2 Thurs 29/11/07	SITE C Day 3 Fri 30/11/07	SITE C Day 4 Sat 1/12/07
0100		SAPS 4 depths	CTD (STS) DIEL	
0200				
0300	Drifter		CTD (STS) DIEL	
0330	FISH (TMS)			
0400	FISH (TMS)			
0500	CTD (STS) Pre-dawn	CTD (STS) DIEL Pre-dawn	CTD (STS) DIEL Pre-dawn	CTD (STS) Pre-dawn
0600				
0700		CTD (STS) DIEL		
0800	CTD (TIT)	CTD (STS)	CTD (STS)	CTD (STS)
0900		CTD (STS) DIEL		
1000				NSS & RIB
1100		CTD (STS) DIEL		
1200				
1230	OPTICS cast start	OPTICS cast start	OPTICS cast start	OPTICS cast start
1300				
1330	OPTICS cast end	OPTICS cast end	OPTICS cast end	OPTICS cast end
1340	CTD (STS) Solar noon	CTD (STS) DIEL Solar noon	CTD (STS) Solar noon	CTD (STS) Solar noon
1400				
1500	SAPS Single depth	CTD (STS) DIEL	NSS & RIB	NSS & RIB
1600				
1700		CTD (STS) DIEL		
1800				
1900		CTD (STS) DIEL		
2000				
2100		CTD (STS) DIEL		
2200				
2300		CTD (STS) DIEL		
2400				

Some aspects of the research carried out onboard involved the immediate analysis of iodocarbon concentration distributions. In addition a range of incubation experiments were done to examine how iodocarbon concentrations vary versus measurements that indicate biological, chemical and photochemical processes. For example, the project examined how the exposure of water samples to UV light, different light intensities, zooplankton grazing of phytoplankton, plankton death and decay and bacterial growth influenced the concentrations of the iodocarbons measured. The turnover of isotopically labelled compounds was also investigated. In addition, a range of independent biological, chemical and optics data was collected to support the iodocarbon data and provide the background context for the study. Figure 3.3 shows the large number of on-deck seawater flow-through incubators that were in use. In addition samples were stored for post-cruise studies and analysis. More details can be found in the individual reports in section 7.

4. Main shipboard achievements.

Most of the work we wanted to cover during the INSPIRE cruise was done as we had planned. However, weather conditions meant that we did less sampling from the RIB and NSS. At the time of writing the following achievements can be noted, but a lot of data remains to be analysed and interpreted so we anticipate more.

Assessment of photochemical loss of CH_2I_2 and production of CH_2CII in natural seawater (Archer, Goldson & Nightingale). In on-deck incubations conducted during the INSPIRE cruise we did isotopic enrichment experiments to measure the photochemical loss of CH_2I_2 and the subsequent production of CH_2CII in natural seawater. This is the first time that such measurements have been made in the field. Results indicate that the production of CH_2CII and loss of CH_2I_2 are broadly in line with predictions based on laboratory experiments.

A link between particulate organic carbon (> 10 micron) and iodocarbon production in the tropical Atlantic (Hughes & Malin). Incubation studies carried out during the INSPIRE cruise have shown that iodocarbon compounds are produced by (> 10 micron) particles collected from regions of high, medium and low productivity in the tropical Atlantic Ocean. The rates of production varied with depth and higher production rates were seen in particles collected in the upper water-column. In general, there is good agreement between the rate of iodomethane production and the level of (> 10 micron) particulate organic carbon in the experiments. This finding builds on our previous work which has shown that the iodocarbons are produced by biogenic particles collected in other ocean regions (Hughes et al., 2008 *Limnology & Oceanography* 53: 867-872). These results contribute to our knowledge of the processes controlling iodocarbon concentrations in seawater.

First measurements of the bacterial oxidation of CH_3I (Archer, Stephens & Nightingale). The first measurements of the bacterial oxidation of CH_3I have been made using a radiotracer technique as part of the INSPIRE experiment. The results indicate that biological oxidation of CH_3I by marine bacteria is unlikely to be an important sink for CH_3I in oligotrophic waters. Air-sea gas transfer and chemical reactions dominate the loss of CH_3I in the waters of the tropical Atlantic. However,

there may well be an important role for biological oxidation at higher latitudes when the chemical loss rates are much slower due to the colder water temperatures.

A new source of volatile organoiodine compounds in surface seawater (Martino, Mills, Woeltjen and Liss). We have identified a novel, and potentially ubiquitous, sea-surface source of the short-lived volatile organoiodine compounds CH_2I_2 , CHClI_2 and CH_3I . These compounds were formed when seawater was exposed to ambient levels of ozone. The volatiles are produced via the reaction of marine dissolved organic matter with hypiodous acid/molecular iodine, which are formed at the sea surface when ozone reacts with dissolved iodide. The same 3 compounds were formed when we incubated seawater of different productivity levels with molecular iodine during the INSPIRE research cruise in the tropical Atlantic Ocean. We suggest that the presence of dissolved iodide, dissolved organic matter and ozone can lead to the sea-surface production of CH_2I_2 , CHClI_2 and CH_3I . As such, this process could provide a ubiquitous source of iodine to the marine atmosphere. Following emission to the air these compounds photodissociate within minutes to days, releasing iodine atoms that are known to catalytically destroy tropospheric ozone, form IO radicals and play a role in new particle formation in coastal areas. Published in: Martino et al. A new source of volatile organoiodine compounds in surface seawater. *Geophysical Research Letters* 36, L01609, doi:10.1029/2008GL036334, 2009.

Nitrate availability influences the photochemical formation of iodomethane in seawater (Hughes, Martino, Liss, Malin and others who are not formally involved in the INSPIRE project). Incubation studies were conducted at UEA and some of these used seawater collected during the INSPIRE project. The data show that nitrate availability influences the photochemical formation of iodomethane (CH_3I) in seawater. Samples of natural seawater or NaCl solutions spiked with acetone and iodide as the C- and I-precursors were exposed to light covering the wavelengths 280-700 nm. The results reconfirm the photochemical route for iodomethane formation. However, the extent to which NO_3^- influenced the rate of CH_3I production was shown to be dependent on the concentration of the carbon-precursor. At relatively high acetone concentrations (20 μM) increasing concentrations of NO_3^- did not impact on the rate of CH_3I photoproduction, but at 5 μM acetone iodomethane production decreased by 46 % between 0-20 μM NO_3^- . We suggest that this reflects competition between the products of NO_3^- photolysis and the iodine-precursor for CH_3I formation. This would provide an explanation for our earlier field data sets where inverse correlations were found between photoproduction of CH_3I and NO_3^- concentrations. In addition, the rate of photoproduction of methyl nitrate (CH_3ONO_2), a known source of oxidized nitrogen to the remote marine atmosphere, increased at higher concentrations of NO_3^- . These novel findings suggest that the photochemical formation of CH_3I , an atmospheric ozone ‘depleter’, and CH_3ONO_2 , an ozone ‘producer’, may represent competitive processes in the marine environment. A manuscript is in preparation for submission to *Environmental Chemistry*.

Novel outputs from the INSPIRE research cruise optics and aerosol data (Smyth). Optics data collected during the INSPIRE research cruise was used to develop an in-water UV radiative transfer model which is driven by Inherent Optical Properties. This is a very significant achievement because it is the first model of this type. In addition software has been developed for processing hyperspectral radiometry and retrieve water leaving radiances which offers considerable advances over

proprietary software. Also as part of a collaboration with NASA AERONET INSPIRE oceanic aerosol optical data has been contributed to their database at: http://aeronet.gsfc.nasa.gov/new_web/maritime_aerosol_network.html This data along with data for in-water parameters (UV, CTD, FRRF, ac9) and above water radiometry (hyperspectral and UV) has been fully processed and submitted to BODC. A manuscript entitled 'The marine aerosol network' has been submitted to the Journal of Geophysical Research Atmospheres.

5. Personnel.

5.1. Scientific & Technical Personnel

NAME	INSTITUTION
Gill Malin (INSPIRE Principal Scientist & D325 Principal Scientific Officer)	University of East Anglia, UEA.
Claire Hughes (INSPIRE Researcher Co-Investigator)	UEA
Gareth Lee	UEA
Janina Woeltjen	UEA
Philip Nightingale until 27/11/07 (INSPIRE Co-Investigator)	Plymouth Marine Laboratory, PML
Stephen Archer (INSPIRE Co-Investigator)	PML
Timothy Smyth (INSPIRE Co-Investigator)	PML
Amanda Beesley	PML
Darren Clarke	PML
Denise Cummings	PML
Joanna Dixon	PML
Laura Goldson	PML
Carolyn Harris	PML
Susan Kimmance	PML
Andrew Rees	PML
John Stephens	PML
Glen Tarran	PML
Gavin Tilstone	PML
Malcolm Woodward	PML
Rosemary Chance	University of York
Rachel Shelley	University of Plymouth
John Wynar (Technical Liason Officer)	National Marine Facilities Division (NMFD), Southampton. Technician
Christopher Barnard	NMFD Technician.
Daniel Comben until 27/11/07	NMFD Technician.
David Teare	NMFD Technician.
David Turner from 27/11/07	NMFD Technician.

5.2. Officers and Crew

NAME	RANK
Roger Chamberlain	Master
Richard Warner	Chief Officer
Malcolm Graves	2 nd Officer
Michael Hood	3rd Officer
David Hartshorne	Purser Catering Officer
George Parkinson	Chief Engineer
Stephen Bell	2 nd Engineer
Allan MacLean	3 rd Engineer
Ian Collin	3 rd Engineer
Dean Hurren	Electrical technical Officer (ETO)
Andrew Smith	Engineer Cadet
Iain Thomson	Chief Petty Officer (Deck)
Stephen Smith	Chief Petty Officer (Science)
Mark Moore	Petty Officer Deck (POD)
Gerry Cooper	Seaman (SG1A)
Paul Farley	Seaman (SG1A)
Colin Atkinson	Seaman (SG1A)
Lee Stephens	Seaman (SG1A)
Leslie Hillier	Engine Room Petty Officer (ERPO)
Peter Lynch	Head Chef
Wilmot Isby	Chef
Jeffrey Orsborn	Steward

6. Record of activities.

6.1 Outline of scientific activities.

Day	Date	Activity	Chl a / Production	location
Fri	09/11/2007	Travel		
Sat	10/11/2007	Mobilise		
Sun	11/11/2007	Mobilise		
Mon	12/11/2007	Mobilise		
Tue	13/11/2007	Sail		
Wed	14/11/2007	Transit		
Thu	15/11/2007	Transit		
Fri	16/11/2007	SITE A preliminary survey		
Sat	17/11/2007	Site A Day 1	Medium 1	17deg45'N 22deg45'W
Sun	18/11/2007	Site A Day 2		
Mon	19/11/2007	Site A Day 3		
Tue	20/11/2007	Site A Day 4		
Wed	21/11/2007	Transit		
Thu	22/11/2007	Site B Day 1	High 1	16deg55'N 24deg45'W
Fri	23/11/2007	Site B Day 2		(Nr UK-SOLAS Atmospheric Sampling Site)
Sat	24/11/2007	Site B Day 3		
Sun	25/11/2007	Site B Day 4		
Mon	26/11/2007	Transit/spare		
Tue	27/11/2007	Mindelo Port Stop		
Wed	28/11/2007	Site C Day 1	High 2	16degN23deg40W
Thu	29/11/2007	Site C Day 2		(West of island of Boa Vista)
Fri	30/11/2007	Site C Day 3		
Sat	01/12/2007	Site C Day 4		
Passage overnight		Transit		
Sun	02/12/2007	Site D Day 1	Medium 2	17deg40'N 22deg50'W
Mon	03/12/2007	Site D Day 2		Near Site A
Tue	04/12/2007	Site D Day 3		
Wed	05/12/2007	Site D Day 4		
Thu	06/12/2007	Transit		
Fri	07/12/2007	Site E Day 1	Low 1	20deg30'N 25degW
Sat	08/12/2007	Site E Day 2		
Sun	09/12/2007	Site E Day 3		
Mon	10/12/2007	Site E Day 4		
Tue	11/12/2007	Transit		
Wed	12/12/2007	Site F Day 1	Low 2	26degN 24deg'W
Thu	13/12/2007	Site F Day 2		
Fri	14/12/2007	Site F Day 3		
Sat	15/12/2007	Site F Day 4		Set course for Tenerife at 1637
Sun	16/12/2007	Transit		
Mon	17/12/2007	Transit		arrived Tenerife 1502
Tue	18/12/2007	Demobilise		Some flights to UK. Remainder overnight onboard.
Wed	19/12/2007	Travel		Remainder of flights to U.K.

6.2. Detailed log of scientific activities

<u>Date</u>	<u>Time (UT)</u>	<u>Event</u>
10/11/07	0930	Captain Roger Chamberlain joins vessel in Santa Cruz De Tenerife Mobilisation for Cruises 325 already underway
11/11/07	1315	Ships RIB launched for testing and pre-cruise trials Discovery of steering cable problems. Immediate sourcing for new cable launched via local agents, then via NMF SS. No luck.
	1540	RIB re-stowed for making up a tiller arrangement so that the RIB can be used for the forthcoming cruise.
12/11/07	0900	Commence loading Fresh Water
	1500-1600	Familiarisation of Scientists and signing them on.
	1720	Commence loading BUNKERS
	1900	Finished loading Fresh Water
	2047	Finished Bunkering - Took 169 Tonnes
13/11/07	0810-45	Final Pre-sailing checks to all critical equipment and propulsion
	0845	Pilot on board
	0914	All gone and clear of berth
	0922	Pilot disembarks off breakwater
	0924	FULL AWAY on passage East B/water bore 353° T x 0.34M Course 199° T
	1117	a/c to 216° T Pta De Agora bore 293° T x 3.80M
	1200	Position Latitude 28 00.9 N Longitude 016 27.2 W
	1615-40	Emergency and Lifeboat Musters and lectures.
14/11/07	0000	Position Latitude 26 06.9 N Longitude 017 58.4 W
	0900-40	Cruise Planning Meeting underway 24 45.8N 019 02.4 W
	1048	Hove to for CTD Trials
	1057-1143	Stainless CTD cast outboard to 500 metres 24 30.6N 019 14.1 W
	1237-1329	Titanium CTD cast outboard to 500 metres 24 30.4N 019 14.3 W
	1401	Resumed passage at full speed – Course 216° T
15/11/07	0000	Position Latitude 22 59.3 N Longitude 020 25.4 W
	1054	Hove to TMS Fish deployed 21 22.7N 021 39.6 W Took opportunity to swing both lifeboats out.
	1100	Resumed passage
	1200	Position Latitude 21 15.5 N Longitude 021 45.1 W
	1312	Hove To to test OPTICSics Rig
	1321-42	OPTICSics Cast outboard 21 04.4 N 021 50.8 W
	1344-1403	OPTICSics Cast outboard 21 04.3 N 021 50.9 W
	1415	Resumed passage. Set Course 191° T
	2000	a/c to 196° T 19 58.9 N 022 04.8 W
16/11/07	0000	Position Latitude 19 15.6 N Longitude 022 17.9 W
	0912	Hove To on SITE 'A'
	0914	DRIFTER A 001 deployed 17 44.7 N 022 45.4 W
Site A	0915	Commenced Site 'A' Pre - Survey.
Pre-Survey	1027-59	CTD A 001 (STS) cast to 200 m 17 45.3 N 022 52.8 W
	1226-56	CTD A 002 (STS) (STS) cast to 201 m 17 37.6 N 022 45.9 W
	1500-33	CTD A 003 (STS) (STS) cast to 200 m 17 51.5 N 022 44.6 W
	1705-35	CTD A 004 (STS) (STS) cast to 200 m 17 43.7 N 022 38.2 W
	1830-1905	Engaged in recovery of Drifter
	1905	DRIFTER A 001 all inboard 17 44.8N 022 45.3 W
	1925-55	CTD A 005 (STS) (STS) cast to 200 m 17 44.7 N 022 45.3 W
	1955	End of Pre- Survey
Site A proper	2020-29	DRIFTER A 002 deployed 17 44.7 N 022 45.2 W
	2029	DRIFTER 002 deployed - Air Sampling begins.

17/11/07	0307	TMS A 001 Fish lowered to 9 metres 17 43.5 N 022 44.4 W
	0510-55	CTD A 006 (STS) cast to 200 m 17 42.7 N 022 45.2 W
	0813-52	CTD A 007 (TIT) cast to 100 m 17 42.2 N 022 46.6 W
	0936-1014	RIB launched for test purposes (see log sheets)
	1244-1303	OPTICS A 001 cast to 120 m 17 41.7 N 022 46.6 W
	1347-1448	CTD A 008 (STS) cast to 450 m 17 41.4 N 022 46.8 W
18/11/07	0108	SAPS cable and anchor deployed to 50m
	0111-0359	SAPS A 001 cast outboard 17 41.4 N 022 46.6 W
	0401	Saps cable and weight inboard
	0504-40	CTD A 009 (STS) cast to 200 m 17 40.1 N 022 46.7 W CTD communications problem.
	0632-50	CTD A 010 (STS) cast to 200 m 17 39.8 N 022 46.9 W CTD communications problem.
	0721-50	CTD A 011 (TIT) cast to 200 m 17 39.5 N 022 47.1 W
	0908-21	CTD A 012 (TIT) cast to 65 m 17 39.2 N 022 46.6 W
	1104-11	CTD A 013 (TIT) cast outboard 17 37.6 N 022 47.0 W
	1245-1322	OPTICS A 002 cast to 120 m 17 37.6 N 022 47.0 W
	1348-1423	CTD A 014 (TIT) cast to 65 m 17 37.3 N 022 47.2 W 3 bottles damaged.
	1513-25	CTD A 015 (TIT) cast to 51 m 17 36.8 N 022 47.6 W
	1539-1620	CTD A 016 (STS) cast to 150 m 17 36.7 N 022 47.9 W Testing new cable.
	1703-25	CTD A 017 (STS) cast to 100 m 17 36.5 N 022 48.5 W
	1909-20	CTD A 018 (STS) cast to 50 m 17 36.0 N 022 49.0 W
	2110-16	CTD A 019 (STS) cast to 50 m 17 35.9 N 022 48.8 W
	2305-19	CTD A 020 (STS) cast to 50 m 17 35.7 N 022 48.4 W
19/11/07	0106-31	CTD A 021 (STS) cast to 200 m 17 35.4 N 022 48.6 W
	0306-20	CTD A 022 (STS) cast to 50 m 17 35.3 N 022 48.7 W CTD-STS out of action.
	0510-20	CTD A 023 (TIT) cast to 65 m 17 35.2 N 022 48.7 W
	0607-30	CTD A 024 (TIT) cast to 65 m 17 34.9 022 48.7 W
	0805-30	CTD A 025 (TIT) cast to 100m 17 35.6 N 022 49.0 W
	0920-1130	Vessel left site for some garbage management
	1241-1315	OPTICS A 003 cast to 120 m 17 33.5 N 022 49.2 W
	1344-1417	CTD A 026 (TIT) cast to 101 m 17 33.2 022 49.5 W
	1455	Ships Rigid inflatable Boat (RIB) launched
	1511	NSS A 001 – Near Surface Sampler deployed.
	1456-1555	RIB A 001 (9 samples) launched 17 33.0 022 50.1 W
	1532	NSS A 001 Near Surface bottles Fired 17 33.1 022 50.1 W
	1541	Near Surface Sampler recovered
	1555	RIB A001 – RIB recovered and secured
	2023-34	CTD (TESTING) 101m 17 32.4 N 022 50.8
20/11/07	0506-42	CTD A 027(TIT) cast to 100m 17 32.0 N 022 51.2
	1015	Ships Rigid inflatable Boat (RIB) launched 17 31.8 N 022 51.9 W
	1018	RIB A 002 (9 samples) launched 17 31.8 022 51.9 W
	1038-1111	NSS 002 – Near Surface Sampler deployed 17 31.7 022 52.1 W
	1130	RIB 002 – RIB recovered and secured
	1238-1312	OPTICS A 004 cast to 120 m 17 31.0 N 022 52.5 W
	1514-48	Engaged in recovery of Drifter
	1548	DRIFTER A 002 all inboard 17 30.9N 022 52.4 W
	1636-2011	SAPS A 002 cast outboard to 146 m 17 30.9 N 022 52.5 W
	2048	Set Course 252° T for Site ‘B’

21/11/07	0800	Hove To on SITE 'B' 16 56.0 N 024 45.3 W
	0900	Commenced Site 'B' Pre – Survey 16 56.3 N 024 45.2 W
	0951	altered course to 051° T 16 57.9 N 024 52.6 W
	1143	altered course to 204° T 17 09.7 N 024 38.1 W
	1320	Hove to on station
	1321-38	OPTICS B 005 cast to 120 m 16 55.8 N 024 44.0 W
	1426-44	OPTICS B 006 cast to 120 m 16 51.5 N 024 45.9 W
	1602-20	OPTICS B 007 cast to 120 m 16 50.4 N 024 46.5 W
	1710	Set Course 010° T 16 50.9 N 024 46.7 W
	1736	altered course to 270° T 16 53.2 N 024 46.1 W
	1805	Hove to on station
	1820-40	OPTICS B 008 cast to 120 m 16 53.7 N 024 49.8 W
22/11/07	0333	TMS B 002 Fish lowered to 7 metres 16 53.5 N 024 50.1 W
	0521-45	CTD B 028(TIT) cast to 100m 16 53.8 N 024 50.4 W
	0805-41	CTD B 029(TIT) cast to 100m 16 53.6 N 024 49.9 W
	1243-1310	OPTICS B 009 cast to 70 m 16 53.4 N 024 50.1 W
	1342-1414	CTD B 030 (TIT) cast to 84m 16 53.4 N 024 50.2 W
	1448	set course 090° T
	1642	altered course to 043° T 16 50.0 N 024 35.5 W
	1730	Vessel hove to 16 54.9 N 024 30.1 W
	2106	Returning to Site 'B'
	2343	Hove to on station 16 53.3 N 024 50.0 W
23/11/07	0518-0600	CTD B 031(TIT) cast to 100m 16 53.8 N 024 50.3 W
	0806-26	CTD B 032(TIT) cast to 100m 16 54.0 N 024 50.2 W
	1248-1324	OPTICS B 010 cast to 70 m 16 53.3 N 024 49.8 W
	1353-1427	CTD B 033(TIT) cast to 101m 16 53.4 N 024 50.0 W
	1521-1840	SAPS B 003 cast outboard to 79 m 16 53.6 N 024 50.3 W
24/11/07	0526-0600	CTD B 034(TIT) cast to 100m 16 53.6 N 024 50.2 W
	0806-31	CTD B 035(TIT) cast to 100m 16 53.6 N 024 50.2 W
	1246-1341	OPTICS B 011 cast to 85 m 16 52.9 N 024 49.3 W
	1408-47	CTD B 036(TIT) cast to 86m 16 53.3 N 024 50.0 W
	1524	Vessel positioning for SAPS Station
	1616-1925	SAPS B 004 cast outboard to 80 m 16 54.0 N 024 50.2 W
25/11/07	0518-52	CTD B 037(STS) cast to 100m 16 53.9 N 024 50.3 W
	0933	TMS Fish inboard 16 54.2 N 024 50.3 W
	1248-1340	OPTICS B 012 casts to 100 & 65m 16 53.0 N 024 49.8 W
	1416-49	CTD B 038(TIT) cast to 100m 16 53.4 N 024 50.2 W
	1900	Completed air sampling Set Course 045° T 16 53.6 N 024 50.0 W
		Incineration and garbage management whilst on passage.
	2204	Hove to (AIR SAMPLING STATION) 17 00.5 N 024 42.7 W
26/11/07	0000	Position Latitude 17 00.9 N Longitude 024 42.6 W
		Air Sampling throughout day
	1200	Position Latitude 17 00.6 N Longitude 024 42.7 W
		Air Sampling throughout day
27/11/07	0000	Position Latitude 17 00.5 N Longitude 024 41.4 W
	0600	Set Course 260° T towards Mindelo at full speed
	0700	All criticals tested – hand steering faulty 16 59.4N 024 50.5W
	0745-0940	Hove to to fix Hand steering problems
	0940	Resumed Pilotage into Mindelo 16 58.2N 024 53.1W
	1044	Pilot on Board outside Porto Grande, Mindelo
	1130	Vessel alongside Mindelo – Berth 4
	1200-1700	Receiving Airfreight, stores and water alongside.
	1755	All criticals tested
	1809	Pilot On Board

	1830	All gone and clear from berth
	1833	Pilot away
	1842	Full away on passage course 313° T
	1848	Altered course to 270° T 16 54.0N 025 01.6W
	1850	Altered course to 240° T 16 54.0N 025 02.5W
	1900	Altered course to 220° T 16 53.5N 025 04.0W
	1915	Altered course to 200° T 16 51.2N 025 06.0W
	1918	Altered course to 180° T 16 50.7N 025 06.2W
	1927	Altered course to 124° T 16 48.9N 025 06.1W
	2025	Hove to to deploy TMS and PES Fishes
	2034	TMS Fish outboard 16 44.2N 025 00.2W
	2040	PES Fish (10 kHz) fish outboard – resumed passage
28/11/07	0000	Position Latitude 16 28.4 N Longitude 024 31.6 W
	0610-15	DRIFTER C 003 deployed 16 00.1 N 023 39.9 W
	0630	TMS C 003 Fish lowered to 7 metres 16 00.1 N 023 39.9 W
	0634-0710	CTD C 039(TIT) cast to 200m 16 00.3 N 023 39.82 W
	0906-42	CTD C 040(TIT) cast to 100m 16 00.4 N 023 40.4 W
	1102-29	CTD TEST (STS) cast to 200m 16 00.5 N 023 40.8 W
	1237-1340	OPTICS C 013 2 x casts to 120m 16 00.4 N 023 41.0 W
	1354-1441	CTD C 041(STS) cast to 450m 16 00.3 N 023 41.1 W
	1531-1830	SAPS C 005 cast outboard to 94 m 16 01.0 N 023 41.7 W
	1920	TMS Fish hauled 2m 16 01.3N 023 42.3W
29/11/07	0125-0427	SAPS C 006 cast outboard to 144 m 16 01.0 N 023 42.7 W
	0507-50	CTD C 042(STS) cast to 200m 16 01.3 N 023 43.7 W
	0707-28	CTD C 043(STS) cast to 100m 16 01.3 N 023 43.7 W
	0804-25	CTD C 044(STS) cast to 100m 16 00.9 N 023 44.0 W
	0903-21	CTD C 045(STS) cast to 100m 16 01.3 N 023 44.3 W
	1102-21	CTD C 046(STS) cast to 100m 16 01.7 N 023 44.8 W
	1238-1330	OPTICS C 014 cast to 120m 16 01.8 N 023 45.2 W
	1340-1425	CTD C 047(STS) cast to 100m 16 01.7 N 023 45.5 W
	1510-28	CTD C 048(STS) cast to 100m 16 01.6 N 023 46.3 W
	1702-17	CTD C 049(STS) cast to 100m 16 01.7 N 023 46.5 W
	1902-18	CTD C 050(STS) cast to 100m 16 02.4 N 023 46.4 W
	2101-20	CTD C 051(STS) cast to 100m 16 02.3 N 023 46.3 W
	2302-25	CTD C 052(STS) cast to 100m 16 01.8 N 023 46.4 W
30/11/07	0102-20	CTD C 053(STS) cast to 100m 16 01.5 N 023 46.1 W
	0258-0321	CTD C 054(STS) cast to 100m 16 01.3 N 023 46.2 W
	0503-30	CTD C 055(STS) cast to 100m 16 01.3 N 023 46.4 W
	0814-40	CTD C 056(STS) cast to 100m 16 00.9 N 023 47.0 W
	1238-1334	OPTICS C 015 2 x casts to 120m 16 00.1 N 023 47.2 W
	1343-1428	CTD C 057(STS) cast to 100m 16 00.0 N 023 46.9 W
		RIB launch cancelled due to lively seas
	1500-0503	Standing by drifter and continuing to AIR SAMPLE
01/12/07		Position Latitude 15 59.1 N Longitude 023 47.6 W
	0505-35	CTD C 058(STS) cast to 100m 15 57.2 N 023 49.4 W
	0807-28	CTD C 059(STS) cast to 100m 15 58.1 N 023 50.6 W aborted.
	0845-0905	CTD C 060(STS) cast to 100m 15 57.9 N 023 50.9 W
	1234-1335	OPTICS C 016 2 x casts to 120m 15 56.9 N 023 52.1 W
	1346-1423	CTD C 061(STS) cast to 100m 15 56.8 N 023 52.2 W
	1457-1555	Engaged in recovery of Drifter
	1555	DRIFTER C 003 all inboard 15 56.8N 023 53.6 W
	1602	Set Course 360° T for Site 'D' course for receiving email
	1622	Altered course to 124° T 15 58.9N 023 53.9W

02/12/07	0000	Position Latitude 16 54.9 N Longitude 023 18.1 W
	0600	Position Latitude 17 30.6 N Longitude 022 55.9 W
	0755	Hove to on Site 'D' 17 39.9N 022 50.1W
	0807-10	DRIFTER D 004 deployed 17 39.9 N 022 50.1 W
	0826-0910	CTD D 062(STS) cast to 200m 17 40.2 N 022 49.9 W
	1235-1334	OPTICS D 017 2 x casts to 120m 17 40.5 N 022 51.9 W
	1346-1433	CTD D 063(STS) cast to 451m 17 40.9 N 022 52.2 W
	1512-1822	SAPS D 007 cast outboard to 100 m 17 41.1 N 022 52.8 W
	1822-50	Engaged in recovery of Drifter
	1850	DRIFTER D 004 all inboard 17 40.9N 022 53.6 W
03/12/07	0124-0440	SAPS D 008 cast outboard to 144 m 17 41.4 N 022 53.8 W
	0445	TMS D 004 Fish lowered to 9 metres 17 42.2 N 022 53.5 W
	0510-50	CTD D 064(STS) cast to 100m 17 42.3 N 022 53.6 W
	0706-22	CTD D 065(STS) cast to 100m 17 42.7 N 022 54.0 W
	0811-46	CTD D 066(TIT) cast to 100m 17 42.8 N 022 53.9 W
	0919-46	CTD D 067(STS) cast to 101m 17 42.9 N 022 53.9 W
	0957-9	DRIFTER D 005 deployed 17 43.0 N 022 53.9 W
	1101-20	CTD D 068(STS) cast to 100m 17 43.3 N 022 53.8 W
	1234-1336	OPTICS D 018 2 x casts to 120m 17 43.8 N 022 53.8 W
	1350-1430	CTD D 069(STS) cast to 95m 17 44.0 N 022 53.8 W
	1511-33	CTD D 070(STS) cast to 97m 17 44.4 N 022 54.4 W
	1705-22	CTD D 071(STS) cast to 100m 17 45.2 N 022 54.8 W
	1901-20	CTD D 072(STS) cast to 100m 17 45.2 N 022 54.8 W
	2100-17	CTD D 073(STS) cast to 100m 17 45.1 N 022 55.3 W
	2300-20	CTD D 074(STS) cast to 100m 17 44.8 N 022 55.6 W
04/12/07	0100-19	CTD D 075(STS) cast to 100m 17 45.0 N 022 55.6 W
	0302-19	CTD D 076(STS) cast to 98m 17 45.1 N 022 56.4 W
	0505-40	CTD D 077(STS) cast to 100m 17 45.2 N 022 56.5 W
	0806-36	CTD D 078(STS) cast to 100m 17 46.5 N 022 56.8 W
	1235-1331	OPTICS D 019 2 x casts to 120m 17 47.4 N 022 58.2 W
	1347-1443	CTD D 079(STS) cast to 450m 17 47.6 N 022 58.2 W
05/12/07	0000	Position Latitude 17 48.6 N Longitude 023 04.5 W
	0508-45	CTD D 080(STS) cast to 100m 17 48.6 N 023 07.4 W
	0607	TMS D 005 Fish lowered extra 4 metres 17 48.5 N 023 07.7 W
	0807-29	CTD D 081(STS) cast to 100m 17 48.0 N 023 09.7 W
	1200	Position Latitude 17 48.6 N Longitude 023 13.3 W
	1240-1334	OPTICS D 020 2 x casts to 120m 17 48.8 N 023 13.8 W
	1347-1421	CTD D 082(STS) cast to 100m 17 49.0 N 023 14.1 W
	1437	TMS Fish recovered 17 49.2N 023 14.4W
	1447-1545	Engaged in recovery of Drifter DRIFTER D 005
	1545	Drifter beacon buoy ONLY recovered 17 48.1N 023 16.9W
	1601-30	Deliberating whether or not to search for rest of drifter
	1630	decision made to abandon Drifter D 005
	1630	Set Course 329° T for Site 'E' 17 48.6N 023 16.2W
06/12/07	0000	Position Latitude 18 53.9 N Longitude 023 58.7 W
	0600	Position Latitude 19 42.3 N Longitude 024 29.5 W
	1200	Hove to on Site 'E' 20 30.0N 025 00.1W
	1235	TMS E 006 Fish lowered port quarter 20 30.1 N 025 00.1 W
	1249-1331	OPTICS E 021 cast to 180m 20 30.2 N 025 00.2 W
	1448-1653	CTD E 083(STS) cast to 2500m 20 30.6 N 025 00.6 W
07/12/07	0000	Position Latitude 20 35.7 N Longitude 024 59.7 W
	0501-45	CTD E 084(STS) cast to 200m 20 38.8 N 024 57.3 W
	0901-0946	CTD E 085(TIT) cast to 200m 20 39.9 N 024 58.0 W
	1238-1324	OPTICS E 022 - 2 x casts to 160m 20 41.1 N 024 57.8 W
	1351-1444	CTD E 086(STS) cast to 450m 20 41.8 N 024 57.9 W

1606-1852		SAPS E 009 cast outboard to 84 m 20 44.0 N 024 59.2 W
08/12/07	0100-0420	SAPS E 010 cast outboard to 124 m 20 49.0 N 025 01.2 W
	0505-55	CTD E 087(STS) cast to 197m 20 50.2 N 025 00.3 W
	0555	TMS Fish hauled up 2 metres
	0705-37	CTD E 088(STS) cast to 200m 20 51.7 N 025 00.4 W
	0902-47	CTD E 089(STS) cast to 200m 20 52.6 N 025 01.0 W
	1107-37	CTD E 090(STS) cast to 200m 20 54.1 N 025 02.0 W
	1230	OPTICS CAST CANCELLED due to weather
	1340-1448	CTD E 091(STS) cast to 458m 20 56.2 N 025 02.2 W
	1705-27	CTD E 092(STS) cast to 200m 20 58.4 N 025 02.4 W
	1903-25	CTD E 093(STS) cast to 200m 20 59.3 N 025 03.1 W
	2108-39	CTD E 094(STS) cast to 200m 21 01.1 N 025 02.8 W
	2302-38	CTD E 095(STS) cast to 200m 21 02.6 N 025 02.9 W
09/12/07	0104-30	CTD E 096(STS) cast to 200m 21 04.3 N 025 02.7 W
	0301-27	CTD E 097(STS) cast to 200m 21 05.3 N 025 02.5 W
	0504-45	CTD E 098(STS) cast to 200m 21 06.0 N 025 02.3 W
	1230-1344	OPTICS E 02 - 2 x casts to 160m & 120m 21 11.6 N 025 01.7 W
	1402-51	CTD E 099(STS) cast to 200m 21 12.2 N 025 01.5 W
	1544-1645	CTD E 100(STS) cast to 1200m 21 13.7 N 025 01.0 W
	1835-1930	CTD E 101(STS) cast to 950m 21 15.4 N 025 00.7 W
10/12/07	0000	Position Latitude 21 17.3 N Longitude 025 00.2 W
	0504-40	CTD E 102(STS) cast to 196m 21 18.2 N 024 57.2 W
	0805-40	CTD E 103(STS) cast to 200m 21 18.9 N 024 57.2 W
	1237-1345	OPTICS E 024 - 2 x casts to 160m & 120m 21 20.6 N 024 57.6 W
	1355-1440	CTD E 104(STS) cast to 200m 21 21.0 N 024 57.7 W
	1451	TMS lowered to 10 metres
	1506	Set Course 011° T for Site 'F' 21 21.9N 024 57.1W
11/12/07	0000	Position Latitude 22 44.3 N Longitude 024 40.3 W
	1200	Position Latitude 24 40.2 N Longitude 024 16.6 W
	1954	Hove to on Site 'F' 26 00.1N 023 59.9W
	1958-2000	DRIFTER F 006 deployed 26 00.1 N 023 59.9 W
	2055	TMS F 007 Fish raised to 2 metres 26 00.9 N 023 59.9 W
12/12/0	0505-55	CTD F 105(STS) cast to 200m 26 02.7 N 023 59.4 W
0809-46		CTD F 106(STS) cast to 200m 26 03.0 N 023 59.7 W
1235-1351		OPTICS F 025 - 2 x casts to 160m & 120m 26 03.6 N 023 59.6 W
1402-55		CTD F 107(STS) cast to 450m 26 04.2 N 023 59.6 W
1535-1847		SAPS F 011 cast outboard to 144 m 26 04.7 N 023 59.6 W
13/12/07	0117-0425	SAPS F 012 cast outboard to 174 m 26 05.8 N 023 59.7 W
	0440	TMS F 008 Fish lowered to 7 metres 26 06.6 N 023 59.4 W
	0505-45	CTD F 108(STS) cast to 200m 26 06.6 N 023 59.5 W
	0708-28	CTD F 109(STS) cast to 200m 26 06.7 N 023 59.8 W
	0806-54	CTD F 110(TIT) cast to 200m 26 06.8 N 023 59.9 W
	0915-39	CTD F 111(STS) cast to 200m 26 07.0 N 024 00.3 W
	1102-25	CTD F 112(STS) cast to 200m 26 07.3 N 023 59.6 W
	1232-1339	OPTICS F 026 - 2 x casts to 160m & 120m 26 07.7 N 023 59.9 W
	1402-27	CTD F 113(STS) cast to 200m 26 07.7 N 024 00.1 W
	1701-22	CTD F 114(STS) cast to 200m 26 08.2 N 023 59.7 W
	1900-24	CTD F 115(STS) cast to 200m 26 08.4 N 023 59.6 W
	2103-28	CTD F 116(STS) cast to 200m 26 08.7 N 023 59.8 W
	2302-28	CTD F 117(STS) cast to 200m 26 08.6 N 023 59.8 W

14/12/07	0110-39	CTD F 118(STS) cast to 200m 26 09.2 N 023 59.6 W
	0308-32	CTD F 119(STS) cast to 200m 26 09.8 N 023 59.5 W
	0505-41	CTD F 120(STS) cast to 200m 26 10.0 N 024 00.0 W
	0805-37	CTD F 121(STS) cast to 200m 26 10.2 N 023 59.7 W
	1201-1343	OPTICS F 027 - 2 x casts to 150m & 120m 26 10.9 N 023 59.7 W
	1353-1438	CTD F 122(STS) cast to 200m 26 11.0 N 023 59.6 W
	1504	Ships Rigid inflatable Boat (RIB) launched 26 11.1 N 023 59.4 W
	1520	RIB F 003 (10 samples) away from ship 26 11.1 023 59.4 W
	1604	RIB Crew aboard safely
	1612	RIB F003 – RIB recovered and secured 26 11.1 N 023 59.0 W
15/12/07	0503-52	CTD F 123(STS) cast to 200m 26 13.1 N 023 59.3 W
	0803-29	CTD F 124(STS) cast to 200m 26 13.4 N 023 58.9 W
	1049	Ships Rigid inflatable Boat (RIB) launched 26 13.4 N 023 59.1 W
	1055-1115	RIB F 004 (10 samples) away from ship 26 13.0 N 023 59.1 W
	1130	RIB Crew aboard safely
	1134	RIB F 004 – RIB recovered and secured 26 12.7 N 023 59.1 W
	1232-1332	OPTICS F 028 - 2 x casts to 160m & 120m 26 13.3 N 023 59.2 W
	1347-1429	CTD F 125(STS) cast to 200m 26 13.3 N 023 59.3 W
	1500-33	NSS F 003 – Near SurfaceSampler deployed 26 13.5 023 59.0 W ABANDONED and recovered
	1520	Ships Rigid inflatable Boat (RIB) launched 26 13.4 N 023 59.3 W
	1520-48	RIB F 005 – Too rough – NO SAMPLES TAKEN
	1548	RIB Crew aboard safely
	1620	RIB F 005 – RIB recovered and secured 26 14.3 N 023 59.0 W
	1625-37	Recovering TMS and PES Fishes
	1637	SCIENCE ENDS Set Course 076° T for passage to Tenerife 26 14.8 N 023 58.8 W
18/12/07	0800 (prov)	ETA Santa Cruz De Tenerife

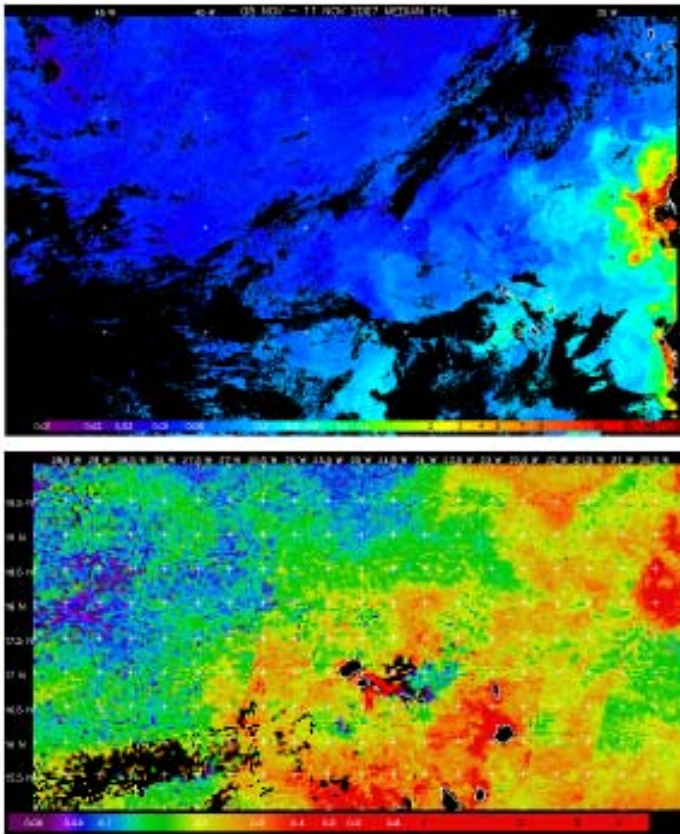
END OF REPORT

7.1 Study Site Selection

Gill Malin

University of East Anglia

The selection of the six, four-day duration sites for INSPIRE was guided by processed surface ocean colour satellite images that were supplied to us on a daily basis daily by email by the UK Natural Environment Research Council (NERC) Earth Observation Data Acquisition and Analysis Service (NEODAAS <http://www.neodaas.ac.uk/>) at Plymouth Marine Laboratory. A range of different satellite data was used (SeaWiFS, MODIS and MERIS) and images with a focus on different areas and with altered colour scales were sometimes requested. Examples of a couple of the images received during the early part of the cruise are shown below and a composite image for the whole cruise period, with sampling stations and cruise track superimposed is shown in section 3.



Top: 7-day composite Modis aqua for the period prior to sailing: 5 to 11/11/2007.

Bottom: 7-day composite SEAWIFS for the 11 to 18/11/07. Focusing on major area of interest near the Cape Verde Islands.

Images courtesy of NEODAAS (NERC Earth Observation Data Acquisition and Analysis Service).

We were looking for sites that matched to our aim of occupying 2 sites each of approximately low, medium and high productivity (relative to the productivity levels prevailing over this area of the North Atlantic). We wanted to stay upwind of the Cape Verde Islands and between them and the Canary Islands, such that we would be sampling the waters whose emissions fall within the footprint of the SOLAS air monitoring station on Cape Verde. Given our use of drifters we looked for sites that had fairly homogeneous chlorophyll levels relative to the likely scale of the drift and avoided areas with obvious transitions in chlorophyll. For this reason we avoided waters that were very clearly associated with the upwelling off Africa.

The choice of locations for the 6 sites was further constrained due to the time available. It was necessary to take into account the distances the ship would need to cover between stations and to and from the ports in Cape Verde and the Canary Islands, the prevailing weather conditions and weather forecasts. Time constraints also meant that it was not feasible to do the desired survey to map water column conditions and iodocarbon concentrations prior to commencing sampling at every site.

Inevitably, some compromises had to be made. Chlorophyll levels were high at Station B close to Sao Vicente, but the waters were relatively shallow and the currents and tide were strong. This meant that it was not possible to deploy a drifter buoy and sub-surface drogue. Instead we held a geographic position immediately upwind of the land-based SOLAS atmospheric sampling station. It was perhaps hardest to locate sites with spatially consistent high chlorophyll level, so our second high chlorophyll site, Station C, was located west of the Island of Boa Vista which south east of the SOLAS air sampling station though still in it's rather broad air trajectory footprint. Our medium chlorophyll were in approximately the same geographic location.

We considered sampling at the TENATSO Tropical Eastern North Atlantic Time-Series Observatory site at (17° 35.390' N 24° 15.120' W). This deepwater, open ocean sampling site was set up by the German SOLAS project and IfM-GEOMAR-Kiel and it is ~6 hours sailing distance from Mindelo. We had hoped that our data could then mesh in with the sites monthly sampling programme that had been planned to start in the late summer of 2007 using the small vessel *Islandia*. However, onboard email discussions with Doug Wallace and Letitica Cotrim da Cunha (IfM-GEOMAR-Kiel) revealed that this sampling series had not yet started. In addition the satellite images suggested that the chlorophyll concentration in this area were quite homogeneous so we decided to choose another site.

In conclusion, we pretty much achieved our aim of selecting 2 sites each of approximately low, medium and high chlorophyll and productivity. Preliminary primary production data can be seen in the section 7.8 Figure 1 and section 7.13. Extracted chlorophyll data can also be found in section 7.13.

Many thanks to NEODAAS for supporting the INSPIRE cruise. Thanks to Tim Smyth for helping with the interpretation of the satellite images, and Malcolm Woodward and the Officers for help with calculating transit times between stations. The scientific need to position the ship head-to-wind for much of the time led to a lot of down time for the scientific email system. I am grateful to Captain Roger Chamberlain who kindly agreed to all emails from NEODAAS being copied to him on the alternative email system.

7.2 Halocarbon Measurements, Drifter and Near-Surface Sampler Deployments

*Phil Nightingale, Amanda Beesley, Denise Cummings, John Stephens
Plymouth Marine Laboratory*

A purge and cryogenic trap system was used with electron capture detection (ECD) on two gas chromatographs (an HP5890 and a Shimadzu GC-14A) to determine concentration levels of six primary species of halo-carbons in the water column. The purge was of 20min. duration with a purge gas flow rate of 60 ml/min. The instruments were calibrated using liquid standards diluted in methanol and prepared by Claire Hughes and Gareth Lee (UEA).

Primary species identified were:

CH ₃ I	: iodo-methane	CH ₂ I ₂	: di-iodo-methane
CH ₂ ClI	: chloro-iodo-methane	CH ₂ BrI	: bromo-iodo-methane
CHBr ₃	: tri-bromo-methane	C ₂ H ₅ I	: iodo-ethane

A total of 6, four-day stations were worked (Stations A-F) and samples taken for analysis are shown in Table 1.

A diel cycle for each station concentrated primarily on the mixed layer with one sample being analysed at the near surface and one in the mid to lower boundary every two hours, with an additional sample being analysed at the chlorophyll maximum every four hours. Samples were taken from CTD casts.

Station B was the only station for which a diel cycle was not undertaken since we were not drifting with the water column but holding a geographic position upwind of the land based atmospheric sampling station on Ilha de Sao Vicente, of the Cap Verde Islands.

At Stations A samples were also taken from the surface 2m of the water column using a near-surface sampling device (NSSD). This piece of equipment was not used at the other sites due to the rough nature of the sea-surface and consequent mixing processes associated with these conditions preventing the formation of near surface gradients. An attempt was made at Station F but failed due to rough seas.

Additional surface monitoring of halo-carbons was also undertaken using samples from the TowFish at a set depth of 2m. at Stations A, E and F. The fish was used in preference to the ships' non-toxic supply because there was reduced contamination.

The duration of the sampling periods were:-

Station A - 18th-19th Nov. 2007 commensurate with diel sampling.

Station E - 8th - 9th Dec. 2007 approx. hourly sampling.

Station F - 12th - Dec. 2007 approx. two hourly sampling.

Samples were also analysed for four grazing experiments: -

Expt. 1. T₀ 5th Dec. 2007, T_{Final} 7th Dec.2007

Expt. 2. T₀ 9th Dec. 2007, T_{Final} 10th Dec.2007

Expt. 3. T₀ 12th Dec. 2007, T_{Final} 13th Dec.2007

Expt. 4. T₀ 14th Dec. 2007, T_{Final} 15th Dec.2007

TABLE 1 : D325 INSPIRE : HALO-CARBON - (CTD) SAMPLING SUMMARY**STATION A : 17th-20th November 2007**

CTD_A006	Date: 17/11/2007	Time GMT: 05:40hrs	Lat: 17 42.6N	Long: 22 45.3W
CTD_A008	Date: 17/11/2007	Time GMT: 14:37hrs	Lat: 17 41.1N	Long: 22 46.8W
CTD_A024	Date: 19/11/2007	Time GMT: 06:32hrs	Lat: 17 34.89N	Long: 22 48.68W
CTD_A027	Date: 20/11/2007	Time GMT: 05:00hrs	Lat: 17 31.99N	Long: 22 51.15W
NSSD_01	Date: 19/11/2007	Time GMT: 15:30hrs		
NSSD_02	Date: 20/11/2007	Time GMT: 10:00hrs		
DIEL CYCLE	Date: 18_19/11/2007			

STATION B : 22nd-25th November 2007

CTD_B028	Date: 22/11/2007	Time GMT: 05:30hrs	Lat: 16 54.01N	Long: 24 50.57W
CTD_B030	Date: 22/11/2007	Time GMT: 14:30hrs	Lat: 16 53.47N	Long: 24 50.17W
CTD_B031	Date: 23/11/2007	Time GMT: 05:30hrs	Lat: 16 53.92N	Long: 24 50.48W
CTD_B033	Date: 23/11/2007	Time GMT: 14:30hrs	Lat: 16 53.44N	Long: 24 50.03W
CTD_B034	Date: 24/11/2007	Time GMT: 05:30hrs	Lat: 16 53.59N	Long: 24 50.21W
CTD_B036	Date: 24/11/2007	Time GMT: 14:30hrs	Lat: 16 53.44N	Long: 24 50.03W
CTD_B037	Date: 25/11/2007	Time GMT: 05:20hrs	Lat: 16 53.87N	Long: 24 50.22W
CTD_B038	Date: 25/11/2007	Time GMT: 14:50hrs	Lat: 16 53.52N	Long: 24 50.21W

STATION C : 28th November - 1st December 2007

CTD_C039	Date: 28/11/2007	Time GMT: 07:20hrs	Lat: 16 00.37N	Long: 23 39.79W
CTD_C041	Date: 28/11/2007	Time GMT: 14:30hrs	Lat: 16 00.31N	Long: 23 41.09W
CTD_C055	Date: 30/11/2007	Time GMT: 05:03hrs	Lat: 16 01.27N	Long: 23 46.43W
CTD_C057	Date: 30/11/2007	Time GMT: 14:20hrs	Lat: 15 59.95N	Long: 23 46.95W
CTD_C058	Date: 01/12/2007	Time GMT: 05:10hrs	Lat: 15 57.10N	Long: 23 49.27W
CTD_C061	Date: 01/12/2007	Time GMT: 14:15hrs	Lat: 15 56.83N	Long: 23 52.20W
DIEL CYCLE	Date: 29 - 30/11/2007			

STATION D : 2nd - 5th December

CTD_D062	Date: 02/12/2007	Time GMT: 08:30hrs	Lat: 17 40.06N	Long: 22 49.94W
CTD_D063	Date: 02/12/2007	Time GMT: 14:30hrs	Lat: 17 40.72N	Long: 22 52.03W
CTD_D064	Date: 03/12/2007	Time GMT: 05:30hrs	Lat: 17 42.36N	Long: 22 53.59W
CTD_D069	Date: 03/12/2007	Time GMT: 13:30hrs	Lat: 17 43.99N	Long: 22 53.81W
CTD_D077	Date: 04/12/2007	Time GMT: 05:00hrs	Lat: 17 45.08N	Long: 22 56.33W
CTD_D079	Date: 04/12/2007	Time GMT: 13:47hrs	Lat: 17 45.53N	Long: 22 58.23W
CTD_D080	Date: 05/12/2007	Time GMT: 05:00hrs	Lat: 17 48.62N	Long: 23 07.37W
CTD_D082	Date: 05/12/2007	Time GMT: 14:00hrs	Lat: 17 48.96N	Long: 23 14.04W
DIEL CYCLE	Date: 03 - 04/12/2007			

STATION E : 7th - 10th December

CTD_E082	Date: 07/12/2007	Time GMT: 05:20hrs	Lat: 20 38.77N	Long: 24 57.36W
CTD_E086	Date: 07/12/2007	Time GMT: 14:00hrs	Lat: 20 44.45N	Long: 24 57.78W
CTD_E087	Date: 08/12/2007	Time GMT: 05:10hrs	Lat: 20 50.24N	Long: 25 00.23W
CTD_E091	Date: 09/12/2007	Time GMT: 13:40hrs	Lat: 20 54.94N	Long: 25 21.49W
CTD_E098	Date: 09/12/2007	Time GMT: 05:00hrs	Lat: 21 05.97N	Long: 25 02.33W
CTD_E099	Date: 09/12/2007	Time GMT: 14:00hrs	Lat: 21 12.08N	Long: 25 01.56W
CTD_E102	Date: 10/12/2007	Time GMT: 05:00hrs	Lat: 21 18.13N	Long: 24 57.53W
CTD_E105	Date: 10/12/2007	Time GMT: 13:50hrs	Lat: 21 18.13N	Long: 24 57.53W
DIEL CYCLE	Date: 8_9/12/2007			

STATION F : 12th - 15th December

CTD_F105	Date: 12/12/2007	Time GMT: 05:20hrs	Lat: 25 02.52N	Long: 23 59.40W
CTD_F107	Date: 12/12/2007	Time GMT: 14:30hrs	Lat: 26 04.08N	Long: 23 59.57W
CTD_F120	Date: 14/12/2007	Time GMT: 05:20hrs	Lat: 26 10.06N	Long: 23 59.69W
CTD_F122	Date: 14/12/2007	Time GMT: 14:00hrs	Lat: 26 10.98N	Long: 23 59.68W
CTD_F123	Date: 15/12/2007	Time GMT: 05:20hrs	Lat: 26 13.11N	Long: 23 59.09W
CTD_F125	Date: 15/12/2007	Time GMT: 14:00hrs	Lat: 26 13.29N	Long: 23 59.24W
DIEL CYCLE	Date: 13_14/12/2007			
NSSD_03	Date: 15/11/2007	Time GMT: 15:30hrs	Failed	

Figure 1 below shows a mean concentration for Station A, CTD's during the 4 day station. Six halo-carbon species are shown but the values must be treated with caution since final calibration checks need to be undertaken. All plots are to the same scale.

D325 : INSPIRE : STATION A : Mean CTD Profiles

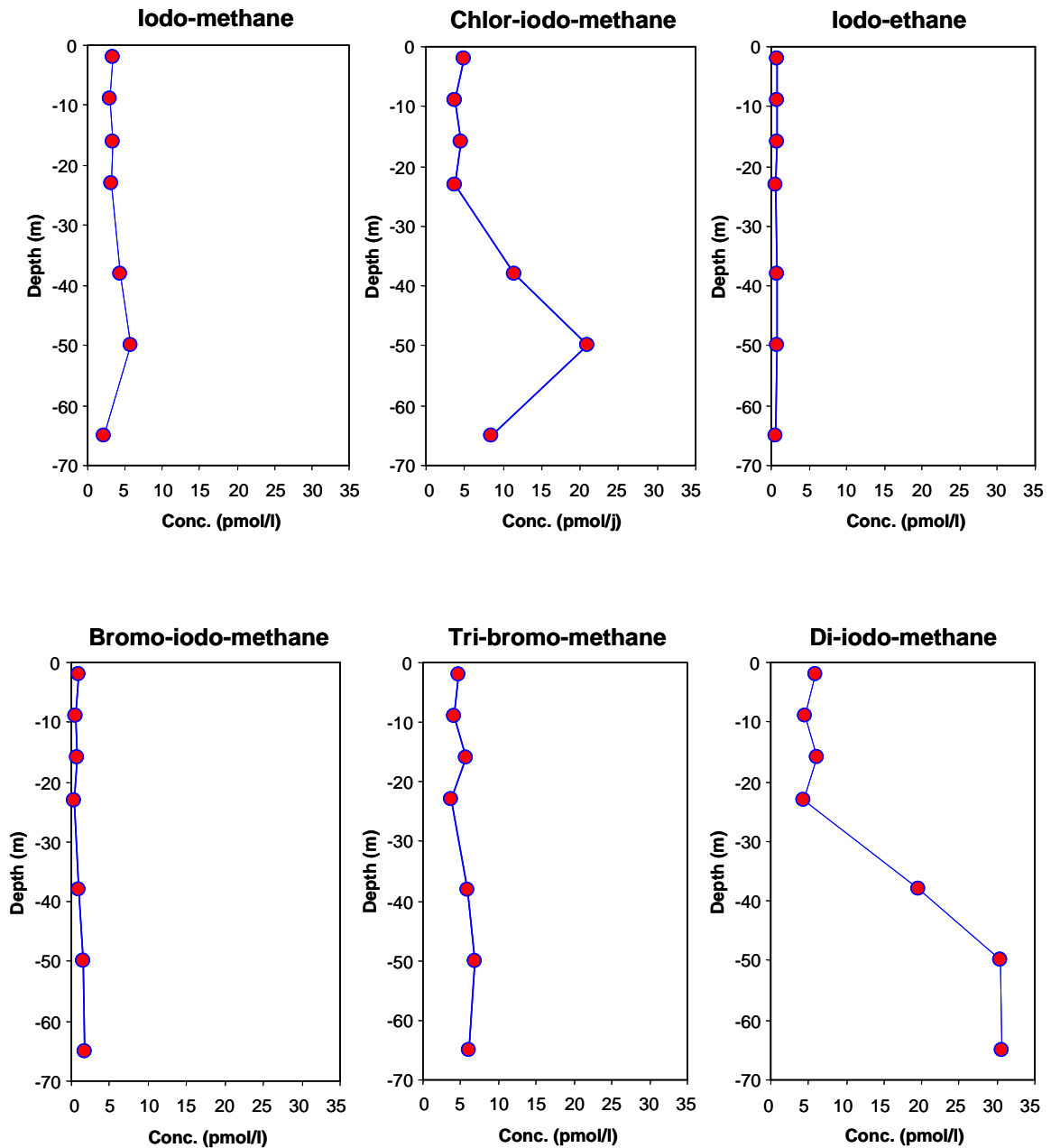


Figure 1: Relative abundance of six halo-carbon species presented as a mean from the analysis of four CTD casts during the four day station.

Figure 2 below shows the contrast between Station A and Station B for vertical profiles of halocarbon abundance. Two halo-carbon species are shown but the values must be treated with caution since final calibration checks need to be undertaken. All comparative plots are to the same scale.

D325 : STATIONS A and B : Vertical Profile Comparisons

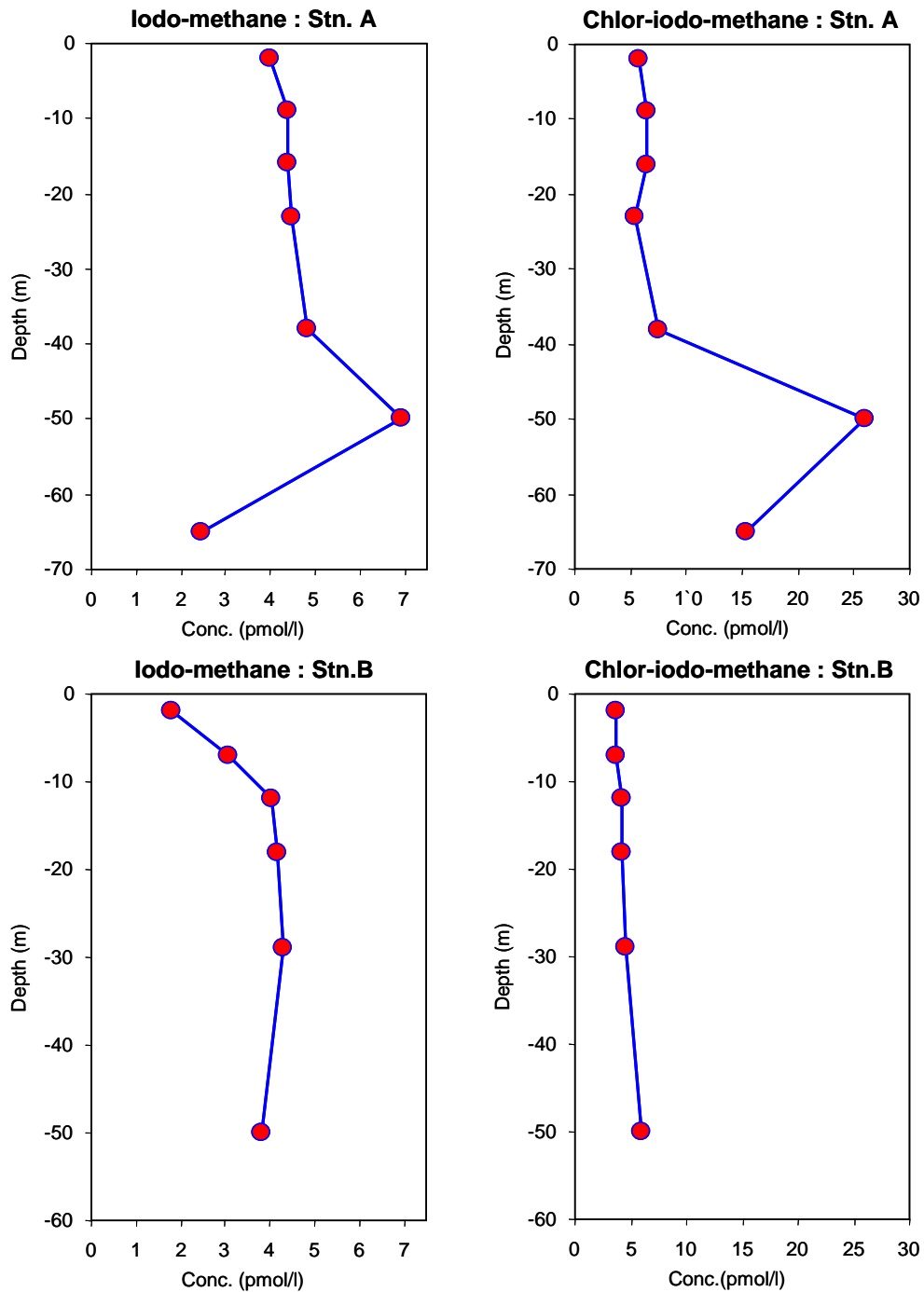


Figure 2: Relative abundance of two halo-carbon species at Stations A and B for a single CTD cast in each case.

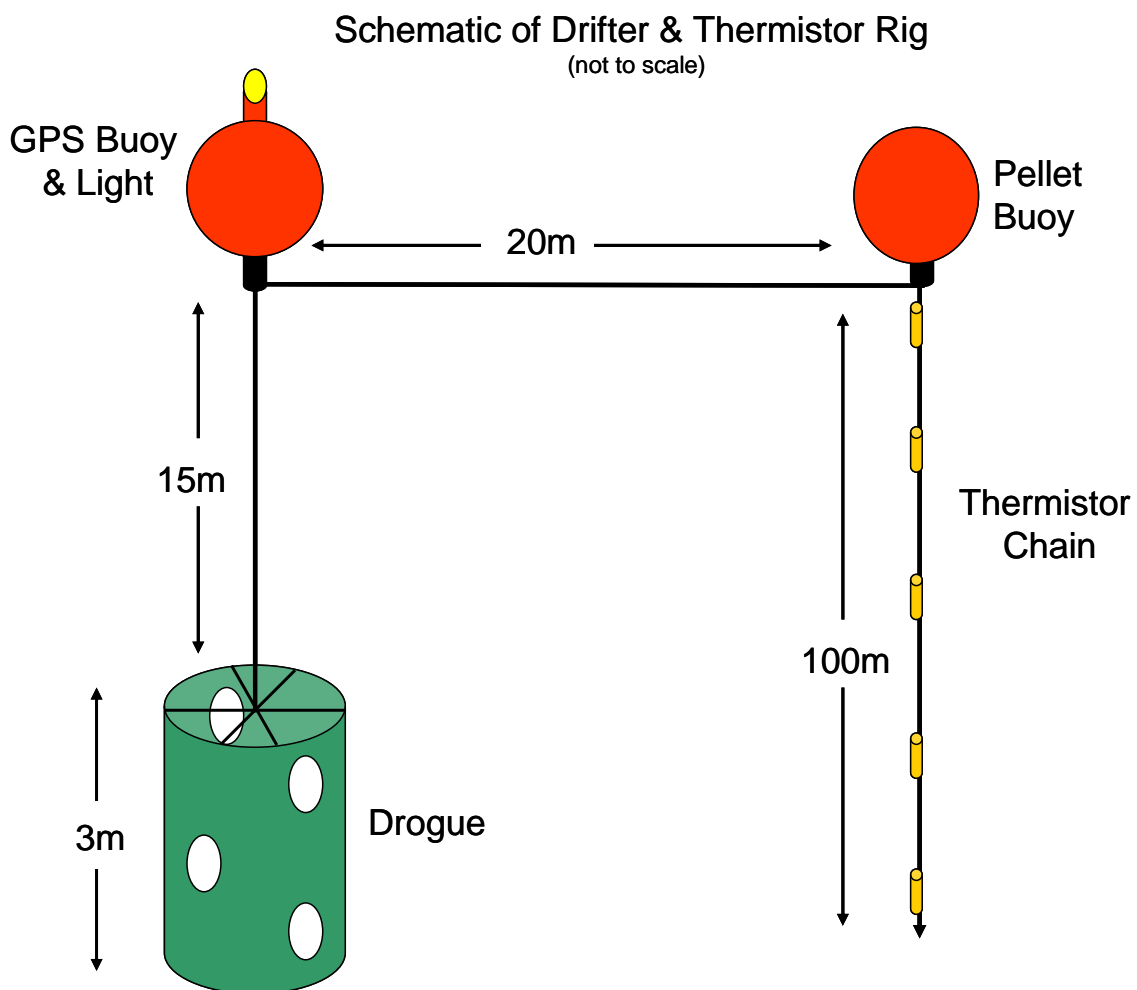
Drifter Deployments

A drifter buoy attached to a sub-surface drogue was deployed at the start of each station in an effort to maintain a close proximity to the water column being sampled during the four-days on station. The buoy sent GPS positions to a PC on the bridge every 5 minutes enabling the ship to track and plot its movements. The ship used hourly positions to determine the drifter tracks (Figs. 3 and 4).

At Station A, a thermistor chain was also attached to the drifter assembly with 10 thermistors at depths of 2, 8, 10, 12, 21, 32, 44, 51, 71 and 102m.

The nature of Station B precluded a drifter deployment due to the strong currents in the vicinity of Ilha de Sao Vicente, of the Cap Verde Islands and the need to maintain a geographic position upwind of the atmospheric sampling station situated on the island.

At Station C, a similar deployment to Station A was undertaken with attached thermistor chain with depths of 3, 8, 11, 15, 21, 31, 38, 45, 67 and 99m.



At Station D the sea state was quite rough (> force 6) and the drifter buoy stopped sending its position and was recovered. Once on deck it resumed sending a correct GPS position. It was concluded that the buoy was working correctly but that the continual submersion of the buoy in rough seas was preventing it picking up a satellite fix and thus not able to update the PC on the ship. When the sea state dropped the buoy was redeployed and several hours later it was determined that it had speeded up. On recovery at the end of the station the buoy was found floating high in the water and had parted company from the drogue and thermistor chain (which were subsequently considered lost). The shackle swivel which had attached the buoy to the drogue cable despite being suitably tightened and seized with a plastic cable tie had in the rough sea managed to come undone and part company from the buoy.

At Station E it was deemed too rough to deploy the drifter buoy, the rough sea state and weather exceeding force 6 which had previously swamped the buoy and prevented it from obtaining a satellite fix.

At Station F the drifter was deployed without a thermistor chain.

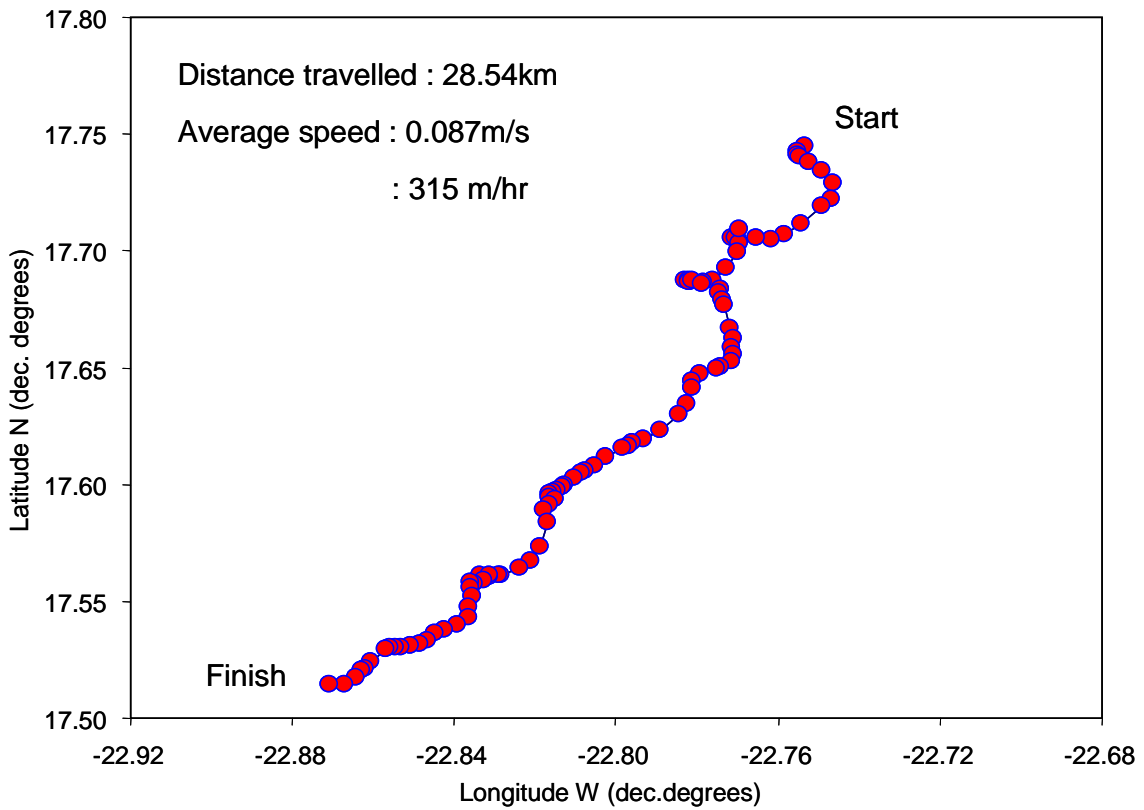
Summary deployment table for drifters :

Station	Event ID	Event	Notes
A	Drifter.001	Test deployment	No thermistor chain
A	Drifter.002	Station deployment	Thermistor Chain
C	Drifter.003	Station deployment	Thermistor Chain
D	Drifter.004	Station deployment	Thermistor Chain
D	Drifter.005	Station deployment	Thermistor Chain Lost
F	Drifter.006	Station deployment	No thermistor chain

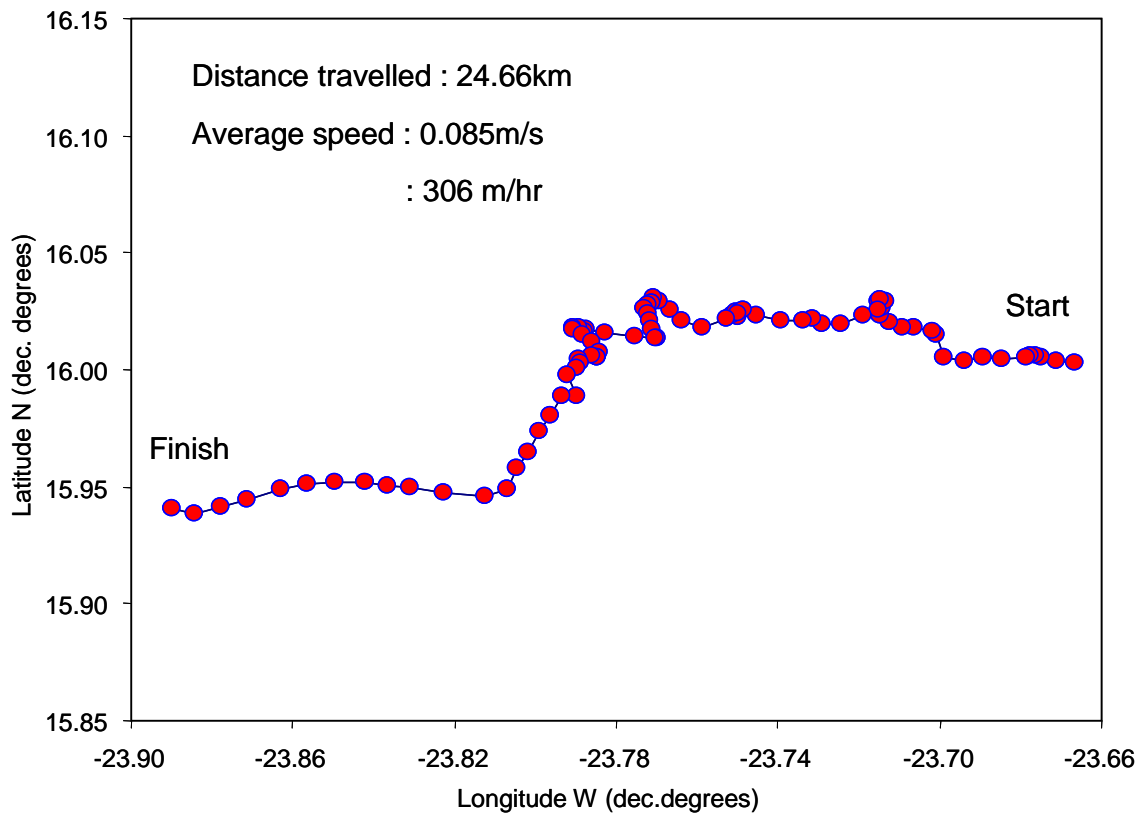
Table showing straight line distance travelled by drifters:-

Station	Deployment Latitude (N)	Deployment Longitude (W)	Recovery Latitude (N)	Recovery Longitude (W)	Distance travelled (km)	Average speed (m/hr)
A.002	17 44.700	22 45.200	17 30.841	22 52.247	28.541	315
C.003	16 00.182	23 39.976	15 56.450	23 53.387	24.664	306
D.005 (1)	17 43.030	22 59.930	17 48.520	23 01.026	16.136	529
D.005 (2)	17 48.520	23 01.026	17 48.310	23 15.504	24.728	1302
F.006	26 00.110	23 59.910	26 14.219	23 58.978	26.193	234

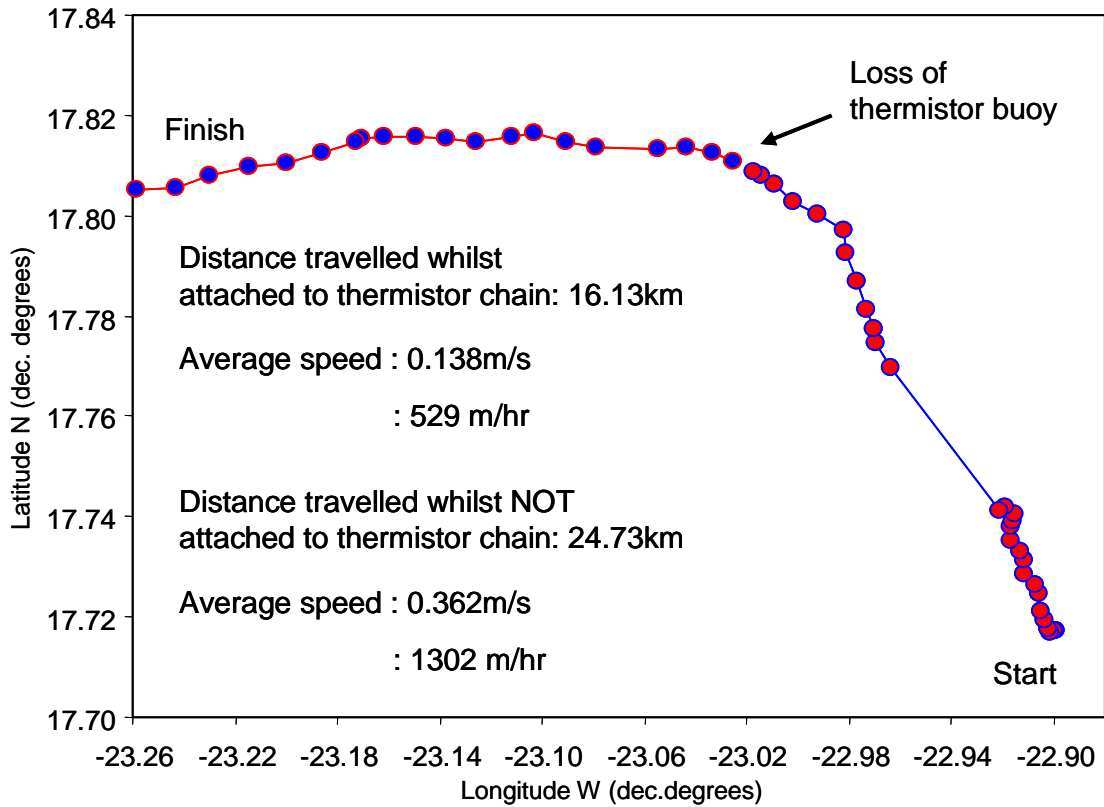
D325 Station A - Drifter Track : 16th - 20th Nov 2007



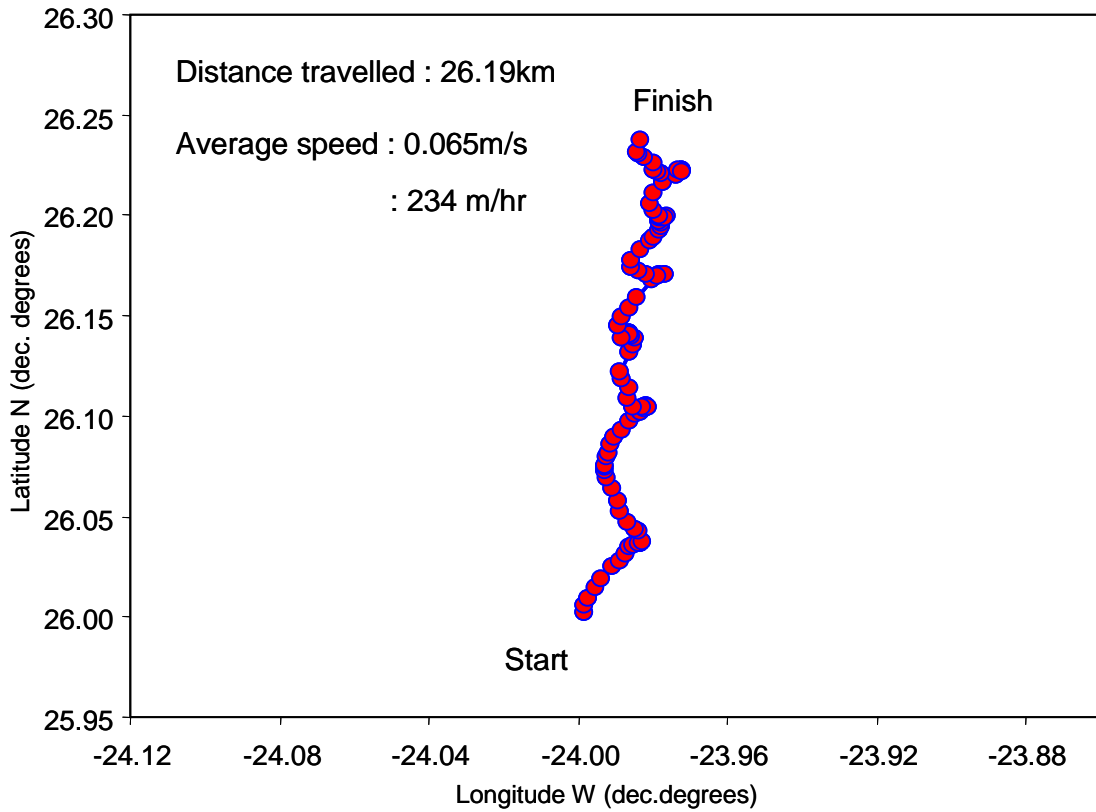
D325 Station C - Drifter Track : 28th Nov - 1st Dec 2007



D325 Station D - Drifter Track : 3rd - 5th Dec 2007



D325 Station F - Drifter Track : 11th – 15th Dec 2007



7.3. Iodocarbon production by biogenic marine aggregates

Claire Hughes

University of East Anglia

1. People involved:

Claire Hughes (UEA) Iodocarbon analysis and particulate organic carbon

Andy Rees/ Jo Dixon (PML) Bacterial heterotrophic production

Ruth Airs (PML) HPLC pigment determinations

2. Rationale:

We have previously shown that biogenic marine aggregates sampled in both temperate and polar areas are a source of iodocarbon compounds in seawater (Hughes *et al.*, 2008). In this study we examined whether aggregates collected from the tropical Atlantic are also a source of these compounds.

3. Methodology:

Sampling and experimental design

Sampling of the aggregates was carried out using Stand-alone pumps (SAPS). Details of each SAPS deployment are given in **Table 1**. The SAPS were fitted with 10 μm nylon mesh to concentrate particles greater than this diameter. After collection the SAPS material was also filtered across a 200 μm nylon mesh to remove any large zooplankton. Two SAPS deployments were carried out at each of the 6 sites. The first deployment was of a single pump which collected aggregates from the particle maximum, defined by examination of the CTD transmissiometer profile. The second deployment was of 4 pumps which sampled aggregates from within and below the mixed layer. Again the depths at which the 4 pumps were deployed were defined by CTD data. All incubations of SAPS material were performed in glass bottles held on roller tables in the dark.

Incubation 1 was carried out using material from the first (single) SAPS deployment and was designed to examine iodocarbon production over time. A seawater water sample collected from the same depth as the SAPS deployment (but with no particle concentration) was used as the control. These incubations were carried out over a period of 48 hours with samples generally taken at 0, 6, 12, 24 and 48 hours. Alongside the iodocarbon analyses, bacterial heterotrophic production was also carried out during the cruise. Samples were also collected for analysis after the cruise for particulate organic carbon, and HPLC determination of photosynthetic pigments and associated breakdown products.

Incubation 2 was carried out using material collected during the second (multiple) SAPS deployment and was designed to examine variations in iodocarbon production by aggregates from different depths in the water column. Samples for iodocarbon analysis, particulate organic carbon and HPLC pigments were taken at T=0 and T=24 hours.

Iodocarbon analysis

Iodocarbon analysis was carried out using an Agilent gas chromatograph-mass spectrometer (GC-MS) coupled to a Markes Unity thermal desorption unit (TDU) and

Ultra autosampler. The iodocarbons were extracted from seawater by purging with nitrogen gas at a flow rate of 95 ml min⁻¹. The compounds were then trapped and concentrated on 3-bed solid sorbents (tenax, carbograph and carboxen) held in stainless steel tubing. The sorbent tubes were held at 2 °C using a peltier-cooled aluminium block built at UEA during sampling to ensure effective trapping of the more volatile compounds (e.g. iodomethane). Following collection the samples were desorbed from the sample tubes using the Unity and Ultra system and introduced in to the GC column. An oven temperature programme was using to separate the iodocarbons which were then identified and quantified in the MS. The MS was operated in single-ion mode (SIM) throughout the campaign. Calibrations were carried out using liquid standards gravimetrically prepared in methanol prior to the cruise at UEA.

Table 1. Details of all stand-alone pump (SAPS) deployments carried out during RRS *Discovery* cruise D325 in the tropical Atlantic including sample site, date, SAPS event ID, position, SAPS depths sampled, total water depth and SAPS volume filtered. In the ‘depth/s sampled’ and ‘volume filtered’ columns the depths and volumes are given for SAPi, SAPii, SAPiii and SAPiv in the sequence they were deployed in the water column. SAPi is the pump deployed closest to the surface and SAPiv refers to the pump deployed the deepest. The low volumes filtered in SAPSE009 and SAPSF012(SAPii) were due to pump failures and not enough material was collected for incubations from these deployments.

Site	Date	SAPS event	Position	Depth/s sampled SAPi, SAPii (m)	Water depth (m)	Volume filtered SAPi, SAPii (L)
A	18/11/07	SAPSA001	17°41.44'N, 22°46.57'W	45	3403	746
A	20/11/07	SAPSA002	17°30.87'N, 22°52.49'W	20, 55, 60, 90	3403	2943, 2958, 2929, 3213
B	23/11/07	SAPSB003	16°53.35'N, 24°50.15'W	35	200	2688
B	24/11/07	SAPSB004	16°57.78'N, 24°49.66'W	20, 50, 70, 100	400	2786, 2747, 2916, 3215
C	28/11/07	SAPSC005	16°00.44'N, 23°41.07'W	65	3660	2950
C	29/11/07	SAPSC006	16°00.91'N, 23°42.80'W	18, 50, 65, 100	3660	2793, 2647, 2419, 2911
D	02/12/07	SAPSD007	17°41.53'N, 22°53.98'W	65	2669	2833
D	03/12/07	SAPSD008	17°41.40'N, 22°53.74'W	9, 23, 65, 100	3419	1927, 2861, 2734, 2837
E	07/12/07	SAPSE009	20°43.16'N, 24°58.51'W	80	4680	29
E	08/12/07	SAPSE010	20°48.35'N, 25°01.36'W	20, 50, 80, 120	4764	2853, 2887, 2588, 2500
F	12/12/07	SAPSF011	26°04.76'N, 23°59.60'W	100	5043	3090
F	13/12/07	SAPSF012	26°05.92'N, 23°59.74'W	20, 50, 100, 150	5045	3108, 3, 2962, 2446

References:

Hughes, C., G. Malin, C. M. Turley, B. J. Keely, P. D. Nightingale, and P. S. Liss. 2008. The production of volatile iodocarbons by biogenic marine aggregates. *Limnol. Oceanogr.* 53: 867-872.

7.4 Attempt to quantify biological oxidation of methyl iodide in oceanic waters.

Stephen Archer

Plymouth Marine Laboratory

Background

One potential loss process for volatile iodine containing compounds (VICs) in surface waters is biological metabolism. Stable isotope approaches have indicated rapid loss rates of CH_3Cl and CH_3Br attributed to biological activity occur in some oceanic waters and biological oxidation of radiolabelled CH_2Br_2 and CH_3Br have been measured in estuarine and coastal seawater. If such processes occur for VICs, they will impact on the surface concentrations and hence, air-sea flux of these compounds. In this case I've chosen to focus on methyl iodide (CH_3I); primarily because we know from previous studies that it is one of the main vectors of volatile iodine into the remote oceanic atmosphere and secondly, it is the most readily available radiolabelled VIC. The 'lagrangian' nature of the proposed study and the detailed analyses of *in situ* concentrations (see Stephens et al., this report) should allow the significance of biological removal to be assessed against known loss processes including air-sea flux and nucleophilic substitution.

Hypothesis: bacterial oxidation is the major loss process of CH_3I in ocean surface waters and so represents an important control on air-sea gas exchange of this VIC.

Method

Oxidation of radiolabelled $^{14}\text{CH}_3\text{I}$ was measured using modifications of approaches by Goodwin et al. (1998) and Kiene and Hoffmann Williams (1998). Seawater samples from near surface, 7 % light levels and/or chlorophyll maximum were incubated in glass syringes in the dark in an on-deck incubator, or in a temperature-controlled cool box. $^{14}\text{CH}_3\text{I}$ was added at nM concentrations in order to provide sufficient radioactivity to quantify oxidation rates. Produced $^{14}\text{CO}_2$ was captured by precipitation with SrCl_2 or following acidification, trapped on a NaOH-soaked wick.

Results

Preliminary analyses indicate bacterial oxidation rates of $^{14}\text{CH}_3\text{I}$ of 0.0005 to 0.0140 d^{-1} . Making several assumptions, this corresponds to approximately 0.001 and 0.05 $\text{pmol dm}^{-3} \text{d}^{-1}$ of ambient $^{12}\text{CH}_3\text{I}$ and equates to turnover rates of the ambient standing stocks of between 50 and >1000 days.

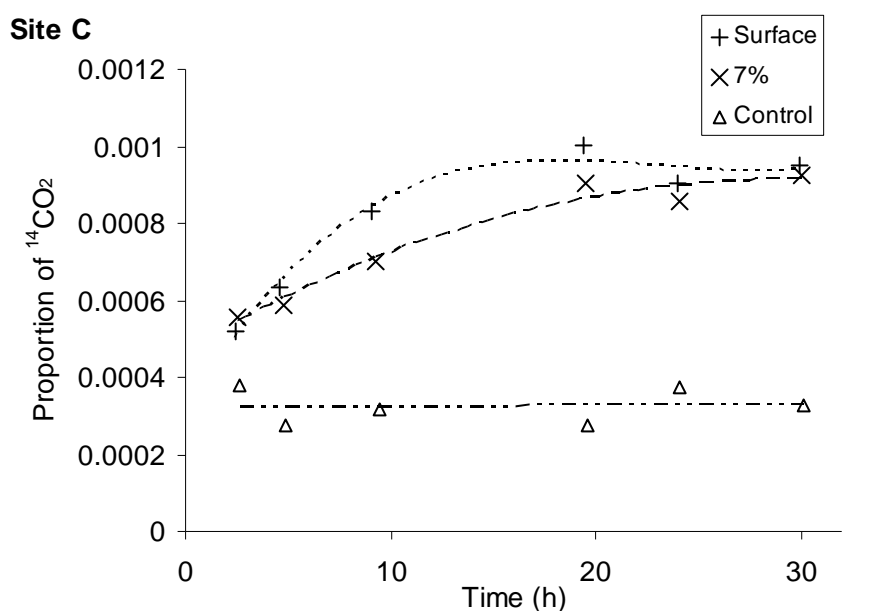


Figure 1. An example of the production of $^{14}\text{CO}_2$ from $^{14}\text{CH}_3\text{I}$, in seawater collected at Site C. Surface (97 %) and 7 % light levels were sampled. Rates were calculated from the steepest portion (i.e. 3 - 4 points) of the curves and corrected for control values.

A total of 19 experiments were carried out at the 6 sites. Not all experiments yielded results that could be interpreted; with method sensitivity a constant issue. However, I expect these are amongst the lowest oxidation rates of any compound measured in oceanic waters. They are approximately 2 to >20 fold lower than measured for CH₃Br in estuarine and coastal seawater (Goodwin et al. 1998).

My intention is to compare these rates to calculated air-sea flux and nucleophilic substitution rates for the same water in order to assess the significance of the biological removal of CH₃I. This could involve extrapolating the biological oxidation rates to the mixed layer depth, hopefully based on bacterial abundance and/or production (Dixon / Tarran, this report) and the measured ambient CH₃I concentrations (Stephens et al. this report). Combining the three loss processes may allow us to determine a 'semi-gross' production rate in the mixed layer. Hopefully we can back this up with the ¹³CH₃I data being generated by the GC-MS – incubation approach (see Goldson, this report).

Acknowledgements: Jo Dixon for helpful advice; Andy Rees for musical accompaniment; and NMF, Officers and Crew.

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7.5 Determination of Iodocarbon Production and Destruction Rates Using Stable Isotope Addition Experiments.

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Introduction

Iodocarbons possess multiple oceanic sources and sinks. Photochemical and biological iodocarbon production and removal have been observed with an additional chemical loss occurring through nucleophilic substitution with the chloride ion (Moore and Zafirou, 1994; Tokarczyk and Moore, 1994; Elliot and Rowland, 1993). While the level of understanding of these production/destruction pathways is improving, there is a need for quantification of the rates at which these processes occur in order to predict the impact of these climatically active gases. Here, stable isotope addition experiments were used to determine iodocarbon loss and production rates in Tropical Atlantic surface waters. The processes which were targeted in these studies were:

- 1) Rates of photochemical, biological and chemical loss of methyl iodide ($^{13}\text{CH}_3\text{I}$ addition).
- 2) Rates of photochemical, biological and chemical loss of diiodomethane ($^{13}\text{CH}_2\text{I}_2$ addition).
- 3) Rates of photochemical production of chloriodomethane as a photolysis product of diiodomethane ($^{13}\text{CH}_2\text{I}_2$ addition).
- 4) Rates of photochemical, biological and chemical loss of chloriodomethane (CD_2I addition).
- 5) Rates of methyl iodide production following methyl donor addition (^{13}C S-adenosyl methionine addition).

Methods

Seawater was sub-sampled into 2 L ground glass stoppered bottles from 10 or 20 litre steel sprung Niskin bottles on the CTD sampling rosette. The water was then transferred to a 1 L glass stoppered bottle (no headspace) and either $^{13}\text{CH}_3\text{I}$, $^{13}\text{CH}_2\text{I}_2$ or CD_2I was added with a gas tight syringe (Hamilton) at approximately 3-50 times the surface concentration. The process was repeated with 300 kDa filtered water (see S. Kimmance's report for filtration details). Following a 30 minute mixing period the labelled water was transferred into 100 ml glass stoppered bottles and foil wrapped for dark incubations or 100 ml quartz tubes for light incubations. Prior to addition, serial dilutions (primary and secondary) of the primary compounds were carried out in 60 ml of milli-q filtered water or, in the case of $^{13}\text{CH}_2\text{I}_2$, in methanol and then milli-q due to its low solubility. All incubations were carried out in on-deck incubators with flow through seawater. Forty ml aliquots of the incubated seawater were filtered through a GF/F filter (0.7 μm pore size, Fisher) into a 100 ml glass stripper. Seawater was purged for 20 minutes with high purity helium (Built in purifier (BIPTM)). Water vapour was removed with a NafionTM counter-flow (Perma-Pure, USA) drier and iodocarbons were cryogenically trapped in an unpacked steel loop at -150°C . Samples were desorbed at 100°C prior to injection onto a DB-VRX capillary column (60 m x 0.32 mm x 1.8 μm film thickness) and analysed on an Agilent 6890/5973 Network GC-MS with mass selective detector operating in selective ion monitoring mode

(SIM). During stripping, 40 pmol of CD₃I (99% CK Gas, UK) was injected from a 100 ul gas loop (10 ppb) into the helium flow upstream of the seawater sample to use as an internal standard). For calibration of the individual iodocarbons liquid standards of known concentrations were injected into pre-purged filtered seawater and analysed using the same method as the sample analysis.

The experiments which were carried out as well as the CTDs and sampling times are listed in Table 1.

Table 1: List of experiments with dates and sampling details.

25/11/07	D325_BO37 TIT surface	¹³ CH ₃ I whole seawater + filtrate; dark incubations
28/11/07	D325_BO39 TIT surface	¹³ CH ₃ I whole seawater + filtrate; dark incubations
29/11/07	D325_CO44 STS surface	¹³ CH ₃ I whole seawater + filtrate; dark incubations
12/12/07	D325_F105 STS surface	¹³ CH ₃ I whole seawater + filtrate; light and dark incubations
14/12/07	D325_F120 STS surface	¹³ CH ₃ I whole seawater + filtrate; light and dark incubations
30/11/07	D325_CO55 STS surface	¹³ CH ₂ I ₂ whole seawater + filtrate; light and dark incubations
02/12/07	D325_D062 STS surface	¹³ CH ₂ I ₂ whole seawater + filtrate; light and dark incubations
04/12/07	D325_D077 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
05/12/07	D325_080 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
07/12/07	D325_E084 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
08/12/07	D325_E089 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
10/12/07	D325_E102 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
13/12/07	D325_F120 STS surface	¹³ CH ₂ I ₂ + CD ₂ CII whole seawater + filtrate; light and dark incubations
8/12/07	D325_E089 STS 88 metres/chl-a max	¹³ C adenosyl methionine addition

Preliminary results

Rates of iodocarbon removal and production have yet to be calculated. Some incubations showed clear evidence of losses of methyl iodide in light and dark however, others were not so clear-cut. The inconsistencies between experiments requires further investigation and may be due to intermittent shading of the tanks. It is hoped that rates of photochemical, chemical and biological losses of ¹³CH₃I can be separated and determined. As in the case of the methyl iodide addition experiments there were some inconsistencies in the results of the ¹³CH₂I₂ and CD₂CII additions. However, in general, rapid destruction of ¹³CH₂I₂ was observed with a concurrent increase in ¹³CH₂CII (Figure 1). In addition, losses of CD₂CII were observed in the

filtered and whole seawater incubations in the light. Unfortunately there was no measurable incorporation of the ^{13}C methyl donor in any of the iodocarbons in the S-adenosyl methionine addition experiment.

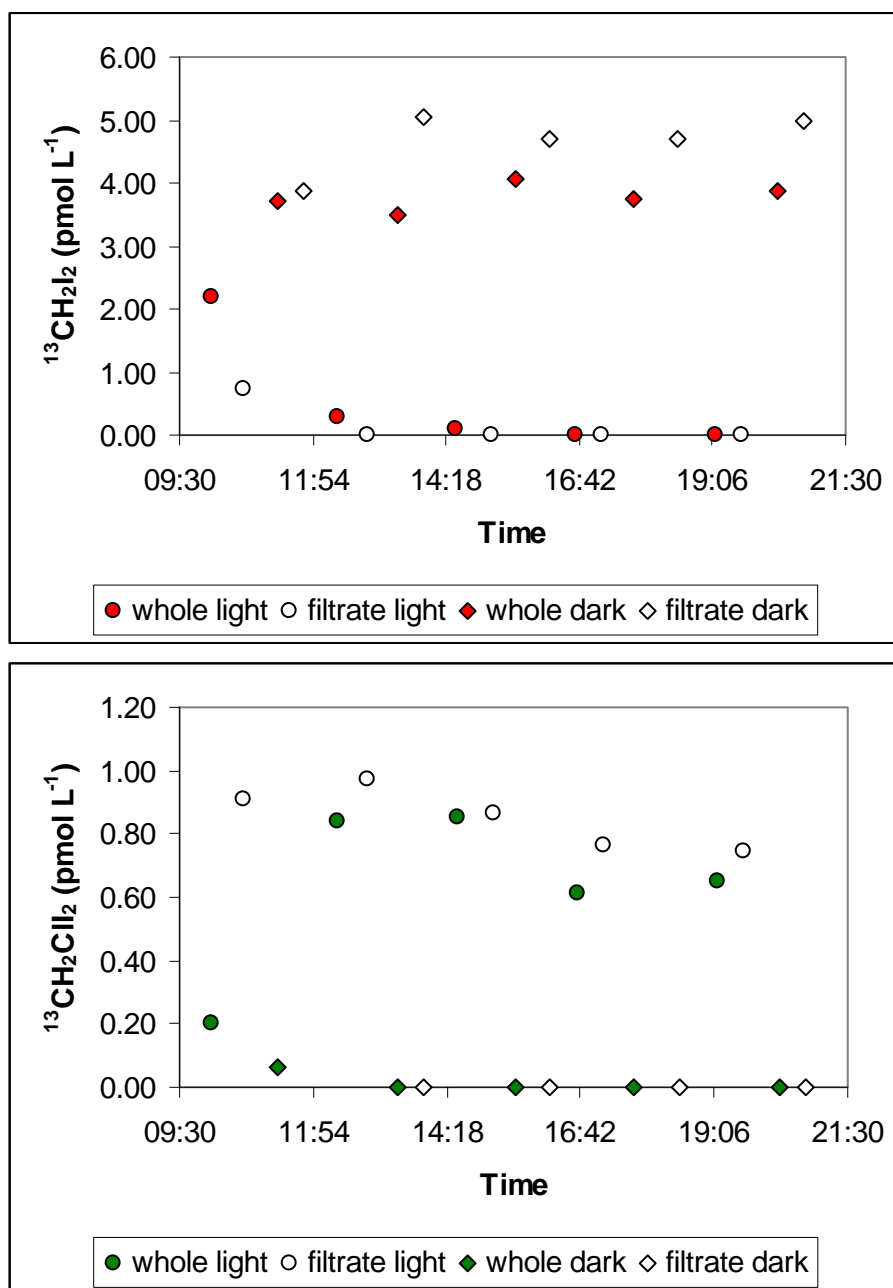


Figure 1: Concentrations of $^{13}\text{CH}_2\text{I}_2$ and $^{13}\text{CH}_2\text{ClI}_2$ over time in whole surface seawater and 300 kDa filtrate kept in on deck incubators in light and dark treatments (30/11/07).

Acknowledgements

Many thanks to the captain and crew of the *RRS Discovery*. Also thanks to the NMFers for CTD operations and technical support. In addition, thanks to Susan Kimmance for the daily supply of 300 kDa filtrate, to Gareth Lee and Claire Hughes for providing the liquid iodocarbon standards and to Janina Woeltjen for the loan of a column and column cutter.

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7.6 Photochemical and chemical production of iodocarbons

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Summary:

Our main task during the Inspire cruise was the investigation of photochemical production of iodocarbons in surface seawater. Photochemical production has previously been observed in shipboard incubation experiments carried out in the tropical Atlantic (Richter and Wallace, 2004). Our aims were to quantify production rates under varying levels of sunlight and to investigate the influence of dissolved organic matter concentrations on iodocarbon production in ocean surface water (photochemical production experiments).

We also investigated the production of iodocarbons via the reaction of molecular iodine with organic matter (molecular iodine addition experiments). This formation pathway might be important in the sea-surface, where molecular iodine is formed by the reaction of iodide with ozone (Garland and Curtis, 1981).

Additionally, we explored the effect on iodocarbon formation of increasing the iodide concentration of deep-seawater (by adding potassium iodide) to levels typical of tropical surface seawater.

To meet these aims, on-deck incubation experiments of 0.2 μm filtered and 200 μm filtered surface seawater under natural sunlight were performed during the cruise. Molecular iodine was added to some incubations of surface seawater and deep-seawater was incubated with added iodide. Changes in iodocarbon concentrations with time were measured and samples were taken for the determination of iodide, iodate, CDOM, DOC and flow cytometric measurements.

Experimental detail:

Water sampling

Seawater for the incubation experiments was collected at the beginning of each station using the CTD rosette, as detailed in table 1. For the photochemical production experiments and the molecular iodine addition experiments, surface seawater was taken from the predawn cast. For the iodide addition experiments, seawater from 450 m depth was taken from the solar noon cast. Prior to each incubation experiment starting, samples for coloured dissolved organic matter (CDOM) and dissolved organic carbon (DOC) determination were taken from the collected seawater. The CDOM samples were filtered through a 0.2 μm nylon filter and measured directly using a Perkin Elmer Lambda UV/VIS spectrometer. The DOC samples were filtered through a GF/F Whatman filter, acidified with HCl and stored at 4°C until analysis upon return to the UK.

Table 1:

Summary of seawater sampled from the stainless steel (STS) and the titanium (TIT) CTD for incubations of 200 um filtered (BIO) and 0.2 um filtered (NON-BIO) seawater, and 0.2 um filtered seawater spiked with molecular iodine (+ I₂) or iodide (+KI); time = Greenwich Mean Time

Event number	date	time	station	bottle no.	depth, m	latitude	longitude	purpose
D325_A_023TIT	19/11/07	05:20	A	21, 22, 23, 24	2	17°35.1750	22°48.6973	Bio, + I ₂
D325_A_027TIT	20/11/07	05:15	A	20	50	17°31.9624	22°51.21725	Bio, Non-Bio
D325_B_028TIT	22/11/07	05:30	B	23	2	16°53.80532	24°5033658	Bio, Non-Bio
D325_B_033TIT	23/11/07	14:10	B	24	2	16°53.38494	24°4993981	+ I ₂
D325_C-039TIT	28/11/07	06:30	C	10, 11, 12	2	16°00.35700	23°39.80542	Bio, Non-Bio, + I ₂
D325_D_062STS	12/02/07	08:25	D	24	2	17°40.06096	22°49.93969	Bio, Non-Bio, + I ₂
D325_D_079STS	12/04/07	14:15	D	1	450	17°47.59582	22°58.2454	+ KI
D325_E_084STS	12/07/07	05:45	E	23, 24	2	20°38.80354	24°57.3898	Bio, Non-Bio, + I ₂
D325_E_091STS	12/08/07	14:10	E	1, 2	450	20°56.05801	25°02.11703	+ KI
D325_F_105STS	12/12/07	05:45	F	24	2	26°02.6771	23°59.45642	Bio, Non-Bio, + I ₂

Photochemical production experiments

For the photochemical production experiments, part of the collected seawater was filtered through 200 μm nylon mesh to remove zooplankton and part of it was filtered through 0.2 μm nylon filter to remove all micro-organisms larger than 0.2 μm . The filtered and unfiltered seawater was distributed to 180 ml quartz and pyrex vessels and deployed in the dark and light incubators. The incubators were constantly flushed with seawater from the non-toxic supply in order to maintain sea surface temperatures during the experiments; the water depth was such that the incubation vessels were just covered, so as to imitate light conditions at the sea surface. Quartz tubes, which allow penetration of UV-light, were used for the light incubations, while the dark controls were contained in pyrex tubes wrapped in aluminium foil in a covered incubator.

At the first station (station A), two 12 hour test incubations were performed, with time points every 3 hours. The first incubation was performed with 200 μm filtered seawater to measure the overall production of iodocarbons. For the second incubation, both filtered and unfiltered seawater from the chlorophyll-a maximum (50 m depth at this station) was used, in order to investigate the influence of higher concentrations of organic matter. Neither experiment revealed significant iodocarbon production over the 12 hour period, so at subsequent stations, all incubations were performed for 72 hours or longer with time points every 24 hours. Therefore, one photochemical incubation experiment was performed per station. At station C, bacterial numbers were measured in filtered and unfiltered samples at each time point, using a Becton Dickinson Facsort Flow Cytometer following preservation with glutaraldehyde; this work was done by Dr. Glen Tarran (PML).

Molecular iodine addition experiments

For the molecular iodine (I_2) addition experiment, surface seawater was filtered through 0.2 μm nylon filters and spiked with I_2 to give an approximate end concentration of 100 nM I_2 . The I_2 spiking solution was prepared by adding approximately 0.1 g I_2 crystals to 20 ml of LC-MS grade water and leaving the mixture to equilibrate for 24 hours; the same solution was used in all experiments. The dissolved I_2 concentration in the spiking solution was measured spectrophotometrically (using the iodate method, see below) and found to be 240 ± 65 μM . Immediately after spiking, filtered seawater aliquots with and without I_2 were distributed to the quartz and pyrex tubes and placed in the light and dark incubators as for the photochemical incubation experiments described above.

At station A, one 12 h I_2 addition experiment with time points every three hours was performed. At station B, a 96 hour experiment with sampling points every 24 hours was performed to measure longer term formation of DOI and iodocarbons, this experiment began on day 2 of the station and lasted over the transit day and the port call in Cape Verde. At the remaining stations, the iodine addition experiments were combined with the main photochemical production experiments. This way, the same seawater could be used for all incubations and less incubation tubes were needed, as the photochemical incubations of 0.2 μm filtered seawater could act as the I_2 free controls in the I_2 addition experiment. Net iodocarbon production following I_2 addition was greater in the dark than the light incubations, presumably due to loss of photolabile species in the light. Therefore, at stations C and F, only dark incubations of I_2 spiked seawater were conducted. At station F, additional tubes containing seawater

spiked to give approximate I₂ concentrations of 20 nM and 50 nM I₂ were included in the incubation experiment.

Iodide addition experiments

For the iodide (+KI) addition experiments, seawater from 450 m depth, which is well documented to have lower iodide concentrations than surface water (e.g. Elderfield and Truesdale, 1980; Campos et al., 1996) was collected from the solar noon cast. (This water collection time was chosen to avoid collision with sampling points for the photochemical and I₂ addition experiments detailed above). Potassium iodide solution was added to the deep seawater to give a final iodide concentration of around 200 nM, which is equivalent to typical surface iodide concentrations in tropical waters (e.g. Elderfield and Truesdale, 1980; Campos et al., 1996). Deep seawater with and without the iodide spike was distributed to the quartz and pyrex tubes, and incubated in the dark and light, as for other experiments described in the preceding sections. Iodide addition experiments were performed at stations D and E. At station D, a 48 hour incubation was performed with time points at the beginning and the end of the experiment. At station E, a 72 hour incubation experiment, with time points at the beginning and after 48 and 72 hours of incubation, was performed. The iodide addition experiments were started on day 3 at station D and day 2 at station E, and continued over the transit days between stations.

Sample analysis

The parameters sampled for in each incubation experiment, at each station, are summarised in table 2. For each time point and each treatment during the incubations, duplicate sample tubes were taken out of the incubators and immediately analysed for iodocarbons. For this analysis, 40 ml sample from each tube was sub sampled into gastight 100 ml glass syringes and an internal standard of CD₃I and deuterated 2-iodopropane were injected. The iodocarbons were extracted using cryogenic liquid nitrogen purge and trap (Martino, 2006) and analysed with an Agilent Technologies gas chromatograph mass spectrometer (GC/MS). CH₃I, C₂H₅I, 2-iodopropane, 1-iodopropane, CH₂ClI, CH₂BrI, CH₂I₂ were measured quantitatively using halocarbon standards for calibration, CHCl₂I, CH₂ClI₂ and CHI₃ were measured qualitatively. All gas chromatographs on board were calibrated using the same halocarbon standards to achieve consistency between the different experiments. Additionally, water samples for iodate, iodide and dissolved organic iodine (DOI) were taken from selected experiments (see table 2). Samples for the determination of iodide and iodate were filtered through GF/F papers and stored at -20°C for return to the UK. Iodide will be determined using cathodic stripping square wave voltammetry (Luther et al., 1988; Campos, 1997) and iodate (strictly, all inorganic iodine present in oxidation states between 0 and +5, though this fraction is dominated by iodate) will be determined spectrophotometrically (Jickells et al., 1988). Samples for DOI were either applied to a solid phase extraction column, or filtered as above, and stored at 4°C for return to the UK. DOI will be investigated qualitatively using liquid chromatography-tandem mass spectrometry (LC-MS-MS) and, if a suitable method is available, total DOI may also be determined.

Table 2:

Summary of analytes sampled for during incubations of 200 μ m filtered (BIO) and 0.2 μ m filtered (NON-BIO) seawater, and 0.2 μ m filtered seawater spiked with molecular iodine (+ I₂) or iodide (+KI); experimental protocols given in the main text. V = volatile organic iodine; I = iodide & iodate; D = dissolved organic iodine (* = dark only); C = CDOM; O = dissolved organic carbon; F = flow cytometer samples.

station	expt	t0	t1	t2	t3	t4
A	BIO	V, O	V	V	V	
	NON-BIO	V, I, C	V	V	V	
	+ I ₂	V, I, D	V, D	V, D	V, D	
B	BIO	V, O	V	V	V	
	NON-BIO	V, I, C, D	V, I, D*	V, I, D*	V, I, D*	
	+ I ₂	V, I, D	V, D	V, D	V, D	V, D
C	BIO	V, I, O, F	V, I, F	V, I, F	V, I, F	
	NON-BIO	V, I, C, D, F	V, I, D*, F	V, I, D*, F	V, I, D*, F	
	+ I ₂	V, I, D	V, D*	V, D*	V, D*	
D	BIO	V, I, O	V, I	V, I	V, I	
	NON-BIO	V, I, C, D	V, I, D*	V, I, D*	V, I, D*	
	+ I ₂	V, I, D	V, D*	V, D*	V, D*	
	+ KI	V, I, O, C	V, I			
E	BIO	V, I, O	V, I	V, I	V, I	
	NON-BIO	V, I, C, D	V, I, D*	V, I, D*	V, I, D*	
	+ I ₂	V, I, D	V, I, D	V, I, D	V, I, D	
	+ KI	V, I, O, C, D	V, I, D	V, I, D		
F	BIO	V, I, O	V, I	V, I	V, I	
	NON-BIO	V, I, C	V, I	V, I	V, I	
	+ I ₂ conc 1	V, I	V, I	V, I	V, I	
	+ I ₂ conc 2	V, I	V, I	V, I	V, I	
	+ I ₂ conc 3	V, I	V, I	V, I	V, I	

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7.7 Iodine speciation in the surface ocean and lower atmosphere

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1. Summary

In order to compliment measurements of volatile organic iodine (VOI) compounds made during the INSPIRE cruise (D325), a variety of samples were collected for the determination of inorganic and dissolved organic iodine species. With the exception of a limited amount of on-board iodate analysis, all samples will be analysed upon return to the UK. Seawater samples were collected for the determination of iodide (I^-), iodate (IO_3^-), and, if a suitable method is available, total dissolved iodine. Additional seawater samples were applied to solid phase extraction (SPE) columns for subsequent investigation of dissolved organic iodine (DOI) speciation. Water and SPE samples were also taken from incubation experiments conducted by other members of the scientific party. Samples of marine aerosol were collected with the aim of investigating DOI speciation, and possibly also determining iodide and iodate concentrations. Starch coated glass denuder tubes were deployed for the measurement of molecular iodine (I_2) in marine air. Atmospheric ozone (O_3) was also measured continuously throughout the cruise.

2. Seawater sampling and incubation experiments

2.1. Inorganic iodine (iodide and iodate)

The main aims of investigating inorganic iodine speciation in seawater during the INSPIRE cruise were as follows:

1. To investigate whether there is a link between VOI production and iodide concentration, as suggested by Chuck et al. (2005).
2. To investigate whether there is a link between iodide levels and biological productivity, as has been debated in the literature (see Chance, 2007)
3. To investigate the possible photochemical interconversion of iodide and iodate, as demonstrated previously (Spokes and Liss, 1996).

Samples were collected from CTD casts and also from incubation experiments conducted in collaboration with other members of the scientific party. Photochemical incubation experiments were conducted with Janina Woeltjen (University of East Anglia) and are detailed in a separate cruise report. Samples were also taken from a marine aggregate time series experiment (Claire Hughes, University of East Anglia) and an atmospheric dust addition experiment (Jo Dixon/Andy Rees, Plymouth Marine Laboratory). The samples taken are summarised in table 1.

Table 1. Summary of water samples collected during cruise D325 for the determination of inorganic iodine species. BIO indicates an incubation experiment using 200 μ m filtered seawater, NON-BIO indicates an incubation experiment using 0.2 μ m filtered seawater and $\pm I_2$ indicates experiments using iodine spiked, 0.2 μ m filtered seawater.

Station	Description	Number of samples
A	Depth profile Diel cycle $\pm I_2$ incubation expts	8 depths from 450 m to surface 10 time points 2 x t0 samples
B	Depth profile $\pm I_2$ incubation expts NON-BIO incubation expts	7 depths from 80 m to surface 2 x t0 samples 7
C	Depth profile Diel cycle $\pm I_2$ incubation expts NON-BIO incubation expts BIO incubation expts	8 depths from 450m to surface surface and chl-a max, 12 time points 2 x t0 samples 7 7
D	Depth profile $\pm I_2$ incubation expts NON-BIO incubation expts BIO incubation expts Deep water KI addition	8 depths from 450m to surface 2 x t0 samples 7 7 4
E	Depth profile Diel cycle $\pm I_2$ incubation expts NON-BIO incubation expts BIO incubation expts Deep water KI addition	8 depths from 450m to surface 13 x surface water 7 7 7 10
F	Depth profile $\pm I_2$ incubation expts NON-BIO incubation expts BIO incubation expts Aggregate time series Dust addition expt	8 depths from 450m to surface x 3 conc.'s dark only 12 7 7 8 12

Samples were filtered through GF/F filters and stored frozen for transport back to the UK. Iodide will be determined using cathodic stripping square wave voltammetry (Luther et al., 1988; Campos, 1997), using an instrument at the University of East Anglia. Iodate will be determined by spectrophotometry (Jickells et al., 1988) using an instrument at the University of York. Some iodate analysis was conducted during the INSPIRE cruise, but due to poor instrument performance at sea, this was limited. Where measured, iodate depth profiles (figure 1) were consistent with other measurements of iodide/iodate in tropical waters (e.g. Campos et al., 1996).

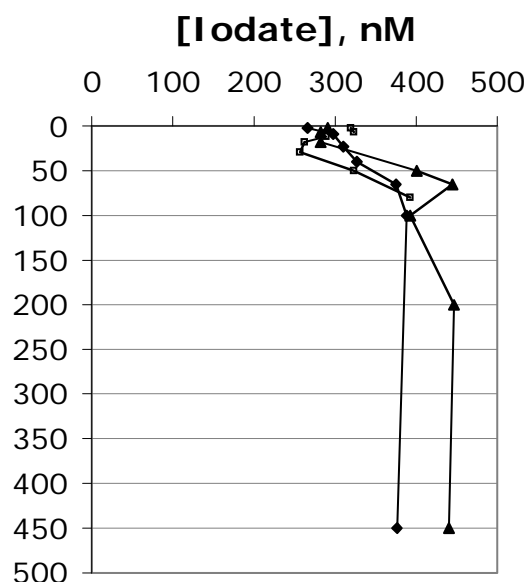


Figure 1. Variation in iodate concentration with water depth at stations A (◆), B (□) and C (▲) during cruise D325.

2.2. Dissolved organic iodine

A variable fraction of the dissolved iodine present in seawater is organic (Wong, 1991), but the nature of this material is unknown. In order to investigate the speciation of DOI, both in natural seawater and during experimental manipulations, samples were applied to reversed phase solid phase extraction (SPE) columns (Strata-X by Phenomenex). The columns were stored at 4°C for return to the UK. The columns will be eluted using a variety of solvents and the extracts analysed by liquid chromatography – tandem mass spectrometry (LC-MS-MS) at the University of York. The aim of this work is to obtain structural information about any DOI species present in sufficient amount to be analysed, and furthermore to obtain “DOI fingerprints” which will allow qualitative comparison of samples from different sources. Additional water samples were GF/F filtered and stored at 4°C for return to the UK, where they will be used for the determination of total dissolved iodine (and thus DOI by difference) if a suitable method is available. Aliquots of these water samples may also be desalted by dialysis and analysed for DOI by LC-MS-MS as above. The samples taken are summarised in table 2.

Table 2. Summary of samples collected during cruise D325 for the investigation of dissolved organic iodine speciation.

Station	Description	Sample number
A	Surface & Chl-a max ± I2 incubation expts aggregate t24	SPE x 2 SPE x 4 SPE x 1
B	Chl-a max ± I2 incubation expts aggregate t0 & t48	SPE x 2 & water sample x 1 SPE x 10 SPE x 2
C	surface and chl-a max ± I2 incubation expts aggregate t0 & t24	SPE x 4 & water sample x 2 SPE x 8 SPE x 2
D	surface and chl-a max x 2 ± I2 incubation expts aggregate t0 & t24	SPE x 4 SPE x 14 SPE x 2
E	surface and chl-a max ± I2 incubation deep water KI addition aggregate t48	SPE x 4 & water sample x 2 Water samples x 14 SPE x 10 SPE x 1 & water sample x 2
F	surface and chl-a max ± I2 surface & chl-a max blanks	SPE x 4 & water sample x 2 SPE x 4 & water sample x 2 SPE x 8

3. Atmospheric sampling

3.1. Atmospheric aerosol

Recent work has suggested that DOI might represent a significant fraction of the iodine present in marine aerosol (Baker, 2005). In order to investigate the nature of any such DOI, aerosol samples (non size-segregated) were taken using a high volume air sampler located on the monkey island (figure 2). Samples were collected onto pre-ashed glass fibre filters over periods of about 24 or 48 hours. As far as was practicable, the ship was kept head to wind in order to avoid contamination from the stack. When ship operations were likely to cause contamination (e.g. incineration events in low winds, lifeboat engine testing, ship manoeuvres) the sampler was turned off. A total of 24 samples (including blanks) were taken. It was noted that at station D there was a large amount of red dust on the filters, presumably due to a Saharan dust deposition event. One filter from this station was used in a dust addition experiment conducted by Jo Dixon and Andy Rees (Plymouth Marine Laboratory). All other filters were stored frozen for return to the UK. Samples will be extracted using a variety of solvents and the extracts analysed for DOI by LC-MS-MS as above. There may also be opportunities to determine iodide, iodate and total DOI in the aerosol extracts through collaborations with Alex Baker (University of East Anglia) and Ben Gilfedder (Heidelberg).

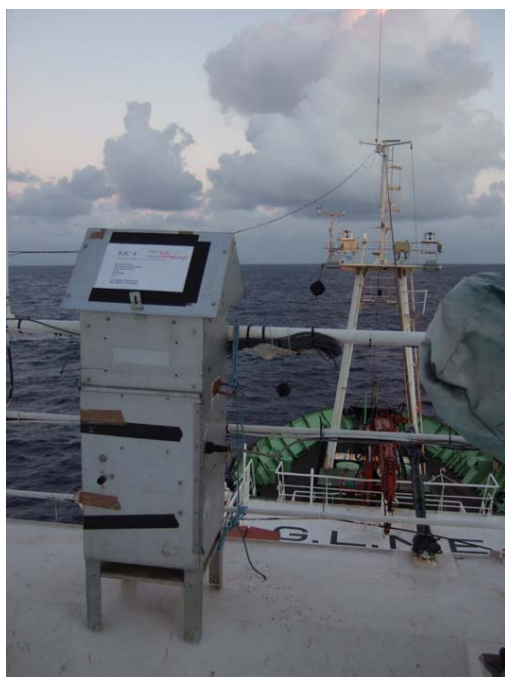


Figure 2. High volume aerosol sampler on monkey island of R.R.S. Discovery during cruise D325.

3.2. Molecular iodine

Molecular iodine (I_2) in air was sampled using starch coated, glass denuder tubes, after the method described by Hongwei (2005). The tubes were deployed on the monkey island (figure 3). Samples were taken for 12 hour periods or multiples thereof, with tubes being changed at dawn and/or dusk in order to differentiate between light and dark I_2 concentrations. The tubes will be returned to the UK as frozen stow. The tubes will be eluted with the solvent TMAH, and the iodine concentration of the eluate determined by ICP-MS using facilities at Central Science Laboratories (CSL), York.

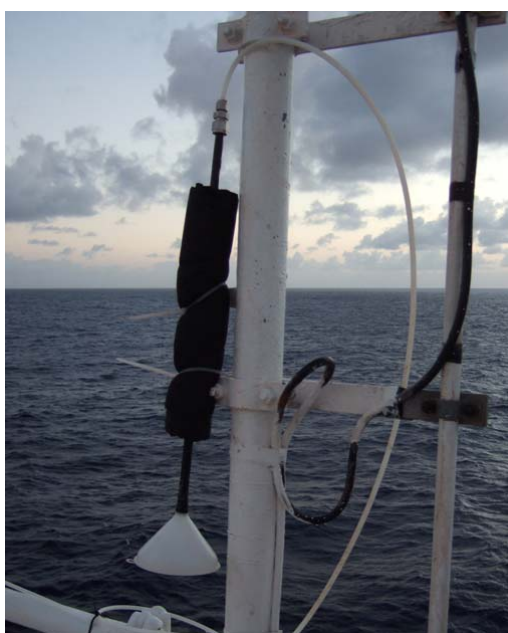


Figure 3. Denuder tube in sampling position on monkey deck of R.R.S. Discovery during cruise D325.

3.3. Ozone

An ozone (O₃) monitor ran continuously from 16/11/07 to 17/12/07, with hourly average ozone concentrations (ppbv) being logged. This data will be used by James Lee (University of York) for inter-comparison with ozone measurements made at the SOLAS Cape Verde Atmospheric Observatory.

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7.8 Phytoplankton photosynthesis and primary production in relation to iodocarbon production.

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OBJECTIVES.

91 photosynthesis – irradiance curves, 20 primary production measurements and 41 iodocarbon – irradiance experiments were made during D325 to assess whether there is a link between phytoplankton photosynthesis and iodocarbon production. To support these measurements, 185 samples were taken for the determination of phytoplankton pigments and 165 samples were taken to measure phytoplankton absorption coefficients. These measurements aim to fulfil the following objectives within the NERC SOLAS INSPIRE project:

- **Hypothesis 3:** biological iodocarbon production is the main source of iodocarbon compounds in surface seawater.
- **Hypothesis 4:** environmental factors play an important role in determining the biological iodocarbon production rate; **Light stress:** Exposure to excess light causes oxidative damage to the photosynthetic apparatus resulting in a decrease in photosynthetic efficiency.

METHODS. Water samples were taken from 20l niskin bottles on a stainless steel or titanium CTD rosette frame from at least 6 depths in the euphoic zone from 20 stations to measure the photo-physiology of phytoplankton. Coincident measurements of iodocarbons of CH₃I, C₂H₅I, CH₂ClI & CH₂I₂ were also conducted during the photosynthesis – irradiance experiments at 4 to 5 different irradiance levels.

Phytoplankton photosynthesis and primary production. 91 Photosynthesis-Irradiance experiments were conducted on seawater collected from 20 CTD casts (Table 1). Photosynthetrons illuminated by 50 W, 12 V tungsten halogen lamps (Plate 1) were used following the methods described in Tilstone *et al.* (2003). Each incubator houses 15 sub-samples in 60 ml polycarbonate bottles which were inoculated with between 185k Bq (5 μ Ci) and 370 kBq (10 μ Ci) of ¹⁴C labelled bicarbonate. The samples were maintained at *in situ* temperature using the ships non-toxic supply. After a 2 h incubation, the suspended material was filtered through 25 mm Whatman GF/F filters and the filters were exposed to concentrated HCl fumes for 12 h, then immersed in scintillation cocktail and ¹⁴C disintegration time per minute (DPM) was measured on board using the onboard Perkin Elmer 1414 liquid scintillation counter and the external standard and the channel ratio methods to correct for quenching. The broadband light-saturated Chla-specific rate of photosynthesis P_m^B [$\text{mg C (mg chl a)}^{-1} \text{ h}^{-1}$] and the light limited slope α^B [$\text{mg C (mg chl a)}^{-1} \text{ h}^{-1} (\mu\text{mol m}^{-2} \text{ s}^{-1})^{-1}$] were estimated by fitting the data to the model of Platt *et al.* (Platt *et al.*, 1980). The photosynthetically active radiation absorbed by phytoplankton [E_{PUR} ($\mu\text{mol m}^{-3} \text{ s}^{-1}$)] at each position in the incubator and for each sampling depth was estimated according to (Dubinsky, 1980). The maximum quantum yield of carbon fixation [ϕ_m mol C fixed (mol photons absorbed)⁻¹] will be determined by fitting the Chla-specific photosynthetic rates P_z^B [$\text{mg C (mg chl a)}^{-1} \text{ h}^{-1}$] to the photosynthetically available radiation absorbed by phytoplankton [E_{PUR} ($\mu\text{mol m}^{-3} \text{ s}^{-1}$)] following Figueiras *et al.* (Figueiras *et al.*, 1999). The daily integrated PP (mgCm^{-1})

$^2d^{-1}$) will be estimated using a bio-optical model which inputs E_{PUR} , Chla and spectral photosynthetic parameters calculated from measurements of the phytoplankton absorption coefficient ($a_{ph}(\lambda)$) and integrates primary production at minute by minute intervals, down to 0.1% irradiance depth following Tilstone *et al.* (Tilstone et al., 2003).



Plate 1. LEFT; Gareth Lee preparing a sample for the analysis of iodocarbons, RIGHT; Gavin Tilstone loading samples into the photosynthesizers to measure carbon fixation by phytoplankton.

Iodocarbon Determination.

Iodocarbon measurements were made on 41 photosynthesis-irradiance experiments. CH3I, C2H5I, CH2ClI, 1-IP, 2-IP & CH2I2 were determined at 4 to 5 light treatments during each experiment. Iodocarbon samples were taken from niskin bottles into 70ml polycarbonate bottles using dissolved gas sampling techniques. The samples were stored in the dark, at 17°C prior to analysis. Samples were trapped using a Markes ultra and unity tube desorption device and analysed on an Agilent 6890 GC with mass selective detector (GCMS). Iodocarbon compounds in the initial seawater were determined immediately and then sample bottles were placed in the photosynthesizers at 4 to 5 irradiance levels along the light gradient. Each sample was introduced into the photosynthesizer at 30 minute intervals and then incubated for 2 hrs. For Methyl Iodide (CH3I), a dual purge and trap system was used and then analysed immediately using a short GCMS method (GL1CH3I). The other compounds were stored at -20°C and analysed overnight using standard GCMS methods.

On deck incubations of ^{14}C uptake and iodocarbon production:

Two 24 hr experiments were conducted in an on deck incubation system (Plate 2) to determine the relationship between the uptake of ^{14}C and production of iodocarbons in the following size fractions to evaluate whether phytoplankton or bacteria are causing the release of these compounds:

- 1.) unfiltered seawater,
- 2.) 0.2 μ filtered seawater,

3.) unfiltered autoclaved seawater.

^{14}C uptake and iodocarbons were determined every 3 hrs for 24hrs, bottles or syringes both in the light and in the dark (sample vessels wrapped in foil; see Fig. 2). For ^{14}C uptake, three replicate bottles were used for each light and dark treatment.

Bench Top Fast Repetition Rate Fluorometer (FRRF).

The NMF fast repetition rate fluorometer was employed in bench top mode, to assess the variability in the photo-physiology of phytoplankton in parallel with the photosynthesis-irradiance curves at 2 stations (C_060 & E_103). The experiments were abandoned due to problems with the FRRF data in both light and dark channels.



Plate 2. On deck incubations for the coincident determination of ^{14}C uptake and iodocarbon production.

Phytoplankton pigments and phytoplankton absorption coefficients. Water samples from six or more depths at 24 stations were filtered onto GFF filters for the analysis of phytoplankton pigments by High Performance Liquid Chromatography (HPLC) using the methods described in Barlow et al. (1997), and particulate, phytoplankton and detrital absorption coefficients (aph) using the methods described in Tassan and Ferrari (1995) and Tilstone et al. (2004).

The Effect of UV on the absorption of Coloured Dissolved Organic Material (CDOM). Sea water was taken from the surface and Chla maximum at 2 stations to determine whether UV has an effect on CDOM. Unfiltered and $0.2\ \mu$ filtered water was placed in 1 litre quartz or glass flasks and exposed to the following treatments in an ‘on deck’ incubation system with different light filters: 1.) PAR only; 2.) PAR +

UVA; 3.) PAR + UVB + UVA. After 24 & 48 h incubations, replicate water samples were filtered through 0.2 μ filters for the analysis of absorption coefficient of coloured dissolved organic matter (CDOM) on the UEA Perkin Elmer lambda 25 spectrophotometer following the methods outlined in Tilstone et al. (2004). During the course of the experiments there appeared to be considerable baseline drift in the instrument, so only a limited number of experiments were conducted.

***Table 1.** Stations at which photosynthesis-irradiance curves, iodocarbons, bench top FRRF and CDOM measurements were made and phytoplankton pigments and absorption coefficient samples were taken.*

Station; CTD No.	Date	Time In water GMT	Lat	Long	depths (m)	Measurements taken†
SITE A						
A 001 STS	16 Nov	10:27	17° 45.38'N	22° 52.76'W	60	CDOM
A 006 TIT	17 Nov	05:40	17°42.6'N	22°43.3'W	2, 9, 16, 23, 48, 65	HPLC, aph
A 007 TIT	17 Nov	08:14	17°42.20'N	22°46.54'W	2*, 16*, 33 ^{†,□} , 43* ^{†,□} , 65 [†]	PE, Iodo*, HPLC [‡] , aph [□]
A 011 TIT	18 Nov	07:50	17°39.43'N	22°47.15'W	2, 48	CDOM UV
A 024 TIT	19 Nov	06:32	17°34.89'N	22°48.68'W	2, 9, 16	HPLC, aph
A 025 STS	19 Nov	08:05	17°34.60'N	22°44.00'W	2*, 16, 38, 55*, 65 ^{†,□} , 75* ^{†,□}	PE, Iodo*, HPLC [‡] , aph [□]
A 027 TIT	20 Nov	05:06	17°31.99'N	22°51.15'W	2, 9, 16, 23, 38, 50, 65	HPLC, aph
SITE B						
B 028 TIT	22 Nov	05:06	16°54.01'N	24°50.57'W	2, 7, 12, 18, 29, 50	HPLC, aph
B 029 TIT	22 Nov	08:05	16°53.56'N	24°49.80'W	2*, 7, 12, 30*, 51, 66 ^{†,□}	PE, Iodo*, HPLC [‡] , aph [□]
B 031 TIT	23 Nov	06:31	16°53.92'N	24°50.48'W	2, 7, 12, 18, 29, 45, 50	HPLC, aph
B 032 TIT	23 Nov	08:06	16°53.83'N	24°50.08'W	7, time series; 3, 6, 9 hrs.	PE, Iodo, HPLC, aph
B 034 TIT	24 Nov	05:18	16°53.84'N	24°50.16'W	2, 7, 12, 18, 29, 50	HPLC, aph
B 035 TIT	24 Nov	08:06	16°53.51'N	24°50.23'W	2*, 7, 18, 29*, 50, 65*	PE, Iodo*, HPLC, aph
SITE C						
C 039 TIT	28 Nov	07:20	16°00.37'N	23°39.79'W	2, 7, 12, 18, 29, 50	HPLC, aph

C 040 TIT	28 Nov	09:06	16°00.43'N	23°40.37'W	2, 12, 29, 44* ^{‡,□} , 50, 65 ^{‡,□}	PE, Iodo*, HPLC [‡] , aph [□]
C 042 STS	29 Nov	05:20	16°01.29'N	23°43.69'W	2, 9, 16, 23, 32, 39, 64	HPLC, aph
C 044 TIT	29 Nov	08:04	16°00.88'N	23°44.04'W	50 ^{‡,□}	PE; 3 replicates, HPLC [‡] , aph [□]
C 055 STS	30 Nov	05:40	16°01.27'N	23°46.43'W	2, 9, 16, 23, 32, 65	HPLC, aph
C 056 STS	30 Nov	08:10	16°08.95'N	23°47.06'W	2, 9, 23, 32, 50 ^{‡,□} , 65	PE, HPLC [‡] , aph [□]
C 058 STS	1 Dec	05:10	15°57.10'N	23°49.27'W	2, 9, 16, 23, 32, 64	HPLC
C 060 STS	1 Dec	08:45	15°57.97'N	23°50.83'W	2, 23, 45	PE, Iodo, FRRF, HPLC, aph
SITE	D					
D 062 STS	2 Dec	08:26	17°40.06'N	22°49.93'W	2 ^{a,*} , 9, 16, 23 ^a , 45 ^a , 56 ^{a,*} , 65 ^a , 80 ^{a,*}	PE ^a , Iodo*, HPLC, aph
D 064 TIT	3 Dec	05:30	17°42.36'N	22°53.59'W	2, 9, 18, 25, 41, 55, 70	HPLC, aph
D 066 TIT	3 Dec	08:06	17°42.77'N	22°53.95'W	2, 9, 25, 44, 55, 70	PE, HPLC, aph
D 077 STS	4 Dec	05:30?	17°45.08'N	22°56.33'W	2, 9, 18, 25, 41, 62, 70	HPLC, aph
D 078 STS	4 Dec	08:06	17°46.55'N	22°56.84'W	2*, 9, 25, 41, 58* ^{‡,□} , 63*	PE, Iodo*, HPLC [‡] , aph [□]
D 080 STS	5 Dec	05:40	17°48.62'N	23°07.37'W	2, 9, 18, 25, 41, 56, 70	HPLC, aph
D 081 STS	5 Dec	08:07	17°48.05'N	23°09.97'W	56	on deck incubations, EXP 1, 14C, Iodo, HPLC
D 081 STS	6 Dec		17°48.05'N	23°09.97'W	56	on deck incubations, EXP 2, 14C, Iodo, HPLC
SITE	E					
E 084 TIT	7 Dec	05:01	20°38.77'N	24°57.36'W	2, 23, 33, 55, 90, 95	HPLC, aph

E 085 TIT	7 Dec	08:07	20°52.49'N	25°00.96'W	2, 23, 55, 90, 95, 110 ^{†,□}	PE, HPLC [†] , aph [□]
E 087 STS	8 Dec	05:10	20°50.24'N	25°00.23'W	2, 33, 23, 75, 86	HPLC, aph
E 089 STS	8 Dec	09:02	20°52.49'N	25°00.96'W	2*, 33, 80, 88*, 100	PE, Iodo*, HPLC, aph
E 098 STS	9 Dec	05:00	21°05.97'N	24°02.33'W	2, 13, 23, 33, 55, 95	HPLC
E 102 STS	10 Dec	05:40	21°18.13'N	24°57.53'W	2, 13, 23, 33, 55, 95, 100	HPLC, aph
E 103 STS	10 Dec	08:05	21°18.88'N	24°57.08'W	50	PE, Iodo*, HPLC, aph, FRRF
SITE	F					
F 105 STS	12 Dec	05:05	25°02.52'N	23°59.40'W	2, 17, 31, 46, 75, 130	HPLC, aph
F 106 STS	12 Dec	08:09	26°02.94'N	23°59.69'W	2*, 46, 100 ^{†,□} , 130*, 150* ^{†,□} , 170 ^{†,□}	PE, Iodo*, HPLC [†] , aph [□]
F 109 TIT	13 Dec	05:30	26°06.66'N	23°59.46'W	2, 13, 24, 35, 58, 100	PE, Iodo, HPLC, aph
F 110 TIT	13 Dec	08:06	26°06.81'N	23°59.88'W	58	PE, Iodo, HPLC, aph
F 120 STS	14 Dec	05:02	26°10.06'N	23°59.69'W	2, 13, 24, 35, 58, 100, 115	HPLC, aph
F 121 STS	14 Dec	08:06	26°10.24'N	23°59.61'W	89	PE, Iodo, HPLC, aph
F 123 STS	15 Dec	05:03	26°13.11'N	23°59.09'W	2, 13, 24, 35, 58, 100, 115	HPLC, aph
F 124 STS	15 Dec	08:03	26°13.35'N	23°58.97'W	100	PE, Iodo, HPLC, aph

†PE – photosynthesis-irradiance experiments, Iodo* - iodocarbon measurements made on PE bottles, HPLC – phytoplankton pigments by High Performance Liquid Chromatography, aph – particulate, phytoplankton & detrital absorption coefficients, FRRF – bench top fast repetition rate fluorometer measurements, CDOM – absorption coefficient of coloured dissolved organic material, 14C - on deck incubations of carbon uptake, CDOM UV – CDOM analysis under different UV treatments.

Preliminary Results.

Maximum photosynthetic rates and primary production increased in surface waters from 1.4 mgC hr⁻¹ at Site A to 8 mgC hr⁻¹ at Site B (Fig 1 & 2). At both sites, CH3I increased with increasing irradiance, whereas there was no corresponding increase in C2H5I, CH2ClI & CH2I2. In contrast, maximum photosynthetic rates were 2.5 mgC hr⁻¹ at Site C, but there was no change in CH3I and the other iodocarbon compounds with increasing irradiance. At Sites D and E, the maximum photosynthetic rates decreased to 1 mgC hr⁻¹ and <0.8 mgC hr⁻¹ respectively, but iodocarbon concentrations were the highest of all sites and tended to increase with increasing irradiance with a sudden inhibition at high irradiance levels. At Site F photosynthetic rates were lowest of all the Sites (0.2 mgC hr⁻¹) and iodocarbon concentrations were relatively low, but comparable with Site C, which exhibited the second largest primary production (Fig. 1).

Using the empirical satellite primary production (PP) model of Behrenfeld et al. (1998) which estimates PP as a function of surface Chla values, PP was highest at Site B (>350 mgCm⁻²d⁻¹) and gradually decreased from Site B to F where it reached the lowest levels recorded (<130 mgCm⁻²d⁻¹; Fig 1). The photosynthesis-irradiance curves will be used in conjunction with the phytoplankton pigment HPLC samples and the light field of the water column, to calculate both in situ primary production and photosynthetic parameters to further assess whether there is a link between phytoplankton photosynthesis and iodocarbon production in the area, in relation to different chlorophyll a concentrations and phytoplankton groups.

Figure 1. Primary production at each site estimated from the model of Behrenfeld et al. (1998).

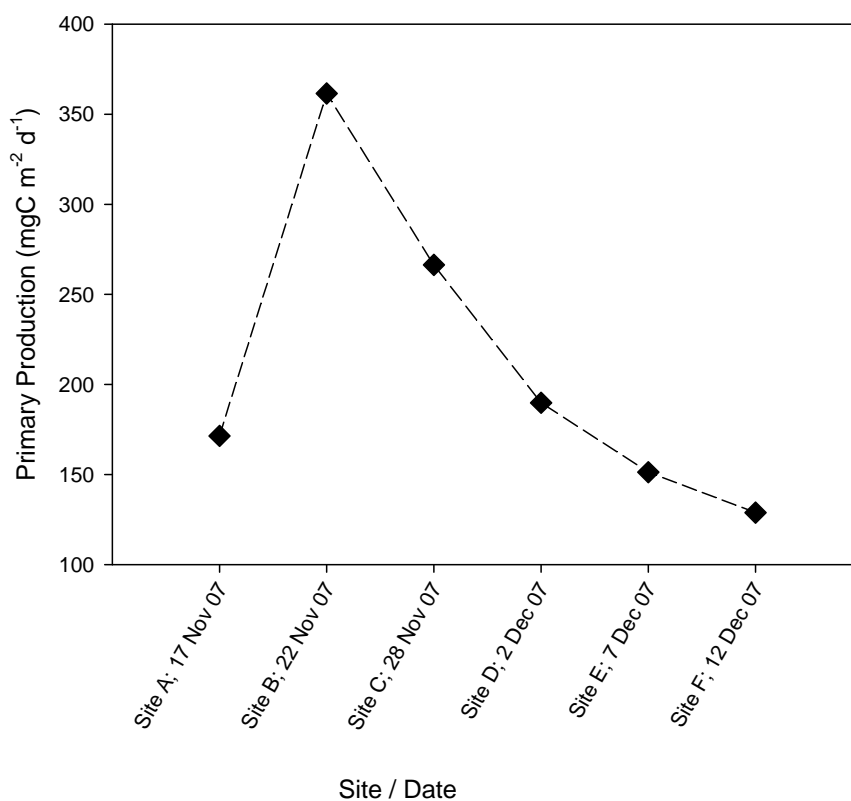
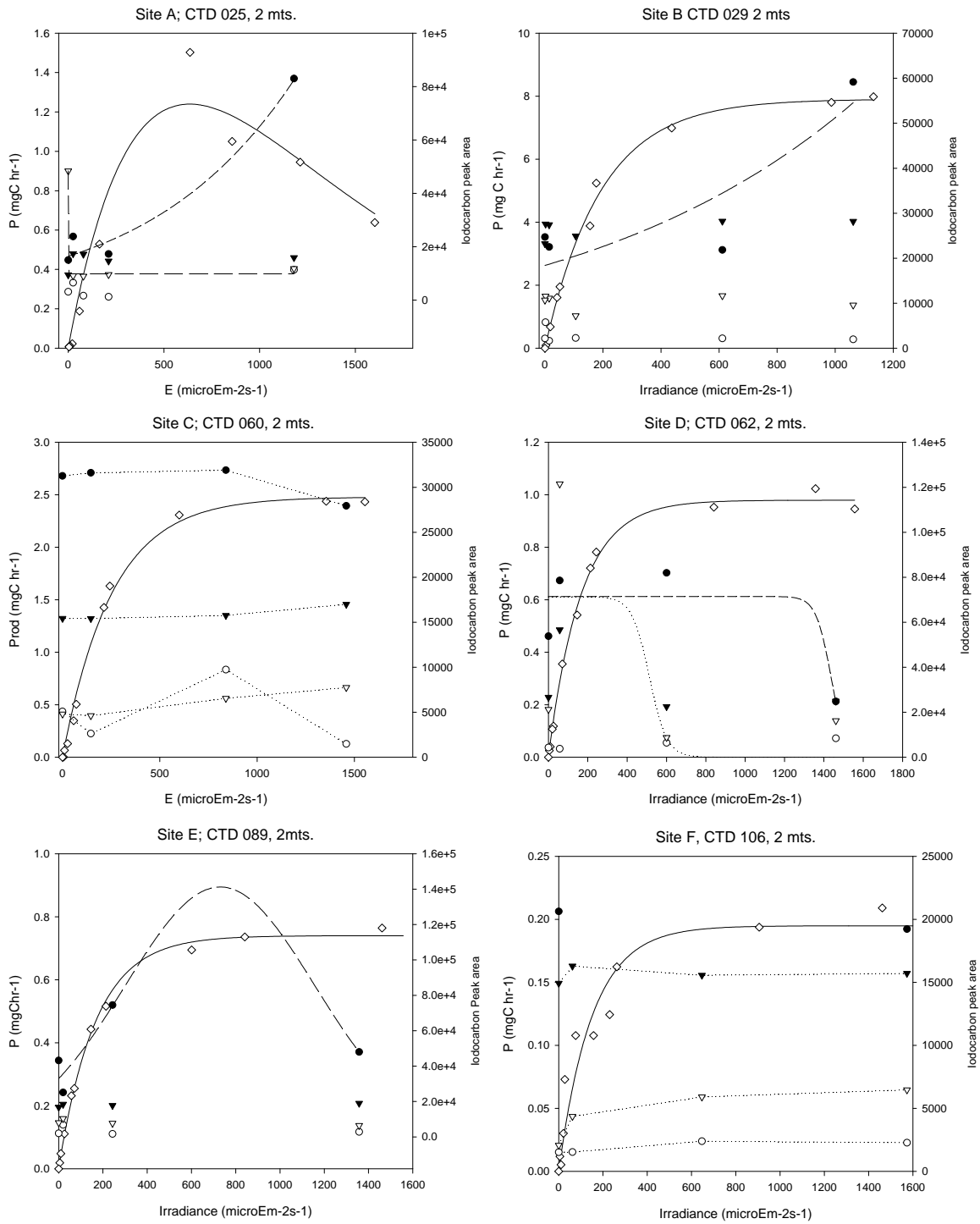


Figure 2. Photosynthesis-Irradiance curves in the surface waters at each site and corresponding iodocarbon concentrations. Open Diamonds & solid line – 14C production (mgC hr^{-1}); filled circles – CH3I (GCMS peak area); open circles – C2H5I; inverted filled circles – CH2CII; open inverted circles – CH2I2; dashed and dotted lines – trend in iodocarbon production.



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7.9 Quantifying microzooplankton grazing and viral-induced mortality rates of phytoplankton

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Lysis by viruses and grazing by protozoa represent two fundamentally different pathways by which carbon and nutrients may cycle within a food web. Viral lysis diverts primary production away from higher trophic levels as a result of completely transforming phytoplankton cells to DOM, cell fragments, and inorganic nutrients. This contrasts with the fate of primary production when cells are grazed. It has been estimated that $\geq 26\%$ of primary production may be channelled through the 'viral shunt' to DOM as a result of viral lysis of phytoplankton, bacterioplankton and grazers.

Grazing and viral lysis are two of the most important loss processes in terms of microbial food web functioning and the importance of these processes in relation to production and loss of iodocarbons is unclear at present. In the context of INSPIRE we aimed to determine rates of phytoplankton mortality as a result of these two loss processes in waters of varying productivity. By comparing these measurements with concentrations of iodocarbon compounds *in situ* we hoped to further understand the role that grazing and viral lysis may play in the flux of these compounds.

Methods:

A series of on-deck incubation experiments were conducted to:

1. quantify the mortality of phytoplankton cells through viral lysis compared to that of grazing using the modified dilution technique (Evans et al. 2003).
2. quantify algal virus and bacteriophage production rates using 2 methods: 1) viral dilution approach (Wilhelm et al. 2002) and 2) viral production estimated directly from distinct phytoplankton populations.

Modified dilution experiments:

To set up dilution incubations, fresh seawater collected at the 55 % light level (varied with site location; 9-13 m depth) was siphoned into clean 20 L polypropylene carboys through a 200 μm mesh, which removed large grazers. Two series of dilution incubations were set-up in parallel, one using diluent filtered through a 0.2 μm pore size filter and the second through a 300 kDa tangential flow system. The diluent and whole water were added to 4 L polycarbonate carboys in the correct proportions to create the t0 dilutions, i.e., 20, 40, 70 and 100 % whole water. These dilutions created a gradient of grazing and viral lysis pressure. Triplicate 500 ml polycarbonate bottles were filled from each t0 carboy and placed into the on-deck incubators with neutral density screening providing 55 % light. Sub-samples were taken from the t0 carboys for phytoplankton abundance (live, analytical flow cytometry, AFC), virus abundance (fixed, AFC). Samples for fixed viral analysis were preserved with glutaraldehyde (0.5% final concentration) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at -80°C. Sampling was repeated at t24 from the triplicate 500 ml polycarbonate bottles. Viral lysis rates, grazing rates, and phytoplankton growth rates, were determined from changes in phytoplankton abundance in the 500 ml experimental bottles between t0 and t24.

Viral productivity:

In addition to the virus measurements taken during the dilution incubations, a series of experiments were conducted to measure changes in viral productivity at the six different sites. Two

methods were used to determine viral production rates. For the first approach the rate of virus production was determined from the appearance of new viral particles after the dilution of the *in situ* viral community using flow cytometry. Water from the 55 % light level was collected from CTD casts and gently vacuum filtered through 47 mm diameter, 0.2 µm pore-size Supor membrane filters (Pall Gellman). During this process, the sample was kept mixed, while volume was maintained (>50 ml, final volume = 400 ml) by adding virus-free, ultrafiltered seawater (300 kDa). This resulted in viruses being diluted to ~10-20 % of the initial abundance. Samples (100 ml) of this virus-reduced retentate were placed in foil-wrapped 125 ml polycarbonate bottles (to exclude light) and incubated in the on-deck tanks at *in situ* temperatures. Sub-samples (2 ml) for viral enumeration, were collected every 2 h for 12 h and fixed with glutaraldehyde (0.5 % f.c.) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at -80°C, for analysis back at PML. Virus production rates will be determined from regressions of viral abundance vs. time for triplicate incubations.

The second method for estimating viral production rates was more phytoplankton specific in that, distinct populations of the most dominant phytoplankton groups (typically, *Synechococcus* spp., and *Prochlorococcus* spp.) were single-cell sorted and collected using flow cytometry. Triplicate incubations were set-up from the sorted populations and placed in the on-deck tanks; one set was dark-incubated (foil-wrapped) and one set was exposed to 55 % light. Sub-samples (2 ml) for production of viral particles over time were collected every 2 h for 12 h using the same protocol as above.

Preliminary results:

Preliminary data from the modified dilution experiments show that there were differences between stations for both phytoplankton growth rates and microzooplankton grazing rates. Phytoplankton growth rates were highest at the high productivity sites. However, grazing rates were highest at the mid-productivity sites. Unfortunately, results from the low productivity sites are difficult to interpret because the experiments did not work as well. This may be due to the difficulty of conducting dilution experiments in oligotrophic waters where grazer and phytoplankton cell numbers are low. Thus, small changes over a 24 hr period may be difficult to ascertain. Virus samples from the modified dilutions and viral productivity experiments are still to be analysed, so as yet we have no knowledge of the changes in viral productivity between stations. We expect fixed virus sample analysis to be completed by March 2008, after which point the variation between sites may become clearer.

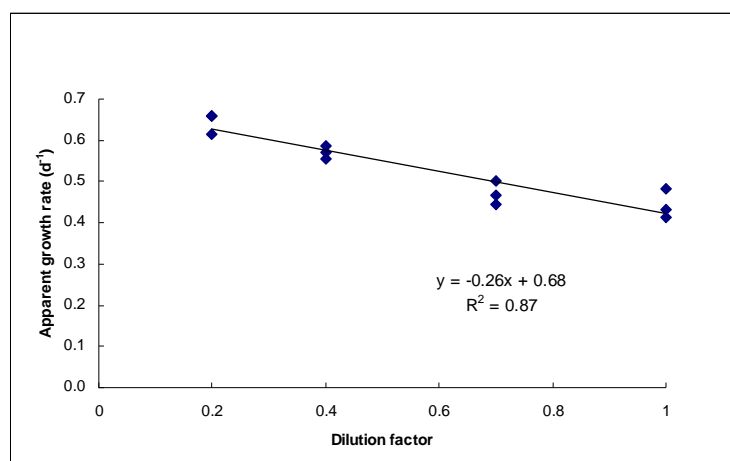


Figure shows an example of the data obtained from one of the modified dilution experiments. The graph shows that at Site C, on day 1, the apparent net growth rate of *Prochlorococcus* spp. was 0.68 (μ, d^{-1}) and that *Prochlorococcus* spp. were being grazed by microzooplankton at a rate of 0.26 (d^{-1}).

Table 1 summarises the CTD casts sampled and analyzed during the cruise; VPD = viral productivity dilution experiment; VPS = viral productivity sorting experiment.

DATE	CTD#	TIME (GMT)	DEPTHS SAMPLED	BOTTLE NOS.	PARAMETERS MEASURED
17/11/07	D325_A006	05:30	9m	18-21	Modified dilution 1: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates Viral production rates: VPS1
18/11/07	D325-A012 TIT	09:00	65m	13-18	Viral production rates: VPS2 and VPD1
19/11/07	D325-A023 TIT	05:00	60m	13-20	Modified dilution 2: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates
22/11/07	D325-A023 TIT	05:00	9m	4-9	Modified dilution 3: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates
23/11/07	D325-BO32 TIT	08:00	9m	13-22	Viral production rates: VPS3 and VPD2
24/11/07	D325-BO34 TIT	06:00	7m	1-8	Modified dilution 4: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates

25/11/07	D325-BO37 TIT	05:30	7m	23-26	Viral production rates: VPD3
28/11/07	D325-BO39 TIT	06:00	8, 200m	1-9	Modified dilution 5: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates
29/11/07	D325-CO44 STS	08:05	9m	3-6	Viral production rates: VPS4 and VPD4
30/11/07	D325-CO55STS	05:33	10m	11-16	Viral production rates: VPS5
30/11/07	D325-CO60STS	08:00	9m	5-10	Viral production rates: VPS6 and VPD5
03/12/07	D325-DO64STS	05:10	9m	20-21	Viral production rates: VPS7 and VPD6
04/12/07	D325-DO77STS	05:05	9m	19-21	Viral production rates: VPS8 and VPD7
05/12/07	D325-DO80STS	05:08	9m	20-21	Viral production rates: VPS9
07/12/07	D325-EO84STS	07:00	13m	18-21	Modified dilution 6: Phytoplankton growth rates Microzooplankton grazing rates Viral lysis rates
08/12/07	D325-EO89STS	09:47	13m	15-18	Viral production rates: VPS10 and VPD8
09/12/07	D325-EO98STS	05:00	13m	20-22	Viral production rates: VPS11

12/12/07	D325-F105STS	05:05	14m	18-21	Modified dilution 7: Phytoplankton growth rates Microzooplankton grazing rates Viral production rates: VPS12
13/12/07	D325-F120STS	05:00	13m	22-23	Viral production rates: VPD9
14/12/07	D325-F120STS	05:00	13m	19-21	Modified dilution 8: Phytoplankton growth rates Microzooplankton grazing rates Viral production rates: VPS13

Many thanks to the Captain, crew, and my scientific colleagues on Discovery (D325) for their help and for making this research cruise a very enjoyable experience.

7.10 Plankton community structure and grazing induced mortality using flow cytometry

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Objectives

- 1) To study differences in planktonic communities in oligotrophic, low production waters through to productive waters in the Eastern subtropical Atlantic Ocean using flow cytometric analysis of live samples from predawn CTD profiles for phytoplankton and preserved stained samples for bacteria. Data to provide context information for iodocarbon studies.
- 2) Develop and test novel techniques to determine mortality of specific plankton groups through grazing by serially saturating seawater samples with surrogate prey (beads) and measuring grazing/growth in time course experiments with Stephen Archer and Susan Kimmance.
- 3) Test utility of saturation experiments mentioned above for analysing production of iodocarbons through grazing with Steve Archer, Denise Cummings, Amanda Beesley and John Stephens.
- 4) Analyse samples from established dilution grazing experiments to determine autotrophic picoplankton abundance; with Susan Kimmance and Stephen Archer. (See Susan's cruise report for details).

Methods and initial findings

1) Plankton abundance from CTDs

Fresh seawater samples were collected from CTD casts in clean 250 mL polycarbonate bottles from a Seabird CTD system containing, either 24 x 10 L Trace Metal Niskin bottles or 24 x 20L Niskin bottles. Samples were stored in a refrigerator until analysed (less than 1 hour). 3 mL samples were used for immediate flow cytometric analysis to characterise and enumerate prochlorophytes, cyanobacteria, pico-eukaryotes and nanophytoplankton based on their light scattering and fluorescence properties. The flow cytometer used was a Becton Dickinson FACSort instrument. Of the 3 mL, approx 1.5 mL of sample was actually analysed to provide vertical profiles of phytoplankton abundance per millilitre, at the 6 depths used for incubation experiments (1, 7, 20, 33, 55 and 97% of incident light), plus the chlorophyll maximum. Samples from the same depths were also preserved immediately for bacterial abundance analysis after 30 min fixation with 0.5% glutaraldehyde (final concentration) at 4°C and 1 hour staining at room temperature with a mixture of Sybr Green I DNA stain and potassium citrate buffer. Table 1 summarises the CTD casts sampled and analysed during the cruise.

Table 1: CTD casts sampled for plankton community structure

DATE	JULIAN DAY	TIME ON DECK (GMT)	SITE	SITE PROD'N	CTD CAST	LAT N	LON W	DEPTH RANGE SAMPLED
17 Nov	321	05:58	A	Medium	D325_A006STS	17.71	22.75	2 - 65 m
17 Nov	321	14:47	A		D325_A008STS	17.69	22.78	2 - 65 m
19 Nov	323	06:32	A		D325_A024TIT	17.58	22.81	2 - 65 m
20 Nov	324	05:44	A		D325_A027TIT	17.58	22.81	2 - 65 m
22 Nov	326	05:44	B	High	D325_B028TIT	16.89	24.84	2 - 50 m
23 Nov	327	05:59	B		D325_B031TIT	16.90	24.84	2 - 50 m
24 Nov	328	06:04	B		D325_B034TIT	16.89	24.84	2 - 50 m
25 Nov	329	05:49	B		D325_B037TIT	16.90	24.84	2 - 50 m
28 Nov	332	07:11	C	High	D325_C039TIT	16.01	23.66	2 - 50 m
29 Nov	333	05:53	C		D325_C042STS	16.02	23.73	2 - 64 m
30 Nov	334	05:32	C		D325_C055STS	16.02	23.77	2 - 64 m
01 Dec	335	05:36	C		D325_C058STS	15.95	23.82	2 - 64 m
02 Dec	336	09:11	D	Medium	D325_D062STS	17.67	22.83	2 - 65 m
03 Dec	337	05:50	D		D325_D064STS	17.70	22.89	2 - 70 m
04 Dec	338	05:40	D		D325_D077STS	17.75	22.94	2 - 70 m
05 Dec	339	05:45	D		D325_D080STS	17.81	23.12	2 - 70 m
07 Dec	341	05:46	E	Low	D325_E084STS	20.65	24.96	2 - 95 m
08 Dec	342	05:43	E		D325_E087STS	20.84	25.00	2 - 95 m
09 Dec	343	05:44	E		D325_E098STS	21.10	25.14	2 - 95 m
10 Dec	344	05:43	E		D325_E102STS	21.30	25.96	2 - 100m
12 Dec	346	0.24375	F	Low	D325_F105STS	26.04	23.99	2 - 130 m
13-Dec	347	0.238889	F		D325_F108STS	26.11	23.99	2 - 108 m
14-Dec	348	0.238194	F		D325_F120STS	26.17	23.99	2 - 115 m
15-Dec	349	0.247917	F		D325_F123STS	26.22	23.98	2 - 112 m

Data for CTD profiles will be available after the cruise.

2) Bead saturation experiments

The rationale behind these experiments is that the established method for measuring grazing using a dilution approach to dilute natural seawater to uncouple grazing from phytoplankton growth involves filtering large volumes of water which, because of the filtration process are likely to contain enhanced nutrients and other dissolved compounds. This means that if one wants to study production of compounds such as iodocarbons then there is the probability that the experimental setup itself will contribute to production of the compounds which are the subject of study. Therefore it is desirable to find an alternative method involving as little manipulation of the seawater to be studied as possible. During the cruise we have been developing and testing an approach which involves the addition of beads at different concentrations to act as prey for grazers. As the bead concentration increases, the grazers are saturated with bead 'prey' and don't come into contact (and therefore eat) as many phytoplankton prey, thus allowing the phytoplankton to grow. Figure 1 provides an overview of the expected results when cell populations are quantified at the beginning and end of a time course experiment. There were several questions inherent with trying to use this approach: Will grazers ingest the beads (are they selective)? Are the beads toxic to prey/grazers? Do the saturation levels chosen actually saturate grazing? Do beads contain iodocarbons?

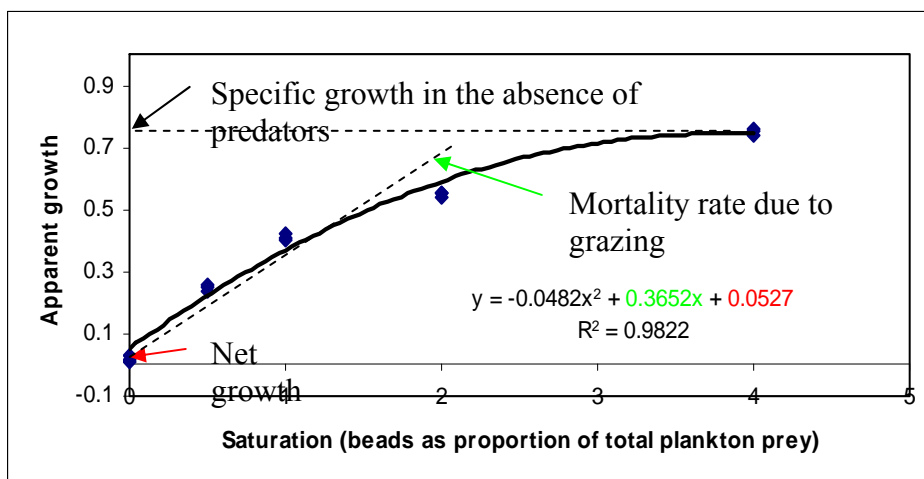


Figure 1: Theoretical results from saturation grazing experiment using beads as surrogate prey: phytoplankton growth/mortality

To begin with, an initial experiment was set up using 0.5, 2 and 6 μm beads to mimic bacteria, picophytoplankton and nanophytoplankton prey. 5 x 1 L acid rinsed polycarbonate bottles were filled to the neck (approx. 1.25 L) with seawater from the 55% light depth from the solar noon (1340 GMT) CTD. 1 bottle acted as a control, with no beads added. The other 4 bottles had beads added according to the abundance estimates for plankton from the predawn CTD analysed on the same day. 1 bottle had beads added at 50% of ambient prey concentrations (0.5 saturation), a second bottle had beads added at the same concentration as ambient prey concentrations (1 saturation) and so on for 2 and 4 saturation levels. Triplicate samples were taken from each bottle for immediate analysis of pico- and nanophytoplankton by flow cytometry and for fixation and Sybr Green I staining to quantify bacteria. Once the samples had been taken the experimental bottles were placed in an on-deck incubator with non-toxic seawater from 6.5 m running through and a 55% light screen on top. Bottles were incubated for a total of 24 hours. During the hours of darkness a cover was placed over the incubator to prevent any influence from the ship's lights. After 24 h, samples were again analysed to quantify pico- and nanophytoplankton and bacteria and grazing/growth rates calculated for *Synechococcus* sp., *Prochlorococcus* sp., picoeukaryotes, nanoeukaryotes, high nucleic acid (HNA)-containing bacteria and low nucleic acid (LNA)-containing bacteria. Results were promising, particularly for the *Synechococcus* and *Prochlorococcus*.

As the cruise progressed, the experimental design was modified:

- increasing the number of experimental bottles to provide duplicates,
- using only 0.6 μm beads (doublets, triplets etc. probably acted as larger prey),
- diluting the beads in seawater before adding them to experimental bottles to improve accuracy of beads added (small pipetting volumes led to variable bead concentrations in bottles),
- not analysing for nanoeukaryotes as they were not abundant enough to provide statistically reliable numbers,
- analysis of preserved samples to quantify heterotrophic grazers using Sybr Green I DNA stain.

Once the experimental design had been modified and finalised we began to analyse samples from the experimental bottles to quantify iodocarbons. In theory, if grazing is a factor contributing to the production of iodocarbons then there should be a

reduction in the concentration of iodocarbons as the bead saturation increases as shown in figure 2 below.

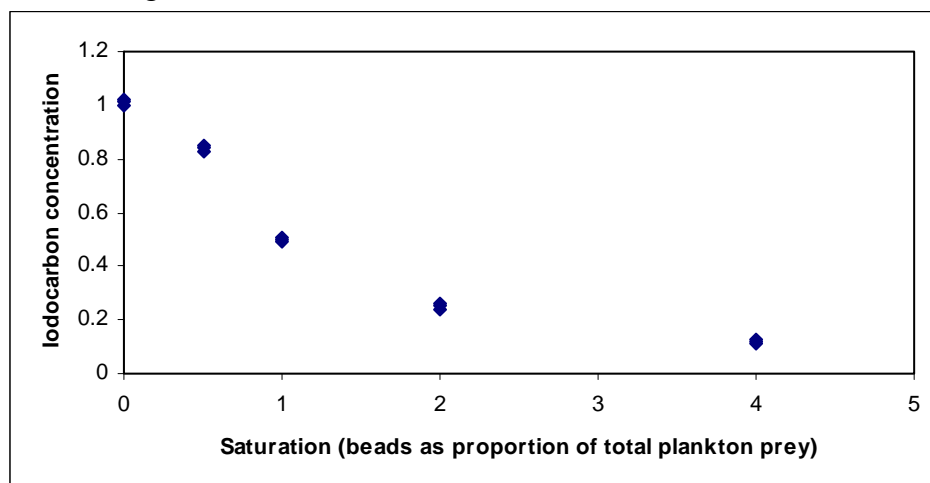


Figure 3: Theoretical results from saturation grazing experiment: : iodocarbon production

With the last 5 experiments, samples were also taken for the analysis of iodocarbons. A total of 11 saturation experiments were conducted as outlined in Table 2.

Results for experiments will be analysed in detail back in the laboratory, but an initial look at some of the data looks promising.

Table 2: CTD casts sampled for saturation grazing experiments

EXPT	DATE	JULIAN DAY	TIME ON DECK GMT	SITE	CAST	LAT N	LON W	DEPTH (m)	iodo-CARBONS MEASURED
SA1	19 Nov	323	14:17	A	D325_A026TIT	17.55	22.82	9	
SB1	22 Nov	326	14:13	B	D325_B030TIT	16.89	24.84	7	
SB2	24 Nov	328	14:47	B	D325_B036TIT	16.89	24.83	7	
SC1	28 Nov	332	14:41	C	D325_C041STS	16.01	23.68	7	
SC2	30 Nov	334	14:30	C	D325_C057STS	16.00	23.78	9	
SD1	02 Dec	336	14:32	D	D325_D063STS	17.68	22.87	9	
SD2	04 Dec	338	14:44	D	D325_D079STS	17.79	22.97	9	✓
SE1	07 Dec	341	14:44	E	D325_E086STS	20.69	24.96	13	✓
SE2	09 Dec	343	14:50	E	D325_E099STS	21.20	25.03	13	✓
SF1	12 Dec	346	14:54	F	D325_F107STS	26.068	23.99	17	✓
SF2	14 Dec	348	14:39	F	D325_F122STS	26.183	23.99	13	✓

3) Dilution grazing experiments

Live samples from dilution grazing experiments set up by Susan Kimmance and Stephen Archer were analysed at the beginning and end (T24 hours) of experiments to determine autotrophic picoplankton abundance. (See Susan's cruise report for details). Samples were also taken, preserved and stored at -80°C for quantification of heterotrophic grazers in experimental bottles after the cruise.

7.11 Optics

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Aims and objectives

Prior to the cruise I had been developing a coupled atmospheric in-water UV optical model. The model required measurements of chlorophyll and CDOM to extrapolate the signal measured in the visible (400 – 700 nm) to the UV (300 – 400 nm). On this cruise I hoped to take measurements of spectral inherent optical properties (using an ac-9) with which to better parameterise, and coincidental in-water spectral UV with which to validate the model. The atmospheric component of the model would be validated against the deck measured incident UV measurements. The final aim, which fits into the larger picture of INSPIRE, is to include chemistry to investigate the photo-dissociative effects of UV on Iodocarbons.

In addition I have taken measurements of phytoplankton physiology using an FRRF; PAR, to determine the light levels through the water column for the various incubation experiments; hyperspectral water leaving reflectance; and opportunistic measurements of aerosol optical depth for the NASA AERONET project.

Methodology

In-water optics

On the optics rig the following instruments were deployed: Wet Labs ac-9; Wet Labs flow cells; Fast Repetition Rate Fluorometer (NMF supplied); Satlantic UV sensor; Seabird SBE19+ CTD (see appendix for instrument details).

The optics rig was deployed from the starboard aft quarter of the ship using a winch / crane combination on 200 m of Dyneema at 12.30 pm daily. Optical protocols state that deployments should be on the sunward side of the ship; the prevailing wind direction and orientation of the sun meant that this criterion was always met. The instruments were switched on and the instrument package lowered into the water and kept at the surface for four minutes. The rig was then lowered at a fairly fast rate (0.5 m/s) down to a predetermined depth (120 m at the high and 160 m at the low production stations). The upcast is the important part of the deployment and this was carried out at 0.1 m/s. Two casts made up each deployment: the first had Supracap 0.2 μm filters attached to the ac9; the second had no filters. The filtered cast was to determine the absorption by coloured dissolved organic matter (CDOM); the unfiltered was to determine total absorption. If the sun was covered by clouds periodically, such as on a day where there are broken fields of cumulus, the cast was halted until strong sunshine re-appeared.

Upon recovery, data from the instruments was downloaded: hyperterminal was used to download the FRRF and WLHost the ac-9, UV sensor and CTD combination.

The FRRF data was processed using V6 of the Sam Laney (WHOI) Matlab code. This requires the FRRF to be characterised using 0.2 μm filtered water, at each of the gain settings (0, 1, 4, 16, 64, 256) for both the light and dark chambers, in a black bucket. This was done at each of the six (A-F) stations. The primary outputs of the FRRF data stream were the maximum fluorescence (F_m) and the ratio of the variable to maximum fluorescence (F_v/F_m); the PAR output was used to determine the percentage light levels for the following day's pre-dawn CTD casts. This was done by bespoke IDL routines written on the cruise. The final FRRF data product will consist of the phytoplankton physiological parameters binned to 2 m depth resolution.

The ac-9 data was pre-processed using the Wetlabs WAP (v4.28a) software which essentially extracts the separate data streams from the instrument binary and then merges the different datastreams back into ascii format. The ac9 data need to be corrected for the effects of temperature, salinity and scattering (Zanefeld et al. scheme) which was done using bespoke IDL routines. The ac-9 also needs to have regular field calibrations done by running milliQ water through a thoroughly cleaned instrument (methanol used to clean optics and tubes). This was done on two occasions and the necessary offsets removed. The final ac-9 product will consist of the spectral ac-9 signal merged with the Satlantic UV-sensor (4 channels); CTD and flow cells.

Atmospheric optics

Surface UV measurements

A Trios Rameses ACC UV sensor was setup on the roof of the CTD winch cab and configured to log hyperspectral UV between 200 and 500 nm at 2.5 nm resolution every 5 minutes through daylight hours. The data can either be kept as hyperspectral (to force e.g. in-water light field models) or integrated over broadband (UV-A and UV-B) ranges (this was done on the cruise using bespoke IDL routines). Data is available for 29 days of the cruise.

Satlantic Hypersas

A Satlantic HyperSAS system was also mounted on the roof of the CTD winch cab. The instrument has three sensors measuring i) sea upwelling radiance (angled at 45 degrees downwards); ii) sky downwelling radiance (angled at 45 degrees upwards) and iii) downwelling radiance (pointing vertically). The data is merged with GPS information and data processing for water leaving reflectance will be carried out back at the laboratory. Data is available for 29 days of the cruise.

Microtops sun photometer

A Solar light Co. microtops sunphotometer was opportunistically used to determine the spectral aerosol optical thickness at 340, 440, 675 and 870 nm as part of the NASA AERONET project. The instrument was used on 23 days of the cruise and data processing done by Dr. Sasha Smirnov.

Results

Date	Begin	End	Station	Cast ID	Filter	FRRF	Lat	Lon	Depth 1	Depth 2	Comments
15/11/2007	13:21	14:03	S	OPTS000	fu	N	21 04.4 N	021 50.8 W	120	120	shakedown station
17/11/2007	12:44	13:26	A	OPTA001	fu	N	17 41.7 N	022 46.6 W	120	120	high level Cs / Ci
18/11/2007	12:45	13:22	A	OPTA002	fu	N	17 37.6 N	022 47.0 W	120	120	chaotic sky
19/11/2007	12:41	13:15	A	OPTA003	fu	N	17 33.5 N	022 49.2 W	120	120	
20/11/2007	12:38	13:12	A	OPTA004	fu	Y	17 31.0 N	022 52.5 W	120	120	
21/11/2007	13:21	13:38	B	OPTB005	u	Y	16 55.8 N	024 44.0 W	120		survey station
21/11/2007	14:26	14:44	B	OPTB006	u	Y	16 51.5 N	024 45.9 W	120		survey station
21/11/2007	16:02	16:20	B	OPTB007	u	Y	16 50.4 N	024 46.5 W	120		survey station
21/11/2007	18:20	18:40	B	OPTB008	u	Y	16 53.7 N	024 49.8 W	120		survey station
22/11/2007	12:43	13:10	B	OPTB009	uf	Y	16 53.4 N	024 50.1 W	70	70	mod / rough sea
23/11/2007	12:48	13:24	B	OPTB010	f	Y	16 53.3 N	024 49.8 W	70		tube off ac9
24/11/2007	12:46	13:41	B	OPTB011	fu	Y	16 52.9 N	024 49.3 W	85	85	mod / rough sea
25/11/2007	12:48	13:40	B	OPTB012	fu	Y	16 53.0 N	024 49.8 W	100	65	hit bottom (1)
28/11/2007	12:37	13:40	C	OPTC013	f	Y	16 00.4 N	023 41.0 W	120	120	mod / rough sea
29/11/2007	12:38	13:30	C	OPTC014	f	Y	16 01.8 N	023 45.2 W	120	120	freq clouds
30/11/2007	12:38	13:34	C	OPTC015	fu	Y	16 00.1 N	023 47.2 W	120	120	
01/12/2007	12:34	13:35	C	OPTC016	fu	Y	15 56.9 N	023 52.1 W	120	120	freq clouds
02/12/2007	12:35	13:34	D	OPTD017	fu	Y	17 40.5 N	022 51.9 W	120	120	rough sea
03/12/2007	12:34	13:36	D	OPTD018	fu	Y	17 43.8 N	022 53.8 W	120	120	rough sea
04/12/2007	12:35	13:31	D	OPTD019	fu	Y	17 47.4 N	022 58.2 W	120	120	rough sea; Cs
05/12/2007	12:40	13:34	D	OPTD020	fu	Y	17 48.8 N	023 13.8 W	120	120	rough sea
06/12/2007	12:49	13:31	E	OPTE021	u	Y	20 30.2 N	025 00.2 W	180		rough sea
07/12/2007	12:38	13:24	E	OPTE022	fu	Y	20 41.1 N	024 57.8 W	160	160	rough - very rough
09/12/2007	12:30	13:44	E	OPTE023	fu	Y	21 11.6 N	025 01.7 W	160	120	rough - very rough
10/12/2007	12:37	13:45	E	OPTE024	fu	Y	21 20.6 N	024 57.6 W	160	120	mod / rough sea
12/12/2007	12:35	13:51	F	OPTF025	fu	Y	26 03.6 N	023 59.6 W	160	120	mod sea
13/12/2007	12:32	13:39	F	OPTF026	fu	Y	26 07.7 N	023 59.9 W	160	120	freq clouds
14/12/2007	12:31	13:43	F	OPTF027	fu	Y	26 10.9 N	023 59.7 W	160	120	
15/12/2007	12:32	13:32	F	OPTF028	fu	Y	26 13.3 N	023 59.2 W	160	120	showers on horizon

Table 1: Description of the optics stations sampled. The filter order is given as e.g. fu for filtered followed by unfiltered. A simple yes (Y) and no (N) is given for the presence of usable FRRF data; meteorological and sky conditions are recorded in log book.

Table 1 shows the details of the optics stations sampled during the INSPIRE cruise. Stations A and D were designated ‘medium production’ sites; B and C ‘high production’ and E and F ‘low production’. Figures 1 and 2 show the FRRF parameters associated with the medium (mesotrophic) stations ‘A’ and ‘D’ respectively. Both show a chlorophyll maximum (from the Fm parameter), strongly peaked at around 50 m. In the surface layers Fv/Fm is likely photochemically quenched giving low (0.2) values; this rises towards a maxima of 0.6 at and just below the fluorescence maximum and then decreases towards 0.2 below this level as the phytoplankton become increasingly light limited. The 1% light level for stations ‘A’ and ‘D’ were 58 and 69 m respectively.

For the highly productive (figures 3 and 4; this is a relative term as the estimated surface chlorophyll from satellite was still only 0.3 mg m⁻³) stations the fluorescence maximum is around 30 m; station B was not deep enough (< 100 m) to show a decrease in Fv/Fm below the fluorescence maxima. Station B was also strongly influenced by steep changes in bathymetry, tides and strong onshore winds. Both B and C had a 1% light level between 60 and 70 m. The greatest differences can be seen in the oligotrophic stations E and F. Figures 5 and 6 show that the fluorescence maximum was around 100 – 120 m; this represented approximately the depth of the

1% light level and the maximum in Fv/Fm. Both oligotrophic stations seemed to be highly light stressed in the surface layer; have healthy populations at the chlorophyll (fluorescence) maxima and then show a decrease of Fv/Fm in the light limited region. Figures 7 – 9 show the spectral UV light penetration through the water column and, despite there being stronger surface UV light at the southernmost stations (A-D) there is greater penetration of UV (unsurprisingly) at the more oligotrophic stations (E and F). At 320 nm the light level at station F is around $0.001 \text{ W m}^{-2} \text{ nm}^{-1}$ at 50 m whereas for stations A and C this light level is attained at around 30 m. At stations A and F there is a change in slope in Ed 380 nm around the chlorophyll maximum; indicative of the absorption of UV by phytoplankton.

Figures 10 and 11 show the attenuation and absorption at four out of the nine ac9 wavelengths. The difference between the filtered and unfiltered curves shows the amount of absorption / attenuation caused by particles and phytoplankton; the difference between the attenuation and absorption curves (unfiltered) gives the amount of scatter throughout the water column. It is therefore possible, using this optical configuration to describe the whole suite of IOPs (absorption (a); scatter (b) and attenuation (c)) and attempt to partition what is causing it. Figure 11 shows that there is more absorption due to phytoplankton at 440 nm than at the other wavelengths; this is consistent with the peak in the phytoplankton action spectrum. If the ac9 is well characterised there should be a minimal difference between the filtered attenuation and absorption curves as CDOM is essentially non-scattering in the classical sense. The differences between figure 10 and 11 show that there is more scattering in the surface layers than below the chlorophyll maximum. In addition it shows that CDOM is lower in the mixed layer than beneath the thermocline. This is somewhat of a tantalising result and seems to be consistent throughout the dataset. It may be hypothesised therefore, that in this particular region of the tropical Atlantic, that CDOM is being strongly photo-bleached in the mixed layer. Beneath the thermocline it seems, ancient CDOM (the lifetime in the ocean of CDOM may be several millennia) resides. There is certainly a change in the spectral slope of CDOM at several stations beneath the mixed layer. The main inter-station differences are in the optical effects due to phytoplankton. There is only a small difference in the CDOM signature measured. This possibly represents a de-coupling of the co-varying signal of chlorophyll – CDOM which is usually assumed in bio-optical modelling; this is probably due again to strong photobleaching of CDOM. The next step back in the laboratory is to use the IOP results and attempt to model the UV light field simultaneously measured (examples shown in figures 7 – 9). This can then be extended into the field of iodacarbon photo-chemistry.

Figures 12 and 13 show the differences between the southern and northern stations in terms of surface UV on fairly clear days; the spikes in the otherwise smooth sinusoidal are caused by clouds blocking the sun. The southern stations generally show much higher surface UV; one contributory factor will be the lower sun angle in the north, but also the ozone values could be higher in the north compared with the south – the tropics are quite a dynamic zone in terms of stratospheric ozone and values can vary between 80 – 600 DU. These measurements will be used to validate the atmospheric UV model which is in turn used to drive the in-water UV model.

Finally, figure 14 shows the aerosol optical depth derived from the sun photometric measurements. The time-series shows generally low values of AOD around 0.1 (unitless) at 675 nm which is typical of clean marine atmospheres; however there are a few departures from this up to around 0.2 which could represent more Saharan desert injections of dust and certainly the values around 0.7 at the start of the cruise

are likely induced by the Canary Islands. There was little or no impact of the Cape Verde Islands as we sampled upwind of them.

Integration:

The UV modelling work will be integrated with the Iodacarbon measurements to produce a coupled chemical – radiative transfer model.

Datasets produced:

In water optics:

i) Merged dataset of ac9, UV and CTD; 29 days of data divided into 2 casts (filtered and unfiltered), median binned into 2 m depth intervals. Filenaming convention:

D325_OPTSSSS_ac9_SUV_CTD_fff_yymmdd.txt

where SSS is the station ID (e.g A001); ac9 (ac9), SUV (Spectral UV), CTD (CTD), fff is flt (filtered) or unf (unfiltered), yy (year), mm(month), dd (day).

ii) Binned dataset of FRRF parameters into two separate casts (where appropriate). Filenaming convention: D325_OPTSSSS_frrf_castx_yymmdd.csv

Atmospheric measurements:

i) hyperspectral files every 5 minutes for duration of cruise; these could be binned into broadband files (UVA – UVB). Number of files and process yet TBD.

ii) hyperspectral reflectance every 6 minutes for duration of cruise. Number of files and process yet TBD.

iii) Single spreadsheet of aerosol optical depth measurements taken opportunistically during the cruise.

Figures

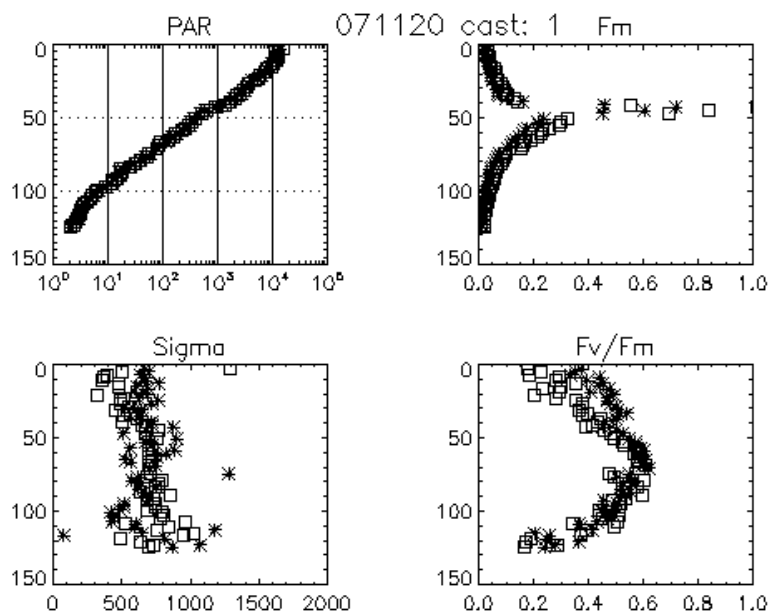


Figure 2: FRRF parameters for station A (OPTA004)

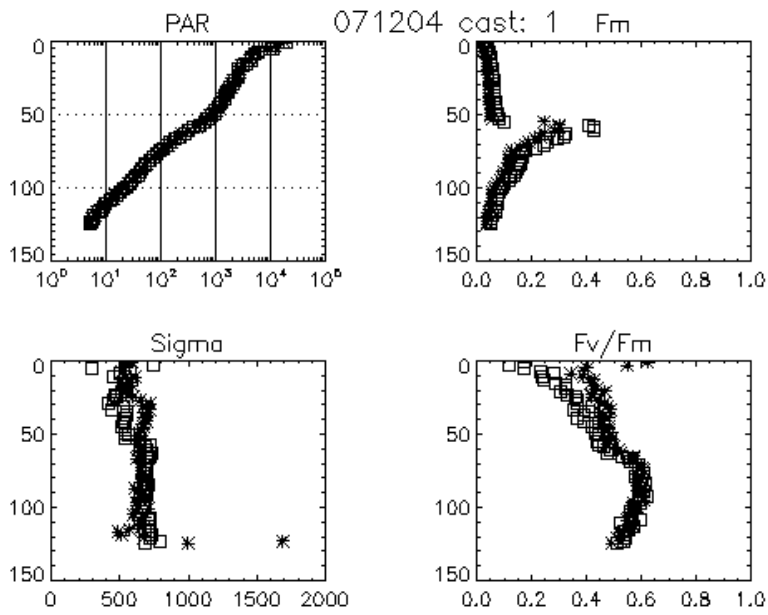


Figure 3: FRRF parameters for station D (OPTD019)

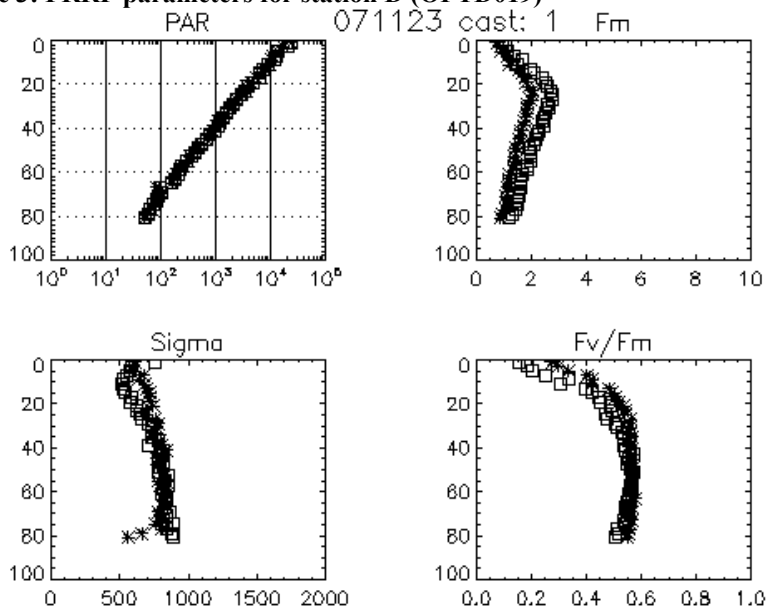


Figure 4: FRRF parameters for station B (OPTB010)

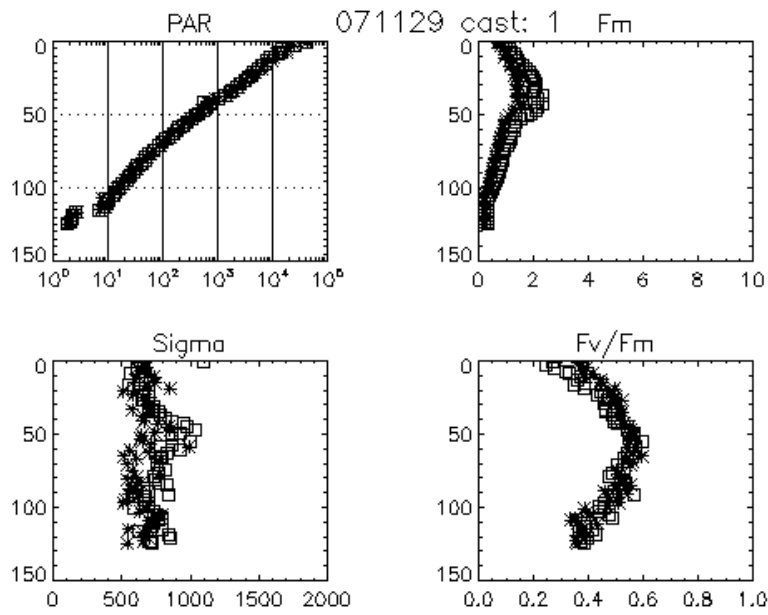


Figure 5: FRRF parameters for station C (OPTC014)

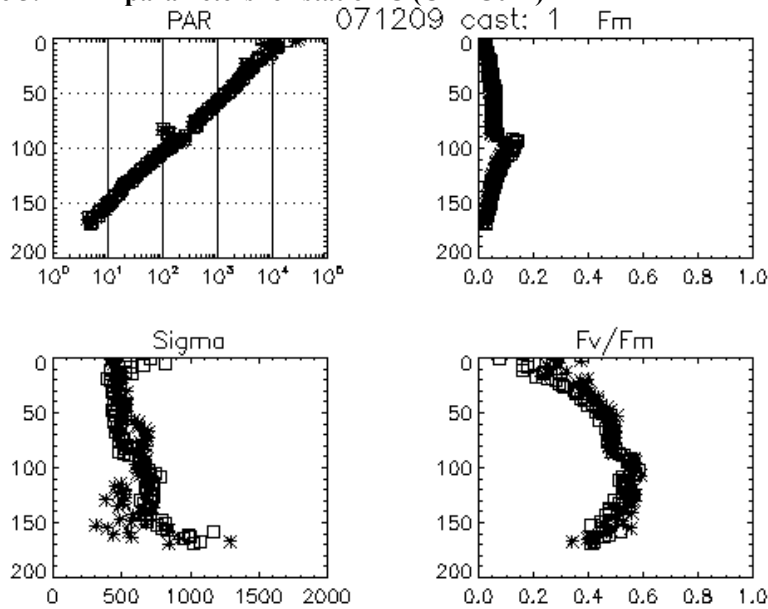


Figure 6: FRRF parameters for station E (OPTE023)

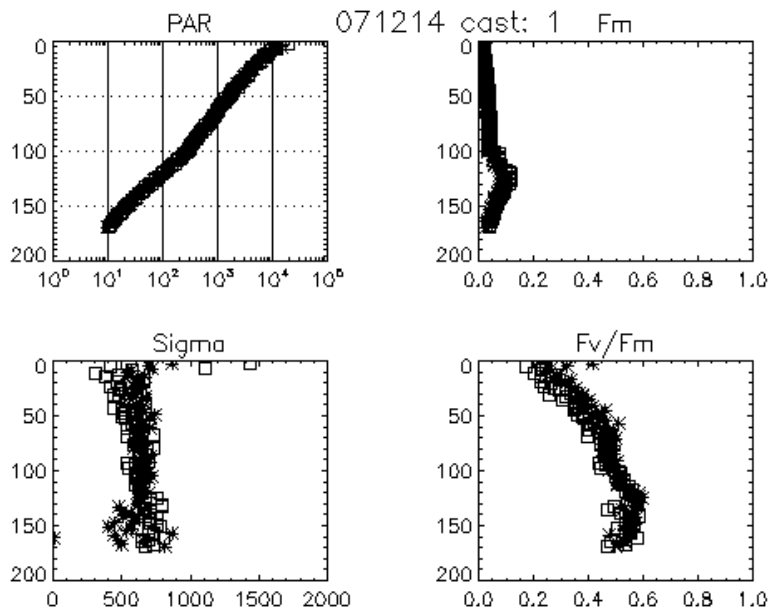


Figure 7: FRRF parameters for station F (OPTF027)

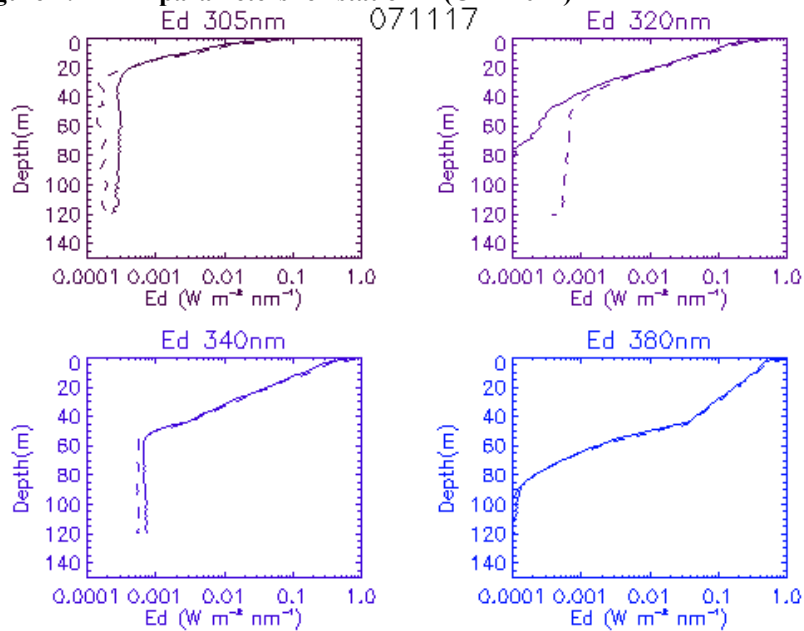


Figure 8: Spectral UV at station A (OPTA001); solid line is cast 1, dashed line is cast 2.

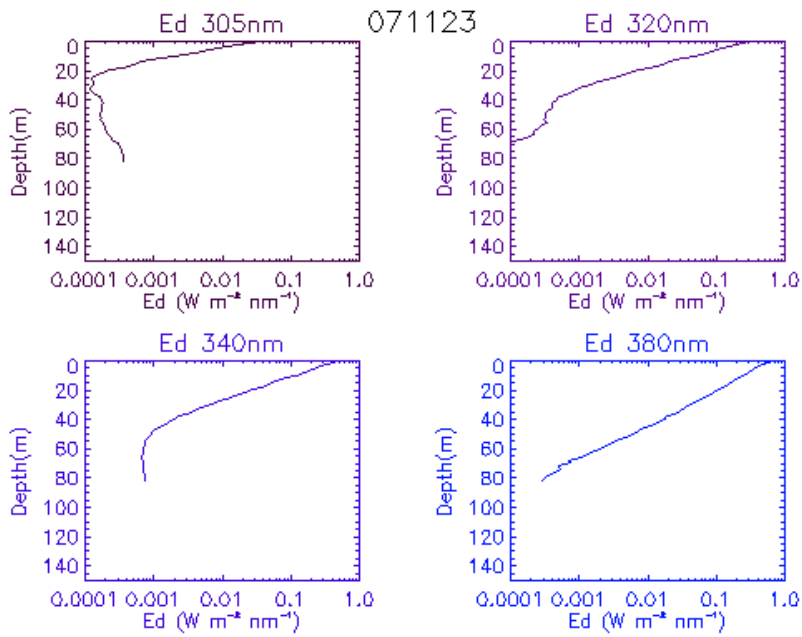


Figure 9: Spectral UV at station B (OPTB010).

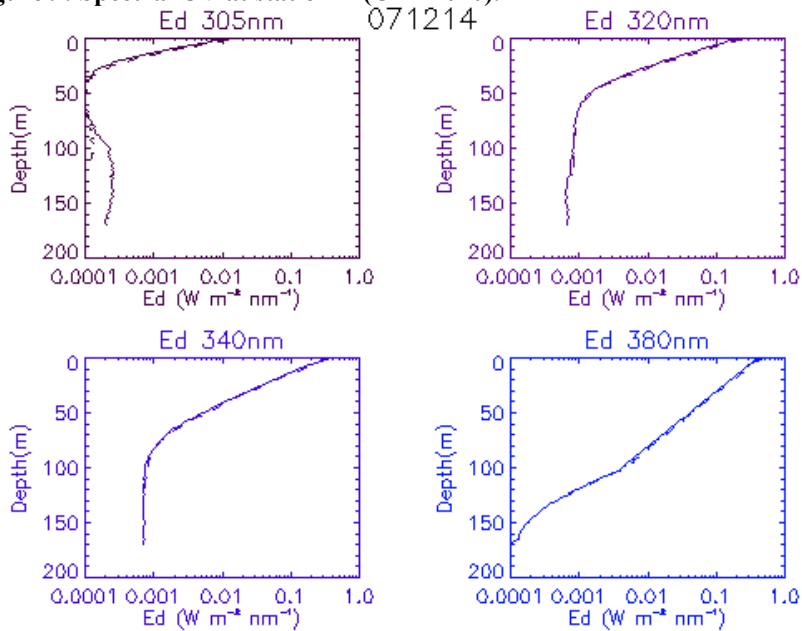


Figure 10: Spectral UV at station F (OPTF027); cast 1 is solid line, cast 2 is dashed.

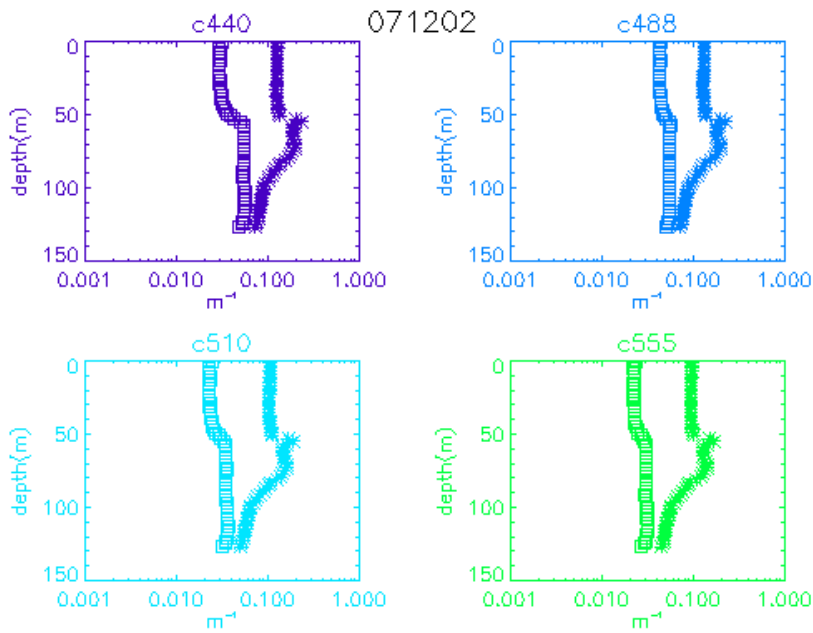


Figure 11: Attenuation at 440, 488, 510 and 555 nm measured using the ac9 at station D. Open squares represent a filtered cast through 0.2 μm supracaps and represent the CDOM signal. Crosses show the unfiltered cast and show total (not including pure water) attenuation.

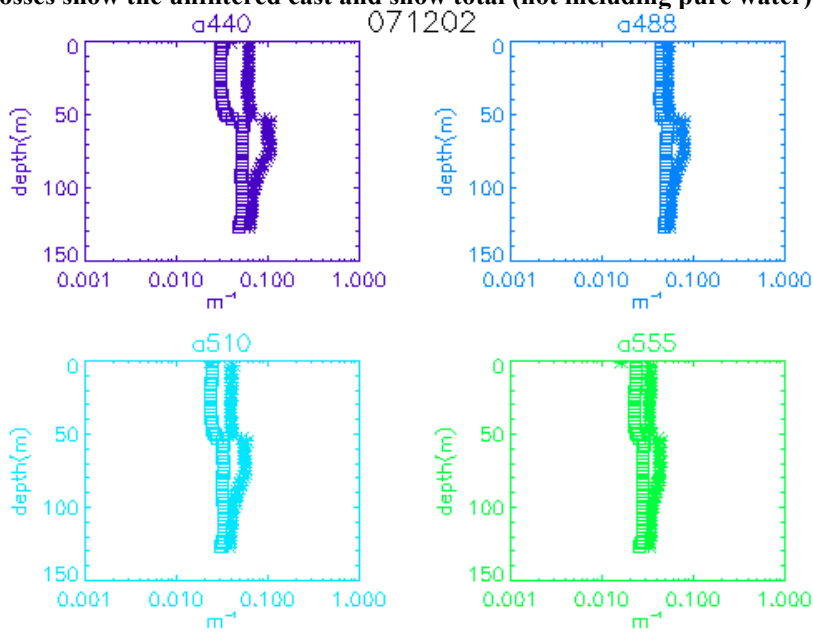


Figure 12: As for figure 10 but absorption.

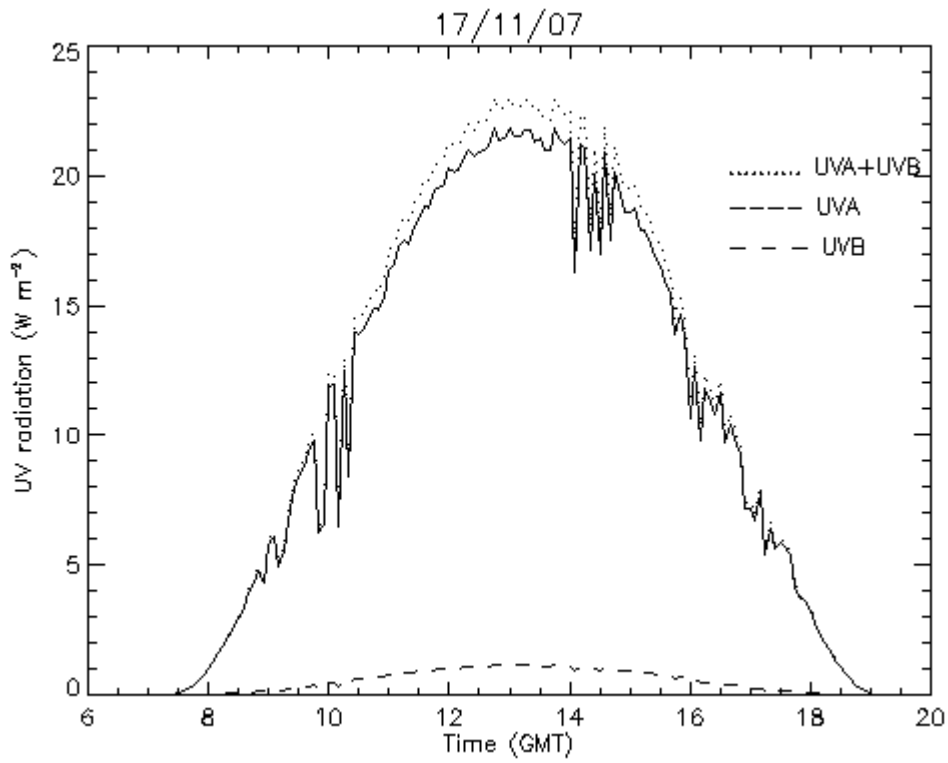


Figure 13: Surface UV light levels at station A

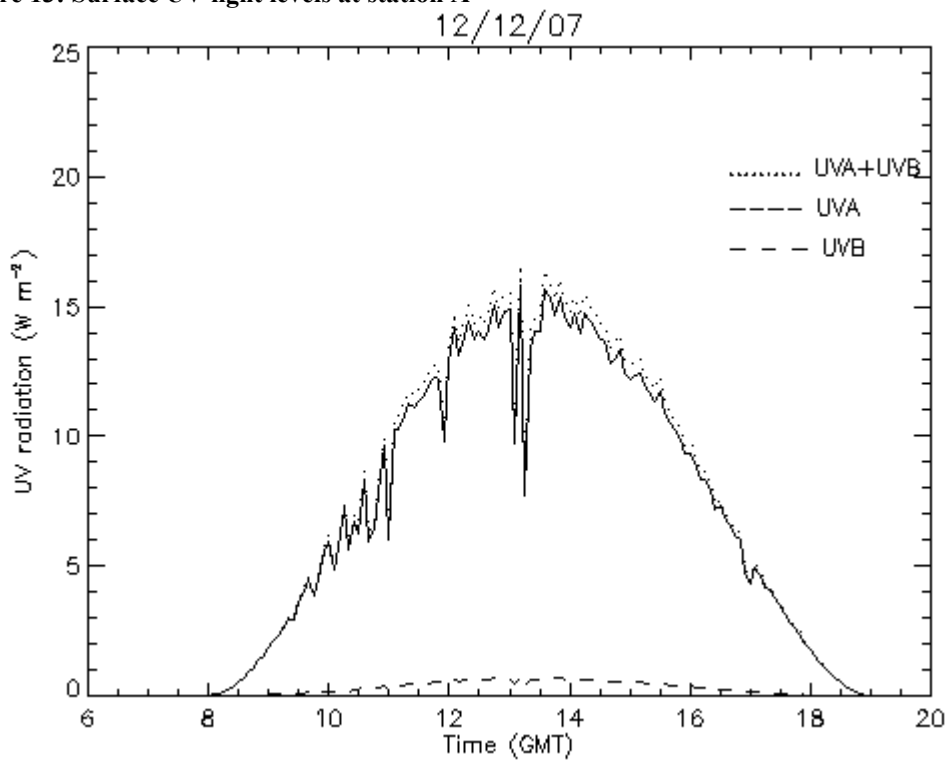


Figure 14: Surface UV light levels at station F.

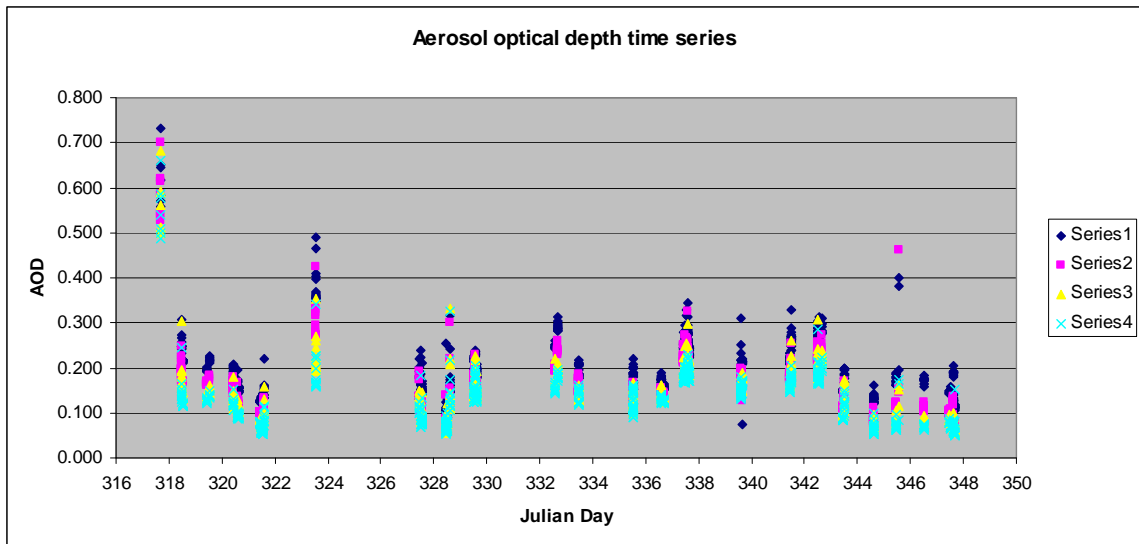


Figure 15: Aerosol optical depth measurements over the duration of the cruise. Blue squares – 340 nm; pink squares 440 nm; yellow triangles 675 nm; cyan crosses 870 nm.

Appendix

Measurement	Instrument	Manufacturer	Model	Serial number
In-water UV (305, 320, 340, 380 nm)	UV sensor	Satlantic	507-UV	168
phytoplankton phys.	FRRF	Chelsea	FRRF 1	182043
PAR	PAR sensor	Chelsea	0046-3097	046058
Depth	Depth sensor	Druck	PTX 1830	2500106
Temperature, Salinity absorption / attenuation at 412,440, 488,510,532,555,650,676, 715 nm	CTD	SeaBird	SBE19+	19P27903-4180
Incident UV (200 – 500 nm at 2.5 nm resolution)	ac-9 Hyperspec.UV sensor	Wetlabs Trios	ac9+ ACC2 UV	ac90265P 010-05-501F
HyperSAS	Radiometer - vertical	Satlantic	OCR-R	258
	Radiometer -45	Satlantic	OCR-R	023
	Radiometer +45	Satlantic	OCR-R	022
Aerosol Optical Depth	sunphotometer	SOLAR light co.	microtops II	03125

Table 2: description and serial numbers of instruments used. Highlighting is used to show instruments used as a unit.

7.12 Micro and Nanomolar Nutrients
Malcolm Woodward and Carolyn Harris
Plymouth Marine Laboratory

OBJECTIVES:

To investigate the spatial and temporal variations of the micromolar nutrient species Nitrate, Nitrite, Silicate and Phosphate, and also the nanomolar nutrient concentrations for Nitrate, Nitrite, Phosphate and Ammonium, during a research cruise to the Eastern Tropical Atlantic studying contrasting areas of productivity. The sea areas studied were to the north and north-west of the Cape Verde Islands, plus a high productivity site to the south. Where possible samples would be analysed from small boat sampling, using a novel high technology ‘pole’ sampler to sample 9 depths from the upper 2.5 metres of the water column to investigate ammonia production and losses in this near surface area. Samples would also be analysed from the NSS, the Near Surface Sampler system where deployed.

ANALYTICAL METHODOLOGY:

We deployed an ammonium analytical system with a nanomolar detection limit, which utilises a fluorimetric detection technique. Following ammonia gas diffusion out of the samples due to pH differential chemistry, the gas crosses across a 5 micron hydrophobic teflon membrane into a fluorescent reagent and then is subsequently detected.

For the other nano-nutrient species of nitrate, nitrite and phosphate we used a three-channel nanomolar analytical system which combines sensitive segmented flow colorimetric analytical techniques with 2 metre flow-length Liquid Waveguide Capillary Cells (LWCC).

The micro-molar analyser was a Bran and Luebbe AIII segmented flow, colorimetric, autoanalyser,

Water samples were taken from a 24 x 20 litre stainless steel CTD/Rosette system (SeaBird), and also from a 24x10 litre titanium frame CTD for the trace metal studies. These CTD bottles were sub sampled into acid clean 60 mls HDPE (nalgene) sample bottles and analysis for the nutrient samples was in most cases complete within 3-4 hours of sampling. Clean handling techniques were employed to avoid any contamination of the samples, particularly for the nanomolar nutrients. No samples were stored.

Samples were also analysed from the Trace metal ‘fish’ deployed over the port quarter which were taken by the trace metal experimental scientists.

CTD SAMPLES ANALYSED.

Details of all the samples analysed are in the cruise information spreadsheet.

CTD	CTD	SAMPLE DEPTHS
17 th November	A006-STs	2,9,16,23,38,48,55,65,70,100,200
	A007-TIT	2,9,16,23,38,43,65,80,100
	A008-STs	2,9,16,23,35, 38,40, 42,44,52,65,100
18 th November	A011-TIT	2,9,16,23,32,38,48,65,100
	A014-TIT	2,9,16,23,28,32,35,38,40,45, 65,100
19 th November	A024-TIT	2,9,16,23,38,42,47,51,65

	A026-TIT	2,9,16,26, 33, 40,46,48,51,55,65,80,100
20 th November	A027-TIT	2,9,16,23, 30, 38,45,50,52,55,65,80,100
21 st November	B028-TIT	2,7,12,18,29,50
	B029-TIT	2,7,12,18,29,50,55,60,65,80,100
	B030-TIT	2,7,12,18,29,50,55,60,65,80
23 rd November	B031-TIT	2,7,12,18,29,35,40,45,50,65,80,100
	B033-TIT	2,7,12,18,29,38,45,50,65,80,100
24 th November	B034-TIT	2,7,12,18,29,50,55,60,65,80,100
	B036-TIT	2,7,12,18,29,35,40,45,50,65,100
25 th November	B037-TIT	2,7,12,18,29,35,40,45,50,65,100
	B038-TIT	2,7,12,18,29,35,40,45,50,65,100
28 th November	C039-TIT	2,7,12,18,29,35,42,50,55,65,100, 200
	C040-TIT	2,7,12,18,29,29,32,38,44,50,65,100
	C041-STS	2,7,12,18,24,29,32,38,44,50,65,80,100, 200, 450
29 th November	C042-STS	2,9,16,23,27,32,35,39,45,55,64,100,200
	C047-STS	2,9,16,23,32,36,40,45,50,64,100
30 th November	C055-STS	2,9,16,23,32,36,40,45,55,64,100,200
	C057-STS	2,9,16,23,32,36,40,45,64,100
1 st December	C058-STS	2,9,16,23,32,36,40,45,50,64,100
2 nd December	D062-STS	2,9,16,23,38,44,48,52,56,60,65,70,80,100
	D063-STS	2,9,16,23,38,50,65,80,100
3 rd December	D064-STS	2,9,18,25,36,41,46,50,55,58,63,67,70,100
	D066-TIT	2,9,18,25,32,39,44,55,60,70,100
	D069-STS	2,9,18,25,41,46,52,55,60,70
4 th December	D077-STS	2,9,18,25,41,50,54,58,62,70,103
	D079-STS	2,9,18,25,41,52,56,60,64,70,100
5 th December	D080-STS	2,9,18,25,41,45,48,50,56,58,65,70,100
	D082-STS	2,9,18,25,41,45,54,57,60,70,100
7 th December	E083-STS	200, 500, 800, 900, 1100, 1200, 1500, 2000, 2500
	E084-STS	2,13,23,33,55,75,85,90,95,100,150,200
	E085-TIT	2,13,23,33,55,70,85,90,95,100,200
	E086-STS	2,13,23,33,55,70,73,80,90,95,100,120,200
8 th December	E087-STS	2,13,23,33,55,70,75,83,90,95,100,200
	E091-STS	2,13,23,33,55,85,90,95,98,100,104,120,200
9 th December	E098-STS	2,13,23,33,55,75,85,90,93,95,100,120,200
	E100-STS	933
	E101-STS	933
10 th December	E102-STS	2,13,23,33,55,80,88,92,95,100,120,200
	E104-STS	2,13,23,33,55,75,88,92,95,98,100,120,150,200
12 th December	F105-STS	2,13,31,46,75,90,95,100,105,110,120,130,200
	F107-STS	2,17,31,46,75,90,95,100,110,130,160,200
13 th December	F108-STS	2,13,24,35,55,89,90,100,108,130,160,200
	F110-TIT	2,13,24,35,58,90,100,120
14 th December	F120-STS	2,13,24,35,58,90,100,105,115,150,200
	F122-STS	2,13,24,35,58,80,100,105,110,114,118,130,150,200
15 th December	F123-STS	2,13,24,35,58,80,90,95,100,104,108,112,120,150,200
	F125-STS	2,13,24,35,58,90,100,111,120,130,180,200

OTHER SAMPLES:

Trace Metal Fish samples:

17/11/07

21/11/07

28/11/07

3/12/07

7/12/07

13/12/07

Ammonia Pole samplings, depths in metres

19th November: 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5

20th November: 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5

14th December: 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5

15th December: 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5

NSS samplings, depths in metres

19th November: 0.2, 0.4, 0.8, 1.0, 1.3, 1.6, 2.0

20th November: 0.2, 0.4, 0.8, 1.0, 1.3, 1.6, 2.0

CRUISE SUMMARY

Overall a very successful cruise and thanks to the ships officers and crew for helping to provide a good working platform. Also thanks to scientific colleagues and PSO Gill Malin for making the cruise very enjoyable.

The nutrient analysers worked very well throughout the cruise apart from the odd early morning start-ups for the nanomolar systems, however a very minimal number of samples were lost.

The nutrients in the surface waters demonstrated a variation across the 3 differing sampling regions with decreasing surface water concentrations out to the low productivity oceanic site F. Here less than 5nm of phosphate and nitrate were seen. Also the depth of the mixed layer and the nutricline increased as we progressed through high, medium to low productivity stations.

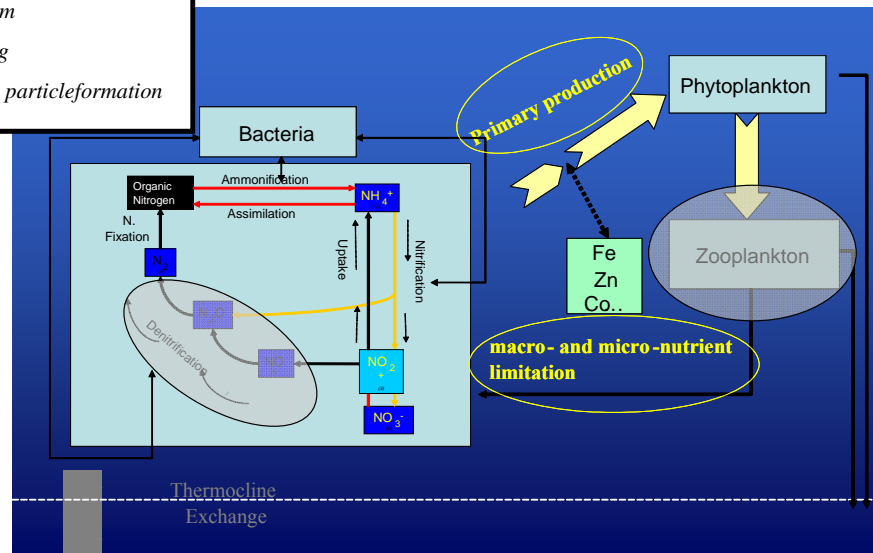
On the 9th December we also took 2 deep CTDs to 933 metres which was the depth of the nitrate maximum and salinity minimum at site E. The water was collected into provided 25 litre cubitainers and will be sent to the Japanese Kanso laboratory for making a new quality Nutrient Reference Material that will be representative of Atlantic waters with the correct nutrient ratios.

7.13

Nitrogen Cycling & Microbial Productivity

Box B	Biology (B)
	Variables: <ul style="list-style-type: none"> • composition and biomass • phytoplankton processes • phytoplankton stress • bacterial metabolism • zooplankton grazing • algal senescence & particle formation

Darren Clark, Joanna Dixon, Andy Rees
Plymouth Marine Laboratory
Rachel Shelley
University of Plymouth



In order to complement the biological objectives of the INSPIRE project and to address key objectives of OCEANS 2025 Theme 2 (WP2: *To reduce key uncertainties in the microbial cycling of the major elements*) we have performed a series of experimental procedures to address specific objectives 3 and 4 of WP2:

iii. To define rates of oceanic new production.

iv. To identify the limiting/co-limiting factors for the microbial cycling of carbon and nitrogen

At each of six oceanographic stations occupied, rate and state measurements (see methods for list) were made under a semi-lagrangian framework and involved:

- a) A vertical profile between the surface and base of euphotic zone
- b) A diel survey over 24 hours from surface waters
- c) A bioassay experiment to assess limitation of microbial processes by essential trace metals; Fe, Zn, Co, Cu (& N)

Acknowledgements – We would like to be upfront in thanking a number of people who have contributed to this work. In particular, Gill Malin has performed an excellent job as principal scientist in organising and maintaining a smooth operation throughout. Susan Kimmance, Tim Smyth, Carolyn Harris and Malcolm Woodward have all contributed to the completion of this work.

Methods

Vertical profiles were performed using water collected from the titanium CTD rosette in pre-cleaned (10% HCl), 10 litre “Niskin” bottles, whilst seawater was collected from a towed fish deployed from the port aft quarter for delivery of diel and bioassay

surveys. Bioassay experiments were performed under a strict trace metal clean regime and involved the collection of 120 litres seawater from the depth equivalent to 55% of surface PAR, into an acid clean HDPE container, which was housed in the trace metal clean container. This was then distributed into triplicate 4.6 litre bottles for the treatments listed below in the sampling log. Following amendment with nutrients these bottles were placed in on-deck incubators at surface temperature and 55% incident irradiation for a conditioning period of 48 hours, after which rate and state variables listed below were determined.

Carbon Fixation (JD): Seawater was distributed into triplicate 60 ml polycarbonate bottles and amended with $\sim 10 \mu\text{Ci } ^{14}\text{C}$ -bicarbonate. Incubations were performed in on-deck incubators under simulated in-situ light conditions and temperature controlled by surface seawater. Experiments were terminated by filtration onto 0.2 μm Supor 200 membrane filters which were fumed with HCl prior to onboard liquid scintillation counting.

Bacterial production (JD): Incorporation of L-[4,5- ^3H]Leucine into bacterial protein in seawater samples was determined following the method of Smith and Azam 1992.¹ 1.7 ml seawater samples were inoculated with 25 nM ^3H Leucine (7 μl) (as determined by a Vmax experiment carried out on 01/05/04) and incubated in the dark at in situ temperature for 1 hr. Samples were terminated with 100 μl TCA (5% final concentration) and incorporated ^3H extracted following procedures outlined in Smith & Azam 1992 before being measured by liquid scintillation counting.

Nitrogen Fixation (AR): Seawater was distributed into triplicate 1 litre polycarbonate bottles and amended with 2 ml of ^{15}N - N_2 . Following incubation in the on-deck incubators for approx 6 hours, experiments were terminated by filtration onto 25 mm GF/F filters which were dried onboard and pelleted into tin capsules prior to stable isotope mass spectrometer analysis which will take place at PML.

Nitrification, Ammonium regeneration, N uptake (DC): Seawater was distributed into 3 x 2.4 L vessels with either $^{15}\text{NH}_4^+$, $^{15}\text{NO}_2^-$ or $^{15}\text{NO}_3^-$ added at $\approx 10\%$ ambient [DIN] and placed in on-deck incubators for 6 hours. Incubations were terminated by filtration onto pre-ashed 25mm GF/F. The filter was frozen and will be used to measure N-assimilation rate by IRMS. A sub-sample of filtrate was frozen and will be used for DON analysis. Reagents were added to the remaining filtrates for dye development (indophenol for NH_4^+ , sudan-1 for NO_2^- ; NO_3^- was quantitatively reduced to NO_2^- using a cadmium column) and the dyes were collected by solid phase extraction. The dye were eluted from SPE columns and will be returned to PML for GC/MS analysis, providing measurements of DIN pool concentration and rates of NH_4^+ regeneration, NH_4^+ oxidation and NO_2^- oxidation.

Urea uptake (AR): Triplicate samples were collected into 0.64 litre polycarbonate bottles and each amended with an addition of 5 nmol/l ^{15}N -urea. These were then incubated for approx 6 hours in on-deck incubators and terminated by filtration onto 25mm GF/F filters. ^{15}N analysis will be performed at PML. Unfortunately the analysis of urea concentration, on which the rate equation relies, was largely unsuccessful and may render these samples unuseable.

Urea concentration (AR): Room temperature digestion of triplicate samples with thiosemicarbazide and diacetylmonoxime according to Goeyens et al (1998) was performed on a number of samples collected into amber medicine bottles.

¹ Smith, D.C and Azam, F. 1992 Marine Microbial Food webs 6(2): 107-114.

Unfortunately, for reasons unknown this did not work, and so a number of samples have been collected and frozen at -80°C for later analysis at PML.

Chlorophyll concentration (AR): Seawater samples (150 – 250 ml) were filtered onto 47mm 0.2µm polycarbonate filters, extracted in 90% acetone at -20°C overnight and Chlorophyll a determined according to the method of Welschmeyer (1994) using a Turner instruments fluorometer.

AFC (JD): Duplicate 1.8 ml samples were fixed with paraformaldehyde and stored at -80°C for later analysis by flow cytometry at PML (for diel and bioassay experiments only).

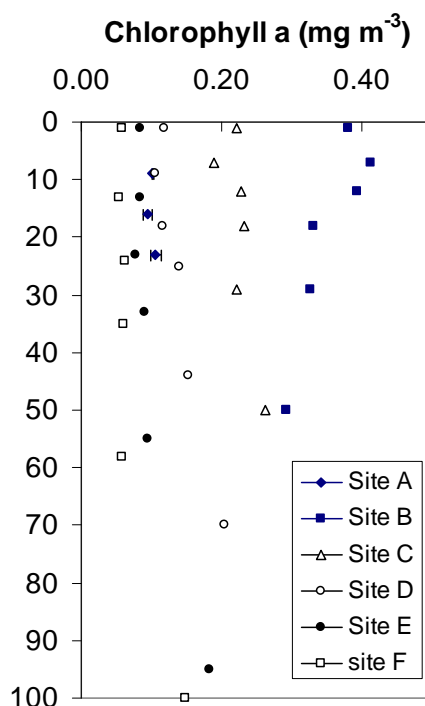
Trace Metal Analysis (RS) : One seawater sample (250 ml; acid cleaned HDPE bottles) was taken from each of the 4.6 l incubation bottles and filtered through an acid cleaned 0.2µm nuclepore membrane, using a vacuum pump filtration system with Teflon components. The filtrate was collected in 125 ml HDPE bottles and acidified to pH2 using ultra high purity HCl. All operations were carried out in clean room conditions under a laminar flow hood. The HDPE sample bottle cleaning protocol followed that of Achterberg *et al.* (2001).

Analysis for dissolved trace metals (Fe, Zn, Co, Cu) will be carried out at the University of Plymouth (UoP) according to previously published flow injection techniques. In addition two membranes from each treatment were retained for analysis of particulate trace metals. This analysis is also to be carried out on return to the laboratory at UoP.

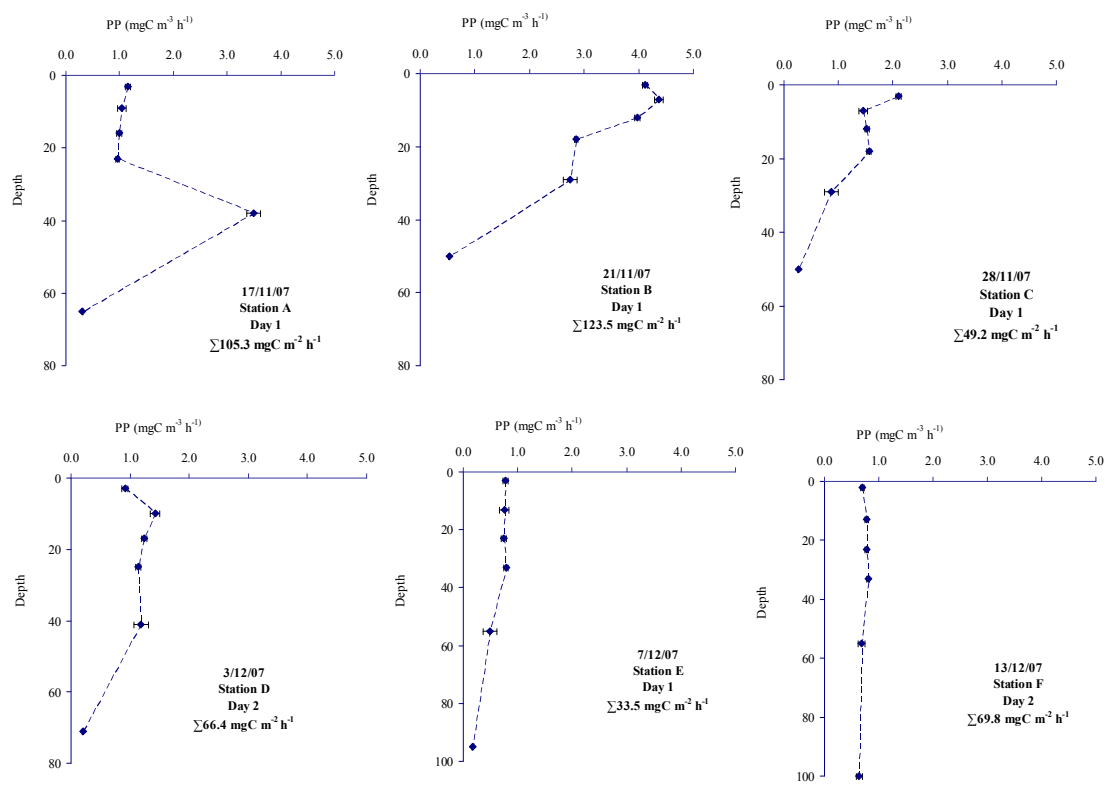
Achterberg *et al.* (2001) *Analytical Chimica Acta* 442: 1-14.

Preliminary results

There is very little information available at this stage as most of what has been done requires analysis at PML and will be available in the order of 6 months after the cruise. Chlorophyll analysis was performed onboard and clearly indicates the difference in trophic conditions experienced over the 6 stations.



Preliminary rates of primary production from titanium CTD casts



Sampling Log

DATE /TIME	SITE /STATION	VERTICAL PROFILE	BIOASSAY	DIEL	OTHER
17 Nov 0409	A day 1 TMS-A001		Control, +Fe, +Zn, +Co, +Cu, Mix		
0815	CTD-A007tit	Surf – 60m			
18 Nov	A day 2			N-fixation 4 hourly sampling (0600 – 0200 19/11) Particulate methanol uptake, total methanol oxidation, AFC samples and bacterial production every hour.	

				N-cycling (6 hourly sampling)	
20 Nov					Bacterial production comparison between NSSD & Pole
22 Nov 0434	B day 1 TMS-B002		Control, +Fe, +Zn, +Co, +Cu, Mix		
0805	CTD- B029tit	Surf – 50m			
28 Nov 0650	C day 1 TMS-C003		Control, +Fe, +Zn, +Co, +Cu, Mix		
0906	CTD- C040tit	Surf – 50m			
29 Nov	C day 2			N-fixation 4 hourly sampling (0640 – 0145 30/11) Particulate methanol uptake, total methanol oxidation, AFC samples and bacterial production every hour. N-cycling diel (4 x 5 hr)	
03 Dec 0525	D day 2 TMS-D004		Control, +Fe+N, +Zn+N, +Co+N, +Cu+N, +N		
0811	CTD- D066tit	Surf – 70m			
04 Dec	D day 3			N-fixation 4 hourly sampling (0615 – 0224 05/12)	
05 Dec					Bacterial production for UEA light/dark

					incubation experiment.
07 Dec 0530	E day 1 TMS-E005		Control, +Fe, +Zn, +Co, +Cu, Mix		
0901	CTD- E085tit	Surf – 95m			
08 Dec	E day 2			N-fixation 4 hourly sampling (0620 – 0155 09/12) N-cycling 4 x 5 hr	
12 Dec	F day 1			N-fixation 4 hourly sampling (0610 – 0230 13/12) Particulate methanol uptake, total methanol oxidation, AFC samples and bacterial production every hour. N-cycling (4x5hr)	
13 Dec 0530	F day 2 TMS-F006		Control, +Fe+N, +Zn+N, +Co+N, +Cu+N, +N, +Dust		A dust addition bioassay expt (collected from aerosol filters) was carried out in conjunction with York/UEA for Iodine chemistry and methyl halides respectively.
0806	CTD- F110tit	Surf-100m			

AFC denotes samples preserved for analysis by flow cytometry. In addition bacterial production samples were taken to support aggregate experiments undertaken by Claire Hughes UEA.

7.14 CTD and SAP Operations

Dave Teare

NMFSS

Two CTD systems were used during the cruise. A 'standard' stainless steel unit for general sampling plus a titanium unit for trace metal sampling. Both units were fitted with Seabird CTDs and associated equipment.

CTD configurations

The stainless CTD package comprised of the following instruments. Seabird 911+ CTD with dual pumped temperature and conductivity sensors. The primary sensor pair were vane mounted to reduce salinity spiking. A Seabird SBE 43 oxygen sensor was fitted in the secondary duct. Seabird carousel type SBE 32. Chelsea instruments Alphatracka (transmissometer) and Aquatracka (fluorometer). PML 2pie PAR light sensors for up welling and down welling light. Chelsea Instruments FRR-fluorometer with its own PAR sensor. Benthos altimeter type 915T. Wet-Labs light back scatter sensor. Twenty four, 20 litre OTE Water bottles.

The titanium CTD comprised of, Seabird 911+ CTD with dual pumped temperature and conductivity sensors, both pairs were mounted on the CTD. A Seabird SBE 43 oxygen sensor in line with the secondary sensor duct. SBE 32 carousel. Chelsea Instruments Alphatracka and Aquatracka. PML 2 pie PAR light sensors, one for down welling and one for up welling light. WetLabs back scatter sensor. Trittech P200 altimeter. Twenty four, 10 litre OTE trace metal water bottles.

Equipment performance.

Generally both systems performed well. The only major problem was the Stainless Steel system carousel, which developed a fault early in the cruise. The Titanium system was used in its place, until a spare unit was collected at the mid-cruise port call. After fitting the replacement, the Stainless Steel system worked with few problems. The 20 litre water bottles had a 'sealing failure' rate of below one bottle per cast. This is quite normal with these bottles, the bottom end cap being the source of failure.

Stand Alone Pumps (SAP)

All the pumps were Challenger Oceanics MK3, with one experimental unit, which had a micro-controller timer fitted. The pumps were deployed a total of twelve times, two deployments at each of the six stations. Each station had a single instrument deployment followed, approximately twelve hours later, by a four instrument (string) deployment.

Equipment performance

All the 'standard' pumps worked well, pumping between 2500 and 3000 litres. The experimental unit was not so reliable. Out of its seven deployments, three test and four real, the unit failed twice. Both failures were under real deployment conditions with filters fitted.

7.15 Computing and Instrumentation Report

For any further information on this report please contact:

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RVS LEVEL ABC System

The LEVEL ABC system is a system comprised of multiple components that can be adjusted and altered to suit the needs of the cruise in progress. The system is due to be retired due to its age and the difficulty in acquiring spares. The ABC system is created of 3 tiers:

- Level A - The Level A's role in the system is to acquire the data from an instrument, parse the data stream into the necessary format to be recorded by the level B and also place a timestamp on each piece of data. The instruments are connected to the Level A's via RS-232 and are also connected to the level B in the same way. This allows simple interrogation of messages when attempting to track a problem with the system.
- Level B - The level B is sent all data from the Level A's and allows you to view all the data as it is coming in. The Level B allows the backup of the data to magnetic disks which are backed up on the Level C in compressed Zip format. The Level B transmits the data to the Level C and the data is parsed directly into the RVS data files that we use now. All data, errors, comments can be viewed for each individual instrument.
- Level C - The level C system is a Sun Solaris 10 UNIX Workstation discovery1 also known as ABCGATE. The RVS software suite is available on this machine. This suite of software allows the processing, editing and viewing of all data within the RVS data files. This system also has monitors that allow us to ensure that the level C is receiving data from the level B.

The Level A's acquire their timestamp from a Radio code GPS Clock that is distributed via the RVS Master / Slave Clock System.

The ABC system still remains the main data logging format for the ship, this is being run in parallel with the new Ifremer Techsas Sensor Acquisition System. This system is currently being proven and a database of drivers being built to enable us to interface with the instruments on board.

This system will then become the primary system for data logging.

For this cruise the Level A system were used to log:

- 1) Ashtech ADU-2 multi antenna GPS with attitude (gps_ash)
- 2) Ashtech GPS G12 integral to the FUGRO Seastar DGPS receiver (gps_g12)
- 3) NMFD Surface-water and Meteorology instrument suite (surfmet)
- 4) NMFD Winch Cable Logging And Monitoring CLAM (winch)

The RVS level ABC system suffered no major issues during the cruise with the exception of the full loss of power to all ships systems, total loss of data was around 2 hours for most instruments, mainly due to the need to reset almost all devices that are used in the data logging process. During the power outage the computer room clean supply was turned off incase of spiking in order to protect equipment. This was successful and no further damage occurred to the ABC system or the Ifremer Techsas system.

Ifremer Techsas System

The Ifremer data logging system is the system that will inevitably replace the existing Level A + B system while for the most part the Level C will remain as the main system for outputting, viewing and editing the acquired data.

The Techsas software is installed on an industrial based system with a high level of redundancy. The operating system is Red Hat Enterprise Linux Edition Release 3. The system itself logs data on to a RAID 0 disk mirror and is also backed up from the Level C using a 200GB / 400GB LTO 2 Tape Drive. The Techsas interface displays the status of all incoming data streams and provides alerts if the incoming data is lost. The ability exists to broadcast live data across the network via NMEA.

The storage method used for data storage is NetCDF (binary) and also pseudo-NMEA (ASCII). At present there are some issues on some data streams with file consistency between the local and network data sets for the ASCII files. NetCDF is used as the preferred data type as it does not suffer from this issue.

The Techsas data logging system was used to log the following instruments:

- 1) Trimble GPS 4000 DS Surveyor (converted to RVS format as gps_4000)
- 2) Chernikeef EM speed log (converted to RVS format as log_chf)
- 3) Ships Gyrocompass (converted to RVS format as gyronmea)
- 4) Simrad EA500 Precision Echo Sounder (ea500d1)
- 5) NMFD Surface-water and Meteorology (SURFMET) instrument suite
- 6) ASHTECH ADU-2 Altitude Detection Unit (adu2)
- 7) NMFD Winch Cable Logging And Monitoring CLAM (winch2)

8) Ashtech GPS G12 integral to the FUGRO Seastar DGPS receiver (gps_g12T)

This system is still being trial run by the platform systems as the replacement to the aging RVS system, no major issues occurred during this cruise and no substantial data losses occurred. The recent upgrade of the software on both TECHSAS systems allows the software to continue logging without the memory leak issue which was causing crashes in the system every few days.

Techsas NetCDF to RVS Data Conversion

During this cruise there is no reliance upon the data provided by Techsas, however it has been included on the data archive in the standard rvs form using a piece of software used to make it compatible with the RVS ASCII data structure. The University of Rhode Island instruments were logged using the Techsas system and had to be converted to the RVS format in order to be able to create data logs that included multiple variables from other RVS streams.

An in house application was used to handle the conversion of NetCDF files to the RVS format. This was then parsed back to the data file and was processed as normal. These 2 new applications being ncvars and nclistit.

These new binaries require to environment variables in order to function:

`$NCBASE` – the base for the NetCDF binaries system, set to `/rvs/def9`

`$NCRAWBASE` – the base for the raw data files, set to `/rvs/pro_data/TECHSAS/T1backup/D325/NetCDF`

The existing `$PATH` variable must also include the path to the nc binaries, the path `/rvs/def9/bin` was appended to the `$PATH` variable.

All Techsas data file names are in the format of `YYYYMMDD-HHMMSS-name-type.category` with the data/timestamp being the time the file was created by Techsas.

The files were each processed in the following way for this cruise:

```
nclistit 20060813-000001-gyro-GYRO.gyr - | sed s/head/heading >
$DARAWBASE/gyro.225
```

At this stage the data is converted to the correct format and its header replaced by the header required by the RVS software suite.

Another issue with the conversion of the files to the RVS format is that the top timestamp is always outputted as `00 00/ 00:00:00`. The file outputted with `nclistit` is then edited in `VI` in order to alter that timestamp to the correct time and day. This is done as it would not be imported into the RVS data format with this timestamp error.

The file is then passed to the `titsil` application which simply reads the data from the text file that was created and enters it as records in the RVS data file.

cat \$DARAWBASE/gyro.225 | titsil gyronmea –

This command reads the gyro.225 file in the /rvs/raw_data directory and passes it to titsil for input in the gyronmea file. The – dictates that all variables will be included.

The TECHSAS system was set to create a new file for each day, however on days when errors occurred multiple files were created as that is normal practice for Techsas when it is restarted.

During this cruise techsas was successfully used to log 3 new sensors bought on board by the University of Rhode Island, after slight tinkering due to differences in data output (lost in translation in e-mail correspondence) the logging procedure began and there were few issues with techsas logging these instruments. Despite having checked the devices cabling and route to the system some confusion at the beginning of the cruise resulted in the 2 of the devices (both Gas Tension devices) being logged by the opposite name. The devices were swapped at the beginning of the cruise and it is now apparent that they should not have been. This is easily rectified using the RVS systems applications.

Fugro Seastar DGPS Receiver

The Fugro Seastar is the source of custom differential corrections based on its position fixed by its internal Ashtec G12 GPS module. It outputs corrections via RS-232 using the standards RTCM message. The message is distributed among all GPS receivers where they are used to compute their own DGPS positions.

The Fugro Seastar functioned correctly throughout the cruise. There have been issues with this system previously not detecting the correct satellites due to location. However in this instance it performed correctly and differential positions were calculated throughout the cruise.

The module for logging this instrument was written prior to the cruise sailing and was run during the cruise. The system reported no errors however it failed to log the ‘sec’ field that holds the utc time of the data sent from the gps. This field appears blank in the NetCDF files for this system PASHRPOS-G12.PASHR.

The Level A B system has correctly logged this data for the entirety of the cruise and was used in bestnav calculations.

The issue was resolved during the cruise however due to problem with the way techsas work you cannot change the code and compile a binary without shutting down logging to ensure it creates a new file. As this means that logging ceases I was not willing to make the change during science.

Trimble 4000 DS Surveyor

The Trimble 4000DS is a single antenna survey-quality advanced GPS receiver with a main-masthead antenna. It uses differential corrections from the Fugro Seastar unit to produce high quality differential GPS (DGPS) fixes. It is the prime source of scientific navigation data aboard RRS Discovery and is used as the data source for

Navigation on the ships display system (SSDS). This system worked reliably during the cruise following its replacement during the port call prior to sailing. This antenna is directly on top of the mast and suffers from negligible interference from other items on the mast. It is also almost directly at the centre point of the ship making it an ideal navigation system.

Ashtec ADU-2

This is a four antenna GPS system that can produce attitude data from the relative positions of each antenna and is used to correct the VMADCP for ship motion. Two antennae are on the Bridge Top and two on the boat deck.

The Ashtec system worked reliably throughout the cruise with some gaps that are quite usual with this system due to the amount of calculations necessary. No Large data gaps are present. The ADU-2 forms part of the bestnav system which is an assembly of multiple GPS signals including the gyronmea and emlog stream in order to calculate the best possible position, speed heading pitch and roll of the ship. The Ashtec is not as reliable as the G12 and the 4000DS mainly due to its low position on the ship it is hard for this system to maintain locks on satellites when the ship is maneuvering and the bridge and main mast come into its direct line of sight with the satellites.

Gyronmea

The Gyronmea is a file that receives its data from the Ships gyro compass located on the bridge. There are two such Gyros on the bridge and we are able to use either one of them as a source of heading. The selected Gyro is logged by the TECHSAS system and is used as part of the bestnav calculation.

RDI Ocean Surveyor 75KHz Vessel Mounted ADCP (VMADCP)

Data from the RDI Ocean Surveyor was logged throughout the cruise and backed up to the /data32 shared data area. The ADCP 75 was setup to follow the settings as agreed with Ricardo Torres. The system was reconfigured to 4 meter bins in order to achieve a better resolution through the mixed layer.

50 Bins

4 m

8 m Blanking Distance

This can also be viewed in the command files that were used for both legs of the cruise that are included in the ADCP area of the data archive.

RDI 150KHz Vessel Mounted ADCP (VMADCP)

Following several difficulties in the previous cruises with this system the transducer head was replaced prior to sailing D317. The ship was attended by a Teledyne RDI consultant who assisted in checking over the setup of the ADCP 150Khz and ADCP 75Khz systems. The transducer had been giving several errors during the cruise which would indicate that the transducer head was damaged. Problems also existed with the PC that was in use. No navigation signals were being received by the unit and the ensemble out would not function. This ensemble out allows the RVS system to grab data on a 2 minute interval from the ADCP 150Khz system. Following the visit by the

RDI Consultant the system was able to handle both navigation input and ensemble output. However that seems to have now changed once more. The ADCP 150 is still receiving the GPS messages and still has the setup within its file to handle the data however it does not seem to function correctly. This appears to be a fault in the way that the VMDAS software is handling the navigation or possibly the comm ports. The system was logged without navigation to the local hard disk and also to the RVS Level C where it can be concatenated with the navigation data. This system is due for upgrade next year during the 2008 dry dock.

50 Bins
4 m
8 m Blanking Distance

Chernikeef EM log

The Chernikeef EM log is a 2-axis electromagnetic water speed log. It measures both longitudinal (forward-aft) and transverse (port – starboard) ships water speed.

The EM log was not calibrated prior to the cruise and was reading at -0.8 knots astern when alongside (-0.8 knots)

The system was logged by the TECHSAS logging system.

Simrad EA500 Precision Echo Sounder (PES)

The PES system was used throughout the cruise, with a variation between use of the Fish and use of the hull transducer. The PES was deployed on the fish due to the inaccuracy of the Echo sounder around mindelo, up to that point the hull transducer was used.

The PES outputs its data to a stream called ea500d1 on the TECHSAS System.

EA500 on Hull Transducer 07 317 095859
EA500 on Fish 07 330 100500
EA500 off 07 331113500
EA500 on PES 07 331 1800
EA500 on Hull 07 3501600
EA500 off at 07351090304

Surfmet System

This is the NMFD surface water and meteorology instrument suite. The surface water component consists of a flow through system with a pumped pickup at approx 5m depth. TSG flow is approx 25 litres per minute whilst fluorometer and transmissometer flow is approx 3 l/min. Flow to instruments is degassed using a debubbler with 40 l/min inflow and 10/l min waste flow.

The meteorology component consists of a suite of sensors mounted on the foremast at a height of approx 10m above the waterline. Parameters measured are wind speed and

direction, air temperature, humidity and atmospheric pressure. There is also a pair of optical sensors mounted on gimbals on each side of the ship. These measure total irradiance (TIR) and photo-synthetically active radiation (PAR).

The Non Toxic system was enabled as soon as we were far enough away from land.

Surfmet Non Toxic On 073170950

Surfmet Non Toxic Off 073310825 (Port Call)

Surfmet Non Toxic On 073311800

Surfmet Non Toxic and Logging Stops 07351090304

Salinity samples were taken on a daily basis while the Non toxic supply was taken, 1 ample a day were taken for calibration of the TSG. For Times and Salinity Values Please see the Excel Sheet in the tsg_salin folder

The data here shows a good standard trend for all data points used. Some data points were removed due to them affecting the regression. This amounted to a small number of points and indicates a bad sample. The TSG shows that it is reading quite a bit higher salinity value than the autosal samples done.

There are several files in the system for Surfmet due to the Level B having a time error.

Surfmet is the Level B logged file

Surfmet2 is the TECHSAS Logged file

Surftmp is the cleaned level B file

Surftmp2 is the cleaned techsas logged file

Protsg is the protsg version of the level B data set

Protsg2 is a product of a matlab program that I produced during the cruise. IT simply takes the protsg as an input file, uses the coefficients from the Excel Autosal file and applies them to all the data.

Meteorological Instrumentation

Measurement	Wind Speed	Spec : Range 0.4-75m/s, output: 0-75m/s = 0-750Hz, Accuracy: +/- 0.17m/s ²
Manufacturer	Vaisala	
Model N^o	WAA151	

Measurement	Wind Direction	Spec : Range: 0-360°, output: 6bit parallel grey code
Manufacturer	Vaisala	
Model N^o	WAV151	

Measurement	PAR	Spec : Range 350-700nm output depends on sensor, (see cal sheet), Accuracy: +/-5%
Manufacturer	ELE	
Model N^o	DRP-5	

Measurement	TIR	Spec : spectral Range 335-2200nm (95%) irradiance 0-1440W/m ² , Sensitivity 9-15uv/W/m ²
Manufacturer	Kipp & Zonen	
Model N^o	CM 6B	

Measurement	Temp & Humidity	Spec : Temp, -20 - +60°C, accuracy at 20°C, +/-0.4°C Humidity, 0-100% RH Accuracy, +/-4%
Manufacturer	Vaisala	
Model N°	HMP45	

Measurement	Barometric Pressure	Spec : Range 800-1060mbar, Accuracy at 20°C : +/-0.3mbar
Manufacturer	Vaisala	
Model N°	PTB100A	

Surface Sampling

Measurement	Housing Temperature	Spec Range:-2 - +32°C, accuracy: +/-0.003°C, res:0.0001°C Stability: +/-0.0005 °C
Manufacturer	FSI	
Model N°	OTM	

Measurement	Remote Temperature	Spec Range:-2 - +32°C, accuracy: +/-0.003°C, res:0.0001°C Stability: +/-0.0005 °C
Manufacturer	FSI	
Model N°	OTM	

Measurement	Conductivity	Spec : Range 0.4-75m/s, output: 0-75m/s = 0-750Hz, Accuracy: +/-0.17m/s ²
Manufacturer	FSI	
Model N°	OCM	

Measurement	Turbidity	Spec : Range 0-100% or 90-100%, Output: 0-5vdc Or -5 - +5vdc Accuracy: 0.1%
Manufacturer	Seatech	
Model N°	20cm	

Measurement	Fluorescence	Spec : Output ∞ emitted light at 685nm Output: 0-+5vdc
Manufacturer	Wetlabs	
Model N°	WETStar	

Plots

Plots were made using the standard bestnav system on DVD1.

Plots were made for each station using Matlab 2006b. These can be found on the DVD along with the RVS Cruise Data.

CASIX PCO2 System

This system is an autonomous pCO₂ system developed by PML and Dartcom. I am not entirely sure of the full details of this and so I'm not going to pretend like I do for fear of being incorrect. I advise that you contact Nick Hardman-Muntford at PML for information. The system was run at the same time as the Surfmet system and cleaned periodically. The PCO₂ ProForma can be found on the data archive.

PCO₂ On 073170952

PCO₂ No Water 073310825 – 07331180000

PCO₂ Off 073510900

Network Services

The networking system was used continually throughout the cruise with connections on the monkey island being used for computers logging GPS and Drifter buoy positions. The system in general performed well, however some comments on the speed were submitted. The ships old 10base2 network that is available in cabins is currently being replaced in order to help improve services and speed.

Wireless network

Previous known network issues had been addressed prior to the cruise allowing the existing system to continue to work uninterrupted. Wireless worked throughout the cruise where available.

E-mail system

The email system worked fairly well for the entire length of the cruise. There were several issues due to the heading of the vessel which were unavoidable at certain stations due to the head to wind requirement. Email's were done at opportunistic times whenever the samplers were turned off or we were required to re maneuver back to station

Data Storage

Two USB external hard drives are being use as a RAID 0 mirror hosted by Discovery3 at the /data32 export. The mirror uses the modern meta device commands available in Solaris 10. This increases storage robustness by providing another layer of redundancy at the online storage level. The maintenance and administration of the disk set is minimal and the performance more than adequate.

All cruise data except for the /rvs path were stored on this storage area. Access was given to scientists to some of the folders via Samba shares.

All CTD, FRRF and Minilog data was backed up to these drives on acquisition.

Level C data was logged to the discovery1 internal disk, Techsas backs its data to here under /rvs/pro_data/TECHSAS and also stores it on its own internal raided drive array.

Data Backups

Backups of the Level C data were done twice daily as a tar file to DLT tape and LTO tape. Alternating between the standard backup below and a full /rvs backup. The following paths were included in the tar file:

/rvs/raw_data

/rvs/pro_data
/rvs/def7/control
/rvs/users

In addition to the redundancy provided by the RAID 0 pair, daily backups of the /data32 directory were done by a level tar of the file system to the LTO 2 tape. The whole disk was backed up not just current cruise data.

The LTO2 system was backed up on a daily basis in a rolling 2 tape system.

Data Archiving

The proposed data archive will consist of the following components.

- 1) All CTD data
- 2) All FRRF data
- 3) All TECHSAS NMEA and NetCDF data files
- 4) All RVS Data Streams including Listit Text file outputs
- 5) All Drifter data from miniloggers.

All data was written to DVD with 10 copies made.

1 copy for BODC (LTO)

1 copy for PSO

1 copy for RRS DISCOVERY

1 copy for return to NOC

A Backup was also put on my personal hard drive and the hard drive of the PSO as a 'just in case' measure.

8. Disclaimer

All data in this Cruise Report are provisional. As the various data sets are finalised they are being archived by the British Oceanographic Data Centre (BODC <http://www.bodc.ac.uk/>). No data from this report should be published or otherwise presented without the express permission of the originators named in the Scientific Reports.

9. Acknowledgements

A research cruise demands a huge amount of work from those who sail onboard and a whole host of people who stay onshore. The efforts extend over many months both before and after the research cruise itself. This means that there are lots of people to thank - sincere apologies if I have forgotten anyone!

For their support onboard RRS Discovery: First and foremost a huge vote of thanks to the Master, Roger Chamberlain and all of the Officers, Engineers and Crew of RRS Discovery D325 for the excellent service and support they provided throughout the INSPIRE research cruise. We are also very grateful to have had an excellent technical team onboard from the National Marine Facilities Division (NMFD): our thanks to John Wynar, Dave Teare, Chris Barnard, Dan Comben and Dave Turner for their expert help in keeping all the various sampling and computing systems running.

For shore-based support we are grateful to: Phil Williamson, the co-ordinator for the UK SOLAS programme for all his excellent help and support before, during and following D325. The Southampton-based NMFSS staff for their support. Hamilton Y Compania S.A., the ships agents in Tenerife. Gwen Moncoiffe and Jenny Andrew at BODC for their help, advice and data archiving. The NEODAAS 'Cruise Support' team, especially Rory Hutson, Jamie Shutler, Peter Miller, Stephen Willey and Mike Grant, for providing the satellite images. Dawn Ashby at PML and Rosie Cullington at UEA for web support for the INSPIRE blog. Special thanks to Malcolm Woodward (PML) for dealing with all the pre- and post-cruise logistics.

I would like to thank the whole INSPIRE science team for all the excellent work done right from the initial stages of writing the research proposal through to the D325 research cruise itself and beyond. We set ourselves some challenging tasks, managed to do most of them and produced some great data.

Last but not least thanks to the NERC UK-SOLAS programme for funding the INSPIRE project.

Gill Malin

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I11. Photo Gallery

SCIENTISTS & TECHNICIANS



Gill Malin



Claire Hughes



Gareth Lee



Janina Woeltjen



Phil Nightingale



Steve Archer



Tim Smyth



Amanda Beesley



Darren Clark



Denise Cummings



Jo Dixon



Laura Goldson



Carolyn Harris



Susan Kimmance



Andy Rees



John Stephens



Glen Tarran



Gavin Tilstone



Malcolm Woodward



Rosie Chance



Rachel Shelley



John Wynar



Chris Barnard



Dan Comben



Dave Teare



Dave Turner

OFFICERS & CREW

(Names are given left to right)



David Hartshorne (Purser Catering Officer), George Parkinson (Chief Engineer), Richard Warner (Chief Officer), Roger Chamberlain (Master) and Steve Bell (2nd Engineer).
Photo: Claire Hughes.



Malcolm Graves (2nd Officer), Roger Chamberlain (Master) and Michael Hood (3rd Officer). Photo: Steve Bell.



ENGINEERING STAFF
Back Row: Dean Hurren (ETO Electrical Technical Officer); Ian Collin (3rd Engineer); Stephen Bell (2nd Engineer); Leslie Hillier (ERPO Engine Room Petty Officer or Motorman); George Parkinson (Chief Engineer).
Front row: Allan MacLean (3rd Engineer); Andrew Smith (Engineer Cadet).
 Photo: Colin Atkinson

CATERING STAFF & STEWARD
 Wilmot Isby (Chef), Peter Lynch (Head Chef), Jeffrey Orsborn (Steward).
 Photo: Rachel Shelley.



DECK CREW
Back Row: Paul Farley (Seaman), Iain Thomson (Chief Petty Officer Deck), Colin Atkinson (Seaman), Mark Moore (Petty Officer Deck). **Front row:** Lee Stephens (Seaman), Gerry Cooper (Seaman), Stephen Smith (Chief Petty Officer Scientific).
 Photo: Gill Malin.

D325 End of cruise group photo



Names are given left to right

Back row: John Stephens, Steve Archer, John Wynar (NMF Technician), Janina Woeltjen, Jeff Orsborn (Steward), Gerry Cooper (Seaman), Dave Teare (behind post! NMF Technician), Carolyn Harris, Dave Turner (NMF Technician), Amanda Beesley, Mark Moore (Seaman), Rachel Shelley, Steve Smith (Chief Petty Officer Scientific), Andy Rees, George Parkinson (Chief Engineer), Chris Barnard (NMF Technician), Dave Hartshorne (Purser Catering Officer), Ian Collin (3rd Engineer).

First row standing: Paul Farley (Seaman), Gareth Lee, Tim Smyth, Darren Clark, Claire Hughes, Rosie Chance, Gill Malin, Gavin Tilstone, Glenn Tarran, Jo Dixon, Denise Cummings, Mike Hood (3rd Officer), Roger Chamberlain (Captain).

Front row sitting: Steve Bell (2nd engineer), Malcolm Woodward, Susan Kimmance, Laura Goldson. Photo: Colin Atkinson

12. Cruise blog

Throughout the D325 research cruise some of the scientists, officers and Crew wrote 20 short pieces and/or provided photographs they had taken onboard for the cruise blog. In most cases the blogs were posted on the web within 24 hours of writing. The idea was to share our experiences of life onboard, including aspects of the research, with family, friends and colleagues. The INSPIRE cruise blog (which includes some of the photographs above) can be accessed via

<http://web.pml.ac.uk/solas/inspire/inspire.htm> and
<http://www.uea.ac.uk/env/research/LGMAC/fieldwork/inspire>

