1. Data document sheet:

Reactive Halogens in the Marine Boundary Layer (RHaMBLe) Atlantic Ocean Cruise, RRS Discovery D319

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Abstract:
Discovery cruise D319 formed the basis of WP2 of the RHaMBLe project, aiming to provide a detailed latitudinal characterisation of marine atmospheric halogen chemistry, thereby feeding validation and constraint data to regional and global models in linked projects. A range of state-of-the-science atmospheric and water sampling instruments were deployed in D319 and the cruise transected from Lisbon, leaving on 19th May 2007, through Biscay, south past the west coast of Africa, to Cape Verde at the same time as the intensive deployment in RHaMBLe WP1 prior to passing into the Mauritanian upwelling region to assess the relative contribution to atmospheric halogens from productive and less productive waters. GC/MS instruments were deployed to measure a variety of halocarbons in both water column and atmosphere and tropospheric measurements of I2, OIO and IO were made by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS). A compact version of the FAGE system was deployed to measure IO, permitting direct assessment of RHS-induced changes in the oxidising environment through the upwelling region. A range of trace gas monitors were also simultaneously deployed on the ship to measure O_3 and NOx, with aerosol number and size distribution measurements from 3 nm to 20 μm being made by a range of mobility (SMPS) and optical instrumentation, (OPC and FSSP). Prevailing meteorological conditions and remote sensing products from NEODAAS support were used to direct the cruise in terms of geographical positioning and measurement interpretation, e.g. i) exploitation of any broad flow connection between Cape Verde and the ship to interpret measurements as process studies and ii) identification of in- and out-of-plume conditions to contrast chemistry influenced and uninfluenced by upwelling region emissions. Significant additional aerosol measurements were made as part of the UK SOLAS-funded ACMME project and measurements of pigments by HPLC were provided by collaboration with Dr Keely.

Keywords:
Atmospheric, Halogen, Iodine, Chemistry, Ozone destruction, Radicals, Aerosol

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2. Cruise scientific personnel:

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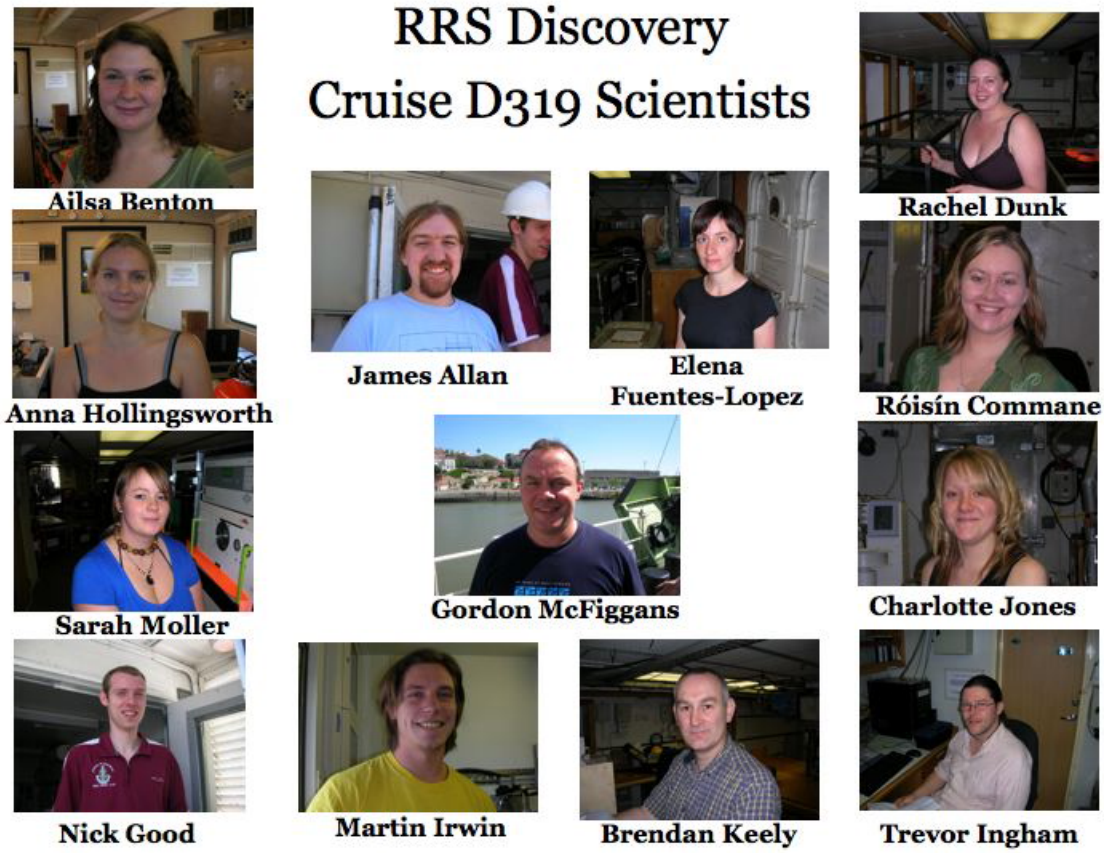
E	Dr Elena Fuentes-Lopez	Bubble tank	Dr Gordon McFiggans g.mcfiggans@manchester.ac.uk Dr James Allan james.allan@manchester.ac.uk	CAS, SEAES, University of Manchester, Simon Building, Oxford Road, Manchester, M13 9PL
F	Dr James Allan, Mr Nick Good, Mr Martin Irwin	AMS & other HTDMA, DMPS CCN		
G	Ms Sarah Moller	NO_{xy} & O_3	Dr James Lee	Dept. of Chemistry, University of York, York, YO10 5DD
H	Dr Brendan Keely	HPLC Pigments	Dr Brendan Keely	Dept. of Chemistry, University of York, York, YO10 5DD

Principal Scientist: Gordon McFiggans

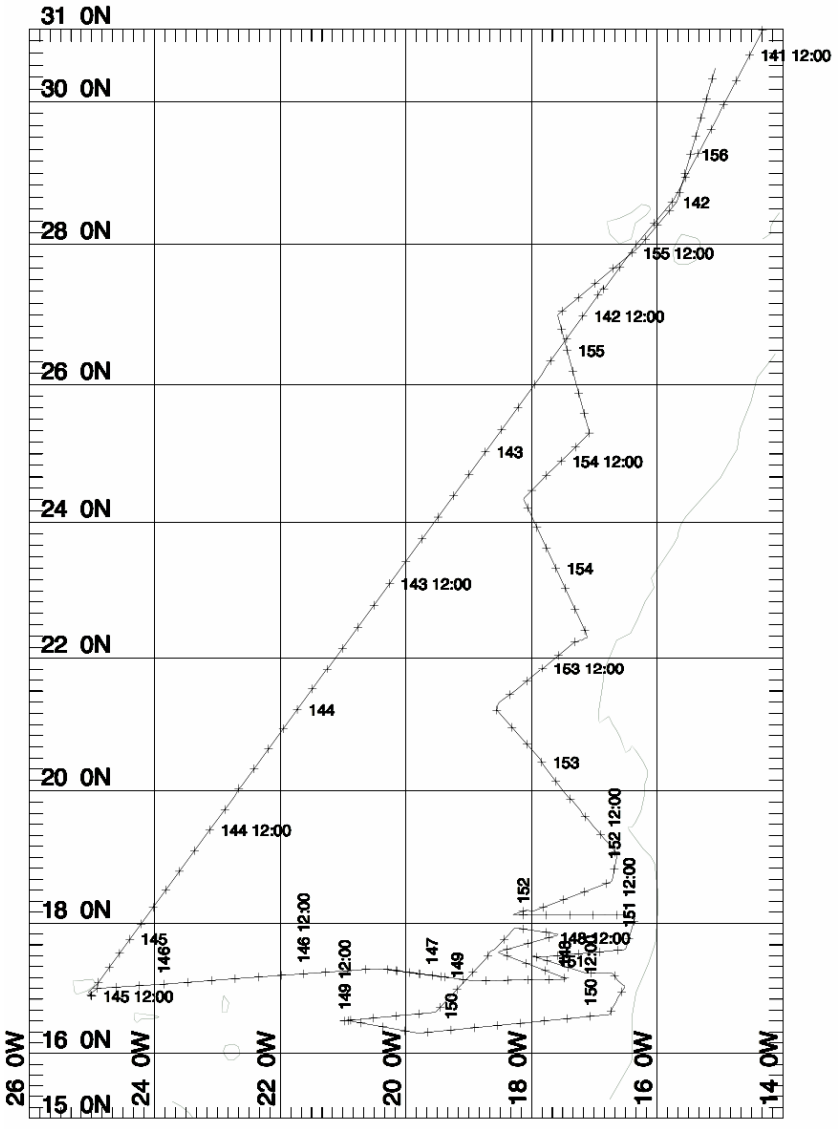


3. Scientific objectives:

Objectives: To quantify marine halocarbon emission variability and latitudinal variation, characterise *in situ* open ocean atmospheric reactive iodine latitudinal variability and characterise oxidative chemistry perturbation due to oceanic emission of halogens from the Mauritanian upwelling region.
Rationale: Transecting from the UK through Biscay, south past the west coast of Africa, through the Mauritanian upwelling, to pass Cape Verde simultaneous to the intensive deployment at the UK SOLAS Observatory on Sao Vicente, the measurements made on Discovery cruise D319 are intended to provide a detailed latitudinal characterisation of marine atmospheric halogen chemistry. This will feed validation and constraint data to regional and global models in projects linked to RHaMBLe. In addition the cruise will address a number of key scientific questions required to determine the global importance of iodine chemistry and to further our understanding of the controls of halogen chemistry in the remote ocean: i) How heterogeneous are the direct halogen sources and on what scale is the heterogeneity – does the upwelling region produce more or less halogens than the "background" region? ii) What are the relative contributions of I atoms to the remote MBL from I_2 and organic iodine? iii) Is sufficient iodine released to the remote MBL to sustain aerosol nucleation or to significantly affect the ozone budget and free radical populations?

4. Cruise overview:

Steaming down from Lisbon, between Tenerife and Gran Canaria then straight towards Sao Vicente, the southbound leg was predominantly used just to get the instrumentation calibrated and stabilized before the scientifically interesting investigations out from the Cape Verde Islands and on the return leg. On departure from Mindelo after the port call on 25th May, the Discovery headed towards the Mauritanian upwelling waters. MODIS Chla retrievals were used to guide the cruise track across the steepest gradients in biological activity to maximise potential reactive halogen signal. To maintain the maximum exposure to uncontaminated airflow, the track zig-zagged across the Chla fronts, slowly and steadily returning northwards. Prevailing meteorological conditions were used to direct the cruise in terms of geographical positioning and



D319 Cape Verde Track (2 hour ticks)

measurement interpretation, e.g. i) exploitation of any broad flow connection between Cape Verde and the ship to interpret measurements as process studies and ii) identification of in- and out-of-plume conditions to contrast chemistry influenced and uninfluenced by emissions from the upwelling region.

5. Diary cruise narrative:

The following narrative has been directly extracted from the PSO log and is a reflection of the daily science and other meetings throughout cruise D319. Very many of the perceived problems were ironed out post-cruise, hence the reporting of a measurement problem is no indication of a data problem and the reader is referred to section 7 for operational details relating to measurements.

Daily, throughout the cruise, synoptic meteorological charts, the MODIS satellite chlorophyll *a* product and modelled oceanic mixed layer depth were sent by Steve Groom of PML through the remote sensing support agreement with UK SOLAS. Forward and back trajectories, calculated using the Hysplit programme, were provided by Karen Hornsby from Lucy Carpenter's group at the University of York. Along with the remote sensing product, the trajectories were used to plan the cruise track in consultation with the Master.

Tuesday 15th May 2007 – Friday 18th May 2007.
Mobilisation in the Port of Lisbon.

Friday 18th May 2007

Scientists officially joined ship.
12:30 Signing onto ship
13:00 Safety brief
16:15 Safety muster

A brief status report on scientific instruments:
Carpenter (York). Halocarbon GC/MS, 1st instrument settled, calibrated and ready, 2nd instrument stabilising after initial "leak" problem addressed.
Keely (York). Pigment HPLC. Detector & software comms. requiring attention, otherwise functional.
Ball / Jones (Leicester / Cambridge). BBCEAS, green system aligned and operational, blue system aligned and operational. To be calibrated.
Heard (Leeds). FAGE, installed at NOC, but no major progress has been possible owing to excessive heat during mobilisation and inability to use the underway seawater cooled container air conditioning whilst alongside in Lisbon. Operators will start laser when the AC cooling capacity is sufficient.
McFiggans / Allan (Manchester). Owing to lack of power to container until 15:00 on 17th May, the Manchester mobilisation has been somewhat delayed. However, most instruments are in a state of readiness. DMPS2, CCN, Grimm1, Grimm2, Andersen1, Andersen2, MAAP, Bubble-tank & SMPS are all functioning correctly. HTDMA requires minor attention to RH probe3. DMPS1 is having problems; we are unsure as to their origin at present, but they manifest as unrealistic distribution shape. The CO and NO_x instruments to be operated by Leeds / Leicester / Cambridge in the UKORS container as required.

Saturday 19th May 2007

08:00 Cast off from mobilisation berth to move to a bunker berth to take on fuel.

12:30 Leave bunker berth. Finally underway.

Brisk winds expected along with a reasonable swell as we move into the Atlantic. We weren't to be disappointed.

15:00 Science meeting – status report for start of cruise:
Carpenter (York). Halocarbon GC/MS, 1st instrument is working and ready to sample water, 2nd instrument is not identifying peaks from standard. The fallback position is to sample from bottles using GC/MS1 when not sampling water.
Lee (York). The NO_{xy} is running well on a single channel switching between NO and NO_2
Keely (York). Pigment HPLC. The instrument is now communicating with the detector and the detector to its logging system. There is still some work to be done on logging system.
Ball / Jones (Leicester / Cambridge). BBCEAS, both systems are behaving reasonably but losing sensitivity with time; possibly due to aerosol deposition on mirrors. There are several avenues for investigation. Both spectral radiometers are operating correctly.
Heard (Leeds). FAGE, the air conditioning is operational, so operators are continuing with instrument setup and performing calibrations.
McFiggans / Allan (Manchester). DMPS2 (Dry), Grimm1, Grimm2, Andersen1, Andersen2, MAAP, Bubble-tank & SMPS are all functioning correctly. CCN flow problem and HTDMA requiring minor attention to RH probe3. DMPS1 (wet) is completely non-functional.
Sampling via the trace metal standard "Fish" is problematic. Apparently sampling is severely compromised by the wake. Unsure why the fish was moved forward as it was requested to be in the aft position. There are 3 options: sample at around 5 – 10 m depth off the starboard side if we can move the winch further out whilst underway, ii) sample of the non-toxic supply at around 5 – 10m depth or iii) move the winch to the aft position at the port call.

Sunday 20th May 2007

Significant swell and brisk northerlies are making for a good roll on the southbound leg.

08:30 Cruise management meeting; daily brief to raise points for action throughout day based on previous day's activity:
Action points for the upcoming day:
Requirement to establish container communications for emergencies and general safety purposes. A check-in and check-out procedure will be adopted, with instructions being made clear on the bridge and in the containers.
A port call has been requested at Mindelo from 08:00 GMT on 25th May until 17:00 GMT.
The bar and safety committee's will be meeting soonest and @ 10:30 on Tuesday respectively.
Incinerator and lifeboat engine emissions will affect scientific outcomes. This will be addressed at the scientific meeting at 10:30. On the southbound leg, these will be less of a problem, but on the northbound leg, any such activity will only occur after consultation.
Winch for the fish will be moved towards the side when the weather is fine and / or to the bow during the Mindelo port call.

10:30 Scientific meeting with crew:
Restrictions on crew activities were explained to the crew from all departments by scientists representing each group. These referred in particular to smoking, painting, chipping and solvent use with particular regard to location wrt the inlets.

15:00 Science meeting – status report:
Carpenter (York). Halocarbon GC/MS, 1st instrument working, ready to sample water with 2 hours frequency during daytime and air with full 24 hour coverage. 2nd instrument under investigation. 1 to 2 phytoplankton samples will be collected each day for cell counting.
Lee (York). NO_{xy} is running well on a single channel, the instrument will be taking 3 hours per day to take zeros and perform calibrations. There is up to 300 ppb of NO observed, so the sample stack is hugely impacting on the bow inlets at midships.
Keely (York). Pigment HPLC. The instrument is ready to test and awaiting solvents to be made up. Logging system is still misbehaving but there is a likely route forward.

Ball / Jones (Leicester / Cambridge). BBCEAS systems are both much improved. Green system has a slightly poorer alignment but drifts less; this is encouraging. The blue system is misbehaving more fundamentally; it is holding its alignment but giving an incorrect absorption signal. Both spectral radiometers are operating well.
Heard (Leeds). FAGE is running as well as it ever has in the lab; work is underway to improve its sensitivity from an estimated 2 ppt.
McFiggans / Allan (Manchester). DMPS2 (Dry), Grimm1, Grimm2, Andersen1, Andersen2, MAAP, Bubble-tank & SMPS all functioning correctly. CCN still has a flow problem at high supersaturation. HTDMA working well, but giving surprisingly low GF_D, we need to calibrate using $(NH_4)_2SO_4$ and NaCl at 90%. DMPS1 (wet) now has a slightly low counting long DMA. AMS working fine (barring power cuts!).

Monday 21st May 2007

Winds still brisk and northerly, but sea state a little calmer.

08:30 Cruise management meeting:
Action points for the upcoming day:
Container communications procedure has been established.
Port call at Mindelo still on schedule from 08:00 GMT on 25th May until 17:00 GMT, Katie Read on Sao Vicente will make local arrangements. Scientific crew from Dornier (James Lee / Ally Lewis) will attend ship visit in CV – hope to discuss airband / VHF comms etc...
Bar committee will meet 12:55 today.
Winch for the fish will be moved towards the side late pm today or early am tomorrow in lee of one of the Canaries (for calmer conditions) and / or to the bow during the Mindelo port call.

12:55 Bar committee meeting, Captain's Day Room.

15:00 Science meeting – status report:
Carpenter (York). Halocarbon GC/MS, 1st instrument was working until the Helium was turned off to this instrument rather than to the non-working 2nd instrument (which is still being difficult!). Now the 1st instrument (that which will be used for water sampling) will be ready to sample in the morning of 22nd after all internal components are cleaned. The 2nd (air sampling) instrument is still being investigated.
Lee (York). The NO_{xy} is still running well on single channel. The O_3 instrument has intermittent power problems – likely resulting from the power supply and voltage regulator assembly. This is a non-serviceable unit and the effect of lowering the temperature on its performance will be investigated (since there is an indication that the unit is overheating).
Keely (York). Pigment HPLC. The instrument is behaving well now (the minor problems with changing the gradients etc… have been solved) and the instrument is ready to measure the standards.
Ball / Jones (Leicester / Cambridge). Both BBCEAS instruments require NO_2 for calibration of the mirrors. The green system has better alignment than yesterday and is free from drift. The blue system still has problems with a strange spectral shape and the mirrors are suspected. It will be possible to characterise and calibrate both systems once the problems with the gas cal. / NO_x box combination have been sorted out. As a fallback, it is possible to titrate NO with O_3 to produce NO_2. Both spectral radiometers are behaving well.
Heard (Leeds). Still working to improve FAGE sensitivity from an estimated 2 ppt by reducing the laser scatter by improved baffle design. The aim is to be ready by Friday.
McFiggans / Allan (Manchester). Grimm1, Grimm2, Andersen1, Andersen2, CCI, MAAP all functioning correctly. The bubble-tank, Grimm & SMPS are being tested using water from the non-toxic supply. DMPS2 (Dry) has had serious problems; the logging computer operating system was reinstalled and the locking up problem hopefully rectified (it was initially thought to be a hardware problem and there still may be driver complications). The CCN flow problem at high supersaturation was cured by operating at a more gradual gradient. HTDMA working well; $(NH_4)_2SO_4$ $GF_{D,90\%}$ looks reasonable and it's currently being used as a training instrument! The

long DMA of DMPS1 (wet) is dismantled. The AMS is working fine but is still subject to occasional power cuts.
The winch carrying the trace metal standard “Fish” will be moved further out in the calmer waters expected in the lee of the Canaries tomorrow morning.

Tuesday 22nd May

The waters are much calmer today. Bright and still, the ship was relatively motionless first thing this morning as the crew repositioned the winch carrying the “Fish” closer to the side of the ship. After setting off again, it was found that it still ran too close to the ship and it was decided to run from the gantry crane. This proved satisfactory, holding the “Fish” in exactly the correct position, some 1 to 1.5 m below the surface.

Arrangements are in place for a bus from the port to the observatory and back and for a meal near the port. Thanks to Katie Read. There will be a meeting at the observatory and a reciprocal visit from the ground-based scientists to the ship. 2 local dignitaries (Bruno & Oscar) will attend the ship visit and (up to) 4 ship crew will attend the lunch.

10:30 Safety Committee Meeting, Library; no major problems affecting the scientific crew were highlighted.

15:00 Science meeting – status report:
Carpenter (York). Halocarbon GC/MS, 2 working instruments; the air instrument had a sticking solenoid valve which has been fixed and the water instrument has now been cleaned up. The former is running air standards and is ready to sample air immediately. There is already an indication that bromocarbons are observable in the air. The water instrument is seeing the whole range of halocarbons in the non-toxic supply and will run from the “Fish” once the line is passivated.
Lee (York). The NO_{xy} is still running well on single channel. The O_3 instrument is dead, but one can be borrowed from the observatory in CV. The NO_{xy} is currently seeing around 100 ppt of NO; whilst this is not quite marine background it’s 3 orders of magnitude down on stack emissions. The ship is making its own headwind by beating the rather slack northerlies.
Keely (York). Pigment HPLC. The instrument has run all standards successfully and is now running 3L samples from the non-toxic supply.
Ball / Jones (Leicester / Cambridge). Both BBCEAS still require NO_2 for calibration of the mirrors and hence cannot provide a quantitative signal. A N_2 flush flow is helping to keep the mirrors clean from seasalt, so we’re hopeful that a calibration may demonstrate that the mirrors have not degraded. There is the possibility of titrating NO with O_3 from clean air exposed to a mercury lamp to produce NO_2. Both spectral radiometers behaving well after data from one was lost for 6 hours.
Heard (Leeds). FAGE laser scatter has been reduced to 1/5 that in the lab by improved baffle design. Operators are starting to calibrate.
McFiggans / Allan (Manchester). Grimm1, Grimm2, Andersen1, Andersen2, CCI, MAAP all functioning correctly. The first set of impactor substrates will probably not be useful due to stack contamination but were a useful test of the system. The bubble-tank, its Grimm & SMPS are now using water from the “Fish”. The SMPS needs sheath drying to overcome arcing problems. DMPS2 problems seem to have been resolved. The CCN is working well and is being calibrated; the same applies to the HTDMA. The long DMA of DMPS1 (wet) is still reading lower than that of DMPS2. The AMS is working fine but is still subject to occasional power cuts.

The provision of satellite products is converging on a mature configuration & trajectories are starting to arrive (possibly in need of a little refinement, but they will be useful).

Wednesday 23rd May

Today is another calm one. The weather is bright and still, with a few fair weather cumulus. Wind from NW (330 degrees), so coming across starboard.

08:30 Cruise management meeting:
Action points for the upcoming day:
Port call at Mindelo still to be confirmed for 08:00 GMT on 25th May until 17:00 GMT, customs declaration to be signed by all crew (incl. scientific). The Master has requester that a representative from the Dornier operations crew attend the ship visit in CV.
Emergency drill & boat muster to take place at 16:15 today.
At Mindelo, the winch for the fish will be moved aft to redeploy it. The Master is unhappy with its deployment from the starboard gantry.

15:00 Science meeting – status report:
Carpenter (York). Halocarbon GC/MS, 2 working instruments; the air instrument is sampling continuously from ambient and the water instrument is alternating between the fish and non-toxic supplies. There are bubbles visible in the line from the fish but not in samples decanted from the line. So far as halocarbons are concerned, there appears to be little difference between each water source, with all halocarbons present. Comparison between each supply will continue for halocarbons (and also for pigments & cytology). In the air samples it appears that there are bromo- and possibly chlorocarbons, but not iodocarbons.
Lee (York). The NO_{xy} is still running well on single channel and the O_3 instrument is still dead. The NO_{xy} is currently seeing around 50 to 100 ppt of NO and 500 to 600 ppt NO_2; again, this is not quite marine background but is almost 3 orders of magnitude down on stack emissions.
Keely (York). Pigment HPLC. The instrument has run a few samples from the non-toxic supply, on filters from 3L samples. The chlorophyll level is around 0.06 microgramme / L, indicative of oligotrophic, very low productivity waters. For comparison, the fluorescence instrument is giving readings below the concentration of its blank and so is not directly useful. Comparison will be made between the non-toxic supply and the fish supply.
Ball / Jones (Leicester / Cambridge). It has been decided to calibrate the BBCEAS systems using the absorption in the O_4 band (and a water absorption feature in the green instrument) rather than NO_2. The mirror characterisation that is achieved will be applied to data after the event. Both spectral radiometers generally behaving well, though one has lost a little data in the last 24 hours; there is 50% redundancy in the system, so this loss is not critical.
Heard (Leeds). FAGE is being calibrated (using CF_3I that will not contaminate other groups, apparently) and will be ready to measure by tomorrow.
McFiggans / Allan (Manchester). Grimm1, Grimm2 and MAAP all functioning correctly. Seeing clean marine coarse mode and black carbon loading. Andersen1 (quartz), Andersen2 (cellulose), CCI (foam) all been sampling well. The bubble-tank, its Grimm & SMPS are now using water from the "Fish" and the relationship between flow and aerosol distribution is being tested. The SMPS is measuring dry using a sheath drier. DMPS2 (dry) is measuring high wrt total CPC and DMPS1 (wet) has a long-standing software problem causing it to read the flows (and hence calculate number and size) incorrectly. The CCN is working well and has been calibrated, though the calibration needs to be repeated at the mid-range sizes. The HTDMA has no problems. The nitrate calibration for the AMS is being processed and the size calibration is yet to be done. It is currently sampling from ambient.

Discussion of the satellite and meteorological product availability and use is still underway. It is likely that we will need to do relatively extensive mapping in a grid pattern and process the data *a priori*.

16:15 Emergency drill & boat muster replaced with a "safety quiz" and demonstration donning of an immersion suit.

Thursday 24th May

Another calm and steady, bright day in NW (330 degrees) light winds, more humid than yesterday.

08:30 Cruise management meeting:
Action points for the upcoming day:
Port call at Mindelo has been confirmed for 08:00 GMT on 25th May.
A piracy policy (essentially "minimum resistance") and possible lockdown strategies, to secure essential spaces, were discussed.
Users of the fish and non-toxic water supplies to be asked when the former should be lifted and the latter closed when approaching port.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS, instruments are running; the air instrument is sampling continuously from ambient and the water instrument is alternating between the fish and non-toxic supplies, doing 4 samples per day from each supply, with shift working for coverage. Both instruments will be calibrated to provide concentrations by tomorrow. In air it is possible to detect $CHBr_3$, $CHCl_3$, CH_2Br_2, CCl_4 etc… - but generally no iodine species (possibly CH_2I_2 in 1 sample).
Lee (York). The NO_{xy} is still running well on single channel and the O_3 instrument is still dead. The NO_{xy} is currently seeing around 50 to 60 ppt of NO and around 400 ppt NO_2; again, this is not quite marine background but is almost 3 orders of magnitude down on stack emissions. Overnight last night, there were fewer NO emissions than previous night, but the 10 minute average values are still definitely non-zero and are comparable to daytime levels.
Keely (York). Pigment HPLC. A comparison has been made between the fish and non-toxic supplies , but unfortunately the pigment values were too low to quantify, being around the limit of detection. Two more samples are being prepared for this afternoon's analysis, however the fish samples take several hours to filter whilst the non-toxic supplied samples only take around 20 minutes – an indication that there is a difference between water sampled at 5 – 7 m and 1.5 – 2 m.
Ball / Jones (Leicester / Cambridge). Both the blue and green BBCEAS systems are sampling ambient air at present. The data is being inspected, but the blue system (IO) is seeing very little and we do not yet know about the green (I_2) system.
Heard (Leeds). The FAGE inlet is in position and is sampling ambient air. IO is below the detection limit, which is 2 (0.8, 0.6) ppt for 1 (5, 10) minute integration times.
McFiggans / Allan (Manchester). Grimm1, Grimm2 functioning correctly, capturing clean marine coarse mode. The MAAP is seeing background black carbon loadings – though has been picking up e.g. ship / island plumes. Andersen1 (quartz), Andersen2 (cellulose), CCI (foam) all been sampling well. We will now synchronise the CCI and Andersen using cellulose filters to enable an intercomparison of ion loadings using IC. The bubble-tank has been modified to use two water jets and evaluate the effects of the modified flow on the aerosol size distribution using the Grimm & SMPS instruments with water from the "Fish". DMPS2 (dry) is still measuring high wrt total CPC and is currently still being used to calibrate the CCN. The software on DMPS1 (wet) has been changed. The CCN is still being calibrated. The HTDMA has no problems. The AMS is sampling ambient air with no problems.

Fish to be brought in and non-toxic supply switched off at 22:00 in preparation for landing at Mindelo tomorrow.

Friday 25th May

We've chosen a hot, bright and calm day in light winds for our port call in Mindelo.

08:00 Brought alongside in Porto Grande, Mindelo.

09:30 (08:30 CV time = GMT – 1) Our bus arrived at the port to take us to the observatory.

10:00 Site visit at the observatory providing an opportunity for the ship scientists to familiarise themselves with the measurements being made at the observatory and the personnel involved.

11:45 The bus departed to take us back to the ship.

12:15 We arrived back at the ship to provide an opportunity for the observatory scientists to familiarise themselves with the measurements being made onboard and the personnel involved. The Dornier aircrew were already on the bridge, liaising with the Master for the following day's flying.

14:00 A splendid lunch was thrown at the Porto Grande Hotel; many thanks to Katie Read for organising this.

16:00 All ship scientists returned onboard.

17:00 The Discovery departed Mindelo, into slightly rougher seas, with an easterly bearing.

19:00 The scientific crew and the Master had a lengthy and necessary discussion about the cruise track planning, using all satellite data, windfields, trajectories and online monitoring facilities to select the most scientifically appropriate course. This is to be reviewed daily in the light of emerging information.

Saturday 26th May

We've set off eastwards into more overcast skies with heavier northerly winds. Cutting across the prevailing winds is causing some roll which, though not particularly drastic, is more uncomfortable than the calm passage prior to the port call.

08:30 Cruise management meeting:
The subject of piracy was briefly addressed and the authorities in Kuala Lumpar have advised that there have been no recent reported incidents in the local waters, but that due vigilance should be employed. Communication with the aircraft was discussed.
The fish was redeployed on the starboard side of the aft deck at Mindelo. This has caused problems with no turn to port being possible.

10:00 Communication with James Lee (representing the Dornier crew) over Iridium:
It was stated that the Discovery position at 12:00 CV time (13:00 GMT) will be 17°13′N 21°21′W, heading 086° at 10.5 knots. We will continually monitor 123.4 MHz on the airband radio. The overflight is scheduled for around 1.5 hours after take-off at 13:00 GMT. Information about the next flying day on offer, and the ability to deploy from Sal, was requested.

10:30 Security briefing to address the policy on the occasion of piracy.

14:30 Dornier overflight. Approached from stern at 500 feet, performing stack to 10000 feet over the ship before continuing beyond the ship on the same bearing and returning to base on Sao Vicente. Visual contact from 14:45 until 15:30. Difficulty with radio and satellite phone communication.

15:30 Science meeting – status report:
Carpenter (York). The calibrations on both halocarbon GC/MS instruments appear fine with minor queries about a few of the standard compound in the air instrument; the air instrument is sampling continuously from ambient and the water instrument is largely measuring from the non-toxic supply. The fish is sampling too obviously in the wake to be of use and it is necessary to move it to the gantry again. In air it is possible to detect $CHBr_3$, $CHCl_3$, CH_2Br_2, CCl_4 etc… and from 11:00 CH_2I_2 has been observed.

Lee (York). The NO_{xy} instrument is now running well in dual channel configuration (the zeros are now comparable after it has settled down) and the new O_3 instrument (brought onboard in Mindelo) is working well, even though a large calibration correction must be applied. The NO_{xy} is currently seeing less than about 20 ppt of NO (compared with its DL of about 8 ppt on minute averages) and around 400 ppt NO_2; the O_3 instrument is measuring around 30 to 40 ppt.
Keely (York). Pigment HPLC. There has been no great benefit to further sampling in the non-productive waters experienced recently. Since the fluorescence has been rising, a new sample from 12:00 has been put on for analysis.
Ball / Jones (Leicester / Cambridge). Both the blue and green BBCEAS systems are sampling ambient air at present. There is significant extinction in both cavities, but most, if not all, of this is likely due to aerosol. There are significant problems with alignment in the cross-winds, and procedures must be put in place to ensure alignment and calibration are carried out safely. The spectral radiometers are performing well.
Heard (Leeds). There has been little signal observed in the FAGE instrument above the detection limit, though there is an indication that the signal is higher outside the container than inside. There is a possible systematic negative offset on the order of 1 ppt, possibly due to NO_2. This needs to be tested by providing known NO_2 concentrations. The instrument is sampling ambient air. The IO detection limit is now 0.5 (0.3) ppt for 1 (10) minute integration times.
McFiggans / Allan (Manchester). Grimm1, Grimm2 functioning correctly, capturing clean marine coarse mode. The MAAP is seeing background black carbon loadings. All impactors have been sampling as planned and the CCI and Andersen using cellulose are now synchronised. The bubble-tank using two water jets is being used to compare samples from the fish and the non-toxic supply. DMPS2 (dry) is still measuring high wrt total CPC and DMPS1 (wet) is running well on dry, but cannot yet be humidified. The CCN has been calibrated and is awaiting calibration validation. The HTDMA has no problems but requires D_0 and NaCl calibration. The AMS is sampling ambient air with no problems.

The fish is to be redeployed from the starboard gantry.

Sunday 27th May

Overnight we tracked eastwards across a biologically productive feature and back again with the intention of traversing the same patch this morning to make a day / night comparison. The productivity as indicated by the fluorescence chlorophyll proxy is showing good correspondence (mirror-imaging) for the first two legs, giving confidence that the track is effective. We've set off eastwards again, into similar conditions as yesterday (overcast skies with relatively heavy northerly winds).

08:30 Cruise management meeting:
There is still a pronounced list to starboard, not helped by the fish on the gantry. This will be largely corrected by using and redistributing the fuel onboard.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, and in air CH_2I_2 has been observed continuously from 11:00 yesterday with CH_2ICl from early today.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration seeing 400 to 600 ppt NO_2 (1 to 2 ppb earlier today) and slightly higher NO than yesterday. The new O_3 instrument is still measuring around 30 ppt.
Keely (York). Pigment HPLC. The instrument has been running from the non-toxic supply and the type of pigments observed indicate a healthy community of primary producers with no senescence. It is not yet clear whether the concentrations track the fluorescence measurements.
Ball / Jones (Leicester / Cambridge). The mirrors in both the blue and green BBCEAS systems are experiencing heavy salt deposits. Though these are readily removed, it will be necessary to try to prevent this occurring to alleviate signal degradation. There are various options available including shielding some of the cavity length. The alignment problems (operator soaking

included!) are significant. It was decided to coordinate the alignment with the ship track planning to reduce the exposure to poor conditions (turning around dawn and dusk, shielding the alignment from the worst of the weather). Both spectral radiometers are behaving well but need cleaning.
Heard (Leeds). There is an indication that IO is being observed by FAGE its detection limit sporadically, but we must try to understand the negative offset. 2 tests are required; i) overfilling the inlet with N_2 to see if the offset disappears and ii) providing known NO_2 concentrations and observing any correlation with offset.
McFiggans / Allan (Manchester). All instruments running well on ambient with a few minor problems, the following noteworthy; significant motion has caused the bubble-tank outlet to feed water to the Grimm OPC. This has been dried out, but recurrence must be avoided. DMPS2 (dry) is still measuring high wrt total CPC and DMPS1 (wet) is awaiting humidification correction (e.g. by warming bubbler). The CCN is still awaiting calibration validation. The HTDMA D_0 and NaCl calibrations are still required.

The intention is to conduct further "sawtooth" passes across the predicted fronts in biological activity.

Monday 28th May

Yesterday we continued in an easterly direction to cut into the inshore upwelling region for the first time before heading back out in a WNW direction to conduct the first sawtooth across this productivity "hotspot" feature. We arrived in relatively dead waters for this morning. The productivity as indicated by the fluorescence chlorophyll proxy is not entirely tracking the satellite maxima. The conditions are similar to yesterday (overcast skies with relatively heavy northerly winds).

08:30 Cruise management meeting:
The MAAP instrument in the forward container has been indicating high concentrations of black carbon corresponding to the ship turning at the waypoints. It was noted that, since the fish has been redeployed from the gantry, all turns have been conducted to starboard to avoid collision with the hull. This has meant that turns to starboard at the end of eastbound legs have exposed the ship to stack emissions. Henceforth all turns will be into the wind to avoid such problems as far as possible.
It was asked whether the coordination of the ship turning and the BBCEAS alignment was improving the comfort, safety and effectiveness of the action. This was confirmed.
It was also decided to pass the ship's satellite phone number to the aircraft liaison personnel to improve communication.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, with CH_2ICl spiking whilst the other compounds remained broadly constant. In air CH_2I_2 has continued to be observed overnight and dropped across dawn, reducing further through the day. CH_2ICl has also reduced. This could show some correspondence with photolytic destruction.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration (DL around 7 ppt) seeing a peak NO concentration yesterday around 10 am, dropping throughout the day and decreasing to zero at night. The NO_2 is high (order of 1 ppb), but with occasional reductions to between 800 and 900 ppt. The new O_3 instrument is still measuring around 30 ppt.
Keely (York). Pigment HPLC. The instrument is working well. The onboard underway fluorescence instrument has previously been measuring around 0.5 μg / L with a maximum of around 1 μg / L in an obvious satellite hotspot, but an all time high of 2.3 at 17:21 on 26th May where the satellite image has been masked above the Cape Verde Plateau. Preliminary HPLC analyses indicate that this could be a factor of 2 overestimate (though there is some chlorophyll-c present which may be contributing to the fluorescence and leading to the chlorophyll-a overestimate).

Ball / Jones (Leicester / Cambridge). The signal degradation resulting from heavy salt deposition on the mirrors in both systems has been alleviated by shielding some of the cavity length with tubing inserts. The effective cavity lengths are 40 cm shorter, but there is much lower falloff in signal (the blue system lost only 3% of the counts overnight, the green system only lost 1/5 of the signal loss from the previous night. In addition, the alignment is much safer and effective now it has been coordinated with the ship track planning. Both spectral radiometers are behaving well but one lost 12 hours data.
Heard (Leeds). FAGE has been monitoring ambient air continuously and it's possible, though not yet reportably so(!) that IO has been observed above the instrument detection limit around 8:00 (with sunrise) and 13:00. The negative offset has not yet been resolved and it will be useful to obtain the Roscoff NO_2 data.
McFiggans / Allan (Manchester). All instruments running well on ambient with a few minor problems, the following noteworthy; DMPS2 (dry) is still measuring high wrt total CPC and DMPS1 (wet) is awaiting humidification correction (by use of water bath to warm the bubbler) using the technical help onboard. The CCN is still awaiting calibration validation. The HTDMA D_0 and NaCl calibrations are good. All 3 impactors have just been changed. One of the cellulose substrate strips is being analysed by HPLC (for biological pigments), since its colour is comparable to the residue after filtration of the seawater samples. The top stage quartz substrates are similar in colour, but the finer quartz are greyer. We need to eliminate dust & anthropogenic influences (including ship plumes etc…). The MAAP instrument is showing significant absorption (100 to 200 ng m^{-3}), but this could be pigments, dust etc…

Tomorrow there is the opportunity for one last Dornier overflight. Speaking with Ally Lewis, the previous flight (on Saturday 26th) indicated a very low boundary layer (around 800 ft) above the ship which was some 250 miles towards east of Sao Vicente. Above the island the BL was around 5000 feet. Air in the BL was north-easterly with a haze layer aloft moving south-easterly. It was not felt that the NO_x measured onboard was significantly unusual given the likelihood that much of the air was of African origin.

Tuesday 29th May

Yesterday we tracked back into the inshore upwelling for midday, then back west across the gradient into poorer waters, before tracking south-westerly overnight through the offshore "hotspot" to prepare for the Dornier overflight, due initially at 11:30 at 16.5°N21.0°W. The conditions again are similar to yesterday (overcast skies with relatively heavy northerly winds).

No messages from Dornier ground or flight crew until I speak to James Lee, then Ally Lewis calls at 11:00 to inform about delay until 13:15.

Dornier makes 6 overpasses between 300 and 8000 feet on a true bearing of 100°. It appears that we are in a very thin (c. 100 m) surface layer of mid-Atlantic air (with O_3 concentrations of c. 30 ppb) capped by an extremely strong inversion of around 9°C, above which O_3 depleted air is moving in a south-easterly flow. The surface layer develops into a full MBL of depth around 5000 ft by Cape Verde. The only possible reason for this very thin layer so very far from the coast (few hundred miles) can be strong surface cooling; there is no change in roughness length out here.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, CH_2ICl reached a maximum at 16:00 on 28th with quite unusual variability. In air CH_2I_2 has continued to be observed and CH_2ICl is further reduced.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration measuring very little, if any, NO but up to 6 ppb NO_2. However, the NO_2 calibration seems fine at 800 ppt, so confidence may be placed in the levels.
Keely (York). The pigment HPLC chlorophyll measurements agree very well for 6 points with the fluorescence instrument over previous days. The data from 28th will shortly be available for further validation.

Ball / Jones (Leicester / Cambridge). The tubing inserts have reduced sensitivity for the BBCEAS instruments owing to reduction in path length. Suggestions from afar have included the construction of an "iris" type mechanism to reduce spray, but allow light for full cavity length. The blue system has been measuring positive signal, but below the detection limit. The green system data is to be worked up. Both spectral radiometers are behaving well with no data loss.
Heard (Leeds). FAGE has now been monitoring ambient air for 3 days continuously. It can be stated that, when out of the ship stack influence, the signal is flatlining with a very slight negative bias. It has been reaffirmed that between 12:00 and 14:30 on 28th it is possible, but by absolutely no means certain, that IO has been observed above the instrument detection limit.
McFiggans / Allan (Manchester). All instruments running well on ambient with a few minor problems, the following noteworthy; DMPS2 (dry) is still measuring high wrt total CPC and DMPS1 (wet) is spanning the ambient RH with the short DMA nearly saturated and long DMA at 80%. The CCN salt calibration is not looking very accurate compared with theory. The AMS high resolution mass spectrometry mode data is being lost sporadically. The cellulose Andersen impactor and CCI are on 24 hour cycling and the quartz Andersen is switching between 24 hour and 3 day sampling. The extraction of material from the heavily-coloured cellulose substrate strip was found to be clear. It is therefore highly likely that the coloured material is dust. The MAAP instrument is showing significant absorption (100 to 200 ng m^{-3}), cycling at low frequency (diurnal?), again likely to be dust.

Wednesday 30th May

After the Dornier pass yesterday, we tracked broadly east across the offshore "hotspot" area (south of our westerly crossing on the night of 28th / 29th) and closing on the coast to within a distance of 12 miles or so, moved into the inshore upwelling for midday. We then ran parallel to the coast for 3 hours or so, before heading back offshore (WNW dead leg). Today was calmer than it has been and apparent headwind was maintained for most of the day.

08:30 Cruise management meeting:
The MAAP instrument in the forward container has been indicating high concentrations of black carbon corresponding to the ship turning at the waypoints. It was noted that, since the fish has been redeployed from the gantry, all turns have been conducted to starboard to avoid collision with the hull. This has meant that turns to starboard at the end of eastbound legs have exposed the ship forward of the stack to stack emissions. Henceforth all turns will be into the wind to avoid such problems as far as possible.
It was asked whether the coordination of the ship turning and the BBCEAS alignment was improving the comfort, safety and effectiveness of the action. This was confirmed.
It was also decided to pass the ship's satellite phone number to the aircraft liaison personnel to improve communication.

Noteworthy observations throughout today:
i) In the forward container we made unambiguous measurements of nucleation between 11:55 and 12:10 on both DMPS instruments and the total CPC. Checking with the NO_{xy}, unfortunately, revealed that this corresponded to elevated NO and NO_2. It must therefore have been a ship plume, but requires further screening.
ii) The radar on the bridge showed a phenomenon appearing like rain throughout the early afternoon. This was persistent and holding at several miles distant from, and to the NNE of, the ship. This has been tentatively identified as an extensive deck of lofted dust, with the nearest being invisible to the radar which has an elevation of only 24°. Apparently, this has been observed on several occasions over the past few days. The implications of such a dust loading should inform all data analysis.
iii) When relatively close to the coast, the birdlife and shipping brought to the area by the abundance of fish was obvious. The nutrients brought to the surface by the upwelling cold waters are driving the avian and human food chains. It has to be recognised that the biological productivity in the waters represents an entire food web and cannot be well approximated by primary productivity.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, at reasonably high levels but with no drastic changes. In air, CH_2I_2 and CH_2ICl have been seen along with most other halocarbons for the past 3 or so days. From 06:00 and 07:00 CH_2ICl and CH_2I_2 have been respectively absent. There appears to have been no direct correspondence with the fluorescence "productivity" proxy through the elevated "hotspots". There is possibly some interesting relationship to be explored between the halocarbons and HPLC pigments on 28th between 14:00 and 16:00 (though the fluorescence instrument disagrees with these).
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. Background NO is around 25 ppt with NO_2 at 600 ppt. In relatively short-lived (several minute) plumes (probably ships) NO is reaching 100s of ppt whilst the NO_2 peaks at the few ppb level. O_3 is being observed at around 40 ppb and there may be an indication of O_3 production from 11:30 am.
Keely (York). The pigment HPLC has been providing hourly coverage of chlorophyll measurements from 10:30 this morning. After 28th, the HPLC pigment loading does not track the fluorometer measurements well (HPLC gives higher loading). The divergence appears greatest with the highest productivity / turbidity. There are several possible explanations, all pointing to a negative bias in the fluorometer with increased productivity. One that has been proposed is that the aggregation of algae into larger clumps using their exudates reduces the efficiency of the fluorescence. Also, it is difficult to see how a detection of fluorescence in turbid waters, optically thick at the fluorescence wavelength, can yield a linear response with chlorophyll concentration in a finite volume some thickness of sample away from the detector.
Ball / Jones (Leicester / Cambridge). The cork iris technique is to be tried this evening on the green BBCEAS instruments to overcome the sensitivity reduction caused by the reduction in path length using the tubing inserts. Both systems have been running continuously for the last day and both have been using NO_2 for a mirror calibration. Both spectral radiometers are behaving well with no data loss and a preliminary look at the data analysis is underway.
Heard (Leeds). FAGE is still running continuously and measuring levels in the noise. It will be undergoing further calibration between 15:00 and 23:00.
McFiggans / Allan (Manchester). All instruments running well on ambient with a few minor problems, the following noteworthy; DMPS2 (dry) is still measuring high wrt total CPC and DMPS1 (wet) is now running with the short DMA dry and the long DMA at ambient; it appears much happier this way! The CCN salt calibration can be compiled with previous calibrations and used to back out data satisfactorily. The HTDMA RH3 sensor has been changed to remove downtime. There appears to be a significant amount of dust on all impactors. The MAAP instrument is still showing significant absorption, cycling at low frequency. The bubble-tank Grimm instrument requires attention to its pump.

Thursday 31st May

We've been in the most recent long "live" leg with strong apparent headwind since turning in the small hours to head onshore again into relatively calm bright conditions (less overcast and hazy today). This will continue until around 11:00, when we head north for several hours, parallel to the coast in the cold upwelling waters just off Nouakchott.

08:30 Cruise management meeting:
Today we will be turning slightly short of our previously intended coastal approach to Nouakchott and staying around 20 miles offshore owing to our lack of diplomatic clearance for Mauritania.
There was discussion about demobilisation arrangements and plan changes. The UKORS container must be emptied dockside and both this, and the forward container, must be lifted quickly once berthed. Packing lists must be provided for arrival in Falmouth as must the registration numbers of all vans and cars coming down to meet the cruise. It may be sensible to arrange for empty gas bottles to be collected in Falmouth, rather than shipping them.

15:00 Science meeting – status report:
Carpenter (York). There were problems with the air conditioning and the compressor overnight causing some operator and instrument discomfort! However, both halocarbon GC/MS instruments are still sampling satisfactorily. In water, all compounds present as usual, at the high end of the levels measured throughout the cruise. $CHBr_3$ is being observed at up to 3 times its previous highest values. In air, CH_2I_2 and CH_2ICl were observed to drop again over dawn and have absent thereafter.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. There was no measurable NO overnight until around 07:00 when it was observed at ppb levels. The NO_2 increased from overnight levels in the high hundreds of ppt to ppb levels, Generally NO_2 > NO, but with very occasional incidence of stack emissions where NO exceeds NO_2. Today we've generally been in a photochemical stew, with significant fishing traffic, particularly inshore. There may be evidence of sea-land breeze effects, with a significant westerly component in the wind.
Keely (York). The pigment HPLC system is currently running a 24 hour batch of samples and will provide further data shortly. It will be necessary to interpret the fluorometer measurements in the light of these measurements as well as the satellite estimates of Chl-a and the sea surface temperature.
Ball / Jones (Leicester / Cambridge). The green BBCEAS instrument is running as well as it ever has been in the lab in Leicester (in terms of, for example, its light intensity at any given wavelength). It has been running continuously since 21:00 yesterday evening with no degradation in alignment. The blue instrument has been misbehaving slightly. The LED has now been changed and there have been difficulties with mirror calibration again. This will be repeated at 16:00. One spectral radiometer is behaving well, the computer for the other is locking up and we are awaiting resolution of a few problems with the data analysis software.
Heard (Leeds). FAGE is still running continuously. It has been measuring levels of IO of around 1 ppt (i.e. above DL) both at night and during the day. This is strange, but appears to be true! The signal appeared at about 01:30 and has persisted until around dawn when it started to disappear. The signal then increased again to similar levels with increasing solar intensity. It is postulated that the nighttime signal could perhaps result from NO_3 reactions in the cell but that the daytime signal is real atmospheric IO. This all needs to be investigated.
McFiggans / Allan (Manchester). All aerosol instruments are running well on ambient samples, measuring anthropogenically influenced, dust-laden marine air! The impactor substrates on the coarse stages were yellow when changed.

Friday 1st June

Overnight we headed ENE inshore again on a relatively long "live" leg before heading north east for several hours tracking to within 15 miles or so of the coast. Whilst bright early on, and calm all day, the light quickly became diffuse as a strong haze developed and visibility was never more than 5 or 6 miles all day. There were significant numbers of large and small fishing boats with their associated pollution

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, CH_2ICl has risen to its cruise maximum, $CHBr_3$ is still relatively high and CH_2I_2 is quite low. In air, CH_2I_2 was present until 07:30 and CH_2ICl was present only after 09:30 (i.e. the pattern is not the same as yesterday).
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO and NO_2 have both indicated polluted conditions (with NO_2 up to 20 ppb). It is clear that this is not stack emissions (NO_2 > NO, unlike when our own stack is sampled). NO was lower overnight. O_3 has been variable, with levels from 25 ppb up to 50 ppb (highest in cruise so far).
Keely (York). The pigment HPLC system has been working well with an indication that the measurements are very different from the fluorometer measurements, though the correspondence in absolute numbers and the trends have yet to be fully evaluated. Chlorophyll-a

levels were up to around 2 μg / L in the offshore productive patch earlier in the cruise and have been comparable (up to around 3 μg / L in the upwelling, but with an indication of transformation products absent in the earlier measurements.
Ball / Jones (Leicester / Cambridge). The green BBCEAS instrument has been running continuously since 21:00 on 30th with a little degradation in alignment. Measurement was stopped at 14:00 today at the start of the current dead-leg to clean the mirrors which had salted up despite the shielding of the tube inserts. The blue instrument has been running continuously for 24 hours with a second new LED. It too has been stopped for the dead-leg. There are tentatively observations of IO at around 2 ppt (which corresponds to an optimistic estimate of the detection limit!). The calibration using NO_2 is working well and the observed gradual loss of sensitivity in the blue system throughout the project probably corresponds to gradual degradation of the mirrors. The specrads are both now working, but the analysis software is being infuriating…
Heard (Leeds). The FAGE system has been running continuously up until the last recent turn to the west. It has been measuring levels of IO of up to 1.5 ppt (i.e. above DL) both at night and during the day. Over the last 24 hours the night and day values have been comparable (whereas yesterday, the night-time values were higher). The signal dropped off just around dawn and increased again with increasing light levels. Again, this all needs to be investigated.
McFiggans / Allan (Manchester). All aerosol instruments are, in general, running well with the following noteworthy points: the wet DMPS system 3025 CPC wick has become waterlogged and is undergoing drying. Short DMA data has been lost between sometime after 03:00 and 13:00. The Grimm OPC operating on the bubble tank was not operating for a short while, reporting a power supply error. There may have been a loss of data from the monkey island based Grimm OPC, owing to WiFi dropout. On changing the CCI and cellulose Andersen impactor, it was again noted that there was significant dust contamination. The quartz filter was not changed as we are waiting for an improvement in the probability of clean marine air as we move to more open ocean waters. It should be noted that the valves to the impactors have switched many times in the last 24 hours. This may possibly be due to absorption by dust as well as by BC from ships. This needs to be remembered during analysis.

As a general synopsis of conditions in the area of the upwelling which we have just left, it can be stated that everything probably appears to be telling a consistent, but complex story. Firstly, it seems we've been in anything but pristine marine air. According to the Dornier, there is a 9° temperature inversion about 100 metres aloft capping us off from above. This can only be driven by the extremely cold upwelling waters stabilising the surface air. However, the upwelling currents are very patchy and we can be in water as much as 6 degrees warmer in 10 miles. I've no quantitative idea what this does to the boundary layer, but it must stimulate convective mixing. Back trajectories have previously told us that we should be receiving clean mid-Atlantic air at low levels (though this is not the case now!). For the last few days (but again, not today) the ship's radar has been picking up a large echo, holding at around 10 to 15 miles NNE of us. It appears as a bank of rain would, but is more stable and has tentatively been interpreted as an extensive sheet of lofted dust; the nearfield material is above the radar's detection since it has a maximum elevation of 24°. We have been getting significant dust on our impactor substrates and the NO_2 levels are much higher than clean marine background. It may be that earlier in the week, although the prevailing flow would mean that we should be receiving clean marine air capped off from the layer above by strongly stabilising cold waters, air from layers aloft have has been entrained into the surface layer upwind over warmer waters where there is much weaker stabilisation, hence the elevated dust and NO_x. The higher pollution levels in onshore waters from fishing boats is further adding to the deviation from clean marine air. The upwelling region is qualitatively showing correspondence between colder waters and higher chlorophyll-a as measured by the fluorometer. The fluorometer measurements do not quantitatively agree with the HPLC pigment analyses, and the halocarbon concentrations in water and air do not generally track the indicators of primary productivity, indicating an alternative first order effect on their concentrations. The tentative IO identification has been made on live-legs only. Again, there seems to be no obvious first order correspondence with primary productivity.

16:15 Safety muster at boat stations followed by emergency stations.

Saturday 2nd June

Overnight we headed NNW offshore on a "dead" leg before heading north east for towards the coast for the first of 2 parallel 12 hour "live" legs. It is much clearer, cloud-free and hot. We are apparently north of the dust front. Now we are heading directly into the NE trades and adverse currents, the ship is pitching severely and it's quite lively in the foredeck container!

08:30 Cruise management meeting:
The turn around dawn was taken early to avoid shipping traffic. However, it was not sufficiently easterly to get apparent headwind. The scientists should ensure that the bridge are informed that this is a primary requirement. We require a further offshore leg to obtain apparent wind across dusk. The problem with condensate leaking into the main lab will be ongoing whilst there is no drain in the air conditioning room. This will improve once the list to starboard is corrected. We have been informed that the demobilisation at Falmouth is from the Queen's wharf – apparently this is not the best for working on the ship, but it should be OK.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, at similar levels to before we surveyed the upwelling region. In air, few iodocarbons are present, but there are plenty of chloro- and bromocarbons.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO and NO_2 both indicate slightly polluted conditions (NO at 70 ppt and NO_2 at 500 to 700 ppt). O_3 has been measured at around 30 ppb.
Keely (York). The pigment HPLC system is rattling through the collected samples – it is confirmed that measurements are sometimes very different from those made by the underway fluorometer. For example, the fluorometer has read levels of 0.5 2 μg / L when the HPLC analysis is seeing Chlorophyll-a at levels up to 2.5 μg / L. This may be a result of fluorescence quenching in particularly turbid water. The discrepancy is not consistent, sometimes the two instruments are agreeing at high levels. This requires confirmation. Owing to the relatively barren waters expected on the homeward leg, it is not intended to continue sampling continuously by HPLC, but only when the underway fluorescence indicates some sort of biological change.
Ball / Jones (Leicester / Cambridge). The blue BBCEAS instrument has been operating continuously with similar sensitivity to yesterday; again, a new LED has been used, but this appears to be bright at the wrong wavelengths, so it may be changed back again. There is a tentative indication of IO at around the detection limit around and post dawn. There is the intention to change to measuring NO_3 north of Tenerife. The green system has been out of operation since the "dead"-leg yesterday afternoon, owing to difficulty with realignment and wet briny deposits on the mirrors. A fresh alignment attempt will be made this afternoon. The air-conditioning in the port container has been misbehaving and will be investigated. The specrads are both working, but the analysis software is being infuriating…
Heard (Leeds). The FAGE system had been running at very reduced laser power and has now not worked from 05:00 to 14:00. It is now working with more power than usual and has been observing levels of IO between 2 and 2.5 ppt (but with high variability and dropouts in signal). The timescales of this variability are comparable to the integration timescales to get useful signal to noise… It is suggested that, this afternoon, the ship track makes "steps" between orienting itself broadside to the wind and obliquely across the wind to the port side to investigate possible wind-ramming or turbulent effects. It is also desirable to complete the FAGE diurnal profile by making more measurements across sunset and between 19:00 and 24:00.
McFiggans / Allan (Manchester). All aerosol instruments in the container are, in general, running well with the following noteworthy points: the total CPC is measuring between 1000 and 1500 /cc. This is high for marine. The dry DMPS is seeing modes at 38 nm and 150 nm. The HTDMA is still measuring relatively low $GF_{D,90\%}$ (1.7 ish) for almost all sizes, with only the largest dry size (300 nm) showing evidence of a few seasalt particles. The bubble tank is giving an indication that the difference in aerosol mode sizes between the fish and the non-tox is shrinking – we need to check whether this is a result of line passivation. The CCI, cellulose and quartz impactors have all

been changed today. The WiFi is now behaving unreliably and the Grimm on the monkey island and the valve switching cannot be assumed to be operational.

Sunday 3rd June

Overnight we headed NNW offshore on a "dead" leg before heading north east towards the coast for the 2nd parallel 12 hour "live" leg at 07:00. It is much clearer, cloud-free and hot (hot enough for sunburn for the stupid!) Trevor and Roisin want to move the FAGE inlet – it appears that the air reaching the bluff body of the container is leading to too much variability in the air flow and the nozzle, flush with the container wall, is in the ship's boundary layer. Today we will cut short the "live" leg to help make up some time.

08:30 Cruise management meeting:
Since the FAGE measurements are too variable and it appears that this is due to flow disturbances, not chemistry or source fluctuation, it was decided not to use the "zig-zag" approach to evaluate the inlet characteristics.
The fish and the non-toxic supply will continue until no longer needed or the Master advises that it will stop.
This morning there will be spot risk assessment inspections from the Master.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, at similar levels to before surveying the upwelling region. In air, no CH_2I_2 present since dawn yesterday and no CH_2ICl present, but there are plenty of chloro- and bromocarbons.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO is zero and NO_2 is around 400 ppt. O_3 is present at around 40 ppb.
Keely (York). The pigment HPLC system is continuing to analyse the collected samples, further illustrating the discrepancy between the HPLC and the fluorometer with the former measuring Chlorophyll-a at levels up to 3.5 μg / L.
Ball / Jones (Leicester / Cambridge). Both the blue and the green BBCEAS instruments have been operating continuously since yesterday. The green system has had similar sensitivity and the blue system has lost around 25% of its intensity. The specrads are both working.
Heard (Leeds). The FAGE system has been diagnosed with a sampling problem. It is thought that the nozzle does not extend sufficiently far away from the container to place it outside of the boundary layer of the ship. This is causing flow problems (slackening of air at the container wall) and probably sampling artefacts. The cell is being extended with a bored plastic insert to transport the end of the nozzle outside the ship's BL. This inlet design will be tested as soon as it is built.
McFiggans / Allan (Manchester). All aerosol instruments in the container are, in general, running well with the following noteworthy points: the wet DMPS is operating with one channel fewer as it started to arc. The MAAP is seeing around 100 ng m^{-3} black carbon, which is slightly elevated. The CCI and the cellulose Andersen impactors showed no sign of dust contamination. It has been decided to sample the quartz Andersen to 27.5° N before changing it, hopefully for a clean marine sample! The Grimm from the monkey island replaced that from the bubble tank. The former is not logging since the WiFi is intermittent and the pump in the latter is broken. The bubble tank aerosol modal diameter discrepancy between fish and non-toxic supply water is even lower than yesterday.

Monday 4th June

Overnight we made our way north before turning ENE at 03:30 towards the ship control system between Tenerife and Gran Canaria. We arrived at the start of the system at around 13:30 and made our way between the islands by around 19:00 today. Today was very hot and quite calm until north of the Canaries when the headwind and swell was sufficient to make progress difficult and it became quite overcast.

08:30 Cruise management meeting:
The air conditioning condensate no longer leaks into the lab.
FAGE is measuring much more believably and will measure intensively. The water is barren according to HPLC and fluorometer and therefore the HPLC and GCMS instruments are not working intensively. It was suggested that the fish and the non-toxic supply will continue only for one more day owing to the convergence in the bubble tank results.
There was discussion about the packup arrangements. It was suggested that the foredeck container will be unplugged on Saturday (ending calibrations and science Friday night). The scientists are all to be polled on their packup requirements today.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, at similar levels to before surveying the upwelling region. In air, no iodocarbons present, but there are plenty of chloro- and bromocarbons.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO measuring low ppt during night and NO_2 from 500 – 600 ppt. At 09:00 to 13:30 the NO and NO_2 increased dramatically to 8 and 12 ppb respectively (with large variation). At 13:30, NO_2 increased to 40 ppb whilst NO dropped to 20 ppt. We are downwind of southern Tenerife, but this is a lot of NO_x. O_3 has been measuring from 30 to 60 ppb.
Keely (York). The pigment HPLC system is continuing to analyse the collected samples which should all be ready shortly.
Ball / Jones (Leicester / Cambridge). The green BBCEAS system has now been running for 48 hours continuously with sensitivity as good as in the lab (other than the path shortening). The blue instrument has been operating fine since its recent nitrogen flush. From 23:00 to 07:00 there was no signal loss, but from 07:00 to 13:00 there was around 20% signal loss, retrievable with further mirror cleaning. There is a deep interest in switching to measure NO_3 which is being negotiated with the PS! One of the specrads has been misbehaving and the other has been fine other than a glitch between 07:00 and 07:15.
Heard (Leeds). The FAGE system appears to be working exceptionally well! The extended inlet was in place from 02:30 and running properly from 03:30. There has been no IO observed overnight with scatter in the signal about zero and all below DL. An after dawn steady increase to a maximum around 1.5 to 2 ppt with short timescale variability. The new inlet design has reduced the solar background signal and largely offset any loss of sensitivity resulting from the increased inlet length. DL is now around 0.2 (0.5) ppt at 30 (10) minutes.
McFiggans / Allan (Manchester). All aerosol instruments are, in general, running well with the following noteworthy points: the impactors will be changed, hopefully for a clean marine sample, once outside the influence of the Canaries. The bubble tank aerosol modal diameter discrepancy between fish and non-toxic supply water is back! Possibly organics in polluted water? Temperature?

Tuesday 5th June

Overnight we continued our direct northbound homeward passage; still at a relatively laboured pace (8.5 knots ish). Since dawn it has been relatively overcast, with sunny spells. As the morning has progressed, the wind and swell has eased and the sun has burnt off much of the cloud. From around 10:00 we have made better progress through the calmer waters.

08:30 Cruise management meeting:
Passage has been quite slow overnight, but there is still reasonable hope that the winds will slacken and progress will speed up. The headwind and swell were significant overnight and the attendant spray over the bow was large. Any repetition may require curtailment of foredeck activities.
There is a scientific focus around the FAGE instrument which is behaving more reasonably, but still with some need to make careful interpretation of the measurements. It has been suggested

that the fish seawater supply will continue for one more measurement to investigate whether there is re-convergence in the bubble tank results between the fish and non-toxic supplies.
There was further discussion about the pack-up arrangements. Scientists will need to inform about the arrangements for the collection of gas bottles and about the registration numbers of vehicles meeting the ship. A barbeque was tentatively arranged for Thursday or Friday dependent on weather and seas – it is projected that we will either be leaving Finistere or entering Biscay.
The cruise debrief has been scheduled for 10:30 on Thursday 7th June.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily. In water, all compounds present as usual, at similar low concentrations to before surveying the upwelling region. In air, no iodocarbons present, but chloro- and bromocarbons are present. Duplicates are being sampled and analysed with the water instrument to quantify variability.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO measuring around 10 ppt background and NO_2 around 500 ppt. Between 01:00 and 03:00 both NO and NO_2 experience spikes and broad elevation. O_3 dropped from 55 ppb at 02:00 to 30 ppb around lunchtime but has risen to around 40 ppb since lunch.
Keely (York). The pigment HPLC system is currently running through its last set of analyses and should be completed by the evening of 6th June. Highest chlorophyll-a level so far recorded is around 4 μg / L on day 152 (1st June) at 14:48.
Ball / Jones (Leicester / Cambridge). The green BBCEAS system has now been running for 72 hours continuously with sensitivity as good as in the lab (other than the path shortening). The data are still to be worked up. Alignment of the blue instrument was too risky last night, but a pre-dawn alignment has yielded the best sensitivity for a week. This had dropped by 30% by the nitrogen flush at 11:00 but was back to earlier levels by the time of the next flush. Between 06:00 and 11:00, there appeared to be a sensible increasing profile of IO, but at the detection limit of 1 to 2 ppt. Between 11:00 and 15:00, the profile was less sensible. It is intended to measure NO_3 from just after dusk today. One of the specrads crashed last night, the other has been fine; there has been no data loss.
Heard (Leeds). The YAG laser in the FAGE system has failed. Prior to this, there was a full sensible diurnal profile of IO from yesterday (increase from zero after dawn, midday max at a ppt or so, and drop to zero just after dusk), plus an additional overnight rise after dusk, peak around midnight and fall well pre-dusk.
McFiggans / Allan (Manchester). All aerosol instruments are, in general, running well with the following noteworthy points: the CCI and cellulose Andersen impactors have be changed. The quartz substrates have been left loaded. The 3025 CPC from the dry DMPS has developed a large butanol leak, probably inside the female fill connector. There are around 2000 total particles /cc being seen, with the MAAP indicating 100 ng m^{-3} and the DMPS observing a broad mode at around 120 nm. Overnight has been cleaner with a trimodal distribution. The HTDMA is recording a lower $GF_{D,90\%}$ mode but with the dominant mode still at 1.7. There is no longer a bubble tank aerosol modal diameter discrepancy between fish and non-toxic supply, we have therefore finished with the fish.

Wednesday 6th June

Overnight we have made much better progress on our direct northbound homeward passage through calmer waters. Winds are slack and the weather is clear, fairly bright, though a little overcast.

08:30 Cruise management meeting:
The York and Manchester groups have now finished with the fish and it will be brought back onboard. The laser on the FAGE instrument is not functioning and will no longer be driving our science. All other atmospheric measurements are continuous and will neither affect, nor be affected by, our homeward transit leg. Clocks will advance one hour on Friday night giving us one hour extra in bed after the barbeque. It is possible to lift the pumps for the forward container from the hydraulics hold on Saturday whilst underway, provided the weather is still fine.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments are sampling satisfactorily, as yesterday. In water, all compounds present as usual, at similar low concentrations to before surveying the upwelling region, possibly very slightly higher than yesterday. In air, no iodocarbons present, but chloro- and bromocarbons are present. Again, running duplicates today, after which the instruments will be calibrated and no further ambient samples will be taken.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO measuring around 20 ppt background and NO_2 is between 400 and 500 ppt background. NO_2 was experiencing spikes between 16:00 and 19:00 yesterday. O_3 levels are between 30 and 50 ppb all day.
Keely (York). The maximum chlorophyll-a level analysed by the pigment HPLC system is around 6 μg / L on day 152 (1st June). There was no sample taken simultaneously with the highest fluorometer reading. The fluorescence had only been elevated for 25 minutes during this period. It should be noted that the fluorometer had a full scale deflection of 5V corresponding to around 75 μg / L. This gives a highest fluorometer reading of about 37.5 μg / L on 1st June, slightly after the HPLC highest value.
Ball / Jones (Leicester / Cambridge). The green BBCEAS system had no evidence of salt deposits on the mirror when inspected. There was a possible loss of data from 19:30 yesterday to 13:00 today. An I_2 crystal experiment was conducted slightly downwind of the cavities just prior to 18:30. Data has yet to be analysed. The blue instrument stopped sampling ambient at 16:00 yesterday and the red instrument was brought online from 22:00. Light intensity was good, but software had some minor glitches. The instrument needs to have wavelength shifts applied and full calibration.
Heard (Leeds). The FAGE system is currently not operational. It may be useful to arrange for a diurnal cycle of IO to be measured on Cape Verde if the system there is operational.
McFiggans / Allan (Manchester). All aerosol instruments are, in general, running well with the following noteworthy points: the HTDMA was not operational from 06:00 to 11:30 as the RH was not maintained (the bubbler was empty). The total particle number is around 1000 / cc and the MAAP instrument is measuring less than 50 ng / m^3 of black carbon. The two DMPS instruments are measuring the same – there seems to be agreement in clean airmasses, but not in polluted. The impactors possibly experienced a spiking on turning the ship.

Thursday 7th June

Again, we have made very good progress on our homeward passage through calm waters in slack winds on a clear, bright day with little cloud.

10:30 Cruise debrief:
See debrief report and Principal Scientist's Cruise Assessment form.

15:00 Science meeting – status report:
Carpenter (York). Both halocarbon GC/MS instruments have stopped measuring ambient, the water instrument at 17:30 on 6th June and the air instrument at 12:00 on 7th. They are currently being calibrated and will then be packed.
Lee (York). The NO_{xy} instrument is still running well in dual channel configuration as is the 2B O_3 instrument. NO measuring around 20 ppt background, spiking to 200 ppt and NO_2 measuring between 300 and 600 ppt. O_3 levels are between 30 and 50 ppb all day. Ambient measurements will cease later today for calibration and packup.
Keely (York). The pigment HPLC system has been switched off. Pigment abundances have been calculated and will be quality assured on return.
Ball / Jones (Leicester / Cambridge). The green and red BBCEAS systems are both running well. The red system lost data between 06:30 and 09:30. Neither system had lost signal overnight. It may be possible to remove some of the tube shielding the green system to improve sensitivity since there is little evidence of any contamination in the still air.

Heard (Leeds). The FAGE system has been miraculously resurrected thanks to Trevor's pig-headed persistence! It has been operational since 02:00 after adjusting a trim pot. on a laser control card. It has been sampling ambient since, but with no data to report as yet.
McFiggans / Allan (Manchester). The MAAP, AMS and Grimm have been running on ambient air for the morning only (with nothing overnight). The other instruments have been working on nebuliser and bubble tank experiments with seawater. The impactors are sampling blank without motors running for calibration. The pump on the Andersen for the cellulose filters has broken.

6. Instrumentation:

Measurement Description: Measured species included a variety of halocarbons in both water column and atmosphere and atmospheric boundary layer measurements of I_2, IO (and NO_3) by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS). A compact version of the FAGE system, developed for the FAAM BAe-146, was deployed to provide measurements of IO or OH / HO_2, permitting direct assessment of RHS-induced changes in the oxidising environment through the upwelling region. A range of trace gas monitors was simultaneously deployed to measure O3 and NO_x. Aerosol number and size distribution measurements from 3 nm to 20 micron diameter were also made by a range of mobility (DMPS) and optical instrumentation, (OPC). Note, significant additional aerosol measurements were provided as part of the NERC-funded ACMME project (PI Allan). Measurements of pigments in the surface waters were made by HPLC.

7. Operations:

No station work was conducted during D319 and, with the exception of halocarbon, pigment analysis and sampling for the bubble tank, all measurements were atmospheric.

A GC/MS analysis of halocarbons in air and surface seawater
Provider: Dr Lucy Carpenter, University of York, ljc4@york.ac.uk
Personnel: Dr Rachel Dunk, Dr Charlotte Jones

Instrument specifications:Two Perkin-Elmer Turbomass GC - quadrupole mass spectrometers coupled to Perkin-Elmer Turbomatrix thermal desorption units were deployed. One was dedicated to making continuous automated measurements of halocarbons in air (24 hour coverage, sample frequency of 70 minutes) while the second instrument was used in conjunction with a purge and trap system to analyse for halocarbons in seawater samples (approximately every 2-2.5 hours, with 16-20 hour coverage each day).

Calibration information: Both instruments were calibrated using a permeation oven technique. Calibration was achieved

using fixed volume (10 μl) injections of the output of thermostatted permeation tubes into a stream of nitrogen gas in order to dilute parts per million by volume (ppmv) mixing ratios into parts per trillion by volume (pptv). Full calibrations were carried out twice during the cruise - once during the port call to Cape Verde (25th May) and then again at the end of the cruise (Thursday 7th / Friday 8th June). In addition a gas standard containing the halocarbons of interest in nitrogen was analysed once a day on each instrument in order to determine any day to day variations in instrument sensitivity.

Detection limits, accuracy and precision: Not yet known

Air sampling: Air was analysed for halocarbons from 21st May to 7th June inclusive. Bromocarbons CH_2Br_2 and $CHBr_3$, and chlorocarbons CCl_4 and $CHCl_3$ were present for the duration of the measurements. The iodocarbons CH_2ICl and CH_2I_2 were detected in air whilst the ship was in the productive regions west of Mauritania, although often CH_2I_2 levels dropped off with sunrise to close to / below the limit of detection of the instrument.

Water sampling: Measurements of halocarbons in seawater were made between 21st May to 6th June inclusive. Water samples were taken from the ships non-toxic water supply and the fish, with the majority of samples from the non-toxic supply. The bromocarbons and chlorocarbons were detected in all water samples analysed, as were the iodocarbons CH_2I_2, CH_2ICl and CH_2IBr. Levels of $CHBr_3$ and CH_2ICl were seen to increase significantly in the upwelling region.

Phytoplankton counts: Water samples were collected and filtered for phytoplankton counting periodically (between 1 and 6 times a day) to coincide with water sample analyses for halocarbons. Phytoplankton counts will be determined following post cruise analysis.

Data coverage & downtime:

1. Air instrument: Periods of continuous measurements of halocarbon mixing ratios in air (24 hour coverage, sample frequency of 70 minutes, but note for 2-3 hours each day the instrument was offline in order to analyse gas standards for calibration purposes):

14:00 23/05/07 – 10:45 24/05/07
Port call to Sao Vicente, Cape Verde
04:00 26/05/07 – 13:15 29/05/07
20:00 29/05/07 – 00:30 31/05/07
06:30 31/05/07 – 12:00 07/06/07

There were 2 notable periods of downtime each lasting a few hours between 23/05 & 07/06:

Downtime on the afternoon of the 29/05 was due to trouble shooting a problem with the instrumentation (Valco valve not switching in the Automated Thermal Desorber due to loose electrical connection).

Downtime early on the 31/05 was again due to an instrumentation problem - on this occasion the air compressor was not achieving high enough pressures & was overheating due a to a leak in the compressed air line.

2. Seawater instrument: Halocarbon concentrations in seawater samples from the ships non-toxic supply (~6 m depth) were typically analysed every 2-3 hours, with 16-20 hour coverage each day. Occasionally seawater sampling was less frequent (up to 5 hours between measurements) due to experimenting with alternative water sampling techniques, as well as instrument problems on the morning of the 31/05 (see above). Periods of measurement were:

18:00 22/05/07 – 21:00 24/05/07
Port call to Sao Vicente, Cape Verde

06:45 26/05/07 – 17:45 07/06/07

Brief summary of main findings:

The CH_2ICl surface seawater concentration was elevated within the productive Mauritanian upwelling region compared to the pelagic open ocean (concentrations of up to ~16 pmol dm^{-3} were detected in the upwelling, while typical background levels outside these waters were 1-4 pmol dm^{-3}).

Unlike CH_2ICl, there was no obvious increase in the CH_2I_2 seawater concentration in the upwelling region compared to the open ocean waters. CH_2I_2 concentrations were generally between 1 and 6 pmol dm^{-3}, although occasionally higher concentrations of up to ~ 11 pmol dm^{-3} were detected. The mean CH_2I_2 concentration in seawater across all measurements was 3.3 pmol dm^{-3}.

CH_3I concentrations in seawater ranged from 2-30 pmol dm^{-3}, with a mean average cruise concentration of 11 pmol dm^{-3}, but like CH_2I_2 the CH_3I concentration was not significantly elevated in the upwelling region.

Concentrations of other iodocarbons in seawater were considerably lower than those of CH_3I, CH_2ICl & CH_2I_2; the mean average concentrations of CH_2IBr & C_2H_5I were 1.6 & 0.9 pmol dm^{-3} respectively.

Concentrations of the bromocarbons $CHBr_3$ & CH_2Br_2 in seawater increased within the upwelling, but less rapidly than CH_2ICl. Mean average concentrations were 8.3 & 2.4 pmol dm^{-3} for $CHBr_3$ & CH_2Br_2 respectively, with a maximum $CHBr_3$ concentration within the upwelling of ~25 pmol dm^{-3}.

Mean average iodocarbon mixing ratios in air were ~0.15 pptv CH_2ICl & ~0.01 pptv CH_2I_2. CH_2IBr was detected in air occasionally, with an average mixing ratio of ~0.02 pptv. The air instrument could not be used to monitor CH_3I due to issues associated with the chromatography, & C_2H_5I was below the detection limit of the air instrument for the duration of the cruise.

The mean $CHBr_3$ mixing ratio in air throughout the cruise was ~0.5 pptv, although the highest value detected was ~1.9 pptv. The mean CH_2Br_2 mixing ratio was 0.2 pptv.

The next stage of the data analysis will be to use the simultaneous air & seawater concentrations in order to determine instantaneous sea-air fluxes for these iodocarbons & bromocarbons.

B Determination of Atmospheric Molecular Iodine, I_2 by Broad Band Cavity Enhanced Absorption Spectroscopy (BBCEAS).

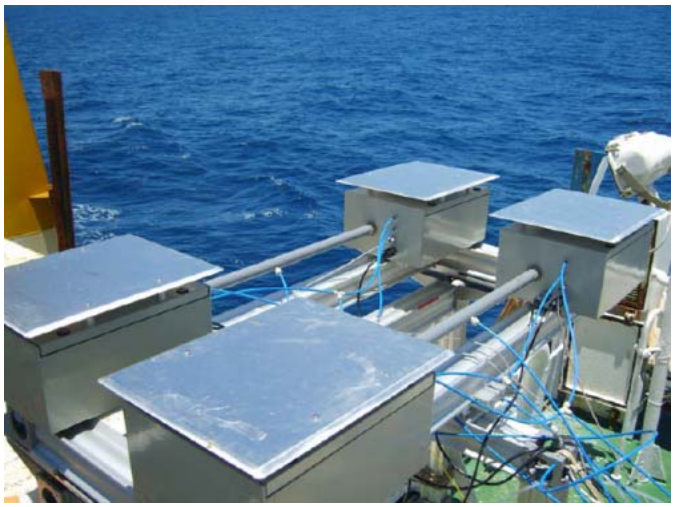
Provider: Dr Steve Ball, University of Leicester, sb263@le.ac.uk
Personnel: Ms Anna Hollingsworth

Measurement technique: An optical absorption spectrometer capable of quantifying sub-ppbv amounts of atmospheric trace gases via their electronic absorption spectra at visible and near-UV wavelengths. Its basic components are a broad band light source – in this case a light emitting diode – coupled to a high finesse optical cavity and a spectrometer detector. More details of this instrument can be found in *Ball et al 2004*.

For this deployment, the BBCEAS instrument was configured to operate in a where molecular iodine has strongly structured absorption bands. The very high reflection efficiency (R ≈ 99.94%) of the cavity's mirrors enabled the absorption spectra of ambient atmospheric samples to be measured over an effective path length of 2.2 kilometres in a cavity of length d = 117 cm, thus providing a sensitive in situ detection method for I_2. Differential Optical Absorption Spectroscopy (DOAS) is then used to fit the various contributions to the atmospheric absorption spectrum and

hence to accurately determine I_2 concentrations in the presence of other absorbing/scattering species.

Instrument parameters:
Cavity length: 117 cm.
Cavity mirrors: layertech 1 inch green
LED: Luxeon III star (LXHL LM3C)
Spectrometer: Ocean optics HR4000 mini spectrometer
Input fibreoptic: 10m long 400 um diameter ocean optics armoured fibre
Output fibre: 15m long 400um diameter ocean optics armoured fibre
Bandwidth sampled: 520nm ≤λ< 560 nm



Sampling position: Port side

Sampling mechanism: Air samples. Air passes through instrument unperturbed with no inlet or filters.

Measurement time:

Leicester BBCEAS Anna Hollingsworth

Hour	00:00	01:00	02:00	03:00	04:00	05:00	06:00	07:00	08:00	09:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00	22:00	23:00
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07/06/2007									f	x,o							f,x							
08/06/2007										f,x						f	x							
09/06/2007									f,x															

f nitrogen flush
running for all or part of hour open path
x NO2 calibration
o Oxygen dimer calibration

Table 1.

The BBCEAS I_2 instrument was run almost continuously from 13:49pm ship time on 25th May to 8:15am on the 9th June 2007 as indicated by dark green regions in Table 1. A more detailed account is in text below.

Calibration methods: The BBCEAS method measures the absorption spectrum of a sample, in this case an atmospheric sample, by comparing the steady state light intensities leaking from the high finesse cavity in the presence of the sample, I(λ), and with the cavity flushed with a non-absorbing gas $I_0(\lambda)$:

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \times \frac{d}{1 - R(\lambda)} \qquad \text{Equation 1}$$

Thus periodically it was necessary to suspend atmospheric sampling to flush the cavity with dry, aerosol-free nitrogen in order to measure $I_0(\lambda)$. These times are indicated by an "F" in Table 1. These breaks were also used to record the detector's dark current and to record a calibration spectrum by flushing the cavity with pure oxygen ("O" in Table 1).The BBCEAS method can only be made quantitative if the reflectivity of the mirrors is known as a function of wavelength, R(λ). An initial estimate of R(λ) is available from information supplied by the mirror manufacturer, however the actual values of R(λ) depend on the precise optical alignment of the cavity and whether the reflectivity has been degraded by, for example, ambient aerosol, salt and seawater depositing on the mirrors.
Thus periodic cleansing of optical components and (re-)calibrations were necessary throughout cruise D319
Recording the BBCEAS spectrum of oxygen dimer absorption bands in samples of pure oxygen provided a method through which the mirror reflectivity could be iteratively adjusted until the measured BBCEAS spectrum matches that expected for pure oxygen. Towards the later parts of the cruise NO2 was also available to provide an additional route to mirror reflectivity determination.

Detailed Measurement times and reasoning:
OP = Open Path measurements

23rd May 2007

OP 14:01 until 16:11 (1 s x 10 averages = 10s data)
Calibration, dark and flush spectra recorded
OP 16:45 until 18:39
Calibration, dark and flush spectra recorded
OP 20:45 until 24th May 2007 01:43, computer crashed at 01:43 unsure why!

24th May 2007
Calibration, dark and flush spectra recorded 09:00
OP 09:31 until 12:57
Calibration, dark and flush spectra recorded
OP 13:10 until 16:02
Calibration, dark and flush spectra recorded
OP 16:41 until 19:53
Computer needed restarting, other programs not functioning correctly
OP 20:12 until 21:45
Down time: Alignment too dangerous.

25th May 2007
Aligned, Calibrated and flush spectra recorded 7am
OP 07:33 until 12:50
flushes recorded.
OP 13:09 until 18:56
Calibration, dark and flush spectra recorded at 1900
Cleaned optics and tried realigning, winds strong, so had to abandon until morning.

26th May 2007
Calibration, dark and flush spectra recorded at 0900
OP 09:39 until 16:24
Calibration, dark and flush spectra recorded at 1615
OP 16:48 until 18:19
Cavity mirrors very dirty. Optics cleaned and cavity realigned, not much signal improvement, winds strong, causing added difficulty to alignment procedures.
Calibration, dark and flush spectra recorded at 2030
OP 21:06 until 08:46 27th May 2007

27th May 2007
Calibration, dark and flush spectra recorded at 0845 for end of overnight run.
Not running open path due various factors. Ships heading may cause sampling of stack. Sensitivity loss, need to clean optics and realign cavity, not able to do so. Wait till dusk or dawn to be able to observe light beam.

28th May 2007
Newly aligned cavity: Calibration, dark and flush spectra recorded at 0630
OP 06:58 until 13:07
Flushes at 13:16
OP 13:31 until 18:59
Calibration, dark and flush spectra recorded at 1900

29th May 2007
Calibration, dark and flush spectra recorded at 0700
OP 07:42 until 14:08
Flushes at 14:12
Increased Integration time to 1.5 s x 10 averages =15 s data try to get more light,hence sensitivity at shorter wavelengths
Calibration, dark and flush spectra recorded at 14:20
OP 14:50 until 20:06

Calibration, dark and flush spectra recorded at 2015
OP 20:40 until 30th May 2007, 06:00

30th May 2007
Calibration NO2, dark and flush spectra recorded at 0615
OP 06:49 until 12:54
Flushes at 13:00
OP 13:22 until 16:38
Calibration NO2, dark and flush spectra recorded at 1700
Cavity mirrors cleaned and realigned. Best signal so far in trip.
Integration time 1 s x 10 averages = 10 s data
Calibration, dark and flush spectra recorded at 1930
OP 20:54 until 31st May 2007, 08:32

31st May 2007
Calibration NO2, dark and flush spectra recorded at 08:40
OP 10:25 until 11:46
OP 11:57 until 16:10
Calibration NO2, dark and flush spectra recorded at 16:20
OP 16:55 until 1st June 2007, 06:31

1st June 2007
Calibration NO2 and O2, dark and flush spectra recorded at 0640
OP 07:43 until 11:40
Flushes at 11:44
OP 11:57 until 14:17
Calibration NO2, O2, dark and flush spectra recorded at 14:17
Cleaning and realigning not working today, lots of sea spray onto optics as trying to refit them. Eventually too wet/ windy and late to continue. Try again tomorrow.

2nd June 2007
Early/ pre-dawn alignment not able to the get signal back to sensible level.
Spent all day cleaning and realigning.
Calibration NO2 and O2, dark and flush spectra recorded at 1840
OP 19:37 until 08:55 3rd June 2007
3rd June 2007
Calibration NO2, dark and flush spectra recorded at 0900
OP 10:25 until 17:00
Calibration NO2, dark and flush spectra recorded at 1710
OP 19:07 until 07:15 on 4th June 2007

4th June 2007
Calibration NO2, dark and flush spectra recorded at 0815
OP 08:53 until 12:25
Flushes and darks at 12:30
OP 12:45 until 16:10
Calibration NO2, dark and flush spectra recorded at 16:20
OP 17:08 until 07:25, 5th June 2007

5th June 2007
Calibration NO2, dark and flush spectra recorded at 08:55
OP 09:30 until 12:44
Flushes at 12:48
OP 13:10 until 16:55
Experiment with iodine vapour from crystals below cavities between 17:20 and 1900hrs
OP 19:05 until 1930, computer program crashed, data not saved.

6th June 2007
Calibration NO2, dark and flush spectra recorded at 12:45
OP 13:30 until 08:49, 7th June 2007
NOTE: overnight flood lights on deck on and off intermittently. May see in detector.

7th June 2007
Calibration NO2 and O2, dark and flush spectra recorded at 0855
OP 09:57 until 16:10
Calibration NO2, dark and flush spectra recorded at 1640
OP 17:05 until 08:55 8th June 2007

8th June 2007
FOG/ Mist this morning, this kills signal to detector. Goes back up to usual levels when flushing. Open path measurements will have high aerosol extinction.
Calibration NO2, dark and flush spectra recorded at 0940
OP 10:05 until 15:38
Calibration NO2, dark and flush spectra recorded at 15:45
OP 16:25 until 08:15, 9th June 2007

9th June 2007
Calibration NO2, dark and flush spectra recorded at 08:24
Light rain from approx 430am and during these last calibration/flushes.

End of data collection.

Problems encountered during D319: The anti-vibration mounting unit for the cavity were not secured by bolts to the deck as previously agreed. The mounting was lased to the deck and railings by strapping, which appeared sure but could result in noise on spectra caused by cavity rail movement.
The feed trough (exit-hole) of the Lab container was positioned at the forward-end, resulting in a distance between the outside cavity and the internal electronics of greater than the 10m maximum specified throughout each planning stage and meeting. This caused stain on fibres that can result in additional noise to the measurements.
Weather conditions often made cavity mirror realignment difficult and this was not attempted at all on some days for safety reasons.
Malfunction of the Lab (port side container) air-conditioning unit caused huge temperature differences. This causes drift in the LED emission spectrum, which can result in large signal/noise ratio and some data to be discarded.

Summary of Findings: The problems encountered during the cruise have added to the complicated post campaign analyses of this data and it can therefore not yet be reported.
It is hoped that a detection limit for I_2, and NO_2 (which can also be retrieved from this data set) will be derived and any species present in concentrations above these be reported.

Expected Data formats: Data will be averaged to minute resolution. All data was collected using spectra suite software supplied by manufacturers with the spectrometer and analysed using a program written in Mathcad by Anna Hollingsworth

Date; Time; I_2 concentration; uncertainty in fitted I_2; NO_2 concentration; uncertainty in fitted NO_2; standard deviation in residual spectrum remaining after subtraction of fitted absorbers.

Reference: Ball SM, Langridge JM, Jones RL, Broadband cavity enhanced absorption spectroscopy using light emitting diodes, Chem Phys Lett, 2004, 398 (1-3): 68-74.

B Solar Irradiance Measurements by Spectral Radiometer
Provider: Dr Steve Ball, University of Leicester, sb263@le.ac.uk
Personnel: Ms Anna Hollingsworth

Measurement technique: Spectral Radiometers recorded the solar actinic flux, F(λ), as a function of wavelength between 280 and 700nm through an upward pointing 2π hemisphere.

These instruments recorded flux data in a continuous mode for the duration of the D319 cruise, with post deployment work-up of the data to calculate photolysis rates of any user-selected trace gas for which the absorption cross sections and quantum yields are available from laboratory data (e.g. the IUPAC recommendations).

Sampling positions: Port and Starboard sides of monkey deck.

Preliminary Analysis of the spectral radiometer 45935 data is now complete, and photolysis rates are available on one minute averages for the following species:
Column 1: date (dd/mm/yyyy)
Column 2: time (hh/mm)
Column 3: date and time (dd/mm/yyyy hh/mm)
Column 4: J(O^1D)
Column 5: J(NO_2)
Column 6: J(NO_3)
Column 7: J(I_2)
Column 8: J(OIO)
Column 9: J(Br_2)
Column 10: J(CH_2I_2)
Column 11: J(CH_2ClI)
Column12: J(CH_2BrI)
Column 13: actinic flux
Column 14: J(INO)
Column 15: J(IO)
Column 16: J(CH_3I)
Column 17: J(HOI)
Column 18: J($IONO_2$)
Column 19: J(IONO)
Column 20: J(BrO)
Column 21: J(IBr)
Column 22: J(HOBr)
Column 23: J(BrNO)
Column 24: J(BrN)
Column 25: J(BrO)

Measurement times: Spectral radiometer 45935 ran almost continuously from 11:50 on 18th May 2007 to 14:15 on 9th June 2007 (with occasional breaks for computer malfunctions & power outages). Data available from 45935 instrument:

11:49 18/05/2007 to 23:48 26/05/2007
06:35 28/05/2007 to 02:11 01/06/2007
23:30 02/06/2007 to 14:17 09/06/2007

Details: Times are in GMT/ UTC
Data from instrument 45935 - 0.5 second integration time
jO(^1D) temperature dependence from RSS Discovery onboard Met data.
No data value = -1.00E+04
No temperature data value (jO(^1D)) = -1.00E+04

Cross Sections and Quantum Yields Used
jO1D - Malicet and Matsumi
jNO2 - Coquart and Troe
jNO3 - Yokelson and Orlando
jI2 - Saiz-Lopez
jOIO - Bremen
jBr2 - Passchier
jCH2I2 - Roehl
jCH2ClI - Roehl
jCH2BrI - Mossinger

References:

Malicet, J., D. Daumont, J. Charbonnier, C. Parisse, A. Chakir and J Brion. (1995)
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Matsumi, Y., F. J. Comes, G. Hancock, A. Hofzumahaus, A. J. Hynes, M. Kawasaki,
and A. R. Ravishankara, Quantum yields for production of O(1D) in the ultraviolet photolysis of ozone: Recommendation based on evaluation of laboratory data
JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. 0, 10.1029/2001JD000510, 2002

Coquart, B., A. Jenouvrier, and M. F. Merienne, The NO2 Absorption Spectrum. II. Absorption Cross-Sections at Low Temperatures in the 400-500 nm Region (298 K) J. Atmos. Chem., 21, 251-261, 1995

J. Troe "Are primary quantum yields of NO2 photolysis at lambda less than or equal to 398 nm smaller than unity?" Z. Phys. Chem. 214, 573 – 581, 2000.

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Peter Spietz, "Absorption cross-sections for iodine species of relevance to the photolysis of mixtures of I_2 and O_3 and for the atmosphere", PhD thesis, 2005

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J.C. Mössinger, D.E. Shallcross, and R.A. Cox, "UV-VIS absorption cross-sections and atmospheric lifetimes of CH_2Br_2, CH_2I_2, and CH_2BrI," J. Chem. Soc. Faraday Trans. 94, 1391-1396, 1998

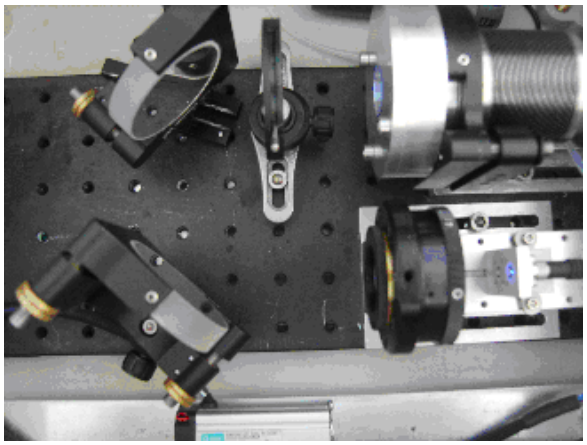
C Determination of Atmospheric Iodine Monoxide (IO) and Nitrate (NO_3) Radicals by Broad Band Cavity Enhanced Absorption Spectroscopy (BBCEAS)

Provider: Prof. Rod Jones, University of Cambridge, rlj1001@cam.ac.uk
Personnel: Ms Ailsa Benton

Using absorption bands between 420 and 480nm for IO and between 620-680nm for NO_3

Instrument Specifications:
Cavity Length: 1.17m.
Spectrometer: Acton SpectraPro 2300i.
CCD Camera: Acton Pixis 400.
Optical Fibre specifications: Input and output fiber both 400µm (Thorlabs Inc. BFL37-400, and RoMack Inc. Custom-made).
LEDs: For IO measurement: Luxeon 3-star 3W LXHL-LR3C (royal-blue), powered at 1A.
For NO_3 measurement: Roithner Lasertechnik JET-655-10 (red), powered at 350mA.
Mirrors: IO: Los Gatos Research Inc. 6m roc, 1inch diameter, 1x 430nm peak wavelength and 1x 460nm peak wavelength.
NO_3: Layertec, 1 inch diameter, roc=1m, 660nm peak wavelength.
Time resolution for IO/NO_2 data: 30s.
Time resolution for NO_3 data: 10s.
Calibration Method: Cavity was filled with a known concentration of O_2 (NO_2 when available) and measured absorbances compared to known absorption cross sections to calculate a mirror reflectivity function. Repeated 2-3 times per day or as required.
Instrument Position: Above and aft of the Port-side container, forward of the ship's exhaust funnel. Cavity was open-path to ambient air flow: no filters or pumps into the cell was required.

Position of BBCEAS Cavities on RRS Discovery



Optics

All data was collected and analysed using a program written in National Instruments' LabVIEW Version 8 by J. M. Langridge.

All experiments and data analysis detailed in this report were carried out by A. K. Benton.

University of Cambridge BBCEAS instrument uptimes: All times in UTC. Only full minutes of complete data are included.

Measuring in blue region for IO

23 May 2007, 13:09 until 23 May 2007, 16:06

23 May 2007, 20:59 until 24 May 2007, 09:00
24 May 2007, 09:49 until 24 May 2007, 12:53
24 May 2007, 13:17 until 24 May 2007, 14:45
24 May 2007, 16:34 until 24 May 2007, 18:56
25 May 2007, 07:39 until 25 May 2007, 12:48
25 May 2007, 13:06 until 25 May 2007, 18:51
26 May 2007, 08:11 until 26 May 2007, 09:36
26 May 2007, 09:55 until 26 May 2007, 12:44
28 May 2007, 07:07 until 28 May 2007, 13:06
28 May 2007, 13:33 until 28 May 2007, 18:47
29 May 2007, 07:51 until 29 May 2007, 11:12
29 May 2007, 11:29 until 29 May 2007, 14:21
29 May 2007, 15:05 until 29 May 2007, 20:08
30 May 2007, 07:10 until 30 May 2007, 11:23
30 May 2007, 11:36 until 30 May 2007, 14:28
30 May 2007, 14:43 until 30 May 2007, 16:37
31 May 2007, 16:34 until 31 May 2007, 18:59
31 May 2007, 20:06 until 01 June 2007, 06:28
01 June 2007, 07:29 until 01 June 2007, 11:26
01 June 2007, 11:45 until 01 June 2007, 14:18
02 June 2007, 06:39 until 02 June 2007, 08:43
02 June 2007, 09:31 until 02 June 2007, 18:32
02 June 2007, 21:04 until 03 June 2007, 06:22
03 June 2007, 06:42 until 03 June 2007, 07:45
03 June 2007, 08:28 until 03 June 2007, 13:02
03 June 2007, 13:23 until 03 June 2007, 16:38
03 June 2007, 23:17 until 04 June 2007, 08:16
04 June 2007, 09:15 until 04 June 2007, 12:25
04 June 2007, 12:46 until 04 June 2007, 16:41
04 June 2007, 17:29 until 04 June 2007, 20:44
04 June 2007, 21:03 until 05 June 2007, 05:23
05 June 2007, 06:46 until 05 June 2007, 11:07
05 June 2007, 11:25 until 05 June 2007, 14:25
05 June 2007, 14:46 until 05 June 2007, 16:56

Measuring in red region for NO_3

05 June 2007, 22:25 until 06 June 2007, 00:47
06 June 2007, 01:00 until 06 June 2007, 08:48
06 June 2007, 09:04 until 06 June 2007, 13:21
06 June 2007, 13:34 until 06 June 2007, 18:10
06 June 2007, 18:41 until 07 June 2007, 06:23
07 June 2007, 10:12 until 07 June 2007, 16:35
07 June 2007, 17:18 until 08 June 2007, 08:56
08 June 2007, 10:10 until 08 June 2007, 15:39
08 June 2007, 16:03 until 09 June 2007, 08:36

Problems associated with downtime: Calibration was required 3-4 times per day, resulting in instrument downtime for a period of around 1 hour.

Realignment was required on intermittent time periods depending on deposition rate of salt particles onto mirrors. Despite various prevention methods, including purging and protective bellows, sea-salt and particle deposits on the cavity mirrors caused constant degradation of their performance which was rectified to some extent with regular cleaning. However, this resulted in further down-time and a higher than expected limit of detection on affected data.

Broken permeation tube in transit resulting in no available NO_2 for calibration until a new tube was constructed on 30th May 2007. Prior to this, O_4 was used for calibration resulting in larger error boundaries from less accurate calibration.

Weather conditions often made cavity mirror realignment difficult and this was not attempted at all on some days for safety reasons.

Malfunction of the in-container air-conditioning unit caused temperature changes beyond limits of control of the internal *Peltier* LED-cooling system. This caused significant drift in the LED emission spectrum, leading to large signal/noise ratio and some data to be discarded.

The anti-vibration mounts and stand for the cavity were not secured by bolts to the deck as previously agreed. Strapping of cavity appeared tight but could have resulted in further noise on spectra caused by cavity rail movement.

The exit-hole on the container was positioned at the forward-end, resulting in a distance between the outside cavity and the internal electronics of greater than the 10m maximum specified. A longer optical fiber therefore had to be used. Tension on the fiber may also have increased noise.

Summary of Findings: The various problems detailed above resulted in data that requires a much more sophisticated analysis procedure than has been previously required in laboratory studies and it can therefore not yet be reported. Much of the data has a very high signal:noise ratio and some will have to be discarded. Additional parameters to account for drifts associated with temperature and particle depositions are in process of being applied. It is hoped that a detection limit for IO, and NO_2 (for blue-region measurements) and NO_3 (for red-region measurements) will be derived and any species present in concentrations above these be reported. Data format will include the following: Date; Time; [IO]; detection limit for IO; standard deviation in fitting; [NO_2] detection limit for NO_2; standard deviation in fitting; [NO_3] detection limit for NO_3; standard deviation in fitting spectra.

References: Ball, S.M.; Langridge, J.M.; Jones, R.L., Broadband cavity enhanced absorption spectroscopy using light emitting diodes. Chem. Phys. Lett., 2004, 398 (1-3): 68-74.

Langridge, J.M.; Ball, S.M.; Jones, R.L., A compact broadband cavity enhanced absorption spectrometer for detection of atmospheric NO2 using light emitting diodes. Analyst, 2006, 131, 8,: (916-922).

D Iodine monoxide (IO) detection by Laser Induced Fluorescence (LIF)

Provider: Prof. Dwayne Heard, University of Leeds, d.e.heard@leeds.ac.uk
Personnel: Dr Trevor Ingham, Ms Roisin Commane

Measurement of the concentration of atmospheric iodine monoxide (IO) radicals by the FAGE technique using Laser Induced Fluorescence (LIF): an all solid-state Nd:YAG pumped Ti:Sapphire laser operating at approximately 445 nm was used to excite the (2,0) band of the IO $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ electronic transition, with off-resonance fluorescence in the (2,5) band detected at 521 nm. The sensitivity of the instrument was determined by calibration. IO (between 2 and 40 pptV) was generated in a turbulent flow system following the 184.9 nm photolysis of $N_2O/CF_3I/N_2$ mixtures with NO actinometry used to determine the photolysis flux. The detection limit was determined to be 0.23 pptV for a 30 minute integration period (signal-to-noise = 1), with an uncertainty of 23% (1σ).

Data time integration: 30 mins

Data Summary: For all data analysed to June 2008, maximum IO mixing ratios of 1.9 pptv were observed during the day with 1.2 pptv observed during the night-time.

Clean data: collected continuously from 03:00 04/06/07 until 12:00 05/06/07 (30 minute data). These 33 hours of data represent the first open ocean measurements of IO in the marine boundary layer. For this time period: daytime mean = 1.2 pptv, night-time mean = 0.9 pptv, ave limit of detection: 0.7 pptv IO.
(33 hours = 66 x 30 min)

Subsequent data: (0100 07/06/07 – 1200 09/06/07) may be influenced by fog.
(59 hours = 118 x 30 min)
The validity of this data will be in doubt until other data (such as radiometer data) is submitted to verify the cleanliness of the samples.

Prior to 04/06/07: the data collected may be subject to influence from the boundary layer of the ship and will not be considered as valid measurements.
Data with sampling issues (data taken but may be influenced by ship boundary layer):
14 hrs 27/05/07, 10 hrs 28/05/07, 8 hrs 29/05/07, 5 hrs 30/05/07, 16.5 hrs 31/05/07, 14.5 hrs 01/06/07, 3 hrs 02/06/07, 3 hrs 03/06/07
(74 hours = 148 x 30 min)

Most of the data not logged during the campaign were due to 'dead' legs where the wind was passing through the ship and cannot be considered open ocean measurements. However, notable exceptions are a laser re-alignment period (02/06/07) and a laser repair period (05/06/07 – 07/06/07).

Total clean samples:	66 x 30 min
Data to be verified:	118 x 30 min
Data questionable:	148 x 30 min

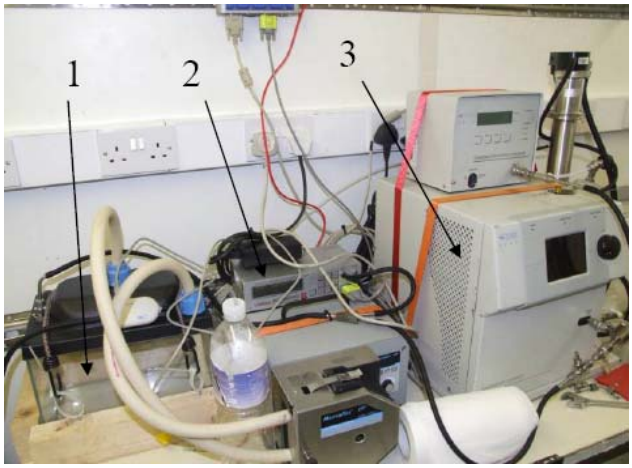
E, F Aerosol-related measurements

Providers: Dr James Allan, Dr Gordon McFiggans, University of Manchester, james.allan@manchester.ac.uk, g.mcfiggans@manchester.ac.uk
Personnel: Dr Elena Fuentes-Lopez, Mr Nick Good, Mr Martin Irwin

Fwd. container (ambient sampling)

1. Hygroscopicity tandem differential mobility analyser (HTDMA): Used to measure the size changes that occur within submicron particles when exposed to high (90%) humidity. Particles are dried, electrostatically selected according to size, humidified, then sized a second time before being counted using a condensation particle counter.
2. Thermo Electron multi angle absorption photometer (MAAP): Collects ambient aerosols onto a filter tape and measures the optical absorbance, which can in turn be used to estimate the concentration of black (elemental) carbon.

3. Differential mobility particle sizers (DMPS): These use electrostatic selection to separate particles according to size before counting with condensation particle counters, allowing the number and size of particles between 3 and 800 nm to be measured. In one instrument, the particles are dried, giving the particle sizes without any water content, whereas the other is operated at ambient (~85%) humidity, showing the size distribution representative of the outside atmosphere.
4. Droplet Measurement Technologies cloud condensation nuclei (CCN) counter: This instrument sets up temperature gradients within a wetted column to create supersaturated conditions typically seen during cloud formation (~0.07-0.15%SS), before counting the activated particles optically. This allows the number concentration of potential cloud particle seeds for a given supersaturation to be counted. On alternate hours, the instrument samples particles of specific sizes from the dry differential mobility particle spectrometer, allowing the cloud condensation nuclei concentration to be delivered as a function of dry particle size.
5. Aerodyne time-of-flight aerosol mass spectrometer (AMS): Uses an aerodynamic lens to focus particles into a beam before the majority of the gas from the sample is skimmed off. Particles between around 40 and 700 nm are impacted on a heated surface, where they flash vapourised. The resulting vapours are ionised using 70 eV electrons and the ions analysed using a Tofwerk high resolution orthogonal extraction mass spectrometer, allowing non-refractory components of the ambient particles (nitrate, sulphate, organic matter and ammonium) to be quantified. Aerodynamic sizing allows size-resolved data collection and the additional information on the organic fraction can be obtained through inspection of the mass spectra.



Fwd. container (seawater analysis) These measurements were provided to supplement the core RHaMBLe data in addition to the core measurements and are therefore not subject to the UK SOLAS data policy.

1. Bubble tank. Seawater (from either the clean water "fish" or the ship's non-toxic inlet) is flowed continuously using a peristaltic pump and onto the water surface in the tank, creating bubbles and generating particles, which are delivered to the other instrumentation.

2. GRIMM optical particle counter. Uses a laser to count and size particles of 600nm and greater.

3. TSI Scanning mobility particle sizer (SMPS). In a similar manner to the differential mobility particle spectrometers, uses electric fields and a condensation particle counter to count and size particles between 10 and 600 nm.

Fwd. container (mast)

1. Main aerosol inlet. Serves the instrumentation inside the container.

2. GRIMM optical particle counter. Used to measure the number and size of ambient particles above 600nm, mounted outside to minimise stack interferences that can affect larger particles.

3. Inlet for compact cascade impactor (CCI). The impactor cassette is mounted at the bottom of the stack and is used to collect aerosol samples for offline analysis, separated aerodynamically according to size. An automated switching mechanism inside the container can be used to shut off the collector if pollution is detected.

4. Vaisala temperature and humidity probe

5. In-line cyclone. Used to remove particles of a size greater than 4 μm before delivery to the sampling manifold inside the container.

Monkey Island

1. Andersen high-volume cascade impactors. Collect aerosol samples over periods of days onto quartz or cellulose (paper) substrates, separating particles aerodynamically according to size. Analysis of samples will be performed offline in the laboratory.
2. GRIMM optical particle counter. Identical to those associated with the container. Data sent back to container via a wireless network.

Performance: Most of the aerosol instrumentation in the fore container started collecting data in earnest on the 23/05/07. Prior to this, most of the instruments (AMS, dry DMPS, wet DMPS, CCN, CPC and HTDMA) were being set up and calibrated. Also, all of these instruments were being used to support the bubble tank experiments from 06/06/07 onwards, resulting in only partial coverage of ambient sampling during the return leg. Problems were encountered with the wet DMPS, which due to problems with the software and humidification system, only began to collect data properly on 31/05/07. Also, the dry DMPS experienced a pump failure on 04/06/07, resulting in partial data coverage. The HTDMA performed three humidograms, on 22/05/07, 29/05/07 and 04/06/07.
The MAAP, fore GRIMM and monkey island GRIMM all measured continuously during the entire cruise. There were some sporadic issues with the MAAP pump, resulting in partial data coverage on 22-24/05/07 and 06/06/07. Problems with the wireless communication resulted in a degradation in coverage for the monkey island GRIMM from 31/05/07, culminating in the loss of the measurement on 03/06/07. However, the data from the two GRIMMs were found to be identical for the period that they were both operating.
The compact cascade impactor (CCI) mounted on the container collected 17 24-hour sample sets during the course of the cruise, of which 2 were blanks and 4 were possibly of low quality (due to technical issues or sampling emissions from the ship or terrestrial sources). The first monkey island Anderson impactor collected 17 24-hour sample sets on cellulose substrates, including 2 blanks and 4 of possible low quality. The second Anderson collected 7 sets of samples on quartz substrates of varying duration (between 1 and 3 days), including 1 blank and 1 of possible low quality.

Preliminary findings: Analysis of the impactor samples is currently ongoing and will be available in due course. Preliminary data from the online instruments indicates that the nonseasalt fraction contained sulphate, organics, ammonium and desert dust. The dust appears to have originated from aloft, possibly through gravitational settling. There appears to have also some influences from terrestrial sources that may include the Canaries, western Africa or longer-range transport. The fore container instrumentation appears to have received minimal contamination from the ship itself. Work to apportion the different aerosol types to the different sources is ongoing.

Date	AMS	Dry DMPS	Wet DMPS	CCN	CPC	HTDMA	MAAP	Fore GRIMM	Monkey GRIMM	CCI	Cellulose Anderson	Quartz Anderson
05/19/2007	Set up		DMA1 broken			Cal						
05/20/2007	Electrical problems										Loaded incorrectly	
05/21/2007		Computer problems										
05/22/2007		CCN Cal		Cal		Humidogram	Pump problems					Blank
05/23/2007	Alignment		Counts wrong									
05/24/2007										Blank	Blank	
05/25/2007				Switching started								
05/26/2007			Humidifier problems									
05/27/2007												
05/28/2007												
05/29/2007						Humidogram						
05/30/2007												
05/31/2007									Wireless problems			
06/01/2007												
06/02/2007												
06/03/2007												
06/04/2007		Pump died				Humidogram						
06/05/2007		3025 butanol leak										
06/06/2007	Bubble experiments										Pump died	
06/07/2007										Blank	Blank	
06/08/2007												

Down	
Concerns	
Up	

G Nitric Oxide (NO), Nitrogen Dioxide (NO_2) and Ozone (O_3) Sampling

Providers: Dr James Lee, University of York, jdl3@york.ac.uk
Personnel: Ms Sarah Moller, sjm133@york.ac.uk

2 x Eco Physics NO analyser type CLD780 – Chemiluminescence detectors

Eco Physics Photolytic Converter – Conversion of NO_2 to NO

2B Technologies O_3 analyser

NO Analysers and Photolytic Converter: Gives NO and NO_2 concentrations in ppb from an inlet situated at ~ 8.5m above sea level through ¼ inch PFA tubing.

Data coverage: Run from 19/05/07 to 08/06/07, continuous sampling (except during calibrations and when running zeros; usually undertaken when sampling was affected by ship emissions)

From 19/05/07 to 24/05/07 run on one Eco Physics NO analyser, measuring both NO and NO_2, with the other Eco Physics NO analyser measuring only NO.

From 19/05/07 to 22/05/07 run on 2 min internal averaging

From 22/05/07 to 24/05/07 run on 1 min internal averaging

No sampling from 24/05/07 16:40 until 25/05/07 20:30, port call and instrument alterations as detailed below.

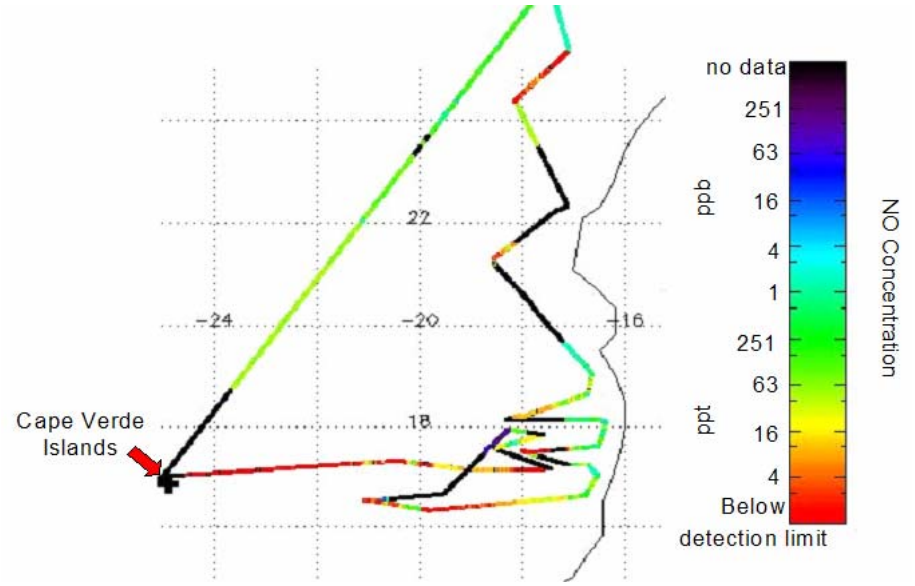
From 25/05/07 to 08/06/07 run with one Eco Physics NO analyser measuring NO and the other measuring NO_2 on 1 min internal averaging

Calibration: The NO analysers and photolytic converter were calibrated regularly (from every day to every three days depending on times when conditions meant that meaningful data could not be taken). They were calibrated using an Eco Physics PAG003 pure air generator, an Environs calibration gas blender 6100 and cylinder of 450 ppb NO in nitrogen. The NO standard was diluted using the gas blender to ~ 4ppb. The photolytic converter efficiency is also determined as part of the calibration using an ozone generator to perform a gas phase titration of NO to NO_2.

Zero air was run through the system on several occasions to allow more accurate determination of the systematic artefact and detection limit (LOD). .

Results: All data is averaged to 10 min and the submitted dataset has calibration and zero data removed. Data has been labelled according to whether the ship's heading suggests that ship emissions are being sampled. Throughout the cruise the NO_2 concentrations were considerably elevated above expected clean marine levels. It is believed that this is not reliable data and that an undiagnosed instrument fault or interference is the origin of the high NO_2. NO data, however, is highly logical and agrees well with preliminary black carbon data (supplied by Dr James Allan), so it is believed that this data was unaffected by the interference in NO_2.

NO data shows near zero values when around the Cape Verde Islands (below detection limit) and increasing concentrations as the African coast is approached both. Influence from the ship's stack can clearly be seen by extremely high values (hundreds of ppb) and rapid fluctuations; the degree of influence varies depending on wind direction, wind speed, ship's heading and ship speed.



NO:
Precision = 4 ppt
2σ LOD = 3 ppt
Accuracy ~ 10 %
Total uncertainty at 20 ppt = 20 %

NO_2:
Precision = 6 ppt
2σ LOD = 6 ppt
Accuracy ~ 20 %
Total uncertainty at 20 ppt = 35 %

Ozone analyser:
Gives O_3 concentration in ppb from an inlet situated at ~ 8.5m above sea level through ¼ inch PFA tubing.

Data coverage: Electrical fault identified in instrument on 21/05/07, data taken before identification was discarded as fault makes it unreliable (details of this instrument not included as no data used).

Alternative instrument (specifications given at beginning) obtained from Cape Verde Observatory on 25/05/07

Run from 25/05/07 to 08/06/07, continuous sampling

Run on 1 min internal averaging

Precision = 2 ppb
All values were well above the LOD (exact value not known)
Calibration was carried out at atmospheric observatory before instrument was taken onboard.

Results: All data is averaged to 10 min. Average ozone whilst around the area of interest is of the order of 40 ppb. Levels measured in close proximity to the Cape Verde Islands compare reasonably well with the instrument at the Cape Verde Observatory. When NO is highly elevated due to emissions from the ship (~400 ppb) a corresponding low in ozone is seen (~10 ppb). The influence of the Canaries can also be seen with an ozone high downwind of the islands, and a low when between the islands resulting from the presence of fresh pollution. As the ship travelled north towards Europe there is a general increase in ozone as would be expected.

H Determination of photosynthetic pigments by HPLC
Provider: Dr Brendan Keely, University of York, bjk1@york.ac.uk
Personnel: Dr Brendan Keely

High performance liquid chromatograph. Determination of photosynthetic pigments (abundances and distributions) in water samples collected from the non-toxic supply. Analyses provide a measure of the productivity of the waters and the health of the primary producers in the waters sampled.

These measurements were provided to supplement the core RHaMBLe data in addition to the core measurements and are therefore not subject to the UK SOLAS data policy.

No further information is available about these measurements.

H Underway ship's data
Provider: Martin Bridger, UKORS
Personnel: Martin Bridger

Logged Data (RAW)

GPS_4000	Trimble Navigator 4000		*Techsas
	Lat	= lat	
	Lon	= lon	
	Gndcourse	= hdg	
	Gndspeed	= hvel	
Logged but not used:	Alt		
	Prec		
	Nbseen		
	Nbused		
	HDOP		
	VDOP		

	PDOP	
GPS_G12	Fugro G12 GPS	*LevelB
	Type	
	Svc	
	Utc	
	Lat	
	Lon	
	Alt	
	Cmg	
	Smg	
	Vvel	
	Pdop	
	Hdop	
	Vdop	
	Tdop	
GPS_ASH	Ashtec Attitude Detection Unit 2	*LevelB
	Sec	
	Lat	
	Lon	
	Hdg	
	Pitch	
	Roll	
	Mrms	
	Brms	
	Attf	
WINCH	Cable Monitoring System	*LevelB
	Cabltype	
	Cablout	
	Rate	
	Tension	
	Btension	
	Comp	
	Angle	
EA500D1	10kHz Echo Sounder	*Techsas & LevelB
	Depth	
	Rpow	
	Angfa	
	Angps	
GYRONMEA	Gyrocompass	*Techsas
	Heading	
LOG_CHF	Chernikeef Log (EM LOG)	*Techsas
	Speedfa	
	Speedps	
SURFMET	Surface and Meteorological Instruments	*Techsas & *LevelB
	Temp_h	
	Temp_m	
	Cond	
	Fluo	
	Trans	
	Pres	
	Ppar	
	Spar	
	Speed	
	Direct	
	Airtemp	
	Humidty	

Ptir
Stir

Data Logging

*Techsas Logged on Techsas Logger (Replacment to Level A & B)
*LevelB Data was logged using the previous generation LevelA and LevelB

Processed Data (PRO)

RELMOV inputs: GYRONMEA, LOG_CHF
Output: RELMOV
Vn
Ve
Pfa
Pps

BESTNAV inputs: RELMOV, GPS_4000, GPS_G12, GPS_ASH
Output: BESTNAV
Lat
Lon
Vn
Ve
Cmg
Smg
Dist_run
Heading

BESTDRF
Vn
Ve
Kvn
Kve

WINDCALC inputs: bestnav, surfmet*
Outputs: pro_wind
Abswspd (knots)
Abswdir

PROTSG inputs: surfmet
Output: protsg
Temp_m
Temp_h
Cond
Salin
Sigmat

PRODEP inputs: EA500D1
Output: PRODEP
Uncdepth
Cordepth
Cartarea

Some temporary files were created to aid data editing SURFTMP is a editing copy of SURFMET RAWDEP is a editing copy if EA500D1

Level C

All data processing was done on Sun Workstation 'Level C' using rvs data format and rvs data processing tools. Data was converted from NetCDF where necessary.

Data Integrity

Gaps in data of more than 60 seconds:

GPS_4000
GPS_ASH
LOG_CHF
GYRONMEA
SURFMET

Cruise Data Archive
The cruise DVD(s) contains the following files:
Rvs data files. These are located in raw_data and pro_data, which refer to raw data from instruments and processed data that is derived from the raw data files e.g. pro_wind, protsg etc…
SBWR
Data files from the Shipborne Wave Recorder.
Techsas/NetCDF
NetCDF files logged on Techsas
Techsas/NMEA
NMEA files logged on Techsas
Ascii
All Cruise Data in ascii text format
Plots
Any plots and graphs produced during the cruise.
Weather
Weather charts from the Met Office sorted by type and date.
Misc
TSG water samples compared measured using Autosal compared to TSG Salinity with protsg.

Daily Data Processing
Data logged by was converted to RVS formatted files. The files converted were: position (log), gyro and log (Chernikeef). To convert the data we used the nclistit command e.g.
Nclistit [file to convert] – titsil –o [target stream] [variable list]
Bestnav - Takes navigation inputs from multiple navigation files and generates a continuous navigation file.
Relmov - Relmov is used to calculate the relative motion of the ship from gyro and log data.
Pro_wind - Used to derive absolute wind speed and direction from relative wind speed and direction, course and speed made good, and ships heading

Backups
Daily backups of data were taken throughout the duration of the cruise. Two tapes were used to ensure that data was retained for a period of 48 hours.

Data Cleaning
Data was manually edited to flag out bad data. Each variable is given a status flag of:
20 = REJECT
30 = SUSPECT
50 = GOOD
A value of less than 50 indicates that it is suspect value and is likely to have been flagged out or rejected.

PCO_2
The PML PCO_2 was continuously running throughout the cruise. There were occasions when it was out of while diagnosing an Iridium communications fault. The Iridium modem ceased to work on 29th May. The D319.paf and log files are located in the PCO_2 folder of the cruise DVD.

Surfmet (Continuous Surface Water and Meteorological Measurements)
Surfmet consists of thermosalinograph (temperature, conductivity) Transmissometer, Fluorometer, and remote temperature sensor connected to the ships non-toxic system in the wet lab.

Meteorological instruments are located on the fore mast. They consist of Port and Starboard PAR and TIR sensors. A temperature and humidity sensor. Wind speed and direction sensors, and a barometric pressure sensor.
For more information about sensors used please refer to the file:
D319 Surfmet Instrument List.doc

TSG Calibration.
Water samples were taken twice daily during the cruise to establish a relationship between the thermosalinograph and a standardised Autosal located in the constant temperature lab. The results of this calibration can be found in the file: D319_Autosal_Protsg.xls
Log sheets of water samples, cleaning and maintenance can be found in the files: TSG Maintenance Log.pdf & Salinity Log Sheet 1-36.pdf

The File Surfmet Cal Coefficients.doc contains information about the calibration coefficients entered into the Surfmet computer and used for the protsg processing routine. Protsg.cal.rtf is the actual calibration file protsg uses.