Gas Exchange Southern Ocean Experiment Cruise Report

NOAA Ship RONALD H. BROWN, cruise: RB-08-02



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2 Summary

The Southern Ocean GasEx experiment was conducted aboard the NOAA ship Ronald H. Brown with 31 scientists representing 22 institutions, companies and government labs. The cruise departed Punta Arenas, Chile on 29 February, 2008 and transited approximately 5 days to the nominal study region at 50°S, 40°W in the Atlantic sector of the Southern Ocean. The scientific work concentrated on quantifying gas transfer velocities using deliberately injected tracers, measuring CO₂ and DMS fluxes directly in the marine air boundary layer, and elucidating the physical, chemical, and biological processes controlling air-sea fluxes with measurements in the upper-ocean and marine air. The oceanic studies used a Lagrangian approach to study the evolution of chemical and biological properties over the course of the experiment using shipboard and autonomous drifting instruments. The first tracer patch was created and studied for approximately 6 days before the ship was diverted from the study site, 350 miles to the south, to wait near South Georgia Island for calmer seas. After more than 4 days away, we returned to the study area and managed to find some remnants of the tracer patch. After collecting one final set of water column samples and recovering the two drifting buoys deployed with the patch, we relocated to the northwest, closer to the area where the first patch was started. A second tracer patch was created and studied for approximately 15 days before we had to break off the experiment and transit to Montevideo, Uruguay for the completion of the cruise. During the transit we hit rough weather and had to hove-to for two days. We were scheduled to arrive on 10 April, 2008. We pulled into the Montevideo harbor on 11 April, but there was not room at the pier. We were forced to anchor out for a night and dock on Saturday 12 April.

3 Introduction

Currently, large uncertainties in the air-sea flux of CO₂ prevent verification of the partitioning of fossil fuel CO₂ between the ocean and the terrestrial biosphere. These uncertainties limit the ability of models to realistically predict future atmospheric CO₂ levels. Techniques are now in hand to improve estimates of air-sea fluxes. Given the paucity of data, however, there is a clear need to quantify gas transfer velocities at wind speeds in excess of 10 m s⁻¹ (e.g., see *Ho et al.*, 2006). The Southern Ocean represents a poorly sampled but globally significant CO₂ sink (*Takahashi et al.*, 2002). It frequently experiences the higher wind speeds that need to be studied. It is also entirely possible that the Southern Ocean CO₂ flux is governed by factors other than just wind speed and Δ pCO₂ such as biological processes and wave formation. Therefore, with financial support from NOAA, NASA and NSF, the Southern Ocean Gas Exchange (SO GasEx) experiment was designed to address the following questions:

- What are the gas transfer velocities at high winds?
- What is the effect of fetch on the gas transfer?

- How do other non-direct wind effects influence gas transfer?
- How do changing pCO₂ and DMS levels affect the air-sea CO₂ and DMS flux, respectively in the same locale?
- Are there better predictors of gas exchange in the Southern Ocean other than wind?
- What is the near surface horizontal and vertical variability in turbulence, pCO₂, and other relevant biochemical and physical parameters?
- How do biological processes influence pCO₂ and gas exchange?
- Do the different disparate estimates of fluxes agree, and if not why?
- With the results from Southern Ocean GasEx, can we reconcile the current discrepancy between model based CO₂ flux estimates and observation based estimates?

4 Order of Events

The NOAA Ship *Ronald H. Brown (RHB)* departed from Punta Arenas, Chile on 29 February, 2008 with 31 scientists aboard (Table 1). Departure was a day later than originally scheduled because several shipments, including two containers of equipment essential to the project, were delayed in arriving to Punta Arenas. One container, with the SuperSoar equipment, arrived on 28 February. The second container, which contained the MAPCO₂ buoy, arrived on 29 February and was loaded shortly before the ship departed. Three shipments did not arrive in time to make the ship: the French Carioca buoys, a hydrophone mooring that we were going to deploy as a piggyback project, and a spare SuperSoar cable. These items did finally arrive in Punta Arenas on 3 March, three days after the *Ron Brown* had already departed.

After departure, the ship proceeded east into the southwest Atlantic towards the nominal study site at 50°S, 40°W plus or minus five degrees (Figure 1). As we have learned from previous open ocean gas exchange studies, the study site selection is critical for ensuring the success of the experiment. The general study area of SO GasEx was chosen to satisfy the following criteria:

- to have a ΔpCO₂ of at least 40 µatm to ensure a large enough signal to noise for direct eddy-covariance measurements of CO₂
- be a relatively stable water mass (i.e., weak currents and low mesoscale eddy variability) to allow ³He/SF₆ patch to be followed for up to 25 days,
- have mixed layer depth of less than 50 to 70 m to constrain the tracers,
- have relatively high wind speeds, long fetch and large waves,
- and proximity to South American ports to minimize transit time.

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Table1. Cruise Participants



Figure 1 Map of South Atlantic showing the locations of relevant ocean fronts and the proposed study site.

After a 5 day transit to the study region, a site survey was started. Significant variability is known to occur in the Southern Ocean so remote sensing products of ocean color, altimetry and sea surface temperature (SST) were used to refine the nominal study region from 40°W to 38°W to avoid a broad area with a strong northward current. After an initial survey of the nominal study area using the surface underway systems, the plan was to use the SuperSoar to develop a detailed image of the subsurface structure. The SuperSoar went in the water on March 6, but after approximately 7 hours of successful operation the instrument struck an underwater object. The SuperSoar was successfully recovered but the tow cable was damaged beyond repair. The site survey was continued using the surface underway systems until the tracer injection started on 7 March. The underway seawater systems were secured and a GPS drifter was deployed at 50°36'S, 38°40'W. The ship circled around the GPS drifter while injecting the tracer at about 6m depth. Creation of an 8 km wide patch took approximately 13 hours. Once the injection was completed (8 March) the GPS drifter was recovered and the MAPCO₂ system was deployed. The ASIS buoy was deployed in the patch on 10 March. Optical casts were conducted from 13:00-14:30 GMT and CTD casts were conducted at 15:00 and 23:00 each day. In between casts the patch was surveyed with the underway systems.

When the MAPCO₂ system was first deployed it was sitting lower in the water than intended so the buoy was recovered on 12 March, reconfigured with less weight and two fewer drogues, then redeployed on 13 March. The afternoon of 13 March we received a warning from the Navy of high wind and wave conditions approaching our study area, the exact conditions for which we had been planning and waiting. However, the ship experienced a combination of mechanical and software failures on items that were overdue for maintenance that could impact the ship's ability

to handle rough seas. The Captain decided to move the ship to a safer location; in this case, 350 miles to the south near South Georgia Island where the ship could duck behind the island to avoid the wind and waves if necessary (Figure 2).

On17 March we were cleared to return to the study site. We reached the MAPCO₂ buoy in the evening and surveyed the area until morning. Although we did find some tracer near the buoy, we decided that we needed to create another patch as soon as possible. On 18 March the MAPCO₂ buoy was recovered, the ASIS buoy was recovered and then we transited back towards



the original tracer injection spot to create the second patch.

The injection for the second patch was started the evening of 20 March after two days of surveying to find the best site. The conditions (particularly the currents) were not quite as favorable as the first injection. The GPS drifter was deployed at 51°9'S, 38°29'W. The tracers were pumped at a higher rate and the ship did smaller circles so a 4 km wide patch was created in a little over 6 hours. Once the injection was finished, the MAPCO₂ system was deployed in the patch and the GPS drifter was recovered. After an initial patch survey the CTD and optical time series measurements were started on 21 March.

Figure 2 Track for Ronald H. Brown on SO GasEX.

On 31 March the MAPCO₂ buoy was recovered because it had moved approximately 50 km southeast of the primary patch. The shipboard surveys and time series CTD/rosette casts were continued until 5 April when the ship started its transit to Montevideo, Uruguay. During the transit we hit rough weather and had to hove-to for two days. We were scheduled to arrive on 10 April, 2008. We pulled into the Montevideo harbor on 11 April, but there was not room at the pier. We were forced to anchor out for a night and dock on Saturday 12 April.

5 Science Implementation

In order to investigate the questions and problems posed in the research objectives of SO GasEx, a series of projects were funded which roughly fall into the following categories:

	Research Projects	Mathad		
	Research Trojects	ivicinou		
1	Direct Flux Measurements (CO_2 , ozone and DMS)	Air-sea CO ₂ (NDIR), Ozone and DMS (APIMS) flux systems		
2	Bulk Meteorology and Turbulent Fluxes (winds, momentum, water vapor, temp, IR, Solar radiation, etc.)	Sonic anemometer, thermometer, pyranometer, pyrgeometer, MicroSAS		
3	Integrated Gas Transfer Velocities with Deliberate Tracers (SF ₆ and 3 He)	Continuous and discrete SF_6 systems (GCs) and He isotope mass spec		
4	Surface and Subsurface variability (CO ₂ , nutrients, calcite, DMS, chlorophyll)	Shipboard underway systems, NDIR CO ₂ systems, GC, EcoVSF, ICPOES, fluorometer, ACS, ISUS, SuperSoar/TOMASI		
5	Autonomous Platforms	MAPCO ₂ , SAMI, ASIS, surface drifters, SOLO floats		
6	Surface and near-surface ocean processes (wave spectra, white capping, currents)	Shipboard radar; microwave altimeter, video camera, ADCP		
7	Water column hydrography, carbon and related tracers (DIC, pCO ₂ , Talk, temp, sal, O ₂ , nutrients, DOC, CDOM, PIC, O ₂ /Ar/N ₂ , DMS, particles, TSM, Chl., POC)	SOMMA, NDIR, titration, CTD, Winkler, nutrient autoanalyzer, spectrophotometer, mass spec., GC, HPLC, fluromoter		
8	Primary production/new production	¹⁴ C and ¹⁵ N incubations, O ₂ /Ar, spectral absorption, radial photosynthetron		
9	Ocean Optics	PAR sensor, FRRF, IOP cage, HTSRB, MVSM		

Table 2. Categories of research projects on SO Gasex.

5.1 Direct Flux measurements

A number of instruments for making atmospheric concentration and flux measurements were mounted on a mast at the bow of the ship (e.g. Figure 3). These instruments are summarized in Table 3 and described in the following sections.



Figure 3 Overall picture of the instrument setting on jackstaff; three sonic anemometers, five Licors, and two Vaisala sensor probes with their respective bee-hives.

Measurement	Methodology	Scales	Comments
Closed-path, open-path, null, shipboard Air-Sea CO ₂ flux	Direct Covariance of CO ₂	100 m ² ; 20 min	Short-term measurements.
Latent and Sensible Turbulent Heat Fluxes	Direct covariance of virtual temperature and water vapor	20 min	Short-term measurements.
Momentum Flux	Direct Covariance using wind velocity	20 min	Short-term measurements.
Shipboard motion correction package	Integrated accelerometer and tilt	20 min	
Longwave Radiative Fluxes	Pyrgeometer	20 min	
Shortwave Radiative Flux	Pyranometer	20 min	
Wind Speed	3-D Anemometer	20 min	Accurate mean wind speeds.
Waves	WaMoS II	20 min	Directional Spectra
Waves	Laser Altimeter	20 min	Significant wave height, Spectra.
Waves	Microwave Altimeter	20 min	Significant wave height, Spectra
Whitecapping	2 Video Cameras	100 m ² ; snapshots	Whitecap coverage, breaking frequency
Global Position System	GPS (Dual-Antenna)		Heading, Location and Timestamp

Table 3. Components of flux systems.

5.1.1 CO₂ Flux (Zappa, Cifuentes, Bariteau)

In a collaboration between NOAA Earth System Research Laboratory, the University of Connecticut (UConn) and Lamont-Doherty Earth Observatory (LDEO), numerous atmospheric CO₂ measurements have been made on this cruise. There were five LI-7500's up on the foremast sampling at 10-20 Hz. Three Licor 7500 were mounted at the top of the mast as an open path system (direct atmospheric sampling) these three open path systems are from the University of Connecticut; two more Licors from NOAA PSD complete the set of five. The set was operated with one Licor acting as a Null (completely enclosed without air flow) and one Licor operating under a sleeve (enclosed but with an air flow-through). The Null is intended to be used as a white noise filter due to high frequency oscillations related to the ship motion and mast vibration. The air sampled by the sleeved Licor previously went through a mixing chamber that acted as a high frequency filtering function. The sleeved Licor was intended to provide weather proof measurements. All the units, except the null one, are washed regularly in order to remove any sources of contaminations.

Three Licor 6262 units were mounted in the University of Hawaii DMS van on the 02 foredeck. These units provided by LDEO were set to sample at 5 Hz. The air was drawn from up the mast to the van by three pumps. Pump fluctuations are taken out by setting a mixing chamber between the pump and the Licor units at the end of the sampling line. These chambers stabilize the unit pressure improving the CO_2 and H_2O measurements. These systems provide solid CO_2 concentrations and are used as a core measurement in the direct flux estimates in conjunction with the faster sampled Licor 7500 units.

By the end of the cruise we accumulated approximately 15 gigabytes of data that needs to be analyzed. The time series will need to be averaged and filtered in order to get the high frequency variations due to turbulence (eddies) and get rid of the white noise due to artifact issues or motion contamination from the ship. Motion correction from the ship's tilt, roll and yaw will also be needed previous any flux calculation can be made plus correction from the ship's own velocity over ground.

During the cruise the data analysis was limited to daily plots of the time series in order to check that the instruments were in good shape and running. Daily plots also helps the selection of good periods were the time series are well behaved, meaning the noise levels are low. The Licor units 7500 mounted up in the mast are sensitive to weather conditions (relative humidity and precipitation) under these conditions the time series clearly shows high noise levels and reporting erroneous readings.

Figure 4 shows the instrument sensitivity to weather conditions and the need for further analysis of the time series. The flux calculations are based upon the signal fluctuations around the mean, it is therefore very important to get a good signal to noise ratio.



Figure 4 Julian day 86 hour 15, shows noisy series of CO₂ and H₂O for a rainy day. CO₂ and H₂O units are mmol/ m³.

Spectral analysis of CO_2 and H_2O were also made in order to check the Licors 6262 and 7500 signal response and coherence. Initial CO_2 variance spectra in Figure 5 computed from the data shows the signal levels for the closed and open path sensors appear to agree out to 0.2 Hz and the null sensors indicate fairly low noise. The coherence between the open and closed path sensors will improve after we have compensated for the lag between the closed-path (6262) and open-path (7500) sensors.



Figure 5 Comparison of the CO₂ variance spectra for the 3 Licor 6262 sensors and 4 of the 5 Licor 7500 sensors.

For the flux measurements, it is best to have head winds to minimize flow distortion by any platform and structure. Periods for when the Sonic Anemometers are aligned into the wind must be identified. The wind time series need to be motion corrected and aligned into the main wind stream. The motion correction is a necessity before calculating any flux. Aligning the wind into the main stream is preferred instead of working with the wind velocity components. It is preferred at least a period of one hour under this conditions of alignment for flux measurements, this is required in order to achieve a solid mean wind velocity and the corresponding velocity perturbations.

5.1.2 Ozone Flux (Bariteau)

Ozone concentration was also present in the standard ESRL flux package. The first-ever direct eddy correlation (EC) measurements of ozone flux from the ship were made with this system. This fast ozone sensor was designed in Boulder as a collaborative effort between NOAA and INSTAAR to help understand more about the destruction of ozone at the ocean's surface. This sensor was setup in the University of Hawaii's container on the 02 deck. A sampling line runs to the jackstaff with the sampling inlet near the sonic anemometer. Two additional slow ozone monitors were used as well for calibration purposes and low frequency measurement.

Time series of ozone concentration is shown on Figure 6 for March 2nd to April 6th, 2008. As for the aerosol systems, most of the drops in the signal are caused by the ship's exhaust. The NO released by the ship interacts with ozone. Some drops are due to lag time testing on the system. All of these bad data points will be removed later during post-processing.





Figure 6 Ozone concentrations from the fast ozone instrument, from JD 62 to JD 97 (2 March to 6 April, 2008).

The ambient level of ozone has been pretty low in this part of the ocean. The maximum ozone peak encountered was about 27ppbv on Julian Day 81. An interesting feature is the difference in concentration between the two surveys. During the first patch, the mean ozone concentration was about 15.5 ppbv, whereas it reached a mean level of 20 ppbv for the second survey. A closer look to other parameters will be done in order to understand why.

5.1.3 DMS Flux (Blomquist)

University of Hawaii (PIs Huebert, Blomquist) operated an atmospheric pressure ionization mass spectrometer (APIMS) for 20 Hz measurements of dimethylsulfide (DMS) in ambient air. In cooperation with NOAA/PSD (PIs Fairall, Bariteau, providing 10 Hz wind data) and Plymouth Marine Lab (PI Archer, providing underway seawater DMS data) we will compute the flux and sea/air transfer velocity of DMS during the on-site tracer/buoy studies and for much of the underway transit to and from the study area. Additionally, we have configured the APIMS for seawater DMS measurement during portions of the transit legs and will conduct an intercomparison of the APIMS and purge and trap DMS methods.

As of 3/28/08, we had 24 days of nearly continuous 20 Hz atmospheric DMS data (Figure 7) and operations continued until we reached the Uruguay EEZ on the in-bound transit leg. The figure illustrates how the hourly average DMS has varied over the course of the cruise. The general trend has been a decrease in concentration, punctuated by periods of higher concentrations, presumably arising from upwind advection over DMS-enriched areas of the ocean. We note that computation of the DMS sea/air flux depends on the variability in DMS concentration over short time scales and not on the mean concentration, so flux cannot be inferred from this plot. Flux is also largely determined by local seawater conditions and not by conditions more than a few kilometers upwind of the ship.



Figure 7 atmospheric DMS concentrations on SO Gasex cruise.

The APIMS performed well on this cruise, exhibiting high sensitivity (generally > 200 cps/ppvt). Other than minor maintenance no significant instrumental problems have occurred. We have computed fluxes for a few days thus far and the data appear acceptable. Figure 8 shows a covariance spectrum for DMS and vertical wind velocity illustrating a positive covariance at frequencies from 0.001-1 Hz, which is typical for fluxes measured from surface platforms. In this case, the integrated co-spectrum yields a flux of 6.14 μ moles DMS/m²/day.



Figure 8 covariance spectrum for DMS and vertical wind velocity.

Mean wind speeds have ranged from less than 5 m/s to more than 15 m/s. Fluxes and derived transfer velocities will therefore span a useful range of conditions, extending our previous measurements to higher wind speeds and providing more robust data set for development and validation of gas exchange models.

5.2 Bulk Meteorology and Turbulent Fluxes

The NOAA/ESRL Physical Science Division (PSD) air-sea flux group collaborated with LDEO and University of Connecticut to conduct measurements of near-surface bulk meteorology in the Southern Ocean at 50°S Latitude, 40°W Longitude. The systems were installed initially on the *RHB* in Charleston, SC, in early October 2007. Then it was used during the fall for the STRATUS 2007 cruise off the coast of South America (20°S, 85°W). Finally, it was tested and brought back into full operation in Punta Arenas, Chile, in late February, 2008. The official start of the SO GASEX experiment and data collection was around 1600 GMT 29 February, 2008 (JD 61). We arrived on the study site station on day 65 (5 March, 2008). The first tracer patch survey was from JD 68 to 73 (8 March to 13 March, 2008), and the second patch period was from JD 81 to 96 (21 March to 5 April, 2008). At about 1400 GMT on day 96 (5 April, 2008), the *RHB* departed the site to begin its transit to Montevideo, Uruguay.

5.2.1 Aerosol and Sea Spray Measurements (Bariteau)

Atmospheric aerosols were measured with a Particle Measurement Systems (PMS) Lasair-II aerosol spectrometer. The Lasair-II draws air through an intake and uses scatter of laser light from individual particles to determine the size. Particles are counted in six size bins: 0.1-0.2, 0.2-0.3, 0.3-0.5, 0.5-1, 1-5, and greater than 5.0 μ m diameters. The PSD system was mounted in the University of Hawaii's seatainer on the 02 deck with the intake on the upwind side of the container. The system ran at 1.0 cfm (0.028 m³/min) sample volume flow rate with a count deconcentrator that reduces the counts a factor of 10 (to prevent coincidence errors).

Another aerosol instrument from University of Leeds was deployed on the foremast, near the sonic anemometer. This Compact Lightweight Aerosol Spectrometer Probe (CLASP) is used to make high frequency measurements of aerosol spectra suitable for direct eddy correlation determination of the sea spray particle flux. This device is capable of measuring 8-channel size spectra for mean radii between 0.15 and 3.5 µm at 10 Hz.

Data from the PMS Lasair-II aerosol spectrometer is shown in Figure 9. The instrument size range includes most of the so-called accumulation-mode aerosols that represent most of the particles activated to form droplets in clouds. Thus, the total number of aerosols counted by this device is expected to correlate with cloud condensation nuclei and the number of cloud drops. The Lasair-II only observes the large particle size mode. The concentration varies with a time scale of several days. This is the result of the complex interaction between entrainment, advection, production and scavenging of aerosols. Spikes in the graph are caused by the ship's exhaust. We can observe that most of the aerosol concentration variation correlates with the variations in the heat fluxes (Figure 10), especially with the net longwave radiation which is connected to energy emitted from aerosols.



Figure 9 Aerosol concentrations from Lasair-II spectrometer from JD 62 to JD 97 (2 March to 6 April, 2008). Upper panel: total number concentration for aerosols larger than 0.1 micron diameter. Spikes are caused by the ship's exhaust. Lower panel: size fractionated concentrations.



Figure 10 Surface fluxes during SO GasEx from JD 62 to JD 97 (2 March to 6 April, 2008). From the top, the panels show the longitudinal component of the wind stress (N m^{-2}), the net heat flux (W m^{-2}), the solar flux (W m^{-2}), the net longwave radiation flux (W m^{-2}), the sensible heat flux (W m^{-2}) and the latent heat flux (W m^{-2}).

5.2.2 The NOAA/ESRL PSD Bulk Meteorological Measurement Package (Bariteau)

In addition to the measurements discussed above, the PSD air-sea flux system includes:

- a fast turbulence system with ship motion corrections mounted on the jackstaff. The jackstaff sensors include: GILL Sonic anemometer and a Systron-Donner motion-pak,
- a mean Temperature/Relative Humidity sensor in an aspirator on the jackstaff,
- solar and infra-red radiometers (Eppley pyranometers and pyrgeometers) mounted on top of a wood pole on the 02 deck,
- a near surface sea surface temperature sensor consisting of a floating thermistor deployed off port side of the ship with an outrigger,
- a Riegl laser rangefinder wave gauge mounted on the bow tower, and
- an optical rain gauge mounted on the bow tower.

Slow mean data (T/RH, PIR/PSP, etc) are digitized on a Campbell 23x datalogger and transmitted via RS-232 as 1-minute averages. A central data acquisition computer logs continuously all sources of data via RS-232 digital transmission and wireless radio modem network. A GPS system is also included to define the heading and ship location as well as providing a uniform time stamp for the analysis

At sea, programs are run each day for preliminary data analysis and quality control. As part of this process, we produce a quick-look ASCII file that is a summary of fluxes and means. The data in this file come from three sources: The PSD sonic anemometer (acquired at 10 Hz), the Ship's Computer System (SCS) (acquired at 0.5 Hz), and the PSD mean measurement systems (sampled at 0.1 Hz and averaged to 1 min). The sonic is 5 channels of data; the SCS file is 17 channels, and the PSD mean system is 77 channels. A series of programs are run that read these data files, decode them, and write daily text files at 1 min time resolution. A second set of programs reads the daily 1-min text files; time matches the three data sources, averages them to 5 and 30 minutes, computes fluxes, and writes new daily flux files.

5.2.3 LDEO/U. Conn. Bulk Meteorological Measurements (Zappa, Cifuentes)

Two Sonic Anemometers measured the wind velocities (u, v and w) and the corresponding perturbations. Sampling frequency was 20 Hz. The Sonics were mounted in the front line up in the mast to avoid flow distortion; one is set on the port side the other one to starboard a third sonic from NOAA is set in between completing a 3 Sonic system which will provide the velocity ensemble for flux calculations.

Two Motion Packages (mounted as one unit with the Sonic Anemometers) measured linear accelerations (x, y and z), angular rates and platform displacement (roll, yaw and pitch) in order to apply motion correction accounted by the ship's motion. Sampling frequency was 20 Hz.

Two Vaisala systems provided redundancy in temperature and relative humidity to calculate specific humidity for the latent heat flux. Sampling frequency was 1 Hz.

The data acquisition system (DAS) was based on the Spipacq4 software and was run in a Dell Laptop placed inside the main lab, instruments were powered and controlled from the same spot. Connection was made by 120 feet cables run from the mast into the lab.

NOAA's instruments located up in the mast are logged by a signal splitting box located in the main lab, the signal splitting box also enables us to send our signal to NOAA PSD data acquisition system creating a more solid data ensemble for us and for NOAA PSD.

5.2.4 Above-Water Radiance Measurements (Drapeau)

In order to check satellite PIC algorithm performance, free of atmospheric error, water-leaving radiance, sky radiance and downwelling irradiance were measured from the bow of the *RHB* using a Satlantic SeaWiFS Aircraft Simulator (MicroSAS). The same wavelengths used in the 2-band and 3-band calcite algorithms were measured with the MicroSAS. The system consists of a down-looking radiance sensor and a sky-viewing radiance sensor, both mounted on the bow. A downwelling irradiance sensor was mounted at the top of the jackstaff. These data were then used to estimate normalized water-leaving radiance as a function of wavelength. The radiance detector was set to view the water at 40° from nadir as recommended by Mueller et al. (2003b). Sensors were rinsed regularly with Milli-Q water in order to remove salt deposits and any dust.

The water radiance sensor was able to view over an azimuth range of $\sim 270^{\circ}$ across the ship's heading with no contamination from the ship's wake. The direction of the sensor was adjusted constantly to view the water 120 ° from the sun's azimuth, to minimize sun glint. This was done using a computer-based system that calculated the sun's azimuth angle relative to the ship's heading and elevation constantly. The system used the ships gyro-compass to determine the heading of the ship. Depending on the ship's course, the computer controlled a stepping motor that turned the sensors to the proper viewing angle. Protocols for operation and calibration were performed according to Mueller (Mueller et al. 2003a; Mueller et al. 2003b; Mueller et al. 2003c). Data was collected between about 1100 and 1800 GMT when the sun was above 20 ° elevation. Post-cruise, the 16Hz data will be filtered to remove as much residual white cap and glint as possible (we accept the lowest 5% of the data). Also we will attempt to use the ships pitch/roll data to correct for angular changes in post processing. Several calibrations with 10% reflectance plaque were performed during the cruise.

5.2.5 High Volume Air Sampling (Zappa, Cifuentes)

Six high volume air samples (approximately 24 hr sampling per sample) were collected during steam time to and from station and an additional 19 samples were collected while on station. The sampler was mounted on the O3 deck below the bridge at the bow of the ship to minimize sampling of exhaust gases from the stacks. The sampling train comprised a glass fiber filter for particle phase collection followed by a polyurethane foam (PUF)/XAD-2 sandwich for trapping gas-phase compounds. The sandwich consisted of 10g XAD-2 resin between two PUF plugs (80 mm diameter, 75 mm thick (top), 15 mm thick (bottom)). Average ambient air temperatures during sampling were in the range 3 to 10°C. Surface water temperatures were in the range 3 to 5°C. Fluoropolymer gaskets were not used on the high volume sampler to eliminate potential contamination of target compounds. Field blanks (n = 4) for PUF/XAD sandwiches were collected by inserting the media to the sampling system and running the pump on for ~1min. Four field blanks for GFFs were collected. Samples are to be shipped cold and stored at -4°C until extraction in Vlahos's lab at UConn.

5.3 Deliberate Tracers

5.3.1 Tracer Injection (Sullivan, Reid, Schmieder, Ho)

Two tracer injections were made during SO GasEx. For each, approximately 4800 L of seawater were infused with SF₆ and ³He, and released into the surface mixed layer. A large tracer infusion tank on the fantail was filled with seawater en route to the study site, and a headspace of ca. 1 L was continuously flushed with SF₆. The SF₆ was circulated from the headspace and pumped into the water via a diffusion hose until the water was presumed to be saturated. A few hours before tracer injection, the SF₆ circulation was stopped and a headspace of ³He with volume ca. 1 L was created in the tank. This headspace was bubbled through the water for several hours in a closed loop. As the ³He dissolves in the water, another 1 L headspace was created. A total of approximately 10 L of ³He was infused into the water for each injection.

³He and SF₆ saturation was to be determined by measurement using a gas chromatograph equipped with a thermal conductivity detector (GC/TCD). However, due to instrumental problems, we were forced to carry out the injection without measuring the saturation level of the ³He and SF₆ in the infusion tank. Based on previous experience, the infusion times should have been long enough for SF₆ and ³He.

Before beginning the tracer injection, a GPS-enabled drifter with a line-of-sight VHF transmitter was deployed, marking the center of the water parcel and allowing the injection to proceed in a Lagrangian fashion with the ship following a track marked by waypoints at the vertices of expanding hexagons, each centered on the up-to-date position of the GPS drifter.

During tracer injection, the top of the tank was fitted with a weather balloon. As water was pumped out of the tank with a peristaltic pump, the weather balloon was gravity-fed with seawater from a header tank to ensure that a headspace, which would allow ³He and SF₆ to be exchanged and thus altering the ³He/SF₆ ratio, did not develop.

The first injection took place on March 8, 2008, and lasted almost 13.5 hours at a flow rate of 6 L min⁻¹, creating a patch with an area of ca. 50 km^2 . The second injection, in a different water parcel, was on March 21, 2008, and lasted 6.5 hours at a flow rate of 10.2 L min⁻¹, creating a patch with an area of ca. 12.5 km^2 . Nominal injection depth for both patches was about 5-6 m. The smaller patch had two distinct advantages over the first patch:

Because the volume of SF_6 and ³He infused water that we injected was the same for both, a smaller initial patch injected at a higher flow rate resulted in higher SF_6 and ³He concentrations, and enabled us to follow the patch for a longer period.

Because of the limited time for surveying the patch, having a smaller patch meant that we could more fully survey the patch over time.

5.3.2 Underway SF₆ System (Reid, Schmieder, Ho)

An Underway SF_6 System, described in detail in Ho et al., [2002] was used to monitor the advection and dispersion of the SF_6 (and ³He) tracer patch. The system was used to determine the center of the patch (i.e., the area of maximum tracer concentration) for the twice-daily CTD casts.

The system receives water from the uncontaminated seawater line, and consists of 2 main units: The gas extraction unit, and the gas separation and analysis unit. It has a sampling interval of 1.25 min and a detection limit of 1 x 10^{-14} mol L⁻¹. The main component of the gas extraction unit is the membrane contactor (Liqui-Cel MiniModule), which contains thousands of microporous (0.05 µm) polypropylene hollow fibers. Water flows on the inside of the hollow fibers, while ultra-high purity (UHP; 99.999%) N₂ flows countercurrent on the outside of the hollow fibers, resulting in rapid transfer of dissolved SF₆ from the liquid phase to the gas stream. There are also two dissolved oxygen sensors (DO) located before and after the membrane contactor, which give an indication of the DO stripping efficiency. The SF_6 extraction efficiency is then calculated from an empirical relationship between O_2 and SF_6 extraction derived in the laboratory.

At approximately one minute intervals, the gas stream is diverted to the gas separation and analysis unit, through a physical (Nafion) and a chemical (Mg(ClO₄)₂) dryer. After filling a sample loop, the sample is injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD) by UHP (99.999%) N₂ carrier gas. The SF₆ is separated from other gases at room temperature with a molecular sieve 5A column. Typically, 8 samples are bracketed by standards. During data reduction, the sample concentrations are calculated from time-weighted standards. Four different sample loops were used during SO GasEx (2.58, 3.13, 4.85, and 7.60 ml). The analytical precision, based on repeated measurements of the standard over 24 hour periods, is $\pm 2.9\%$, $\pm 4.4\%$, $\pm 2.2\%$, and $\pm 2.5\%$ for the 2.58, 3.13, 4.85, and 7.60 ml loops, respectively.

Valve control and data acquisition are handled by a combination of hardware and software (LabView) running on a personal computer. The hardware is connected to the computer via Universal Serial Bus (USB) and contains digital input/output (I/O) ports and 24-bit analog to digital (A/D) data acquisition ports. In addition to the signal from the GC-ECD, the A/D also acquires signals from the water flow meter. Communication with the global positioning system (GPS) and the DO sensors is accomplished via RS-232. During each analysis, the analog output of the GC-ECD is converted to a digital signal by the data acquisition board and analyzed by a commercially available chromatography package (WillStein). The results are stored on the computer.

The SF₆ tracer patch was surveyed in a lawnmower pattern in north-south or east-west lines when weather permitted. During periods of sustained winds above 10 m s⁻¹, the ship followed diagonal tracks into the wind to minimize rolls. In general, a course bearing $\pm 30^{\circ}$ of the wind direction was chosen to ensure favorable conditions for the groups performing atmospheric flux measurements. In addition to trends in the tracer concentration, ADCP data as well as the MAPCO₂ buoy position were used to predict the advection of the patch.

The center of the tracer patch at the completion of the first injection was 50.6042°S, 38.6308°W. SF₆ concentrations as high as 440 fmol L⁻¹ were measured during the initial survey following tracer injection. The final CTD performed before leaving the area for the vicinity of South Georgia Island was Station 10 on 14 March, 2008 at 50.862°S, 38.239°W, and the surface SF₆ concentration at this location was 29 fmol L⁻¹. The tracer patch thus migrated approximately 40 km over the six days of the survey. After a few days at South Georgia Island, we returned to survey in the vicinity of the MAPCO₂ buoy. Very low SF₆ concentrations of 10 fmol L⁻¹ were

detected near the buoy. Station 13 was conducted at the approximate center of the residual patch before moving on to locate a site for a second tracer injection.

The second tracer patch was created on 21 March, 2008 and was centered on 51.1442°S, 38.4042°W. The maximum SF₆ concentration following the injection was 999 fmol L⁻¹. The final CTD performed in this second patch was on 5 April, 2008 and located at 51.4650°S, 37.4072°W. The surface SF₆ concentrations located at this location were ~6 fmol L⁻¹. The second patch advected 77 km over the 15 days of the second experiment.

5.3.3 Discrete SF₆ system (Sullivan)

An analytical system to measure the sulfur hexafluoride (SF₆) concentration on discrete samples was used to quantify the vertical distribution of one of the added tracer gases. The distribution of SF₆ guided the collection of samples for Helium analyses. The SF₆ instrument, patterned after Law et.al. [1998], was built in 1998 at AOML. In short, the dissolved gases in about 269 ml of sample water were purged and then collected on a Carboxen 1000 trap held at -68°C. After several minutes, the trap was isolated and heated to 150°C. The purged gases were swept onto a molecular sieve 5A column where the SF₆ was separated from oxygen and other gases. The SF₆ was measured with a Shimadzu electron capture detector (ECD). The detector was calibrated using six standards with concentrations of 5.7, 55.1, 112, 167, 345, and 1109 pptrillion (v/v). The custom software was used for instrument control, acquisition of the ECD output, and reintegration of the chromatographic peaks.

Discrete samples for SF_6 analyses were collected immediately after all Helium samples and at additional times. The 550 ml glass sample bottles were rinsed and then filled from the bottom with at least 800 ml of water. The ground glass stoppers were inserted to ensure no gas bubbles were enclosed. Rubber bands held the stoppers in place. If the samples could not be analyzer within 10 hours, the bottles were stored immersed in water. There were 598 samples collected on 41 CTD casts, 56 samples collected from the underway scientific seawater line at 19 locations, and 11 samples collected on the 2 stations employing the submerged pump. Over 40 pairs of duplicate samples were drawn from a Niskin, normally in the mixed layer. The precision of the duplicates was typically better than 2%.

For the CTD casts done in the tracer patches, the SF_6 concentration was essentially uniform throughout the mixed layer. After the patches evolved several days, one depth sampled near the bottom of the mixed layer on some of the casts had less SF_6 than the water above but still well above background SF_6 concentration. Over the 10.5 days that CTD casts were done in the first tracer patch, the SF_6 in the mixed layer decreased to less than 5% of the initial concentration but remained over four times higher than background. The initial concentrations in the second patch were over four times greater than the first patch. Over the 14 days CTD casts were done on the second tracer patch, the mixed layer SF_6 concentrations decreased to less than 2% of the initial concentration but remained over eight times higher than background concentration. Substantial data processing will be necessary before the exact concentrations will be available. An additional effort is needed to ensure that the results from the discrete measurements and the underway measurements are consistent with each other.

The discrete SF_6 analytical system performed well throughout the cruise in spite of some challenges. One of the more severe challenges was the presence of nearly pure SF_6 being vented while dosing the water tank. When the winds were from the stern, the ship's laboratories were bathed in a cloud containing levels of SF_6 many orders of magnitude higher that was being analyzed. Additionally, the fresh water on the ship was made from the surface seawater. While the ship was surveying the tracer patches, the fresh water contained substantial amounts of SF_6 . These situations are believed to be partially responsible for higher blank levels during the second patch.

The higher initial water concentrations in the second patch measured with the underway SF_6 analytical system suggested that the response on the discrete analytical system would be off-scale. A test sample collected from the underway seawater line confirmed the suspicion. The ECD setting was changed from 2 nanoampere (nA) to 1nA standing current. Reducing the sensitivity of the ECD by a factor of two allowed the chromatographic peaks to remain on-scale. All of the analyses for the second patch were done at the lower sensitivity setting.

To span the largest peak from the first water analyses of the second patch, six regular gas loops (1.606 ml) of the most concentrated standard (1109 pptr) had to be trapped. Possible changes in peak shape are a concern when trapping that many loops sequentially. A second gas sample valve with a larger loop (~7 ml) was added to the instrument. Software changes were made to accommodate the use of the larger loop with standard and blank gases. The exact volume of the new gas loop will be determined at AOML.

5.3.4 ³He samples (Ho)

361 ³He samples (with volume ca. 40 cc) were drawn from 40 CTD casts and 2 pumped stations to be used in conjunction with SF₆ to calculate the gas-transfer velocity and to determine the extent of horizontal and vertical mixing. Typically, 8 to 10 depths per station were sampled, covering the mixed layer, thermocline, and below. The samples are stored in copper tubes closed tightly at both ends by means of stainless steel pinch-off clamps. The ³He measurements will be performed at Lamont-Doherty Earth Observatory of Columbia University's Noble Gas Laboratory. ³He and other gases will be extracted from the copper tubes and transferred to glass ampoules containing activated charcoal using a vacuum extraction system [Ludin et al., 1998]. The extracted gases are flame-sealed and stored in glass ampoule with low helium permeability. The ⁴He concentration and the ³He/⁴He ratio are measured on a dedicated VG-5400 He isotope mass spectrometer. Prior to introduction into the mass spectrometer, He will be separated from all other gases by a series of cold traps. ⁴He will be measured using a Faraday Cup and ³He will be measured using a channeltron. Neon is measured in parallel on a quadrupole mass

spectrometer [Ludin et al., 1998]. Precision is expected to be about 0.5 % in ³He for samples with very high ³He excesses ($100\% < {}^{3}\text{He} < 1000\%$), and 0.2 to 0.5 % for samples with lower ³He excesses ($-1.7\% < {}^{3}\text{He} < 100\%$). Precision of the ⁴He and Ne measurements is expected to be about 0.2 to 0.5, and 0.5 to 1%, respectively.

5.4 Surface and Subsurface Variability

5.4.1 SCS System (ship's survey tech - Shannahoff)

Nearly all of the *RHB* sensors are integrated into the Scientific Computing System (SCS), which allows for centralized data acquisition and logging from numerous sensors with different sampling rates. The following sensors are integrated into the ship's SCS: Trimble GPS (Precise Positioning GPS, Magnavox MX200 GPS, Northstar GPS Receiver/Navigator, ODEC Doppler Speed Log, MK37 Gyro Compass, Ship's Gyro Compass, Raytheon RD-500 Depth Recorder (Chart Recording Fathometer to 500m), Digital barometer, RM Young Met Translator 1, Wind Speed (Bridge), Wind Direction (Bridge), Rain Gauge (1-4), RM Young Met Translator 2 (Bridge), Rain Gauge (5-9), WOCE-IMET Pak, Relative Humidity/Air Temp, Short Wave Radiation, Long Wave Radiation, Precipitation, Air Temperature, Relative Humidity, Relative Wind Speed/Direction, True Wind Speed/Direction (Calculated from relative wind and ship's heading), Seabird hull mounted Thermo-salinograph (sea surface temperature, conductivity, salinity).

5.4.2 Seabeam (ship's survey tech - Shannahoff)

The *RHB* has a Seabeam 2112 (12 Khz) swath bathymetric sonar system. The system, originally used for high accuracy (Seabeam Classic) charting of the U.S. Exclusize Economic Zone (EEZ), is capable of hydrographic charting and seafloor acoustic backscatter imaging in water depths of 50 to 11,000 meters with up to 151 beams. Swath coverage varies as a function of depth, from 150 degrees at 1,000 meters, to 120 degrees at 5,000 meters, and 90 degrees at 11,000 meters, with a resolution of two degrees. The system regularly operates in 4000+ meters of water but is effective in shallower applications (less than 500m). The swath of coverage on the ocean floor is approximately 75% of the water depth. The system operates at an acoustic frequency of 12 KHz and uses transducer arrays that are flush-mounted on the hull in a T-shaped configuration centered on the ship's keel.

5.4.3 Underway pCO₂ System (Castle, Sullivan)

During the Southern Ocean Gasex (SO Gasex) cruise there were two automated underway pCO₂ systems from AOML situated in the Hydro Lab. The first system (CN system for the designer/builder Craig Neill) has been collecting data on the *RHB* since 1999. The second system (GO System purchased from General Oceanics) was newly designed and built, and was installed just before this cruise. If the performance of the GO system proves to be acceptable over several cruises, it will replace the first system on the *RHB*. The CN system runs on an hourly cycle during which 3 gas standards, 3 ambient air samples, and 8 headspace samples from

its equilibrator are analyzed. The GO system runs 3 gas standards, 5 ambient air samples, and 55 headspace samples from its equilibrator in 2.6 hours. Both systems used the same gas standards (CA06745, CA05398, CA05344), with concentrations of 289.06, 370.90, and 411.42 ppm CO_2 in compressed natural air. The standard gases were purchased from NOAA/ESRL in Boulder and are directly traceable to the WMO scale.

Both systems include an equilibrator where surface seawater from the bow intake is equilibrated with headspace. One of the major differences between the systems is the size of the equilibrator. The approximate volumes of the enclosed headspace and water in the CN system are 16 and 8 liters, respectively; while for the GO system enclosed water is about 0.6 liters and the headspace is 0.8 liters. The approximate water flow rates were 10 liters per minute in the CN system and 2 liters per minute in the GO system.

On both systems, the equilibrator headspace is circulated through a non-dispersive infrared analyzer (IR) and then returned to the equilibrator. On the CN system the analyzer is a Licor 6251; the GO system includes a Licor 6262 analyzer. When ambient air or standard gas is analyzed the sample output of the analyzer is vented to the lab rather than connected to the equilibrator. Both systems employ KNF pumps to draw marine air from separate intakes on the bow mast through 100 m of 0.95 cm (= 3/8") OD DekoronTM tubing at a rate of 6-8 l/min. A filter of glass wool at each intake prevents particles from entering the gas streams. Both air inlet lines are constantly being flushed. Both systems dry the environmental samples prior to analyses. Both system has a column of magnesium perchlorate while the GO system has two PermaPure Naphion drying tubes to present environmental samples to the analyzers with very little water vapor. The Licor 6262 internally compensates for any residual water vapor in the sample gas streams.

Custom developed programs run under LabView^{$^{\text{M}}$} control the systems and graphically display the air and water results. The programs record the output of the infrared analyzers, the water flow, the gas flows, the equilibrator temperature, the barometric pressure, the GPS position, and a variety of other sensors. The programs write all of this data to disk at the end of each measurement phase. The details of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1998).

The uncontaminated seawater system was shut down twice during the cruise, from 7 March at 23:50 to 8 March at 21:20 GMT and on 21 March from 04:03 to 15:20. During that time, the systems continued to run and collect air sample data but no valid sea surface measurements were made. The CN system operated throughout the entire cruise with only minor problems. On 3 occasions, gas flow from the equilibrator stopped resulting in 6 hours of lost data. Also, the equilibrator thermistor does not read below 6°C due to an improper calibration. Since the raw resistance values are stored in the data file, the thermistor can be recalibrated at the lab and the

temperature values corrected. The GO system ran well until near the end of the cruise when the computer froze twice – once on 4 April at 11:40 and again on 4 April at 23:51. The first occasion resulted in a 24 minute data dropout and the second one resulted in a 14.5 hour data dropout. Also, on 5 April at 21:25, the GPS signal stopped and remained off until 8 April at 16:38.

5.4.4 Underway DMS (Archer)

We used an automated system to measure DMS concentrations in seawater at approximately 10 minute intervals. The system uses an equilibrator linked to a cold-adsorbent trap and Varian GC with PFPD detector; seawater to the equilibrator was supplied from the ship's non-toxic system. Discrete DMS measurements were measured using a purge system linked to the same cold-adsorbent trap. The discrete measurements were made from CTD-depth profiles (5 to 100m), from surface samples (0 - 0.2 m) collected by bucket and from the ship's seawater supply (~ 5m) to compare with equilibrator-derived measurements.

'Continuous' DMSsw measurements were made during both transects to and from the study location, on the transects to and from South Georgia and during both $SF_6/^3$ He experiments. Depth profiles were made for each of the 'in-patch' CTD depth profiles made during the second experiment. Samples from the depth profiles for total DMSP have also been saved for subsequent analysis.

This data will be used:

- 1. to generate DMS transfer velocity estimates, in collaboration with groups from University of Hawaii and NOAA/PSD (see above); and
- 2. be used to attempt to understand the controls on DMSsw concentration in the second SF6-patch. We hope to be able to derive: i.sea to air flux; ii.dilution; iii.vertical mixing losses; and iv.rates of net change in DMSsw concentration from the mixed layer of the SF₆-labelled patch-water.
- 3. The DMSsw will add data from a very undersampled region of the oceans to the global PMEL –DMSsw data base.

DMSsw concentrations in surface water were approximately 3.5 nM in the first SF₆ patch. In the second patch DMSsw began at > 2 nM and decreased during the experiment to < 0.8 nM (see Figure 11). Concentrations were generally constant through the mixed layer, decreasing to 0.2 nM by 100 m.



Figure 11 Profiles of seawater DMS at the beginning and end of the second tracer patch experiment.

The equipment worked considerably more reliably than I had hoped, producing almost continuous data throughout the study period only interrupted by mistakes on my part or during discrete DMSsw measurements. We believe this is the most comprehensive coverage of DMSsw concentrations for any Lagrangian experiment. It should provide a sound basis for the transfer velocity estimates and enable us to calculate the influence of directly-quantified physical processes on DMSsw concentrations, using a mass balance approach. Together with the DMSPt estimates, we hope to be able to link this information to phytoplankton composition and productivity.

5.4.5 Flow-through bio-optical system (Drapeau)

This system operated semi-continuously with water from the ships uncontaminated seawater supply. The Wetlabs EcoVSF (green) instrument was started on March 4 at 12:46 GMT and ran until the seawater supply was shut down at the end of the cruise. Every 4-6 minutes it measured temperature, salinity, chlorophyll fluorescence, total backscattering at 532nm (bb_{tot}), acidified backscattering (bb_{acid}; backscattering of the seawater suspension after the pH has been lowered to dissolve calcium carbonate), acid labile backscattering (bb'; the difference between the bb_{tot} and bb_{acid}), absorption and attenuation at 9 visible wavelengths (412, 440, 488, 510, 555, 630, 650, 676, and 715 nm), and dissolved absorption and attenuation at same wavelengths after water was routed through 0.2um filters (during alternating 2 minute segments). Preliminary data from underway acid labile backscattering suggests significant and highly variable amounts of PIC in the surface waters in and around the study area.

5.4.6 Underway Particulate Inorganic Carbon (Drapeau)

Discrete underway samples were collected from the manifold in the main lab about 4-5 times per day while surveying for particulate inorganic carbon (PIC), coccolith and cell counts, and biogenic silica. We will also be looking at discrete underway chlorophyll extractions from Vaillancourt for fluorometer calibrations. PIC samples are collected on 0.4 µm polycarbonate filters, rinsed with Potassium Tetraborate buffer, stored in metal free centrifuge tubes, and analyzed by ICPOES for particulate calcium. Coccolith and cell counts are collected on HA (nitrocellulose) filters, rinsed with Potassium Tetraborate buffer and stored frozen. The filters are then cleared with Canada Balsam and enumerated by birefringence microscopy (Haidar and Thierstein 2001; Haidar et al. 2000). Biogenic silica (BSi) samples are filtered onto 0.4 mm polycarbonate filters, frozen in clean centrifuge tubes, and analyzed following Brezinsky and Nelson (1989).

5.4.7 Multispectral Absorption-Attenuation Sensors (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

Two WetLabs' acs (Multispectral absorption-attenuation sensors) and a SBE 49 CTD were connected to the Brown's clean seawater. Data were collected continuously until we entered Uruguayan territorial waters. One acs was fitted with a high volume 0.22 μ m filter to measure CDOM absorption, while the other acs was left unfiltered to measured total absorption and beam attenuation. Clean water calibrations were done every ~3 days. Underway data shows low variability in all measurements of absorption and beam attenuation obtained during sampling at the experiment site. Values of $a_g(\lambda)$, $a(\lambda)$, $c(\lambda)$ and $b(\lambda)$ will be available after post-processing.

Volume Scattering Function (VSF noted β) of the surface seawater has been measured from pumped water samples using the uncontaminated seawater line. To obtain the VSF for particles β_p , the contribution of seawater is subtracted from in situ measurements of β . Then, the particulate scattering b_p and backscattering b_{bp} coefficients are computed by integrating the VSF over the whole and the half range of scattering angle θ , respectively.

During the cruise, 14 measurements of VSF have been collected, 10 simultaneously with CTD and optical profiles. The values of b_p and b_{bp} obtained by integration of β_p at 510 nm are within the range 0.44 – 0.82 m⁻¹ and 0.002 – 0.005 m⁻¹, respectively. The values of the backscattering ratio B_p , which represents the b_{bp} to b_p ratio, at 510 nm are within the range 0.003 – 0.007 m⁻¹. The angular structure in the shape of the VSF looks good in comparison with the Petzold's VSF and the Fournier-Forand VSF calculated as in Mobley et al. (2002) for a B_p value corresponding with the minimum and the maximum observed during the cruise (Figure 12).



Figure 12 VSF $\beta p(\theta)$ for particles collected during the SO GasEx III cruise at 510 nm (black curves) together with seawater VSF (dashed curve), Petzold's VSF at 514 nm (blue curves), and the two Fournier-Forand VSFs (red curves).

Figure 13 shows the spectral shape of b_p , b_{bp} and B_p . We can observe that the spectral variation of b_p presents non linear features between 440 and 620 nm. This may be compared with the usual parameterization of b_p as a λ^{-1} power law for the case I water, which is realistic if the marine particles are non-absorbing and distributed according to a power law with a Junge parameter of 4. The spectral shape of b_{bp} shows a spectral dependence following a $\lambda^{-\gamma}$ power law with a mean value of γ of 1.93 ± 0.13. Similarly, the spectral shape of B_p shows a spectral dependence following a $\lambda^{-\gamma}$ power law with a mean value of γ of 1.87 ± 0.17.



Figure 13 Spectral shape of (A) b_p (B) b_{bp} and (C) B_p derived from the in situ VSF.

5.4.8 Multi-channel Fluorometer (Hargraves)

A multi-channel fluorometer was used to acquire bio-optical data to help interpret the absorption and photosynthesis measurements (see section 4.8). This instrument is a Turner Designs C6 profiling fluorometer equipped with sensors for chlorophyll-a, cdom, phycoerythrin, phycocyanin, turbidity, temperature, and pressure. It was used in two ways: (1) with the ship's underway seawater along with two AC-S instruments (one measuring whole water and one measuring particle-free water) and a CTD unit in the sink of the ship's Wet Lab and as part of a profiling package (either the ship's CTD rosette package or the optical package). Eleven profiles were completed from 30 March – 5 April 2008. Daily files of underway seawater fluorescence combined with ship GPS data and PAR irradiance were created for 4-30 March and 5 April to the end of the point at the end of the cruise (approximately 10 April) when the seawater flow was shut off.



Figure 14 near surface phytoplankton absorption and extracted chlorophyll during SO Gasex cruise.

The use of the C6 fluorometer for both underway monitoring using its flow cell and automated wiper and as a self-contained package added quickly to the ship's CTD-rosette system established its versatility and value for this type of bio-optical research. The pigment fluorescence profiles provide valuable biological information on the phytoplankton response to sunlight (non-photochemical quenching and photoinhibition/photod amage) by comparing day and night profiles, the extent of the mixed layer and the depths where light is likely to be a limiting factor for sustaining phytoplankton populations. There is also evidence in the phytoplankton absorption spectra of a response to ultraviolet radiation (many samples show the presence of UV-B screening protective pigments). The absence of Phycoerythrin pigments in the vertical profiles will also be helpful during our interpretation of the photosynthesis experiments.

The cdom fluorescence data in the vertical profiles has also been useful to the Optics Group as they explore the sources and sinks for organic carbon and possible contributions to carbon dioxide in the mixed layer. On two sunny or partly sunny days there was evidence from the cdom fluorescence profiles that photochemical breakdown of cdom fluorescence exceeded the rate of mixing and/or biological production. Because the cdom fluorescence pattern differs with depth somewhat from the cdom absorbance pattern, there is an opportunity to use the ratio of the two measurements to create an optical fingerprint related to the source of the water and its exposure to sunlight. I am also exploring with Roberta Hamme a possible link between biological productivity (which she measures with oxygen-argon ratios) and grazing after my underway monitoring of fluorescence showed some regions where cdom and chlorophyll vary inversely to each other (Roberta saw some cases where high productivity was correlated with high cdom and low chlorophyll).



Figure 15 Profile of fluorometric data from CTD cast 47.

5.4.9 Chlorophyll (Lance)

Fluorometric chlorophyll was measured to provide near real-time concentrations of chlorophyll biomass in the surface waters from the ships underway seawater system and station profiles at 6 to 8 depths from surface to ~ 100m. These measurements were used by other researches to calibrate their voltage-based observations. Samples were filtered onto GFF filters (nominal pore size ~0.7 μ m) and on some occasions through polycarbonate filters (2, 5 and or 20 μ m pore sizes) and extracted in 100% methanol for at least 24 h (but not more than 30h). Approximately 60 surface underway Fl-Chls were measured during various transits and surveys which ranged from 0.3 to 4.8 mg m⁻³.

Approximately 15 surface underway HPLC's were collected during various transits, surveys and underway "diel" experiments. Samples were filtered onto GFF filters and stored in liquid N_2 for

later analysis of suite of phytoplankton pigments. Samples will be analyzed by Analytical Services of Horn Point Laboratory Pigment Analysis Facility, HPL-UMCES.

5.4.10 SuperSoar/TOMASI (Hales/Strutton/Hebert)

The Oregon State University SuperSoar is a towed undulating sampling/sensing vehicle, including full-suite CTD measurements and high-volume sampling pump. In situ measurements included dual T/S sensor pairs, O₂, beam-c, PAR, chlorophyll fluorescence, CDOM fluorescence, optical backscatter, pCO₂, TCO₂, and nitrate (ISUS and shipboard analysis). TOMASI is a microstructure instrument that could be strapped to the SuperSoar for measuring turbulent mixing rates.

The SuperSoar went in the water on 6 March, but after approximately 7 hours of successful operation the instrument struck an underwater object. The SuperSoar was successfully recovered but the tow cable was damaged beyond repair. Seven hours of SuperSoar data were collected. These data consisted of approximately 50 10-60m profiles. Data for T, S, chl, O₂, beam attenuation, optical backscatter, CDOM fluorescence, PAR, NO₃ (ISUS-based), and pCO₂. TCO₂ analyzer was not working due to elevated CO₂ content in the chopper cell of the LI6262. Shipboard NO₃ analyzer was not online. TOMASI was not deployed on SuperSoar for this first survey.

The shipboard analysis systems that were originally associated with the SuperSoar were adapted to operate on the ship's uncontaminated seawater line (see next section).

On 27 March an attempt was made to make a low-speed deployment of TOMASI on a reducedpayload, short-cable configuration of SuperSoar. However, the TOMASI pressure case flooded upon deployment and no data were collected.

5.4.11 OSU Underway Systems (Hales, Hubbard)

On 8 March three of the OSU SuperSoar analysis systems were adapted to operate on the ship's uncontaminated seawater line: pCO_2 , NO_3^- (wet-chemical analysis), NO_3^- (ISUS). On 12 March the DIC instrumentation was repaired and started making underway measurements. All systems were run until the seawater lines were shut down at the end of the transit back to Montevideo.

Near surface seawater pCO₂ data was collected at 1Hz frequency using the methods of Hales et al. (2004). CO₂ gas standards and an atmospheric sample were run every 2-4 hours. pCO₂ was also configured to record the analog (0-5V) outputs of a WetStar chlorophyll fluorometer, a CStar beam transmissometer, an SBE43 O₂ electrode, and the output of a SBE45 thermosalinograph. Reported TSG T was about 0.7°C warmer than true SST. Salinity data is believed to be more accurate than Ship's Ssalinity data. Chl-fluorometer, beam transmissometry, and O₂ electrode signals will be calibrated with discrete Chl, POC, and O₂ measurements of the underway seawater.

Wet-chemical-analysis NO_3^- data was collected following Gordon et al. (1993) as modified by Hales et al., (2005).

The ISUS NO_3^- sensor was brought online on 8 March and has run nearly continuously since then, except for a period of down-time while stationed off South Georgia Island. Post-processing will include comparison with analytical NO_3^- data and corrections, if necessary.

 TCO_2 is determined by acidifying the seawater, extracting the gas and analyzing it with a LI6262 NDIR following the method of Bandstra et al. (2006). Liquid and gas standards were run every 2-4 hours. TCO_2 data collection was initiated on 9 March, but problems with pump instability make the first few days of data collection plagued with drop-outs. Data is nearly continuous from about 12 March onward.

5.5 Autonomous Platforms

5.5.1 MAPCO₂ Buoy (Sabine, Zappa, Lebon)

A drifting autonomous buoy was designed by NOAA/PMEL to make high frequency physical and biogeochemical measurements in the tracer patch during the experiment. The buoy was approximately 1.5m in diameter and 2m high (half above the water and half below the water). Below the buoy was a 118m sting of instruments and 6 tubular canvas drogues that were 10m long by 1m diameter (Figure 16). At the bottom of the string was 350 pounds of weight.

The buoy contained a MAPCO₂ non-dispersive infrared analyzer based system for measuring the CO₂ concentrations of the surface water and atmosphere every 30 minutes. A Gill sonic anemometer measured the wind speed and direction at approximately 0.9m above the water surface. A 10 minute average reading was recorded every 30 minutes. The wind sensor was damaged half way through the second deployment and was replaced with a spare for the third deployment. A SeaBird 37 Microcat sensor measured the temperature and conductivity of the water at approximately 1m depth every 15 minutes. All of these data, together with the GPS location of the buoy, were transmitted via Iridium satellite to NOAA/PMEL four times per day. These data were automatically processed and posted to a web site that could be accessed from the Ron Brown to get near real time information about the waters being sampled by the MAPCO₂ buoy. The buoy also had a second, independent Iridium/GPS system that transmitted GPS fixes and information from a load cell located immediately below the buoy back to NOAA/PMEL once per hour. These data were also posted to the web. The hourly GPS fixes were also emailed to Chris Sabine and several of the ship's officers so the ship would know where to find the buoy at any time.

There were several instruments mounted to the buoy at approximately 1m depth to determine near surface turbulence, relative currents and bubble characteristics. The MAVS (Modular Acoustic Velocity Sensor) measures 3-axis velocity at a single point (1000 cm³). The technology is time-of-flight. However, battery problems prevented the instrument from operating

properly so no data was recovered from this instrument. The Sontek 10 MHz ADV (Acoustic Doppler Velocimeter) measures 3-axis velocity at a single point (1 cm³). This instrument uses backscatter from particles in the water to make its measurement. The measurement was made at a sampling frequency of 25 Hz for 10 minutes every 30 minutes. The RDI 1200 KHz ADCP measures vertical profiles of 3-axis velocity over 15 m of water column with a blanking distance of 1-2 m. There are roughly 75 bins of 25 cm each. A profile was sampled every 2.5 seconds throughout the deployments. There was also an underwater camera that took photos every 90 minutes. These photos will be analyzed to characterize the bubble dynamics under different wind and wave conditions.



Figure 16 Diagram of MAPCO₂ drifter.

Just below the buoy at 2m depth was a Nortek 2 MHz Aquadopp HR which measures alongbeam velocity over a profile of 1 m with 1.7 cm bins. This allowed us to determine the wavenumber spectra for velocity which allowed us to estimate the turbulent kinetic energy dissipation rate. A profile was sampled at 4 Hz for roughly 3 minutes every hour.

A SAMI-pH sensor was mounted on the buoy at 1m depth. Six SAMI-CO₂ sensors were deployed below the buoy at 5, 19, 34.5, 50, 75, and 105m. The SAMI instruments used a colorimetric dye to measure pH or pCO₂ every half hour. All of the SAMI instruments also had dissolved oxygen sensors. Beam-C instruments were mounted to the 5 and 75m SAMIs. PAR sensors were located on the 34.5, 50, and 105m SAMIs. A fluorometer was mounted on the 19m SAMI. All instruments were programmed to sample every 30 minutes.

Onset water temperature PRO V2 sensors were located below the buoy at 5, 19, 25, 34, 34.5, 40.5, 49.5, 50, 56, 65, 65.75, 74.75, 75.25, 81.25, 90.25, 91, 100, and 105m. They sampled every 30 minutes with an accuracy of 0.1° C and precision of 0.02° C.

The first MAPCO₂ buoy deployment was on 8 March, immediately after the tracer injection was completed. The buoy was deployed adjacent to the GPS drifter used for the patch creation. When the buoy was released from the ship we noticed that it was sitting lower in the water than expected. When large waves would pass, the waves would ride over the buoy instead of the buoy riding over the waves. Unfortunately, the buoy could not be recovered until 12 March to fix the situation.

On 13 March the buoy was redeployed in the patch with four drogues instead of six. We also removed half the weight at the bottom of the drifter string and added a cylindrical float from the ASIS buoy at a depth of about 20m. The only instrument affected by these changes was the 105m SAMI which was 10m shallower on the second deployment. The buoy rode much better with this configuration and was not getting topped by the waves nearly as often. The load cell readings on the bottom of the buoy were also lower and, more importantly, did not show the large spikes observed in the first deployment. A few hours after the buoy was redeployed the ship left the study area for South Georgia Island because of approaching heavy weather. Based on the load cell data, it appears that the 20m float was compromised sometime between 14 and 15 March. The maximum loads on the load cell got significantly higher and the frequency of large spikes increased.

The MAPCO₂ buoy was recovered the morning of 18 March, after returning to the study site from South Georgia Island. The buoy was sitting a little lower in the water than when it was deployed, but not as bad as the first deployment. When the ASIS float we added was lifted out of the water it had clearly been crushed and was full of water. Because the float was filled with foam, we believe that it still had a small net positive buoyancy but not the original 250 pounds of flotation.
The MAPCO₂ buoy was deployed in the patch for the third and final time on 21 March, immediately after the second tracer injection. The configuration was the same as the second deployment except without the float at 20m. A piece of nylon rope was inserted in place of the float so the instrument depths were not affected.

Although the drogues made the drifter difficult to deploy and retrieve, the MAPCO₂ buoy did an excellent job of staying with tracer patch. During the first two deployments and the first week of the third deployment the buoy was providing a useful navigation tool for mapping the patch and recording its movements. Suddenly around 27 march the tracer completely stopped moving while the buoy continued on its southeasterly course. Each day as the ship stayed with the patch the buoy got farther and farther away. Unfortunately, we were not able to go retrieve the buoy because the ship's propulsion systems repeatedly failed throughout the weekend and it was all we could do to keep track of the patch. On 31 March we decided that we must make the 50 km trek to retrieve the buoy before it got too far away. As we approached the buoy, however, we discovered that there were significant concentrations of tracer moving with the buoy. Apparently the patch had sheared in two. The portion of the patch near the buoy continued moving to the southeast while the core of the patch got caught up in a small stable eddy. Because the ship's propulsion systems were failing so often and we were concerned about having to make a sudden early departure from the study site, we chose not to redeploy the buoy again.

5.5.2 ASIS Buoy (Rebozo)

ASIS is the University of Miami's "Air-Sea Interaction Spar" buoy. At 6 x 2 x 2 m (36 x 6 x 6 ft), and weighing close to a ton, it is indeed one on the larger pieces of kit on the deck. The role of ASIS in SO GasEx is to make measurements at, and close to, the ocean surface. Above the surface, we measure basic meteorological parameters, as well as the air-sea fluxes of CO₂, water vapor, heat and momentum. In collaboration with Ian Brooks and Sarah Norris of the University of Leeds, we are also measuring aerosol fluxes and concentrations. At the surface, we measure surface waves and wave slopes at various scales. This is particularly important for gas transfer work, as small scale waves are thought to be significant control on gas transfer rates. Below the water, we measure temperature, salinity and energy dissipation rates (a measure of surface mixing, which acts as a control on gas transfer). There is also one of Mike DeGrandpre's SAMI CO₂ systems measuring carbon dioxide, dissolved oxygen, and light (PAR). Finally we also measure how ASIS moves in the water. ASIS is equipped with three ARGOS beacons giving position. While many of these atmospheric measurements are also made on board the *RHB*, a ship disturbs the near surface too much to measure many air-sea processes, such as small scale waves. ASIS was designed precisely to fill the need for a platform for such high resolution nearsurface measurements.

The ASIS was deployed in the first tracer patch on 10 March, 2008. A 10m drogue, identical to the MAPCO₂ drogues, was attached to the bottom of the spar to reduce the impact of the wind on the spar trajectory. Despite the drogue, however, it still quickly moved out of the patch travelling

down wind. The ASIS was recovered on 18 March, approximately 60 miles downwind of the first patch, before steaming back to the original study area to deploy the second tracer patch.

5.5.3 Surface Drifters and SOLO floats (Castle)

Five drifting buoys were deployed during SO Gasex. Three were deployed in the first tracer patch immediately after it was created. One was deployed in the second tracer patch immediately after it was created. One was deployed at 41°S during the transit to Montevideo.

Serial #	Date	Time	Latitude	Longitude
70930	3/8/2008	15:30	-50.6091	-38.6245
70931	3/8/2008	15:33	-50.6091	-38.6245
70932	3/8/2008	15:35	-50.6091	-38.6245
70935	3/21/2008	13:48	-51.1418	-38.3991
70936	4/10/2008	2:00	-41.0154	-51.7195

These floats are part of the Global Drifter Program (GDP), which is the principle component of the Global Surface Drifting Buoy Array, a branch of NOAA's Global Ocean Observing System (GOOS) and a scientific project of the Data Buoy Cooperation Panel (DBCP). The objectives of the GDP are to maintain a global 5x5 degree array of 1250 ARGOS-tracked drifting buoys to meet the need for an accurate and globally dense set of in-situ observations of mixed layer currents, sea surface temperature, atmospheric pressure, winds and salinity. The data collected from these drifters is to be processed and provided for scientific use. Further information regarding these instruments is available at: <u>http://www.aoml.noaa.gov/phod/dac/gdp.html</u>.

Five SOLO floats were deployed during the transit to Montevideo. These floats are part of the ARGO network of profiling floats contributing to the Global Ocean Observing System (GOOS).

Serial	Startup	Startup time	Deployment	Deployment		
Number	date	(GMT)	Date	time (GMT)	Latitude	Longitude
778/71591	4/4/2008	22:01	4/5/2008	2:23	-51.4651	-37.4071
817/6510	4/6/2008	0:22	4/6/2008	3:07	-48.0153	-42.7216
777/71590	4/6/2008	12:36	4/6/2008	16:23	-46.001	-45.2768
810/9060	4/6/2008	12:32	4/9/2008	14:21	-42.4834	-50.3838
756/71580	4/6/2008	12:34	4/10/2008	14:54	-38.9955	-53.2993

The ARGO profiling floats spend most of their time at their ballasted depth, collecting temperature and salinity data. South Atlantic floats are ballasted for 1800 m and tropical floats, for 1100m. Upon deployment, the cardboard box they are packaged in opens and permits the float to slide out and sink, collecting a temperature and salinity profile. Most floats immediately ascend and send position and data to the ARGOS satellite. After a few hours on the surface, it again sinks for typically a 10 day mission at depth, ascending again in its cycle to relay data to the satellite. Their normal life is 3-4 years. AOML/PhOD is responsible for deployments in the North and South Atlantic, using floats supplied by the WHOI Float Group.

5.6 Surface and Near-surface Ocean Processes

5.6.1 Wave Height (Zappa)

Figure 17 shows a time series of the significant wave height as determined from 3 comperable systems deployed on this cruise: WaMoS[®] II, the TSKA wave height sensor, and the Riegl altimeter. Note that a preliminary correction for ship motion (heave) has been applied to the TSKA and Riegl. Comparison of the WaMoS[®] II and TSKA systems show agreement during periods when the ship is stationary and heading into the wind. When the ship is moving, the TSKA and WaMoS[®] II diverge which suggests that more comprehensive motion correction needs to be performed for the wave height analysis.



Figure 17 Time series of wind speed, ship speed, and significant wave height for the entire SO GasEx 2008. waves are shown for the WaMoS II and TSKA systems.

5.6.1.1 WaMoS[®] II

Directional ocean wave spectra, significant wave height, peak wave period, and peak wave direction were obtained with a Wave and Surface Current Monitoring System (WaMoS[®] II). The WaMoS[®] II also has the capability to resolve two-dimensional maps of surface elevation snapshots and allowed for real time measurement with the significant advantage of continuous availability of wave data in rough seas, under harsh weather conditions with limited visibility, and at night. The system used the unfiltered output from a marine X-Band radar to determine wave and surface current parameters. The measurements were based on the radar backscatter from the ocean surface (sea clutter) that shows the wave patterns. The WaMoS[®] II capabilities on the *RHB* provided directional wave spectra and individual wave state components at larger scales (>100m). The WaMoS[®] II had a dedicated PC acquisition computer with 4 external hard drives to store the 2 terabytes of data.

5.6.1.2 TSKA Wave Height Sensor

Significant wave height was measured using a the nadir-looking TSKA microwave system. The system was deployed from the bow of the *RHB*, similar to the system used during GasEx 1998. Motion of the ship (heave) is required to be removed for accurate wave heights. The sampling rate is 10 Hz.

5.6.1.3 Riegl Laser Altimeter

Significant wave height was measured using measured using a Riegl model LD90-3100VHS laser altimeter. The system was deployed from the bow of the *RHB*, similar to the system used during GasEx 2001. Motion of the ship (heave) is required to be removed for accurate wave heights. The sampling rate is 10 Hz.

5.6.2 Imperx Video Cameras (Zappa)

We deployed two high-resolution Imperx digital cameras on the flying bridge to provide wavebreaking statistics. We took 108 runs of video of the ocean's surface during daylight hours. Each run of wave breaking video lasted for roughly 20 minutes at a sampling rate of 5 Hz. There is nearly 5 terabytes of wave breaking video data that will be analyzed.

The Imperx video cameras send data and communication via the Camera Link protocol. In order to run extended distances (50 m in this case), the system includes Fiber Optic nodes. The IO Industries data acquisition system uses two CL-160 frame grabbers and the data is acquired using Streams software. The two frame grabber boards are set up in a master-slave configuration to insure synchronized image acquisition. A GPS card was installed to lock the computer clock onto GMT for timing within $\pm 5 \,\mu$ s of GMT at all times.

5.6.3 ADCP (ship's survey tech –Shannahoff, Hebert)

Data from the *RHB* hull mounted 75 kHz Ocean Surveyor acoustic Doppler current profiler (ADCP) was operated in two modes, broad-band and narrow-band, throughout most of the cruise using the University of Hawaii Data Acquisition System (UHDAS). Preliminary processing using the UH CODAS package was conducted at sea. This provided the science party with several valuable pieces of information. First, it assisted in site selection by giving estimates of velocity and shear distributions. Second, progressive vector calculations gave predictions of patch trajectories and assisted with the patch tracking/mapping exercises. Third, advective corrections applied to survey tracks gave more robust estimation of the patch-survey 'snapshots', correcting for apparent temporal/spatial variability that resulted from advection of hydrographic features within the surveys. Final processing will be performed by Jules Hummon at UH.

5.7 Water Column Hydrography, Carbon and Related Tracers

5.7.1 CTD (Purkey)

CTD casts were conducted at 12-hour intervals during times spent in the tracer patch. The basic CTD/rosette package consisted of two salinity sensors, two temperature sensors, one pressure

sensor, one dissolved oxygen sensor and 24 Niskin bottles for water samples. In addition a PAR sensor and fluorometer were attached for a number of casts. The standard maximum cast pressure was 500 dbar. One 4600-dbar cast was conducted at the beginning of the experiment, three 1500-dbar casts, and seven 100-dbar casts were taken during the cruise (see Table 4). About once a week, one reference CTD was conducted outside the patch. A total of 41 casts were completed.

Station	Latitude	<u>Longitude</u>	Date	Time	<u>Maximum Pressure</u>
1	-50 45.0	-38 29.9	6-Mar-08	15:20	4600
2	-50 42.8	-38 35.1	10-Mar-08	4:44	500
3	-50 43.9	-38 33.3	10-Mar-08	15:08	500
4	-50 45.3	-38 28.5	11-Mar-08	3:09	500
5	-50 45.5	-38 26.5	11-Mar-08	15:19	500
6	-50 47.4	-38 24.6	12-Mar-08	3:07	500
7	-50 48.2	-38 21.3	12-Mar-08	15:05	500
8	-50 52.0	-38 18.4	13-Mar-08	4:01	100
9	-50 52.5	-38 14.0	13-Mar-08	15:05	500
10	-50 51.7	-38 14.4	14-Mar-08	1:15	1500
13	-51 2.4	-37 41.9	18-Mar-08	7:16	500
14	-50 56.8	-37 47.8	20-Mar-08	15:25	1500
16	-51 8.4	-38 22.5	22-Mar-08	3:10	500
18	-51 11.5	-38 18.3	22-Mar-08	15:49	500
19	-51 11.4	-38 15.9	23-Mar-08	3:13	500
21	-51 12.0	-38 8.1	23-Mar-08	15:11	500
22	-51 13.3	-38 1.1	24-Mar-08	3:13	500
24	-51 14.4	-37 59.8	24-Mar-08	14:57	500
25	-51 15.5	-37 52.1	25-Mar-08	3:45	500
26	-51 17.7	-37 41.2	25-Mar-08	15:18	500
27	-51 19.6	-37 33.8	26-Mar-08	2:11	500
28	-51 18.0	-37 30.2	26-Mar-08	13:36	500
29	-51 17.5	-37 25.6	27-Mar-08	1:43	500
30	-51 19.1	-37 20.8	27-Mar-08	13:34	500
31	-51 19.1	-37 18.8	28-Mar-08	1:12	500
34	-51 17.7	-37 15.0	29-Mar-08	13:26	500
35	-51 18.3	-37 17.1	29-Mar-08	18:05	500
37	-51 18.7	-37 17.8	30-Mar-08	2:41	500
38	-51 17.8	-37 19.8	30-Mar-08	15:11	500
39	-51 18.2	-37 21.0	31-Mar-08	1:13	500
40	-51 18.2	-37 20.5	31-Mar-08	14:05	500
41	-51 47.6	-36 53.1	31-Mar-08	18:37	100
42	-51 16.8	-37 21.8	1-Apr-08	1:33	100
43	-51 20.2	-37 26.0	1-Apr-08	13:05	500

Table 4. CTD station information.

44	-51 20.4	-37 27.8	2-Apr-08	1:33	500
45	-51 22.0	-37 28.4	2-Apr-08	13:17	500
46	-51 23.0	-37 28.0	3-Apr-08	1:10	100
47	-51 24.4	-37 31.0	3-Apr-08	13:11	500
48	-51 26.2	-37 28.6	4-Apr-08	2:27	100
49	-51 27.2	-37 26.3	4-Apr-08	13:16	500
50	-51 27.0	-37 15.0	4-Apr-08	19:21	1500
51	-51 27.9	-37 24.4	5-Apr-08	1:03	200

5.7.1.1 Water Sampling Packages

All CTD/O₂ profiles were collected using Sea-Bird instrumentation mounted vertically in one of two 24-position aluminum frames. The first package was used for stations 1-31 and had 24 11-L Niskin-type Bullister bottles and 400 lbs of lead weights. Instruments used included a Sea-Bird Electonics (SBE) 24-position carousel s/n 471 and a SBE 9plus CTD s/n 209 with primary 3plus temperature sensor s/n 03P-4211, primary 4C conductivity sensor s/n 04-2887; secondary temperature sensor model 03-02/F s/n 03-1455, secondary 4C conductivity sensor s/n 04-2882, and SBE-43 oxygen sensor s/n 315. A load cell and pinger were also mounted on the underwater package. A WET Labs fluorometer s/n ws35-418p was added before station 2 but removed after station 7 when corrosion was found in its underwater connector. A Biospherical instruments PAR sensor s/n 4623 was added for all stations with a maximum pressure less than 600 m. The CTD was mounted vertically in a SBE CTD frame attached to a plate welded in the center of the rosette frame under the pylon. The rosette system was suspended from a UNOLS-standard three-conductor (0.322") electro-mechanical sea cable using the *RHB's* forward winch.

After the first package was accidentally pulled into the winch block, a second frame and CTD were used. The second packages had 20 11-L Niskin-type Bullister bottles (16 recovered from the first package), 4 10-L Niskin bottles and 400 lbs of lead weights. Instruments included a SBE 24-position carousel s/n 471 and a SBE 9plus CTD s/n 315 with primary 3plus temperature sensor s/n 03P-4341, primary 4C conductivity sensor s/n 04-3157, secondary 3plus temperature sensor s/n 03P-4335 secondary conductivity sensor model 04-02/0 s/n 04-1467, and SBE-43 oxygen sensor s/n 664. Again, the Biospherical instruments PAR sensor s/n 4623 was added for all stations with a maximum pressure less than 600 m. The CTD was mounted vertically to the outside of the center of the frame. The rosette system was suspended from a UNOLS-standard three-conductor (0.322") electro-mechanical sea cable using the Ronald H. Brown's aft winch.

Both packages' SBE4 conductivity and SBE3plus temperature sensors and their respective pumps were mounted vertically as recommended by SBE. Pump exhausts were attached so water flowed directed downward and away from the intake. The fluorometer was mounted vertically without a pump and the PAR sensor was attached to the top outside ring of the frame.

The deck watch prepared the rosette 15-60 minutes prior to each cast. The bottles were cocked and all valves, vents and lanyards were checked for proper orientation. The CTD was powered

up about 10 minutes prior to station. Once stopped on station, the data acquisition system in the computer lab was started when directed by the deck watch leader. The rosette was unstrapped from its tied down location on deck. The syringes were removed from the CTD intake ports. The winch operator, directed by the deck watch leader, raised the rosette and quickly lowered it into the water. The package was lowered to at least 10 meters and held there for 2 minutes while the sensor pumps turned on and air bubbles were purged from the plumbing. The winch operator was then directed to bring the package back to the surface, zero the winch wire-out, and begin the descent at 30 m/min. The depth of each cast varied from 95m to 4500m. During the up-cast the winch operator was directed to stop the winch at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle to insure the package wake had dissipated and the bottles were flushed, then an additional 10 seconds after bottle closure to insure that stable CTD comparison data had been acquired. Once a bottle had been closed, the console operator directed the winch operator to bring up the package to the next bottle stop. When multiple bottles were fired at one depth, the CTD console operator waited 30 seconds between tripping each bottle. Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks to attach tag lines. The rosette was secured on deck under the block for sampling. The bottles and rosette were examined before samples were taken, and anything unusual noted on the sample log.

Each bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette. Bottle position was used for sample identification. No bottles were replaced on this cruise during the use of either frame, but various parts of bottles were occasionally changed or repaired. Routine CTD maintenance included soaking the conductivity cells and rinsing the dissolved oxygen sensors in dilute Triton-X solution between casts to maintain sensor stability by eliminating any accumulated biofilms. Rosette maintenance was performed on a regular basis. O-rings were changed and lanyards repaired as necessary. Bottles were raised and lowered if they were not firing properly. Bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

5.7.1.2 CTD Data Acquisition and Rosette Operation

The CTD data acquisition system consisted of a SBE-11plus (V1) deck unit and a networked generic PC workstation running Windows XP. SBE SeaSave software was used for data acquisition and to close bottles on the rosette. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. After the CTD had been deployed, soaked at 10 m for 2 minutes, and brought back to the surface, the console operator checked the CTD data for proper sensor operation, paused for 10 seconds, and then instructed the winch to descend to a target depth (wire-out). Profiling rates were usually 30 m/min to 50 m, 45 m/min to 200 m, and 50 m/min deeper than 200 m. Sometimes these rates were varied with sea cable tension and sea state.

The console watch monitored the progress of the deployment and quality of the CTD data through interactive graphics and operational displays. Additionally, the watch created a sample log for the deployment that would be used later to record the correspondence between rosette bottles and analytical samples taken. Bottles were closed on the up cast by operating an on-screen control. Bottles were tripped 30 seconds after stopping at the trip location to allow the rosette wake to dissipate and the bottles to flush. The winch operator was instructed to proceed to the next bottle stop 10 seconds after closing bottles to insure that stable CTD data were associated with the trip. After the last bottle was closed, the console operator directed the deck watch to bring the rosette on deck. Once out of the water, the console operator terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.



Figure 18 Typical depths sampled during the CTD casts. The blue trace is salinity and the red trace temperature.

5.7.1.3 CTD/O₂ Data Processing

The reduction of profile data began with a standard suite of processing modules (process.bat) using Sea-Bird Data Processing Win32 version 5.37e software in the following order:

- DATCNV converts raw data into engineering units and creates a .ROS bottle file. Both down and up casts were processed for scan, elapsed time(s), pressure, t0, t1, c0, c1, and oxygen voltage. Optical sensor data were converted to voltages but not carried further through the processing stream. MARKSCAN was used to skip over scans acquired on deck and while priming the system under water. MARKSCAN values were entered at the DATCNV menu prompt.
- 2. ALIGNCTD aligns temperature, conductivity, and oxygen measurements in time relative to pressure to ensure that derived parameters are made using measurements from the same parcel of water. Primary conductivity is automatically advanced in the V1 deck unit by 0.073 seconds. Secondary conductivity was advanced by .073 seconds in ALIGNCTD. It was not necessary to align temperature or oxygen.
- BOTTLESUM averages burst data over an 8-second interval (+/- 4 seconds of the confirm bit) and derives both primary and secondary salinity, primary potential temperature (θ), primary potential density anomaly (σ_θ), and oxygen (in µmol/kg).

- 4. WILDEDIT makes two passes through the data in 100 scan bins. The first pass flags points greater than 2 standard deviations; the second pass removes points greater than 20 standard deviations from the mean with the flagged points excluded. Data were kept within 100 of the mean (i.e. all data).
- 5. FILTER applies a low pass filter to pressure with a time constant of 0.15 seconds. In order to produce zero phase (no time shift) the filter is first run forward through the file and then run backwards through the file.
- 6. CELLTM uses a recursive filter to remove conductivity cell thermal mass effects from measured conductivity. In areas with steep temperature gradients the thermal mass correction is on the order of 0.005 PSS-78. In other areas the correction is negligible. The value used for the thermal anomaly amplitude (α) was 0.03. The value used for the thermal anomaly time constant (β^{-1}) was 7.0 s.
- 7. LOOPEDIT removes scans associated with pressure slowdowns and reversals. If the CTD velocity is less than 0.25 m s⁻¹ or the pressure is not greater than the previous maximum scan, the scan is omitted.
- 8. BINAVG averages the data into 1-dbar bins. Each bin is centered on an integer pressure value, e.g. the 1-dbar bin averages scans where pressure is between 0.5 dbar and 1.5 dbar. There is no surface bin. The number of points averaged in each bin is included in the data file.
- 9. DERIVE uses 1-dbar averaged pressure, temperature, and conductivity to compute primary and secondary salinity.
- 10. TRANS converts the binary data file to ASCII format.

Package slowdowns and reversals owing to ship roll can move mixed water in tow to in front of the CTD sensors and create artificial density inversions and other artifacts. In addition to Seasoft module LOOPEDIT, MATLAB program deloop.m computes values of density locally referenced between every 1 dbar of pressure to compute the square of the buoyancy frequency, N^2 , and linearly interpolates temperature, conductivity, and oxygen voltage over those records where N^2 is less than or equal to -1×10^{-5} s⁻². Program calctd.m reads the delooped data files and applies final calibrations to primary temperature and conductivity, and computes salinity and calibrated oxygen.

5.7.1.4 CTD Shipboard Calibration Procedures

CTD s/n 93450-0209 was used for station 1-31 and CTD s/n 09P8431-0315 was used for stations 34-51. The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE. The primary temperature and conductivity sensors were used for all reported CTD data. In-situ salinity and dissolved O_2 samples collected during each cast were used to calibrate the conductivity and dissolved O_2 sensors.

CTD Pressure: Pressure calibrations for the CTD instrument used during this cruise were precruise. No additional adjustments were applied. On deck pressure readings prior to each cast were examined and remained within 0.5 dbar of calibration. *CTD Temperature:* In addition to a viscous heating correction of -0.0006 °C, a linearly interpolated temperature sensor drift correction using pre and post-cruise calibration data for the midpoint of the cruise will be determined. Viscous and drift corrections are applied to profile data using program calctd.m, and to burst data using calclo.m.

CTD Conductivity: Seasoft module BOTTLESUM creates a sample file for each cast. Program build_table.m collected CTD bottle data and matched it with the sampled salinity and oxygen data. Primary sensors s/n 2887 and 3157 were selected for calibration. For s/n 2887, program calcos1.m produced the best results for an overall linear fit of sample data from stations 1-31:

number of points used: 46total number of points: 50% of points used in fit: 92fit standard deviation: 0.002291fit bias: -0.019446226min fit slope: 1.0008241max fit slope : 1.0008822min fit slope: 1.0008241

For s/n 3157, program calcos1.m produced the best results for a station-dependent linear fit for station 35-51:

number of points used: 28total number of points: 32% of points used in fit: 87.5fit standard deviation: 0.002228fit bias: 0.006286064min fit slope: 0.99994206max fit slope: 1.0001011min fit slope: 0.99994206

Conductivity calibrations were applied to profile data using program calctd.m, and to burst data using calclo.m.

Primary sensor CTD - bottle conductivity differences plotted against station number (Figure 19) and pressure (Figure 20) are used to allow a visual assessment of the success of the fit.



Figure 19 difference between CTD salinity and bottle salinity versus station number.



Figure 20 difference between CTD salinity and bottle salinity versus pressure.

5.7.1.5 CTD Oxygen Calibration

Program build_table.m collected CTD bottle data and matched it with the sampled salinity and oxygen data. Because of sensor hysteresis, programs match_sgn_315p_new.m (stations 1-31) and match_sgn_664_new.m (stations 35-51) were used to match upcast oxygen data to downcast oxygen data by potential density anomalies referenced to the closest 1000-m interval. The oxygen sensors were calibrated to the bottle oxygen by minimizing the residuals using a non-linear least-squares fitting procedure using programs run_oxygen_cal_ml_315.m (stations 1-31) and run oxygen cal_ml_664.m (stations 35-51):

Station	Slope	bias	lag	tcor	pcor
1-31	0.376208	-0.582029	5.255248	0.000340	0.039223
35-51	0.396214	-0.521007	6.989878	0.001015	0.039901

The oxygen was calculated using:

$$O_2 = slope \times (oxvo + bias + lag \times e^{(d_1 \times P + d_2 \times T)} \times \frac{dv}{dt}) \times f_{sat}(S, T, P) \times e^{(tcor \times T + \frac{pcor \times P}{273.15 + T})}$$
(eq. 1)

where:

O_2	= Dissolved O_2 concentration in ml/l;
oxvo	= Oxygen voltage from dissolved oxygen sensor;
fsat(S,T,P)	= O_2 saturation concentration at S,T,P from Garcia & Gordon (1992) (ml/l);
S	= Salinity at O_2 response-time;
Т	= Temperature at O_2 response-time (°C);
Р	= Pressure at O_2 response-time (decibars);
dv/dt	= change in voltage output over time (using an x-second window)
d ₁	= 1.964e-4 (constant nominal value from SeaBird)

Primary sensor CTD - bottle oxygen differences plotted against station number (Figure 21) and pressure (Figure 22) are used to allow a visual assessment of the success of the fits.



Figure 21 Calibrated CTD oxygen - bottle oxygen versus station number.



Figure 22 Calibrated CTD oxygen – bottle oxygen versus pressure.

5.7.1.6 Problems

The secondary conductivity sensor showed irregular variations for stations 2-13. The problem was remedied when the secondary pump was replaced and there were no signs of the problem for the rest of the cruise.

The Wet Lab fluorometer stopped transmitting voltage outputs during the downcast of station 7. When it was removed from CTD s/n 209, corrosion was discovered on the pins of the CTD bulkhead connector. The fluorometer was not used for the remainder of the cruise.

At the beginning of station 32 cast 1, the package was pulled up into the winch block causing the frame, load cell, sea cable and 8 Niskin bottles to break. In addition the forward winch block fell off. There was no visible damage to the CTD or any of the CTD sensors but they were not used for the duration of the cruise. All stations after 32 were taken using a different frame and a different CTD and sensors. The 16 undamaged 11-L bottles plus four spares of the same type where used on the second package. Four 10-L bottles were used to fill the 24 position rosette. The aft winch was used for the remaining stations.

Because of time needed to properly set up the second rosette, water samples were drawn at the regular times for stations 32 cast 2 and station 33 using a submersible pump. A description of how water samples were acquired during that operation is given below.

During station 34, power was lost to the winch due to boat generator problems. The CTD sat at 200 m for approximately 10 minutes and then came directly back onto the deck without firing the remaining bottles. No water samples were taken from this cast. Station 35 was completed and sampled two hours later in the same location when the generators were back online.

5.7.1.7 Submersible pump (stations 32-33)

A submersible pump was used for stations 32 and 33 to pump water to the surface for water samples. Water were pumped through a length of reinforced Tygon tubing and split to control flow rate. The tubing was connected to a rope with a 25 lb weight attached to the end. Desired depths were marked onto the rope and then the rope was let out to the correct depth. Water samples were collected from 20m, 25m, 31m, and 38m for station 32 and 5m, 10m, 20m, 30m, 40m, 45m, and 50m for station 33. A SBE-37-SI MicroCAT C-T sensor was connected to the pump for station 33.

5.7.2 Salinity (Purkey)

All sampled salinity measurements were made using Guildline 8400B salinometer S/N 61668, located in an enclosed laboratory in the hydro-lab. The salinometer was connected to a computer interface for computer-aided measurement. Two samples were collected from each cast, one from a Niskin bottle closed in the surface mixed layer and one from the deepest Niskin bottle closed. Samples were collected in 200 ml Kimax high-alumina borosilicate bottles sealed with custom-made plastic insert thimbles and Nalgene screw caps. Each sample was rinsed a minimum of three times with sample water prior to filling. The laboratory was kept just below 24°C to help stabilize readings and improve accuracy. Fluctuations in the laboratory were monitored using a wall-mounted thermometer. A logging thermometer recorded ambient temperature in 1-minute increments throughout the cruise. The samples were allowed to

equilibrate in the lab for at least 12 hours before being run. Samples were run approximately once every three days during the cruise. Approximately 100 sample salinity measurements were made during the cruise.

The Autosal bath temperature was set to 24°C. A bottle of standard sea-water (batch P-147) was used to standardize the salinometer before and after each batch of samples was run. No more than 24 samples were run in each group. The salinometer outputs were logged to a computer file by the interface software, which prompted the analyst to flush the instrument's cell and change samples when appropriate. For each sample, the salinometer cell was initially flushed at least 4 times before a set of conductivity ratio readings were taken. At least three readings were taken for each sample. Distilled water remained in the cell between uses.

PSS-78 salinity (UNESCO, 1981) was calculated for each sample from the measured conductivity ratios. The offset between the initial standard seawater value and its reference value was applied to each sample. Then the difference (if any) between the initial and final vials of standard seawater was applied to each sample as a linear function of elapsed run time.

5.7.3 DIC (Lebon)

The DIC analytical instrumentation was set up in a seagoing container modified for use as a shipboard laboratory. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) used simultaneously on the cruise. Each system consisted of a 5011 coulometer (UIC, Inc.) coupled with a system designed to improve upon the original SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system. The original SOMMA was developed by Ken Johnson (Johnson et al., 1985,1987, 1993; Johnson, 1992; Wilke et al., 1993) of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, all carbonate species are converted to CO_2 (gas) by addition of excess hydrogen to the seawater sample, and the evolved CO_2 gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated hydroxide. CO_2 is thus measured by integrating the total charge required to balance the reaction.

For the SO GasEx Cruise, our primary standard Certified Reference Materials (CRMs) were supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). The CRM accuracy is determined shoreside manometrically. The CRMS were run approximately every 24 samples on each analytical system and starting the second week of the cruise, running 2 standards per station vs one. On this cruise, the overall accuracy and precision for the primary CRMs on both instruments has yet to be determined. PMEL1 had a gas loop fan failure during the cruise and PMEL2 showed fluctuations due to the air conditioning unit in the van. This was corrected after the first week but overall statistics for the cruise will be determined post cruise shoreside. Preliminary DIC data reported to the database have not yet been completely corrected to the

Batch 84 CRM value, but a more careful quality assurance to be completed shoreside will have final data corrected to the secondary standard on a per instrument basis.

Samples were drawn from the Niskin-type bottles into cleaned, precombusted 300-mL Pyrex bottles using Tygon tubing with silicone ends. Bottles were rinsed twice and filled from the bottom, overflowing a full volume and taking care not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 6-mL headspace, and 0.2 mL of 50% saturated HgCl₂ solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored at room temperature for a maximum of 12 hours prior to analysis. Over 800 samples were analyzed for discrete DIC; all depths were sampled on every station. Replicate samples were typically taken from the bottom depth out of the Niskin-type bottles. The replicate sample was spaced in the middle and or end of the station analysis for quality assurance of the integrity of the coulometer cell solutions. No systematic differences between the replicates were observed.

5.7.4 pCO₂ (Castle)

Samples were drawn from Niskin-type bottles into 500 ml volumetric flasks using Tygon[©] tubing with a Silicone adapter that fit over the petcock to avoid contamination of DOC samples. Bottles were rinsed while inverted and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. About 5 ml of water was withdrawn to allow for expansion of the water as it warms and to provide space for the stopper, tubing, and frit of the analytical system. Saturated mercuric chloride solution (0.2 ml) was added as a preservative. The sample bottles were sealed with a screw cap containing a polyethylene liner. The samples were stored in coolers at room temperature generally for no more than 8 hours.

The analyses for pCO_2 were done with the discrete samples at 20°C. In addition to the primary water bath, which maintained the analytical temperature within 0.05°C, there was a secondary bath to get the samples close to the analytical temperature. As soon as space was available in the secondary and then primary baths, the sample flasks were moved into the more controlled temperature bath. No flask was analyzed without spending at least 2 hours in a bath close to the analytical temperature.

All CTD stations were sampled. On 500 m stations, 15 to 17 of 18 depths were sampled. On 100 m stations, all depths but one were sampled. On deeper stations, all depths were sampled except for one on the last station. Since the flasks are analyzed in pairs, an odd number of depths would normally be sampled to allow for a set of duplicate samples at one depth. At least one pair of duplicate samples from the same Niskin was drawn at every station to check the precision of the sampling and analysis.

In total, 623 samples were drawn at 41 CTD stations and 6 were drawn from a submersible pump lowered over the side of the ship when the CTD broke down. Of the 629 samples drawn,

10 were flagged as questionable and 17 as bad (QC flags of 3 and 4 respectively). Many of these probably result from errors in the program that calculates fCO_2 and will likely be changed to good (QC flag of 2) when the values are recalculated after the cruise.

Forty-seven sets of duplicate flasks were drawn at numerous depths. One pair of duplicates was obviously bad (difference > 5%). The average relative standard deviation of these 47 pairs was 0.82%. Removing the bad pair, the standard deviation of the 46 good pairs was 0.34%.

The discrete pCO₂ system is patterned after the instrument described in Chipman et al. (1993) and is discussed in detail in Wanninkhof and Thoning (1993) and Chen et al. (1995). The major difference between the two systems is that the Wanninkhof instrument uses a LI-COR[©] (model 6262) non-dispersive infrared analyzer, while the Chipman instrument utilizes a gas chromatograph with a flame ionization detector. Once the samples reach the analytical temperature, a ~50-ml headspace is created by displacing the water using a compressed standard gas with a CO₂ mixing ratio close to the anticipated pCO₂ of the water. The headspace is circulated in a closed loop through the infrared analyzer that measures CO₂ and water vapor levels in the sample cell. The samples are equilibrated until the running mean of 20 consecutive 1-second readings from the analyzer differ by less than 0.1 ppm (parts per million by volume). This equilibration takes about 10 minutes. An expandable volume in the circulation loop near the flask consisting of a small, deflated balloon keeps the headspace of the flask at room pressure.

In order to maintain analytical accuracy, a set of six gas standards (CA05998, CA05989, CA05988, CA05980, CA05984, CA05940) with CO_2 mole fractions of 205.07, 378.71, 593.64, 792.51, 1036.95 and 1533.7, respectively, is run through the analyzer before and after no more than every ten seawater samples. The standards were obtained from Scott-Marin and referenced against primary standards purchased from C.D. Keeling in 1991, which are on the WMO-78 scale.

The calculation of pCO_2 in water from the headspace measurement is done by a data reduction program written in GWBasic[©] in 1992. The CO₂ concentrations in the headspace are determined via second degree polynomial fit using the nearest three standard concentrations. Corrections for the water vapor concentration, the barometric pressure, and the changes induced in the carbonate equilibrium by the headspace-water mass transfer are made. The corrected results are reported at the analytical temperature of 20°C. Since the data reduction program was written, the system has been modified to use the internally calculated pCO₂ output of the LI-COR[©] instead of the millivolt output, and some of the algorithms are no longer appropriate. A new program was written during the cruise and is 95% complete. After the cruise, the program will be finished and the calculations redone. This will cause a small change in the final results.

No instrumental problems occurred during the cruise. The relatively time consuming analyses and the presence of only one analyst limited the total number of samples analyzed.

5.7.5 Talk (Covert)

Potentiometric titration was used to analyze 842 samples for total alkalinity during the SOGasEx cruise, including duplicates, and certified reference materials (CRM). With the exception of a series of bad pH electrodes midway through the cruise, analytical performance and reproducibility was as expected for shipboard analyses.

Preliminary results show no significant change in total alkalinity during the course of either tracer patch study. In general, alkalinity was constant 2280 µmol kg⁻¹ throughout the mixed layer, increasing to around 2340 µmol kg⁻¹ at 500 m. Slight variability in the surface was observed, coincident with the rain event midway through the second tracer patch study.

Samples were drawn from Niskin-type bottles into cleaned, 300 mL borosilicate glass bottles using silicone tubing. Bottles were rinsed three times and filled from the bottom, overflowing by half of the bottle volume, and taking care not to entrain any bubbles. The sample tube was closed off and withdrawn from the sample bottle, leaving a 5.0 mL headspace. Samples were preserved by poisoning with 0.18 mL of a 50 percent saturated HgCl₂ solution. Sample bottles were sealed with ground glass stoppers lightly coated with Apiezon-L grease and stored at room temperature (21–25 °C) for a maximum of 12 hours prior to analysis.

Analysis of seawater for total alkalinity, Talk, was performed using an open cell, potentiometric titration method published by Dickson et al. (2003) and subsequently adopted as one of standard analytical methods for ocean carbon measurements (Dickson et al., 2007). By this method, a measured amount of acid titrant (0.1 N HCl) is added to the sample to reduce the pH to less than 3.55, CO₂-free air is bubbled through the acidified sample to facilitate removal of the evolved CO₂ gas, followed by titration to a pH of less than 3.0. The titration curve is fit to a derivation of the defining equation for alkalinity in seawater using a non-linear least squares approach in which one of the adjustable parameters in the fit equation is Talk.

All titrations were performed at a constant temperature of $25.0 \pm 0.2^{\circ}$ C in a water-jacketed, 250 mL glass beaker. Samples were introduced into the beaker using a fixed volume (108.30 ± 0.03 mL), glass syringe. Prior to titration, all samples were brought to 25° C by placing them in a temperature-controlled water bath for at least one hour prior to analysis. After each titration, the beaker was emptied, rinsed three times with de-ionized water, and dried.

Titration progress was monitored by measuring the electromotive force, E, of a combination glass-reference pH electrode (Radiometer, PHC 2002-8). Temperature, T, during the titration was monitored using a Pt RTD. A National Instruments high-precision data acquisition card (NI-4351) was used to record both titration E and T.

Removal of CO_2 generated by acidification of the sample was accomplished by bubbling CO_2 free air through the sample at 100 mL/min for 5 minutes. Air was dried by flowing through a Drierite column and CO_2 removed by flowing through an Ascarite II column.

A Metrohm Dosimat 765 was used to deliver acid to the sample beaker in increments of 0.050 mL. The acid titrant used was 0.1 mol kg⁻¹ HCl prepared in 0.6 mol kg⁻¹ NaCl background to approximate the ionic strength of seawater (0.7 mol kg⁻¹). A single batch of titrant was used over the course of the cruise: PMEL 071607-1. The acid concentration, determined gravimetrically during preparation, is 0.09923 mol kg⁻¹.

Instrument control and data acquisition was with custom software developed at NOAA/PMEL using the National Instruments LabView programming environment.

Analytical accuracy was assessed by periodic analysis of CRMs (Batch 84: supplied by Dr. A. Dickson of Scripps Institution of Oceanography; <u>http://andrew.ucsd.edu/co2qc/</u>) throughout the cruise. References were analyzed approximately every 24 samples. Standard deviation over the course of the cruise is approximately 2.5 μ mol kg⁻¹. Once electrode drift has been taken into account, it is expected that this standard deviation will decrease to less than 1 μ mol kg⁻¹.

5.7.6 Dissolved Oxygen (Hamme)

The oxygen mass balance of the patch represents an important corollary to the carbon budget as both are partially controlled by biological production and respiration but the timescale of oxygen gas exchange is much faster. These measurements are also used to calibrate the CTD's oxygen sensor. Discrete dissolved oxygen samples were collected at each unique depth on all CTD casts where Niskin bottles were tripped, from two pumped casts, and multiple times from the underway system. Generally, duplicate samples were collected from two Niskins per cast and from the underway sampling, while the mixed layer represents another measure of reproducibility. Samples were preserved and analyzed using a variant of the classic Winkler chemistry. The endpoint of each titration was detected by Chris Langdon's amperometric technique, using an electrode that measures a current proportional to the concentration of the $I_3^$ species. A study looking at titration blanks in seawater showed an average 2.5 µL higher blank when compared with distilled water. The current method calls for the subtraction of a distilled water blank; subtraction of a seawater blank would lower the reported concentrations by 0.5 µmol/kg. Precision on the dissolved oxygen samples was excellent throughout the cruise, with an average standard deviation of duplicates of 0.15 µmol/kg. The Langdon titrator performed very well throughout the cruise. The discrete oxygen samples reveal that the mixed layer in the first patch was several percent supersaturated, while the second patch dropped quickly from barely supersaturated to undersaturated for much of the time series with a recovery back toward equilibrium near the end of sampling.

5.7.7 Nutrients (Fisher)

Nutrient samples were drawn in 20ml HDPE sample bottles that had been stored in 10% HCl. The bottles are rinsed 3-4 times with sample before filling. A replicate was normally drawn from the deep Niskin bottle at each station for analysis. Samples were then brought to room temperature prior to analysis. Dissolved nutrients (phosphate, silicate, nitrate, nitrite and ammonium) were measured by using an automated continuous flow analytical system with segmented flow and colormetric detection. The five channel auto-analyzer was customized with various components from other systems.

The major components of the nutrient system consisted of a WESTCO CS-9000 sampler, two peristaltic pumps, four Perstorp monochrometer detectors (model 510), one Lab Alliance monochrometer detector (model 500) and custom software for digitally logging and processing the chromatograms. In addition, glass micro-coils from Alpkem were used for the mixing of the nutrients. Detailed methodologies are described by Gordon et al. (1993).

Silicic acid was analyzed using a modification of Armstrong et al. (1967). An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybic acid. Oxalic acid was then added to inhibit a secondary reaction with phosphate. Finally, a reaction with ascorbic acid formed the blue compound silicomolybdous acid. The color formation was detected at 660 nm. The use of oxalic acid and ascorbic acid (instead of tartaric acid and stannous chloride by Gordon et al.) were employed to reduce the toxicity of our waste steam.

Nitrate and Nitrite analysis were also a modification of Armstrong et al. (1967). Nitrate was reduced to nitrite via a copperized cadmium column to form a red azo dye by complexing nitrite with sulfanilamide and N-1-naphthylethylenediamine (NED). Color formation was detected at 540 nm. The same technique was used to measure nitrite, (excluding the reduction step).

Phosphate analysis was based on a technique by Bernhart and Wilhelms (1967). An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdate acid. This was reduced to the blue compound phosphomolybdous acid following the addition of hydrazine sulfate. The color formation was detected at 820 nm.

Ammonium was determined by the indophenol method, where the NH4 ion reacts with phenol and NaDTT (Dichloroisocyanuric acid, sodium salt) in the presence of Nitroferricyanide in a basic solution to form an indophenol blue solution. Sodium Citrate and EDTA ((Ethylenedinitrilo) tetraacetic acid) were used as complexing reagents to prevent the precipitation of seawater at elevated pH. This reaction was controlled by a heater set at 60C and measured at 640nM.

Fresh mixed working standards were prepared daily. In addition to the samples, each analysis consisted of 4 replicate standards, 3 DIW blanks and 3 Matrix blanks placed at the beginning and then repeated at the end of each run. Also, one mixed working standard from the previous analytical run was used at the beginning of the new run to determine any differences between the

two standards. Samples are analyzed from deep water to the surface. Low Nutrient Seawater (LNSW) was used as a wash, base line carrier and medium for the working standards.

The working standard was made by the addition of 1ml of primary nitrite standard, 1 ml of ammonium standard and 20 ml of a secondary mixed standard (containing silicic acid, nitrate, and phosphate) into a 500ml calibrated volumetric flask of LNSW. Working standards were prepared daily.

Dry standards of a high purity were pre-weighed at AOML. Nitrite and ammonium standards were dissolved at sea. The secondary mixed standard was prepared by the addition of the nitrate - phosphate primary standard (20 ml) to the silicic acid standard.

Approximately 700 samples were analyzed. Nutrient concentrations were reported in micromoles per liter. Lab temperatures were also recorded for each analytical run. Pump tubing was replaced twice during the cruise.

5.7.8 CDOM (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

Discrete water samples were collected for absorption spectroscopy analysis from ~ 30 hydrocasts. Samples were typically collected from 5, 15, 35, 50, 60, 75, 125, and 200 m. Sample depths were selected after examination of the CTD trace. All samples were filtered through 0.22 μ m nylon filters. Filters were pre-cleaned with ~25 ml of methanol, and ~ 300 ml of nanopure water. Samples were analyzed on board using an Ultrapath liquid waveguide system (Miller et al., 2002). Five replicate absorption measurements were obtained from 270 – 724 nm using the 2m path length cell and a TIDAS fiber optic spectrometer (Figure 2). MilliQ water filtered through a 0.22 μ m nylon was used as a reference for each sample. This method requires a correction for the difference in refractive index between pure water and seawater so post processing is required before data are available. Replicates from ~ 12 stations were stored refrigerated for further analysis by high-resolution, excitation emission matrix fluorescence spectroscopy.

Although our CDOM data still requires correction for the difference in refractive index between seawater and pure water (Miller et al., 2002; Nelson et al., 2007), we can make several comments. In terms of CDOM distribution, the mixed layer was very well mixed. Samples from the mixed layer showed small variability during the cruise. ac9 profiles obtained during optical casts (see 4.9.2) show mixed layer CDOM values - expressed as $a_g 440$ - of ~ 0.050 m⁻¹. Under the mixed layer, $a_g 440$ values drop to ~ 0.025 m⁻¹. This underlying could water mass centered at 125 m could be either nascent Antarctic Intermediate Water, or remnant of winter surface water. In either case, it is unclear what the source of the elevated surface CDOM values is (Figure 23).



Figure 23 Uncorrected CDOM absorption spectra collected during CTD cast 39. The figure shows the low variability in surface CDOM, and the high reproducibility of our method.

5.7.9 DOC/TOC (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

At most stations, sub-samples were collected for total organic carbon (TOC) and dissolved organic carbon (DOC) analysis to be done by P. Vlahos. We do not have high confidence in the cleanliness of sample collection for TOC and DOC. We discovered late in the cruise that the Niskin bottles were not Teflon coated. This could cause contamination of the samples from plastics leaching into the water. We also discovered late in the cruise that the Niskin bottles were cocked at least 30 minute prior to a deployment. In many instances, bottles remained open for 45 min to > 1hour while we searched for the tracer patch. This may have exposed the interior of the bottles to diesel fumes and soot thus contaminating the samples.

5.7.10 PIC (Drapeau)

Water sample were taken from the day CTD stations at 6-8 depths with at least 4 samples in the surface mixed layer, 1-2 in the thermocline and 1-2 between 100m and 500 meters. In addition we would sample the uncontaminated sea water system during the cast for a 3m value to correlate with flow through measurements. These samples will be analyzed for PIC, coccolith and cell counts, and BSi as in section 4.4.5.

5.7.11 Noble Gases and Natural Argon Isotopes (Hamme)

Discrete samples were collected to measure dissolved neon, nitrogen, argon, krypton, and xenon concentrations and natural abundance argon isotopes by high accuracy mass spectrometric methods. While the full geochemical potential of these tracers is still being developed, we expect their large range of solubilities and temperature dependencies to enable us to separate the influences of multiple processes on the gases, including bubble-mediated gas exchange by different mechanisms, temperature change, and atmospheric pressure variation. Samples for

noble gases in the upper 100m were collected on nine casts focusing on higher wind speed events (Stations 2, 4, 13, 14, 22, 25, 37, 46 and 51). Argon isotope samples were collected in the mixed layer coincident with noble gases on those same casts. Additionally, noble gas samples between 150m and 4600m were collected on two casts (Stations 1, 10) to create a full depth profile. Whenever two Niskins were tripped at the same depth, noble gases were sampled on the Niskin not sampled for hydrography. When this was not possible, Niskins were frequently sampled out of order to allow the slower noble gas sampling to keep up. When sharing Niskins with hydrography, order of sampling was after oxygen and before carbon parameters. Sample collection involved flushing of carbon dioxide through the neck of the sample flask, to reduce the possibility of air contamination, followed by sucking the water sample into pre-evacuated flasks. All samples for both noble gases and argon isotopes were collected in duplicate to ensure high precision. Back at the lab, gas samples will be cryogenically purified and exposed to hot gettering alloys to remove interfering gases and analyzed on an isotope ratio mass spectrometer, noble gases at University of Victoria and argon isotopes at University of Washington. An ³⁸Ar spike is added to the noble gas samples to obtain absolute argon concentrations by isotope dilution (Hamme and Severinghaus 2007). Errors for noble gases are expected to be ~0.2% for all the gases based on the standard deviation of duplicates collected on previous cruises. Errors for natural argon isotopes are expected to be near 0.02 permil.

5.7.12 Chlorophyll (Lance)

Fluorometric chlorophyll profiles were measured on most day and evening CTD cast stations and some pump casts which totaled 40 stations. Near surface Fl-Chl at stations ranged from about 0.4 to 1 mg m⁻³ (Figure 24). Size-fractioned Fl-Chl profiles were measured at 6 of these 40 stations and 3 of the 6 coincided with the 3 size-fractioned PP-24h profiles described in section 4.8.1.



Figure 24 near surface fluorometric chlorophyll from CTD stations.

HPLC pigment samples were collected at 28 stations which were a mix of day and night CTD casts from 6 to 8 depths from surface to \sim 100m. Samples were filtered onto GFF filters and stored in liquid N₂ for later analysis of suite of phytoplankton pigments. Samples will be analyzed by Analytical Services of Horn Point Laboratory Pigment Analysis Facility, HPL-UMCES.

5.7.13 TSM (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

On days when optical casts were scheduled, discrete samples were taken for total suspended material (TSM) analysis. Samples were taken from the surface (from the clean seawater source) and at 60 meters. Samples were prescreened with a 64 μ m mesh, then filtered on pre-weighed 0.2 μ m Nucleopore filters. The filters were then frozen for shipping and later analysis. On the last two rosette casts, samples were taken from 5 meters to compare to the inline system. Each time water was taken from the rosette, a full Niskin bottle, including dregs below the spout, was taken, then mixed, and subsamples were taken from that. A total of 64 filters will be analyzed and compared with optical properties.

5.7.14 Particulate Organic Carbon (Strutton)

The POC budget of the patch is an important component of the mixed layer carbon budget. POC was quantified by discrete samples, surface underway mapping (see also section 4.4.7) and vertical optical profiles (see also section 4.9.2). Discrete water samples (1.17L) were taken from six depths between the surface and 100m on each CTD cast. Four samples were usually taken in the mixed (<60m) layer to ensure accurate quantification of changes in mixed layer POC. The remaining two samples were usually obtained from within the thermocline (\sim 75m) and below the thermocline (~ 100 m). These water samples were filtered, the filters dried and will be analyzed on return to the lab. The POC data from the ~9am/11am local CTD casts will be compared with the optical profiles of beam attenuation at \sim 660nm (see section 4.9.2) to obtain continuous vertical profiles of derived POC (Gardner et al., 2003). The near-surface samples from both the morning and evening CTD casts, and occasional calibration samples from the underway seawater line, will be compared with the corresponding data from the surface underway transmissometer (again, beam attenuation at 660nm) to produce high spatial resolution underway maps of POC in and surrounding the patch. The surface underway and CTD data represent complimentary approaches to determining the time rate of change in POC for the patch. Changes in POC were not quantified by measurements during GasEx2001, so this represents a potential improvement on the carbon budget constructed for that experiment.

5.8 Primary Production/New Production

5.8.1 ¹⁴C Incubations (Lance)

Primary productivity was measured in support of two aims: 1) to close the carbon budget of the SO Gas Exchange experiment and 2) to validate primary productivity models based on optical and/or photophysiological parameters. Samples were collected approximately every day during

evening casts (~2100 or 2300 hrs shiptime) from 6 to 8 depths from surface to 50 m. Samples were inoculated with ¹⁴C tracer and incubated in on-deck incubator cooled with flowing surface seawater which contained chambers shaded with blue sheet filters and window screening to simulate 6-8 in situ light levels. Incubation times were 12 and/or 24 hours. Samples were filtered through GFF filters (nominal pore size ~0.7 µm) to give "total" primary productivity and on some occasions through polycarbonate filters (2 and 20 µm pore sizes) to give size-fractioned primary productivity which gives the proportion of primary productivity by 3 operationally defined size classes (picoplankton gff to 2 µm; nanoplankton 2 to 20 µm; and microplankton >20µm). PP-24 h profiles were measured from every night CTD cast and one "pump cast" which totaled 20 stations. Near surface PP-24 values ranged from about 0.5 to 1.5 mmol C m⁻³ d⁻¹ (Figure 25). PP-12 h profiles were measured on 10 of those same 20 (i.e. paired 12 & 24 h incubations). Size-fractioned PP-24 h profiles were done at 3 of the 20 stations (GFF, 2 & 20 μm; except no duplicates on 2 or 20 μm) microplankton, nanoplankton and picoplankton were responsible for approximately 3-9%, 33-37% and 55-60% (respectively) of primary production at those 3 stations. Primary productivity profiles (mmol C $m^{-3} d^{-1}$) will be integrated to provide areal primary productivity to the 1% light depth (mmol C $m^{-2} d^{-1}$).



Figure 25 Near-surface primary productivity based on 24 hour ¹⁴C incubations.

5.8.2 ¹⁵N Incubations (Strutton, Lance)

Given the Lagrangian nature of our experiment, we can assume that new production is approximately equivalent to export production. The LDEO group (previous section) performed ¹⁴C incubations to measure gross and net primary productivity. To quantify new production we performed incubations using the stable isotope ¹⁵N. Discrete water samples (1.17L) were taken from 6 depths between 0 and 50m on the evening CTD casts (usually 5, 10, 15, 25, 35 and 50m).

The samples were kept cold and in the dark until just before local sunrise (~08:30 GMT), whereupon they received an addition of 0.2ml of ~10mM K¹⁵NO₃. This represents an NO₃ enrichment of a little less than 2uM or 10% given the ambient NO₃ concentrations. Samples were incubated for 12-24 hours at light levels approximating those from which the water samples were taken (85, 40, 27, 11, 4 and 1% of surface light) and at surface sweater temperatures in an incubator bath located on the starboard side of the fantail. When the incubations were terminated, the water samples were filtered, the filters dried, and will be analyzed on return to the lab. The amount of ¹⁵N taken up by the phytoplankton community, when compared with the total C uptake, will provide an estimate of the *f* ratio and new production. Data similar to these were used by Strutton *et al.* (2004) and Sabine *et al.* (2004) to close the carbon budget for the mixed layer during GasEx 2001.

5.8.3 Phytoplankton Absorption (Hargraves)

For each of the productivity samples collected I provided (1) daily PAR irradiance data measured at 15 minute intervals at the stern of the ship, and (2) measurements of phytoplankton spectral absorption. PAR irradiance was summarized each day from 5 March until the end of the cruise in daily spreadsheets. Over 300 Phytoplankton absorption measurements were either made using fresh samples (most) or stored for analysis during the summer (several dozen). Daytime measurements of phytoplankton absorption in the upper 5 meters are also being compared with extracted chlorophyll-a data provided by Veronica Lance and spectral radiance reflectance data collected as a first step toward integrating photosynthesis data with Zhong Ping Lee's remote sensing project (Figure 26).



Figure 26 Phytoplankton absorption versus extracted chlorophyll.

The shipboard measurement of over 300 samples for phytoplankton spectral absorption established that the method is feasible in this setting without the need for a delicate laboratory spectrophotometer. The preliminary phytoplankton absorption data and the extracted chlorophyll-a data are currently available. Prior to final adjustments of the absorption spectra, an unusually strong correlation between the chlorophyll red peak (absorption data) and chlorophyll a concentration (extracted in methanol) is seen. The blue peak in the pigment spectra shows two relationships (and thus a somewhat lower r² in the combined regression shown in Figure 26), one for the period early in the study (Station 1-14) and the other for the balance of the time. The higher blue absorption on the earlier dates corresponds to the observations in the spectra of higher UV-B absorption that typically reflects UV-B protective pigments (MAA's). It will be interesting to see if this shift in the spectrum can be correlated with a shift in extractable MAA pigments and/or a change in the photosynthetic efficiency of the phytoplankton from the measurements of my colleagues.

Frozen GFF filter samples will be analyzed for absorption spectra during the summer for the purpose of comparing an established technique with my new technique. I will also be completing several calibration steps for my new method and expect to use the results to refine my preliminary estimates of phytoplankton absorption over the 6-12 months. Comparison of my absorption data and photosynthesis data from the experiments of Lance and Vaillancourt will take place within several months.

The phytoplankton absorption data determined by our optical measurements of particles concentrated on a GFF filter (both my new method and a traditional method) will be compared with two other methods for measuring phytoplankton absorption. First, the in vivo particle absorption spectra (especially the blue peak at 440 nm and red peak at 676nm) determined by optics group's AC-9 measurements in the water column and AC-S measurements in the underway flowing seawater system will be compared with our filter pad measurements of phytoplankton absorption. We expect preliminary data for these comparisons to be available within weeks. Second, frozen samples will be analyzed by HPLC for pigment composition and then concentrations and pigment absorption spectra will be used to reconstruct a total absorption spectrum for photosynthetic pigments. An adjustment must be made in this process to account for the "package effect" of intracellular pigments and this well be guided by the other measurements of phytoplankton absorption. We expect the samples for HLPC pigment analysis (measured by subcontract) to be available within several months.

5.8.4 O₂/Ar Ratios (Hamme)

Mass balance techniques using oxygen/argon ratios can yield high quality estimates of net community production. By ratioing with argon, the biological oxygen signal is corrected for physically-induced signals by bubble-mediated gas exchange and temperature change. The oxygen/argon ratio of surface seawater was near continuously monitored using a membrane equilibrator and quadrupole mass spectrometer developed by Michael Bender's Lab. This ratio is robust to temperature fluctuations and to smaller inputs of air to the underway system. Nitrogen/argon and carbon dioxide / argon ratios were also monitored, but these ratios appeared more sensitive to temperature change and bubbles in the system and may not yield accurate estimates of the true dissolved seawater ratios. Gas ratios in air were monitored for ten minutes

every two hours as a gross standardization of the measurement. The equilibrator inlet mass spectrometer system performed well for much of the cruise, except for periods during March 10-16 when a negative interaction between moisture in the equilibrator and the pick-off capillary caused unstable signals. When finally diagnosed, this problem did not recur for the remainder of the cruise. Discrete samples for high accuracy oxygen/argon measurements were collected from the surface bottle on every CTD Rosette cast except Stations 7 and 8, as well as from the underway system directly. Two short profiles were collected at Stations 6 and 16. All discrete samples will be analyzed for oxygen/argon ratios at Princeton University and used to further calibrate the underway measurements. In the lab, the gas sample is cryogenically purified to remove water vapor and analyzed on an isotope ratio mass spectrometer for gas ratios and isotopes with an expected precision of 0.3% for the oxygen/argon ratio. Additionally, a subset of samples will be chromatographed to remove nitrogen and analyzed for oxygen triple isotopes. with an expected precision of 0.007 per mil on the mass-independent fractionation anomaly of ¹⁷O. Net and gross productivities will be calculated from the oxygen data and an estimate of gas exchange; the later normally contributes most of the uncertainty though we hope that direct measurements made on this cruise will reduce that uncertainty. Preliminary data indicate that the first tracer patch had low but measurable rates of net community production, with some interesting variability. For the most part, preliminary data indicate that the second tracer patch appeared to be characterized by net respiration. Spatial surveys indicated some areas of net productivity, particularly just south of the tracer patch.

5.8.5 Photosynthesis-Irradiance Experiments and FRR fluorometry (Vaillancourt)

5.8.5.1 PE Profiles

Photosynthesis-Irradiance (PE) experiments were performed on water collected during morning ctd casts on 12 separate casts, sampled at 8 depths from the surface (z=5m) to 75 or 100 depth. These maximum depths were likely well below the euphotic depth (depth where PAR irradiance is reduced to 1% of its surface value), estimated using the Morel chlorophyll-light model at approximately 40 m. Actual submarine downwelling irradiance (used to estimate water column profiles of carbon dioxide uptake by phytoplankton from PE data) will be modeled by the optics group (Dierrson, Twardowski, Balch, etc.) using the inherent optical properties of the water column, obtained during separate optical casts just prior to or following morning ctd casts, and meteorological conditions as logged by ship's met systems, as model inputs.

The PE experiments were performed on a 'radial photosynthetron', a ten-position temperaturecontrolled light incubator that is capable of incubating samples from ten different depths, each at identical temperature and light conditions. The purpose of the PE experiment is to 'diagnose' the phytoplankton's ability to incorporate ${}^{14}CO_2$ under a wide set of light intensities. Our first PE incubations (stations 7, 14, and possibly 24) experienced technical difficulties with accurate characterization of the light fields within each incubator box, and these data will likely be thrown out. The technical problem was solved by Station 24 or 30, and each subsequent PE experiment was successful.



Figure 27 Photosynthetic efficiency (left) and maximal photosynthetic rate (right) for eight stations. The error bars represent the standard error of the estimates. Estimates are based on non-linear least squares regressions of data.

Preliminary conclusions on CO₂ uptake patterns based PE data from stations 24 through 49 are as follows:

- a.) The maximum biomass-normalized photosynthetic rate (Pbmax) in the upper 60 m (the isothermal layer) generally varied between 2 and 3 mgC/mg Chl a/h. Below this depth Pbmax generally declined. There is no noticeable trend with time.
- b.) There appears to be a strong temporal trend in biomass-normalized photosynthetic efficiency (α_b) . Stations 24 and 30 (24 & 27 Mar) show low α_b , in the vicinity of 0.02 0.03 mgC/mgChla/h (uE/m²/s)⁻¹ from the surface to 100 m. But for remaining stations 38-49 (Mar 30- Apr 4), α_b increases 3- to 5-fold, between roughly 0.06 and 0.1 mgC/mgChl a/h (uE/m²/s)⁻¹. Generally, the topmost sample at z=5m tended to be lower than values deeper. The z=10 m sample also tended to be very high compared to values above and below. It is possible it is a spurious result from a badly calibrated light field within the incubator box #2, but this has not yet been adequately determined.

Also, for each PE experiment there is a matching set of data for variable fluorescence parameters $(F_v/F_m, \alpha_{PS2}, tau, F_o, F_m)$ taken with the Chelsea Fast Repetition Rate Fluorometer (FRRF). These data have not been processed yet, but should be complete within 6 months of end of cruise. The FRR fluorometer was deployed in benchtop mode. The instrument was set up in the ship's "climate control room", with temperature set constant at ca. 2°C, to match the pre-cruise calibration temperature. Background controls were run for each sample, consisting of a 0.2

micrometer filtered seawater in order to subtract out the fluorescence contribution from CDOM. We expect this contribution to be low and fairly consistent based on CDOM fluorescence results obtained by other means, such as profiling CDOM (Turner C6) fluorometer (Hargreaves) and long-path absorption meter (DeCastillo). Nevertheless, subtraction of CDOM background signal, even when the background is small relative to the signal, has proven important to obtaining meaningful FRRF data.

5.8.5.2 Diel PE Studies

The PE profiles are a measure of CO₂ uptake by phytoplankton on the scale of one to two hours. Extrapolation to daily integrated values of production requires knowledge of how PE parameters vary throughout the diurnal cycle. We attempted to determine this by performing 3 separate diel studies of PE parameters, and one diel study of FRR fluorescence parameters. Diel study #1 was performed during the ship's sojourn on the north side of South Georgia Island. Diel studies #2 and #3 were performed while within the second SF6 patch. Approx 20 Liters of seawater was captured and incubated on deck near the flowing seawater incubators. We sampled the carboy at seven points from one hour prior to sunrise to one hour following sunset for chlorophyll a concentration, PE parameters, and (for Diel study #1 only) FRRF parameters.

The results are equivocal as we cannot separate possible "bottle effects" from actual diel variations when incubation times are < 1day. Nevertheless, there was a noticeable trend in PE parameters that may represent the natural diel variation reported by others. Figure 28 shows these results, with local maxima in both Pbmax and ab near sunrise, and steadily declining values throughout the remainder of the day, with the exception of Pbmax on 28 March.



Figure 28 Results of diel PE Experiments #2 (25 March, blue symbols) and #3 (28 March, red symbols). Chlorophyll –normalized photosynthetic efficiency (alpha, left graph) and maximal photosynthetic rate (right graph) are shown. Data for Diel experiment #1 are not shown.

Diel studies were also performed using FRR flurometery, but only during Diel experiment #1. We had doubts that this water, which was sampled at 7 time points during day while off of South Georgia Island from the ship's flowing seawater line, was from a single water mass, i.e. lagrangian. The PE parameters (not shown) did not show similar patterns to Diels #2 and 3, however the FRR fluorescence was a typical result of irradiance effect on fluorescence (Figure 29).



Figure 29 Solar irradiance during day on March 16 and corresponding suppression of phytoplankton Fv/Fm. Matching Chl a concentrations are shown in green symbols , lower graph.

5.9 Ocean Optics

5.9.1 PAR sensor (Strutton)

A Photosynthetically Available Radiation (PAR, 400-700nm) sensor was mounted on the CTD rosette. PAR data from the morning (~9am/11am) CTDs were used to calculate the diffuse attenuation of solar radiation with depth. These data were then used to calculate the depth of the % light levels that were used for the ¹⁴C and ¹⁵N incubations. These calculations are important because the % light depths are used in the trapezoidal integration of new production and primary production. The PAR attenuation data can also be used to calculate the attenuation of solar radiation for constructing a heat budget for the mixed layer, or as input into a Price-Weller-Pinkel (PWP) model (Price *et al.* 1986).

5.9.2 Optical Casts (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

We deployed our optical instruments that included the deployment of a prototype system that combined instruments from WetLabs-East and the University of Connecticut. Table 5 shows the optical package components. This optical package makes spectral measurements of total and back scattering using different techniques, and standard measurements of beam attenuation and absorption (i.e., ac9). The optical package was deployed at 14 stations close to local noon. At each station the optical package was deployed twice to about 150 m. First, the ac9 was fitted with a 0.2 μ m filter similar to the underway acs to obtain measurements of CDOM absorption. During this cast, the light source on the MASCOT was covered to obtain dark current measurements. On the second cast, the 0.2 μ m filter was removed and the MASCOT light source was uncovered to collect regular scattering measurements. At the beginning or end of this cast, the package was left close to the surface for 30 minutes to measure time-dependant variation in scattering. During this time, a Satlantic HTSRB buoy was deployed to obtain downwelling irradiance and upwelling radiance measurements to calculate spectral Ks and remote sensing reflectance ($R_{rs(\lambda)}$). This tethered buoy is allowed to drift away from the boat to avoid shading and reflection contamination from the boat.

 Table 5. List of instruments deployed on optical profiler and type of measurements

Instrument	Number	Measurements	Legacy
CTD	1	Conductivity, temperature, and pressure	commercial
LISST	3	Near-forward scattering and particle size distribution	commercial
ac9	1	Light absorption and attenuation at 9 wavelengths	commercial
ECO-VSF	1	Volume scattering function to obtain b and bb.	commercial
ECO-bb3	1	Scattering at 3 wavelengths	commercial
AUV-b	1	Total scattering	prototype
MASCOT	1	Scattering at 17 angles from 10 to 170	prototype

During the cruise, $32 R_{rs}$ spectra have been collected whose 21 simultaneously with CTD and optical profiles. These R_{rs} spectra show a weak variability in both magnitude and spectral shape (Figure 30A). The greatest spectral variation is observed between approximately 350 and 490 nm as indicated the standard deviation spectrum (Figure 30B). The weak values in the high wavelengths have been expected and highlight the domination of the organic fraction to the mineral fraction in this part of the ocean.



Figure 30 (A) Rrs spectra obtained during the SO GasEx cruise. (B) The mean and standard deviation spectra calculated from the whole Rrs spectra plotted in (A).

A quality control of our measurements has been done by verifying the consistency of the measured b_{bp} values with those estimated by the inversion of the measured R_{rs} from the Quasi-Analytical Algorithm (QAA; Lee et al., 2002). The results of the comparison are displayed in Figure 31. The Root-Mean-Square-Error (RMSE) value, calculated in the log space, is weaker than 30%. This result may be improved after correction of our R_{rs} and VSF spectra. By consequence, the result of the closure exercise is very encouraging for remote sensing applications in the Southern Ocean.



Figure 31 Comparison of the derived QAA and MVSM particulate backscattering coefficient bbp at 550 nm.

Figure 32A shows the results of the comparison between total absorption subtracted with the pure seawater absorption a_{tot} - a_w measured (at 5 m) and derived at 440 nm. The in situ a_{tot} - a_w have been provided by Scott Freeman. This parameter was measured using the ac9 during the optical profiles. The inversion provides good result with a RMSE weaker than 8% and a regression slope around 0.794.



Figure 32 Comparison between optical properties measured and derived from QAA.

Figure 32B shows the results of the comparison between phytoplankton absorption a_{phy} measured (at 5 m) and derived at 440 nm. The in situ have been provided by Bruce Hargreaves. This parameter was measured using an improved filterpad method (pFPT-TR instrument).

5.9.3 Multispectral Volume Scattering Meter (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

This instrument was developed at the Marine Hydrophysical Institute in Sevastopol, Ukraine (M. E. Lee and M. R. Lewis, 2003). The MVSM performs light scattering measurements at angles going from 0.5° to 179°, with a resolution of 0.3° at eight wavelengths (443, 490, 510, 532, 555, 565, 590, and 620 nm).

5.9.4 Handheld Spectroradiometer and Sunphotometer (Del Castillo, Miller, Freeman, Lubac, Buonassissi)

Measurements of spectral above-water radiance and remote sensing reflectance R_{rs} were made using a handheld spectroradiometer. R_{rs} is computed following the protocol of the method 2 (uncalibrated radiance and reflectance plaque measurements) described by Mueller et al. (2002). A second set of R_{rs} were collected with an ASD at 14 stations.

Measurements of aerosol optical density were made using a sunphotometer (Microtops II). Water's optical properties and phytoplankton absorption coefficients will be derived from measured remote sensing reflectance, and these properties will be compared with data from water sample measurements (taken by collaborators). Satellite (MODIS-Aqua and/or SeaWiFS, MERIS) data will be processed and be compared with in situ measurements.

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Appendix:

NOAA Ship RONALD H. BROWN CTD Incident Report

0900 28 March, 2008

Attached are the statements of all parties involved, a copy of the Deck Log and hourly weather log for that day, and a photo of the damaged CTD package collected by the XO.

Officer Of the Deck (OOD): LT Elizabeth Crapo (on bridge O-4 deck)

Watchstander/Lookout: AB Victoria Carpenter (in winch house O-2 deck)

Chief Survey Technician (CST): Jonathan Shannahoff (initially on deck at CTD deployment location stbd side aft, main deck, near staging bay - Main Deck ext)

Scientific CTD Console Operator: Sarah Purkey (in computer room at CTD control station – Main Deck interior)

Chief Bosun (CB): Bruce Cowden (on deck to respond afterwards)

Investigator - Executive Officer (XO): LCDR Todd Haupt

Commanding Officer (CO): CDR Carl Groeneveld

LT Crapo Statement (1346):

XO,

Here is the statement you asked for:

The CTD was put in the water at 0855. After verifying that the wire angle was not tending in any adverse direction, I commenced the top-of-the-hour weather observations and MOA log entries. I heard the winch operator ask the survey tech to come outside, and when I looked outside the CTD was hanging off the side of the ship, obviously damaged and the block was missing. I did not see the incident occur. The time would have been right around 0800 or 0801.

V/R,

LT Crapo

<u>AB Victoria Carpenter Statement – Taken and Transcribed by XO (0935):</u>

CTD Incident Report according to AB Victoria Carpenter:

 \sim 0845 AB Carpenter went to the winch house in preparation for CTD ops. She checked the cable drum on the way to the winch house and everything checked SAT.

~0853 OOD and CST Shannahoff made the normal radio comms in prep for CTD ops (ie Bridge reports on station, CST visually checks to see that CTD winch operator is ready in winch house, and CST radios CTD console operator to see if they are ready for CTD ops).

 \sim 0854 AB Carpenter visually checks CTD deployment area for any safety hazards, with none noted.

~0855 CST radios AB on winch and boom instructions to deploy CTD in water, per CTD SOP with no incident (ie raise package, boom out, lower package to just below water surface). Once in the water at the surface, CST radios AB to lower package to 10 meters.

~0900 After 2 minutes at 10 meter depth, CST radios AB to bring the package back to the surface per CTD SOP. Once at the surface CST radios AB to clear the meter and then radios CTD console operator with the standard "Computer room the package is yours". CTD console operator responds with the standard "Winch down at 30 (meters/min)". AB checked safety line on deck then turned to observe the CTD cable to her left at the winch house level as she was lowering the package to depth – when in fact she was raising the CTD package (ie taking in cable vs paying out cable).

~0901 AB heard a loud noise and saw the CTD package alongside the ship stbd side outboard and the fwd block from the CTD boom on the main deck below and obviously unusable. She immediately stopped the winch and radioed the CST to on scene. With no immediate response she left the winch house to find the CST. By the time she reached on scene CST was there as well as a couple scientists and crew who had heard the loud noise as well. She started back to the winch house and notified the CO along the way.

~0905 AB is back in winch house. CST radios AB to "boom in". By this time CB and other crew take over operations to safely recover CTD package using the ship's stbd crane.

CST Jonathan Shannahoff Statement (1400):

CTD incident report

CTD operations commenced at approximately 0900 hours on March 28, aboard the RONALD H.BROWN.

The sequence of events is as follows.

I (CST) ask if the bridge was ready, then the computer room. Finally the winch was instructed to put the CTD package in the water.

The package was at the surface and the winch readout was zeroed. The package was then lowered to 10 meters of wire out and held for a 2 minute soak.

The package was then returned to the surface and stopped.

At this time, I (CST) turned the package over to the computer operator to instruct the winch operator to begin the cast.

I (CST) then left the deck to return to the computer room to check that the system is operating properly.

After being in the computer room for only a few seconds, the computer operator said that they had lost the readout (Numbers for sensors). I looked at the deck unit and noticed that it was registering that the pumps were not operating.

At this time the winch operator said over the radio, what sounded to me like, " I came to the surface " and then ask for me (CST) to come out.

As I walked down the passageway I called the winch over the radio to ask what is the problem, I got no answer.

When I stepped out into the staging bay and onto the deck, I saw immediately the problem, the package was hanging off the side of the ship.

I immediately called for the Bosun and proceeded to connect lines to the package to insure it would not break away and sink.

The Bosun came out and we with some deck hands brought the package on deck and secured it.

Jonathan Shannahoff

Scientific CTD Console Operator Sarah Purkey Statement (1224):

Incident Report

March 28, 2008

Sarah Purkey: CTD console operator

This morning at 8:55, after starting up the ctd I gave Jonathan the ok to put the package in the water. Through the radio, I heard Jonathan give instructions to lift the package in to the water, bring it down to 10 m of wire out, sit for 2 min and then bring the package back to the surface.

I let the package sit at the surface for about 20sec then told the winch to go "down at 30". A few seconds later, I looked up at the screen that displays the output from the sensors. I noticed the pressure reading was -0.5 and the pumps were off indicating that the package was out of the water. Before I had time to react the computer gave me an error that connection had been lost. At which point I said something to the extent of, "ummm, Johnny what is going on, something is wrong". Jonathan was making his way over to the computer when the winch operator said "the package is out of the water". Jonathan left the computer room to go out side. I turned of the program and ctd and when out to see what was going on.

CB Bruce Cowden Statement (1345):

CTD incident report 3/28/08 time 0915: Chief Bousun / NOAA Ship Ronald H. Brown

At approximately 0915 I was called to the staging area for CTD operations to investigate a broken block. Upon arrival I noticed the CTD rosette hanging over the side by a single line of 1/2" spectra double braid with a breaking strength around 10,000 lb.

At the time of my arrival the Chief Survey Tech was passing some line around the lifting pad of the CTD for a back up securing line. After a quick survey of the situation to determine whether it was safe to proceed I instructed AB William's to the crane and OS Abraham to procure a 12' lifting strap SWL 10,000 lb.

All unnecessary personal had already been cleared from the working area by the Chief Survey Tech at this time so we went to work. I passed the lifting strap to the CST who passed it through CTDs lifting pad and hung the ends on a cleat until the crane was in position.

The hook was lowered, strap secured on hook, then transferred load to the crane. After the crane took the entire weight of the CTD we looked it over carefully to insure there was no unseen damage that might cause a safety concern, when we determined all was safe, we then brought the CTD back on deck securing it for further investigation.

After further investigation it is apparent that the CTD had two blocked against the Hydro Boom and severed the block and wire causing the CTD to come crashing down against the side of the ship with a considerable amount of force. The only thing holding it from being lost was the second Chinese finger and the spectra safety line put in place for backup.

Bruce Cowden Chief Bosun / NOAA Ship Ronald H. Brown

NOAA FORM 77-138 DECK LOG	- REMARKS SHEE	NATIONAL OU	EARLY AND ATMOSPHERIC (
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NOAA FORM 77-13d (3-76)

U.S. DEPARTMENT OF COMMERCE NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

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