CRUISE REPORT

Ocean Atmosphere Carbon Exchange Study

AOML/OACES designation:

 GAS EX-98, leg 1, leg 2, leg 3

State Department designation:

97-118, RONALD H. BROWN, May 7-July 7, 1998

Cruise designator: RB-98-02

7-May to 7-July 1998

Expocodes:

GasEx-98, leg 1: 33RO19980511
GasEx-98, leg 2: 33RO19980525
GasEx-98, leg 3: 33RO19980628

I. ABSTRACT

This cruise was designed to support research sponsored by the NOAA Climate and Global Change Program under the Ocean-Atmosphere Carbon Exchange Study (OACES), The OACES objective for this study was to determine the air-sea fluxes of CO2 in the North Atlantic. In specific the field components involved:

 COMPONENT METHOD

• Direct flux measurements of CO2 -Co-variance

 -Gradient

 -Eddy Accumulation

• Validation/Verification -Dual deliberate tracer

 - CO2 balance water column

 Biology

 Advection

 -O2 balance

 -Halocarbon thermal disequilibrium

 -Direct fluxes other gases

• Parameterization of gas fluxes -Wind speed

 (gas transfer velocities) -Friction velocity

 -Surface turbulence

 -Whitecaps

• Opportunistic work -Utilize tracer patch for study of

 CH3Br and halocarbon dynamics

 -Utilize gas transfer velocities

 -Intercomparison

II. OVERVIEW OF CRUISE AND ITINERARY

Summary:

Arrive Miami May 2, 1998

In port

Depart Miami May 7

LEG 1 OPERATIONS

Arrive Lisbon May 20

In port May 21

Depart Lisbon May 25

LEG 2 OPERATIONS

 Arrive Ponta Delgada June 26

 In port June 27

Depart Ponta Delgada June 28

LEG 3 OPERATIONS

Arrive Miami July 7

In port/destage July 8-10

 The 3-legged cruise consisted of a leg originating in Miami, Florida on May 7 and arriving in Lisbon, Portugal, May 20; a process study leg between Lisbon and Ponto Delgada, Portugal from May 25-June 26; and a return leg from Ponto Delgada to Miami from June 28-July 7, 1998.

III. CRUISE PERSONNEL

A. Chief Scientists

Leg 1. Jim Butler, CMDL

Leg 2 Rik Wanninkhof, AOML/co-chief Jim Butler, CMDL

Leg 3 Shari Yvon-Lewis, AOML

B. Cruise Personnel GAS EX-98

LEG 1

Name Affiliation Project

Robert Castle NOAA/AOML SF6 tracing/pCO2/DIC

Craig Neill NOAA/AOML SF6 tracing

David Ho Columbia U./LDEO SF6 tracing

Jim Smith NOAA/CMDL closed path dry CO2 flux

Michael Hahn NOAA/CMDL closed path dry CO2 flux

James Butler NOAA/CMDL Halocarbons

Daniel King NOAA/CMDL Halocarbons

Shari Yvon-Lewis NOAA/AOML Halocarbons

Alexander Soloviev Nova U. surface turbulence

Anatoli Arjannikov Nova U. surface turbulence

Terry Thompson NSU and Exploration Technologies, Inc. surface turbulence

Walt McKeown NRL interferometry

Jennifer Hanafin RSMAS/ U. Miami interferometry

Jon Ware WHOI closed & open path CO2 flux

Jeff Hare NOAA/ETL heat & momentum

Andrew Jessup APL/U. Wash IR Imaging

Chris Zappa APL/U. Wash IR Imaging

Jesse Davis APL/U. Wash IR Imaging

Gary Wick APL/U. Wash IR Imaging

Patricial Matrai Bigelow CH3Br/production

Brian Yocis Bigelow CH3Br/production

Wayne Grosko Bigelow CH3Br/production

Heather Wright Bigelow CH3Br/production

Ryszard Tokarczyk RSMAS/ U. Miami CH3Br/degradation

Kevin Sullivan RSMAS/ U. Miami CH3Br/degradation

Michael Reynolds BNL Underway radiance

LEG 2

Rik Wanninkhof NOAA/AOML SF6 tracing

Robert Castle NOAA/AOML SF6 tracing/pCO2

David Ho Columbia U./LDEO SF6 tracing/data/buoy

Kitack Lee NOAA/CIMAS SF6 tracing/data/buoy

Craig Neill NOAA/AOML SF6 tracing

Geoffrey Samuels U. Miami/CIMAS CTD

Marilyn Roberts NOAA/PMEL DIC

Dana Greeley NOAA/PMEL pCO2

Jia-Zhong Zhang NOAA/AOML Nutrients

George Berberian NOAA/AOML Oxygen

Amy Ritchie Bermuda bio. DOC

Jim Smith NOAA/CMDL closed path dry CO2 flux

Michael Hahn NOAA/CMDL closed path dry CO2 flux

James Butler NOAA/CMDL Halocarbons

Daniel King NOAA/CMDL Halocarbons

Shari Yvon-Lewis NOAA/AOML Halocarbons

Alexander Soloviev Nova U. surface turbulence

Anatoli Arjannikov Nova U. surface turbulence

Richard Sikorski RSMAS/ U. Miami interferometry

Goshka Szczodrak RSMAS/ U. Miami interferometry

Jim Edson WHOI heat & momentum

Jeff Hare NOAA/ETL heat & momentum

Mike Ohmart APL/U. Wash IR Imaging

Jesse Davis APL/U. Wash IR Imaging

Wade McGillis WHOI Closed & open path CO2 flux

John Dacey WHOI Closed & open path CO2 flux

Jeff Evan Hamilton College Heat & momentum

Heather Wright Bigelow CH3Br/production

Brian Yocis Bigelow CH3Br/production

Wayne Grosko Bigelow CH3Br/production

Ryszard Tokarczyk RSMAS/ U. Miami CH3Br/degradation

Kevin Sullivan RSMAS/ U. Miami CH3Br/degradation

Robert Moore Dalhousie, Canada Discrete halocarbons

Phil Morneau Dalhousie, Canada Discrete halocarbons

LEG 3

Craig Neill NOAA/AOML Underway CO2

Daniel King NOAA/CMDL Halocarbons

Shari Yvon-Lewis NOAA/AOML Halocarbons

Ajoy Kumar RSMAS/ U. Miami interferometry

Ed Kearns RSMAS/ U. Miami interferometry

Jim Smith NOAA/CMDL closed path dry CO2 flux

Michael Hahn NOAA/CMDL closed path dry CO2 flux

Anatoli Arjannikov Nova U. surface turbulence

Heather Wright Bigelow CH3Br/production

Brian Yocis Bigelow CH3Br/production

Wayne Grosko Bigelow CH3Br/production

Ryszard Torarczyk RSMAS/ U. Miami CH3Br/degradation

Bruce Garrett Amanda, Ohio Teacher at sea

Addresses:

Bermuda Bio. : 17 Biological Lane Ferry Reach Bermuda

Bigelow: Bigelow Laboratory for Ocean Science/University of New England 180 McKown Point W. Boothbay Harbor, ME 04575-475

BNL: Brookhaven National Laboratory, Upton NY 11973

CIMAS: 4600 Rickenbacker Causeway, Miami, FL 33149

Columbia U./LDEO: Route 9W, Palisades NY 10964

NOAA/AOML: 4301 Rickenbacker Causeway, Miami, FL 33149

NOAA/CMDL: 325 Broadway Boulder CO 80303

NOAA/PMEL : OCRD, 7600 Sand Point Way N.E. Seattle WA 98115

Nova U. : Oceanographic Center, 8000 North Ocean Drive, Dania FL 33004

RSMAS/U. Miami: 4600 Rickenbacker Causeway, Miami, FL 33149

APL/U. Wash.: Applied physics laboratory. 1013 NE 40th Street, Seattle, WA 98105

WHOI: Applied physics & Engineering 98 Water Street Woods Hole MA 02543

NRL: Naval Research Laboratory Stennis Space Center, MS 39529

IV. OBSERVERS: None

V. CLEARANCE COUNTRIES: Portugal

VI. OPERATIONS:

a. Operational summary:

 86 Conductivity-Temperature-Depth (CTD) stations during leg 2.

 102 Expendable Bathythermograph (XBT) deployments.

 Continuous along-track ADCP current profiles.

 Continuous along track thermosalinograph records.

 Continuous along track measurements of partial pressure of CO2 (pCO2), halocarbons, total dissolved inorganic carbon (DIC), and chlorophyll.

 Four times a day samples for Oxygen, DIC, and chlorophyll from underway sampling line.

b. Conductivity-Temperature-Depth-Oxygen Stations: 86 stations were occupied, see below for details. A Sea-Bird model 9/11+ CTD was used on the cruise. A 24 bottle Sea-Bird Rosette equipped with nineteen 10-l bottles was used to collect water samples.

c. Niskin Bottle water samples: between six and nineteen bottles were tripped at each CTD station. The chemical and biological analyses on the water are outlined in section VII.

d. Continuous shipboard Acoustic Doppler Current Profiler measurements: hull mounted ADCP data were collected continuously along the track. A hull-mounted RD Instruments 150 Khz narrow-band acoustic Doppler current profiler operated continuously. Velocity data, averaged in earth coordinates using gyrocompass heading, were logged in five-minute (approximately 300 pings) ensembles using RDI Data Acquisition Software version 2.48. Vertical bin size was 8 meters. Range varied from 200 to 400 meters, depending primarily on sea-state. A user exit program (UE4 provided by Eric Firing, U. Hawaii) was used to interface navigation and heading systems. Position was logged at the beginning and end of each ensemble from a Trimble Centurion P-code GPS receiver (estimated position accuracy of 5-10 meters). Mean gyrocompass corrections for each ensemble were recorded from an Ashtech 3DF GPS attitude determination system; 3DF array orientation was calibrated using P-code GPA and ADCP bottom track comparison. These data are used in post-processing to calculate mean ship velocity to reference ensemble means and to compensate for dynamic gyrocompass errors. Estimated errors for an ensemble are 1-2 cm/s for relative velocity and 3-4 cm/s for ship speed errors due to position inaccuracy; errors induced by heading inaccuracies are reduced to less than 1 cm/s using GPS heading data. This total error of 4-6 cm/s over a five minute ensemble is further reduced by averaging during post-processing; fifteen minute averages commonly used represent an average over five kilometers for typical cruising speed, and should be accurate to 1-3 cm/s.

e. Continuous thermosalinograph measurements: continuous TSG measurements were taken along the track-lines

f. Underway measurements: continuous underway pCO2, DIC, halocarbon, and chlorophyll measurements were taken along the track-lines. A description of methods and procedures can be found in section VII.

g. Co-variance measurements: The direct covariance flux system (DCFS) combined the motion corrected velocities from a sonic anemometer with the sonic virtual temperature, a LI-COR CO2/H2O analyzer, an Ophir infrared hygrometer, and an Oak Ridge CO2/H2O sensor to compute estimates of the momentum, buoyancy, moisture, and CO2 fluxes during leg 2. The system was mounted at a height of approximately 18 meters above the sea surface on the forward jackstaff.

h. Bow bridle: Sensors were installed on the bow of the vessel at 1.7-m depth, using a specially designed bow frame. An initial problem with scratching noises produced by the side cables was largely eliminated for the end of leg 2. Three variants of the bow sensor system were tested during Leg 1: bow sensors from TOGA COARE, Chelsea Aquapack CTD with Alpha-Fluorometer, and Mark 317 CTD Idronaut. Most of the observations during leg 2 were performed with the Mark 317 CTD. The frame of the bridle broke during leg 3 and sampling had to be discontinued.

i. Free-Rising Profiler (FRP): The profiler connected with the `shuttle' (winged frame) was deployed from stern of the R/V Ronald H. Brown using a metal frame as launch pad. After leaving the metal frame, the profiler fell into the water and slid outside the ship's wake. At a distance of about 15 to 35 meters from ship's wake it reaches it maximum depth. At the desired depth (20-25 m) the pressure release mechanism released FRP from the `shuttle' and the profiler turned to a vertical orientation to measure temperature, conductivity and turbulence in the upper 25 m.

VII. PROJECT SUMMARY:

## Leg 1 overview by Jim Butler

Leg 1 of GAS EX-98 was a 14-day transit from Miami to Lisbon. Science conducted during this leg focused upon (1) mapping saturation anomalies for CO2 and over 20 halocarbons across the North Atlantic Ocean and (2) testing instruments and procedures for use during Leg 2. Halocarbon saturation anomalies are to be compared with those obtained during Leg 3, after two months warming of the gyre and central ocean waters, to obtain an estimate of the integrated air-sea exchange coefficient. During most of this leg, the ship maintained speeds of 13 kts. or greater over the ground with an eastward flowing current of about 1 kts. and strong following winds. The relative wind speed was often aft of the beam during this leg.

Equilibrium mixing ratios of gases dissolved in the surface waters were obtained by use of two Weiss-design equilibrators, one of which was dedicated to analyses of CO2 by the non-dispersive infrared technique, the other dedicated to halocarbon measurements by two automated GCMS systems. The first few days of measurements were compromised to some extent by leaks in the equilibrator systems and by contamination from the ship. Questions about the integrity of some of the water measurements ultimately necessitated moving the halocarbon equilibrator from the main lab to an outside bulkhead aft of the lab. Realized or not, the potential for contamination by CBrClF2, CHClF2, and CH3Br, among other gases, was higher inside the lab than outside.

All air measurements, taken from Dekabon lines extending to the bow were compromised to some extent by the following relative winds, which tended to blow stack gases (and leaky refrigerants?) from the ship toward the inlets. These conditions persisted during the middle of the leg, during which CO2 measurements were temporarily halted. Atmospheric concentrations of many gases, however, were not influenced significantly by relative wind direction, thus allowing reliable measurements of air concentrations and saturation anomalies.

Slow-down time was allocated toward need and readiness of the various experiments needing dead time or slower speeds, and by the appropriateness of sea-state conditions for the various experiments. Following an initial test of the CTD on the first day, after which a number of scientists returned ashore, about 70% of the slow-down time (dead-stop equivalent) was allocated to surface water microstructure measurements, namely installing and re-installing the bow bridle, testing the free rising profiler, and conducting experiments with catamaran-suspended temperature sensors. The remaining 30% was split evenly between requirements for testing the gradient boom and collecting biological samples (plankton tows and bucket samples).

Considerable effort was put into trouble-shooting the infrared and visible imagers maintained on the bow tower. By the time Lisbon was reached, these systems were working properly.

Overall, most of the work conducted on this leg was successful, with many of the bugs and quirks of initial operation of instruments and sampling systems at sea worked out. This allowed many of the investigators to begin sampling almost immediately during Leg 2, thus allowing the simultaneous measurement of physical and chemical properties in the air and water with minimal interruption.

Notes on the ship during leg 1:

1. The crew has been fantastic during this entire leg. Given the pressure they were working under from Brooklyn to Miami and finally getting us going at sea, they were always there for scientists making and changing requests. All of the scientists were impressed with the sense of cooperation, helpful spirit, and competence of the crew. Also the Captain and officers were accommodating for all of our requests, no mater how often we had to change plans. The ship itself was an excellent platform with almost all of our needs being met easily. A few items recommended for improvement are included in this list.

2. The ship's compressed air needs a greater delivery at higher pressure. 40 psi isn't enough to do much of anything. The line with 100 psi, strung for those in the main lab was apparently attached to a small reservoir, as we experienced some problems when instruments drew air simultaneously.

3. Raw power (in fact all power) in main lab (and throughout ship) seems sufficient for now. Well see how this plays during Leg 2 with a full complement of scientists aboard and running their instruments full time. (Note: Power was fine during leg 2)

4. Seawater system flow seems adequate for two Weiss-type equilibrators and is apparently well insulated. Warming of water through the ship is around 0.3 C at a water temperature of about 17 C. A higher flow (>100 Liters per minute) would decrease warming substantially and would be desired.

5. Drains in the main lab and the hydrolab are extremely slow; essentially inadequate. Floor drain in main lab smells like sewer. Once plugged with duct tape, no problem, but no drain either.

## Leg 2 overview by Rik Wanninkhof

Leg 2 of Gas Ex–98 was a process study in which a water parcel was tagged with the gaseous deliberate tracers sulfur hexafluoride and the isotope He-3. The tracers were both used as a water mass marker and to determine the gas transfer velocity from the change in concentrations of the gases with time.

Leg 2 got underway on Monday May 25 after a chaotic in-port in Lisbon. Guided by altimetry imagery kindly provided by Gustavo Goni of AOML, we steamed to our projected study site near 46 N, 21.5 W. After a day of surveying a water mass with low currents, stable salinities, surface XCO2 values hovering near 285 ppm (yielding us a 85 ppm sink), and 15-20 m mixed layer depths was selected as study site. Surface nutrients were near zero and high chlorophyll values suggested that the region had passed the height of the bloom.

The SF6/He-3 tracer mixture was injected on May 29 in a 3-mile streak along with the deployment of the two pCO2 CARIOCA buoys and a GPS drifter. Following the injection, a low speed survey was performed. During the survey the bow harness with T, S, and O2 sensors for near surface measurements was deployed. The harness was used whenever conditions (low speeds) permitted.

The halocarbon groups found several anomalies in biogenic trace gases. The most noteworthy was the large supersaturation of methyl bromide throughout the area. En route to the study site patches with saturation anomalies of greater than 100% were encountered.

After a week of moderate winds, the first storm has hit the study area during the second week of the process study. From a scientific perspective it was the "perfect storm", greatly changing the conditions in water and air. The persistence of the winds facilitated comparison of bulk versus instantaneous flux measurements under stormy conditions. The near constant winds at 12-14 m/s made it possible to obtain extensive measurements of friction velocity and drag coefficients under these conditions. Water mixed layer depth increased from less than 20 m to over 30 m. For the first time during the study appreciable amounts of nitrate and silicate were observed at the surface. The entrainment also increased total carbon and decreased the air-water pCO2 gradient from -90 to -70 uatm. Surface water halocarbon saturation anomalies, which were for the most part high and well developed, decreased considerably with entrainment of air from above and water from below. The discrete halocarbon measurements also showed that the halogenated by- products of respiration, previously trapped just below the mixed layer, found their way to the surface water.

The buoy trajectories and tracer patch completed a complete counterclockwise circle of about 30 km radius during the first ten days suggesting a warm core eddy with a cold top (SST was 0.2-0.3 lower here compared to surrounding waters). The drogued buoys roughly followed the patch movement. Deliberate tracer (SF6) concentrations decreased dramatically by downward mixing, gas exchange and dispersion. Rather than a well-defined Gaussian patch, large areas of homogeneous SF6 levels were observed that decreased nearly a factor of two every day.

The last week on site offered opportunities to study certain processes in detail and apply some innovations to our measurements techniques. Air CO2 gradient measurements were perfected by measuring CO2 concentrations continuously at a fixed reference level while the gradients were determined making it possible to account for the influence of larger scale eddies. The CO2 co-variance measurements performed by the WHOI group showed a very strong correlation with wind speed (friction velocity) and good agreement with the “Wanninkhof” wind speed-gas exchange relationship. This is the first time that co-variance measurements agree well with the water side isotopic results.

An intensive 18-hour Lagrangian study was performed during the last week to study diel variations in the carbon and nutrient cycles in the patch. During the study there was a balance between potential pCO2 increases to due to day-time heating and pCO2 decreases due to increased photosynthesis. The trace levels of nutrients disappeared within an hour after the sun broke out around mid-day

Methyl iodide and isoprene showed huge supersaturation anomalies (>2000 %) in surface water throughout the experiment with decreasing trends during stormy weather, likely caused by loss due to air-sea gas exchange and downward mixing. Robust production, consumption and flux estimates for methyl bromide were obtained throughout the study.

At the end of the study, the tracer patch had an estimated 20-km diameter and SF6 tracer concentrations had dropped 3 orders of magnitude. However, concentrations were still easily measurable at fifty times higher than background. pCO2 levels increased rapidly en route to the Azores, from undersaturations of –80 uatm at the study site at 46 N to supersaturations of +10 uatm at 39 N.

NOAA ship BROWN completed the process study phase of GAS EX-98 and headed for the Azores on June 26. Preliminary investigations of the rich dataset indicate an extremely successful cruise that has yielded several important breakthroughs in our understanding of air-sea fluxes of CO2 and the biogeochemical cycles of a variety of halogenated compounds. While much of the interpretation and analyses is just beginning some of the highlights of the process study are summarized below:

 The choice process study sites can be much enhanced by use of remote sensing. For our study, altimeter data proved very valuable. As corollary, these sensors will prove very useful to determine biogeochemical mesoscale variability in the surface ocean.

 Tagging water parcels with deliberate tracers and seeding them with drifters appears to be a near essential prerequisite to perform a Lagrangian process study. The tracers can clearly delineate a homogeneous water parcel for the first two weeks or so. At later stages when the patch includes larger chemical heterogeneity, addition (natural) tracers such as salinity and pCO2 are necessary.

 During this study most of the carbon and nutrient input into the mixed layer could be directly related to storm events. It appears that these episodic events to large extent control the evolution of the spring blooms and (pCO2) in the area.

 Direct measurement of friction velocity, u\* and bulk estimates agreed very well suggesting that robust large scale extrapolation of CO2 fluxes is feasible using u\*

 Under the optimal conditions of this study with large CO2 fluxes and small latent heat fluxes the isotopic and micrometeorological flux measurements can be reconciled.

 The ocean plays a non-negligible role in the fluxes of a variety of halogenated tracer species including methyl bromide, isoprene, and methyl iodide.

## Leg 3 overview by Shari Yvon-Lewis

The ship left Ponta Delgada, Azores with 8 groups continuing work that had begun on Legs 1 and 2. These measurements included underway pCO2 with DIC, DOC, and 13C, underway halocarbon saturation anomalies, methyl bromide production, methyl bromide degradation, interferometry, direct flux measurements, and fine thermohaline structure. Bucket samples were collected daily for the methyl bromide degradation and production studies. The underway systems were all performing well as the ship left the Azores.

The bow bridle frame was not strong enough to withstand the constant pounding associated with pitching in the large long-period swell we encountered the first couple of days out of the Azores. On 30 June, the frame snapped at the welds along the backbone. The sensors were undamaged and the both pieces of the frame were successfully recovered thanks to the hard work of Pat Quinanola and the rest of the deck department.

Later in the leg, the direct flux measurement systems, eddy accumulation and eddy correlation, came online and were collecting data for the rest of the leg. On 6 July, the ship stopped for 7 hours pointing bow into the wind to allow for an intensive sampling period for the direct flux measurements. During this time fluxes were measured by the eddy accumulation system.

Overall, the third leg of this ambitious cruise was a success.

OVERVIEW OF INDIVIDUAL PROJECTS.

Sulfur hexafluoride analyses, [SF6] leg 2 only (Rik Wanninkhof PI, AOML; Kitack Lee; Craig Neill; and David Ho): SF6 samples were drawn from most of the 10-bottle CTD casts at every station to map the horizontal and vertical extent of the tracer patch. The patch exhibited homogeneous vertical concentrations down to the depth of the mixed layer. The horizontal extent of the patch was determined with an underway SF6 system drawing water from the bow-intake at two minute intervals using a novel high efficiency equilibrator/stripper. The horizontal extent of the patch was about 15 km in diameter by the end of the experiment. The results from underway system were cross checked using discrete samples every couple of hours from the same bow intake.

The concentrations in the surface water were about 1000 ppt (parts per trillion by volume) at the start of the experiment and decreased by about a factor of 2 per day till the third week at which point the concentrations decreased much slower. We hypothesize that this was caused by the patch reaching the size of the mesoscale eddy at which point lateral advection diminishes. Final concentrations at the end of the process study were about 1 ppt, or about 50 times background level.

Helium-3 Samples, [3He] (Rik Wanninkhof PI, AOML; David Ho; and Craig Neill): 97 3He samples (with volume about 40 cc) were drawn from selected CTD casts. The 3He will be used in conjunction with SF6 to calculate the gas-transfer velocity and to determine the extent of horizontal and vertical mixing. The samples were stored in copper tubes closed tightly at both ends by means of special stainless steel pinch-off clamps. In the laboratory at Columbia University's Lamont-Doherty Earth Observatory, gases will be extracted from the copper tubes using a vacuum extraction system and the helium isotopes will be measured on a mass spectrometer. Neon will be separated from helium before mass spectrometric measurement using a cryogenic cold trap. Precision of the 3He measurement is approximately ± 2 %. Sampling was seized after about three weeks at which point we believe that the He-3 samples were close to background.

CTD OPERATIONS, leg 2 only (Rik Wanninkhof, AOML, PI; Geoffrey Samuels, Dana Greeley, and Jon Shanahoff): CTD casts were conducted using a Sea-Bird SBE 911plus CTD unit equipped with a rosette containing nineteen 10-l Niskin bottles. The CTD unit was equipped with dual temperature and conductivity sensors (there was no oxygen sensor). Post-cast processing using software provided by Sea-Bird produced one decibar pressure averages of in-situ temperature, conductivity, salinity, potential density and potential temperature for both sets of sensors. No bottle salinities were taken. The rosette worked well with an occasional non-trip because of sticky release mechanisms. The problem was remedied by spraying the mechanism with fresh water. The mistrips occurred almost exclusively during the first four days of CTD casts. After the fourth CTD cast, it was discovered that the water flow connections to the Sea-Bird sensor pumps were backwards. This problem was corrected, but the temperature and conductivity data for the first four casts should be considered suspect. Relatively large displacements of the thermocline (two to five meters) between downcasts and upcasts were observed. Investigations have shown no malfunction of the pressure sensor or of the temperature and conductivity sensors so the displacements are probably a real phenomenon. A summary of casts is given below:

Date JD Casts Num Cum. Total

05/26 146 132 - 133 2 2

05/27 147 134 1 3

05/28 148 135 - 140 6 9

05/29 149 141 - 144 4 13

05/30 150 145 1 14

05/31 151 146 - 149 4 18

06/01 152 150 - 153 4 22

06/02 153 154 - 156 3 25

06/03 154 157 1 26

06/04 155 158 - 161 4 30

06/05 156 162 - 164 3 33

06/06 157 165 - 166 2 35

06/07 158 167 - 169 3 38

06/08 159 170 - 172 3 41

06/09 160 173 - 174 2 43

06/10 161 175 - 177 3 46

06/11 162 178 - 179 2 48

06/12 163 180 - 182 3 51

06/13 164 183 - 188 6 57

06/14 165 189 1 58

06/15 166 190 - 193 4 62

06/16 167 194 - 197 4 66

06/17 168 198 - 199 2 68

06/18 169 200 - 202 3 71

06/19 170 203 1 72

06/20 171 204 - 206 3 75

06/21 172 207 - 212 6 81

06/22 173 213-214 2 83

06/23 174 215-216 3 86

Fine Thermohaline Structure and Gas Exchange in Near-Surface Layer of the Ocean (Alexander Soloviev, Nova Southeastern University's Oceanographic Center and Peter Schluessel, Meteorologisches Institut, Universitaet Muenchen, PI’s; Anatoli Arjannikov, Terry Thompson).

The near-surface microstructure measurements were performed under leadership of Arjannikov, Soloviev, and Thompson. Schluessel will retrieve from satellite data the boundary-layer parameters and surface fluxes for a time period covering the Gas-Exchange Experiment at the University of Muenchen.

Bow measurements:

The sensors were installed on the bow of the vessel at a 1.7-m depth, using a specially designed bow frame. An initial problem with scratching noises produced by the side cables were largely eliminated (it, however, might still exist at extreme conditions of full ship speed and rough seas).

Three variants of the bow sensor system were tested during Leg 1: bow sensors from TOGA COARE, Chelsea Aquapack CTD with Alpha-Fluorometer, and Mark 317 CTD Idronaut. Most of observations during Leg 2 were performed with the Mark 317 CTD. The main technical characteristics of Mark 317 CTD with redundant temperature and conductivity sensors are given in Table 1.

TABLE 1. Main technical characteristics of Mark 317 CTD Idronaut

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Range | Accuracy | Resolution | Time Constant |
| Pressure | 0-10 dbar | 0.15% full scale | 0.03% | 50 ms |
| Temperature 1 | -3..+33 oC | 0.003 oC | 0.0005 oC | 50 ms |
| Conductivity 1 | 0.. 70 mS/cm | 0.003 mS/cm | 0.001 mS/cm | 50 ms |
| Temperature 2 | -3..+33 oC | 0.003 oC | 0.0005 oC | 50 ms |
| Conductivity 2 | 0.. 70 mS/cm | 0.003 mS/cm | 0.001 mS/cm | 50 ms |
| Oxygen | 0.. 500%sat | 1% sat | 0.1% sat | 0.9 s or 3 s |

The data acquisition rate is 10 samples per second. The data taken with Mark 317 in Leg 2 in binary format have the following volume: 30 May (25.8 MB), 31 May (22.8 MB), 1 Jun (87.6 MB), 2 Jun (32.6 MB), 3 Jun (88.5 MB), 4 Jun (45 MB), 5 Jun (83.1 MB), 6 Jun (106 MB), 7 Jun (58.3 MB), 11 Jun (81.3 MB), 12 Jun (108 MB), 13 Jun (205 MB), 14 Jun (80.6 MB), 15 Jun (135 MB), 16 Jun (155 MB), 17 Jun (34.8 MB), 18 Jun, 20 Jun, 21 Jun, 22 Jun, 23 Jun (volume of data after 18 June has not yet been estimated). At stations or at very low ship speeds, the bow data can be disturbed by the reciprocal water motions. Undisturbed data will be selected later, using the ship speed information. Preliminary analysis shows that the bow temperature data are useful to calculate the vertical temperature and salinity profiles, the temperature, salinity and density contour plots, and the turbulent mixing coefficient in the upper 3 m layer of the ocean.

Two external channels were reserved for additional fast-response dissolved oxygen (DO) sensors. In total, we had two DO sensors of membrane types (Idronaut and AMT) and a microhole DO sensor (UH/Sea-Bird). Our preliminary conclusion is that the microhole sensor is most suitable for the towing purposes. It, however, has a slow drift and therefore should be used with a slow response membrane-type DO sensor for calibration reference. The CTD DO data from upper bottle are also useful for periodical calibration of the fast response DO sensors. Preliminary analysis of the bow data suggests a close correlation between the fine thermohaline structure and DO features in near-surface layer of the ocean.

Free-Rising Profiler (FRP):

The measurements with FRP were made from the drifting ship. The profiler connected with the `shuttle' (winged frame) was deployed from stern of the R/V Ronald H. Brown with help of a metal frame. After leaving the metal frame the profiler falls into the water and slides outside the ship's wake a distance of about 15 to 35 meters from ship's wake as it sinks. At the desired depth (20-25 m) the pressure release mechanism released FRP from the `shuttle' and the profiler turned to a vertical orientation. The FRP then ascended to the surface with a vertical velocity of 2.5 m s-1. The data acquisition rate is 400 samples per second.

Main technical characteristics of FRP are given in Table 2.

TABLE 2. Main technical characteristics of free-rising profiler

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Range | Accuracy | Stability during one profiling | Resolution | Time Constant or Spatial Resolution |
| Pressure | 0-25 dbar | 0.1 m | 0.01 m |  | 0.01 m |
| Temperature | 14.. 34 oC | 0.1 oC | <0.01 oC | 0.005 oC | 35 ms |
| Fast Temp. | -2.. 35 oC | 0.1 oC | 0.01 oC | 0.005 oC | 3 ms |
| Conductivity | 1.. 6,2 S/m | 0.01 S/m | <0.001 S/m | 0.0008 S/m | ~1 cm |
| Fluct. Velocity | +/-0.25 m/s | 5% | 1 mm/s | 0.6 mm/s | ~1 cm |
| Acceleration | +/- 6 m/s2 | 5% |  |  |  |
| (own vibrations) |  |  |  |  |  |

The total number of casts performed on Leg 2 is 98. Of those, 65 casts can be used for the turbulence analysis. The data with FRP was taken on 3 Jun (4 casts), 5 Jun (12 casts), 6 Jun (12 casts), 13 Jun (12 casts), 16 Jun (10 casts), 19 Jun (9 casts), 21 Jun (23 casts), and 22 Jun (15). 4 Casts on 31 May were done for testing purposes only. Only 1 cast on 19 Jun can be used for turbulence analysis because of problems with pressure release mechanism. 1 Cast on 20 Jun was to test the pressure release mechanism. The obtained data demonstrate dependence of the dissipation rate of the turbulent kinetic energy and the mixing coefficient in near-surface layer on the wind/wave conditions and on the near-surface stratification.

Direct Covariance (Jim Edson, Woods Hole Oceanographic Institute (WHOI), Wade McGillis, WHOI, Chris Fairall, ETL, PI’s; Jeff Hare, NOAA/ETL): The direct covariance flux system (DCFS) combines the motion corrected velocities from a sonic anemometer with the sonic virtual temperature, a LI-COR CO2/H2O analyzer, an Ophir infrared hygrometer, and an Oak Ridge CO2/H2O sensor to compute estimates of the momentum, buoyancy, moisture, and CO2 fluxes. The system is mounted at a height of approximately 18 meters above the sea surface on the forward jackstaff. The system also logs all the mean meteorological measurements required for the bulk aerodynamic method, including wind speed and direction, air temperature, sea temperature, relative humidity, solar and long-wave radiation, and pCO2 concentrations in the air and sea. The data set also includes measurements of the significant wave height using a bow mounted altimeter; and salinity, conductivity and dissolved oxygen using a YSI probe in the sea-water intake line. These systems have been run almost continuously during the cruise. Preliminary results indicate that the momentum flux estimates from the direct covariance and bulk methods are of very high quality. After removal of runs with relative wind directions greater than +/- 90 degrees and heading changes greater than 40 degrees, these estimates agree to within 20 % with a systematic offset of approximately 5%. Preliminary calculations of the transfer velocity from the CO2 flux measurements are encouraging.

Profile Flux Measurements (John Dacey, WHOI; Wade McGillis, WHOI PI’s; Jeff Evans, Hamilton College): The profile system measured vertical profiles of dimethyl sulfide (DMS), CO2 and water vapor. The DMS measurements were made using a micro-GC deployed on the front of the ship, while the CO2 measurements were made using two additional LI-COR sensors. The profile measurements were made by moving the sensor inlets at the end of tubes to various locations well above and/or well outboard of the ship's bow (~7m to port). Measurements extended to 4-5 m below the profiling boom, which is approximately 3-2 meters about the mean water surface. Additional measurements of the DMS concentration in the near surface water were made using a chemiluminescence detector. The DMS measurements show the expected large gradients.

The difficulty in measuring the small CO2 gradients has been offset somewhat through use of two sensors: one unit at a fixed height and other measuring the concentration at the moveable inlet. Referencing the mobile tube to the fixed unit has allowed the measurements of differences on the order of 5-200 ppb (CO2) and 0.001-0.8 ppt (H2O). As expected, water vapor profiles are most pronounced in low humidity (<80% RH) conditions, while CO2 profiles are most consistent at high humidity (80-95% RH) where the fluctuations due to the "Webb correction" are minimized. Preliminary calculations of the transfer velocity from these flux measurements are also encouraging.

IR Remote Sensing (Adrew Jessup and William Asher PI, Applied Physics Laboratory, UW; Jesse Davis, Mike Ohmart, Applied Physics Laboratory, UW): Infrared radiometry was used to obtain sea surface temperature measurements continuously. Four radiometers measured SST while three radiometers provided a sky temperature correction for the imperfect emissivity of water. A constantly towed thermistor provided the bulk temperature at one meter. Infrared imagery was used to determine the bulk-skin temperature difference. IR imagery is a powerful technique due to its ability to resolve thermal structure and turbulent processes involved in heat flux. Our use of imagery emphasizes the observation microscale breaking waves and their role in air-sea heat flux. Results: 200 GB of raw data that we have not yet reviewed. A real whitecap coverage was also measured continuously. We also tried to obtain an temperature-depth profile in the upper one meter. The platform was the 'Husky Cat,' a small catamaran equipped with an assembly of Sea Bird thermistors, at depths of 15 cm, 50 cm, and 1 m. Conditions made routine deployment of this unit impractical, but on a calm day during Leg 1, we measured a thermocline of 1 C in the upper meter alone.

NUTRIENTS [NO3-, NO2- , NH4+, PO43- and H4SiO4](Jia-Zhong Zhang, PI, AOML): During the Gas-Exchange 98 cruise, over 1100 samples from 63 CTD casts were analyzed for nitrate (NO3), nitrite (NO2), ammonium (NH4), phosphate (PO4) and silicic acid (H4SiO4). Samples were collected from the 10-l Niskin bottles in acid washed 25-ml high density polyethylene bottles which were rinsed at least 3 times with sample and analyzed within 1 hour of sample collection. Nutrient concentrations were determined using a shipboard AlpKem Flow Solution Auto-Analyzer and modified EPA’s methods (Zhang et al, 1997).

Low nutrient seawater used for wash and preparation of standards was collected from the surface of the Sargasso Sea after the spring bloom during first leg of this cruise. Standardizations were performed prior to each sample run with standard solutions prepared from pre-weighed high-purity grade standard chemicals.

Nitrite (NO2 ) was determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced was measured at 540 nm and was proportional to the nitrite concentration. A liquid waveguide capillary flowcell in conjunction with a modified 510 monochromator was employed for high sensitivity nitrite detection. The detection limits for nitrite were 0.5 nM. The average relative standard deviation of nitrate analysis for these samples was 0.2%.

Samples for nitrate (NO3) analysis were passed through a home-made copperized cadmium column, which reduced nitrate to nitrite and the resulting nitrite concentration was then determined as described above. The reduction efficiency of column was monitored during analysis and replacement was made in due cause to ensure 100% efficiency. The detection limits for nitrate were 5 nM. The average relative standard deviation of nitrate analysis for these sample was 0.4%.

Ammonium (NH4 ) was determined by indophenol method. Ammonium ion in seawater samples was reacted with phenol and NaDTT in the present of nitroferricyanide as a catalyst in basic solutions to form indophenol blue. Citrate and EDTA were used as complexing reagents to prevent the precipitation of seawater at the high pH. reaction temperature was controlled at 60 oC by a heater. The indophenol blue was measured at 640 nm. The detection limit for ammonium was 10 nM. The average relative standard deviation of ammonium analysis for these sample was 1.6%.

Silicic acid in the sample was analyzed by reacting with molybdate in a acidic solution to form B-molybdosilicic acid. The B-molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 660 nm, was linearly proportional to the concentration of silicic acid in the sample, with a detection limit of 0.01 uM. The average relative standard deviation of silicate analysis for replicate samples was 0.2%.

Phosphate in the samples was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex. This complex was subsequently reduced with ascorbic acid to form a blue complex and the absorbance was measured at 710 nm. The detection limit was 5 nM and the average

relative standard deviation of phosphate analysis for replicate samples was 0.9%.

 Reference

Zhang et al, 1997, Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow analysis. Methods for analysis of chemical substances in estuarine and coastal waters samples, EPA.

Dissolved oxygen (Rik Wanninkhof, PI, AOML; George Berberian): Approximately 920 discrete dissolved oxygen samples were drawn and analyzed from designated depths on the 2nd Leg of the GAS EX-98 Cruise in order to characterize the distribution of dissolved oxygen. Samples were properly drawn and analyzed from approximately 58 CTDs, utilizing the modified Winkler titration methodology.

Most samples were collected from the tracer patch, and some samples were also gathered and analyzed from outside the patch. A very cursory examination of a few of the profiles indicated that the surface waters outside the patch are slightly higher (10-12 umol/l) than the surface waters inside the patch. Also, oxygen values were slightly higher in the waters of 160 to 350 meters, (10-15 umol/l) outside the patch. These kinds of differences are usually attributed to phytoplankton growth, which can cause oxygen saturation in the upper layers of the ocean. However, a thorough examination of the distribution of dissolved oxygen will give us a better understanding of the mechanism and effects of the area studied. Complete set of the distribution of dissolved oxygen, depth profiles and duplicated sample results will be available after examining the data in the NOAA/AOML office.

TOTAL DISSOLVED INORGANIC CO2 [DIC] (Richard Feely, PI, PMEL; Marilyn Roberts; Kitack Lee; and Bob Castle): In order to constrain the gas flux determination, DIC (Dissolved Inorganic Carbon) was measured. Two systems were operated during the cruise: an underway system took samples every 30 minutes during all legs, and two units for discrete samples were used for Leg 2. Both the underway and discrete DIC analyses utilized coulometers coupled with SOMMA (Single Operator Multi-parameter Metabolic Analyzer) inlet systems. Approximately 750 DIC samples were taken from CTD casts on Leg 2. These samples were typically taken throughout the water column to 450m with emphasis on the mixed layer, but occasionally the profiles extended to as deep as 1000m to aid in integration of the data. Subsurface waters showed DIC increasing below the mixed layer to about 2100 umol/kg. In addition, more than 100 discrete samples were drawn and analyzed from the underway water lines to assist in comparison of the underway DIC analyses. On Leg 1 surface values were 2040 umol/kg in the Western Atlantic region and values decreased to 1960 umol/kg as the ship progressed eastward. Surface waters during the process study on Leg 2 changed over a narrow range with highest values encountered immediately after a storm event. The accuracy of the coulometers was checked twice a day using reference water supplied by Dr. Dickson of Scripps (Batch 42). The discrete DIC systems yielded the following accuracy and precision: "PMEL-1" gave an average value of 1981.1+/- 1.5 umol/kg (n=26) while "PMEL-2" gave a value of 1983.6 +/-1.7 (n=40). The underway DIC system (AOML 1) gave an average value of 1981.8+/-2.4 umol/kg (n=40) The manometric value determined at Scripps was 1985.1 +/-1.4 umol/kg. A secondary reference material was analyzed frequently throughout the course of the cruise, and those analyses had a precision of within 2.8 umol/kg (n=60) on both the discrete and underway systems.

PARTIAL PRESSURE OF CO2 [pCO2] (Rik Wanninkhof, PI, AOML; Dana Greeley): Approximately 700 discrete pCO2 taken and analyzed on leg 2 using a analysis system with an infrared (IR) detector. pCO2 was measured in the headspace of a 500 mL volumetric flask at constant temperature of 20 C. Overall precision was 1 uatm over the observed range of 200 to 700 uatm. Discrete pCO2 values showed a similar pattern as DIC suggesting near constant alkalinities in the survey area. Sixty replicates were drawn with a precision of 0.28%

UNDERWAY pCO2 measurements (Rik Wanninkhof, PI; Bob Castle): Quasi-continuous samples were taken of air and water pCO2 using an automated system with sampling lines connected to the bow air intake and the continuous bow water supply. During leg 1 the CO2 was slightly undersaturated compared to the atmosphere. A small leak in the system caused the values to scatter. The leak was fixed at the beginning of leg 2 and the values will be corrected for. At the process site the values reached an undersaturation of –90 uatm, the largest deficit we have encountered to date over the ocean. The system operated with minimal operator intervention

CARBON-13 SAMPLING [DIC-13] (Paul Quay, PI, U. Washington; Marilyn Roberts; Craig Neill): The primary goal of the sampling plan for the carbon isotopic ratio of DIC (DIC-13) was to determine the distribution of the 13C/12C in the North Atlantic and to study the evolution of C-13 over time in the tracer patch. DIC-13 samples were collected every 3 degree spacing on the transit legs. Full depth profiles were taken at 5 stations during the process study. The total samples collected was 200. The samples have been fixed, sealed and prepared for transit. The samples will be stored in a temperature controlled environment on the BROWN until they can be shipped back to Seattle for analysis.

Dissolved Organic Carbon and Nitrogen (Dennis Hansell PI, Bermuda Biological Station for Research; Amy Ritchie, Bermuda Biological Station for Research).

Water column profiles of DOC were determined using the high temperature catalytic oxidation method. The DOC reservoir is an important factor in determining the overall mass carbon balance. DOC and DON samples were obtained from CTD stations occupied on the second leg. An average of 15 depths were collected from the tracer patch during each day, in addition to 5-10 depths collected within each survey site. Initial DOC values appear to be relatively high within the mixed layer, although due to inconsistent concentration resolution, all samples have been archived for further analysis in the lab.

Organohalogen measurements, [CFC's] (Dr. Robert Moore PI, Dalhousie University and Phil Morneau): The objectives of this study are to determine whether the ocean is a source to the atmosphere of a number of volatile organochlorine compounds and to determine whether their distribution in the water column is indicative of production by biological processes.

The compounds, which included methyl chloride, bromide and iodide, dichloromethane, chloroform, tri- and tetra-chloroethylene, were measured in water samples collected from depths of 0 to 450m. Analyses were done by purge-and-trap and GC-MS techniques and calibration was done with gravimetric gas standards. The same compounds were measured in 8 incubation experiments, designed primarily to quantify methyl bromide production.

Methyl iodide showed variable but typically high concentrations in surface and near-surface waters, and methyl bromide was supersaturated. Trichloroethylene was found to be supersaturated, with concentrations increasing with depth in the water column to at least 450m; its profiles are not similar to those normally associated with biogenic gases, such as methyl bromide, methyl chloride and isoprene.

After 23 days of measurements, high levels of noise in the mass-selective detector precluded further analyses.

HALOCARBON THERMAL DISEQUILIBRIUM FLUX MEASUREMENTS (James Butler, CMDL, PI, Dan King, CMDL/CIRES,): The saturation states of a number of conservative and reactive halocarbons including CH3Br were measured continuously during Legs 1, 2, and 3. Water from the continuous underway seawater system flowed through an equilibrator, where headspace samples were collected periodically for analysis by a gas chromatograph/mass spectrometer system (GC/MS). Air was also continuously pumped from an inlet located on the jackstaff, and samples were collected alternately with the equilibrator headspace samples for analysis by the GC/MS system. The difference between the water and air values is a measure of the saturation of a given trace gas. There were some difficulties with the equilibrator during the early part of Leg 1, but the problems were solved by the last quarter of that Leg.

During the course of this cruise, the waters being sampled warmed due to radiative heating. The warming was approximately +1.5 ºC during leg 2 in the intensive study area, and the warming of an area near the Azores that was sampled during Leg 1 and re-sampled at the end of Leg 2 was +2.5ºC. This warming affected the solubility of the halocarbons. The change in solubility is faster than escape to or invasion from the atmosphere. The continuous measurement of the saturation state and the degree of warming that occurred will allow us to calculate the time-averaged air-sea transfer velocities for the conservative trace gases. For the reactive halocarbons, where the temperature and salinity dependent degradation rates are known, similar calculations that include this additional loss in the surface water will be made.

METHYL BROMIDE SATURATION ANOMALIES (Shari Yvon-Lewis, AOML, and James H. Butler, CMDL, PI’s, Dan King, CMDL/CIRES): Atmospheric CH3Br, which is of both natural and anthropogenic origin, has been identified as a Class I ozone-depleting substance in the amended and adjusted Montreal Protocol on Substances that Deplete Stratospheric Ozone. The role of the ocean in regulating the atmospheric burden of this gas is still somewhat uncertain. Saturation anomalies for methyl bromide (CH3Br) were measured with the technique described above. The results from these measurements, when combined with the CH3Br production CH3Br degradation, and organohalogen depth profile measurements made on this cruise, are twofold. First, the surface ocean budget for this class I ozone depleting trace gas is now well defined for the study area at this time of year. Second, by closing the budget, we can apply calculations similar to those mentioned in the thermal disequilibrium section to calculate air-sea transfer velocities for CH3Br.

Methyl bromide production (P. Matrai, PI, Bigelow Laboratory for Ocean Science; B. Yocis, W. Groszko, H. A. Wright): Incubations of surface and deep water were carried over 48h periods semi-continuously during all 3 Legs; methyl bromide and chlorophyll a levels were followed on board. Discrete samples for methyl bromide were analyzed on board with a GC-ECD system; four time points were determined for each incubation and whole water as well as filtered (1 um and 0.2 um) water were monitored in parallel. During each incubation, samples have also been collected for phytoplankton identification, bacterial enumeration, and particulate organic carbon. Surface water was obtained from the bow intake at 5 m depth as well as from CTD casts and as bucket samples; comparisons from all 3 sources yielded no significant differences. Deep samples were also collected during Leg 2 at various depths, determined according to either physical, chemical, or biological characteristics of the water column. During Leg 1, 30 incubations were performed; emphasis was on spatial coverage as well as on sampling, experimental, and analytical replication. Analytical difficulties dramatically slowed our progress during the first half of Leg 2 but were solved, allowing 50 incubations to be done. We expect to do ca. 20 incubations during Leg 3, emphasizing spatial coverage as was done during Leg 1. In addition, during Leg 2, vertical profile samples were collected for chlorophyll and particulate organic carbon. Preliminary results show a slight or no net production of methyl bromide in these seawater incubations while net disappearance of methyl bromide was less common; the data need to be further analyzed back in the laboratory before final conclusions can be drawn.

METHYL BROMIDE DEGRADATION (Eric Saltzman, RSMAS/U. of Miami, PI, Ryszard Tokarczyk, Kevin Sullivan): The rates of degradation of 13-C labeled methyl bromide were measured in the surface water of Atlantic Ocean during the legs 1, 2 and 3. Typically, 2 samples were collected each day and spiked with 13-C methyl bromide to the concentration of about 500 pM and incubated at the same temperature as they were collected. One of the samples was usually filtered prior to spiking through 0.2 micron Anatop filter, second was spiked without any pretreatment. During the leg 1 and 3 water was collected with the bucket directly from the surface. During leg 2 samples were collected from Niskin bottles, typically from 2 depth – about 5 and 20m. A few samples were collected in the deeper layer between 200-500m. An influence of the diurnal cycle at the degradation abilities of water collected at the same sampling site was examined twice during the leg 2.

27 incubation were performed during leg 1. Degradation rates ranged from 8 % per day for open Atlantic waters (37 46 N, 50 33 W, temp 20 C, sal. 36.4) to 66% per day for warm waters of Gulf Stream current (27 C, 36.3 salinity), with the majority of samples falling into the range of about 15-20% per day. The degradation rates observed in filtered samples were usually lower then those observed in untreated ones.

75 incubations were performed during leg 2. The temperature and salinity of surface water remain nearly constant (temperature vary from 15-16 C, salinity from 35.7-35.9). The observed degradation rates were lower then those observed during leg 1, and varied from 6% to 17% per day, with 10-12% as average. The differences between filtered and unfiltered samples were negligible. The results of the diurnal cycle study exhibit that degradation rates were significantly higher in the samples collected late at the day in comparison to samples collected early in the morning.

13 incubations were performed during leg 3. The degradation rates varied from about 10% for open ocean waters to 27% per day for warmer (25 C, 36.4 salinity) waters of west Atlantic.

HALOCARBON GRADIENTS (James Butler, CMDL, PI, Shari Yvon-Lewis, AOML, and Dan King, CMDL/CIRES): Halocarbon vertical profiles were measured with a gas chromatograph/mass spectrometer (GC/MS) system. The sample collection system consisted of a set of flasks that were flushed with air, each from an inlet at a different height above the sea surface. The flasks were closed simultaneously and analyzed sequentially with the GC/MS. The system was completely automated. From 6 to 8 profiles were collected and analyzed per day during Leg 2. Occasional bad weather necessitated removing the lower inlets and pulling in the sampling boom. Therefore, there were some days when gradient measurements were not possible. Post cruise data analysis will determine which of the measured gases are most suitable for calculating gas transfer velocities.

DIRECT FLUX MEASUREMENTS (Pieter Tans, CMDL, PI, Jim Smith, Atmospheric Observing Systems, Michael Hahn, CMDL/CIRES): The objective was direct measurements of the flux of carbon dioxide from the ocean's surface by three separate techniques. Each is based on the same kind of electro-optic analyzer with different methods to process the acquired air streams. All measurements were differential, and the two air streams were always filtered at the source, dried to low dew point corresponding to < 100 ppm water vapor and equilibrated to common temperature and pressure before analysis. Sensitivity ranged from ~10 to 1 ppb in one hour of integration, depending on the stability on the ship. All measurements are in mixing ratio units referred to dry air.

Technique #1 : The Profiler:

Concentrations of CO2 were measured from inlets held at discrete heights above the ocean surface by a rigid boom extending approximately 5 meters from the port side of the ship. A range of discrete heights was possible depending on the ship speed and state of the ocean's surface. Possibilities were -20, -15, -10, 0, and +25' relative to the height of the gunnell. We detected approximately 100 concentration differences from pairs of inlets. Artifacts were evaluated successfully by doing null measurements with pairs of inlets at a common height. The concentration differences, combined with ongoing measurements of momentum transfer, can be used to determine the CO2 flux. Site of measurements was van on deck 02 and back 25 meters from bow.

Technique #2 : The Accumulator:

The continuous air sample was brought to the accumulator through a single gust tube with inlet at the site of the sonic anemometer 25' up jack staff. Air stream was separated into up and down parcels as directed by the anemometer, accumulated into separate cells for 20 min. and then analyzed for CO2 concentrations. This concentration difference, combined with ongoing measurements of the standard deviation of the vertical wind, is a measure of flux. Site of measurements was main lab during leg #3. Can report on 4 days of almost continuous operation.

Technique #3 ; The Correlator:

Like the accumulator, single gust tube brings unbroken stream of air from site of anemometer into main lab at ~24 slpm. But unlike the accumulator where analysis can be slow, the correlator measures fast CO2 fluctuations in the stream. The rate is 2 Hz. Simultaneous with the CO2 measurements, the sonic anemometer is measuring fluctuations in the vertical wind. They are logged continuously by a second computer. The two time series, CO2 and wind, are multiplied and then summed to provide the measure of flux. The correlator ran alongside the accumulator in the main lab for the last three days of leg #3. Our experiment ended with the ship at stop for seven hours to provide exceptionally low noise measurements with both instruments.

INTERFEROMETRY (Peter Minnet, PI, Jennifer Hanafin, Walt Mckeown, Richard Sikorski, Goshka Szczodrak, Ed Kearns, and Ajoy Kumar): For this project, a Marine Atmospheric Emitted Radiance Interferometer (MAERI) was mounted topside to collect a running record (2 minute sampling interval) of the ambient light field emitted both from the sky and the sea surface. These data may be used to derive a variety of useful parameters, not the least of which is the skin temperature of the sea surface. Approximately 150 Mb of data per day, for the periods 5/7/98 to 5/20/98, 5/25/98 to 6/25/98, and 6/28/98 to 7/7/98, were collected (a total of over 6 GB). A continuous record of the sky/clouds conditions were recorded by a time lapse VCR (1 frame every 17 sec) connected to a camera/fish-eye mirror arrangement which was mounted forward on the 03 deck. Regular radiosonde balloon launches were conducted twice a day over the entire period at sea. These radiosonde profile data were saved along with the ship's meteorological and thermosalinograph data for merging with the MAERI data during later analyses. During periods when the ship's speed was 8 knots or less and the sea state was at least moderate (45 times during the course of the cruise), a thermistor was lowered to the water's surface off of the ship's starboard bow, providing a continuous, independent bulk estimate of the sea surface temperature (4 Mb total).

VIII. ACKNOWLEDGMENTS:

The officers and crew of the RONALD H. BROWN performed in an excellent manner as summarized in the attached memorandum to the Captain.

The success of the cruise can, to a large extent, be attributed to hard work and utmost cooperation of scientists with diverse backgrounds. The good interactions and free exchange of preliminary data by the physical, biological, and chemical oceanographers and meteorologists facilitated the creation of a high quality data set.