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**CHEMICAL AND HYDROGRAPHIC MEASUREMENTS DURING THE INDIAN OCEAN 18 REPEAT CRUISE (IR8N) IN SEPTEMBER AND OCTOBER, 1995**

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| E. Peltola    | F. Millero | M. Roche       |
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| J-Z. Zhang    | M. Roberts | A. Huston      |
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Atlantic Oceanographic and Meteorological Laboratory  
Miami, Florida  
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## REMOTE ACCESS TO DATA LISTED IN THIS REPORT

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ADCP data: <http://ilikai.soest.hawaii.edu/sadcp>  
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# CONTENTS

|   |    |
|---|----|
| <b>ABSTRACT</b> .....   | 1  |
| <b>1. INTRODUCTION</b> .....  | 2  |
| 1.1. DESCRIPTION OF STUDY AREA .....  | 3  |
| <b>2. DATA COLLECTION AND ANALYTICAL METHODS</b> .....  | 3  |
| 2.1. HYDROGRAPHIC METHODS.....  | 4  |
| 2.1.1. CTD AND HYDROGRAPHIC OPERATIONS.....   | 4  |
| 2.1.2. NUTRIENT ANALYSIS METHODS.....   | 7  |
| 2.2. CARBON PARAMETERS.....   | 8  |
| 2.2.1. TOTAL DISSOLVED INORGANIC CARBON (DIC) .....   | 8  |
| 2.2.2. FUGACITY OF CO <sub>2</sub> (fCO <sub>2</sub> ).....   | 11 |
| 2.2.3. TOTAL ALKALINITY (TA) .....  | 11 |
| 2.2.4. pH .....   | 14 |
| 2.2.5. TOTAL ORGANIC CARBON AND NITROGEN METHODS .....  | 16 |
| 2.2.6. <sup>13</sup> C/ <sup>12</sup> C OF (DIC).....   | 17 |
| 2.2.7. CHLOROFLUOROCARBONS (CFC).....   | 19 |
| 2.3. BIOLOGICAL PARAMETERS.....   | 21 |
| 2.4. UNDERWAY MEASUREMENT METHODS.....  | 21 |
| 2.4.1. UNDERWAY fCO <sub>2</sub> .....  | 21 |
| 2.4.2. UNDERWAY pH.....   | 22 |
| <b>3. ACKNOWLEDGMENTS</b> .....   | 23 |
| <b>4. REFERENCES</b> .....  | 24 |
| <b>FIGURES</b>  |    |
| 1. Cruise track for the Indian Ocean I8NR cruise in September - October 1995 .....  | 29 |
| 2. Conductivity slope and offset of sensors T <sub>0</sub> and C <sub>0</sub> .....   | 30 |
| 3. Conductivity slope and offset of sensors T <sub>1</sub> and C <sub>1</sub> .....   | 31 |
| 4. Oxygen slope and offset .....  | 32 |
| 5. The difference of CTD and bottle salinity vs. pressure .....   | 33 |
| 6. The difference of CTD and bottle salinity vs. number of samples .....  | 34 |
| 7. The difference of CTD and bottle oxygen vs. pressure .....   | 35 |
| 8. The difference of CTD and bottle oxygen vs. number of samples .....  | 36 |
| 9. The results of the CRM measurements .....  | 37 |
| 10. The difference of the DIC duplicates during the course of the cruise .....  | 38 |
| 11. Potentiometric TA and DIC measurements on the Certified Reference Materials (CRMs) during the cruise .....                | 39 |
| 12. Spectrophotometric and potentiometric pH measurements on the Certified Reference Materials (CRMs) during the cruise ..... | 40 |
| <b>TABLES</b>   |    |
| 1. Station locations .....  | 41 |
| 2. Results for the certified reference material, CRM .....  | 44 |
| 3. Dissolved inorganic carbon duplicates .....  | 47 |
| 4. Replicate dissolved CFC-11 analyses .....  | 52 |
| 5. Replicate dissolved CFC-12 analyses .....  | 54 |
| 6. CFC air measurements .....   | 56 |
| 7. CFC air values (interpolated to station locations) .....   | 58 |
| <b>APPENDICES</b>   |    |
| A. WOCE quality control flags .....   | 61 |
| B. Bottle data .....  | 63 |

# **CHEMICAL AND HYDROGRAPHIC MEASUREMENTS DURING THE INDIAN OCEAN I8 REPEAT CRUISE (IR8N) IN SEPTEMBER AND OCTOBER, 1995**

E. Peltola, R. Wanninkhof, R. Molinari, B. Huss, R. Feely, J. Bullister, J-Z. Zhang, F. Chavez, A. Dickson, A. Ffield, D. Hansell, F. Millero, P. Quay, R. Castle, G. Thomas, R. Roddy, T. Landry, M. Roberts, H. Chen, D. Greeley, K. Lee, M. Roche, J.A. Goen, F. Millero III, K. Buck, M. Kelly, F. Menzia, A. Huston, T. Waterhouse, S. Becker, and C. Mordy

## **ABSTRACT**

This document contains data and metadata from the I8 repeat cruise in the Indian Ocean cruise in 1995 from Fremantle, Australia to Male in the Maldives. From September 22 to October 25, 1995, the National Oceanic and Atmospheric Administration's (NOAA) sponsored an oceanographic research cruise conducted aboard the NOAA Ship MALCOLM BALDRIGE. This report presents the analytical and quality control procedures and data from the cruise that was conducted for the Ocean-Atmosphere Carbon Exchange Study (OACES). Samples were taken at 101 stations.

The data presented in this report includes: hydrography, nutrients, total dissolved inorganic carbon dioxide (DIC), fugacity of carbon dioxide ( $f\text{CO}_2$ ), total alkalinity (TA), pH, total organic carbon and nitrogen data (TOC/TON), chlorofluorocarbons,  $^{13}\text{C}$ , and biological parameters.

## 1. INTRODUCTION

Probably the most significant environmental issue of the next century will be the systematic changes in the earth's climate due to increase in the atmospheric burden of radiatively important trace gases, or "greenhouse gases". CO<sub>2</sub>, as well as other "greenhouse gases" (e.g., water vapor, methane, ozone, chlorofluorocarbons, carbon monoxide and nitrous oxide), serve to reduce radiation of heat from the earth to the stratosphere and space. At present, CO<sub>2</sub> accounts for about 50 % of this effect. This phenomenon has a tight coupling to climate in that it exerts significant controls on the temperature of the troposphere and the Earth's surface. It is, in fact, this "greenhouse" control on temperature that makes the Earth habitable to man, and its variability during glacial and interglacial periods has altered that habitability.

In light of these questions, the NOAA/OGP Ocean-Atmosphere Carbon Dioxide Exchange Study (OACES) was started to determine how the ocean/atmosphere carbon system is functioning, i.e., determine how much carbon, of what origin, is going where. That is the first step required if we are to determine the extent of the CO<sub>2</sub> increases in our global system and their climate impacts. Although coupled ocean/atmosphere models appear the best means of predicting long-term climate impacts resulting from increases of "greenhouse gases" (such as CO<sub>2</sub>) and have already given some provocative projections, they lack sufficient data and information about relevant processes to constrain them adequately for reliable prediction. Data from the field work will be used to test and correct the models so that they result in a proper understanding of the global system and its various components. Models include: (1) atmosphere-ocean CO<sub>2</sub> transport models; and (2) process models of air-sea CO<sub>2</sub> exchange and invasion into the deep ocean.

The National Oceanic and Atmospheric Administration's (NOAA) OACES program sponsored an oceanographic research cruise conducted aboard the NOAA Ship MALCOLM BALDRIGE from September 22 to October 25, 1995. The primary objectives of the cruise were to: (1) extend the data base for carbon fugacity (fCO<sub>2</sub>) in the surface ocean and overlying atmosphere, (2) perform measurements of total dissolved inorganic CO<sub>2</sub> (DIC), and discrete fCO<sub>2</sub> in the surface and deep ocean water masses to provide better estimates of CO<sub>2</sub> exchange and ventilation on seasonal to decadal time scales; and (3) provide a better understanding of physical and biological processes that affect seasonal variations in the distribution of carbon species in the ocean. The data presented in this report includes: hydrography, nutrients, total dissolved inorganic carbon dioxide (DIC), discrete fugacity of carbon dioxide (fCO<sub>2</sub>), discrete partial pressure of carbon dioxide (pCO<sub>2</sub>), total alkalinity (TA), pH, total organic carbon and nitrogen data (TOC/TON), chlorofluorocarbons, <sup>13</sup>C, and biological parameters.

Detailed information of the CTD operations can be found in LDEO-98-1 technical report (Ffield et al, 1998). A description of the analyses and procedures of the underway fCO<sub>2</sub> data has been described by Masters et al. (1997) and total alkalinity (TA) and pH data by Millero et al. (1997).

## 1.1. DESCRIPTION OF STUDY AREA

Samples were taken at 101 stations along a south-north transit. The cruise can be divided into three sections - the 95° E line (stations 3-17), the middle section steaming from the 95° E line to the 80° E line (stations 18-35), and the 80° E line (stations 36-101). The 95° E line was followed from 43° S to 31.65° S latitude with 1° spacing except for the last four stations near the Mid-Indian Ridge which were closer together. The 80° E line was followed from 34° S to 5.8° N with 1° spacing to 15° S and 0.5° spacing northward except for the section from 1° S to 1° N, where 0.25° spacing was used. The cruise track and station locations are presented in Figure 1 and Table 1.

## 2. DATA COLLECTION AND ANALYTICAL METHODS

One hundred and one CTD (Conductivity-Temperature- Depth) hydrographic stations were occupied to collect discrete water samples and hydrographic data. A CTD/Rosette unit with a Seabird-911 CTD instrument equipped with 24, specially designed 10-L samples bottles was utilized for these casts. These bottles have the same outer dimensions as standard Niskin bottles, but are modified to reduce chlorofluorocarbon sample contamination. Water samples were collected for salinity, oxygen, nutrients, chlorofluorocarbons, <sup>13</sup>C, biological parameters, as well as carbon related parameters including total dissolved inorganic CO<sub>2</sub> (DIC), discrete fugacity of CO<sub>2</sub> (fCO<sub>2</sub>), total alkalinity (TA), pH, and total organic carbon/nitrogen (TOC/TON) on all casts during the cruise using these modified “Niskin” style bottles. In the data tables the missing values are assigned a value of -9.0. The WOCE quality control flags have been listed in Appendix A. All the cruise data have been presented in Appendix B. Detailed information on individual data collection, or analyses procedures may be found in the respective method sections.

## 2.1. HYDROGRAPHIC METHODS

### 2.1.1. CTD AND HYDROGRAPHIC OPERATIONS

#### *Description of Measurement Techniques and Calibrations*

##### CTD and in situ O<sub>2</sub>

Depth profiles were obtained with a Seabird 911 plus CTD, deck unit, and rosette pylon. The CTD included 2 temperature sensors, 2 conductivity sensors, 1 Beckman oxygen sensor, 1 Paroscientific pressure transducer, and 2 pumps to decrease the response time. Twenty-four 10 liter PVC bottles were mounted on the frame, along with the CTD, pinger, Lowered Acoustic Doppler Current Profiler (LADCP), and LADCP external battery pack. The bottles were specially designed to reduce chlorofluorocarbon contamination. These bottles have the same outer dimensions as standard 10 liter "Niskin" bottles, but use a modified end-cap design to minimize the contact of the water sample with the end-cap O-rings after closing. The O-rings used in these water sample bottles were vacuum-baked prior to the first station. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing standardly used to close "Niskin" bottles. Seabird software was used to acquire, plot, and process the CTD data on PC's. Raw data were stored on VHS tapes, PC hard drives, and SyQuest drives. Typically each cast sampled to within 10 meters of the sea floor as indicated by the pinger signal. A small subset of stations on this cruise were sampled to 3000 db, rather than the full water column. The CTD/O<sub>2</sub> data were processed and calibrated following Seabird recommendations (CTD Data Acquisition Software and Technical Notes, Sea-Bird Electronics, Inc., 1808 - 136th Place NE, Bellevue, Washington 98005). Exceptional items are noted below. Details can be found in the LDEO-98-1 technical report (Ffield et al, 1998) .

The pressure sensor was calibrated by using the pre-cruise laboratory calibration with a linear offset drift of approximately 0.5 db/year. The linear offset was determined by analyzing CTD pressure measurements at the sea surface.

Pre- and post-cruise laboratory calibrations were obtained for the temperature sensors. The temperature sensors were calibrated using both pre- and post-cruise laboratory calibrations with a linear offset drift over time determined from these calibrations. The reported temperature is an average of the two independently calibrated temperature sensors used on each cast.

Pre- and post-cruise laboratory calibrations were also obtained for the conductivity sensors. The conductivity sensors were calibrated using both pre- and post-cruise laboratory calibrations, with slope and offset drifts determined from the differences between the rosette bottle salinity measurements and the uptrace conductivity sensor measurements converted to salinity. To determine slope and offset drifts, all good bottles below 300 db and within 5 days of each station were used. The nominal Seabird temperature and pressure corrections for the conductivity sensors were used. The calculated drifts were smoothed by a 5 station running mean (Figures 2 and 3). The reported salinity is an average of the salinities calculated from the two calibrated conductivity-temperature sensor pairs used on each cast. A small temperature dependency in the surface values and a small pressure dependency in the deep values remain in the final data. However, the above procedure produced the best overall fit to the rosette bottle salinity measurements. For a few stations there was a problem with one of the conductivity sensors. In these cases, the reported salinity values are only determined from the optimally performing conductivity sensor. The most significant case was the failure of the "C<sub>1</sub>" conductivity sensor between CTD casts 268 and 291.

The oxygen sensor was calibrated by using the pre-cruise laboratory calibration, with slope and offset drifts determined from the rosette oxygen measurements and the uptrace oxygen sensor measurements. A better overall fit was obtained when using the uptrace oxygen sensor measurements, rather than the downtrace measurements as is often the procedure for the oxygen calibration. To determine slope and offset drifts, all good bottles within 5 days of each station were used. Rather than using the Seabird nominal temperature and pressure corrections for the oxygen sensor, the values were adjusted slightly for each sensor. The calculated slopes and drifts were smoothed by a 5 station running mean (Figure 4). Apparent oxygen utilization (AOU) is defined as  $O_2 \text{ measured} - O_2 \text{ sat.}$ , where  $O_2 \text{ sat.}$  is the saturation value at potential temperature and salinity of the sample determined according to Weiss (1970)

Pressure plots and histograms of the differences between the calibrated CTD/O<sub>2</sub> sensors and the rosette bottle measurements are shown for all stations for salinity (Figures 5 and 6) and for oxygen (Figures 7 and 8). The average differences meet WOCE criteria. The CTD data are available through internet address [http://whpo.ucsd.edu/whp\\_data.html](http://whpo.ucsd.edu/whp_data.html)

### Measurement of Currents

A hull-mounted RD Instruments 150 kHz narrowband acoustic Doppler current profiler (ADCP) operated continuously during the cruise. Velocity data, averaged in earth coordinates using gyrocompass heading, were logged in three-minute (approximately 180 pings) ensembles using RDI Data Acquisition Software (DAS) version 2.48. Vertical bin size was 8 meters. The center of the first bin was located at 16 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 equipment. 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 GPS 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 three minute ensemble is reduced further by averaging during postprocessing; fifteen minute averages commonly used represent an average over five kilometers at cruising speed, and should be accurate to 1-3 cm/s. The ADCP data will be available through internet address <http://ilikai.soest.hawaii.edu/sadcp>

On-station velocity profiles were obtained using a RDI 150 kHz Narrowband ADCP (Lowered or LADCP) mounted looking downward from the CTD frame. This technique measures and records velocity shear profiles extending 150 to 350 meters below the instrument approximately once per second. In postprocessing, the individual shear profiles are averaged by depth to produce a full-depth shear profile, which is integrated to estimate the depth dependent (baroclinic) component of the velocity field. The depth-independent (barotropic) component of velocity can be recovered if positions at the start and end of the cast are known; positions were logged on this cruise using a Trimble Centurion P-code GPS receiver, accurate to 5 - 10 meters. Readers are advised to refer to Fischer and Visbeck (1993) for a full explanation of methods and standard processing procedures. The LADCP data will be available through internet address <http://www.nodc.noaa.gov>

### Salinity Technique

A Guildline 8400B autosal was used for the salinity analysis with batch P125 standard water. The autosal van was maintained at 22 °C, and the autosal was set at 24 °C.

### Oxygen Technique

An automatic titration system was used for the oxygen analysis with the Carpenter modification of the Winkler method using a photometric determined endpoint described by Friederich and Codispoti (1991). Reagents for the Carpenter method titration were mixed by the AOML/OCD Group of George Berberian as specified in Friederich's MBARI Technical Report #91-6 (Friederich et al, 1991). Apparent oxygen utilization

(AOU) is defined as  $O_2$  measured-  $O_2$  sat., where  $O_2$  sat. is the saturation value at potential temperature and salinity of the sample determined according to Weiss (1970)

## 2.1.2. NUTRIENT ANALYSIS METHODS

### *Sampling and analytical methods*

Nutrient samples were collected from 10-L "Niskin" bottles in acid washed 25-mL linear polyethylene bottles after three complete seawater rinses and analyzed within 1 hour of sample collection. Measurements were made in a temperature-controlled van ( $20 \pm 2^\circ\text{C}$ ). Concentrations of dissolved nitrite ( $\text{NO}_2^-$ ), dissolved nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ) and silicic acid ( $\text{H}_4\text{SiO}_4$ ) were determined using an Alpkem Flow Solution Auto-Analyzer aboard the ship. The following analytical methods were employed:

#### Nitrate and Nitrite:

Nitrite was determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm (Armstrong et al., 1967; Atlas et al., 1971). Samples for nitrate analysis were passed through an Open Tubular Cadmium Reactor (OTCR, Alpkem) coil, which reduced nitrate to nitrite and the resulting nitrite concentration was then determined as described above. Nitrate concentration was determined from the difference of nitrate + nitrite and nitrite.

#### Phosphate:

Phosphate in the samples was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex at temperature of  $42^\circ\text{C}$ . This complex was subsequently reduced with ascorbic acid to form a blue complex and the absorbance was measured at 880 nm (Armstrong et al., 1967, Grasshoff et al., 1983).

#### Silicic Acid:

Silicic acid in the sample was analyzed by reacting with molybdate in a acidic solution to form  $\beta$ -molybdosilicic acid. The  $\beta$ -molybdosilicic acid was then reduced by stannous chloride to form molybdenum blue (Armstrong et al., 1967; Atlas et al., 1971). The absorbance of the molybdenum blue was measured at 820 nm.

### *Calibration and standards:*

Stock standard solutions were prepared by dissolving high purity standard materials ( $\text{KNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{SiF}_6$ ) in deionized water. Working standards were freshly made at each station by diluting the stock solutions in low nutrient seawater. The low nutrient seawater used for the preparation of working standards, determination of blank and wash between samples was filtered seawater obtained from the surface of the central Indian Ocean. Standardizations were performed prior to each sample run with working standard solutions. Five replicate samples were collected from the "Niskin" bottle sampled at deepest depth at each cast. The relative standard deviation from the results of these five replicate samples were used to estimate the overall precision obtained by the sampling and analytical procedures. The precisions of these samples were 0.2  $\mu\text{mol/kg}$  for nitrate, 0.01  $\mu\text{mol/kg}$  for nitrite, 0.01  $\mu\text{mol/kg}$  for phosphate and 0.1  $\mu\text{mol/kg}$  for silicic acid.

## 2.2. CARBON PARAMETERS

### 2.2.1. TOTAL DISSOLVED INORGANIC CARBON (DIC)

#### *Sampling*

Samples were drawn from 10 l "Niskin" bottles into 0.5 l Pyrex bottles using Tygon tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume while taking care not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5 ml headspace volume. 0.2 ml of saturated mercuric chloride ( $\text{HgCl}_2$ ) solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease. The samples were stored at room temperature in the dark for a maximum of two days.

#### *Analysis*

The DIC analyses were performed by extracting the inorganic carbon in a seawater sample by acidification and subsequent displacement of the gaseous  $\text{CO}_2$  into a coulometer cell. Two coulometers (AOML-1 and PMEL-1) were used on the cruise. Both were equipped with the SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson of Brookhaven National Laboratory (BNL).

For analysis on the SOMMA system, a 0.5 l sample bottle was inserted in a water bath at 20°C. Water from the bottle was displaced by pressurization into a thermostatted pipette using compressed air containing 700 parts per million by volume (ppm) CO<sub>2</sub> in air. The sample was injected into an extraction chamber which contained 1 ml 10% H<sub>3</sub>PO<sub>4</sub> solution previously stripped of CO<sub>2</sub>. The evolved CO<sub>2</sub> gas from the sample was run through a condenser and a magnesium perchlorate drying column to dry the gas stream, and through an ORBO-53™ tube to remove volatile acids, using a carrier stream of CO<sub>2</sub>-free ultra high purity nitrogen. In the coulometer cell the CO<sub>2</sub> is absorbed by a proprietary solution procured from Utopia Instrument Company (UIC). This solution changes color from blue to colorless by addition of the (acid) CO<sub>2</sub> gas. A photo diode detects the color change and causes a current to pass through the cell with electrolytic production of hydroxide ions at the cathode. The titration current is turned off when the solution reaches the original color. The current passed through the cell is measured by a counter and is directly proportional to the amount of CO<sub>2</sub> injected. The details of the system can be found in Johnson (1992) and Johnson et al. (1993). The coulometer cell solution was replaced after 30 milligram of carbon was titrated or when the coulometer runs were less than 9 minutes. This typically was after 18-20 hours of continuous use. Typical sample titration times were 9 to 16 minutes.

Both coulometers were calibrated by injecting aliquots of pure CO<sub>2</sub> using an 8-port valve with two sample loops. The CO<sub>2</sub> gas volumes bracketed the amount of CO<sub>2</sub> extracted from the water samples for the two AOML systems. The gas loops were calibrated at BNL. Liquid certified reference materials (CRMs) consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO) were run on each cell. The results were close to the values determined manometrically by Keeling at SIO as shown below. The CRM results have been presented in Figure 9 and Table 2.

Av. value of CRMs run on AOML-2: 1901.46 μmol/kg ± 1.47 n = 42

Av. value of CRMs run on PMEL-1: 1902.62 μmol/kg ± 1.33 n = 49

The manometric value [SIO reference material batch #29] was 1902.33 μmol/kg ± 1.06 n = 11.

Replicate seawater samples were taken from the deepest "Niskin"™ sample and run at different times during the cell. The first replicate was used at the start of the cell with fresh coulometer solution, the second at the end of the cell after about 30 milligrams of C were titrated, while the third analysis was performed using a new coulometer cell solution. No systematic difference between the replicates was observed. As example, the replicate samples run on SOMMA AOML-2 had an average deviation from the mean of 1 μmol/kg with a standard deviation of 0.6 μmol/kg for 63 sets of duplicates. The deviation is very similar to that observed for the CRMs and suggest no strong

dependency of results with amount of carbon titrated for a particular cell. The results of the duplicate samples have been presented in Figure 10 and Table 3.

The data of the two instruments were normalized using the averages of the reference material for the cruise.

### *Calculations*

The instruments were calibrated three times during each cell solution with a set of CO<sub>2</sub> gas loop injections. Calculation of the amount of CO<sub>2</sub> injected was according to the Department of Energy (DOE) CO<sub>2</sub> handbook [DOE, 1994]. The gas loops yielded a calibration factor for the instrument defined as:

$$Cal. factor = \frac{\text{calculated moles of } CO_2 \text{ injected from gas loop}}{\text{actual moles of } CO_2 \text{ injected}} \quad (1)$$

The concentration of CO<sub>2</sub> ([CO<sub>2</sub>]) in the samples was determined according to:

$$[CO_2] = Cal. factor * \frac{(\text{Counts} - \text{Blank} * \text{Run Time}) * K \text{ } \mu\text{Mol} / \text{count}}{\text{pipette volume} * \text{density of sample}} \quad (2)$$

where "Counts" is the instrument reading at the end of the analysis, "Blank" is the counts/minute determined from blank runs performed at least once for each cell of the solution, "Run Time" is the length of coulometric titration (in minutes), and K is the conversion factor from counts to  $\mu\text{mol}$  which is dependent on the slope and intercept relation between instrument response and charge. For a unit with Ecal slope of 1 and intercept of 0, the constant is  $2.0728 * 10^{-4}$ .

The pipette volume was determined by taking aliquots at known temperature of distilled water from the volumes prior to, during, and after the cruise. The weights with the appropriate densities were used to determine the volume of the syringes and pipette.

Calculation of pipette volumes, density, and final CO<sub>2</sub> concentration were performed according to procedures outlined in the DOE CO<sub>2</sub> handbook (DOE, 1994).

All DIC values were corrected for salinity, volume and CRM. Salinity correction was done using CTD salinity. A volume correction was done due to dilution by 200  $\mu\text{l}$  of saturated mercuric chloride solution. The assumed total water volume in the sampling bottles was 540 ml and therefore the correction factor used was 1.00037. Also, the

following CRM corrections were applied to the data: AOML-2, + 0.87  $\mu\text{mol/kg}$ ; PMEL-1, - 0.29  $\mu\text{mol/kg}$  to normalize results from both SOMMAs to the manometric value.

### 2.2.2. FUGACITY OF $\text{CO}_2$ ( $f\text{CO}_2$ )

#### *Gas Chromatographic (GC) Method*

Approximately 1800 discrete  $f\text{CO}_2$  samples from 101 stations were taken and analyzed on the cruise using a newly developed GC based analysis system (Neill et al., 1997).  $f\text{CO}_2$  was measured in the headspace of a crimp sealed bottle at constant temperature of 20 °C. Overall precision was 3  $\mu\text{atm}$  over the observed range of 200 to 1500  $\mu\text{atm}$ . A comparison of discrete  $f\text{CO}_2$  with the underway  $f\text{CO}_2$  values showed correspondence of values to within 1  $\mu\text{atm}$  suggesting a good accuracy of the analyses as well. Discrete  $f\text{CO}_2$  values showed a similar pattern as DIC except that the bottom waters were less enriched than DIC. Calcite dissolution increases the alkalinity in the bottom water and thereby suppresses the  $f\text{CO}_2$  increase.

### 2.2.3. TOTAL ALKALINITY (TA)

#### *Titration system*

The titration systems used to determine TA consist of a Metrohm 665 Dosimat titrator and an Orion 720A pH meter that is controlled by a personal computer (Millero et al., 1993b). Both the acid titrant in a water jacketed burette and the seawater sample in a water jacketed cell are controlled to a constant temperature of  $25 \pm 0.1^\circ\text{C}$  with a Neslab constant temperature bath. The plexiglass water jacketed cells used during the cruise are similar to that used by Bradshaw and Brewer (1988) except a larger volume (about 200 ml) is used to increase the precision. This cell is closed off with a fill and drain valve which increase the reproducibility of the cell volume.

A Lab Windows-C program is used to run the titration and record the volume of the added acid and emf of the electrodes using RS232 interfaces. The titration is made by adding HCl to seawater past the carbonic acid end point. A typical titration records the emf reading after the readings become stable ( $\pm 0.1$  mV) and then adds enough acid to change the voltage to a pre-assigned increment ( $\sim 13$  mV). In contrast to the delivery of a fixed volume increment of acid, this method gives data points in the range of a rapid

increase in the emf near the endpoint. A full titration (25 points) takes about 20 minutes. Using three systems a 24-bottle station cast can be completed in 3.5 hours.

### *Electrodes*

The electrodes used to measure the emf of the sample during a titration consists of a ROSS glass pH electrode and an Orion double junction Ag, AgCl reference electrode.

### *Standard acids*

The HCl used throughout the cruise were made, standardized, and stored in 0.5 l glass bottles in the laboratory. The 0.2554 M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater (~ 0.7 M). The acid was standardized using a coulometric technique by our group and Dr. Andrew G. Dickson (Taylor and Smith, 1959; Marinenko and Taylor, 1968). Both results agree to within  $\pm 0.0001$  N.

### *Volume of the cells*

The volumes of the cells were determined by comparing the values of TA obtained for Gulf stream seawater with open (weighed amount of seawater) and closed cells ( $V_{\text{cell}} = \text{TA (closed)} \times V \text{ (assigned)} / \text{TA(open)}$ ). The density of seawater at the temperature of the measurements (25°C) was calculated from the international equation of state of seawater (Millero and Poisson, 1981). The nominal volumes of all cells is approximately 200 ml and the values determined before the start of the cruise were:

cell 4: 202.56 ml    cell 17: 206.01 ml    cell 18: 203.49 ml

Results on CRM 29 obtained in the laboratory and during the cruise indicate that the volumes were not accurately assigned in the laboratory before the cruise. Thus, all cruise data (TA and DIC) have been adjusted by about 2 to 4  $\mu\text{mol/kg}$  lower than the original values collected during the cruise.

### *Evaluation of the Carbonate Parameters*

The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point,  $\text{pH}_{\text{equiv}} = 4.5$ , according to the exact definition of total alkalinity (Dickson, 1981)

$$\text{TA} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] + [\text{NH}_3] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] \quad (3)$$

The full titration is used to evaluate TA from any given experiment. This is accomplished with a program that is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982) and Dickson (DOE, 1994). The program determines pH,  $E^*$  (for the electrode), TA, DIC and  $\text{pK}_1$ . The program uses the Levenberg-Marquardt nonlinear least squares algorithm to perform the calculations. The program assumes that the nutrients are negligible in the calculation of TA. Neglecting the concentration of nutrients in the seawater sample little affects the accuracy of TA, but does affect the carbonate alkalinity. The pH and  $\text{pK}_1$  of the carbonic acid used in the program are on the seawater scale,  $[\text{H}^+]_{\text{sw}} = [\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}]$  (Dickson, 1984). The dissociation constants used in the program were taken from Dickson and Millero (1987) for carbonic acid, from Dickson (1990a) for boric acid, from Dickson and Riley (1979) for HF, from Dickson (1990b) for  $\text{HSO}_4^-$  and from Millero (1995) for water. The program requires as input the concentration of acid, volume of the cell, salinity, temperature, measured emf ( $E$ ), and volume of HCl ( $V_{\text{HCl}}$ ). To obtain a reliable TA from a full titration at least 25 data points should be collected (9 data points between pH 3.0 to 4.5). The precision of the fit is less than  $0.4 \mu\text{mol/kg}$  when  $\text{pK}_1$  is allowed to vary and  $1.5 \mu\text{mol/kg}$  when  $\text{pK}_1$  is fixed. Our titration program has been compared to the titration programs used by others (Johansson and Wedborg, 1982; Bradshaw *et al.*, 1981; Bradshaw and Brewer, 1988) and the values of TA agree to within  $\pm 1 \mu\text{mol/kg}$ .

Measurements of TA on 72 samples of Certified Reference Materials (CRMs) gave the following results:  $\text{pH} = 8.004 \pm 0.006$ ,  $\text{DIC} = 1915.0 \pm 2.4 \mu\text{mol/kg}$ , and  $\text{TA} = 2184.3 \pm 1.5 \mu\text{mol/kg}$  (Figure 11). The TA ranges from 2230 to  $2360 \mu\text{mol kg}^{-1}$  in the Indian Ocean. The ranges of surface normalized alkalinity ( $\text{NTA} = \text{TA} \times 35 / S$ ) and DIC (NDIC) nominally along  $80^\circ \text{E}$  are 2290-2325 and  $1940\text{-}2100 \mu\text{mol kg}^{-1}$ , respectively. These values remain constant between  $30^\circ \text{S}$  and  $10^\circ \text{N}$  and increase toward higher latitudes.

A more detailed description of the analyses and procedures of the total alkalinity (TA) data has been described by Millero *et al.* (1997).

#### 2.2.4. pH

The pH measurements of seawater were made using the spectrophotometric techniques of Clayton and Byrne (1993). The pH of samples using m-cresol purple (mCP) is determined from

$$\text{pH} = \text{pK}_{\text{ind}} + \log [(R - 0.0069) / (2.222 - 0.133 R)] \quad (4)$$

where  $\text{pK}_{\text{ind}}$  is the dissociation constant for the indicator and  $R (A_{578}/A_{434})$  is the ratio of the absorbance of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm. The pH of the samples is perturbed by the addition of an indicator. The magnitude of this perturbation is a function of the difference between the seawater acidity and indicator acidity; this correction was quantified for each batch of dye solution. To a sample of seawater (~ 30 ml), a normal volume of mCP (0.080 ml, in this case) was added and the absorbance ratio was measured. From a second addition of mCP and absorbance ratio measurement, the change in absorbance ratio per ml of added indicator ( $\Delta R$ ) was calculated. From a series of such measurements over a range of seawater pH,  $\Delta R$  was described as a linear function of the value of the absorbance ratio ( $R_m$ ) measured subsequent to the initial addition of the indicator (i.e.  $R = -0.03540 - 0.1289 R_m$ ). In the course of routine seawater pH analyses, this correction was applied to every measured absorbance ratio ( $R_m$ ); i.e. the corrected absorbance ratio is calculated as

$$R = R_m - (-0.03450 - 0.1289 R_m) V_{\text{ind}} \quad (5)$$

Where  $V_{\text{ind}}$  (0.08 ml) is the volume of mCP used. Clayton and Byrne (1993) calibrated the m-cresol purple indicator using TRIS buffers (Ramette et al., 1977) and the pH equations of Dickson (1993). They found that

$$\text{pK}_{\text{ind}} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3}) (35 - S) \quad (6)$$

where  $T$  is temperature in Kelvin and is valid from 293.15 to 303.15 K and  $S = 30$  to 37. The values of pH calculated from equations (4) and (6) are on the total scale in units of moles per kilogram. The total proton scale (Hansson, 1973) defines pH in terms of the sum of the concentrations of free hydrogen ion,  $[\text{H}^+]$ , and bisulfate,  $[\text{HSO}_4^-]$

$$\text{pH}_T = -\log[\text{H}^+]_T = -\log\{[\text{H}^+] + [\text{HSO}_4^-]\} = -\log\{[\text{H}^+] (1 + [\text{SO}_4^{2-}] / K_{\text{HSO}_4})\} \quad (7)$$

where the concentration of total sulfate,  $[\text{SO}_4^{2-}] = 0.0282 \times 35 / S$ , and  $K_{\text{HSO}_4}$  is the dissociation constant for the bisulfate in seawater (Dickson, 1990a).

Lee and Millero (1995) redetermined the value of  $pK_{ind}$  from 273.15 to 313.15 K using a 0.04 m TRIS buffer (Ramette et al., 1977). The pH of the TRIS buffer was determined from emf measurements made with the  $H_2, Pt | AgCl, Ag$  electrode system (Millero et al., 1993a). At 25°C the buffer had a pH of 8.0760 and yielded spectrophotometric values of pH that were in excellent agreement ( $\sim 0.0001$ ) with those found using equations (4) and (6). Their results from 273.15 to 313.15 K (0 to 40°C) for  $S = 35$  were fitted to the equation

$$pK_{ind} = 35.913 - 216.404 / T - 10.9913 \log (T) + (2.11 \times 10^{-3})(35-S) \quad (8)$$

with the standard error of 0.001 in  $pK_{ind}$  where the constants are on the total proton scale (moles per kilogram of  $H_2O$ ). The use of equations (4) and (8) from 0 to 40°C makes the assumption that  $R$  is independent of the temperature. The salinity dependence is taken from Clayton and Byrne (1993).

The values of pH calculated from equations (4) and (8) are on the total scale in units of mole per kilogram of  $H_2O$ . The conversion of the  $pH_T$  ( $\text{mol (kg-}H_2O)^{-1}$ ) to the seawater  $pH_{SWS}$  ( $\text{mol (kg-soln)}^{-1}$ ) can be made using (Dickson and Riley, 1979; Dickson and Millero, 1987)

$$pH_{SWS} = pH_T - \log\left\{\frac{(1 + [SO_4^{2-}] / K_{HSO_4} + [F^-] / K_{HF})}{(1 + [SO_4^{2-}] / K_{HSO_4})}\right\} - \log(1 - 1.005 \times 10^{-3} S) \quad (9)$$

where the total concentration of fluoride,  $[F^-] = 0.000067 \times 35 / S$ , and  $K_{HF}$  is the dissociation constant for hydrogen fluoride (Dickson and Riley, 1979). The seawater  $pH_{SWS}$  scale was used in this paper since the carbonate constants used are on this scale (Dickson and Millero, 1987; Millero et al., 1993a).

The absorbance measurements were made using a Diode Array 8452A spectrophotometer. The temperature was controlled to a constant temperature of 25°C with a Neslab refrigerated circulating temperature bath that regulates the temperature to  $\pm 0.01^\circ\text{C}$ . The temperature was measured using a Guildline 9540 digital platinum resistance thermometer.

Spectrophotometric pH measurements were made on 21 samples of CRMs. The average pH of these measurements was  $8.011 \pm 0.001$  (Figure 12). The values of pH (measured at 25°C) for surface waters range from 7.85 to 8.10.

A more detailed description of the analyses and procedures of the pH data has been described by Millero et al. (1997).

## 2.2.5. TOTAL ORGANIC CARBON AND NITROGEN METHODS

### *Total Organic Carbon*

All TOC samples were analyzed by high-temperature combustion using a non-commercial system described more fully in Hansell et al., 1997. In brief, a quartz combustion tube (490 mm x 13 mm) was packed with platinum coated alumina beads (Shimadzu, Inc.), Cuprox (Leeman Labs), and Sulfix (Wako Pure Chemical Industries, Inc.). Four platinum pillows were placed 15 cm from the top of the tube. Below the pillows were 2 g of Cuprox and then 10 g of Sulfix and 10 g of platinum catalyst. The catalyst, Cuprox, and Sulfix were each separated by a thin layer of quartz wool. The packing material was supported from below by a platinum screen (one of the pillows unfolded), which in turn was supported by a quartz rod (0.6 mm O.D.) extending to the bottom of the column. The combustion column was maintained at 750 °C in a Thermolyne 21100 tube furnace.

Samples from Stations 2-41 were run at sea during the cruise, while the remainder were stored frozen for analysis in a shore based laboratory. At the time of analysis, the samples were sparged of inorganic CO<sub>2</sub> following acidification with high purity phosphoric acid (50 µl added to 20 ml of sample). Carbon dioxide generated from 100 µl injections was detected using a LICOR Model LI-6252 NDIR analyzer operated in the absolute mode. Data were acquired on a Macintosh computer running Dynamax Macintegrator 1.3 software (Rainin Instruments, Inc.).

Calibrations were performed 2-4 times daily with a 4-point standard curve using glucose in Milli-Q water (0-100 µmol/l C). The system blank (normally 7-8 µmol/ l C) was determined at intervals of approximately 6 seawater samples using vialled Milli-Q water produced at the Bermuda Biological Station for Research, Inc. The organic carbon content of this water (~ 3 µmol/ l C) was determined by intercomparison with the low-carbon water prepared by Dr. Jon Sharp (Univ. of Delaware) for the TOC intercomparison exercises he organized. Vialled seawater, collected from 2600 m at the U.S. JGOFS Bermuda Atlantic Time-Series Study site in the Sargasso Sea, was also analyzed several times each day to monitor the system blank and the behavior of the analyzer. The percent relative standard deviation (RSD) for all 174 TOC samples at depths >1000 m, with a mean concentration of 42.3 µmol/ l, was 2.0%.

Concentrations of TON were determined by UV photo-oxidation according to the method described by Walsh (1989). Frozen samples were thawed by placing sample bottles in a warm water bath. A 10 ml aliquot was removed from each sample bottle and placed in a 20 ml fused quartz tube equipped with a ground stopper (Quartz Scientific, Inc.). 50  $\mu$ l of 30% hydrogen peroxide was added to each tube and placed in a homemade irradiation unit overnight (17-20 hours). Testing the recovery of known compounds, such as glycine, showed that inconsistent results were obtained with shorter irradiation periods. The irradiation unit contained a 1200 W UV lamp (Hanovia) protected by a quartz jacket. A 2-tiered aluminum tube holder (40 tubes total) fitted around the lamp and held the samples 8 cm from the lamp. A fan placed at the bottom of the unit blew air across the samples for cooling. A hinged aluminum cylinder, open at the top and bottom, was fitted around the samples to keep stray UV light from leaving the system. This entire unit was placed in a fume hood, the front of which was covered with a black curtain while in use (again to collect stray UV light).

After irradiation, aliquots of the samples (which were refrigerated overnight) that had not been oxidized, and the photo-oxidized aliquots, were analyzed for nitrate plus nitrite using a colorimetric method on a Technicon Autoanalyzer II (Knap et al. 1993). Daily calibration was achieved from 4 point calibration curves using both  $\text{KNO}_3$  and  $\text{KNO}_2$ . Cadmium column efficiency was determined by comparing the slope of the  $\text{NO}_3^-$  calibration curve with the slope obtained from  $\text{NO}_2^-$  calibration curve. Due to the photoreduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  (Walsh 1989), it is imperative that the cadmium column be efficient when analyzing samples containing high concentrations of nitrate. Therefore, a new column (i.e. efficiency >98%) was employed when analyzing nitrate samples >10  $\mu\text{mol/l}$ . The column efficiency was generally > 90% when running the low nitrate samples. Low nutrient seawater (Sargasso Sea surface water) was always processed with the samples as a daily quality control measure.

#### 2.2.6. $^{13}\text{C}/^{12}\text{C}$ OF DISSOLVED INORGANIC CARBON

##### *Shipboard Sample Collection Methods*

Samples were collected in pre-washed and baked (450 °C) 250 or 0.5 l ground glass-stoppered bottles using the following method. A length of Tygon tubing was attached to the "Niskin" bottle or seawater line and flushed for a few seconds. The end of the tubing was then placed at the bottom of the upright sample bottle and the bottle was filled, then overflowed with an amount equal to its volume if "Niskin" water volume permitted,

otherwise with at least half its volume. Flow was stopped as the Tygon tubing was removed from the top of the bottle to avoid any splashing in the top. Using a syringe or turkey baster, 10 to 20 ml were withdrawn off the top of the sample to lower the water level to approximately 1 ml below the neck of the bottle, avoiding backwash of water from the turkey baster into the sample. The ground glass joint of the bottle was wiped dry with Kimwipes. Then 100  $\mu$ l of a saturated  $\text{HgCl}_2$  solution (per 250 ml of seawater) was injected beneath the surface of the sample using an Eppendorf pipet. The ground-glass stopper, which had been pre-greased with Apiezon M grease, was then inserted straight into the bottle without twisting. If any air streaked in the grease seal were visible, the stopper was removed, cleaned, and regreased, then the bottle was resealed. Clips (if required for the bottle neck-type) were placed on the necks of the bottles, and two heavy rubber bands were placed around the stopper and bottle to prevent leakage. The sample bottle was then inverted a couple of times to mix the  $\text{HgCl}_2$  throughout the sample.

### *Laboratory Methods*

$\text{CO}_2$  is extracted from the DIC seawater sample using a modification of the helium stripping technique described by Kroopnick (1974) as described in Quay et al (1992). The stripper is comprised of a glass tube with a stainless steel fitting and silicone-greased glass stopcock at the bottom (which connects to the He line), a glass frit which the He passes through, and a stainless steel fitting containing a 3-layer silicone rubber septum at the top. Approximately 1 ml phosphoric acid is injected into the stripper and bubbled with He for 10 minutes. The gas is then evacuated out of the stripper and the stripper is weighed. Then 80 to 125 ml of the sample is drawn into the stripper and it is weighed again to calculate the weight of water analyzed. A stainless steel needle pierces the septum and connects the stripper to the extraction line, which has been evacuated and filled with helium. The sample is stripped with 99.997% pure He at a flow rate of about 200 ml/min for 20 minutes. Water is trapped out in two glass traps submerged in Dewars containing a slush mixture of dry ice and isopropanol at  $-70^\circ\text{C}$ .  $\text{CO}_2$  is collected at  $-196^\circ\text{C}$  in glass loop traps submerged in liquid  $\text{N}_2$ . The  $\delta^{13}\text{C}$  is then measured on a Finnigan MAT 251 mass spectrometer. The efficiency of the extraction method is  $100 \pm 0.5$  percent based on gravimetrically prepared  $\text{Na}_2\text{CO}_3$  standards. The precision of the  $^{13}\text{C}$  analysis is  $\pm 0.02$  per mil based on a replicate analysis of standards and seawater samples.

### 2.2.7. CHLOROFLUOROCARBONS (CFC)

CFC samples were drawn from approximately 70 % of 2300 water samples collected during the expedition. When taken, water samples for CFC analysis were usually the first samples drawn from the 10 liter "Niskin" bottles. Care was taken to co-ordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, total CO<sub>2</sub>, alkalinity and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 10 liter "Niskin" bottles into 100 ml precision glass syringes equipped with 2-way metal stopcocks. The syringes were immersed in a holding tank of clean surface seawater until analysed.

To reduce the possibility of contamination from high levels of CFCs frequently present in the air inside research vessels, the CFC extraction/analysis system and syringe holding tank were housed in a modified 20' laboratory van on the aft deck of the ship.

For air sampling, a ~100 meter length of 3/8" OD Dekaron tubing was run from the CFC lab van to the bow of the ship. Air was pulled through this line into the CFC van using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at about 1.5 atm using a back-pressure regulator. A tee allowed a flow (~100 ml/min) of the compressed air to be directed to the gas sample valves, while the bulk flow of the air (>7 l/minute) was vented through the back pressure regulator. A list of air measurements is given in Table 6 and interpolated values are shown in Table 7.

Concentrations of CFC-11 and CFC-12 in air samples, seawater and gas standards on the cruise were measured by shipboard electron capture gas chromatography (EC-GC), using techniques similar to those described by Bullister and Weiss (1988). For seawater analyses, a ~30-ml aliquot of seawater from the glass syringe was transferred into the glass sparging chamber. The dissolved CFCs in the seawater sample were extracted by passing a supply of CFC-free purge gas through the sparging chamber for a period of 4 minutes at ~70 ml/min. Water vapor was removed from the purge gas during passage through a 7" long x 3/8" diameter glass tube packed with magnesium perchlorate dessicant. The sample gases were concentrated on a cold-trap consisting of a 3-inch section of 1/8-inch stainless steel tubing packed with Porapak N (60-80 mesh) immersed in a bath of isopropanol held at -20 °C. After 4 minutes of purging the seawater sample, the sparging chamber was closed and the trap was held open for an additional one minute to allow nitrous oxide (N<sub>2</sub>O) to pass through the trap and thereby minimize its interference with CFC-12. The trap was then isolated, and the cold isopropanol in the bath was forced away from the trap. The trap was then heated electrically to 125 degrees C. The sample gases held in the trap were then injected onto a precolumn (12 inches of 1/8-inch O.D. stainless steel tubing packed with 80-100 mesh Porasil C, held at 90

degrees C), for the initial separation of the CFCs and other rapidly eluting gases from more slowly eluting compounds. The CFCs then passed into the main analytical column (10 feet, 1/8-inch stainless steel tubing packed with Porasil C 80-100 mesh, held at 90 degrees C), and then into the EC detector.

The CFC analytical system was calibrated frequently using standard gas of known CFC composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column and EC detector were similar to those used for analyzing water samples. Two sizes of gas sample loops were present in the analytical system. Multiple injections of these loop volumes could be done to allow the system to be calibrated over a relatively wide range of CFC concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for a seawater, air, standard or blank sample was about 12 minutes.

Concentrations of CFC-11 and CFC-12 in air, seawater samples and gas standards are reported relative to the SIO93 calibration scale (Cunnold, et. al., 1994). CFC concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts-per-trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles of CFC per kg seawater (pmol/kg). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a CFC working standard (PMEL cylinder 33790) into the analytical instrument. The concentrations of CFC-11 and CFC-12 in this working standard were calibrated before and after the cruise versus a primary standard (36743) (Bullister, 1984). No measurable drift in the concentrations of CFC-11 and CFC-12 in the working standard could be detected during this interval. Full range calibration curves were run at intervals of ~ 3 days during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 1 to 2 hours) to monitor short term changes in detector sensitivity.

Extremely low (<0.01 pmol/kg) CFC concentrations were measured in deep water (>2000 meters) on the 80E section north of ~30 S. Based on the median of CFC concentration measurements in the deep water of this region, which is believed to be nearly CFC-free, blank corrections of 0.0018 pmol/kg for CFC-11 and 0.0015 pmol/kg for CFC-12 have been applied to the data set.

On this expedition, we estimate precisions (1 standard deviation) of about 1% or 0.005 pmol/kg (whichever is greater) for dissolved CFC-11 and 2% or 0.005 pmol/kg (whichever is greater) for dissolved CFC-12 measurements (see listing of replicate samples given in Tables 4 and 5).

A number of water samples had clearly anomalous CFC-11 and/or CFC-12 concentrations relative to adjacent samples. These anomalous samples appeared to occur more or less randomly during the cruise, and were not clearly associated with other features in the water column (eg. elevated oxygen concentrations, salinity or temperature features, etc.). This suggests that the high values were due to individual, isolated low-level CFC contamination events. Measured concentrations for these samples are included in this report, but are given a quality flag of either 3 (questionable measurement) or 4 (bad measurement). A total ~7 analyses of CFC-11 were assigned a flag of 3 and ~9 analyses of CFC-12 were assigned a flag of 3. A total of ~27 analyses of CFC-11 were assigned a flag of 4 and ~69 CFC-12 samples assigned a flag of 4.

### 2.3. BIOLOGICAL PARAMETERS

Samples were collected from 31 discrete stations for biological and bio-optical parameters. A total of 306 primary productivity, 428 chlorophyll, 31 particulate organic carbon, 173 <sup>15</sup>N uptake, 164 epifluorescence microscopy, 257 flow cytometry, 110 A\* (the absorption of light by suspended particles normalized to chlorophyll concentration) and 179 nutrient samples were taken for the characterization of prokaryotic and protistan biomass, growth rates and composition in the upper 300 meters of the water column. The Profiling Reflectance Radiometer was deployed to 100-140 m at the stations which were occupied between 0900 and 1500 hours of local time. In addition underway mapping system continuously measured nitrate concentration, chlorophyll fluorescence, photosynthetically active radiation and transparency, attenuation and absorbance at multiple wavelengths. All the productivity, chlorophyll and much of the epifluorescence microscopy samples have been analyzed aboard ship, however, the A\*, <sup>15</sup>N, POC, and nutrient samples were analyzed in various laboratories. The data is available through the following internet addresses:

<http://www.mbari.org/~reiko/indian/introduction.htm> and  
<http://www.aoml.noaa.gov/ocd/oaces/>

### 2.4. UNDERWAY MEASUREMENT METHODS

#### 2.4.1. UNDERWAY fCO<sub>2</sub>

The Underway pCO<sub>2</sub> System version 1.5 (Ho *et al.* 1997) was used to determine the pCO<sub>2</sub> of surface water and overlying air on a continuous basis (Keeling 1965, Wanninkhof and Thoning 1993). When in operation, seawater is drawn from the uncontaminated seawater intake from the bow bubble approximately 6 meters below the water line to a shower head equilibrator located in the main laboratory, where the

headspace and seawater reach equilibrium on a short time scale. At specific times during an hourly cycle, the content of the headspace is measured by an infrared CO<sub>2</sub> analyzer. Uncontaminated air from the marine boundary layer is drawn continuously from the bow mast to the underway pCO<sub>2</sub> system. At a designated time, air is analyzed by a the infrared CO<sub>2</sub> analyzer, otherwise the air is bled off through a vent .

The CO<sub>2</sub> measurements are made by a Li-Cor differential, non-dispersive, infrared (NDIR) CO<sub>2</sub> analyzer (model 6251), and the result is based on the difference in absorption of infrared (IR) radiation passing through two gas cells. The reference cell is continuously flushed with a gas of known CO<sub>2</sub> concentration using the lowest concentration of three reference gas standards. The sample cell is flushed with one of three reference gas standards, marine boundary layer air, or headspace gas from the equilibrator. Standards were calibrated by NOAA's Climate Monitoring & Diagnostic Laboratory (CMDL) before and after the cruise.

The description of the analyses and procedures of the underway fCO<sub>2</sub> data has been described by Masters et al. (1997). The data may be downloaded via anonymous ftp at <ftp://ftp.aoml.noaa.gov/pub/ocd/carbon/uwpc0295>

#### 2.4.2. UNDERWAY pH

Measurements of pH were made throughout the cruise using an automated, spectrophotometric measurement of pH with a sensitivity of better than 0.001 in pH and with a period of approximately 6 min. (0.1 hr). The potential accuracy of pH measurements measured using this technique has been estimated to be about 0.003. However, this is as yet unconfirmed. The probable sources of uncertainty are in the values that are used for the dissociation constant of the indicator dye and for the various extinction coefficient ratios used in calculating the pH.

The system is capable of being operated in one of two modes: constant temperature, or tracking sea surface temperature. In constant temperature mode, the pH of sea water is a sensitive indicator of the ratio of total alkalinity to total dissolved inorganic carbon in the water mass being measured. Changes in pH are thus indicative of changes in the water mass being monitored. In sea surface temperature mode, the pH is inversely correlated with the sea surface pCO<sub>2</sub> and thus indicates changes in this parameter (note however, that it is probably better to measure pCO<sub>2</sub> directly if accurate measurements are needed).

The system is controlled by computer, and the software provides a near real-time display of sea surface temperature, salinity, and pH (plotted against time) as well as of parameters that are more directly related to instrument performance (which can thus be used to assess whether or not problems exist). Values for sea surface temperature and salinity were obtained from the SCS (Shipboard Computer System), time and position are obtained directly from a GPS (as well as being available from the SCS data stream). During this cruise, the system was operated predominantly in “constant temperature” mode, and despite a number of problem with the valve on the syringe pump — resulting from wear during the previous few months — the system operated for about 80% of the total time of the cruise, *i. e.* it made about 6,500 measurements. The latest update of the data can be obtained from Dr. Andrew Dickson at: [adickson@ucsd.edu](mailto:adickson@ucsd.edu)

### **3. ACKNOWLEDGMENTS**

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#### 4. REFERENCES

- Armstrong, F.A.J., C.R. Stearns, and Strickland, J.D.H., 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon Auto-Analyzer and associated equipment. *Deep-Sea Res.* **14**: 381-389.
- Atlas, E. L., J.C. Callaway, R.D. Tomlinson, L.I. Gordon, L. Barstow, and Park, P.K., 1971. A practical manual for use of the Technicon Autoanalyzer for nutrient analysis, revised. Oregon State University, Technical Report 215, Reference No. 71-22.
- Bradshaw, A. L. and Brewer, P. G., 1988. High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration-1. Presence of unknown protolyte(s)?, *Mar. Chem.*, **23**, 69-86.
- Bradshaw, A. L., Brewer, P. G., Shafer, D. K., and Williams, R. T., 1981. Measurements of total carbon dioxide and alkalinity by potentiometric titration in the GEOSECS program, *Earth and Planet. Sci. Lett.*, **55**, 99-115.
- Bullister, J.L. Anthropogenic Chlorofluoromethanes as Tracers of Ocean Circulation and Mixing Processes: Measurement and Calibration Techniques and Studies in the Greenland and Norwegian Seas, Ph.D. dissertation, Univ. Calif. San Diego, pp. 172
- Bullister, J.L. and Weiss, R.F., 1988. Determination of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in seawater and air, *Deep-Sea Res.*, **35** (5), 839-853.
- Clayton T. and Byrne, R. H., 1993. Calibration of m-cresol purple on the total hydrogen ion concentration scale and its application to CO<sub>2</sub>-system characteristics in seawater, *Deep Sea Res.*, **40**, 2115-2129.
- Cunnold, D.M., Fraser, P.J., Weiss, R.F., Prinn, R.G., Simmonds, P.G., Miller, B.R., Alyea, F.N., and Crawford, A.J., 1994. Global trends and annual releases of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> estimated from ALE/GAGE and other measurements from July 1978 to June 1991, *J. Geophys. Res.*, **99**, 1107-1126.
- Dickson, A.G., 1993. pH buffers for sea water media based on the total hydrogen ion concentration scale, *Deep Sea Res.*, **40**, 107-118.
- Dickson, A. G., 1990a. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Res.*, **37**: 755-766

- Dickson, A. G., 1990b. Standard potential of the ( $\text{AgCl} + 1/2 \text{H}_2 = \text{Ag} + \text{HCl}(\text{aq})$ ) cell and the dissociation of bisulfate ion in synthetic sea water from 273.15 to 318.15 K, *J. Chem. Thermody.*, **22**, 113-127.
- Dickson, A. G. and Millero, F. J., 1987. A comparison of the equilibrium constants for The dissociation of carbonic acid in seawater media, *Deep-Sea Res.*, **34**, 1733-1743.
- Dickson, A. G., 1984. pH scales and proton-transfer reactions in saline media such as seawater, *Geochim. Cosmochim. Acta*, **48**, 2299-2308.
- Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total  $\text{CO}_2$  from titration data. *Deep-Sea Res.*, **28**, 609–623.
- Dickson, A. G. and Riley, J. P., 1979. The estimation of acid dissociation constants in sea water media from potentiometric titrations with strong base-I. The ionic production of water- $K_w$ , *Mar. Chem.*, **78**, 89-99.
- DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. *Version 2.* (A. Dickson and C. Goyet ed.) ORNL/CDIAC-74, 1991.
- Ffield, A., Fleurant, C., Molinari, R., and Wilson, D. NOAA Ship MALCOLM BALDRIGE 1995 Cruises: MB95-02, MB95-04, MB95-07 hydrographic data. LDEO-98-1 technical report, 1998.
- Fischer, J., and Visbeck, M., 1993. Deep Velocity Profiling with Self-contained ADCP'S, *Journal of Atmospheric and Oceanic Technology*, **10**, 764-773.
- Friederich, G.E., Codispoti, L.A., and Sakamoto, C.M., 1991. An easy-to-construct automated Winkler titration system. MBARI Tech. Rep. 91-6.
- Grasshoff, K., Ehrhardt, M. and Gremling, K. (eds), 1983. *Methods of Seawater Analysis*, 2nd edition. Verlag Chemie GmbH., Weinheim, pp.419.
- Hacker, P., Firing, E., Wilson, W. D., and Molinari, R., 1996. Direct observations of the current structure east of the Bahamas, *Geophys. Res. Lett.*, **23**, 1127-1130.
- Hansell, D.A, Carlson, C.A., Bates, N., and Poisson, A, 1997. Horizontal and vertical removal of organic carbon in the equatorial Pacific Ocean: a mass balance assessment. *Deep-Sea Res.II*, **44**, 2115-2130.

- Hansson, I., 1973. A new set of acidity constants for carbonic acid and boric acid in sea water, *Deep Sea Res.*, **20**, 461-478.
- Ho, D. T., Wanninkhof, R., Masters, J., Feely, R.A., Cosca, C., 1997. Measurements of Underway fCO<sub>2</sub> in the Eastern Equatorial Pacific on NOAA Ships MALCOLM BALDRIGE and DISCOVERER from February to September, 1994. NOAA Data Report ERL AOML-30, 52pp.
- Johansson, O. and Wedborg, M., 1982. On the evaluation of potentiometric titrations of seawater with hydrochloric acid, *Oceanol. Acta*, **5**, 209-218.
- Johnson K. M., Wills K. D., Butler D. B., Johnson W. K., and Wong C. S., 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated continuous gas extraction system and coulometric detector. *Mar. Chem.* **44**, 167-189.
- Johnson K. M. and Wallace D. W. R., 1992. The single-operator multiparameter metabolic analyzer for total carbon dioxide with coulometric detection. DOE Research Summary, No. 19, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Keeling C. D., 1965. Carbon dioxide in surface waters of the Pacific Ocean 2. Calculation of the exchange with the atmosphere. *J. Geophys. Res.* **70**, 6099-6102.
- Knap, A. H., Michaels, A.F., Dow, R.L., Johnson, R. J., Gundersen, K., Sorenson, J. C., Close, A. R., Howse, F. A., Hammer, M., Bates, N., Doyle, A., and Waterhouse, T., 1993. BATS Method Manual, U.S. JGOFS Planning Office, Woods Hole, MA.
- Kroopnick, P., 1974. The dissolved O<sub>2</sub>-CO<sub>2</sub>-<sup>13</sup>C system in the equatorial Pacific, *Deep-Sea Res.*, **21**, 211-227.
- Lee, K. and Millero, F. J., 1995. The thermodynamic studies of the carbonate system in seawater. *Deep Sea-Res.*, **42**: 2035-2061.
- LI-COR. 1990. LI-6262 CO<sub>2</sub>/H<sub>2</sub>O Analyzer Operating and Service Manual. 9003-59, LICOR, Lincoln, NB.
- Marinenko, G., and Taylor, J.K., 1968. Electrochemical equivalents of benzoic and oxalic acid. *Anal. Chem.*, **40**, 1645-1651.

- Masters, J., Wanninkhof, R., Ho, D.T., Steckley, M., Feely, R., Cosca, C., 1997. Continuous air and surface seawater measurements of  $f\text{CO}_2$  on board the NOAA Ship MALCOLM BALDRIGE around-the-world cruise during 1995. NOAA data report ERL AOML-31.
- Millero, F.J., Lee, K., Roche, M., Goen, J., and Millero III, F.J., 1997. The Carbonate System Measurements in the Indian Ocean. Ocean Atmosphere Carbon Exchange Study, Leg I. University of Miami Technical Report, No. RSMAS 97-004.
- Millero, F. J., 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochim. Cosmochim. Acta*, **59**, no. 4, 661-677
- Millero, F. J., Zhang, J. Z., Fiol, S., Sotolongo, S., Roy, R., Lee, K., and Mane, S., 1993a. The use of buffers to measure the pH of seawater, *Mar. Chem.*, **44**, 143-152.
- Millero, F. J., Zhang, J. Z., Lee, K., and Campbell, D. M., 1993b. Titration alkalinity of seawater, *Mar. Chem.*, **44**, 153-16.
- Millero, F.J., and Poisson, A., 1981. International one-atmosphere equation of state of seawater. *Deep-Sea Res.*, **28**, 625–629.
- Neill, C., Johnson, K.M., Lewis, E., and Wallace, D.W.R., 1997. Accurate headspace analysis of  $f\text{CO}_2$  in discrete water samples using batch equilibration. *Limnol. Oceanogr.*, **42(8)**, 1774-1783
- Quay P.D., Tilbrook, B., and Wong, C.S., 1992. Ocean uptake of fossil fuel  $\text{CO}_2$ : Carbon-13 evidence, *Science*, **256**, 74-79.
- Ramette, R. W., Culberson, C. H., and Bates, R. G., 1977. Acid base properties of tris (hydroxymethyl) aminomethane (tris) buffers in seawater from 5 to 40°C. *Anal. Chem.*, **49**, 867-870.
- Taylor, J.K., and Smith S.W., 1959. Precise coulometric titration of acids and bases. *J. Res. Natl. Bur. Stds.*, **69A**, 153–159.
- Walsh, T. W., 1989. Total dissolved nitrogen in seawater: a new-high-temperature combustion method and a comparison with photo-oxidation. *Marine Chemistry*, **26**, 295-311.
- Wanninkhof R. and Thoning K., 1993. Measurement of fugacity Of  $\text{CO}_2$  in surface water using continuous and discrete sampling methods. *Mar. Chem.*, **44**, 189-205.

Weiss R. F., Janke R. A., and Keeling C. D., 1982. Seasonal effects of temperature and salinity on the partial pressure Of CO<sub>2</sub> in seawater. *Nature*, **300**, 511-513.

Weiss R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* **2**, 203-215.

Weiss, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.*, **17**, 721-735.

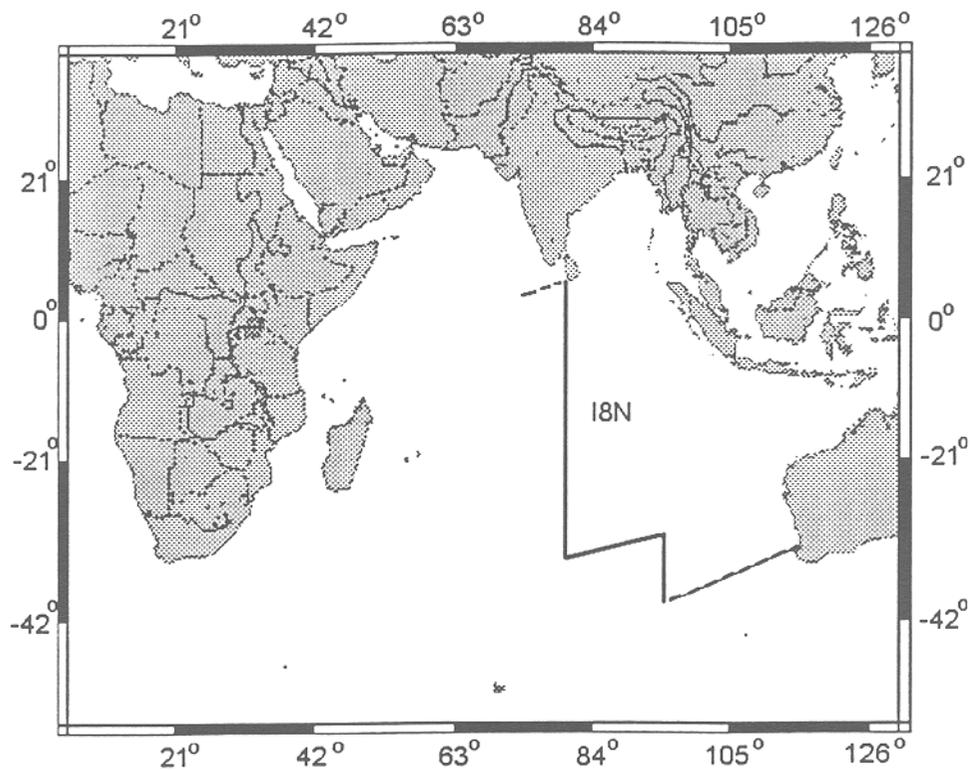


Figure 1. Cruise track for the Indian Ocean I8NR cruise in September-October 1995

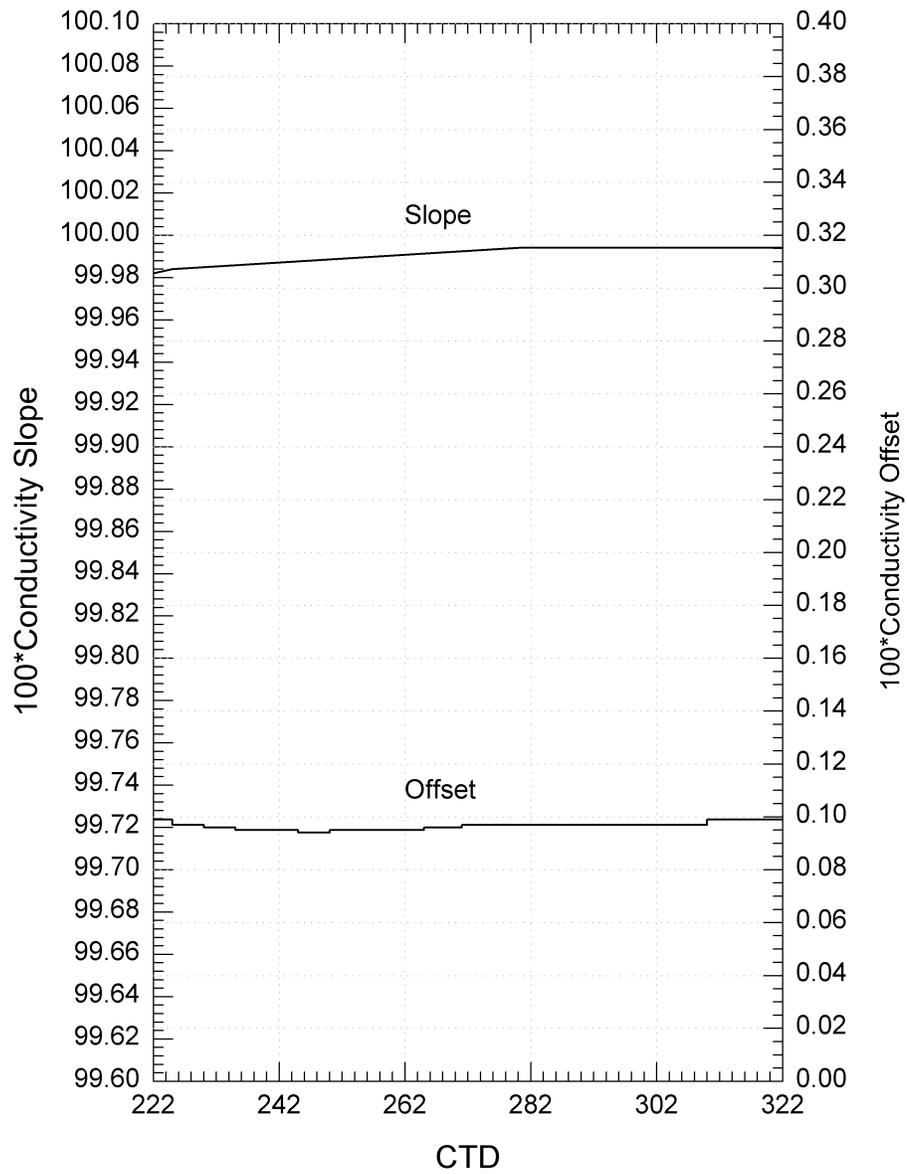


Figure 2. Conductivity slope and offset of sensors  $T_0$  and  $C_0$

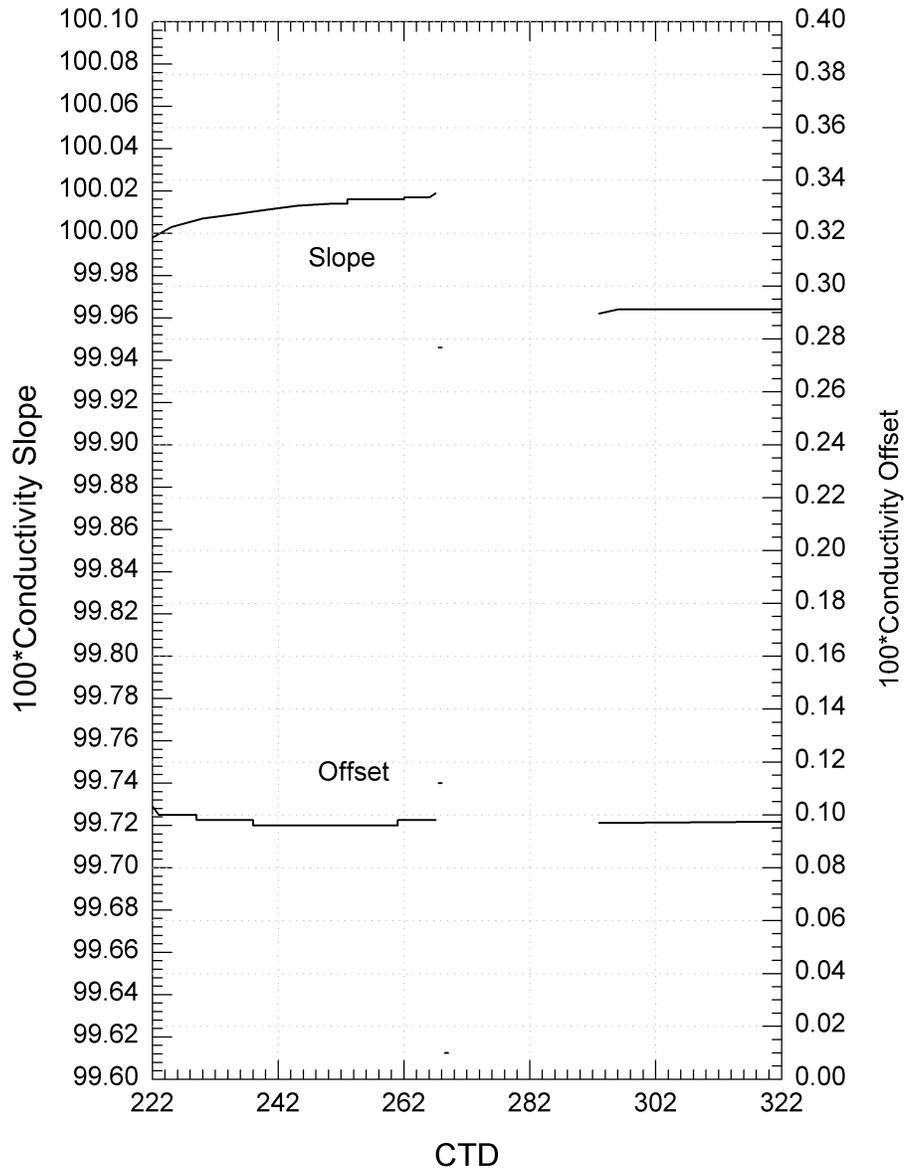


Figure 3. Conductivity slope and offset of sensors  $T_1$  and  $C_1$

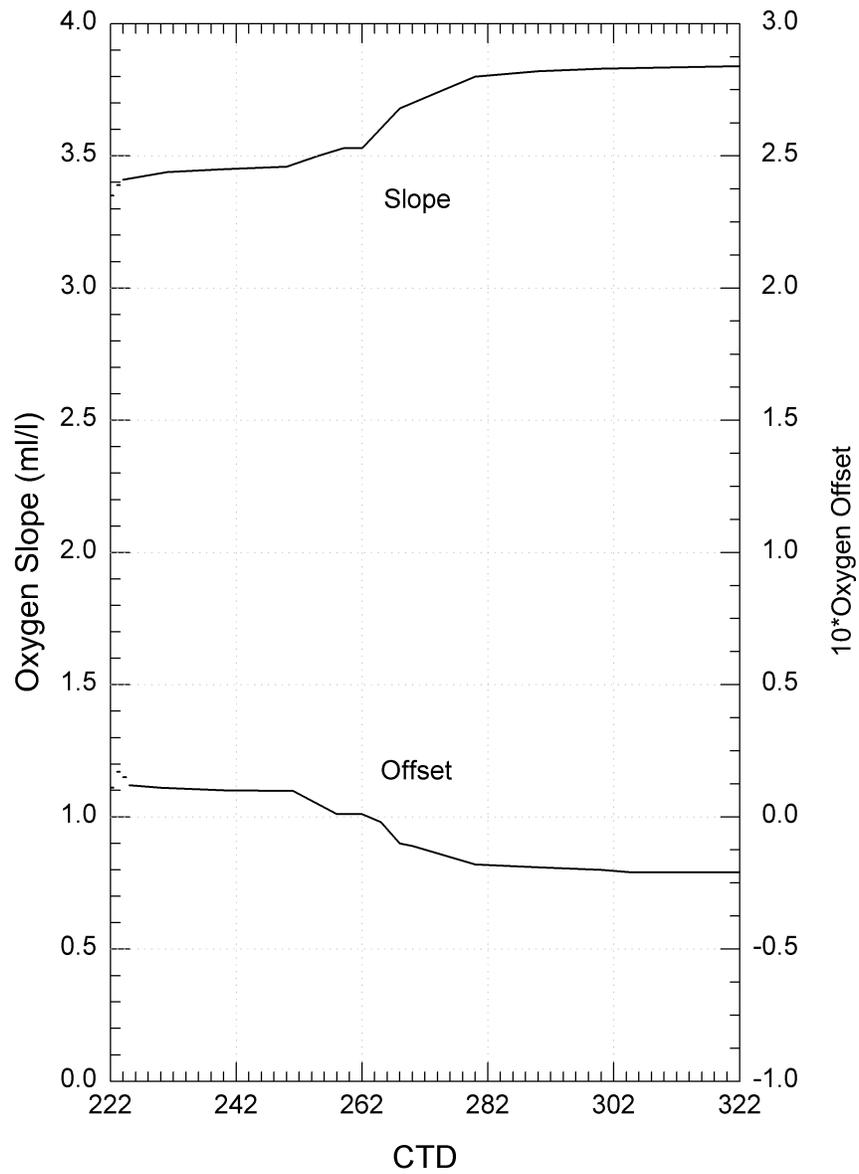


Figure 4. Oxygen slope and offset

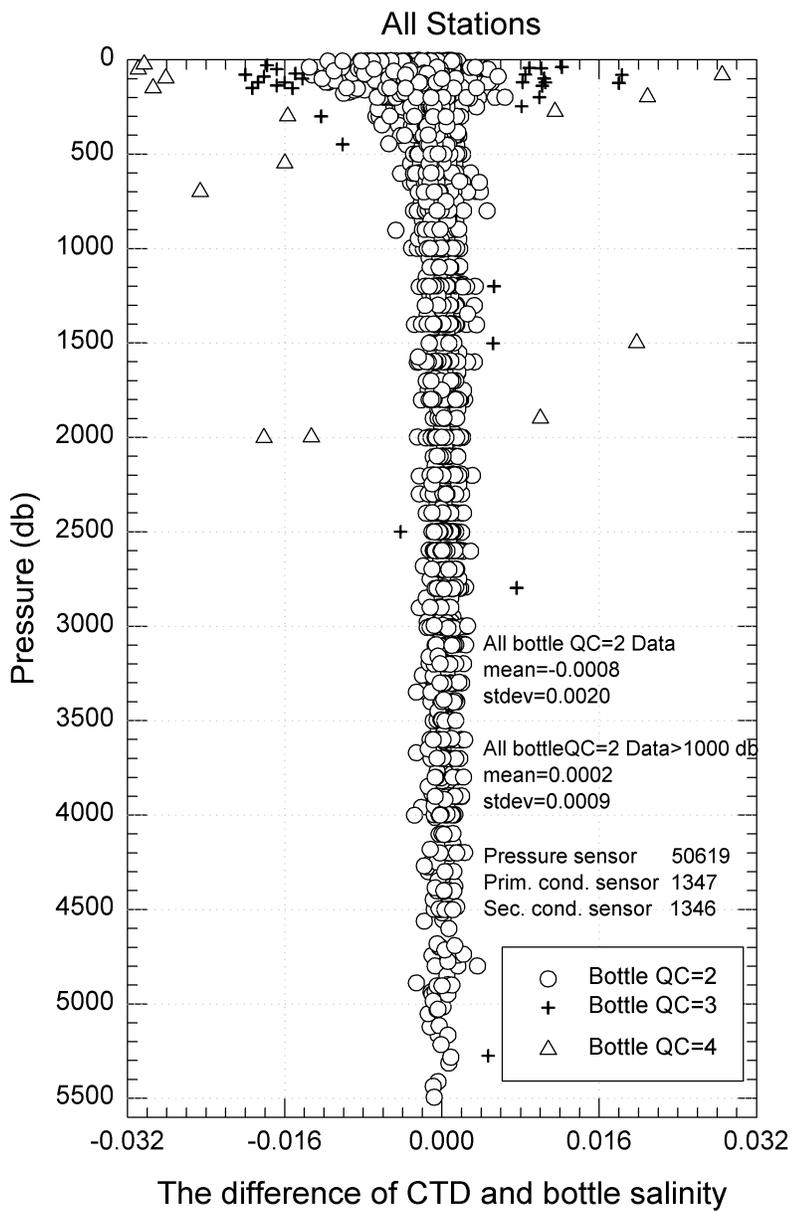


Figure 5. The difference of CTD and bottle salinity vs. pressure

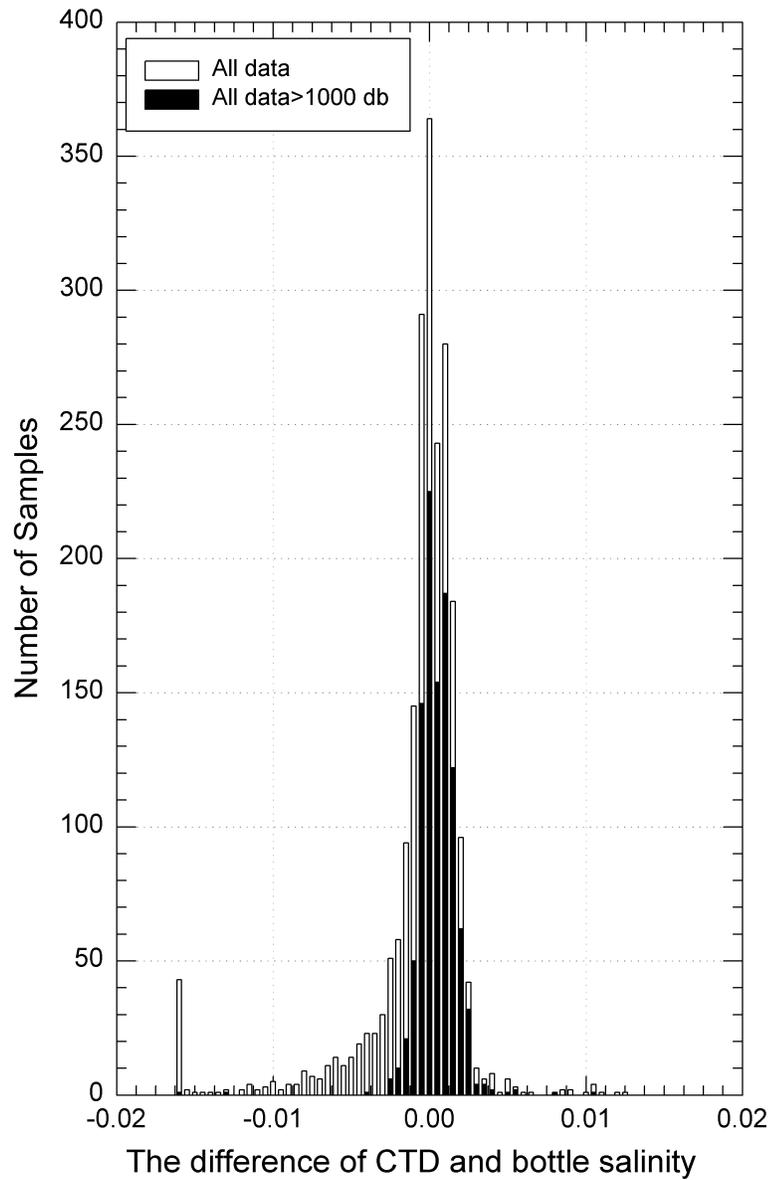


Figure 6. The difference of CTD and bottle salinity vs. number of samples

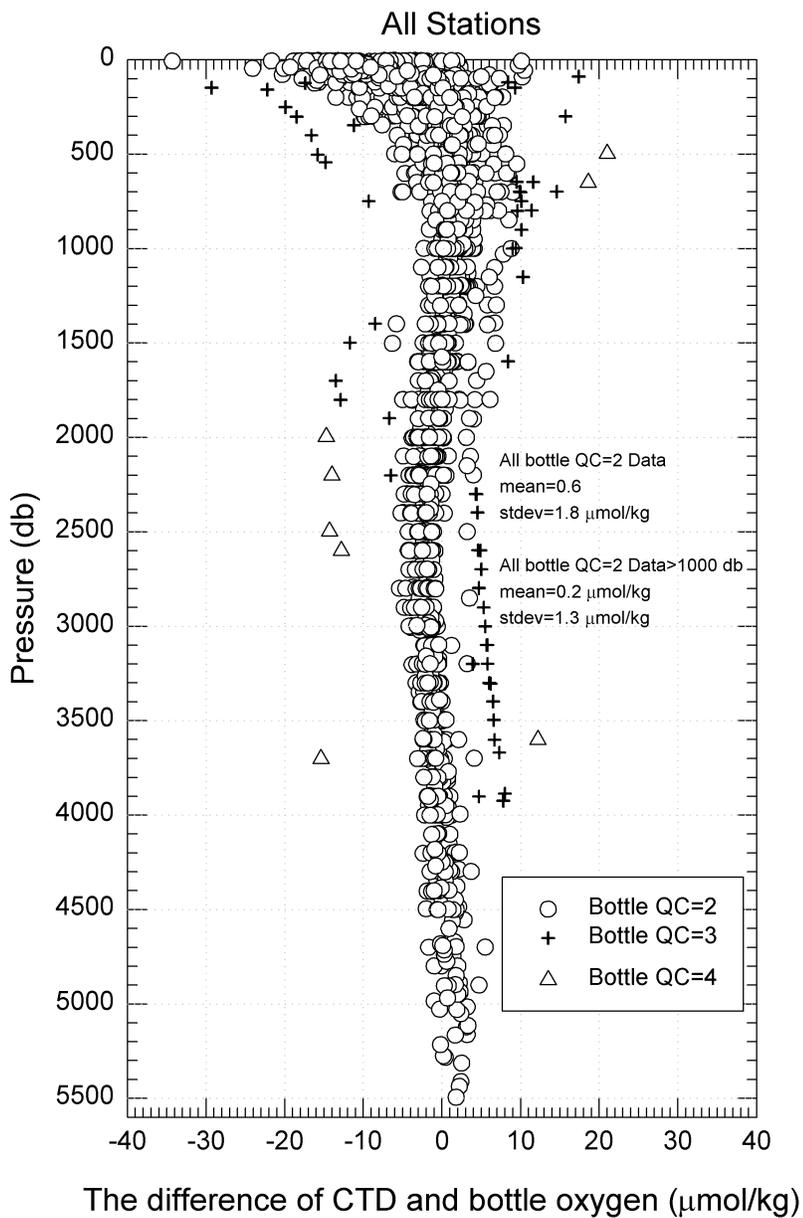


Figure 7. The difference of CTD and bottle oxygen vs. pressure

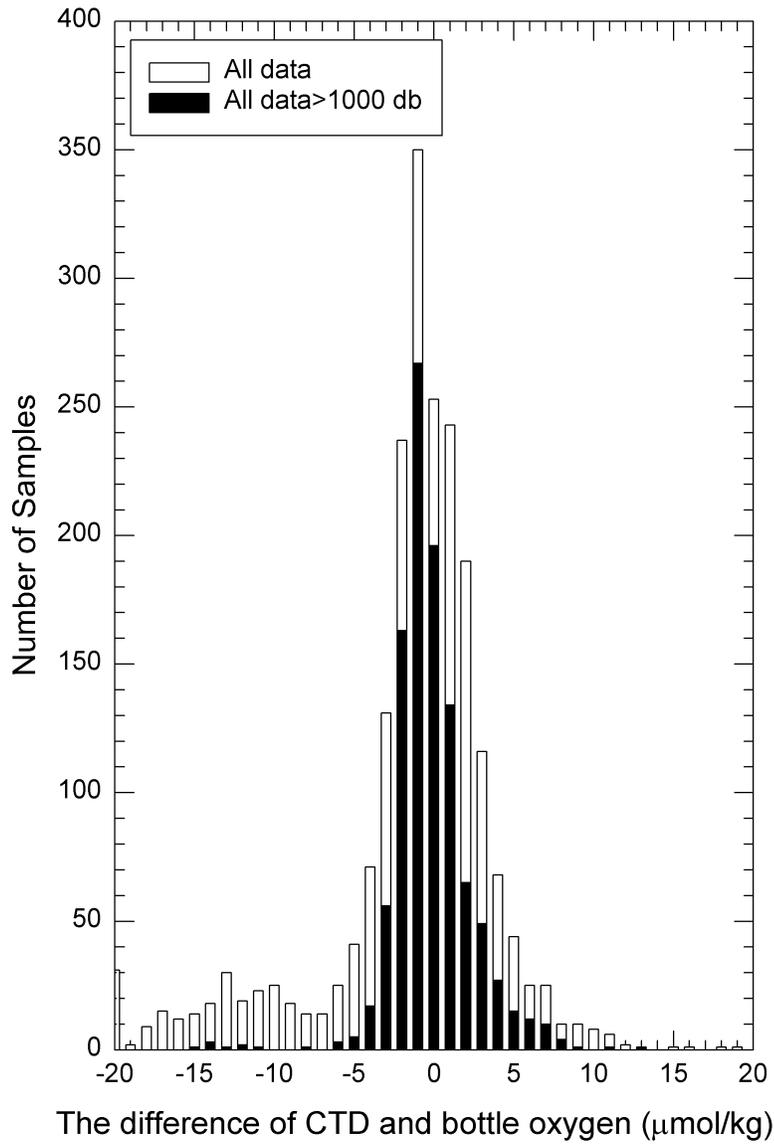


Figure 8. The difference of CTD and bottle oxygen vs. number of samples

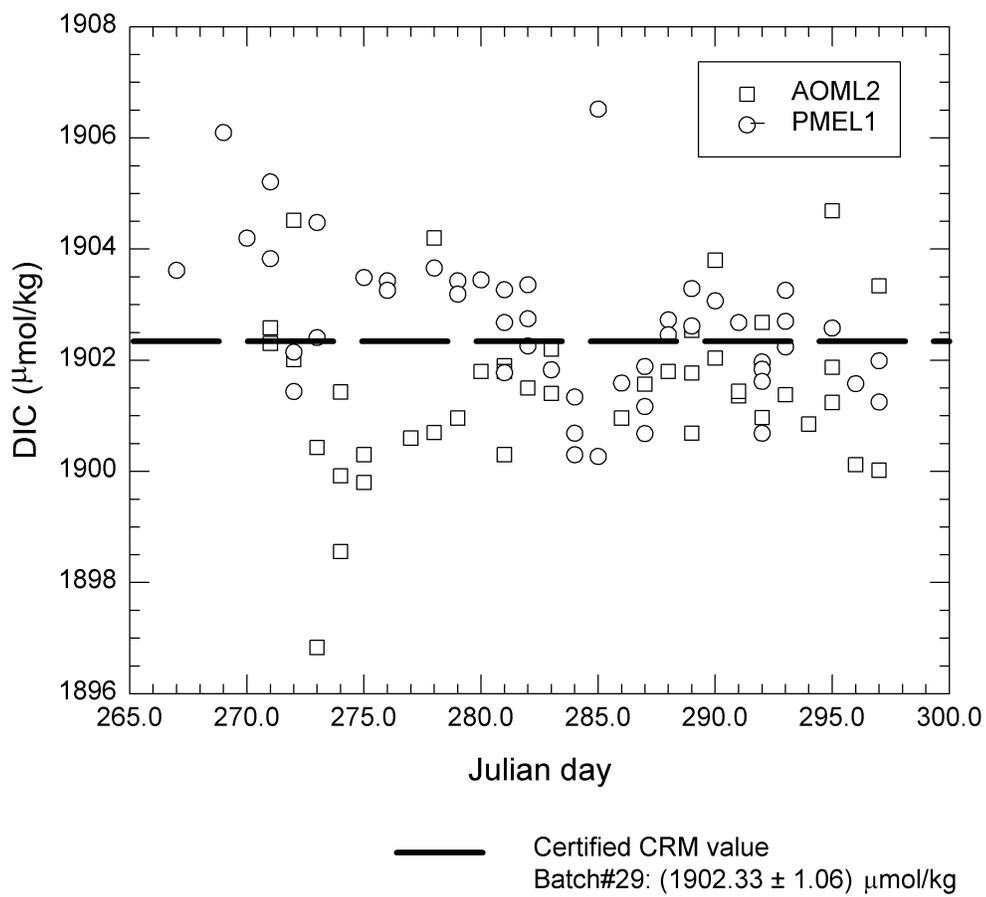


Figure 9. The results of the CRM measurements

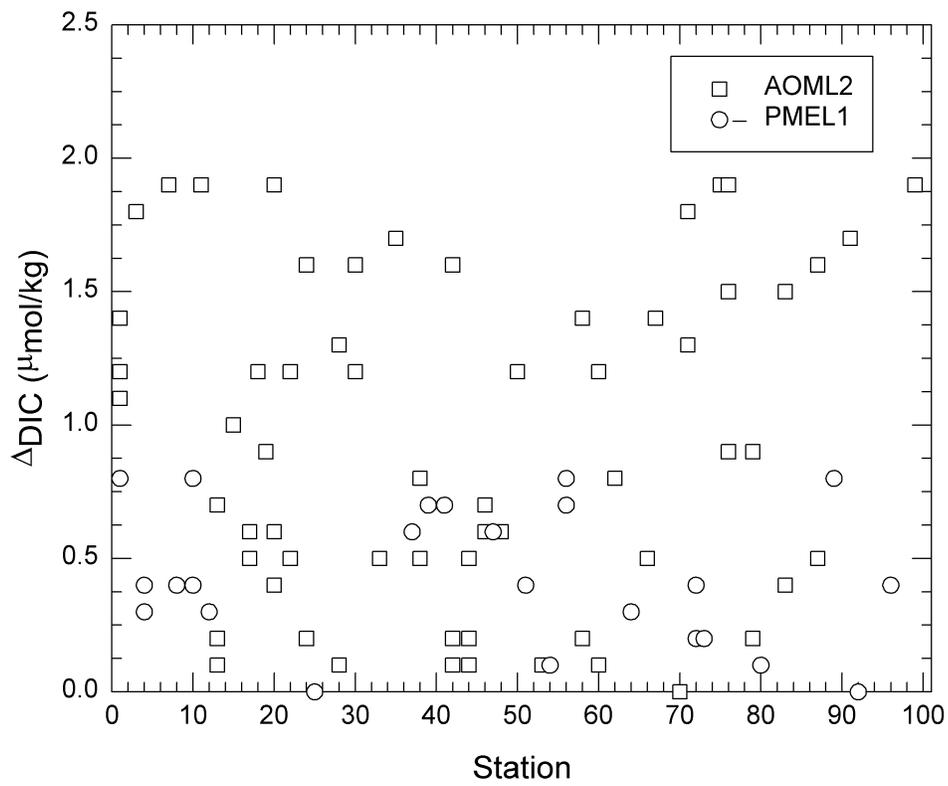


Figure 10. The difference of the DIC duplicates during the course of the cruise

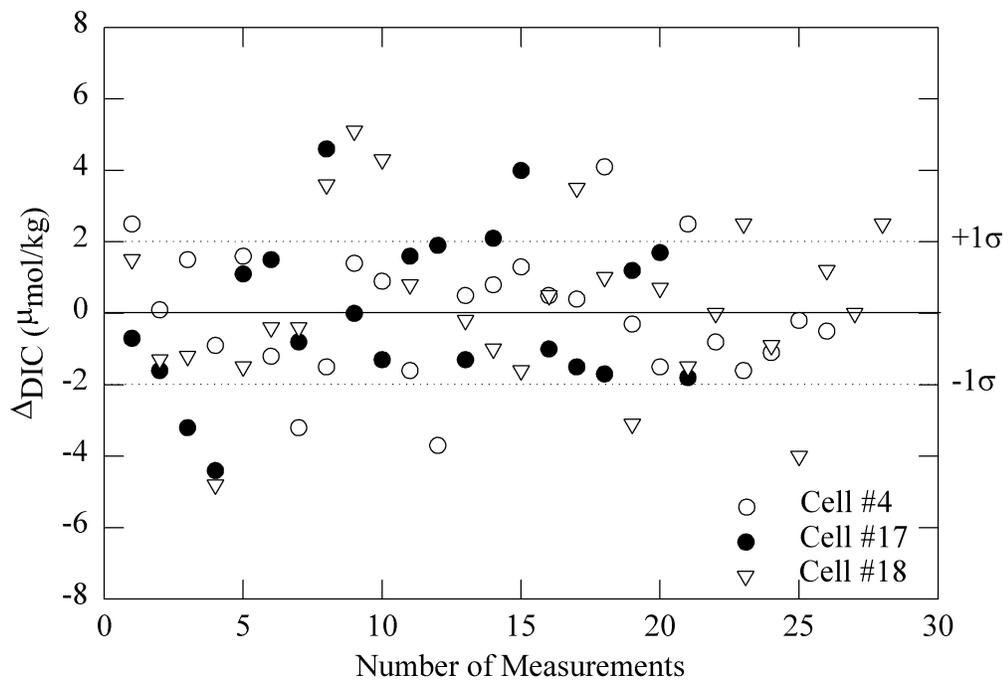
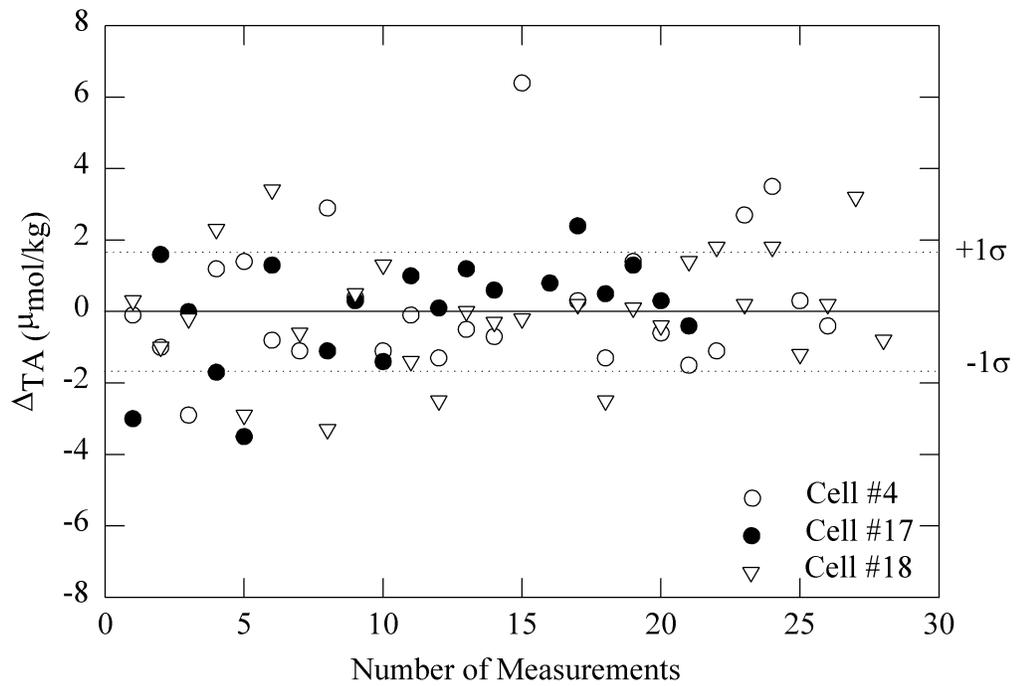


Figure 11. Potentiometric TA and DIC measurements on the Certified Reference Materials (CRMs) during the cruise.

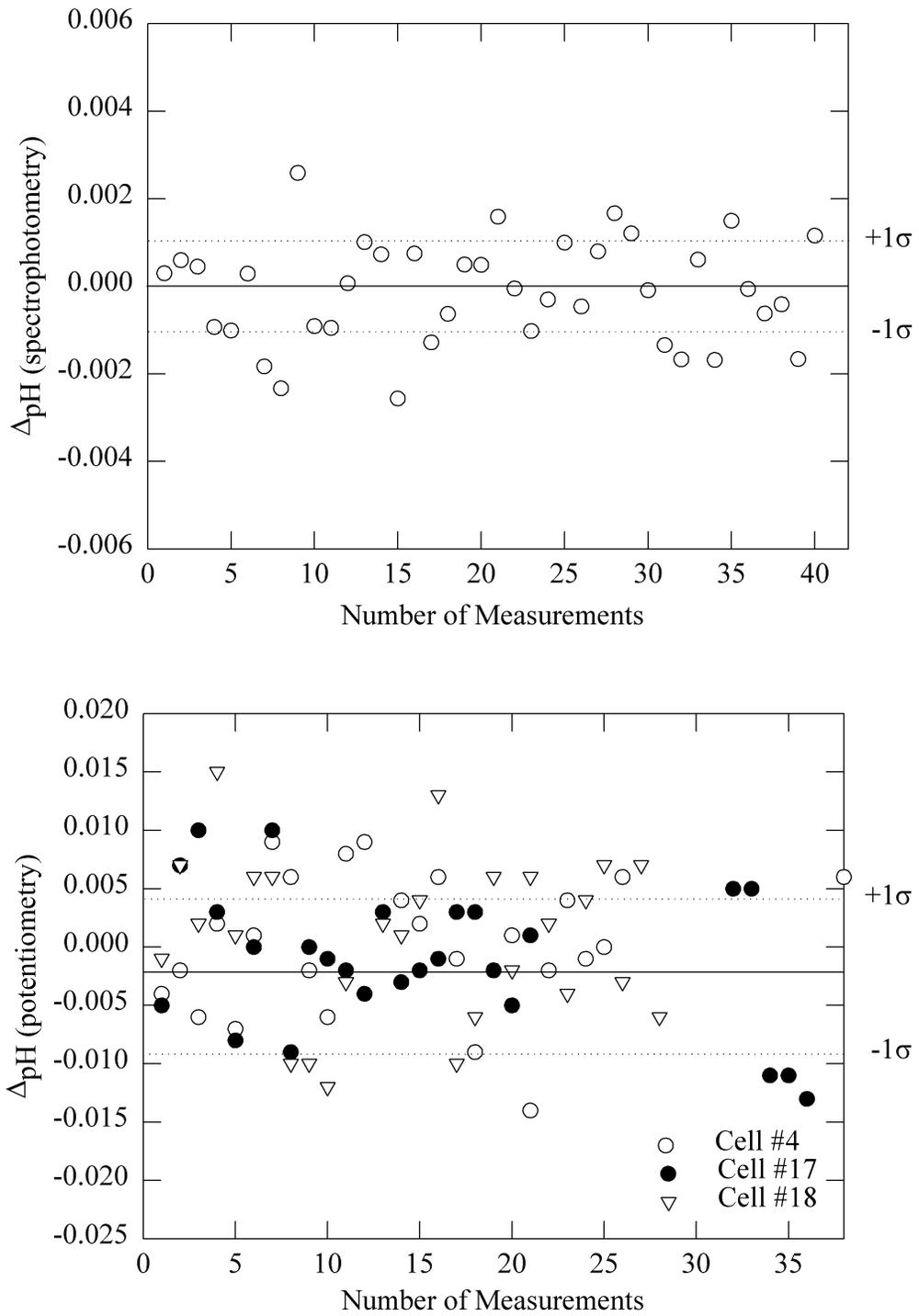


Figure 12. Spectrophotometric and potentiometric pH measurements on the Certified Reference Materials (CRMs) during the cruise.

Table 1. Station locations

| Station | Cast | CTD cast | Latitude    | Longitude    | Date      |
|---------|------|----------|-------------|--------------|-----------|
| 1       | 2    | 222      | 36 1.40 'S  | 112 43.14 'E | 9/23/1995 |
| 2       | 2    | 223      | 40 2.34 'S  | 109 21.2 'E  | 9/24/1995 |
| 3       | 2    | 224      | 43 0.00 'S  | 95 1.12 'E   | 9/28/1995 |
| 4       | 1    | 225      | 41 59.51 'S | 95 1.03 'E   | 9/28/1995 |
| 5       | 1    | 226      | 40 59.95 'S | 94 59.9 'E   | 9/28/1995 |
| 6       | 2    | 227      | 39 59.60 'S | 95 0.91 'E   | 9/29/1995 |
| 7       | 1    | 228      | 39 0.39 'S  | 95 0.86 'E   | 9/29/1995 |
| 8       | 1    | 229      | 38 0.03 'S  | 95 0.15 'E   | 9/29/1995 |
| 9       | 2    | 230      | 36 59.95 'S | 94 59.93 'E  | 9/30/1995 |
| 10      | 1    | 231      | 36 0.82 'S  | 95 1.24 'E   | 9/30/1995 |
| 11      | 1    | 232      | 34 59.92 'S | 94 58.82 'E  | 9/30/1995 |
| 12      | 2    | 233      | 34 0.18 'S  | 94 58.68 'E  | 10/1/1995 |
| 13      | 1    | 234      | 33 0.41 'S  | 95 0.35 'E   | 10/1/1995 |
| 14      | 1    | 235      | 32 30.18 'S | 94 59.81 'E  | 10/1/1995 |
| 15      | 1    | 236      | 32 0.31 'S  | 95 0.05 'E   | 10/1/1995 |
| 16      | 2    | 237      | 31 44.76 'S | 94 59.72 'E  | 10/2/1995 |
| 17      | 1    | 238      | 31 39.14 'S | 95 0.05 'E   | 10/2/1995 |
| 18      | 1    | 239      | 32 27.42 'S | 92 35.84 'E  | 10/2/1995 |
| 19      | 2    | 240      | 33 10.26 'S | 90 10.16 'E  | 10/3/1995 |
| 20      | 1    | 241      | 33 59.95 'S | 87 46.04 'E  | 10/3/1995 |
| 21      | 2    | 242      | 34 10.06 'S | 87 9.3 'E    | 10/4/1995 |
| 22      | 1    | 243      | 34 18.06 'S | 86 37.55 'E  | 10/4/1995 |
| 23      | 1    | 244      | 34 27.17 'S | 86 2.77 'E   | 10/4/1995 |
| 24      | 1    | 245      | 34 36.99 'S | 85 28.12 'E  | 10/4/1995 |
| 25      | 1    | 246      | 34 45.71 'S | 84 52.77 'E  | 10/4/1995 |
| 26      | 2    | 247      | 34 54.17 'S | 84 17.42 'E  | 10/5/1995 |
| 27      | 1    | 248      | 35 3.09 'S  | 83 42.2 'E   | 10/5/1995 |
| 28      | 1    | 249      | 35 13.13 'S | 83 8.62 'E   | 10/5/1995 |
| 29      | 1    | 250      | 35 21.56 'S | 82 33.07 'E  | 10/5/1995 |
| 30      | 2    | 251      | 35 31.82 'S | 81 58.18 'E  | 10/6/1995 |
| 31      | 1    | 252      | 35 27.37 'S | 81 29.01 'E  | 10/6/1995 |
| 32      | 1    | 253      | 35 19.63 'S | 80 49.1 'E   | 10/6/1995 |
| 33      | 1    | 254      | 35 0.13 'S  | 80 20.01 'E  | 10/6/1995 |
| 34      | 1    | 255      | 34 39.67 'S | 79 49.6 'E   | 10/7/1995 |
| 35      | 2    | 256      | 34 20.14 'S | 79 20.6 'E   | 10/7/1995 |
| 36      | 1    | 257      | 33 59.63 'S | 80 0.01 'E   | 10/7/1995 |
| 37      | 1    | 258      | 33 0.01 'S  | 80 0.06 'E   | 10/7/1995 |
| 38      | 1    | 259      | 31 58.96 'S | 80 0.29 'E   | 10/8/1995 |
| 39      | 1    | 260      | 30 59.85 'S | 80 0.6 'E    | 10/8/1995 |
| 40      | 1    | 261      | 30 0.11 'S  | 79 59.77 'E  | 10/8/1995 |
| 41      | 1    | 262      | 28 59.94 'S | 79 59.89 'E  | 10/9/1995 |
| 42      | 1    | 263      | 27 59.71 'S | 80 0.22 'E   | 10/9/1995 |
| 43      | 1    | 264      | 26 59.84 'S | 79 59.9 'E   | 10/9/1995 |
| 44      | 1    | 265      | 25 59.42 'S | 79 59.59 'E  | 10/9/1995 |

Table 1. Station locations (continued)

| Station | Cast | CTD cast | Latitude    | Longitude   | Date       |
|---------|------|----------|-------------|-------------|------------|
| 45      | 2    | 266      | 25 0.38 'S  | 79 59.68 'E | 10/10/1995 |
| 46      | 1    | 267      | 24 0.96 'S  | 79 59.13 'E | 10/10/1995 |
| 47      | 1    | 268      | 22 59.23 'S | 79 59.21 'E | 10/11/1995 |
| 48      | 2    | 269      | 22 0.94 'S  | 80 0.11 'E  | 10/11/1995 |
| 49      | 1    | 270      | 20 59.48 'S | 79 59.67 'E | 10/11/1995 |
| 50      | 1    | 271      | 19 59.46 'S | 80 0.53 'E  | 10/12/1995 |
| 51      | 1    | 272      | 19 0.00 'S  | 80 0.1 'E   | 10/12/1995 |
| 52      | 1    | 273      | 18 0.02 'S  | 80 0.31 'E  | 10/12/1995 |
| 53      | 2    | 274      | 16 58.85 'S | 79 59.64 'E | 10/13/1995 |
| 54      | 1    | 275      | 15 59.63 'S | 80 0.01 'E  | 10/13/1995 |
| 55      | 1    | 276      | 14 59.17 'S | 79 59.95 'E | 10/13/1995 |
| 56      | 1    | 277      | 14 30.03 'S | 79 59.98 'E | 10/14/1995 |
| 57      | 2    | 278      | 13 59.58 'S | 79 59.94 'E | 10/14/1995 |
| 58      | 1    | 279      | 13 29.94 'S | 80 0.01 'E  | 10/14/1995 |
| 59      | 1    | 280      | 13 0.24 'S  | 79 59.64 'E | 10/14/1995 |
| 60      | 1    | 281      | 12 29.85 'S | 80 0.04 'E  | 10/14/1995 |
| 61      | 2    | 282      | 11 59.60 'S | 80 0.35 'E  | 10/15/1995 |
| 62      | 1    | 283      | 11 29.90 'S | 79 59.75 'E | 10/15/1995 |
| 63      | 1    | 284      | 10 59.46 'S | 79 59.52 'E | 10/15/1995 |
| 64      | 1    | 285      | 10 29.48 'S | 80 0.22 'E  | 10/15/1995 |
| 65      | 2    | 286      | 9 59.46 'S  | 80 0.88 'E  | 10/16/1995 |
| 66      | 2    | 287      | 9 29.90 'S  | 80 0.29 'E  | 10/16/1995 |
| 67      | 1    | 288      | 9 0.01 'S   | 80 0.56 'E  | 10/16/1995 |
| 68      | 1    | 289      | 8 24.03 'S  | 80 0.19 'E  | 10/16/1995 |
| 69      | 2    | 290      | 7 59.88 'S  | 80 0.34 'E  | 10/17/1995 |
| 70      | 1    | 291      | 7 30.07 'S  | 79 59.72 'E | 10/17/1995 |
| 71      | 1    | 292      | 7 0.00 'S   | 79 59.43 'E | 10/17/1995 |
| 72      | 1    | 293      | 6 29.26 'S  | 79 59.3 'E  | 10/17/1995 |
| 73      | 1    | 294      | 5 59.72 'S  | 79 58.47 'E | 10/18/1995 |
| 74      | 1    | 295      | 5 29.71 'S  | 79 59.1 'E  | 10/18/1995 |
| 75      | 1    | 296      | 4 59.75 'S  | 80 0.27 'E  | 10/18/1995 |
| 76      | 1    | 297      | 4 29.73 'S  | 80 0.22 'E  | 10/18/1995 |
| 77      | 1    | 298      | 3 59.39 'S  | 80 0.36 'E  | 10/19/1995 |
| 78      | 1    | 299      | 3 29.98 'S  | 80 0.35 'E  | 10/19/1995 |
| 79      | 1    | 300      | 2 59.54 'S  | 80 0.01 'E  | 10/19/1995 |
| 80      | 1    | 301      | 2 30.19 'S  | 80 0.27 'E  | 10/19/1995 |
| 81      | 1    | 302      | 2 0.34 'S   | 80 0.44 'E  | 10/20/1995 |
| 82      | 1    | 303      | 1 29.96 'S  | 80 0.4 'E   | 10/20/1995 |
| 83      | 1    | 304      | 1 0.26 'S   | 80 0.92 'E  | 10/20/1995 |
| 84      | 1    | 305      | 0 45.57 'N  | 79 59.98 'E | 10/20/1995 |
| 85      | 1    | 306      | 0 30.35 'N  | 80 0.48 'E  | 10/20/1995 |
| 86      | 1    | 307      | 0 15.33 'N  | 80 0.35 'E  | 10/21/1995 |
| 87      | 1    | 308      | 0 0.46 'N   | 80 0.35 'E  | 10/21/1995 |
| 88      | 1    | 309      | 0 14.71 'N  | 80 0.35 'E  | 10/21/1995 |

Table 1. Station locations (continued)

| Station | Cast | CTD cast | Latitude   | Longitude   | Date       |
|---------|------|----------|------------|-------------|------------|
| 89      | 1    | 310      | 0 29.77 'N | 80 0.15 'E  | 10/21/1995 |
| 90      | 1    | 311      | 0 44.53 'N | 80 0.06 'E  | 10/21/1995 |
| 91      | 1    | 312      | 0 59.63 'N | 80 0.35 'E  | 10/21/1995 |
| 92      | 2    | 313      | 1 28.65 'N | 80 0.14 'E  | 10/22/1995 |
| 93      | 1    | 314      | 1 59.79 'N | 80 1.01 'E  | 10/22/1995 |
| 94      | 1    | 315      | 2 29.93 'N | 79 59.81 'E | 10/22/1995 |
| 95      | 1    | 316      | 2 59.47 'N | 80 0.1 'E   | 10/22/1995 |
| 96      | 2    | 317      | 3 29.16 'N | 79 59.8 'E  | 10/23/1995 |
| 97      | 1    | 318      | 3 59.35 'N | 79 59.86 'E | 10/23/1995 |
| 98      | 1    | 319      | 4 29.63 'N | 80 0.09 'E  | 10/23/1995 |
| 99      | 1    | 320      | 4 59.61 'N | 79 59.43 'E | 10/23/1995 |
| 100     | 1    | 321      | 5 30.97 'N | 79 59.43 'E | 10/24/1995 |
| 101     | 2    | 322      | 5 47.22 'N | 79 59.83 'E | 10/24/1995 |

Table 2. Results of the certified reference material, CRM  
 (Assigned value by SIO Batch 29 =  $(1902.33 \pm 1.06)$   $\mu\text{mol/kg}$   
 Coulometer: AOML-2

| Date     | Time     | Julian Day | DIC ( $\mu\text{mol/kg}$ ) |
|----------|----------|------------|----------------------------|
| 9/27/91  | 10:01:23 | 271        | 1902.3                     |
| 9/27/91  | 23:15:45 | 271        | 1902.6                     |
| 9/28/91  | 16:33:29 | 272        | 1904.5                     |
| 9/28/91  | 19:54:06 | 272        | 1902.0                     |
| 9/29/91  | 8:54:42  | 273        | 1900.4                     |
| 9/29/91  | 17:47:02 | 273        | 1896.8                     |
| 9/30/91  | 1:41:40  | 274        | 1901.4                     |
| 9/30/91  | 12:43:34 | 274        | 1899.9                     |
| 9/30/91  | 16:06:38 | 274        | 1898.6                     |
| 10/1/91  | 2:12:11  | 275        | 1899.8                     |
| 10/1/91  | 13:36:11 | 275        | 1900.3                     |
| 10/3/91  | 1:47:30  | 277        | 1900.6                     |
| 10/4/91  | 3:26:33  | 278        | 1900.7                     |
| 10/4/91  | 17:42:19 | 278        | 1904.2                     |
| 10/5/91  | 23:21:38 | 279        | 1901.0                     |
| 10/6/91  | 15:25:35 | 280        | 1901.8                     |
| 10/7/91  | 2:53:24  | 281        | 1901.9                     |
| 10/7/91  | 13:40:38 | 281        | 1901.8                     |
| 10/7/91  | 16:38:14 | 281        | 1900.3                     |
| 10/8/91  | 9:46:52  | 282        | 1901.5                     |
| 10/9/91  | 2:53:45  | 283        | 1902.2                     |
| 10/9/91  | 14:28:37 | 283        | 1901.4                     |
| 10/12/91 | 23:27:49 | 286        | 1901.0                     |
| 10/13/91 | 15:00:19 | 287        | 1901.6                     |
| 10/14/91 | 4:46:02  | 288        | 1901.8                     |
| 10/15/91 | 6:58:01  | 289        | 1902.5                     |
| 10/15/91 | 14:30:43 | 289        | 1900.7                     |
| 10/15/91 | 19:21:40 | 289        | 1901.8                     |
| 10/16/91 | 14:13:08 | 290        | 1903.8                     |
| 10/16/91 | 20:12:56 | 290        | 1902.0                     |
| 10/17/91 | 12:51:34 | 291        | 1901.4                     |
| 10/17/91 | 20:08:23 | 291        | 1901.4                     |
| 10/18/91 | 9:34:28  | 292        | 1902.7                     |
| 10/18/91 | 23:16:50 | 292        | 1901.0                     |
| 10/19/91 | 12:43:56 | 293        | 1901.4                     |
| 10/20/91 | 4:21:52  | 294        | 1900.9                     |
| 10/21/91 | 3:52:39  | 295        | 1901.9                     |
| 10/21/91 | 15:55:30 | 295        | 1904.7                     |
| 10/21/91 | 20:39:06 | 295        | 1901.2                     |
| 10/22/91 | 11:46:41 | 296        | 1900.1                     |
| 10/23/91 | 0:51:30  | 297        | 1903.3                     |
| 10/23/91 | 3:07:16  | 297        | 1900.0                     |

Table 2. Results of the certified reference material, CRM (continued)  
 (Assigned value by SIO Batch 29 =  $(1902.33 \pm 1.06)$   $\mu\text{mol/kg}$   
 Coulometer: PMEL-1

| Date     | Time     | Julian Day | DIC ( $\mu\text{mol/kg}$ ) |
|----------|----------|------------|----------------------------|
| 9/23/91  | 19:00:19 | 267        | 1903.62                    |
| 9/25/91  | 13:01:51 | 269        | 1906.10                    |
| 9/26/91  | 13:36:04 | 270        | 1904.20                    |
| 9/27/91  | 8:27:33  | 271        | 1905.21                    |
| 9/27/91  | 15:09:44 | 271        | 1903.83                    |
| 9/28/91  | 9:23:56  | 272        | 1902.15                    |
| 9/28/91  | 15:49:32 | 272        | 1901.44                    |
| 9/29/91  | 11:51:02 | 273        | 1904.48                    |
| 9/29/91  | 22:39:20 | 273        | 1902.41                    |
| 10/1/91  | 7:54:47  | 275        | 1903.49                    |
| 10/2/91  | 8:47:21  | 276        | 1903.43                    |
| 10/2/91  | 19:50:11 | 276        | 1903.26                    |
| 10/4/91  | 9:37:11  | 278        | 1903.66                    |
| 10/5/91  | 6:36:14  | 279        | 1903.43                    |
| 10/5/91  | 21:44:11 | 279        | 1903.19                    |
| 10/6/91  | 12:14:13 | 280        | 1903.45                    |
| 10/7/91  | 2:26:36  | 281        | 1903.27                    |
| 10/7/91  | 14:20:10 | 281        | 1901.78                    |
| 10/7/91  | 17:05:47 | 281        | 1902.68                    |
| 10/8/91  | 6:45:50  | 282        | 1902.26                    |
| 10/8/91  | 15:22:36 | 282        | 1902.75                    |
| 10/8/91  | 19:04:45 | 282        | 1903.36                    |
| 10/9/91  | 10:25:59 | 283        | 1901.83                    |
| 10/10/91 | 3:09:22  | 284        | 1900.69                    |
| 10/10/91 | 13:05:28 | 284        | 1901.34                    |
| 10/10/91 | 20:36:19 | 284        | 1900.30                    |
| 10/11/91 | 13:42:00 | 285        | 1906.52                    |
| 10/11/91 | 14:09:47 | 285        | 1900.27                    |
| 10/12/91 | 12:07:59 | 286        | 1901.59                    |
| 10/13/91 | 4:29:17  | 287        | 1900.68                    |
| 10/13/91 | 16:32:57 | 287        | 1901.17                    |
| 10/13/91 | 21:33:43 | 287        | 1901.89                    |
| 10/14/91 | 7:11:08  | 288        | 1902.73                    |
| 10/14/91 | 10:44:15 | 288        | 1902.46                    |
| 10/15/91 | 4:08:42  | 289        | 1902.62                    |
| 10/15/91 | 18:38:45 | 289        | 1903.29                    |
| 10/16/91 | 10:13:52 | 290        | 1903.07                    |
| 10/17/91 | 4:26:09  | 291        | 1902.68                    |
| 10/18/91 | 5:03:11  | 292        | 1901.97                    |
| 10/18/91 | 7:43:39  | 292        | 1901.84                    |
| 10/18/91 | 18:49:56 | 292        | 1900.69                    |
| 10/18/91 | 19:25:57 | 292        | 1901.62                    |
| 10/19/91 | 4:44:58  | 293        | 1902.24                    |
| 10/19/91 | 13:38:01 | 293        | 1903.26                    |
| 10/19/91 | 17:00:08 | 293        | 1902.70                    |

Table 2. Results of the certified reference material, CRM (continued)  
(Assigned value by SIO Batch 29 =  $(1902.33 \pm 1.06)$   $\mu\text{mol/kg}$ )  
Coulometer: PMEL-1

| Date     | Time     | Julian Day | DIC ( $\mu\text{mol/kg}$ ) |
|----------|----------|------------|----------------------------|
| 10/21/91 | 8:17:04  | 295        | 1902.58                    |
| 10/22/91 | 4:50:48  | 296        | 1901.58                    |
| 10/23/91 | 3:55:10  | 297        | 1901.99                    |
| 10/23/91 | 13:20:23 | 297        | 1901.25                    |

Table 3. Dissolved inorganic carbon duplicates

| Station# | Cast# | Bottle# | Pressure/db | DIC ( $\mu\text{mol/kg}$ ) | Stdev | Coulometer  |
|----------|-------|---------|-------------|----------------------------|-------|-------------|
| 1        | 2     | 2       | 2000        | 2265.5                     | 0.00  | AOML2/PMEL1 |
| 2        | 2     | 1       | 4675        | 2263.9                     | 1.88  | AOML2       |
| 2        | 2     | 23      | 30          | 2087.3                     | 1.59  | AOML3       |
| 3        | 2     | 2       | 3200        | 2254.6                     | 1.27  | AOML4       |
| 3        | 2     | 22      | 50          | 2093.5                     | 1.94  | AOML5       |
| 4        | 1     | 1       | 3293        | 2258.1                     | 0.31  | PMEL1       |
| 4        | 1     | 23      | 50          | 2093.8                     | 0.24  | PMEL1       |
| 5        | 1     | 1       | 3487        | 2259.1                     | 1.74  | AOML2       |
| 5        | 1     | 22      | 100         | 2094.3                     | 2.24  | AOML2       |
| 6        | 2     | 23      | 50          | 2094.6                     | 2.52  | PMEL1       |
| 7        | 1     | 2       | 3400        | 2256.5                     | 3.33  | AOML2       |
| 7        | 1     | 23      | 50          | 2086.0                     | 1.34  | AOML2       |
| 8        | 1     | 1       | 4150        | 2268.5                     | 0.27  | PMEL1       |
| 8        | 1     | 24      | 8           | 2089.4                     | 2.05  | PMEL1       |
| 9        | 2     | 2       | 3900        | 2264.4                     | 3.38  | AOML2       |
| 9        | 2     | 9       | 2200        | 2260.4                     | 4.71  | AOML2       |
| 9        | 2     | 23      | 50          | 2081.2                     | 3.34  | AOML2       |
| 10       | 1     | 2       | 4000        | 2262.7                     | 1.13  | PMEL1       |
| 10       | 1     | 6       | 2500        | 2247.6                     | 0.26  | PMEL1       |
| 10       | 1     | 23      | 50          | 2082.0                     | 2.52  | PMEL1       |
| 11       | 1     | 1       | 4556        | 2266.2                     | 3.10  | AOML2       |
| 11       | 1     | 6       | 3000        | 2253.1                     | 1.37  | AOML2       |
| 11       | 1     | 24      | 10          | 2079.5                     | 2.47  | AOML2       |
| 12       | 2     | 2       | 4200        | 2266.4                     | 1.66  | PMEL1       |
| 12       | 2     | 15      | 1000        | 2138.6                     | 0.24  | PMEL1       |
| 13       | 1     | 2       | 3800        | 2265.2                     | 0.04  | AOML2       |
| 13       | 1     | 9       | 1700        | 2264.6                     | 0.16  | AOML2       |
| 13       | 1     | 23      | 50          | 2072.4                     | 0.52  | AOML2       |
| 14       | 1     | 24      | 7           | 2072.0                     | 1.01  | PMEL1       |
| 15       | 1     | 1       | 4244        | 2266.4                     | 0.74  | AOML2       |
| 16       | 2     | 1       | 3010        | 2256.9                     | 1.21  | PMEL1       |
| 17       | 1     | 2       | 1400        | 2257.4                     | 1.45  | AOML2       |
| 17       | 1     | 6       | 1000        | 2188.1                     | 0.35  | AOML2       |
| 17       | 1     | 22      | 7           | 2075.0                     | 0.45  | AOML2       |
| 18       | 1     | 2       | 4300        | 2267.4                     | 2.65  | AOML2       |
| 18       | 1     | 24      | 9           | 2064.1                     | 0.83  | AOML2       |
| 19       | 2     | 2       | 3600        | 2262.9                     | 2.75  | AOML2       |
| 19       | 2     | 5       | 2700        | 2251.2                     | 2.28  | AOML2       |
| 19       | 2     | 24      | 9           | 2073.9                     | 0.65  | AOML2       |
| 20       | 1     | 1       | 3643        | 2265.1                     | 0.40  | AOML2       |
| 20       | 1     | 4       | 2600        | 2250.8                     | 1.36  | AOML2       |
| 20       | 1     | 24      | 6           | 2078.1                     | 0.30  | AOML2       |
| 21       | 2     | 24      | 7           | 2076.4                     | 0.24  | PMEL1       |
| 22       | 1     | 1       | 3342        | 2260.2                     | 0.32  | AOML2       |
| 22       | 1     | 24      | 7           | 2077.5                     | 0.01  | AOML2       |

Table 3. Dissolved inorganic carbon duplicates (continued)

| Station# | Cast# | Bottle# | Pressure/db | DIC ( $\mu\text{mol/kg}$ ) | Stdev | Coulometer |
|----------|-------|---------|-------------|----------------------------|-------|------------|
| 23       | 1     | 1       | 3342        | 2262.4                     | 0.67  | PMEL1      |
| 23       | 1     | 23      | 40          | 2079.9                     | 1.65  | PMEL1      |
| 24       | 1     | 1       | 3541        | 2263.5                     | 1.13  | AOML2      |
| 24       | 1     | 10      | 1700        | 2258.8                     | 0.11  | AOML2      |
| 25       | 1     | 1       | 3711        | 2263.8                     | 0.03  | PMEL1      |
| 25       | 1     | 24      | 9           | 2080.2                     | 1.15  | PMEL1      |
| 26       | 2     | 1       | 3822        | 2264.3                     | 1.88  | AOML2      |
| 26       | 2     | 24      | 7           | 2080.2                     | 1.77  | AOML2      |
| 27       | 1     | 1       | 3804        | 2265.9                     | 2.12  | PMEL1      |
| 27       | 1     | 24      | 9           | 2078.0                     | 2.99  | PMEL1      |
| 28       | 1     | 1       | 3722        | 2262.7                     | 0.10  | AOML2      |
| 28       | 1     | 24      | 7           | 2076.4                     | 0.95  | AOML2      |
| 29       | 1     | 1       | 3770        | 2264.8                     | 3.22  | PMEL1      |
| 29       | 1     | 24      | 6           | 2075.8                     | 0.45  | PMEL1      |
| 30       | 2     | 1       | 4293        | 2262.2                     | 0.87  | AOML2      |
| 30       | 2     | 24      | 6           | 2077.5                     | 1.12  | AOML2      |
| 31       | 1     | 1       | 2976        | 2259.0                     | 4.21  | PMEL1      |
| 31       | 1     | 24      | 7           | 2077.0                     | 2.14  | PMEL1      |
| 32       | 1     | 1       | 2992        | 2252.3                     | 3.02  | PMEL1      |
| 32       | 1     | 24      | 7           | 2079.1                     | 1.54  | PMEL1      |
| 33       | 1     | 24      | 6           | 2078.2                     | 0.36  | AOML2      |
| 34       | 1     | 1       | 3200        | 2257.9                     | 1.22  | PMEL1      |
| 34       | 1     | 21      | 120         | 2081.6                     | 2.30  | PMEL1      |
| 34       | 1     | 23      | 40          | 2076.3                     | 3.10  | PMEL1      |
| 35       | 2     | 1       | 2973        | 2267.5                     | 2.49  | AOML2      |
| 35       | 2     | 24      | 9           | 2071.9                     | 1.18  | AOML2      |
| 36       | 1     | 1       | 3608        | 2255.3                     | 3.39  | AOML2      |
| 36       | 1     | 24      | 8           | 2073.1                     | 2.75  | AOML2      |
| 37       | 1     | 1       | 3300        | 2258.5                     | 0.42  | PMEL1      |
| 37       | 1     | 24      | 7           | 2071.0                     | 0.91  | PMEL1      |
| 38       | 2     | 1       | 3924        | 2265.6                     | 0.38  | AOML2      |
| 38       | 2     | 24      | 7           | 2066.4                     | 0.55  | AOML2      |
| 39       | 1     | 1       | 3888        | 2268.0                     | 0.49  | PMEL1      |
| 39       | 1     | 24      | 7           | 2063.9                     | 2.02  | PMEL1      |
| 40       | 1     | 1       | 3800        | 2268.8                     | 2.36  | AOML2      |
| 40       | 1     | 24      | 7           | 2062.7                     | 1.42  | AOML2      |
| 41       | 1     | 1       | 4011        | 2273.3                     | 0.47  | PMEL1      |
| 41       | 1     | 2       | 3650        | 2268.3                     | 3.75  | PMEL1      |
| 41       | 1     | 24      | 7           | 2056.9                     | 0.85  | PMEL1      |
| 42       | 1     | 1       | 4252        | 2275.9                     | 0.04  | AOML2      |
| 42       | 1     | 11      | 1250        | 2243.3                     | 0.17  | AOML2      |
| 42       | 1     | 24      | 8           | 2044.3                     | 1.14  | AOML2      |
| 43       | 1     | 1       | 4448        | 2277.3                     | 1.59  | PMEL1      |
| 43       | 1     | 24      | 7           | 2031.6                     | 0.38  | PMEL1      |
| 44       | 1     | 1       | 4336        | 2279.0                     | 0.06  | AOML2      |

Table 3. Dissolved inorganic carbon duplicates (continued)

| Station# | Cast# | Bottle# | Pressure/db | DIC ( $\mu\text{mol/kg}$ ) | Stdev | Coulometer |
|----------|-------|---------|-------------|----------------------------|-------|------------|
| 44       | 1     | 12      | 950         | 2183.2                     | 0.14  | AOML2      |
| 44       | 1     | 24      | 4           | 2006.1                     | 0.36  | AOML2      |
| 45       | 2     | 1       | 3673        | 2278.1                     | 2.62  | PMEL1      |
| 45       | 2     | 24      | 9           | 1993.6                     | 1.22  | PMEL1      |
| 46       | 1     | 1       | 4441        | 2288.5                     | 0.46  | AOML2      |
| 46       | 1     | 24      | 7           | 1994.3                     | 0.42  | AOML2      |
| 47       | 1     | 1       | 4561        | 2290.2                     | 0.41  | PMEL1      |
| 47       | 1     | 24      | 7           | 2003.8                     | 0.13  | PMEL1      |
| 48       | 2     | 1       | 4800        | 2294.3                     | 0.45  | AOML2      |
| 48       | 2     | 24      | 7           | 1982.5                     | 1.75  | AOML2      |
| 49       | 1     | 1       | 4745        | 2293.0                     | 2.68  | PMEL1      |
| 49       | 1     | 24      | 6           | 1967.9                     | 0.17  | PMEL1      |
| 50       | 1     | 1       | 4937        | 2295.8                     | 1.46  | AOML2      |
| 50       | 1     | 24      | 7           | 1973.1                     | 0.83  | AOML2      |
| 51       | 1     | 1       | 4889        | 2294.7                     | 0.30  | PMEL1      |
| 51       | 1     | 24      | 8           | 1950.5                     | 0.34  | PMEL1      |
| 52       | 1     | 1       | 5162        | 2292.7                     | 0.77  | PMEL1      |
| 52       | 1     | 4       | 3900        | 2290.3                     | 3.90  | PMEL1      |
| 52       | 1     | 24      | 7           | 1949.1                     | 0.54  | PMEL1      |
| 53       | 2     | 1       | 5204        | 2296.2                     | 1.48  | AOML2      |
| 53       | 2     | 24      | 6           | 1946.4                     | 0.04  | AOML2      |
| 54       | 1     | 1       | 5117        | 2298.1                     | 0.07  | PMEL1      |
| 54       | 1     | 24      | 9           | 1943.9                     | 0.04  | PMEL1      |
| 55       | 1     | 1       | 5053        | 2298.9                     | 1.56  | AOML2      |
| 55       | 1     | 24      | 8           | 1942.2                     | 1.74  | AOML2      |
| 56       | 1     | 1       | 3000        | 2290.6                     | 0.53  | PMEL1      |
| 56       | 1     | 15      | 50          | 1947.4                     | 0.50  | PMEL1      |
| 57       | 2     | 1       | 5032        | 2298.2                     | 0.69  | PMEL1      |
| 57       | 2     | 24      | 7           | 1942.3                     | 0.10  | PMEL1      |
| 58       | 1     | 1       | 3000        | 2292.9                     | 0.16  | AOML2      |
| 58       | 1     | 16      | 7           | 1952.5                     | 0.99  | AOML2      |
| 59       | 1     | 1       | 4949        | 2297.6                     | 1.44  | PMEL1      |
| 59       | 1     | 24      | 8           | 1950.7                     | 1.14  | PMEL1      |
| 60       | 1     | 1       | 3000        | 2295.6                     | 0.85  | AOML2      |
| 60       | 1     | 14      | 75          | 1998.2                     | 0.04  | AOML2      |
| 61       | 2     | 2       | 5163        | 2299.8                     | 1.34  | PMEL1      |
| 61       | 2     | 24      | 7           | 1959.2                     | 2.01  | PMEL1      |
| 62       | 1     | 1       | 3000        | 2297.1                     | 1.66  | AOML2      |
| 62       | 1     | 16      | 8           | 1949.6                     | 0.53  | AOML2      |
| 63       | 1     | 1       | 5411        | 2296.0                     | 1.76  | AOML2      |
| 64       | 1     | 1       | 3000        | 2296.4                     | 0.20  | PMEL1      |
| 64       | 1     | 16      | 7           | 1932.9                     | 0.11  | PMEL1      |
| 65       | 2     | 1       | 5436        | 2295.4                     | 2.07  | PMEL1      |
| 65       | 2     | 24      | 8           | 1924.1                     | 1.06  | PMEL1      |
| 66       | 1     | 9       | 3000        | 2301.6                     | 1.61  | AOML2      |

Table 3. Dissolved inorganic carbon duplicates (continued)

| Station# | Cast# | Bottle# | Pressure/db | DIC ( $\mu\text{mol/kg}$ ) | Stdev | Coulometer |
|----------|-------|---------|-------------|----------------------------|-------|------------|
| 66       | 1     | 24      | 8           | 1908.2                     | 0.38  | AOML2      |
| 67       | 1     | 1       | 5286        | 2299.2                     | 1.03  | AOML2      |
| 67       | 1     | 24      | 7           | 1899.9                     | 1.66  | AOML2      |
| 68       | 1     | 16      | 6           | 1902.4                     | 1.73  | PMEL1      |
| 69       | 2     | 1       | 5493        | 2294.4                     | 2.52  | PMEL1      |
| 69       | 2     | 24      | 7           | 1900.3                     | 0.58  | PMEL1      |
| 70       | 1     | 16      | 8           | 1885.1                     | 0.03  | AOML2      |
| 71       | 1     | 1       | 4485        | 2294.2                     | 0.92  | AOML2      |
| 71       | 1     | 24      | 6           | 1882.1                     | 1.26  | AOML2      |
| 72       | 1     | 1       | 3000        | 2303.9                     | 0.18  | PMEL1      |
| 72       | 1     | 15      | 40          | 1909.5                     | 0.26  | PMEL1      |
| 73       | 2     | 1       | 5275        | 2293.1                     | 0.16  | PMEL1      |
| 73       | 2     | 24      | 9           | 1882.0                     | 0.22  | PMEL1      |
| 75       | 1     | 1       | 5213        | 2294.7                     | 1.36  | AOML2      |
| 75       | 1     | 24      | 7           | 1912.3                     | 2.57  | AOML2      |
| 76       | 1     | 1       | 3000        | 2307.3                     | 0.66  | AOML2      |
| 76       | 1     | 16      | 8           | 1913.4                     | 1.05  | AOML2      |
| 77       | 2     | 1       | 4861        | 2300.4                     | 0.81  | PMEL1      |
| 77       | 2     | 24      | 6           | 1920.5                     | 0.66  | PMEL1      |
| 79       | 1     | 1       | 5029        | 2299.7                     | 0.66  | AOML2      |
| 79       | 1     | 24      | 6           | 1923.9                     | 0.14  | AOML2      |
| 80       | 1     | 1       | 3000        | 2307.4                     | 0.05  | PMEL1      |
| 80       | 1     | 16      | 6           | 1937.2                     | 1.39  | PMEL1      |
| 81       | 1     | 24      | 6           | 1928.5                     | 0.35  | PMEL1      |
| 82       | 1     | 2       | 2500        | 2308.6                     | 2.26  | AOML2      |
| 83       | 2     | 1       | 4740        | 2305.4                     | 1.09  | AOML2      |
| 83       | 2     | 24      | 9           | 1932.9                     | 0.28  | AOML2      |
| 84       | 1     | 11      | 250         | 2201.6                     | 0.99  | PMEL1      |
| 85       | 1     | 1       | 4773        | 2305.2                     | 3.35  | PMEL1      |
| 85       | 1     | 24      | 6           | 1931.9                     | 1.77  | PMEL1      |
| 86       | 1     | 1       | 3000        | 2312.8                     | 2.46  | PMEL1      |
| 86       | 1     | 16      | 6           | 1944.9                     | 0.21  | PMEL1      |
| 87       | 2     | 1       | 4739        | 2304.5                     | 0.35  | AOML2      |
| 87       | 2     | 24      | 8           | 1946.2                     | 1.13  | AOML2      |
| 88       | 1     | 11      | 250         | 2203.5                     | 0.48  | PMEL1      |
| 89       | 1     | 1       | 4714        | 2305.2                     | 0.55  | PMEL1      |
| 90       | 1     | 1       | 3000        | 2314.4                     | 0.82  | PMEL1      |
| 90       | 1     | 16      | 6           | 1937.1                     | 0.08  | PMEL1      |
| 91       | 1     | 1       | 4691        | 2305.4                     | 3.17  | AOML2      |
| 91       | 1     | 24      | 7           | 1945.7                     | 1.17  | AOML2      |
| 92       | 2     | 1       | 3000        | 2314.8                     | 0.00  | PMEL1      |
| 93       | 1     | 24      | 7           | 1942.5                     | 1.97  | PMEL1      |
| 94       | 1     | 1       | 3160        | 2320.7                     | 1.55  | AOML2      |
| 96       | 2     | 11      | 350         | 2233.8                     | 0.30  | PMEL1      |
| 96       | 2     | 16      | 9           | 1949.3                     | 0.51  | PMEL1      |

Table 3. Dissolved inorganic carbon duplicates (continued)

| Station# | Cast# | Bottle# | Pressure/db | DIC ( $\mu\text{mol/kg}$ ) | Stdev | Coulometer |
|----------|-------|---------|-------------|----------------------------|-------|------------|
| 97       | 1     | 1       | 4402        | 2311.4                     | 1.60  | PMEL1      |
| 97       | 1     | 24      | 7           | 1947.9                     | 1.35  | PMEL1      |
| 98       | 1     | 1       | 3000        | 2327.6                     | 1.50  | AOML2      |
| 99       | 1     | 1       | 4210        | 2310.5                     | 1.32  | AOML2      |
| 99       | 1     | 24      | 7           | 1928.8                     | 1.34  | AOML2      |
| 100      | 1     | 17      | 400         | 2260.7                     | 0.92  | PMEL1      |

Table 4. Replicate dissolved CFC-11 Analyses

| Station | Cast | Bottle | CFC-11<br>pmol/kg | CFC-11<br>Stdev |
|---------|------|--------|-------------------|-----------------|
| 2       | 2    | 18     | 3.632             | 0.004           |
| 2       | 2    | 24     | 3.661             | 0.060           |
| 3       | 2    | 17     | 2.952             | 0.043           |
| 4       | 1    | 12     | 1.431             | 0.004           |
| 5       | 1    | 15     | 2.837             | 0.006           |
| 6       | 2    | 24     | 3.506             | 0.001           |
| 7       | 1    | 7      | 0.029             | 0.005           |
| 7       | 1    | 14     | 2.460             | 0.062           |
| 9       | 2    | 10     | 0.008             | 0.002           |
| 9       | 2    | 24     | 3.264             | 0.005           |
| 10      | 1    | 10     | 0.020             | 0.005           |
| 11      | 1    | 14     | 0.842             | 0.026           |
| 11      | 1    | 20     | 3.358             | 0.020           |
| 12      | 2    | 8      | 0.003             | 0.002           |
| 12      | 2    | 16     | 2.830             | 0.016           |
| 13      | 1    | 6      | 0.003             | 0.001           |
| 13      | 1    | 22     | 3.131             | 0.004           |
| 14      | 1    | 18     | 3.180             | 0.052           |
| 14      | 1    | 21     | 3.091             | 0.015           |
| 15      | 1    | 16     | 3.042             | 0.017           |
| 17      | 1    | 11     | 2.386             | 0.005           |
| 17      | 1    | 21     | 3.019             | 0.019           |
| 18      | 1    | 1      | 0.008             | 0.002           |
| 18      | 1    | 24     | 2.728             | 0.024           |
| 19      | 2    | 14     | 2.129             | 0.010           |
| 19      | 2    | 21     | 2.942             | 0.019           |
| 20      | 1    | 11     | 0.192             | 0.021           |
| 21      | 2    | 11     | 0.751             | 0.000           |
| 23      | 1    | 11     | 0.331             | 0.001           |
| 24      | 1    | 11     | 0.185             | 0.004           |
| 26      | 2    | 14     | 1.564             | 0.014           |
| 28      | 1    | 11     | 0.913             | 0.003           |
| 28      | 1    | 14     | 2.986             | 0.004           |
| 30      | 2    | 11     | 0.198             | 0.001           |
| 30      | 2    | 21     | 3.192             | 0.029           |
| 32      | 1    | 6      | 0.037             | 0.000           |
| 34      | 1    | 11     | 0.772             | 0.004           |
| 34      | 1    | 23     | 3.074             | 0.034           |
| 36      | 1    | 7      | 0.030             | 0.002           |
| 37      | 1    | 10     | 0.379             | 0.004           |
| 38      | 2    | 10     | 0.079             | 0.001           |
| 38      | 2    | 22     | 3.031             | 0.003           |
| 39      | 1    | 11     | 0.432             | 0.008           |
| 40      | 1    | 8      | 0.008             | 0.003           |
| 41      | 1    | 20     | 2.838             | 0.021           |
| 42      | 1    | 21     | 2.901             | 0.013           |
| 43      | 1    | 13     | 0.956             | 0.003           |

Table 4. Replicate dissolved CFC-11 Analyses  
(continued)

| Station | Niskin Bottle |    | CFC-11<br>pmol/kg | CFC-11<br>Stdev |
|---------|---------------|----|-------------------|-----------------|
| 44      | 1             | 21 | 2.316             | 0.024           |
| 45      | 2             | 14 | 1.553             | 0.008           |
| 46      | 1             | 7  | 0.000             | 0.000           |
| 47      | 1             | 14 | 0.017             | 0.002           |
| 48      | 2             | 16 | 2.713             | 0.014           |
| 49      | 1             | 14 | 0.071             | 0.000           |
| 50      | 1             | 17 | 0.319             | 0.004           |
| 51      | 1             | 18 | 2.758             | 0.002           |
| 52      | 1             | 12 | 0.000             | 0.000           |
| 53      | 2             | 18 | 2.238             | 0.011           |
| 54      | 1             | 15 | 0.159             | 0.002           |
| 55      | 1             | 20 | 1.899             | 0.035           |
| 57      | 2             | 14 | 0.026             | 0.002           |
| 59      | 1             | 20 | 1.333             | 0.000           |
| 61      | 2             | 18 | 0.754             | 0.011           |
| 63      | 1             | 19 | 0.794             | 0.000           |
| 65      | 2             | 18 | 0.885             | 0.002           |
| 67      | 1             | 14 | 0.012             | 0.001           |
| 69      | 2             | 17 | 0.484             | 0.003           |
| 71      | 1             | 18 | 0.319             | 0.007           |
| 73      | 2             | 18 | 0.191             | 0.003           |
| 75      | 1             | 20 | 0.778             | 0.004           |
| 79      | 1             | 22 | 1.626             | 0.007           |
| 81      | 1             | 20 | 0.884             | 0.000           |
| 83      | 2             | 18 | 0.446             | 0.003           |
| 85      | 1             | 21 | 1.596             | 0.004           |
| 87      | 2             | 17 | 0.643             | 0.006           |
| 89      | 1             | 16 | 0.126             | 0.004           |
| 91      | 1             | 15 | 0.056             | 0.002           |
| 93      | 1             | 17 | 0.213             | 0.000           |
| 95      | 1             | 18 | 0.474             | 0.001           |
| 97      | 1             | 18 | 0.130             | 0.002           |
| 99      | 1             | 16 | 0.040             | 0.002           |

Table 5. Replicate dissolved CFC-12 Analyses

| Station | Cast | Bottle | CFC-12<br>pmol/kg | CFC-12<br>Stdev |
|---------|------|--------|-------------------|-----------------|
| 2       | 2    | 18     | 1.854             | 0.007           |
| 2       | 2    | 24     | 1.855             | 0.019           |
| 3       | 2    | 17     | 1.456             | 0.012           |
| 4       | 1    | 12     | 0.654             | 0.002           |
| 5       | 1    | 15     | 1.371             | 0.001           |
| 6       | 2    | 24     | 1.770             | 0.001           |
| 7       | 1    | 7      | 0.006             | 0.001           |
| 7       | 1    | 14     | 1.158             | 0.024           |
| 9       | 2    | 10     | -0.001            | 0.002           |
| 10      | 1    | 10     | 0.004             | 0.002           |
| 11      | 1    | 14     | 0.394             | 0.015           |
| 11      | 1    | 20     | 1.706             | 0.002           |
| 12      | 2    | 8      | -0.002            | 0.000           |
| 12      | 2    | 16     | 1.367             | 0.006           |
| 13      | 1    | 6      | -0.001            | 0.000           |
| 13      | 1    | 22     | 1.659             | 0.010           |
| 14      | 1    | 18     | 1.596             | 0.009           |
| 14      | 1    | 21     | 1.620             | 0.033           |
| 15      | 1    | 16     | 1.502             | 0.005           |
| 17      | 1    | 21     | 1.603             | 0.017           |
| 18      | 1    | 1      | 0.004             | 0.001           |
| 18      | 1    | 24     | 1.485             | 0.031           |
| 19      | 2    | 14     | 1.041             | 0.009           |
| 19      | 2    | 21     | 1.561             | 0.004           |
| 20      | 1    | 11     | 0.098             | 0.010           |
| 21      | 2    | 11     | 0.376             | 0.002           |
| 23      | 1    | 11     | 0.169             | 0.001           |
| 24      | 1    | 11     | 0.096             | 0.003           |
| 26      | 2    | 14     | 0.765             | 0.011           |
| 28      | 1    | 11     | 0.436             | 0.005           |
| 28      | 1    | 14     | 1.505             | 0.027           |
| 30      | 2    | 2      | 0.001             | 0.000           |
| 30      | 2    | 11     | 0.093             | 0.005           |
| 30      | 2    | 21     | 1.703             | 0.004           |
| 30      | 2    | 23     | 1.700             | 0.002           |
| 32      | 1    | 6      | 0.018             | 0.000           |
| 34      | 1    | 11     | 0.380             | 0.002           |
| 34      | 1    | 23     | 1.638             | 0.017           |
| 36      | 1    | 7      | 0.017             | 0.002           |
| 37      | 1    | 10     | 0.187             | 0.002           |
| 38      | 2    | 10     | 0.041             | 0.001           |
| 38      | 2    | 22     | 1.628             | 0.003           |
| 39      | 1    | 11     | 0.219             | 0.004           |
| 40      | 1    | 8      | 0.004             | 0.003           |
| 41      | 1    | 20     | 1.520             | 0.002           |
| 42      | 1    | 21     | 1.538             | 0.003           |
| 43      | 1    | 13     | 0.497             | 0.001           |

Table 5. Replicate dissolved CFC-12 Analyses  
(continued)

| Station | Niskin Bottle |    | CFC-12<br>pmol/kg | CFC-12<br>Stdev |
|---------|---------------|----|-------------------|-----------------|
| 44      | 1             | 21 | 1.287             | 0.015           |
| 45      | 2             | 14 | 0.780             | 0.005           |
| 46      | 1             | 7  | 0.000             | 0.000           |
| 47      | 1             | 14 | 0.009             | 0.001           |
| 48      | 2             | 16 | 1.360             | 0.017           |
| 49      | 1             | 14 | 0.044             | 0.001           |
| 50      | 1             | 17 | 0.178             | 0.006           |
| 51      | 1             | 18 | 1.399             | 0.000           |
| 52      | 1             | 12 | 0.001             | 0.001           |
| 53      | 2             | 18 | 1.196             | 0.002           |
| 54      | 1             | 15 | 0.094             | 0.002           |
| 55      | 1             | 20 | 1.086             | 0.029           |
| 57      | 2             | 14 | 0.017             | 0.002           |
| 59      | 1             | 20 | 0.720             | 0.005           |
| 61      | 2             | 18 | 0.389             | 0.010           |
| 63      | 1             | 19 | 0.435             | 0.003           |
| 65      | 2             | 18 | 0.458             | 0.002           |
| 67      | 1             | 14 | 0.006             | 0.002           |
| 69      | 2             | 17 | 0.260             | 0.003           |
| 71      | 1             | 18 | 0.175             | 0.001           |
| 73      | 2             | 18 | 0.111             | 0.001           |
| 75      | 1             | 20 | 0.425             | 0.002           |
| 79      | 1             | 22 | 0.926             | 0.005           |
| 81      | 1             | 20 | 0.495             | 0.007           |
| 83      | 2             | 18 | 0.257             | 0.003           |
| 85      | 1             | 21 | 0.934             | 0.002           |
| 87      | 2             | 17 | 0.363             | 0.000           |
| 89      | 1             | 16 | 0.074             | 0.002           |
| 91      | 1             | 15 | 0.038             | 0.003           |
| 93      | 1             | 17 | 0.128             | 0.001           |
| 95      | 1             | 18 | 0.272             | 0.002           |
| 97      | 1             | 18 | 0.080             | 0.000           |
| 99      | 1             | 16 | 0.025             | 0.003           |

Table 6. CFC Air Measurements  
(Local time = GMT + 5 h)

| Date      | GMT<br>(hhmm) | Latitude  | Longitude  | CFC-11<br>ppt | CFC-12<br>ppt |
|-----------|---------------|-----------|------------|---------------|---------------|
| 24-Sep-95 | 947           | 40 01.5 S | 109 58.7 E | 259.6         | 522.4         |
| 24-Sep-95 | 959           | 40 01.5 S | 109 58.7 E | 260.4         | 520.8         |
| 24-Sep-95 | 1011          | 40 01.5 S | 109 58.7 E | 260.0         | 523.4         |
| 24-Sep-95 | 1023          | 40 01.5 S | 109 58.7 E | 261.5         | 524.2         |
| 25-Sep-95 | 1125          | 40 41.5 S | 107 10.6 E | 261.5         | 516.5         |
| 25-Sep-95 | 1137          | 40 41.5 S | 107 10.6 E | 261.5         | 518.7         |
| 26-Sep-95 | 422           | 41 16.8 S | 103 48.6 E | 259.7         | 519.5         |
| 26-Sep-95 | 434           | 41 16.8 S | 103 48.6 E | 261.0         | 516.7         |
| 26-Sep-95 | 446           | 41 16.8 S | 103 48.6 E | 260.7         | 516.3         |
| 26-Sep-95 | 458           | 41 16.8 S | 103 48.6 E | 261.7         | 514.0         |
| 27-Sep-95 | 935           | 42 39.4 S | 096 46.1 E | 260.2         | 522.5         |
| 27-Sep-95 | 947           | 42 39.4 S | 096 46.1 E | 260.6         | 521.7         |
| 27-Sep-95 | 959           | 42 39.4 S | 096 46.1 E | 260.7         | 522.9         |
| 27-Sep-95 | 1011          | 42 39.4 S | 096 46.1 E | 260.1         | 521.4         |
| 28-Sep-95 | 713           | 43 00.0 S | 095 00.0 E | 261.6         | 520.6         |
| 28-Sep-95 | 725           | 43 00.0 S | 095 00.0 E | 260.8         | 520.5         |
| 28-Sep-95 | 737           | 43 00.0 S | 095 00.0 E | 262.1         | 521.0         |
| 28-Sep-95 | 749           | 43 00.0 S | 095 00.0 E | 260.9         | 519.8         |
| 1-Oct-95  | 800           | 34 00.0 S | 095 00.0 E | 261.5         | 516.8         |
| 1-Oct-95  | 812           | 34 00.0 S | 095 00.0 E | 261.1         | 520.5         |
| 1-Oct-95  | 824           | 34 00.0 S | 095 00.0 E | 261.2         | 522.1         |
| 1-Oct-95  | 836           | 34 00.0 S | 095 00.0 E | 260.7         | 519.2         |
| 3-Oct-95  | 855           | 33 10.5 S | 090 10.5 E | 260.8         | 505.3         |
| 3-Oct-95  | 908           | 33 10.5 S | 090 10.5 E | 260.8         | 512.6         |
| 3-Oct-95  | 921           | 33 10.5 S | 090 10.5 E | 261.0         | 510.2         |
| 3-Oct-95  | 934           | 33 10.5 S | 090 10.5 E | 261.0         | 505.3         |
| 6-Oct-95  | 1711          | 35 19.3 S | 080 49.5 E | 263.2         | 523.7         |
| 6-Oct-95  | 1724          | 35 19.3 S | 080 49.5 E | 263.8         | 526.0         |
| 6-Oct-95  | 1737          | 35 19.3 S | 080 49.5 E | 262.3         | 521.1         |
| 6-Oct-95  | 1750          | 35 19.3 S | 080 49.5 E | -9.0          | -9.0          |
| 8-Oct-95  | 443           | 32 00.0 S | 080 00.0 E | 260.3         | 517.7         |
| 8-Oct-95  | 456           | 32 00.0 S | 080 00.0 E | 261.0         | 518.5         |
| 8-Oct-95  | 509           | 32 00.0 S | 080 00.0 E | 260.9         | 520.4         |
| 8-Oct-95  | 522           | 32 00.0 S | 080 00.0 E | 261.1         | 521.8         |
| 10-Oct-95 | 1033          | 25 00.0 S | 080 00.0 E | 261.5         | 522.9         |
| 10-Oct-95 | 1045          | 25 00.0 S | 080 00.0 E | 262.0         | 522.0         |
| 10-Oct-95 | 1056          | 25 00.0 S | 080 00.0 E | 261.5         | 522.4         |
| 10-Oct-95 | 1108          | 25 00.0 S | 080 00.0 E | 261.5         | 521.6         |
| 13-Oct-95 | 2254          | 15 00.0 S | 080 00.0 E | 261.0         | 524.9         |
| 13-Oct-95 | 2306          | 15 00.0 S | 080 00.0 E | 262.2         | 522.5         |
| 13-Oct-95 | 2318          | 15 00.0 S | 080 00.0 E | 261.2         | 521.5         |
| 13-Oct-95 | 2330          | 15 00.0 S | 080 00.0 E | 261.7         | 531.4         |
| 15-Oct-95 | 1837          | 11 30.0 S | 080 00.0 E | 261.6         | 525.7         |
| 15-Oct-95 | 1849          | 11 30.0 S | 080 00.0 E | 261.3         | 522.1         |
| 15-Oct-95 | 1901          | 11 30.0 S | 080 00.0 E | 261.4         | 522.7         |

Table 6. CFC Air Measurements (continued)  
 (Local time = GMT + 5 h)

| Date      | GMT<br>(hhmm) | Latitude  | Longitude  | CFC-11<br>ppt | CFC-12<br>ppt |
|-----------|---------------|-----------|------------|---------------|---------------|
| 15-Oct-95 | 1912          | 11 30.0 S | 080 00.0 E | 261.5         | 523.2         |
| 16-Oct-95 | 1936          | 09 30.0 S | 080 00.0 E | 262.8         | 523.3         |
| 16-Oct-95 | 1948          | 09 30.0 S | 080 00.0 E | 263.0         | 521.5         |
| 16-Oct-95 | 1959          | 09 30.0 S | 080 00.0 E | 261.6         | 522.6         |
| 16-Oct-95 | 2011          | 09 30.0 S | 080 00.0 E | 261.7         | 520.2         |
| 19-Oct-95 | 613           | 04 00.0 S | 080 00.0 E | 262.3         | 519.8         |
| 19-Oct-95 | 625           | 04 00.0 S | 080 00.0 E | 261.9         | 520.9         |
| 19-Oct-95 | 636           | 04 00.0 S | 080 00.0 E | 261.1         | 527.0         |
| 19-Oct-95 | 648           | 04 00.0 S | 080 00.0 E | 262.3         | 520.4         |
| 23-Oct-95 | 809           | 04 00.0 N | 080 00.0 E | 263.5         | 519.7         |
| 23-Oct-95 | 820           | 04 00.0 N | 080 00.0 E | 263.0         | 522.6         |
| 23-Oct-95 | 832           | 04 00.0 N | 080 00.0 E | 262.4         | 521.1         |
| 23-Oct-95 | 844           | 04 00.0 N | 080 00.0 E | 262.1         | 525.9         |

Table 7. CFC Air values (interpolated to station locations)  
 (Local time = GMT + 5 h)

| Station | GMT<br>(hhmm) | Latitude   | Longitude | CFC-11<br>ppt | CFC-12<br>ppt |
|---------|---------------|------------|-----------|---------------|---------------|
| 2       | 40 02.2 S     | 109 58.6 E | 24-Sep-95 | 260.8         | 521.0         |
| 3       | 42 59.7 S     | 095 00.4 E | 28-Sep-95 | 260.9         | 521.3         |
| 4       | 41 59.6 S     | 095 00.9 E | 28-Sep-95 | 260.9         | 521.3         |
| 5       | 40 59.8 S     | 095 00.0 E | 28-Sep-95 | 260.9         | 521.3         |
| 6       | 39 59.7 S     | 095 00.7 E | 29-Sep-95 | 260.9         | 521.3         |
| 7       | 39 00.1 S     | 095 00.0 E | 29-Sep-95 | 260.9         | 521.3         |
| 8       | 38 00.1 S     | 095 00.0 E | 29-Sep-95 | 261.0         | 520.8         |
| 9       | 37 00.0 S     | 094 59.6 E | 30-Sep-95 | 261.0         | 517.6         |
| 10      | 36 00.9 S     | 095 01.2 E | 30-Sep-95 | 261.0         | 514.0         |
| 11      | 34 60.0 S     | 094 58.7 E | 30-Sep-95 | 261.0         | 514.0         |
| 12      | 34 00.2 S     | 094 58.6 E | 1-Oct-95  | 261.0         | 514.0         |
| 13      | 33 00.5 S     | 095 00.3 E | 1-Oct-95  | 261.0         | 514.0         |
| 14      | 32 30.2 S     | 094 59.7 E | 1-Oct-95  | 261.0         | 514.0         |
| 15      | 32 00.4 S     | 094 60.0 E | 1-Oct-95  | 261.0         | 514.0         |
| 16      | 31 44.7 S     | 094 59.8 E | 2-Oct-95  | 261.0         | 514.0         |
| 17      | 31 39.1 S     | 095 00.0 E | 2-Oct-95  | 261.0         | 514.0         |
| 18      | 32 27.4 S     | 092 35.9 E | 2-Oct-95  | 261.0         | 514.0         |
| 19      | 33 10.3 S     | 090 10.1 E | 3-Oct-95  | 261.0         | 514.0         |
| 20      | 33 59.9 S     | 087 46.0 E | 3-Oct-95  | 261.6         | 516.6         |
| 21      | 34 10.2 S     | 087 09.3 E | 4-Oct-95  | 261.9         | 514.9         |
| 22      | 34 17.9 S     | 086 37.5 E | 4-Oct-95  | 261.9         | 514.9         |
| 23      | 34 27.2 S     | 086 02.8 E | 4-Oct-95  | 261.9         | 514.9         |
| 24      | 34 37.0 S     | 085 28.1 E | 4-Oct-95  | 261.9         | 514.9         |
| 25      | 34 45.7 S     | 084 52.7 E | 5-Oct-95  | 261.5         | 516.6         |
| 26      | 34 54.2 S     | 084 17.4 E | 5-Oct-95  | 261.8         | 521.3         |
| 27      | 35 03.1 S     | 083 43.0 E | 5-Oct-95  | 261.8         | 521.3         |
| 28      | 35 13.1 S     | 083 08.6 E | 5-Oct-95  | 261.8         | 521.3         |
| 29      | 35 21.6 S     | 082 33.1 E | 5-Oct-95  | 261.8         | 521.3         |
| 30      | 35 31.8 S     | 081 58.2 E | 6-Oct-95  | 261.8         | 521.3         |
| 31      | 35 27.4 S     | 081 29.0 E | 6-Oct-95  | 261.8         | 521.3         |
| 32      | 35 19.6 S     | 080 49.1 E | 6-Oct-95  | 261.8         | 521.3         |
| 33      | 35 00.1 S     | 080 19.5 E | 8-Oct-95  | 261.8         | 521.3         |
| 34      | 34 39.7 S     | 079 49.2 E | 7-Oct-95  | 261.8         | 521.3         |
| 35      | 34 20.2 S     | 079 20.6 E | 7-Oct-95  | 261.8         | 521.3         |
| 36      | 33 59.6 S     | 080 00.5 E | 7-Oct-95  | 261.8         | 521.3         |
| 37      | 33 00.0 S     | 080 00.1 E | 7-Oct-95  | 261.8         | 521.3         |
| 38      | 31 59.0 S     | 080 00.3 E | 8-Oct-95  | 261.8         | 521.3         |
| 39      | 30 59.9 S     | 080 00.6 E | 8-Oct-95  | 261.8         | 521.3         |
| 40      | 30 00.1 S     | 079 59.8 E | 8-Oct-95  | 261.7         | 521.7         |
| 41      | 28 60.0 S     | 079 59.9 E | 9-Oct-95  | 261.2         | 520.9         |
| 42      | 27 59.7 S     | 080 00.2 E | 9-Oct-95  | 261.2         | 520.9         |
| 43      | 26 59.8 S     | 079 59.9 E | 9-Oct-95  | 261.2         | 520.9         |
| 44      | 25 59.4 S     | 079 59.6 E | 9-Oct-95  | 261.2         | 520.9         |
| 45      | 25 00.4 S     | 079 59.7 E | 10-Oct-95 | 261.2         | 520.9         |
| 46      | 24 00.9 S     | 079 59.1 E | 10-Oct-95 | 261.2         | 520.9         |

Table 7. CFC Air values (interpolated to station locations, continued)  
(Local time = GMT + 5 h)

| Station | GMT<br>(hhmm) | Latitude   | Longitude | CFC-11<br>ppt | CFC-12<br>ppt |
|---------|---------------|------------|-----------|---------------|---------------|
| 47      | 22 59.2 S     | 079 59.2 E | 11-Oct-95 | 261.6         | 523.6         |
| 48      | 22 00.9 S     | 080 00.1 E | 11-Oct-95 | 261.6         | 523.6         |
| 49      | 20 59.8 S     | 079 59.3 E | 11-Oct-95 | 261.6         | 523.6         |
| 50      | 19 59.5 S     | 080 00.5 E | 12-Oct-95 | 261.6         | 523.6         |
| 51      | 18 59.4 S     | 080 00.1 E | 12-Oct-95 | 261.6         | 523.6         |
| 52      | 18 00.0 S     | 080 00.3 E | 12-Oct-95 | 261.5         | 523.6         |
| 53      | 16 58.9 S     | 079 59.6 E | 13-Oct-95 | 261.5         | 524.3         |
| 54      | 15 59.6 S     | 080 00.0 E | 13-Oct-95 | 261.5         | 524.3         |
| 55      | 14 59.5 S     | 079 60.0 E | 13-Oct-95 | 261.5         | 524.3         |
| 56      | 14 29.9 S     | 079 60.0 E | 14-Oct-95 | 261.5         | 524.3         |
| 57      | 13 59.9 S     | 079 59.9 E | 14-Oct-95 | 261.5         | 524.3         |
| 58      | 13 30.1 S     | 079 60.0 E | 14-Oct-95 | 261.5         | 524.3         |
| 59      | 13 00.7 S     | 079 59.6 E | 14-Oct-95 | 261.5         | 524.3         |
| 60      | 12 29.8 S     | 080 00.0 E | 14-Oct-95 | 261.8         | 523.5         |
| 61      | 11 59.6 S     | 080 00.1 E | 15-Oct-95 | 261.9         | 522.7         |
| 62      | 11 29.9 S     | 079 59.8 E | 15-Oct-95 | 261.9         | 522.7         |
| 63      | 10 59.4 S     | 079 59.5 E | 15-Oct-95 | 261.9         | 522.7         |
| 64      | 10 29.5 S     | 080 00.2 E | 15-Oct-95 | 261.9         | 522.7         |
| 65      | 09 59.4 S     | 080 00.9 E | 16-Oct-95 | 261.9         | 522.7         |
| 66      | 09 29.9 S     | 080 00.3 E | 16-Oct-95 | 261.9         | 522.7         |
| 67      | 08 60.0 S     | 080 00.6 E | 16-Oct-95 | 261.9         | 522.7         |
| 68      | 08 29.7 S     | 080 00.2 E | 16-Oct-95 | 261.9         | 522.7         |
| 69      | 07 59.9 S     | 080 00.3 E | 17-Oct-95 | 261.9         | 522.5         |
| 70      | 07 30.1 S     | 079 59.7 E | 17-Oct-95 | 261.9         | 522.5         |
| 71      | 07 00.0 S     | 079 59.4 E | 17-Oct-95 | 262.1         | 522.0         |
| 72      | 06 29.9 S     | 079 59.3 E | 17-Oct-95 | 262.1         | 522.0         |
| 73      | 05 59.7 S     | 079 58.4 E | 18-Oct-95 | 262.1         | 522.0         |
| 74      | 05 30.0 S     | 079 59.1 E | 18-Oct-95 | 262.1         | 522.0         |
| 75      | 04 59.8 S     | 080 00.3 E | 18-Oct-95 | 262.1         | 522.0         |
| 76      | 04 29.7 S     | 080 00.2 E | 18-Oct-95 | 262.1         | 522.0         |
| 77      | 03 59.5 S     | 080 00.2 E | 19-Oct-95 | 262.1         | 522.0         |
| 78      | 03 29.9 S     | 080 00.4 E | 19-Oct-95 | 262.1         | 522.0         |
| 79      | 02 59.5 S     | 080 00.0 E | 19-Oct-95 | 262.3         | 522.1         |
| 80      | 02 30.2 S     | 080 00.3 E | 19-Oct-95 | 262.3         | 522.1         |
| 81      | 02 00.3 S     | 080 00.4 E | 20-Oct-95 | 262.3         | 522.2         |
| 82      | 01 30.0 S     | 080 00.4 E | 20-Oct-95 | 262.3         | 522.2         |
| 83      | 01 00.3 S     | 080 00.9 E | 20-Oct-95 | 262.3         | 522.2         |
| 84      | 00 45.6 S     | 079 60.0 E | 20-Oct-95 | 262.3         | 522.2         |
| 85      | 00 30.4 S     | 080 00.4 E | 20-Oct-95 | 262.3         | 522.2         |
| 86      | 00 15.3 S     | 080 00.4 E | 21-Oct-95 | 262.3         | 522.2         |
| 87      | 00 00.4 S     | 080 01.3 E | 21-Oct-95 | 262.3         | 522.2         |
| 88      | 00 14.7 N     | 080 00.4 E | 21-Oct-95 | 262.3         | 522.2         |
| 89      | 00 29.7 N     | 080 00.2 E | 21-Oct-95 | 262.3         | 522.2         |
| 90      | 00 44.5 N     | 080 00.1 E | 21-Oct-95 | 262.3         | 522.2         |
| 91      | 00 59.6 N     | 080 00.3 E | 21-Oct-95 | 262.3         | 522.2         |

Table 7. CFC Air values (interpolated to station locations, continued)  
 (Local time = GMT + 5)

| Station | GMT<br>(hhmm) | Latitude   | Longitude | Date  | CFC-11<br>ppt | CFC-12<br>ppt |
|---------|---------------|------------|-----------|-------|---------------|---------------|
| 92      | 01 28.6 N     | 080 00.2 E | 22-Oct-95 | 262.3 | 522.2         |               |
| 93      | 01 59.8 N     | 080 00.0 E | 22-Oct-95 | 262.3 | 522.2         |               |
| 94      | 02 29.9 N     | 079 59.8 E | 22-Oct-95 | 262.3 | 522.2         |               |
| 95      | 02 59.5 N     | 080 00.1 E | 22-Oct-95 | 262.3 | 522.2         |               |
| 96      | 03 29.2 N     | 079 59.8 E | 23-Oct-95 | 262.3 | 522.2         |               |
| 97      | 03 60.0 N     | 079 59.9 E | 23-Oct-95 | 262.3 | 522.2         |               |
| 98      | 04 29.6 N     | 080 00.1 E | 23-Oct-95 | 262.3 | 522.2         |               |
| 99      | 04 59.6 N     | 079 59.4 E | 23-Oct-95 | 262.3 | 522.2         |               |
| 100     | 05 31.0 N     | 079 59.4 E | 24-Oct-95 | 262.3 | 522.2         |               |
| 101     | 05 47.2 N     | 079 59.8 E | 24-Oct-95 | 262.3 | 522.2         |               |