ORNL/CDIAC-103
NDP-064

Surface Water and Atmospheric Underway Carbon Data Obtained During the World Ocean Circulation Experiment Indian Ocean Survey Cruises (R/V *Knorr*, December 1994 - January 1996)

Carbon Dioxide Information Analysis Center

Princeton University

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Environmental Sciences Division
Publication No. 4701

Date Published: November 1997

Prepared for the
Environmental Sciences Division
Office of Biological and Environmental Research
U.S. Department of Energy
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

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LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

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ABSTRACT

Sabine, C. L., and R. M. Key. 1997. Surface Water and Atmospheric Underway Carbon Data Obtained During the World Ocean Circulation Experiment Indian Ocean Survey Cruises (R/V *Knorr*, December 1994–January 1996). ORNL/CDIAC-103, NDP-064. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. 89 pp.

This data documentation presents the results of the surface water and atmospheric underway measurements of mole fraction of carbon dioxide (xCO_2), sea surface salinity, and sea surface temperature, obtained during the World Ocean Circulation Experiment (WOCE) Indian Ocean survey cruises (December 1994–January 1996). Discrete and underway carbon measurements were made by members of the CO_2 survey team. The survey team is a part of the Joint Global Ocean Flux Study supported by the U.S. Department of Energy to make carbon-related measurements on the WOCE global survey cruises.

Approximately 200,000 surface seawater and 50,000 marine air xCO_2 measurements were recorded. Seawater values ranged from 310 ppm to greater than 610 ppm. The lowest values (~50 ppm below atmospheric) were measured in the southwestern Indian Ocean, south of Madagascar. The highest values (more than 250 ppm higher than atmospheric) were found in the Arabian Sea associated with the southwest monsoon upwelling.

All measurements were made using the new fully automated system, designed by the scientists of the Princeton University Ocean Tracers Laboratory. This system was continuously running during all nine Indian Ocean cruises aboard Research Vessel *Knorr*. The system (fully described in Appendix A of this documentation) had a response time of ~1 min and a long-term precision and accuracy of ~0.4 and 1 ppm, respectively. The equilibrator design is a modification of a counterflow disk stripper that has been used in the past to extract soluble gases from seawater. The detector is a dual-beam infrared spectrometer. Calibration and operation of the instrument as well as data logging are computer controlled and require minimal attention. The design is such that other instrumentation can be easily added. Details of the instrument control, calibration, and efficiency tests for this instrument are given to assist others interested in building similar-type systems.

The Indian Ocean underway CO_2 data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of twenty data files, two FORTRAN 77 routines, a readme file, and this printed documentation. The data files and html version of this report can be accessed through the following World Wide Web site: http://cdiac.esd.ornl.gov/oceans/doc.html.

Keywords: carbon dioxide; World Ocean Circulation Experiment; Indian Ocean; partial pressure; carbon cycle; carbonate chemistry; underway measurements

PART 1:

OVERVIEW

1. INTRODUCTION

January 1996 marked the completion of a 14-month, 92,000 km-long hydrographic survey of the Indian Ocean by the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP) (Fig. 1). In addition to the standard WOCE hydrographic parameters measured on these cruises, discrete and underway carbon measurements were made by members of the carbon dioxide (CO_2) survey team. The survey team is a part of the Joint Global Ocean Flux Study (JGOFS) supported by the U.S. Department of Energy (DOE) to make carbon system measurements on the WOCE global survey cruises. As part of the survey team, the Princeton University (PU) Ocean Tracers Laboratory (OTL) constructed an automated system for underway analysis of surface water and marine air CO_2 concentrations (hereafter referred to as the underway system). With the help of the other science team members, the underway system was run aboard Research Vessel (R/V) *Knorr* during all nine legs of the Indian Ocean survey. All measured data and documentation are available to the public through the Carbon Dioxide Information Analysis Center (CDIAC). This report provides a description of the data files, underway system as well as a brief explanation of when and where the data were collected, any problems encountered with the system, and how the data can be accessed through CDIAC.

The underway system was installed by R. M. Key of Princeton University on the R/V *Knorr* in November 1994, prior to the first leg of the survey. Table 1 lists the chief scientist, cruise dates, ports of call, affiliation of the group responsible for discrete carbon sampling, and the analyst in charge of operating the underway system for each of the Indian Ocean legs. On all legs except the first, the CO_2 analyst responsible for operating the underway system was a member of the OTL group.

A majority of the data are of excellent quality. The only major technical problems were encountered on the first leg as a result of failures in the ship's seawater supply system. Approximately 10 days after the R/V *Knorr* departed Fremantle, Australia, for the first leg of the survey, the ship encountered heavy weather that resulted in frequent shutdowns of the ship's uncontaminated seawater pump. On December 19, 1994, the seawater supply for the underway system was switched to a secondary seawater pump. Post-cruise examination of the data revealed that the water from this pump had undergone significant heating, presumably the result of a long (and apparently variable) residence time in the ship. The underway temperature and salinity values recorded during this time are also questionable because they do not track very well with the surface temperature and salinity measured by a conductivity, temperature, and depth sensor (CTD). After careful analysis, much of the data had to be flagged as bad, and the remaining data are much "noisier" than data from subsequent legs. The original uncontaminated seawater supply was back on-line for the second leg and operated with only minor outages for the remainder of the survey. By the end of the survey on January 22, 1996, nearly 250,000 individual measurements of surface water and atmospheric mole fraction of CO_2 (xCO_2) were recorded. Seawater values ranged from 310 ppm to greater than 610 ppm. The lowest values (~50 ppm below atmospheric) were measured in the southwestern Indian Ocean, south of Madagascar. The highest values (more than 250 ppm higher than atmospheric) were found in the Arabian Sea and were associated with the southwest monsoon upwelling.

This report provides details on the calibration and quality control procedures followed in the production of this data set. An extensive account of specific events potentially affecting the CO_2 underway system has been compiled from the original notebooks and is included in Appendix B. The major events are briefly described in the Results section, but a number of minor events (e.g., times when the drying column was changed), which did not appear to have a direct effect on the results, are only recorded in the Appendix B. For further details on additional measured

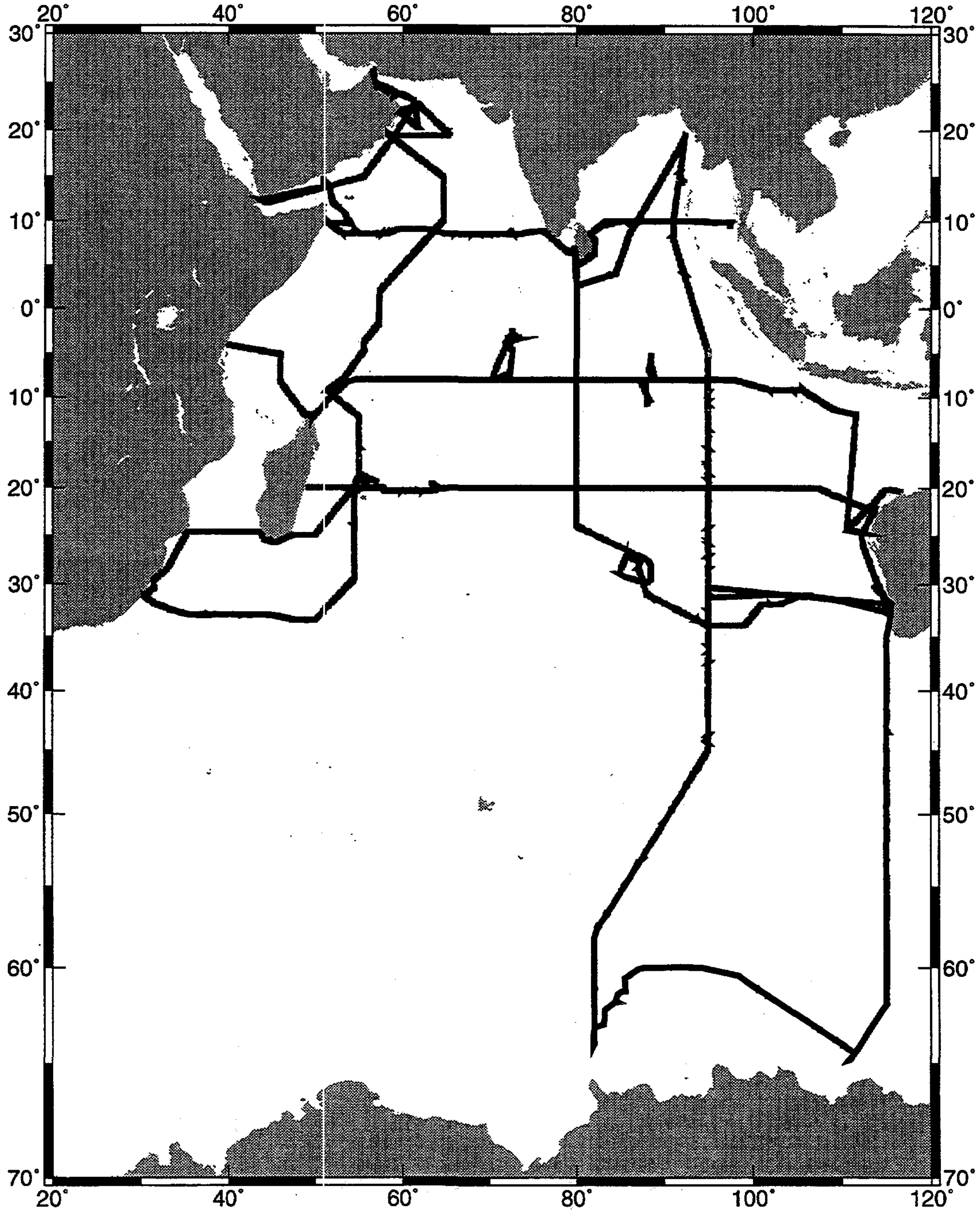

Figure 1. Indian Ocean Survey cruise track.

parameters and the objectives of each leg see the individual WOCE cruise reports produced by the chief scientist (http://www.cms.udel.edu/woce/dacs/whp_dac_one.html).

Table 1. Information on individual legs of WOCE Indian Ocean Survey

WOCE section	Chief scientist	Cruise dates	Ports of call	Carbon group	Underway system analyst
I8S/I9S	M. McCartney	12/01/94 – 01/19/95	Fremantle, AU – Fremantle, AU	BNL[1]	K. Johnson
I9N	A. Gordon	01/24/95 – 03/06/95	Fremantle, AU – Colombo, Sri Lanka	PU[2]	C. Sabine
I8N/I5E	L. Talley	03/10/95 – 04/06/95	Colombo, Sri Lanka – Fremantle, AU	UH[3]	G. McDonald
I3	W. Nowlin	04/23/95 – 06/05/95	Fremantle, AU – Mauritius	UM[4]	R. Key
I5W/I4	J. Toole	06/11/95 – 07/11/95	Mauritius – Mauritius	BNL	T. Key
I7N	D. Olson	07/15/95 – 08/24/95	Mauritius – Muscat, Oman	UH	T. Zahn
I1	J. Morrison	08/29/95 – 10/16/95	Muscat, Oman – Singapore	WHOI[5]	R. Rotter
I10	N. Bray	11/11/95 – 11/28/95	Dampier, AU – Singapore	PU	T. Key
I2	G. Johnson	12/02/95 – 01/22/96	Singapore – Mombasa, Kenya	UH	A. Dorety

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2. MEASUREMENTS, INSTRUMENTATION, AND CALIBRATIONS

The Princeton underway system was designed and constructed by OTL personnel for automated, high-resolution surface water and atmospheric boundary layer CO_2 concentration measurements. The system is controlled by a personal computer that is programmed to perform periodic calibrations, determine detector stability, and alternately measure the seawater and marine air CO_2 concentrations. A dual-beam infrared spectrometer (Li-Cor 6251) is used to measure the CO_2 concentration in the gas stream. The input gas to the detector (either one of four calibrated standards, air-equilibrated with surface seawater or marine air) is selected with an electronic 6-port valve. Prior to entering the detector, the gas is passed through a hygroscopic ion-exchange membrane (Nafion) and a small magnesium perchlorate/Aquasorb™ column to remove water vapor. Marine air is pumped from the bow or stern of the research vessel to avoid contamination from the ship's exhaust. The surface water CO_2 concentration is determined by continuously pumping seawater from the ship's intake (depth ~7m) through the counterflow disk equilibrator. The equilibrator design is a modification of a disk stripper that has been shown to be very efficient at extracting soluble gases from seawater. Water flows through the bottom half of the chamber at a rate of approximately 18 L/min and is then dumped overboard. A fixed volume of air is recirculated through the top half of the chamber in the opposite direction as the water flow. Sixty disks are mounted on a stainless steel shaft that runs along the axis of the chamber. The disks are rotated at 135 rpm so they can pick up a thin film of water on either side, greatly increasing the surface area of the water. Thus, the chamber equilibrates a very large volume of water with a small fixed volume (~6 L) of air. With the rotating disks, the equilibrator's response to an instantaneous change in the CO_2 of the water is an exponential mixing function. Laboratory and "at sea" tests indicate that the response time for this system was approximately 1 minute. The precision of the measurements, estimated from times when the ship was not moving and multiple measurements were made at the same location, was estimated to be approximately 0.4 ppm. This is comparable to the precision obtained from standard gas and marine air measurements. The average water and air sampling frequencies for the Indian Ocean legs were ~2.5 and 9.5 min, respectively. Comparison of these measurements with those from an independent underway system operated by R. Weiss of Scripps Institution of Oceanography (SIO) on the same vessel agreed to better than 1 ppm (R. Weiss, personal communication, 1995). Further details of the underway system design and operation can be found in Sabine and Key (1996), which is reprinted in Appendix A of this documentation.

The infrared detector used during the Indian Ocean survey cruises had an instrumental drift that could be significant on the timescale of a day. The primary calibration method for this system, therefore, was the periodic analysis of gas standards having known CO_2 concentrations. A detailed description of the philosophies and mechanics of how the detector readings were calibrated is given in Appendix A. In addition to the accuracy of the CO_2 standard gases, the accuracy of the final results at *in situ* conditions depends on supporting measurements of temperature, pressure, and salinity. This section discusses the calibration of relevant parameters given in this report.

2.1 CO_2 Standard Gases

The data collection program for the Indian Ocean survey cruises was set up to record five readings from each of the four calibration gases (the reference and three CO_2 standard gases) every three hours. All of the gases were a mixture of CO_2 in artificial air (oxygen, nitrogen, and argon in atmospheric ratios) prepared by Scott Specialty Gases, Inc. The nominal CO_2 concentrations for the three standard gases were 280, 360, and 450 ppm respectively. A reference gas with a nominal concentration of 200 ppm was used on almost all of the cruises to increase the dynamic range of the detector output (see Appendix A for details). Five tanks of calibrated reference gas were put aboard the R/V *Knorr* before the first leg of the survey. However, these tanks were exhausted before a resupply container could be sent with additional calibrated gases. After the first two weeks of leg I7N the reference gas was switched to a CO_2-free air tank. Additional gas tanks were delivered to the ship between legs I1 and I10, so the final two legs (legs I10 and I2) were again run with a 200 ppm reference gas. The exact times that the reference tanks were in use as well as the calibrated concentrations are given in Appendix B. The flow rate on the three CO_2 standards used for calibrations was sufficiently low to make one set of tanks last for the entire survey.

All of the CO_2 standards used for this survey were calibrated by R. Van Woy (SIO) using a technique that employs a gas chromatograph (GC)/flame ionization detector (FID) with catalytic conversion to CH_4 (Weiss 1981). The GC system was calibrated against C. D. Keeling-certified standards with concentrations of 213.14, 296.65, 349.97, and 458.06 ppm. The CO_2 standard gases and the initial five reference tanks were calibrated in September 1994, prior to the first cruise. The overall accuracy of the reported final values was estimated to be ±0.3 ppm. After completion of the last leg of the survey, the three standard gases were returned to R. Weiss' laboratory at SIO for post-cruise calibration in June 1996. Table 2 summarizes the initial and final calibrations of these gases. In all cases the post-cruise calibration was within the estimated accuracy of the initial calibration.

Table 2. Calibrated values for CO_2 standards

Tank ID no.	Date of use	Legs covered	Pre-cruise (ppmv)	Post-cruise (ppmv)
ALM017714	11/27/94–01/22/96	All	456.37 ± 0.21	455.69 ± 0.15
AAL9328	11/27/94–01/22/96	All	361.92 ± 0.18	361.80 ± 0.07
ALM017544	11/27/94–01/22/96	All	284.39 ± 0.18	284.07 ± 0.09
ALM17637	11/27/94–01/03/95	I8S/I9S	198.92 ± 0.13	N/A
AAL1791	01/03/95–02/09/95	I8S/I9S, I9N	199.55 ± 0.14	N/A
ALM008242	02/09/95–04/03/95	I9N, I8N/I5E	198.74 ± 0.15	N/A
ALM027282	04/03/95–05/24/95	I8N/I5E, I3	198.80 ± 0.16	N/A
ALM14400	05/24/95–07/25/95	I3, I5W/I4, I7N	198.63 ± 0.11	N/A
24813	07/25/95–08/15/95	I7N	0.00	N/A
18260	08/15/95–10/13/95	I7N, I1	0.00	N/A
ALM061635	11/01/95–12/29/95	I10, I2	200.88 ± 0.15	N/A
ALM45918	12/29/95–01/22/96	I2	200.92 ± 0.15	N/A

2.2 Underway Sea Surface Temperature, Salinity, and Position

Underway sea surface temperature and conductivity were measured using a Falmouth Scientific thermosalinograph (OCM-TH-212) as part of the R/V *Knorr* improved meteorological (IMET) sensor system. Readings were averaged and recorded at one-minute time intervals together with the global positioning system (GPS) time and location. Underway salinity was calculated relative to the 1978 practical salinity scale from the calibrated temperature and the raw conductivity readings using the equations of Lewis (1980). These data were quality controlled by examining all of the points recorded in two-day intervals and outliers were discarded based on visual inspection. Values were generally discarded when they were more than two standard deviations away from a time local mean. The exact value for the cut, therefore, depended on the instrumental noise at the time. Questionable points were generally left in the data set. The temperature, salinity, latitude, and longitude were then matched to the times when xCO_2 data were recorded. Linear interpolation was used to fill in for values cut in the QC process.

Both the temperature and salinity values were calibrated against the WOCE preliminary surface bottle values at each station. Although the exact trip time is not generally recorded in the WOCE ".SEA" files, the ".SUM" files do record the beginning and ending times of each cast. Since the Niskin bottles were tripped on the upcast, the surface bottle was tripped immediately before the rosette was brought aboard and the cast was completed. The end time for the cast was, therefore, taken as the trip time for the surface bottle at each station. The surface station data were then tied to the underway data by calculating the mean and median values of the underway data for the 15 minutes prior to the recorded cast end time. Although the ship was not underway while the cast was in progress, there was the potential that differences between the underway temperature readings and the discrete samples could have been real in very-high-gradient regions. Stations where the mean and median values were greater than 0.01 units apart were, therefore, flagged as questionable and not considered in the calibration fits.

Since the salinity measurements are a function of temperature, the temperature calibration was performed first. As noted earlier, the temperature data from section I8S/I9S were considerably noisier and appeared to have a different correlation with the CTD data than had data from the other legs. There were no significant differences among the remaining eight cruises, so they were all fit with a single function. Of the 1096 stations occupied after leg I8S/I9S, 201 were flagged as questionable. The remaining data were calibrated with a linear fit to the CTD temperature (Fig. 2). The fitted slope of 1.0013 ± 0.0003 indicates that the sensor had a nearly ideal response. The intercept of 0.095 ± 0.007 indicates that the ship's sensor was reading nearly 0.1°C high. The final calibrated underway temperature values were within ±0.026°C of the CTD values at the stations. The data from section I8S/I9S have a slightly different calibration function because the pump with the thermosalinograph was shut down early in the cruise. Without a constant flow of fresh water across the sensor, the response relied more on diffusion and turbulent mixing at the intake. For this cruise, the sensor slope was significantly different from 1 (1.068 ± 0.007), and the offset was 1.53 ± 0.07°C (Fig. 3). The standard deviation of the difference between the I8S/I9S CTD surface temperatures and the calibrated underway temperatures estimated at 131 stations was 0.44°C.

Underway salinity was calibrated to the preliminary WOCE bottle salinity results. Examination of the salinity data suggested that the calibration for the salinograph varied on a timescale of approximately 1 month (Fig. 4). No obvious correlation was observed between the variability and the *in situ* temperature or salinity. On average, the uncalibrated underway salinity values were approximately 1.3 lower than the bottle salinity values. The reason for the varying

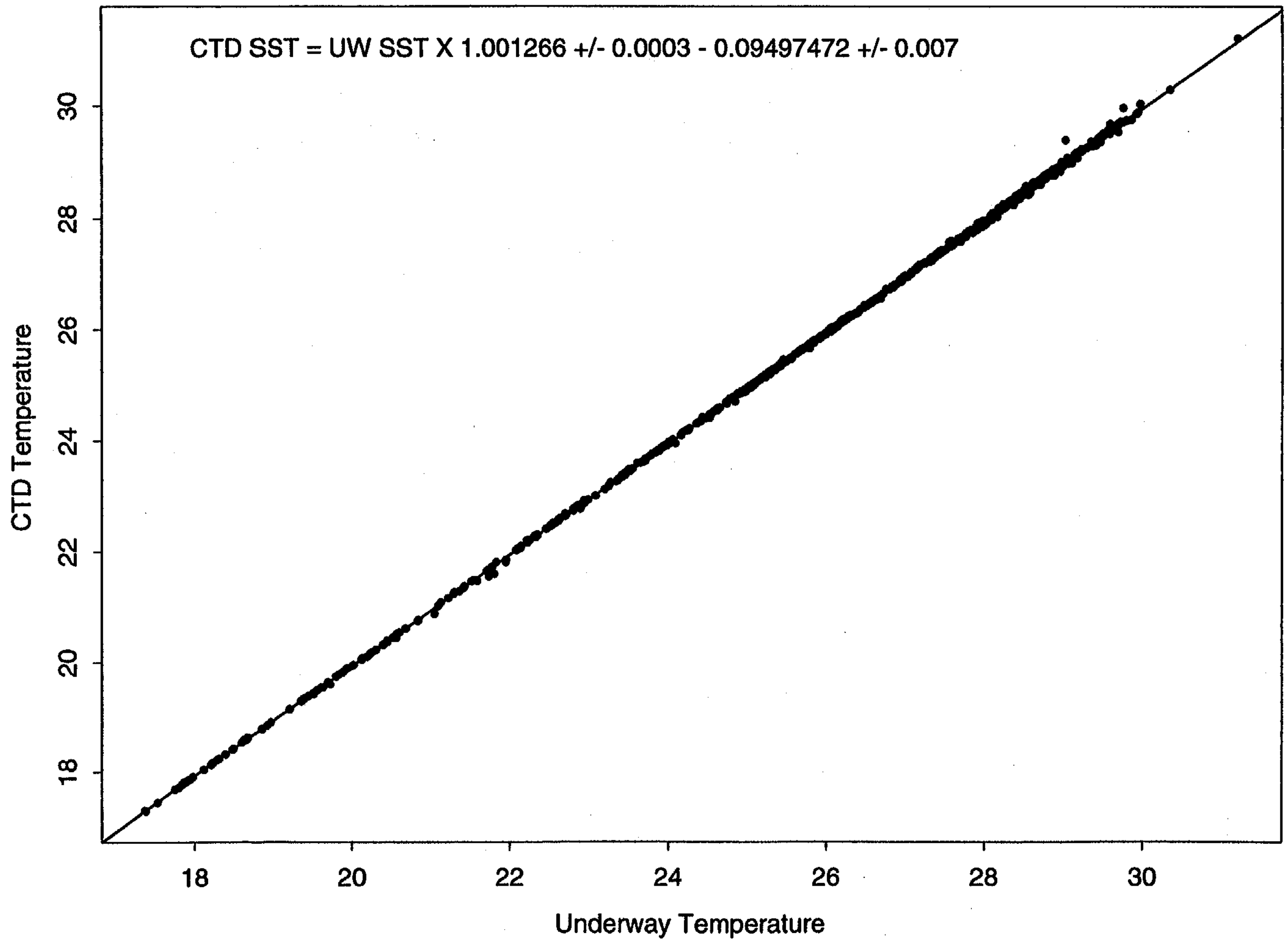


Figure 2. Plot of surface CTD temperature vs the 15-minute mean of the underway temperature for stations occupied on legs I9N–I2. Line and equation are based on linear fit of shown data.

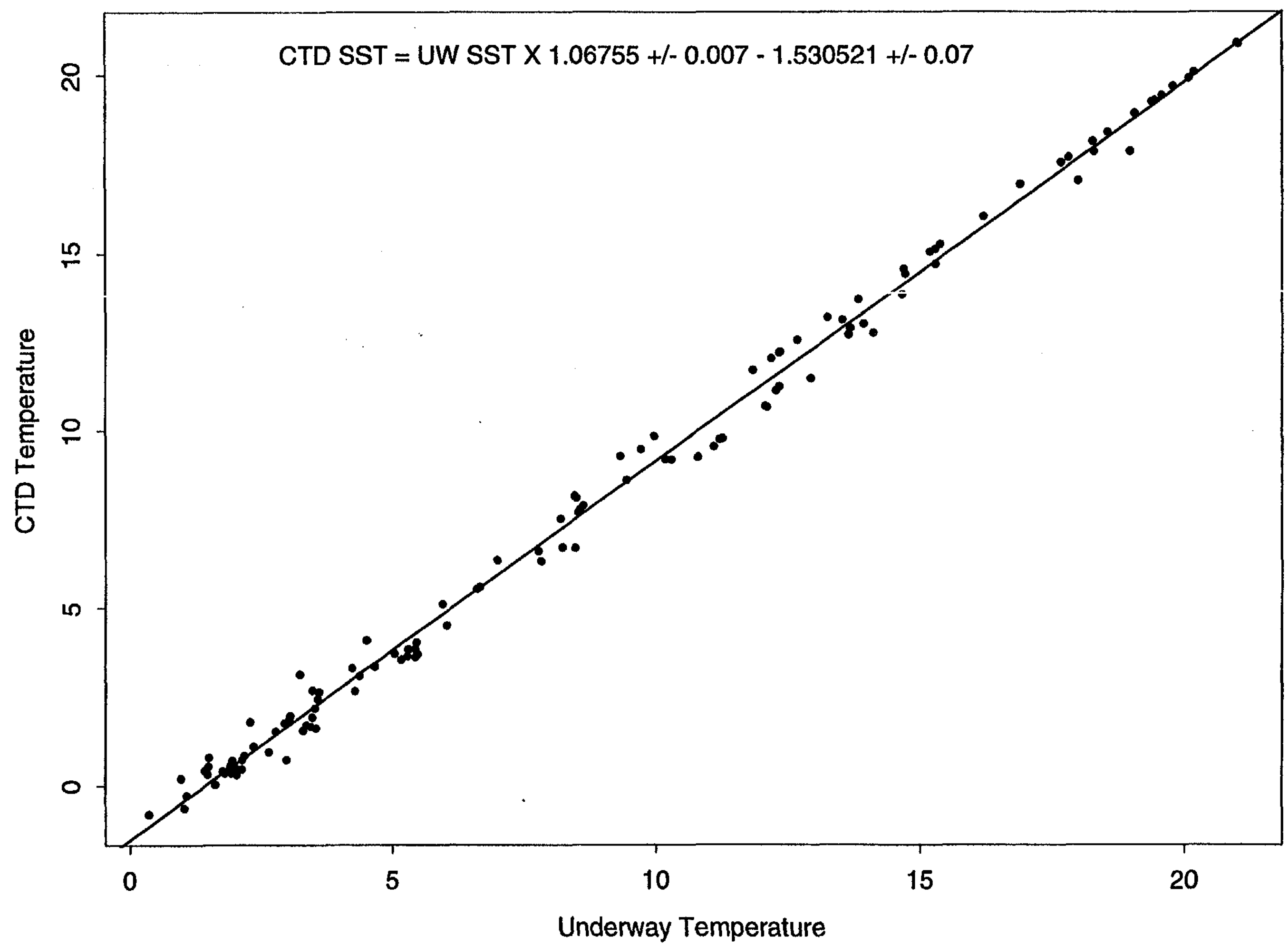


Figure 3. **Plot of surface CTD temperature vs the 15-minute mean of the underway temperature for stations occupied on leg I8S/I9S. Line and equation are based on linear fit of shown data.**

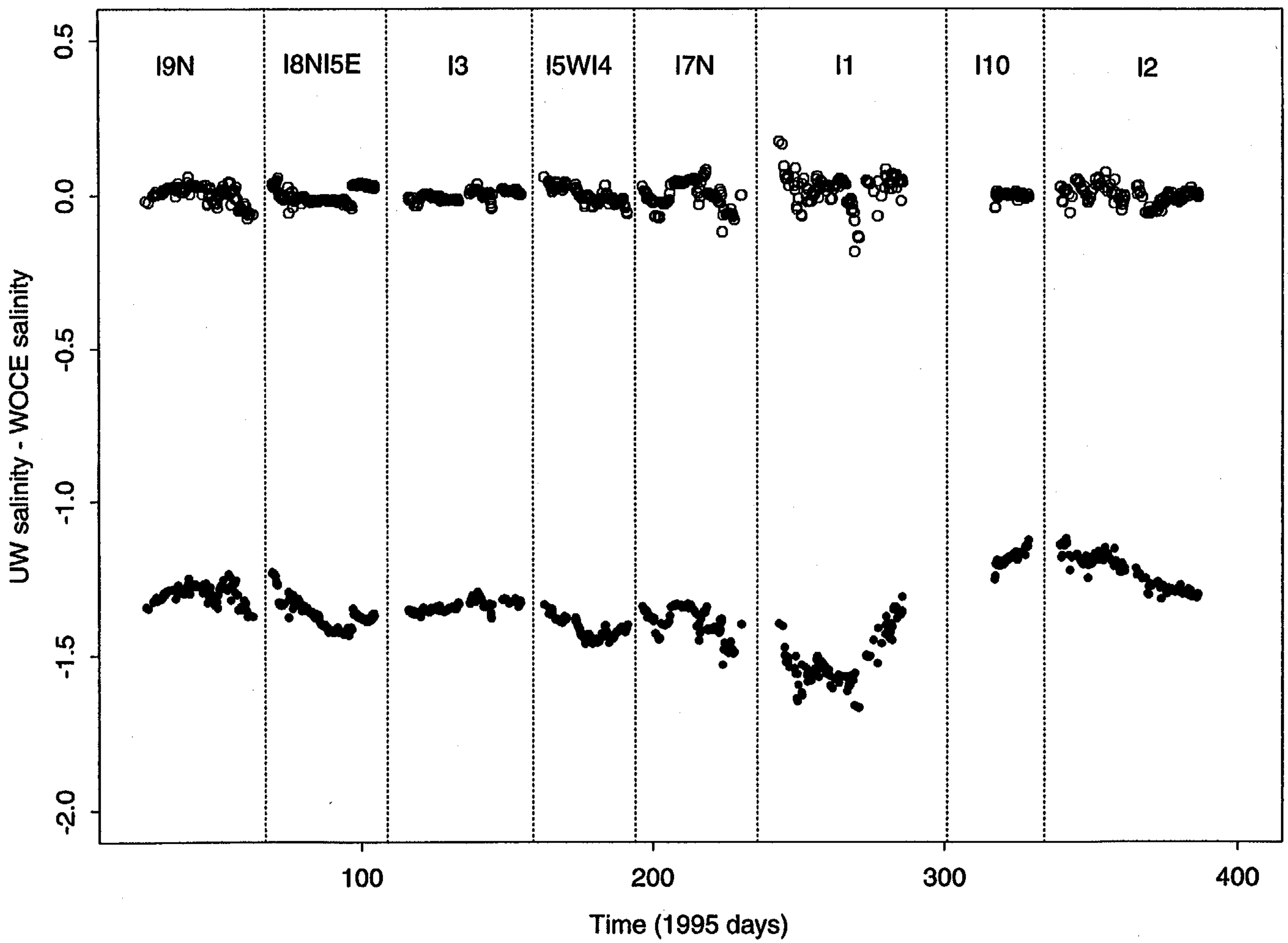


Figure 4. Plot of Δ salinity (underway minus WOCE bottle) as a function of time for all stations occupied after I8S/I9S. Solid dots are based on the raw underway salinity values and the open circles are based on calibrated underway values.

offset is not known, but given this variability the underway data were fit to the station data for each leg individually.

Table 3 lists the coefficients for each leg. The problems with the pump shutdown on line I8S/I9S had a much more drastic effect on salinity than on temperature. The underway salinity values on that cruise did not track the station salinity values and were, therefore, deemed unreliable. The salinity values given in the I8S/I9S data set are simply a linear interpolation of the station data. The thermosalinograph gave much better results on all of the legs after I8S/I9S. The standard deviation of the difference between the WOCE bottle salinities and the calibrated underway salinity values at the stations occupied on legs I9N through I2 was ±0.058.

Table 3. Coefficients for linear calibration of underway salinity

Leg	Intercept	Std. Dev.	Slope	Std. Dev.
I9N	+1.008	0.10	1.0091	0.003
I8N/I5E	–0.459	0.09	1.0539	0.003
I3	–0.335	0.25	1.0495	0.007
I5W/I4	–2.830	0.56	1.1245	0.020
I7N	+0.130	0.20	1.0368	0.007
I1	–0.230	0.20	1.0518	0.006
I10	–0.104	0.09	1.0382	0.003
I2	–1.548	0.14	1.0863	0.004

2.3 Underway CO_2 System Parameters

The temperature of the water inside the equilibrator was monitored with a Rosemont ultralinear platinum resistance thermometer (PRT). The PRT was calibrated in March 1994, prior to the first leg of the survey, by the SIO Ocean Data Facility (ODF) using standard CTD calibration techniques. Estimated accuracy was ±0.003°C on the ITS90 scale. A secondary check on the accuracy of the equilibrator temperature readings was made by frequently comparing temperature readings from a mercury thermometer, located in the equilibrator, to values recorded from the PRT.

Temperature readings from the Li-Cor detector were not explicitly calibrated for this survey because the final results are only a function of the relative changes in temperature between the standard gases and the sample.

The sensor used to monitor the system pressure (Setra Systems Inc.) was factory-calibrated prior to the survey in August 1994 against NIST-traceable primary standards. Estimated accuracy was ±0.05%.

All system inputs were read into the computer as voltages using a National Instruments Lab-PC+ A/D board. Accuracy of the board's readings was confirmed with a Fluke model 8840A 5½-digit voltmeter prior to the survey. The resolution of the readings was a function of the voltage range being measured, but in all cases was at least an order of magnitude smaller than the estimated precision of the measurement.

Data directly recorded by the underway system were tagged with a time based on the internal clock of the PC running the instrument. This clock was manually reset to Greenwich Mean Time (GMT) at the beginning of each leg. The IMET and navigation data recorded by the ship's system were tagged with GMT recorded from the GPS satellite data. A test of how closely the data were in sync was performed on every leg by examining the time offset between the observation of temperature fronts seen in the IMET sea surface temperature versus the equilibrator temperature. Despite the resetting of the PC clock, the equilibrator temperatures lagged the sea surface temperatures by 3.6 min at the beginning of every leg. This offset most likely represented the real time for the water to travel from the pump to the equilibrator (i.e., the residence time of the water in the ship). The offset generally decreased with time to near zero by the end of the longer cruises. The changing offset was attributed to the notoriously bad clocks used in personal computers, which could easily lose more then one minute per month. Under the assumption that the satellite time was correct, all of the xCO_2 data were synchronized to the IMET data before they were merged on the basis of a linear interpolation of the time offsets at the beginning and the end of each leg.

3. QUALITY CONTROL

All of the water and air xCO_2 measurements recorded during the Indian Ocean survey cruises were presented in the OTL original (preliminary) data files. Quality control (QC) flags (qflag) were used to identify "bad" (qflag = 4) measurements (later these measurements were removed from all data files), "questionable" (qflag = 3) measurements, and "good" (qflag = 2) measurements. Although there are several individual readings that can ultimately lead to a bad final value, one overall QC flag is reported for the measurement. This section describes the multilevel QC procedure performed by OTL and used to generate this flag. As described in the previous section, supporting measurements (sea surface temperature, salinity, and position) were filtered for bad values and interpolated to the times of the CO_2 measurements. Anyone interested in investigating the variability of these properties beyond its applicability to these CO_2 data is encouraged to return to the original IMET data set.

The first step in the calibration process was to normalize all of the detector CO_2 voltages to the mean detector temperature for that cruise and a pressure of one atmosphere. The first step in the QC protocols, therefore, was to remove any outliers in the detector temperature and pressure readings. Both of these measurements were very reliable with at most two to four isolated points removed on any given leg. Missing values were replaced with a linear approximation based on adjacent values.

The temperature- and pressure-normalized CO_2 voltages for each of the standards were analyzed for bad values. The collection program's criteria for determining when a CO_2 reading is stable were purposefully generous to prevent undersampling of real variability in the sample gases. Because the stability criteria were the same for sample and standard gases, the first point saved after switching to a new standard generally had not reached the equilibrium value. After visual confirmation of this phenomenon on each leg, the first point from each set of standards was filtered from the data set. Although rare, any exceptional outliers among the four remaining measurements on each standard were also visually identified and removed. The final calibration at each time was based on the mean of the remaining values.

Before the final calibrated values were calculated, a QC check of the equilibrator temperatures was performed. These data were quality controlled by examining all of the points recorded in 2-day intervals and outliers discarded based on visual inspection. Values were generally discarded when they were more than two standard deviations from a time local mean. The exact value for the cut, therefore, depended on the instrumental noise at the time. Questionable points were generally left in the data set. Bad values were replaced with a linear approximation based on adjacent values.

After calibration, the water and air data were broken into separate files. At this stage, every reading contributing to the water and air xCO_2 values has been quality controlled with the exception of the detector voltage. Unusual readings in the final data, therefore, either reflected real variability in the CO_2 concentration of the sample or bad voltage readings. Because it was not always clear which was the case and the final QC step was somewhat based on subjective ideas of how CO_2 behaves in the ocean or atmosphere, QC flags were created for each measurement. Only values that were known to be bad (qflag = 4) were removed from the final data set.

Marine air values showed little variability relative to the water measurements, which made identification of outliers easy. Values that were obvious outliers (qflag = 4) were visually identified by plotting the data from an entire leg as a function of time. High and variable values recorded when the ship was near land were only flagged when there were known detector problems since these values most likely represent real changes in atmospheric concentration. Questionable values (qflag = 3) were identified by carefully examining the data in 1- to 2-day intervals and marking isolated points that did not follow the local trend.

xCO_2 values in the surface seawater were generally much more variable than the marine air readings. A quality flag of "4" was reserved for water values that were clearly bad and for times when the seawater supply was shut down for extended periods, but the automated CO_2 system continued to sample air from the equilibrator (I8S/I9S only). Measurements marked with a quality flag of "3" were either identified as data collected during brief bow pump failures or as single outliers that clearly did not fit with the surrounding data. The times of brief bow pump failure were identified by using the analyst's notes and by plotting the sea surface temperature together with the equilibrator temperature values as a function of time. The two temperatures tracked each other very well except when the bow pump shut down and the two temperature readings would decouple.

The showerhead GC underway xCO_2 system designed by Ray Weiss of SIO was running in parallel with the Princeton non-dispersive infrared (NDIR) instrument (see Appendix A) during all nine Indian Ocean cruises aboard the R/V *Knorr*. Both systems shared the same marine air supply and took water from the uncontaminated bow pump plumbing at essentially the same point. The sampling frequency of the two systems was very different. Approximately 25,000 water measurements and 8,000 air measurements were automatically logged by the Princeton instrument along the 10,000-km cruise track of WOCE leg I9N (from Fremantle, Australia, to Colombo, Sri Lanka). By contrast, the SIO system made approximately 2,000 water and air measurements (two samples per hour) on the same cruise. The high sampling frequency for the Princeton system (average water sample interval was 2.5 minutes) was designed to allow examination of the small-scale spatial variability in surface xCO_2 values. Changes of 10 to 20 ppm over a distance of 10 km are not uncommon in open-ocean surface waters. These gradients can be an order of magnitude greater in frontal regions or in coastal waters. Despite the different designs of the two systems (e.g., GC vs NDIR and shower vs disk equilibrator) the Princeton and SIO underway systems gave nearly identical results. Figure 5 is a plot of ΔxCO_2 (Princeton – SIO) for surface water versus time for WOCE leg I9N. To make a fair comparison, given the very different sampling rates, CO_2 values were interpolated from each data set to 24 evenly distributed times per day (the top of every hour) for the entire cruise. The range of surface water CO_2 concentrations covered in this comparison was approximately 300 to 420 ppm. The mean difference between the two systems (0.86 ± 2.7 ppm) was not statistically different from zero. The standard deviation of the difference not only reflects the potential variability introduced from the interpolations but also any real variability that may have been sampled by one system and missed by the other.

4. RESULTS

Nearly 200,000 surface seawater and 50,000 marine air xCO_2 measurements were made with the Princeton underway system during the 14 months of the Indian Ocean survey. With the exception of leg I8S/I9S, all of the components of the system worked very well and the data are believed to be of the highest quality. This section briefly discusses the overall trends observed in the data and any major events relevant to the final values. All of the events described have been carefully examined and appropriate action has been taken to maintain the quality of the data presented in this report. All times are reported in day of the year relative to 1995 with time of day represented as a fractional day (i.e., noon on 1/1/95 = 1.5) to correspond directly with the time stamp recorded with the data.

As mentioned previously, leg I8S/I9S was the most troublesome of the entire Indian Ocean survey. The R/V *Knorr* departed Fremantle, Australia, on December 1, 1994 (1995 day –29) with the system functioning normally. Aside from short system shutdowns due to overloading circuit breakers, the system worked relatively well until day –20 when the ship encountered strong winds and heavy seas. The ship's bow pump system did not function properly when sea conditions resulted in the uptake of large number of bubbles or when the inlet came completely out of the water. The bow pump was off and on for the next several days. On day –11.33 the seawater supply for the equilibrator was switched to a secondary pumping system that was thought to be more reliable in rough weather. The secondary system, however, significantly heated the water before it reached the equilibrator. The degree of heating was extremely variable and was, at times, as much as 25°C. Although the degree of heating was documented in the difference between the calibrated sea surface temperature and the equilibrator temperature, attempts to correct the xCO_2 values to *in situ* conditions yielded unrealistic results. The data from the first 10 to 20 days of the cruise should be reliable. However, most of the data collected after switching to the secondary pump were deemed unreliable (see Fig. 6). Although some data from the last 20 days of the cruise appeared to be reasonable, care should be taken in placing too much confidence in these results.

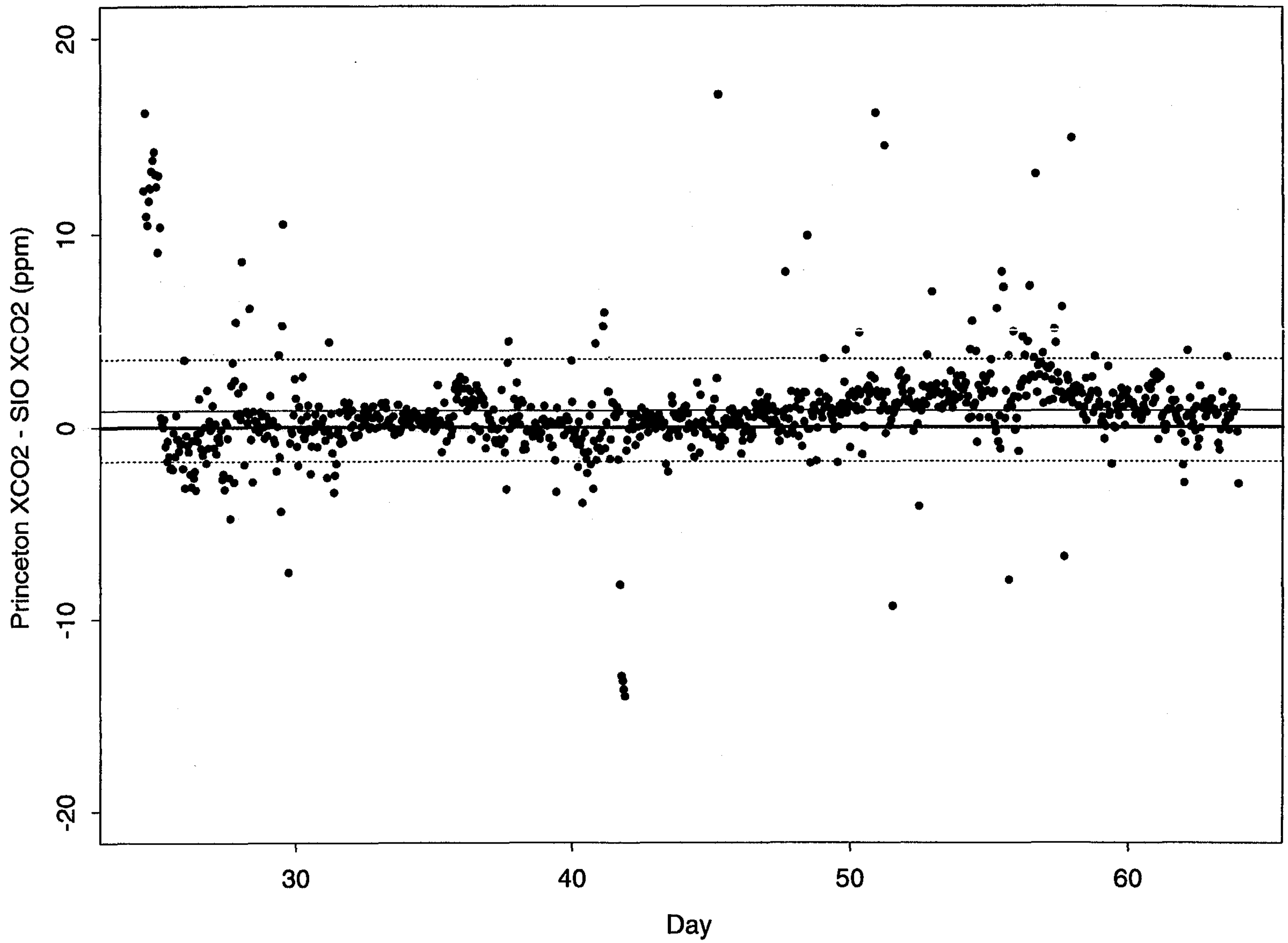


Figure 5. Plot of ΔxCO_2 (Princeton – SIO) for surface waters vs time for WOCE leg I9N.

A

B

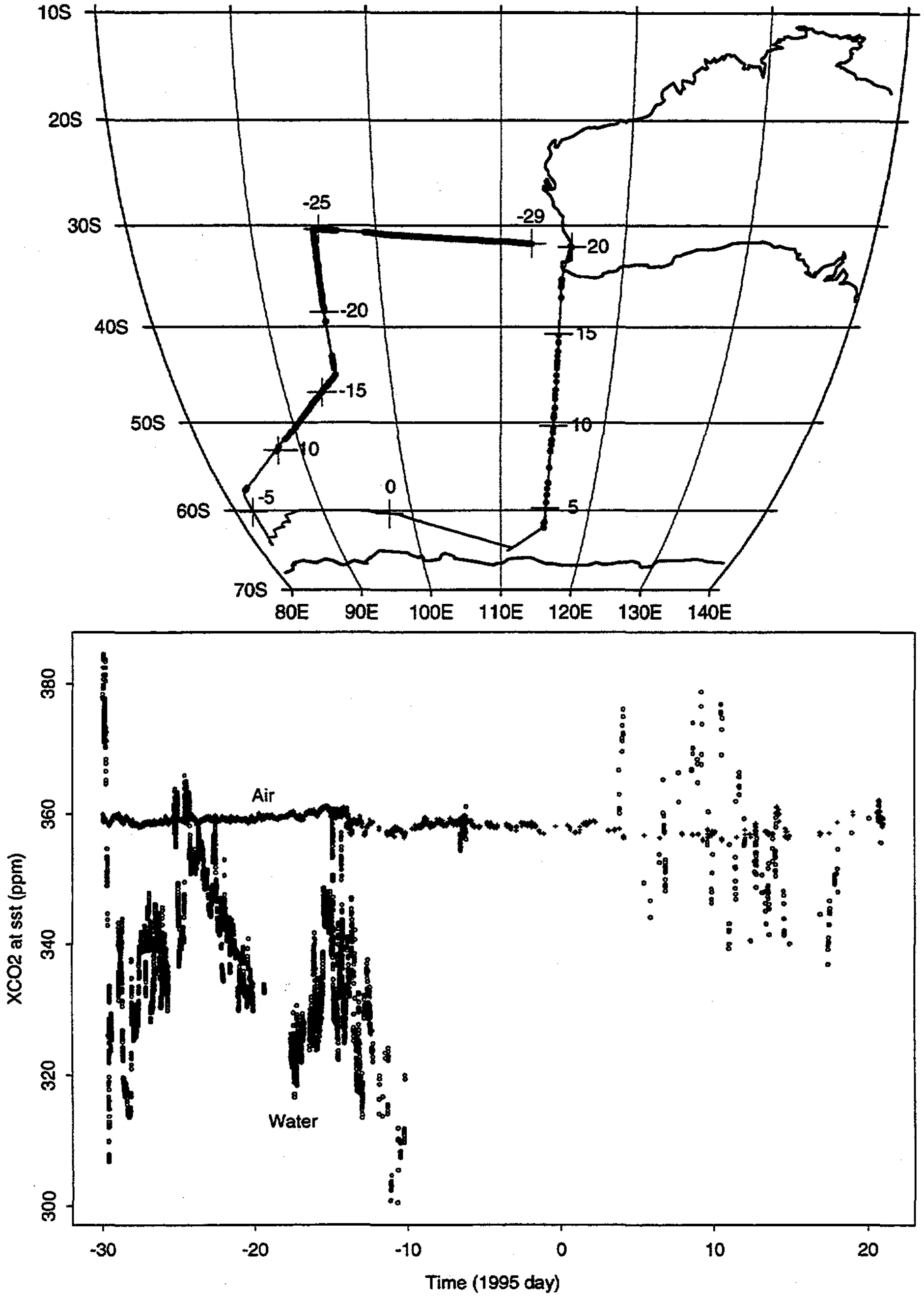


Figure 6. WOCE Indian Ocean Leg I8S/I9S cruise track and data plot. (A) Cruise track with points indicating where good CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I8S/I9S.

After the ship returned to Australia, the system was cleaned up and examined by C. Sabine of PU. Upon examination it was discovered that the CO_2 signal from the detector was unusually noisy (±0.01V). The noise problem was resolved by adjusting the setting on the rack temperature controller from 35 to 33°C. It was later discovered that this model LiCor detector had a substandard timing light emitting diode (LED) that was apparently in the process of failing. Lowering the temperature temporarily fixed the problem until the LED degraded enough to become a problem at the lower temperature (several months later). A replacement detector provided by LiCor was installed at the end of leg I8N/I5E and operated for the rest of the survey.

For leg I9N, lowering the rack temperature to 33°C seemed to fix the problem. The ship departed Fremantle, Australia, on day 24.3333. The water CO_2 concentrations were generally higher than the atmospheric concentrations for most of the cruise, with the exception of the Bay of Bengal where some of the lowest CO_2 concentrations of the survey were observed (Fig. 7). The weather was generally calm, so very few problems were experienced with the bow pump. The reference gas was changed to tank ALM008242 on day 40.3993. On day 59 a new data collection program was installed that read and recorded the IMET and NAV data from the ship's computer whenever a CO_2 data point was collected. Up to this time, the relevant IMET data were extracted after the cruise from the ship's one-minute files. The system was shut down on day 64.125 as the ship made its final approach to Sri Lanka.

Leg I8N/I5E departed Sri Lanka on day 69.5366 and headed south. The CO_2 concentrations of the waters south of Sri Lanka were generally 10 to 20 ppm higher than the atmospheric concentrations, but dropped quickly to values very near atmospheric at around 10° S (Fig. 8). The system generally ran well throughout the cruise, although post-cruise analysis of the data indicates that the time spent trying to analyze the standards started getting significantly longer around day 82. The reason for this lengthening is not known since this phenomenon was not noticed while the system was running. It is possible that the system got noisy again most likely because of the continued degradation of the timing LED in the detector. The problem did not seem to affect the data quality, only the length of time it took for the detector to stabilize and thus the quantity of data collected. When the ship returned to port in Fremantle, Australia, the LiCor was replaced with a new model from the factory.

Leg I3 was the first zonal leg of the survey. The R/V *Knorr* left Fremantle, Australia, on day 113.0040 and headed north along the Australian coast to approximately 20° S. The surface water CO_2 concentrations near the Australian coast were variable, but after the ship turned west there was a general decrease in CO_2 concentration until approximately 135° E, then a slow increase as the ship approached Madagascar (Fig. 9). The data gap between days 145 and 148 was the result of a short port stop in Mauritius. Aside from the detector being changed before the start of this leg, the only significant change to the system was a small modification to the chemicals in the drying column. Prior to this cruise, the chemical drying column was filled with magnesium perchlorate. Because it was difficult to determine when the perchlorate was becoming saturated, all cruises after this point used a column made up half with magnesium perchlorate and half with aquasorb (which changes from purple to black as it absorbs water). The reference tank was changed on day 144.2062, approximately 12 days before the end of the leg.

Leg I5W/I4 departed Mauritius on day 162.19 and returned on day 192 after a short port call in Durban, South Africa, around day 172. The surface water CO_2 concentrations were significantly lower than atmospheric concentrations for the entire leg (Fig. 10). The only significant problems with the system were encountered around day 168 because of a temporary

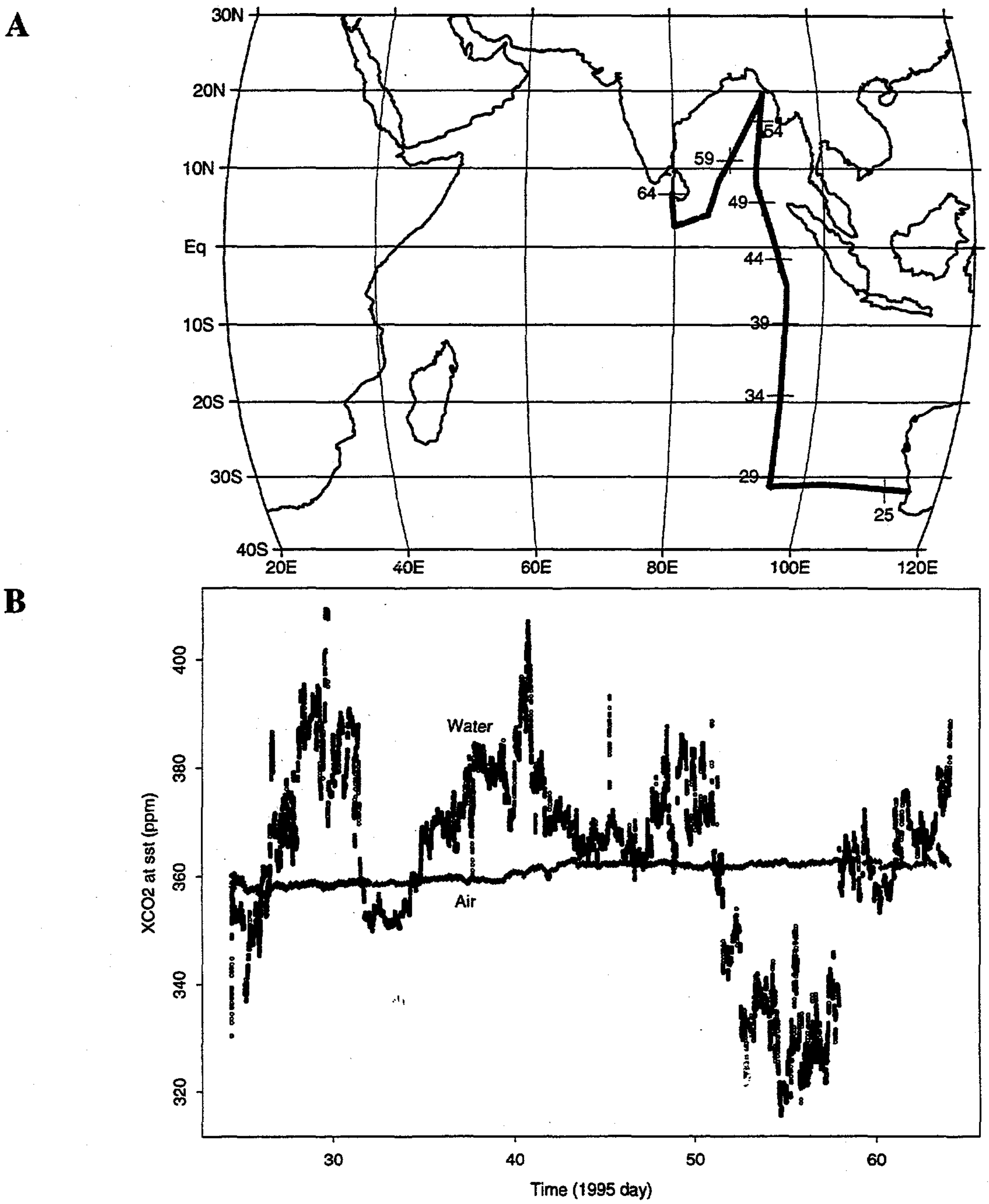


Figure 7. WOCE Indian Ocean Leg I9N cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I9N.

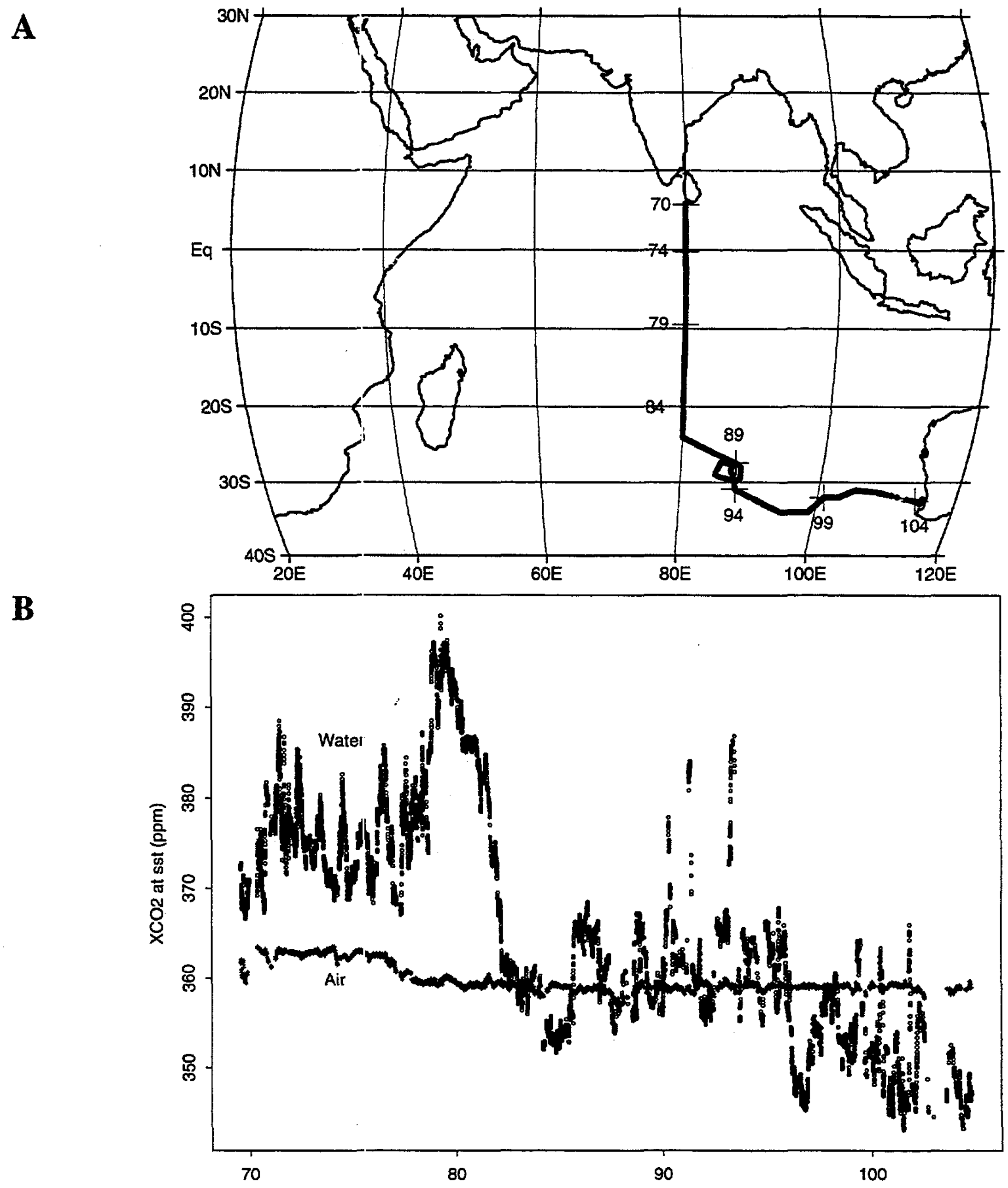


Figure 8. WOCE Indian Ocean Leg I8N/I5E cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I8N/I5E.

A

B

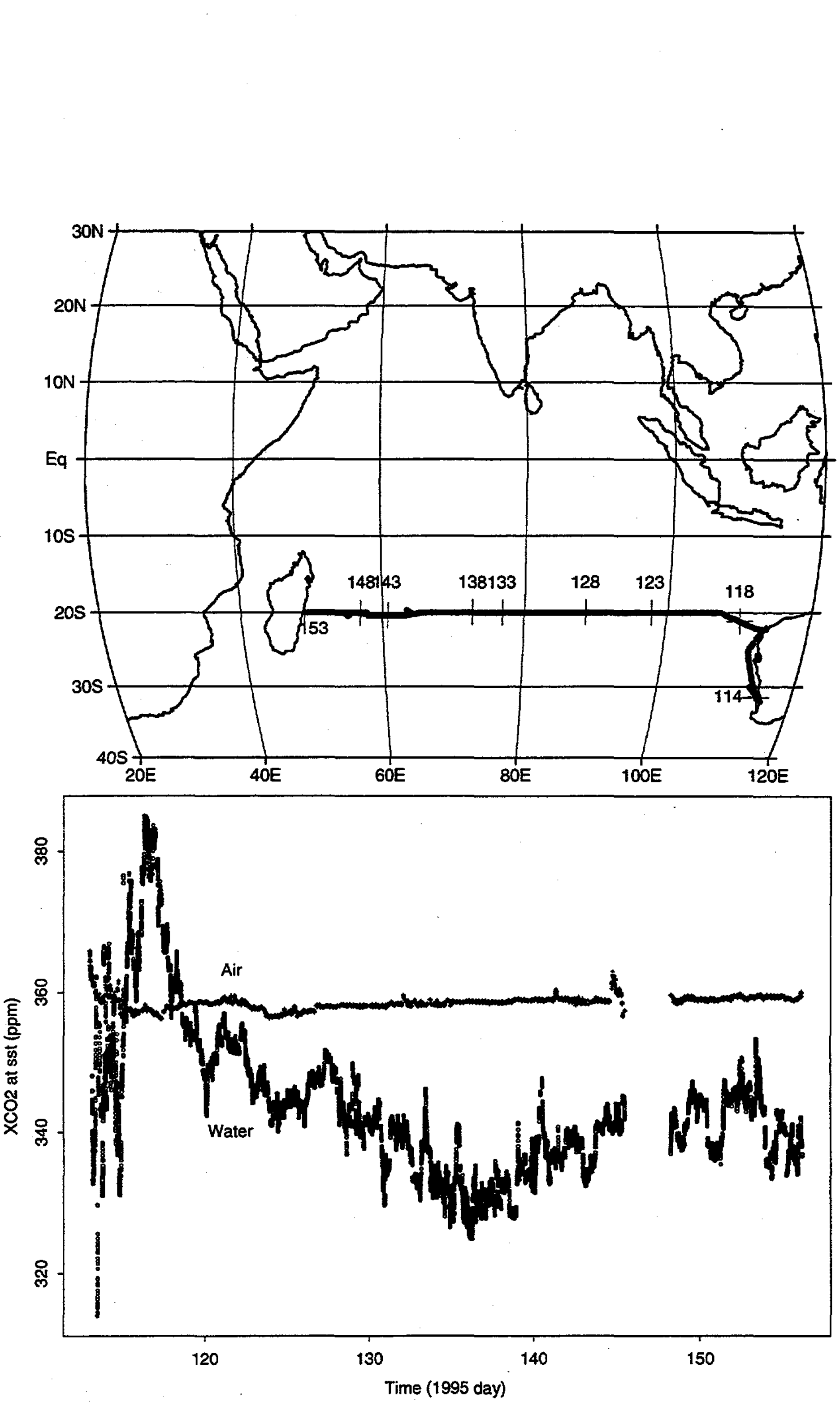


Figure 9. WOCE Indian Ocean Leg I3 cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I3.

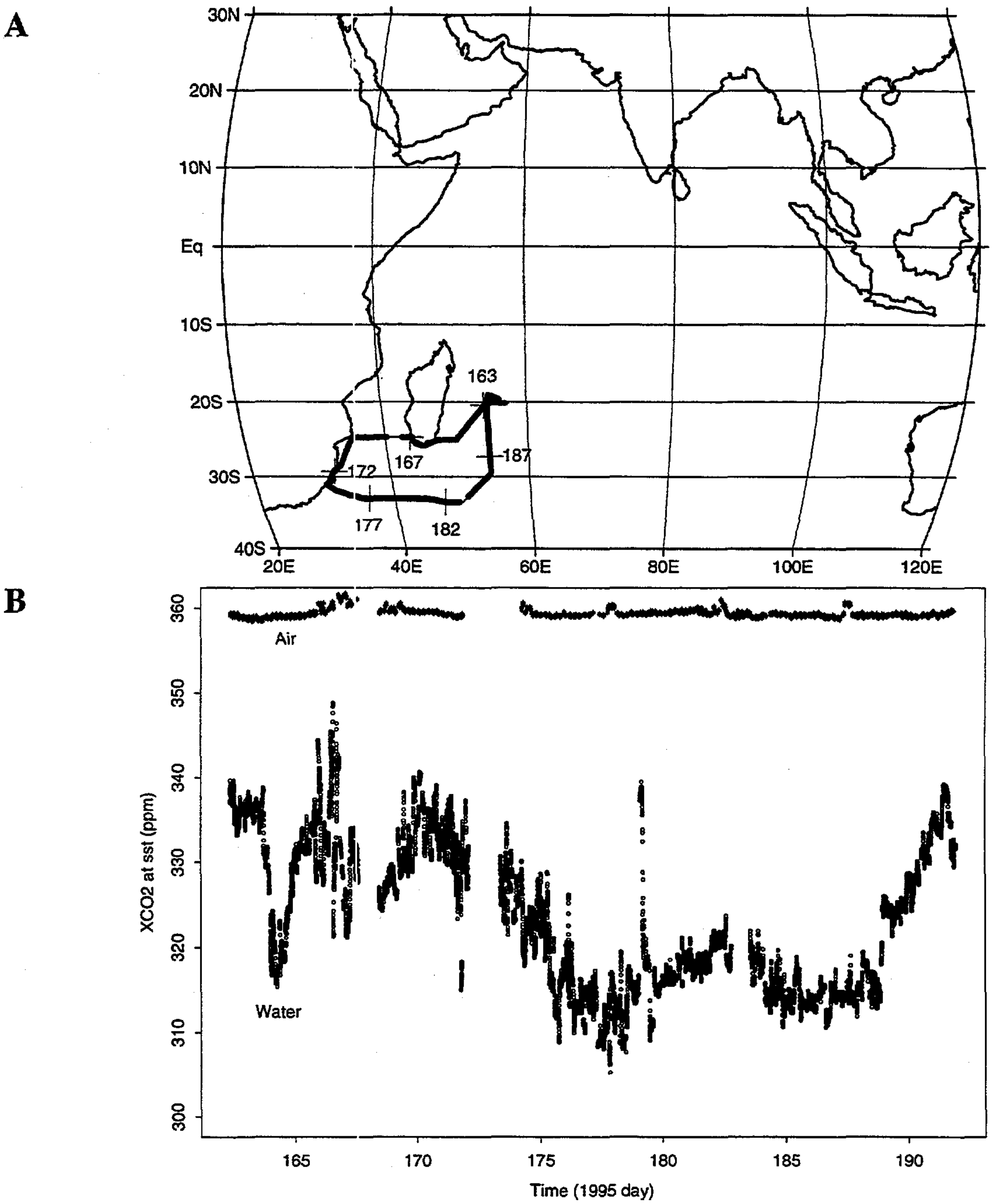


Figure 10. WOCE Indian Ocean Leg I5W/I4 cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I5W/I4.

mechanical problem with the equilibrator and on day 183 because of an extended bow pump shutdown caused by severe weather.

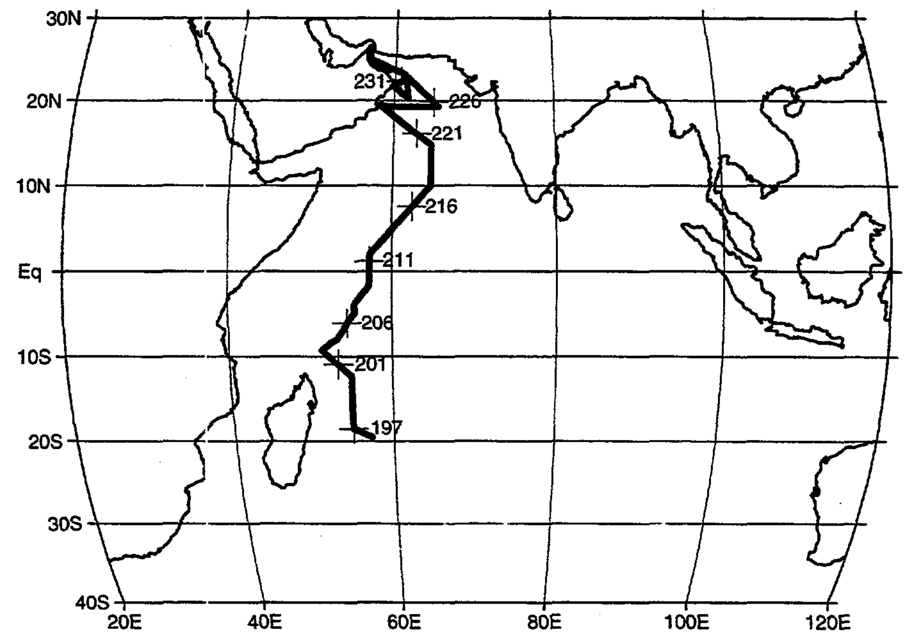
The R/V *Knorr* departed Mauritius on 196.3125 and headed north on leg I7N. Surface seawater CO_2 concentrations increased from approximately 20 ppm below atmospheric concentrations to approximately 20 ppm above atmospheric concentrations near 10° S (Fig. 11). The highest CO_2 concentrations (>600 ppm) were observed off the coast of Oman because of upwelling caused by the southwest monsoon. The monsoon also made the seas very rough, resulting in frequent bow pump failures. The failures were generally short and care was taken to flag the bad data. The reference tank was changed twice during this cruise. The first tank was replaced on day 206.4868 with a zero-CO_2 reference (tank 24813) since the 200 ppm references tanks were all exhausted. Tank 24813 had apparently leaked in shipping since it started with a pressure of only 700 psi. The reference tank was changed again on day 227.3958 to tank 18260.

Leg I1 departed Oman on day 241.4167. Before the system was started, the equilibrator was thoroughly cleaned. Unfortunately, during the cleaning the equilibrator PRT was broken. It was replaced with a spare that was calibrated to the initial PRT in post-cruise data processing. The high surface water CO_2 values observed at the end of leg I7N were also observed at the beginning of leg I1 (Fig. 12). The surface values generally decreased as the ship sailed away from the primary upwelling region. The ship took a short break in Sri Lanka from day 271 to day 273 before continuing on to the Straits of Malacca. The system was shut down as the ship entered Indonesian waters on day 286.4.

All systems were shut down for the 3 weeks that the R/V *Knorr* spent undergoing repairs in Singapore. C. Sabine and G. McDonald boarded the ship on day 303 and thoroughly cleaned and rebuilt the system during the transit from Singapore to Australia. New calibrated reference gases arrived at the ship, so tank ALM061365 was installed as the new reference gas. The LiCor detector also appeared to have had a slow drift in the zero voltage setting over its months of operation. The reference voltage had slowly drifted from 0.1 V when the detector was first set up on leg I3 to nearly 0.6 V by the end of leg I1. This voltage was reset to 0.1 before leg I10 using the zero adjust control on the LiCor. The ship's electronic technician was changing the IMET system around during the transit, so the underway system software had to be modified accordingly. The ship departed Dampier, Australia, for leg I10 on day 315.2943. The surface water CO_2 concentration decreased as the ship traveled south, then increased again as the ship turned north (Fig. 13). The highest xCO_2 values were observed in the Indonesian throughflow waters at the northern end of the section. The system was shut down on day 329.0104 as the ship crossed into Indonesian territorial waters. The only problem noted on the cruise was a loose connector on the atmospheric pressure sensor on day 322. The loose connector resulted in very noisy pressure readings that, in turn, resulted in noisy pressure normalized voltages. The bad pressures during the affected time period (days 322.5 to 323.5) were replaced with the ship's atmospheric pressure readings calibrated to match the underway system pressures preceding and following the affected times.

The final leg of the survey, I2, started on day 339.2764 as the ship cleared the Indonesian territorial waters. The surface water CO_2 concentration generally increased from east to west (Fig. 14). The large data gap seen in Figure 14 from day 361.5 to day 364.3 is the result of a port stop in Diego Garcia. The smaller gaps resulted from frequent system crashes caused by the inconsistent transmission of the IMET data by the ship's computers. The Indian Ocean survey ended in Mombasa, Kenya, on day 386.6076 after covering a total distance of ~92,000 km.

A



B

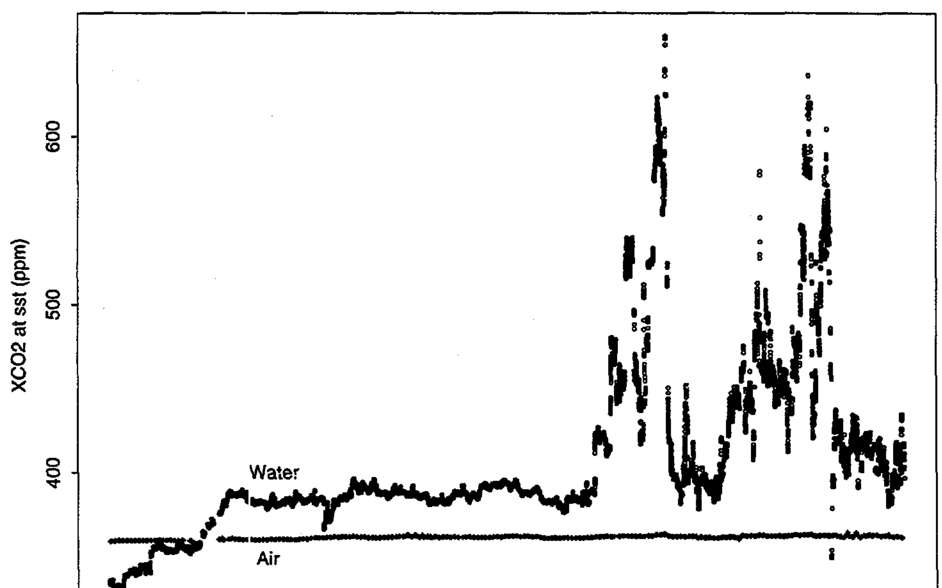
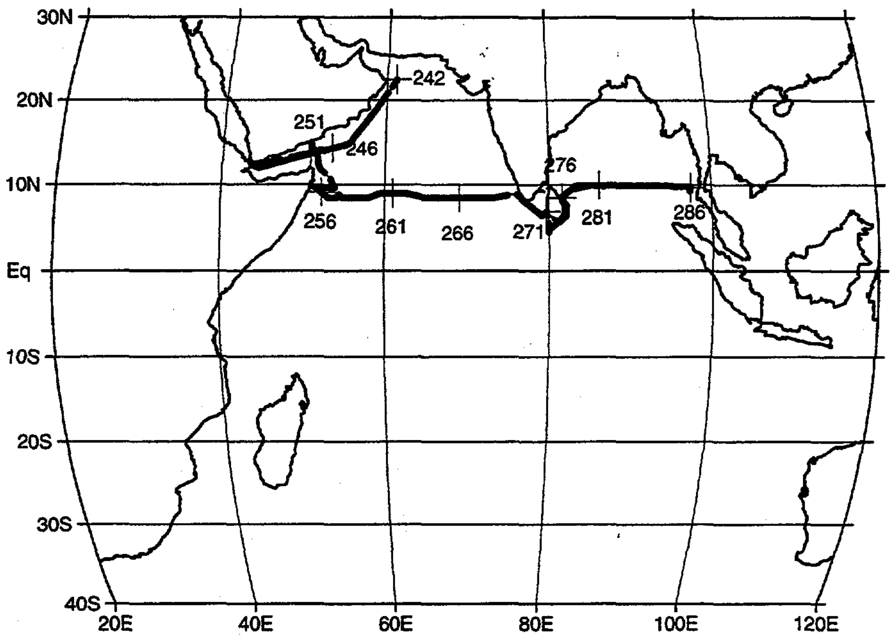


Figure 11. WOCE Indian Ocean Leg I7N cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I7N.

A



B

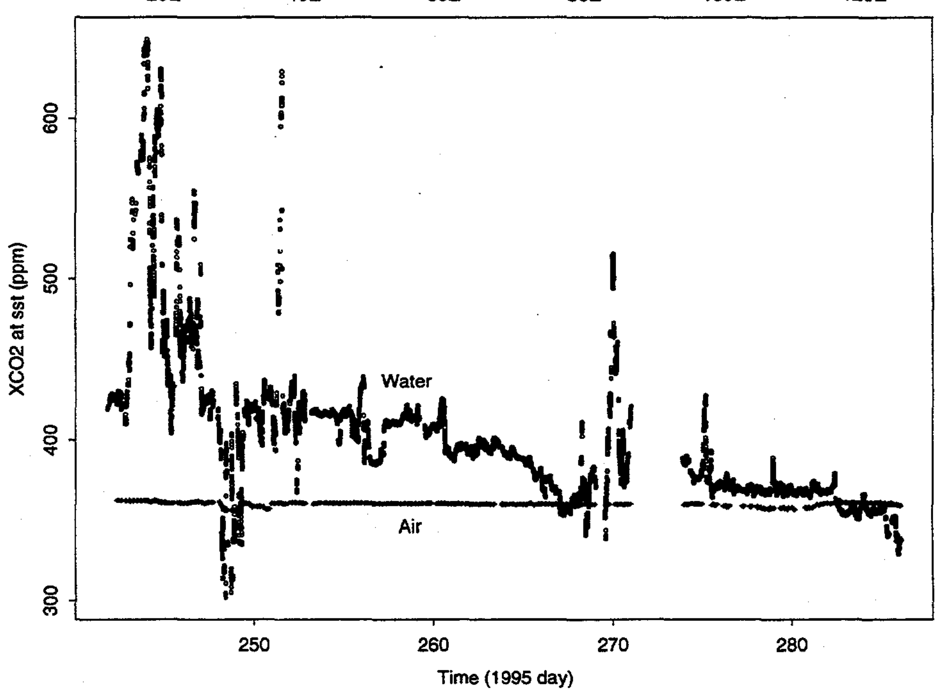
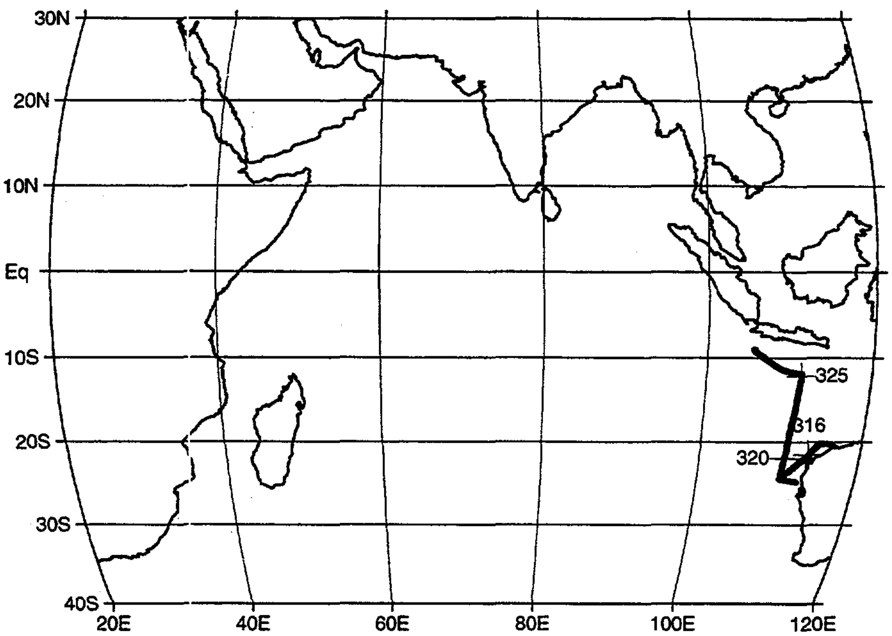


Figure 12. WOCE Indian Ocean Leg I1 cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I1.

A



B

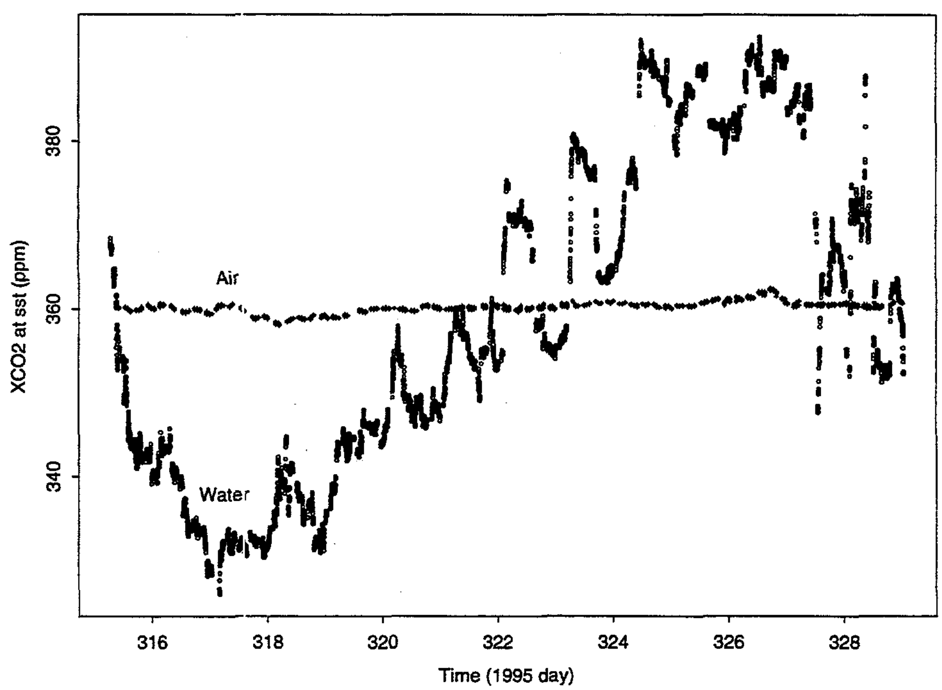


Figure 13. WOCE Indian Ocean Leg I10 cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I10.

A

B

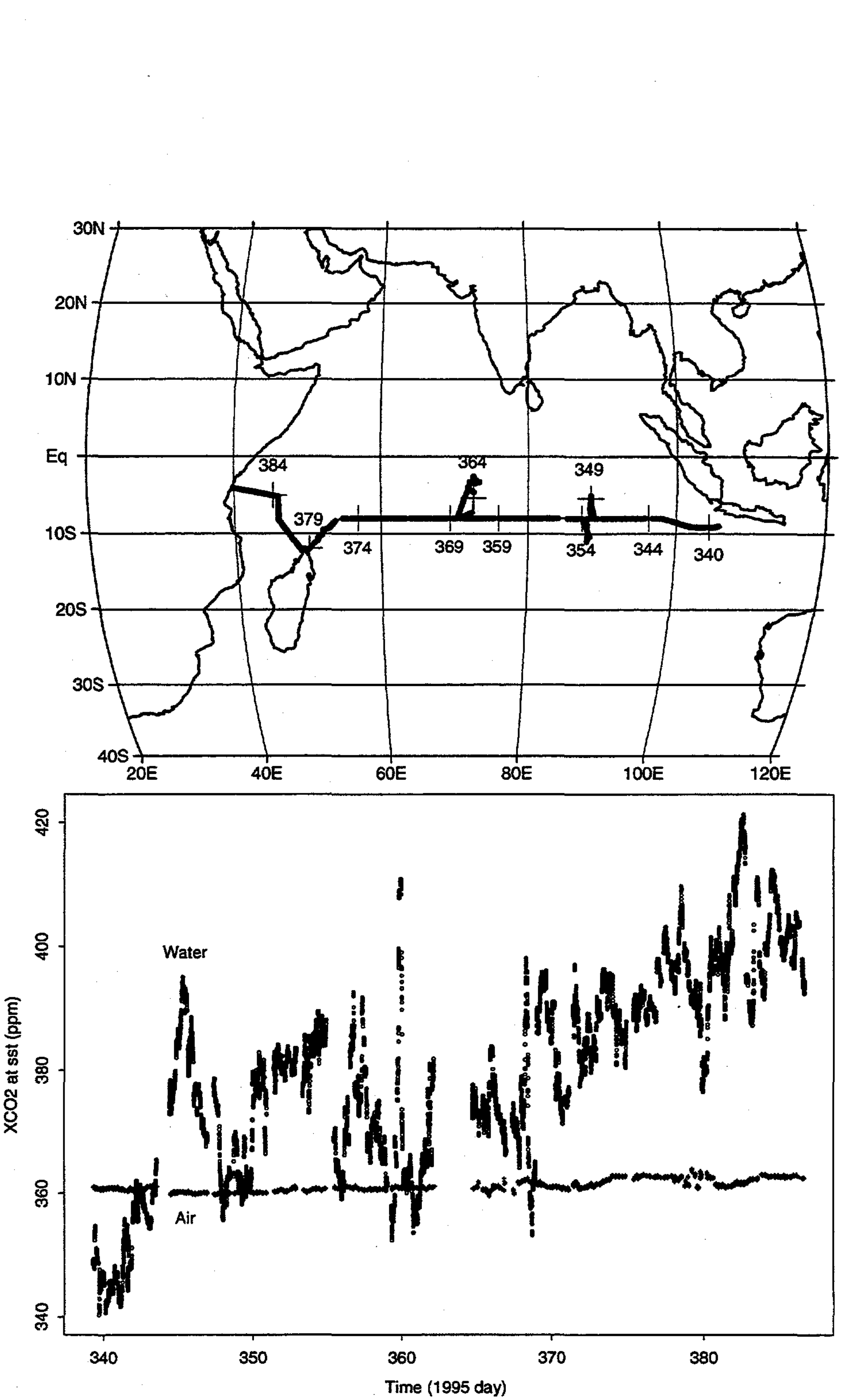


Figure 14. WOCE Indian Ocean Leg I2 cruise track and data plot. (A) Cruise track with points indicating where CO_2 measurements were collected, and tick marks showing location on indicated day (with respect to Jan. 1, 1995). (B) Plot of xCO_2 in air (plus marks) and water (circles) as a function of time for leg I2.

5. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the NDP process at the CDIAC involves the quality assurance (QA) of data before distribution. Data received at CDIAC are rarely in a condition that would permit immediate distribution, regardless of the source. To guarantee data of the highest possible quality, CDIAC conducts extensive QA reviews that involve examining the data for completeness, reasonableness, and accuracy. Although they have common objectives, these reviews are tailored to each data set and often require extensive programming efforts. In short, the QA process is a critical component in the value-added concept of supplying accurate, usable data for researchers.

The following information summarizes the data-processing and QA checks performed by CDIAC on the underway data obtained during the R/V *Knorr* Expeditions in the Indian Ocean (WOCE 9 Sections).

1. All underway measurements were provided to CDIAC as 18 ASCII-formatted files (9 for surface seawater and 9 for marine air CO_2 measurements) by Chris Sabine and Robert Key of PU. A FORTRAN 77 retrieval program was written and used to reformat the original files into uniform formats for "water" and "air" data files.

2. All individual "water" and "air" data files were merged into single "water" and single "air" files that were sorted and arranged chronologically.

3. All data were plotted to check for obvious outliers. Several outliers were identified and removed after consultation with the principal investigators.

4. All data that were marked by quality flag "4" as bad data in original files were removed after consultation with the principal investigators.

5. Dates and times were checked for bogus values (e.g., values of MONTH <1 or >12, DAY <1 or >31, YEAR <1994 or >1996, TIME <0000 or >2400.

6. All cruise tracks were plotted using the coordinates presented in data files and compared with the maps and cruise information supplied by C. Sabine and R. Key.

6. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database is available on request in machine-readable form, without charge, from CDIAC. CDIAC will also distribute subsets of the database as needed. It can be acquired on 9-track magnetic tape; 8-mm tape; 150-MB, 0.25-in. tape cartridge; MAC- or IBM-formatted floppy diskettes; or from CDIAC's anonymous file transfer protocol (FTP) area via the Internet (see FTP address below). Requests should include any specific media instructions required by the user to access the data (e.g., 1600 or 6250 BPI, labeled or nonlabeled, ASCII or EBCDIC characters, and variable- or fixed-length records; 3.5- or 5.25-in. floppy diskettes, high or low density; and 8200 or 8500 format, 8-mm tape). Magnetic tape requests not accompanied by specific instructions will be filled on 9-track, 6250-BPI, nonlabeled tapes with ASCII characters. Requests should be addressed to

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6335
U.S.A.

Telephone: 423-574-0390 or 423-574-3645
Fax: 423-574-2232

Electronic mail: cdiac@ornl.gov

The data files may also be acquired from CDIAC's anonymous FTP area via the Internet:

- FTP to cdiac.esd.ornl.gov (128.219.24.36),
- enter "ftp" or "anonymous" as the user ID,
- enter your electronic mail address as the password (e.g.,"alex@esd.ornl.gov"),[1]
- change to the directory "/pub/ndp064," and
- acquire the files using the FTP "get" or "mget" command.

As an alternative, the data can be accessed through the following World Wide Web site: http://cdiac.esd.ornl.gov/oceans/doc.html.

[1]Please enter your correct address. This address is used by CDIAC to inform data recipients of revisions and updates.

7. ACKNOWLEDGEMENTS

C. Sabine and R. Key would like to thank all of the members of the DOE CO_2 survey team for helpful advice while they were building the underway system and for helping to run the system during the Indian Ocean survey. In particular they thank R. Weiss and R. Van Woy for calibration of standard gases and the captain and crew of the R/V *Knorr* for assistance throughout the survey. They also thank the chief scientists from each leg as well as the U.S. WOCE Hydrographic Programme Office for their assistance and cooperation with the underway measurements. This work was supported by a grant from the U.S. DOE's Office of Biological and Environmental Research (DE-FG02-93ER61540) and the Princeton University Department of Geosciences.

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Weiss, R. F. 1981. Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. *J. Chrom. Sci.* 19:611–16.

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PART 2:

CONTENT AND FORMAT OF DATA FILES

9. FILE DESCRIPTIONS

This section describes the content and format of each of the 23 files that make up this NDP (see Table 4). Because CDIAC distributes the data set in several ways (e.g., via anonymous FTP, on floppy diskette, and on 9-track magnetic tape), each of the 23 files is referenced by both an ASCII file name, which is given in lowercase, boldfaced type (e.g., **ndp064.doc**), and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file. The files are discussed in the order in which they appear on the magnetic tape.

Table 4. Content, size, and format of data files

File number, name, and description	Logical records	File size in bytes	Block size	Record length
1. **ndp064.doc**: a detailed description of the cruise network, the two FORTRAN 77 data-retrieval routines, and the 20 oceanographic data files	1,215	69,710	8,000	80
2. **xco2airdat.for**: a FORTRAN 77 data-retrieval routine to read and print any of ***air.dat** files	45	1,597	8,000	80
3. **xco2waterdat.for:** a FORTRAN 77 data-retrieval routine to read and print any of ***water.dat** files	50	1,883	8,000	80
4. **IOxco2air.dat** underway marine air xCO_2 and surface hydrographic data from all nine Indian Ocean survey cruises	45,834	4,766,434	6,850	137
5. **IOxco2water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from all nine Indian Ocean survey cruises	187,030	26,939,825	6,850	137

Table 4 (continued)

File number, name, and description	Logical records	File size in bytes	Block size	Record length
6. **i8si9sair.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I8S/I9S	4,809	499,834	6,850	137
7. **i8si9swater.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I8S/I9S	10,480	1,466,733	6,850	137
8. **i9nair.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I9N	7,632	793,426	6,850	137
9. **i9nwater.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I9N	25,077	3,510,313	6,850	137
10. **i8ni5eair.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I8N/I5E	4,519	469,674	6,850	137
11. **i8ni5ewater.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I8N/I5E	14,021	1,962,473	6,850	137

Table 4 (continued)

File number, name, and description	Logical records	File size in bytes	Block size	Record length
12. **i3air.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I3	6,430	668,418	6,850	137
13. **i3water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I3	30,549	4,276,393	6,850	137
14. **i5wi4air.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I5W/I4	4,388	456,050	6,850	137
15. **i5wi4water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I5W/I4	20,423	2,858,753	6,850	137
16. **i7nair.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I7N	5,846	607,682	6,850	137
17. **i7nwater.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I7N	29,832	4,176,013	6,850	137

Table 4 (continued)

File number, name, and description	Logical records	File size in bytes	Block size	Record length
18. **i1air.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I1	6,254	650,114	6,850	137
19. **i1water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I1	28,248	4,067,217	6,850	137
20. **i10air.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I10	1,910	198,338	6,850	137
21. **i10water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I10	8,399	1,208,961	6,850	137
22. **i2air.dat:** underway marine air xCO_2 and surface hydrographic data from Indian Ocean WOCE section I2	4,102	426,306	6,850	137
23. **i2water.dat:** underway surface seawater xCO_2, interpolated atmospheric xCO_2, and underway hydrographic data from Indian Ocean WOCE section I2	20,057	2,807,513	6,850	137
Total	467,150	58,175,660		

9.1 ndp064.doc (File 1)

This file contains a detailed description of the data set, the two FORTRAN 77 data retrieval routines, and the 20 oceanographic data files. It exists primarily for the benefit of individuals who acquire this database as machine-readable data files from CDIAC.

9.2 xco2airdat.for (File 2)

This file contains a FORTRAN 77 data-retrieval routine to read and print all ***air.dat** files. The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for ***air.dat** files.

```
c*******************************************************************
c* This is a Fortran 77 retrieval code to read and format the underway
c* air xCO2 and hydrographic measurements from the WOCE Indian Ocean
c* survey cruises (*air.dat files)
c*******************************************************************

       INTEGER  flag
       REAL jday, atmpre, airxco2, lat, lon, temp, sal
       CHARACTER sect*11, date*8, time*8
       OPEN (unit=1, file='input.dat')
       OPEN (unit=2, file='output.dat')
       write (2, 5)

 5     format (2X,'SECTION',7X,'DATE',6X,'TIME',4X,'JULIAN',2X,
     1 'ATM_PRES',5X,'XCO2',5X,'XCO2',2X,'LATIT',3X,'LONGIT',3X,
     2 'SUR_TMP',2X,'SUR_SAL',/,5X,'#',11X,'GMT',7X,'GMT',5X,'DATE',
     3 6X,'ATM',3X,'DRY_AIR_PPM',1X,'QC_FL',3X,'DCM',6X,'DCM',5X,
     4 'DEG_C',5X,'PSS',/)

       read (1, 6)
 6     format (//////)

 7     CONTINUE
       read (1, 10, end=999) sect, date, time, jday, atmpre, airxco2,
     1 flag, lat, lon, temp, sal

 10    format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 2X, F7.5, 3X, F7.3,
     1 5X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X, F7.4)

       write (2, 20) sect, date, time, jday, atmpre, airxco2,
     1 flag, lat, lon, temp, sal

 20    format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 2X, F7.5, 3X, F7.3,
     1 5X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X, F7.4)

       GOTO 7
 999   close(unit=5)
       close(unit=2)
       stop
       end
```

9.3 xco2waterdat.for (File 3)

This file contains a FORTRAN 77 data-retrieval routine to read and print all ***water.dat** files. The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for ***water.dat** files.

```
c***********************************************************************
c* This is a Fortran 77 retrieval code to read and format the underway
c* surface seawater xCO2 and hydrographic measurements from the WOCE
c* Indian Ocean survey cruises (*water.dat files)
c***********************************************************************

       INTEGER  flag
       REAL jday, equitmp, atmpre, eqxco2, lat, lon
       REAL temp, sal, xco2sst, eaxco2
       CHARACTER sect*11, date*8, time*8
       OPEN (unit=1, file='input.dat')
       OPEN (unit=2, file='output.dat')
       write (2, 5)

 5     format (2X,'SECTION',7X,'DATE',6X,'TIME',5X,'JULIAN',2X,
     1 'EQUIL_TMP',2X,'ATM_PRES',3X,'XCO2_DRY_AIR',4X,'XCO2',2X,
     2 'LATIT',3X,'LONGIT',3X,'SUR_TMP',2X,'SUR_SAL',1X,
     3 'XCO2_DRY_AIR', 1X, 'EST_ATM_XCO2',/,5X,'#',11X,'GMT',7X,
     4 'GMT',6X,'DATE',5X,'DEG_C',6X,'ATM',4X,'AT_EQUIL_TMP_PPM',
     5 1X,'QC_FL',3X,'DCM',6X,'DCM',5X,'DEG_C',5X,'PSS',4X,
     6 'AT_SST_PPM',2X,'DRY_AIR_PPM',/)

       read (1, 6)
 6     format (//////)

 7     CONTINUE
       read (1, 10, end=999) sect, date, time, jday, equitmp,
     1 atmpre, eqxco2, flag, lat, lon, temp, sal, xco2sst, eaxco2

 10    format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 3X, F7.4, 4X,
     1 F7.5, 5X, F7.3, 8X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X,
     2 F7.4, 4X, F7.3, 5X, F7.3)

       write (2, 20) sect, date, time, jday, equitmp,
     1 atmpre, eqxco2, flag, lat, lon, temp, sal, xco2sst, eaxco2

 20    format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 3X, F7.4, 4X,
     1 F7.5, 5X, F7.3, 8X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X,
     2 F7.4, 4X, F7.3, 5X, F7.3)

       GOTO 7
 999   close(unit=5)
       close(unit=2)
       stop
       end
```

9.4 *air.dat files

These 10 data files contain the underway marine air xCO_2 measurements and sea surface hydrographic data collected during the WOCE Indian Ocean survey cruises. All files have the same ASCII format and can be read by using the following FORTRAN 77 code [contained in **xco2airdat.for** (File 2)]:

```
      INTEGER  flag
      REAL jday, atmpre, airxco2, lat, lon, temp, sal
      CHARACTER sect*11, date*8, time*8

      read (1, 10, end=999) sect, date, time, jday, atmpre, airxco2,
     1 flag, lat, lon, temp, sal

 10   format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 2X, F7.5, 3X, F7.3,
     1 5X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X, F7.4)
```

Stated in tabular form, the contents include the following

Variable	Variable type	Variable width	Starting column	Ending column
sect	Character	11	2	12
date	Character	8	15	22
time	Character	8	25	32
jday	Numeric	7	35	41
atmpre	Numeric	7	44	50
airxco2	Numeric	7	54	60
flag	Numeric	1	66	66
lat	Numeric	8	69	76
lon	Numeric	8	78	85
temp	Numeric	7	88	94
sal	Numeric	7	97	103

The variables are defined as follows:

sect is the WOCE section number;

date is the sampling date (month/day/year);

time is the sampling time (GMT);

jday is the julian day of the year relative to 1995 with time of the day represented as a fractional day (i.e. noon on 1/1/95=1.5);

atmpre is the atmospheric pressure (atm);

airxco2 is the observed mole fraction of CO_2 in air [ppm (dry air)];

flag is the airxco2 data quality flag:
2 = acceptable measurement of airxco2;
3 = questionable measurements of airxco2;

lat is the latitude of the sampling location (decimal degrees; negative values indicate the Southern Hemisphere);

lon is the longitude of the sampling location (decimal degrees; negative values indicate the Western Hemisphere);

temp is the sea-surface temperature (°C);

sal is the sea-surface salinity [on the Practical Salinity Scale (PSS)].

9.5 *water.dat files

These 10 data files contain the underway surface seawater xCO_2, atmospheric xCO_2 concentrations interpolated to the times when water measurements were made, and hydrographic measurements collected during WOCE Indian Ocean survey cruises. All files have the same ASCII format and can be read by using the following FORTRAN 77 code [contained in **xco2waterdat.for** (File 3)]:

```
      INTEGER  flag
      REAL jday, equitmp, atmpre, eqxco2, lat, lon
      REAL temp, sal, xco2sst, eaxco2
      CHARACTER sect*11, date*8, time*8

      read (1, 10, end=999) sect, date, time, jday, equitmp,
     1 atmpre, eqxco2, flag, lat, lon, temp, sal, xco2sst, eaxco2

 10   format (1X, A11, 2X, A8, 2X, A8, 2X, F7.3, 3X, F7.4, 4X,
     1 F7.5, 5X, F7.3, 8X, I1, 2X, F8.4, 1X, F8.4, 2X, F7.4, 2X,
     2 F7.4, 4X, F7.3, 5X, F7.3)
```

Stated in tabular form, the contents include the following:

Variable	Variable type	Variable width	Starting column	Ending column
sect	Character	11	2	12
date	Character	8	15	22

time	Character	8	25	32
jday	Numeric	7	35	41
equitmp	Numeric	7	45	51
atmpre	Numeric	7	56	62
eqxco2	Numeric	7	68	74
flag	Numeric	1	83	83
lat	Numeric	8	86	93
lon	Numeric	8	95	102
temp	Numeric	7	105	111
sal	Numeric	7	114	120
xco2sst	Numeric	7	125	131
eaxco2	Numeric	7	137	143

The variables are defined as follows:

sect is the WOCE section number;

date is the sampling date (month/day/year);

time is the sampling time (GMT);

jday is the julian day of the year relative to 1995 with time of the day represented as a fractional day (i.e., noon on 1/1/95 = 1.5);

equitmp equilibrator temperature (°C);

atmpre is the atmospheric pressure (atm);

eqxco2 is the observed mole fraction of CO_2 in surface seawater at the equilibrator temperature [ppm (dry air)];

flag is the eqxco2 data quality flag:
2 = acceptable measurement of eqxco2;
3 = questionable measurements of eqxco2;

lat is the latitude of the sampling location (decimal degrees; negative values indicate the Southern Hemisphere);

lon is the longitude of the sampling location (decimal degrees; negative values indicate the Western Hemisphere);

temp is the sea-surface temperature (°C);

sal is the sea-surface salinity (PSS);

xco2sst is the mole fraction of CO_2 in surface seawater corrected to sea surface temperature [ppm (dry air)]. Temperature correction was determined from the equations of Weiss et al. (1982);

eaxco2 is the atmospheric xCO_2 concentrations interpolated to the times when water measurements were made [ppm (dry air)].

APPENDIX A:

REPRINT OF PERTINENT LITERATURE

removed

APPENDIX B:

NOTATIONS FROM AT-SEA NOTEBOOKS, E-MAIL CORRESPONDENCE DURING THE CRUISE, AND THE POST-CRUISE ANALYSIS OF THE DATA

Appendix B

The following notations are compiled from the at-sea notebooks, e-mail correspondence during the cruise as well as post-cruise analysis of the data. Many of the notations did not have a noticeable impact on the final results, but have been included in an attempt to be thorough. All notations are indexed to 1995 days and are broken down into WOCE leg designations.

I8S/I9S

-31	Bob Key set up system in aft port corner of main lab on the R/V Knorr. In setting up the computer, Bob blew the fuse on the A/D board. He replaced blown fuse with spare located on the board.
-30	Water trap on equilibrator line filled with water. Began official data collection at 23:27. Reset run number to 1.
-29.2035	Changed drying column.
-29.3215	Reset computer clock to match GPS.
-29.6875	Ship left the dock. Ken Johnson primary pCO_2 analyst.
-28.6895	System water pump shut off...blown circuit breaker on lab plug.
-27.2708	System water pump back on...rerouted to another circuit.
-25.75	Approximate time of system water pump shutdown due to blown circuit breaker.
-24.25	Replaced air pump.
-20	Frequent system shutdowns due to bow pump failure (caused by heavy seas).
-20	Changed to data disk #2.
-19	Changed drying tube.
-17	Refit air pumps.
-11.33	Seawater supply switched to secondary pumping system.
-10.25	ship's bow pump down. 110 power supply for system water pump fried.
-10.7833	Weather up- ship was hove to.
-7.4181	110 power supply for system water pump repaired by crew.
-1	Changed to data disk #3. Changed drying column.
3.2	Changed to reference tank AAL1791. Notes only stated day...time was estimated by examining the data.
4.7715	Seawater pump down...blown circuit breaker
7	Changed air pump.

11.7972	Circuit breaker blown again.
12	Changed to data disk #4. Changed drying column.
15.1889	Water pump off again.
16	Water meter not recording, but water still flowing OK. Changed air pump.

I9N

24.3333	System turned on as ship was leaving port. C. Sabine was primary CO_2 analyst. While in port, the equilibrator was taken apart and cleaned. The shaft bearing on the left side of the equilibrator was seized to the disk shaft. It was removed and cleaned with steel wool before being replaced (no spare available). Both teflon seals were replaced. Discovered that the circuit breaker kept tripping on the previous cruise because both the disk motor and the water pump were plugged into the same circuit. The two motors together can draw 20 amps from the 15 amp circuit. The water pump was rerouted to a new circuit. The equilibrator air pump was replaced. The water trap on equilibrator air line was replaced with new model. Cleaned air filter on line 5. Noticed that CO2 signal was very noisy (+/- 0.01V). Discovered that noise went away if the temperature controller was set to 33 °C instead of 35 °C. Standard and reference gas use was very high on previous cruise, so the standard gas flow rates were adjusted down to 8-10 mm on the rotometer. The regulator on the 350 standard had trouble maintaining a steady flow rate, so it was swapped with spare.
25.0833	Equilibrator air flow down to 1-2 L/min. Swapped air pumps...flow back up to 7 l/min. Have had following wind since leaving port...using aft intake.
27	Wind has come around so it is no longer from behind (intake switched). Marine air flow jumped from 1L/min to 8L/min. Kevin Sullivan (watching Weiss system) says Weiss flow is still OK.
32.1534	Changed perchlorate drying column just before calibration run.
32.3542	Discovered that marine air rotometer was stuck. After cleaning flow was 4L/min.
33	Marine air flow down to 1.5 L/min. Appears to be some moisture in rotometer again.
34.2431	Bow pump shut off for ~5min. Did not notice whether any samples were collected.
34.9167	Seawater shut off for 15-20 minutes.
34.9653	Seawater back on.
35.0076	Bow pump off...switched computer to run gas calibration
35.0139	Water pump back on.

35.1625	Changed data disk.
40.3993	Program paused to change reference tank to ALM008242 (on sta 192).
40.4313	Program started again.
40.5	Paused program to change drying chemicals. Forced to rerun standards.
47	Examined surface temperature with a bucket and thermometer. Bucket temperatures were as much as 1.5 °C warmer than CTD temps. I believe this represents a real temperature gradient in the upper meter or so of the water column while we are experiencing VERY calm, glass-like conditions and bright sunny days.
47.9590	Changed data disk.
50.8611	System water pump quit and drained equilibrator.
50.8646	Water pump back on.
50.9076	Water pump quit again.
50.9306	Water pump on again.
51.8889	Water pump out 1-2 minutes.
51.1229	Water pump out 1-2 minutes. Believe pump brushes are worn out.
51.4028	Changed drying chemicals. Forced to run calibration.
53.2	Started run East to Andaman Islands to drop off observers.
53.3958	Water pump swapped with spare while system was running standards. Checked old motor and discovered centrifugal switch was warn out.
58.0000	Changed data disk.
59.1471	Stopped program and installed PCO2A3.BAS. This program reads the IMET data in real time. While system was down, the drying chemicals were changed and cleaned the equilibrator rotometer (6).
59.2134	System up and running again.
59.4316	Program crash due to garbage in IMET signal.
59.7271	Program crash.
59.8542	Program crash.
60.0604	Program crash...switched back to PCO2A2.BAS until error trap can be written.
60.3104	Started PCO2A3.BAS
60.3403	Program crashed...fixed.
60.7674	Marine air pump replaced.

62.0104	Program crash.
62.4109	Program crash.
62.4894	Program crash.
63.3022	Bottom of drying column very wet. Stopped program and changed chemicals. Nafion tube seems OK...must have been some plug of water blown through?
63.4295	Program crash.
64.10069	Shut water flow off. Running final standards.
64.125	Program stopped.

I8N/I5E

69.5366	System started after Knorr's departure from Sri Lanka (G. McDonald in charge).
70.3021	Noticed water in perchlorate drying column. Replaced Nafion tube, fixed a clog in Ultra Torr tee on perchlorate column and changed drying chemicals.
71.0010	Marine air pump replaced.
71.1563	Detector voltage seemed "spiky" on standards, lowered rack temperature controller to 32.5 °C.
74.3021	Reset all flow rates based on standard tank pressure dropping. IMET data flaky. System had to be restarted.
77.25	Power shutdown in main lab...system off-line.
77.4167	System restarted after power was restored to lab.
78.0243	Marine air pump replaced.
82	Post cruise analysis of data indicates that the time spent trying to analyze the standards is starting to get significantly longer. The reason for this is not known since Gerry did not notice this while the system was running, but we suspect that the system got noisy again most likely due to the continued degradation of the timing LED in the detector. The problem does not seem to have affected the data quality, only the length of time it takes the detector to stabilize and thus the quantity of data collected.
88.45	Estimated time when reference tank was changed (Gerry's notes somewhat ambiguous). New reference tank number ALM027282.
97.8681	Ship's bow pump down...rough weather.
97.8743	Bow pump running again.
101	Equilibrator air supply low...adjusted back to proper setting.
103.3354	System locked up due to shutdown in IMET data, Rebooted computer at 103.4694.

104.750 Ship's bow pump shut down upon approach into Fremantle.

I3

106	Swapped detector for LiCor replacement. Broke rack temperature controller PRT, replaced with spare.
113.0040	Departed Fremantle, Australia (R. Key running system).
113.6042	Reversed course for medical drop off.
114.0618	Rack temperature controller set temperature lowered from 32.5 to 30.5.
114.1562	Reversed course after medivac.
115.0833	Changed pump heads and changed drying column (started using Aquasorb in drying column instead of Mg-perchlorate).
116.0784	Complete cleaning of equilibrator air lines up to Valco, clean pump, new drying chemicals. Flow greatly improved.
118.0208	New drying column.
119.0001	Data transfer.
120.0799	New drying column.
122.1507	New drying column.
124.5986	New drying column.
126.6153	New drying column.
127.0146	Data transfer.
127.6674	New drying column.
129.7139	New drying column.
132.1500	Cleaned equilibrator pump
132.3785	New drying column.
134.0604	Data transfer.
134.7882	New drying column (started using 1/2 Aquasorb and 1/2 Mg perchlorate in drying column).
137	Lost prime on bow pump several times for a few minutes- (.2882- .2910, .4444-.4514, .4549-.4618, .6389-.6479, .7243-.7264)
139.0417	Lost prime on bow pump - restarted 139.0514.
139.75	System crash due to IMET error - program restarted.
140.4319	System shutdown for 20 min. to check on axle squeak.
141.3549	New drying column.

144.2062	Changed reference tank to ALM14400.
145.4924	Bow pump off approaching Mauritius.
148.1771	Restart program departing Mauritius.
149.4604	Data transfer.
150.4882	New drying column.
151.2083	Swapped leaky reference gas regulator.
154.4465	New drying column.
156.0583	Seawater shut off for final approach to Mauritius.

I5WI4

162.1900	Set sail from Mauritius.
164.2431	Changed drying column.
166.2882	Adjusted all reference and standard gas flows to get system in balance.
167.6321	Noticed some shredded PVC around axle seal - discovered that axle bushing had seized to shaft and was rotating in PVC endplate. Shut system down and took apart equilibrator. Had to get ship's engineers to remove bushing and epoxy spare into endplate.
168.3875	System running again after equilibrator repairs.
168.4826	Data transfer.
168.7521	Changed drying column.
171.7236	Changed equilibrator air pump.
172.1475	Stopped system on approach to Durban.
173.3401	Restarted system after leaving Durban.
174.75	Bow pump off for 9 minutes. Seas have been fairly heavy for several days.
175.1667	Bow pump off and on several times since first shutdown.
175.6236	Changed drying column. Made small adjustments to flow rates.
182.1972	Data transfer.
182.8472	Very rough seas (Swells 15-20'). Bow pump has been off and on. Decided to just run air until things calm down a little.
183.5555	Weather has calmed down a little...bow pump back on line.
184	Have been getting bow pump shutdowns while on station. Small water leak through axle seal...adjusted equilibrator float switch down to lower water level.
185.6667	Changed drying column and data transfer.

188.3757 Changed equilibrator air cadet.

190.4583 System crash due to IMET problems - rebooted. Data transfer.

191.9271 Bow pump shutdown for approach into Mauritius.

I7N

196.3125 Departed Mauritius (T. Zahn in charge).

200.625 Changed drying column. Have had rough weather for past couple of days.

201 Not getting proper sample flow through system ever since changing drying column. Tried all day to find problem...finally discover that the drying column was not being sealed with the O-ring.

203 Data transfer.

205.1875 Bow pump shutdown for repairs...back on at 205.2417

206.4868 Changed to reference tank 24813 (note: this tank is a zero CO_2 gas, started with only had 700 psi).

206.4868 System crashed...when rebooted system was told to run partial standards (note: this option was not supposed to be used, but should not have a noticeable affect on the calibration).

208.5625 Data transfer.

215.6944 Drying column changed.

217.6174 Data transfer.

219.1153 Changed partial standard collection off.

220.8472 Program crash...system rebooted.

221 Bow pump off and on several times during day. Some water leaking through teflon seals.

222 Still having problems with bow pump.

226 Bow pump shut off a couple times during the day...water leak getting worse.

227.3958 Changed reference tank to 18260 (a zero CO_2 standard).

228 Weather very rough...switched to secondary seawater pump 228.4236.

230.3813 Seas calmer...switched back to regular bow pump.

233.6285 Data transfer.

235.3979 Bow pump shut off for approach into Oman.

I1

241.4167	Ship sailed out of Oman (R. Rotter in charge). Equilibrator was taken apart and cleaned. Shaft bushing was replaced and epoxied into endplate. Replaced teflon seals and bypass chamber with spares. Equilibrator PRT and float switch were broken in rebuild and had to be replaced with spares. Collection software was replaced with newer version. Collection scheme was basically the same as the original software, but version had slightly different display and more error trapping.
241.9055	Data collection began.
243.5	Wind and swells up - bow pump off and on.
243.8917	Drying column changed.
244.8403	Bow pump off. Resumed at 244.8458
245	Bow pump frequently shutting off all day.
245.6035	Stopped program temporarily to reset standard flow rates.
246.1632	Bow pump off. Resumed at 246.1764
247.4938	Drying column changed. Data transferred.
248.0215	System set to run partial standards.
248.6618	Power outage - system reset
250.8	Drying column changed.
251.7194	System reset so it would not run partial standards.
2531806	System crash due to bad IMET data.
253	Weather getting rough again water pump off and on all day.
253.9	Drying column changed.
254.4708	Data transferred.
255.6479	Adjusted equilibrator air flow rate.
256.1167	Adjusted equilibrator and marine air flow rates.
256.9118	Drying column changed.
258.0417	System crash due to bad IMET data.
259.0660	System water pump off. Restarted several times, but ultimately had to replace water pump motor with spare.
259.9410	Drying column changed.
260.6160	Data transferred, program restarted.

262.942	Drying column changed.
263.5208	Marine air pump off. Replaced 263.5347
263.7083	Marine air pump off. Replaced 263.7291
264	Weather very hot...noticed that box temperature frequently getting above set temp.
265.5458	System crash due to bad IMET data.
266.7132	Drying column changed.
269.5174	System crash due to bad IMET data.
269.9999	Drying column changed.
271.0556	Bow pump off approaching Sri Lanka.
273.8597	System started after leaving Sri Lanka. Changed set point for rack temperature controller from 30.5 to 31.5 since rack temp has been getting above set point since day 264.
276.8667	Drying column changed.
278.6319	System crash due to bad IMET data.
279.9083	Drying column changed.
281.9736	Data transfer.
282.7840	Drying column changed.
285.4097	System Crash -unknown error.
285.4215	Diskette had bad sector...had to replace with new diskette. Reset system, adjusted flows and changed drying column.
286.1215	Bow pump off as ship enters straits of Malacca. Restarted program without IMET data and ran full standards.
286.4145	Shut down system. Discovered that hard disk was full from 10/7 to 10/13 - Recovered data from floppies. IMET data recovered from ship's 1 minute files.

I10

303-313	C. Sabine and G. McDonald cleaned bypass chamber and equilibrator. It was reassembled with new teflon seals and cleaned bushing. Rebuilt seawater pump...replaced old impeller and link belt. Replaced reference gas with cylinder ALM061635 (new calibrated 200 ppm CO_2 standard). Transferred all data files off of hard disk. Adjusted zero setting on detector to give 0.1V reading on reference gas. Adjusted rack temperature controller back up to 35 °C so it could properly

maintain temperature. System tested on transit from Singapore to Australia. Knorr's ET was aboard making changes to IMET system, so pCO_2 program was modified compensate.

315.2943 System started after leaving Dampier, Australia (G. McDonald in charge).

316.0833 K. Sullivan adjusted main water flow for CFC syringe bath.

316.1388 Bow pump off and on 5 times over next 5 hours (choppy seas).

317.1056 Bow pump off and on 3 times over next 2 hours.

319.5243 System crash - system rebooted.

320.2208 Exited system to confirm data was being collected properly.

321.1097 Changed drying column.

322.225 Transferred data.

323.2215 Noticed that CO_2 concentration signal was noisy. Looked at long term trends and determined that noise started around day 322.5. The noise was due to erratic pressure readings because the 4 pin molex connector was loose. Reconnected plug and signal returned to normal.

323.2674 Changed equilibrator air pump.

324.226 Changed equilibrator air pump to a quieter one.

325.2180 Changed drying column

329.0104 Bow pump shutdown entering Indonesian EEZ.

I2

339.2764 Data collection started after leaving Indonesian EEZ.

342.2319 System crash due to bad IMET data.

342.9861 System crash due to bad IMET data.

344.3833 Changed drying column.

346.9721 System crash due to bad IMET data.

348.4665 System crash due to bad IMET data.

350.8927 System crash due to bad IMET data.

352.9182 System crash due to bad IMET data. Data transferred.

354.9312 System crash due to bad IMET data.

359.0511 System crash due to bad IMET data.

361.5194 Bow pump shutdown entering Diego Garcia.

364	Changed reference gas tank to ALM45918. Had trouble getting reference gas flow down to correct rate (flow is 15 and should be 8-10).
364.3583	System restarted leaving Diego Garcia.
366.9705	System crash due to bad IMET data.
367.6049	Rebuilt needle valve controlling reference flow rate and finally got the correct flow. Standard fits have not been very good for past few days while reference flow was out of whack.
371.8229	System crash due to bad IMET data.
377.3785	Bow pump shutdown for 5 minutes.
377.6468	System crash due to bad IMET data. Readjusted gas flows.
378.6762	System crash due to bad IMET data.
380.6441	System crash due to bad IMET data.
383.6758	System crash due to bad IMET data.
386.6076	Final shutdown approaching Mombasa. Final water flow meter reading 1,146,780 gallons!

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