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Quasi-simultaneous CO₂ Measurements in the Atmosphere and Surface
Ocean Waters from Scripps Institution of Oceanography
DOWNWIND, MONSOON, and LUSIAD Expeditions
1957-1963

Lee S. Waterman, Pieter P. Tans, Todd Aten
U.S. Department of Commerce
National Oceanic and Atmospheric Administration
Boulder, Colorado

and

Charles D. Keeling
University of California, San Diego
Scripps Institution of Oceanography
La Jolla, California

and

Thomas A. Boden
Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
Oak Ridge, Tennessee

“...Man, in his burning of fossil fuels and denudation of the land's surface, may be performing a gigantic geochemical experiment in which the CO₂ cycle is being influenced. It is thought we may be increasing the CO₂ input into the atmosphere by 70% in 40 years, although it is not certain how much of this may be absorbed by the oceans. A substantial increase in CO₂ content in the air would trap more of the earth's radiated heat and cause a warming of temperature.

Data collected during the IGY will be needed for comparison with measurements made 15 to 25 years from now to determine whether the CO₂ content is changing...”

Lill and Revelle
IGY Bulletin
October 1958

ABSTRACT

Carbon dioxide (CO₂) in the surface water and atmosphere of the Pacific, Indian, and Atlantic Oceans was measured by nondispersive infrared gas analyzer on three oceanographic expeditions from October 1957 and August 1963. The data from these expeditions have been reprocessed to eliminate a major error resulting from the use of two-component, CO₂-in-nitrogen calibration gases instead of naturally constituted atmospheric air. The surface water measurements have been recalculated to correct for warming in the process of pumping the water. For the first time hourly atmospheric and surface ocean water values, in the WMO 1985 mole fraction scale, are presented correlated with the position (latitude, longitude) of the vessel.

INTRODUCTION

The first continuous measurements of the partial pressure of CO₂ in surface ocean waters by direct equilibration were made by the Scripps Institution of Oceanography (SIO) Carbon Dioxide Project on the *R/V Horizon* during the Downwind Expedition, October-December 1957. The measurements program was continued on the *R/V Argo* during the Pacific Ocean section of the Monsoon Expedition, January - April 1961, and throughout the Lusiad Expedition, May 1962-August 1963.

The Downwind Expedition was the first extensive SIO cruise undertaken as part of the U.S. International Geophysical Year (IGY) Deep Water Ship Program. The Monsoon and Lusiad Expeditions were the first and second SIO cruises, respectively, made for the International Indian Ocean Expedition (IIOE). The position of individual measurements along the ship track of Downwind, Monsoon, and Lusiad Expeditions are shown in Figure 1.

The individual measurements for both CO₂ in air and equilibrated air (CO₂ in surface ocean water) for Downwind and Monsoon Expeditions were published by Keeling et al. (1965) in the form of averages for 2.5° intervals of latitude. For Downwind, a total of 2280 atmospheric and 1569 surface ocean water CO₂ values are summarized in 38 latitudinal intervals (30°N - 50°S). For Monsoon, the equilibrator was operated only while the research vessel was underway. Totals of 3161 CO₂ air and 1461 CO₂ ocean water values are tabulated in 43 intervals (65°S - 30°N). Individual measurements or hourly means of the data collected on these two expeditions, heretofore, have not been published.

Preliminary results for the Lusiad Expedition were published by Waterman (1965). Later, complete results and interpretation were published by Keeling and Waterman (1968a). The data in these papers are presented only in the form of plots and represent 1° and 2.5° latitudinal or longitudinal averages as dictated by the expedition track. A total of 14,231 air and 12,040 surface ocean water measurements were reduced from the original stripchart records. Data for calculating the interval averages used to prepare the Lusiad graphs were reported in American Documentation Institute Document 9946 (Keeling and Waterman, 1968b). As in the case of the earlier expeditions, individual values and hourly means have never been readily available. Data for

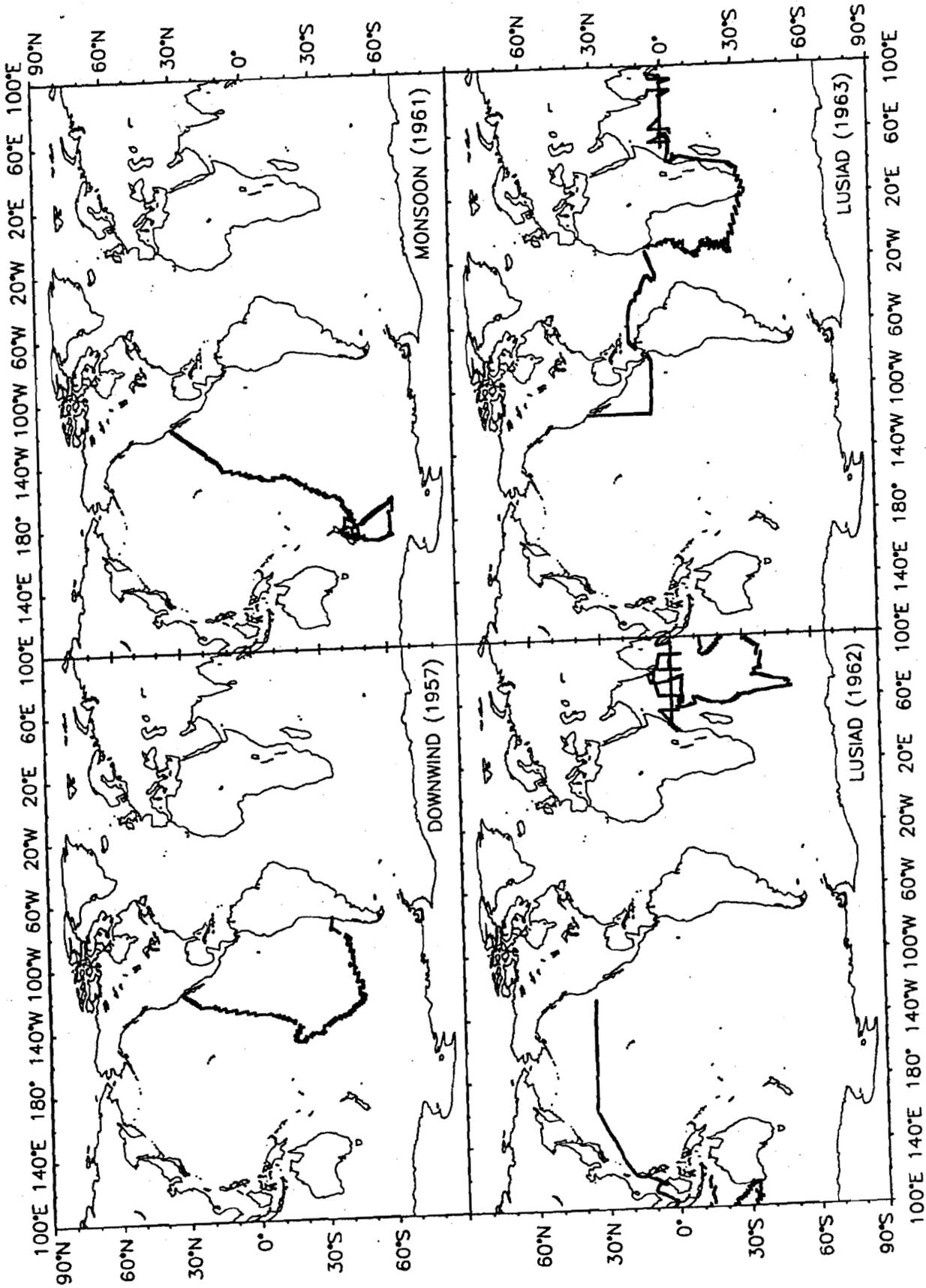


Figure 1. Position of individual measurements along the ship track of Downwind Expedition of 1957, Monsoon Expedition of 1961, and Lusiad Expedition of 1962-1963.

all three expeditions were originally recorded in the ship's local time. For this report everything has been converted to Greenwich Mean Time (GMT).

The published CO₂ measurements from the Downwind, Monsoon, and Lusiad Expeditions were based upon two-component reference gas standards prepared by adding small amounts of CO₂ to high-purity dry nitrogen. The CO₂ concentrations of these mixtures were typically in the range of 300-350 ppm and reference gases were selected to bracket the atmospheric air values. The data were reported in the preliminary SIO "J" scale (Keeling et al., 1976). These measurements are not easily comparable to recent surveys reported in the WMO 1985 manometric scale that is based on standards prepared from natural air (Guenther and Keeling, 1986; Komhyr et al., 1985; Thoning et al., 1987).

EXPERIMENTAL DETAILS

The *R/V Horizon* (Downwind Expedition) was a 143 ft. ocean tug obtained from the U.S. Army Transportation Corps and converted to oceanographic use. There was one large laboratory on the main deck that opened to a fantail weather deck area. The nondispersive infrared NDIR analyzer and the seawater equilibrator were installed on the starboard side of the laboratory.

The analyzer was secured to a plywood panel that was shock mounted from the ship's engine vibration with layers of plastic foam. Vibration isolation of the analyzer was important because the instrument employed a variable-capacitance-type detector. The equilibrator was installed in the laboratory sink and was supplied by the surface water tap designed for scientific use. The location of the seachest that was the source of this water is not known.

The plumbing for the air sampling lines, the equilibrator, and the electromechanical switching system were mounted "breadboard" fashion: on a plywood panel and all parts were easily accessible. All air sample lines inside the vessel were made from soft-drawn copper refrigeration tubing because it was feared higher concentrations of CO₂ in the confined atmosphere inside the ship would diffuse through polyethylene tubing (used for outside air lines) and contaminate the sampling.

The final step for all reference gases and samples (atmospheric air and air from the equilibrator headspace) was to pass through a stainless steel trap suspended in chilled air in a cylindrical chamber of about 4L capacity. The walls of the chamber were cooled by an ultra-low-temperature refrigerator rated to go to -60°C. The achievable low temperature, however, was always dependent on the ship's laboratory ambient temperature and most of the time ranged from -40°C to -50°C as indicated by the gauge mounted on the side of the cabinet.

The outside plastic air lines were run to both the top of the foremast and the mainmast. Relative wind directions were constantly monitored, and air was sampled from the foremast intake when both the wind was forward and abeam. Only when wind directions were aft of the starboard or

port quarters and when there was a clearly defined following wind was the intake shifted to the mainmast line which was in close proximity to the ship's funnel.

The equilibrator was constructed from clear plastic tubing after a design by Levine et al. (1956) that they termed the aspirator unit (their Figure 9). For this application the aspirator unit was encased in a plywood box having a sheet-plastic front cover to observe its operation.

The *R/V Argo*, formerly the *USS Snatch* (ARS 27), was a 213 ft, auxiliary repair ship converted to an oceanographic research vessel. It was used for both the Monsoon and Lusiad Expeditions. The CO₂ measuring apparatus was set up substantially different for these expeditions. For Monsoon, the equipment was installed in the forward cargo hold in the lowest part of the vessel. For Lusiad, the measuring system was located on the port side of the main deck laboratory between the engine room ladderwell and the double hatch opening onto the fantail.

For the Monsoon Expedition the analyzer was placed on plastic foam sheets sandwiched between plywood panels laying on an angle-iron frame located on the port side of the cargo hold. The mounting was similar to the arrangement used on the Downwind Expedition.

The equilibrator is shown in Figure 1 of Keeling, et al. (1965). It is a water spray type constructed from a 20-L Pyrex bottle after one used for special temperature studies at Scripps in 1959 (Takahashi, 1961). The equilibrator headspace accounts for about 20% of the volume for usual operation. It was also located on the port side adjacent to the seachest used for the precision depth recorder (PDR) transducer.

Surface ocean water was obtained from a starboard side seachest, installed for the auxiliary firefighting pump. A separate tap for this program was installed in this seachest and a plastic pipe run athwart ship to the intake of the equilibrator pump. This line was no more than 10-m long. The discharge of the pump was directly to the bilges.

The foremast air lines were run directly down the mast and entered the ship through bulkhead unions installed in the side of a ladderwell enclosure. Lines from the mainmast were run forward and entered the vessel at the same place. Copper tubing was used inside the ship and run four decks down the ladderwell. The reference gas and samples, as on the Downwind Expedition, passed finally through the low-temperature-trap into the analyzer sample cell.

For the Lusiad Expedition the entire CO₂ measuring system, located in the main deck laboratory, was configured in an angle-iron rack about 2.5-m long and 1.5-m deep located next to a specially installed stainless-steel sink. The equilibrator was mounted in the sink. The compact arrangement allowed for short runs of tubing and pipe for both the atmospheric air and the equilibrator plumbing.

The analyzer was suspended in an angle-iron frame, about 1 m off the deck, with elastic shock cord (bungee) producing a fully gimballed effect. Small lengths of plastic tubing were used in the connection of the two gas lines to the analyzer case to further minimize transmission of vibration from the ship's engines to the instrument. This was the most successful method for mounting the

analyzer used on the three expeditions and the noise level as seen in the stripchart record was substantially reduced.

The equilibrator was an improved version of the design used for the Monsoon Expedition. The chamber was a Corning Glass Works 20-L. Pyrex glass organic reaction vessel with a ground-glass flange. The domed top section was a custom-made unit with five necks.

The five openings formed a plus (+) pattern on the top of the cover. The center opening was about 60-mm in diameter and the four encircling openings were each about 35-mm in diameter. This arrangement allowed for separation of the ocean water and air plumbing systems that were crowded into a single opening in the Monsoon equilibrator model. There was also space for installing a U-tube overflow device that virtually eliminated the flooding problems experienced on several occasions during the Monsoon Expedition.

Surface ocean water for the equilibrator was obtained from the same seachest as used for Monsoon Expedition. A dedicated vinyl plastic pipe line was installed between the seachest and the main-laboratory sink. The pipe was insulated with glass wool battings to minimize warming of the water as a result of transport through more than half the length of the vessel.

As on the two previous expeditions polyethylene plastic tubing was used for the atmospheric-air sampling lines. The tubing was strung from both the mainmast and the foremast and run to bulkhead fittings mounted above the portside double hatch leading from the fantail to the main-laboratory. Inside, copper tubing was used on the short runs (less than 5-m) from the bulkhead to the apparatus. The plastic tubing was renewed from time to time when the ship was in port between major segments of the expedition. The output of the gas handling system, as on the other expeditions passed through the low-temperature freezer before entering the analyzer. For this expedition glass thimble-traps were pre-cooled in the freezer chamber and changed easily by switching metal socket joints on the input and output copper-tubing lines.

For all three expeditions, the output of the NDIR analyzer was an analog record of voltages generated by flowing reference gases, atmospheric air, and equilibrated air through the analyzer sample cell. In all cases an individual measurement is defined as the difference, in strip chart scale units, between a reference gas and atmospheric air or equilibrated air.

Several programs were employed using an electromechanical timer, to sequence the three gases in either 20-minute or 30-minute cycles. These schemes usually produces two measurements each of atmospheric air and air equilibrated with ocean water per hour on the Downwind and Monsoon Expeditions. For 22 May to 5 July 1962, three air and three equilibrated measurements per hour were obtained on the Lusiad Expedition. For the remainder of the voyage, four atmospheric air and two equilibrated air determinations were made each hour. When the equilibrator was not in operation, the system was set to alternate atmospheric air and reference gas. Usually four measurements per hour were obtained.

DATA REDUCTION

DOWNWIND EXPEDITION

Preliminary data reductions were accomplished at sea. Stripcharts were measured by hand and the atmospheric air and equilibrated air differences from reference gases were tabulated on forms having spaces for 24 hours of data. An example of a stripchart record is shown in Figure 2 and the Daily Data Sheet is shown in Figure 3. Between 21 October and 23 December 1957 there are 58 data sheets for Downwind Expedition. The original copies of these sheets are on file at SIO.

The procedures for the calculation of revised hourly measurements of atmospheric air and $p\text{CO}_2$ of surface seawater from the Downwind Expedition are documented here.

A database was created with the following information listed for each hour: Time (GMT), Month, Day, Year, Latitude, Longitude, Hourly average air, Hourly average equilibrator, Sea Surface Temperature, Delta T, Pressure Reading (from ship barometer), and Index Values for working reference gas. Index values are analyzer response values converted in a preliminary way to approximate atmospheric mole fractions of CO_2 . All information, except for ship's position data and index values for working reference gases were obtained from the Daily Data Sheets. The ship's position data were obtained from final navigation files inspected and photocopied at the SIO Geological Data Center with the cooperation of Mr. Stuart Smith. The final weighted average index values for the four working reference gases used on this expedition were obtained from the SIO "Shipboard Carbon Dioxide Project Report No. 3: Table 6A (page 89) (Keeling and Waterman, 1968b).

In order to compute the air and $p\text{CO}_2$ hourly values three pieces of information are required. These are (1) the individual measurements of the scale division differences between the atmospheric air (or equilibrated air) and working reference gases. (2) the recorder scale factor (RSF), a measure of the sensitivity of the analyzer detector, and (3) the CO_2 concentration of the working reference gas mixture.

The SIO recorder scale factor (RSF) is defined as the scale difference which is obtained for two reference gases having an index (provisional concentration) difference of 18.00 (parts per million of CO_2 in nitrogen). The RSF is normally determined each time the working reference gases are compared with a set of higher grade standard gases. For the Downwind Expedition the RSF was obtained from one set of 9 standard gas comparisons made on 19 October 1957, just before the start of the expedition (RSF = 18.24) and of 24 comparisons made between 19 October and 3 November 1957 (RSF = 18.16). These data have been combined in a weighted average to yield a single RSF used throughout the expedition, 20 October - 23 December.

$$\frac{9 \times 18.24 + 24 \times 18.16}{33} = 18.18 \quad (1)$$

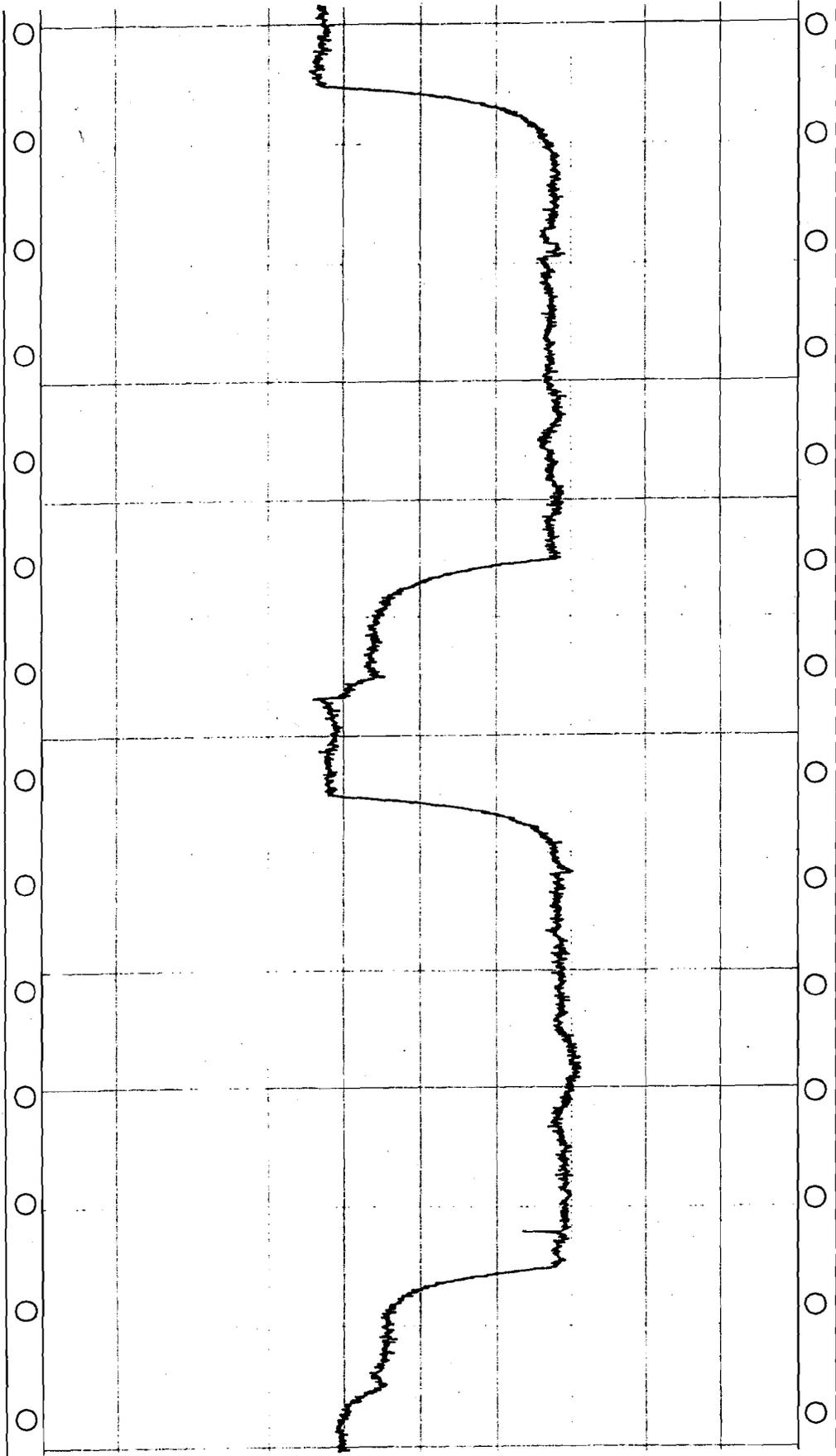


Figure 2. Typical stripchart record for 30-minute cycle of calibration gas (5 min.), atmospheric air (5 min.) and equilibrated air (20 min.)

CARBON DIOXIDE DATA

STATION M.V. HORIZON - DOWNWIND

Sheet No. 3

Span 310 Zero 850 Freezer Temp. _____

Date October 23, 1957

Flow _____ lpm Working Ref. Tank ST One ordinate _____ ppm

Tank Press. _____ psi Obs. _____ From Ref tank test of 28°50'N, 121°W - 26°50'N, 123°W

Time	AN		EQUIL		Dif. Ave.	Sky	Vis.	Weather	Sta. Press	Temp	D.P.	Wind Dir	Wind Vel	RH	Wet Bulb	REMARKS
	1	2	3	4												
0030		6.2														
0100	6.0	6.3	6.2													
0130		6.0		37.2	37.9											
0200	6.0	6.1	6.0		37.6											
0230		6.2		37.8	37.9											
0300	6.1	6.2	6.2		38.2											
0330	6.2	6.0		37.7	38.1											
0400	6.9	6.0	6.3		37.9											
0430		5.9		37.1	38.0											
0500	6.0	6.2	6.0		37.6											
0530	6.4	6.2		38.0	38.9											
0600	6.1	6.0	6.2		38.4											
0630	6.0	6.8		36.8	37.5											
0700	6.0	6.6	6.4		37.2											
0730	5.6	5.6		37.0	37.9											
0800	6.6	6.5	6.1		37.4											
0830	6.6	6.5		36.8	37.5											
0900	6.0	6.2	6.3		37.2											
0930	5.9	6.5														
1000	5.2	5.8	5.8													
1030	6.5	6.5														
1100	6.0	5.9	6.0	37.1	37.2											
1130	6.5	6.4		32.4												
1200	5.7	6.2			32.4											
1230				34.0												
1300	6.4	5.6	6.0	33.9	32.5											
1330	6.2	6.0		37.0	38.4											
1400	6.1	6.0	6.1		37.7											
1430	5.8	5.8		38.1	39.5											
1500	6.5	6.1	6.0		38.8											
1530	5.0	5.5		37.8	38.4											
1600	5.4	6.2	5.5		38.2											
1630	5.8	6.0		37.5	37.0											
1700	6.2	5.2	5.8	34.9	36.5											
1730																
1800																
1830				35.7												
1900				35.9	35.8											
1930																
2000				34.6	34.5	34.6										
2030				34.1	33.5											
2100				34.6	33.2	33.8										
2130				33.6	32.9											
2200	5.9	5.2	5.6	32.4	32.8	32.4										
2230				31.0	32.4											
2300	6.6	6.5	6.6	32.5	32.0	32.7										
2330				32.1	32.2	32.6										
2400																

Figure 3. Carbon Dioxide Data Sheet - the first two handwritten columns contain individual scale division differences for atmospheric air measurements; the third column contains the hourly mean of the air values; columns 4 and 5 contain scale differences for equilibrated air; column 6 contains the hourly mean of the equilibrated air.

The scale division differences for both atmospheric air and pCO₂, columns 3 and 6, respectively, on the Daily Data Sheets are first normalized to a barometric pressure of 30.00 inches of Hg using the expression:

$$\text{Adjust Scale Difference} = \frac{\text{Scale difference} \times 30.00}{\text{Observed barometric pressure}} \quad (2)$$

The observed barometric pressures are hourly readings from the aneroid barometer on the ship's navigation bridge.

The adjusted differences are transformed into index units by the following:

$$\text{Computed Index Difference} = \frac{\text{Adjusted Scale Difference} \times 18.00}{18.18} \quad (3)$$

The hourly index values for atmospheric air and pCO₂ are computed:

$$\text{Index Value} = \text{Computed Index Difference} + \text{Working reference gas index value} \quad (4)$$

In 1959, the index values (provisional CO₂ concentrations) were refined. The SIO original primary reference gases were analyzed using a constant volume manometer. The partial pressure of the CO₂ in the reference gases were directly determined under conditions where the volume and temperature were held constant. These analyses led to a new equation relating index value to mole fraction. The hourly air and pCO₂ index values (3) are changed to adjusted index values (also called the J value) using:

$$\text{Adjust Index Value (J)} = (\text{Index Value} - 311.51)1.2186 + 311.51 \quad (5)$$

Subsequent manometric analyses and derived equations have resulted in the removal of a major error termed the "pressure broadening effect" which resulted from using pure nitrogen instead of naturally constituted atmospheric air for the carrier component in the standard and working gases. The "X" value (mole fraction of CO₂) is derived from the Adjusted Index Value (J) as follows:

$$\begin{aligned} X &= A_0 + A_1J + A_2J^2 + A_3J^3 \quad (6) \\ A_0 &= 86.8076 \\ A_1 &= 0.547493 \\ A_2 &= 3.80939 \times 10^{-4} \\ A_3 &= 7.21640 \times 10^{-7} \end{aligned}$$

X used in this report is the 1985 version (Guenther and Keeling, 1986). Determination of the hourly X values for the atmospheric air measurements completes the revision of the atmospheric air data.

The X values for the hourly pCO₂ were further corrected to take into account the warming of the surface ocean water in the process of equilibration of the dissolved gases with the air in the equilibrators headspace. This warming results in an over-statement of the actual seawater pCO₂ values.

For Downwind Expedition hourly readings of the intake and exit temperatures for the equilibrator water supply were taken as part of the routine of the watchstander. The original Downwind Daily Data Sheets each have a supplementary attachment identified as 1A, 1B, etc. The intake and exit temperatures are recorded on these second sheets.

A three step treatment was used to obtain temperature corrections for the entire pCO₂ data set. First ΔT values were obtained by subtracting the inlet from the outlet temperatures. The inlet temperatures were taken to be equivalent to the sea surface temperatures (SST). Second, both SST and ΔT values were sorted into 1°C bins and averages computed. Third, a plot of ΔT versus SST 1°C averages was prepared and subjected to a straight line fit (Figure 4). The equation of this line is:

$$\Delta T = (-0.0278958)SST + 0.986430 \quad (7)$$

Using the inlet temperature readings (SST) for corresponding hours, each pCO₂ X value obtained from Equation 5 was corrected for temperature using the equation:

$$X' = X - X(0.043)\Delta T \quad (8)$$

where 0.043 is a correction factor determined by Takahashi (Smethie, Takahashi et al., 1985) and ΔT is obtained from Equation 6.

The data in this report are expressed as mole fractions of CO₂ in dry air, which is not the same as the quantity that drives the air-sea exchange flux, namely the fugacity. The latter can be obtained from the mole fractions by correcting for the amount of water vapor present at the interface (up to a few percent) and for the non-ideality of CO₂ in air (about 0.4 percent). A suitable formula is given by Wanninkhof and Thoning (1993), based on Weiss (1974):

$$f_{CO_2} = X_{CO_2} (P - p_{H_2O}) \exp ([B_{11} + 2\delta_{12}] P/RT), \quad (9)$$

in which

$$P = \text{atmosph. pressure in bar}$$

$$R = 83.15 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$$

$$T = \text{temperature in Kelvin}$$

and

$$B_{11} (\text{cm}^3 \text{ mol}^{-1}) = -1636.75 + 12.0408T - 0.0327957T^2 + 3.16528 \cdot 10^{-5}T^3 \quad (10)$$

$$\delta_{12} (\text{cm}^3 \text{ mol}^{-1}) = 57.7 - 0.118T \quad (11)$$

These corrections amount to a multiplicative factor for ΔpCO₂ of up to several percent.

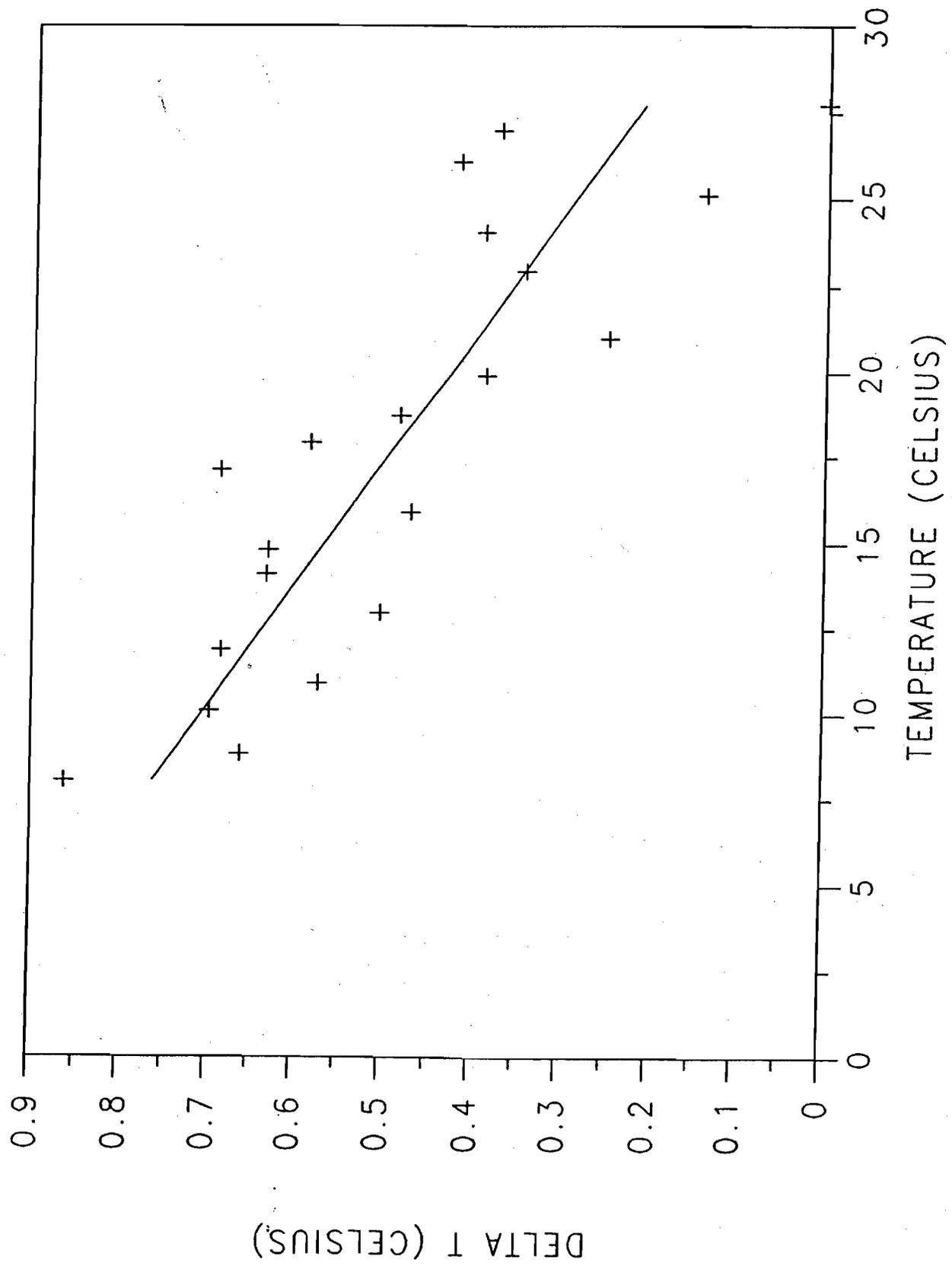


Figure 4. Delta T as a function of Sea Surface Temperature for Downwind Expedition, 22 October to 23 December 1957.

MONSOON EXPEDITION

During this expedition the observers spent virtually all their time on watch monitoring the operation of the analyzer/equilibrator and data collecting. Due to the poor working conditions (equipment installed in the forward cargo hold) and because there were only two watchstanders, a full set of continuous measurements were made only when the ship was underway. Nearly all of the times when the ship was "on station" only the atmospheric air monitoring was operated in an automatic mode.

All data reduction for this expedition was carried out at SIO following completion of the cruise. Tabulations of all data derived from the original stripcharts and from hourly readings at sea of temperature and pressure produced 64 daily data sheets from 31 January through 17 April 1961. This information has been used to create a data base as already described for Downwind Expedition. Once again, the ship's positions were obtained from the final navigation files at the SIO Geological Data Center, and the index values for the four working reference gases used on this expedition are from Keeling and Waterman, 1968b (Table 6B, page 90).

As was the case for the Downwind Expedition, a single RSF was used to transform scale division differences to index differences. Table 8A, Keeling and Waterman, 1968 (page 96), contains data for 34 at sea determinations of the RSF obtained from 31 January through 16 April 1961. These data have been normalized to 30.00" Hg as follows:

$$\text{Adjusted RSF} = \frac{\text{Shipboard RSF} \times 30.00}{\text{observed pressure (inches Hg)}} \quad (1)$$

An average of the 34 adjusted RSF's is 14.77 which is used to calculate all index differences. Comparing the RSF used for Downwind (18.18) with the RSF used for Monsoon (14.77), it can be seen the analyzer was less sensitive for the second expedition. For Downwind one chart division equaled 0.99 index unit (ppm); for Monsoon one chart division equaled 1.22 index units. The hourly average air and pCO₂ "scale differences" were transformed to "computed index differences" as follows:

$$\text{Adjust Scale Difference} = \frac{\text{Scale difference} \times 30.00}{\text{Observed barometric pressure}} \quad (2)$$

$$\text{Computed Index Difference} = \frac{\text{Adjusted Scale Difference} \times 18.00}{14.77} \quad (3)$$

The hourly index values for air and pCO₂ are obtained from:

$$\text{Index Value (I)} = \text{Computed Index Difference} + \text{Working reference gas index value} \quad (4)$$

The (I) to (J) to (X) transformation was carried out as described for the Downwind data set.

A better set of temperature data were obtained for Monsoon than for Downwind. Observations of the seachest water temperature (SST) were made every 30 minutes for all times when the equilibrator was operated. Readings from a thermometer inside the equilibrator chamber were obtained every 10 minutes.

Once again, a multistep procedure was used to obtain ΔT values to be used for calculating temperature corrections for the Monsoon pCO_2 X values. Three ΔT versus SST plots were prepared, one for each major leg of the expedition (Figures 5,6,7). Linear fits of the data were calculated and smoothed ΔT values obtained from the equation.

28 January to 22 February 1961

$$\Delta T = (0.0205505)SST + 0.281999 \quad (5)$$

26 February to 15 March 1961

$$\Delta T = (-0.00108990)SST + 0.292619 \quad (6)$$

23 March to 17 April 1961

$$\Delta T = (0.0000365439)SST + 0.296223 \quad (7)$$

Temperature corrected pCO_2 values, X' , were obtained using the Takahashi (Smethie, Takahashi et al., 1985), factor with the equation:

$$X' = X - X(0.043)\Delta T \quad (8)$$

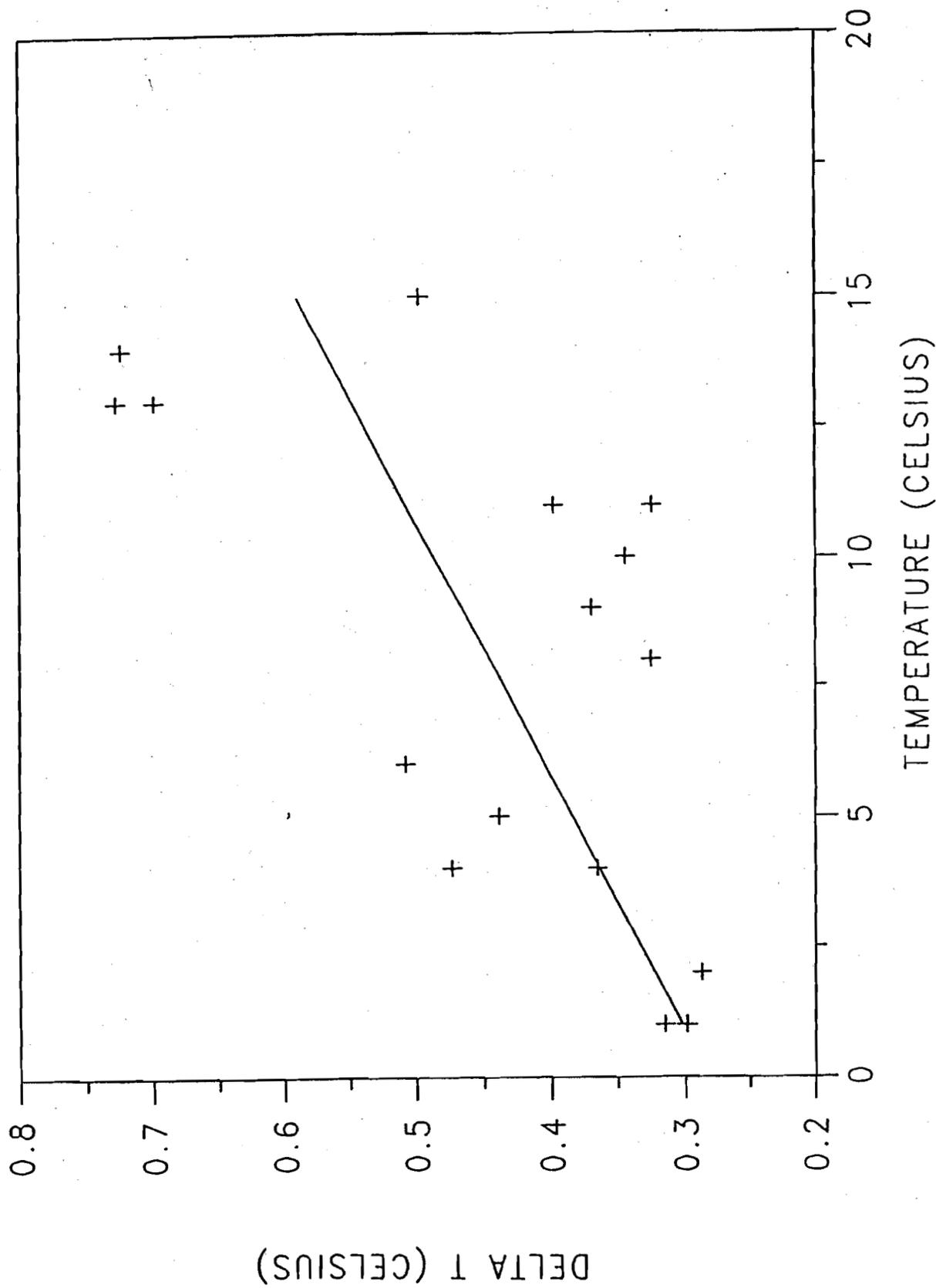


Figure 5. Delta T. as a function of Sea Surface Temperature for Monsoon Expedition, 28 January to 22 February 1961.

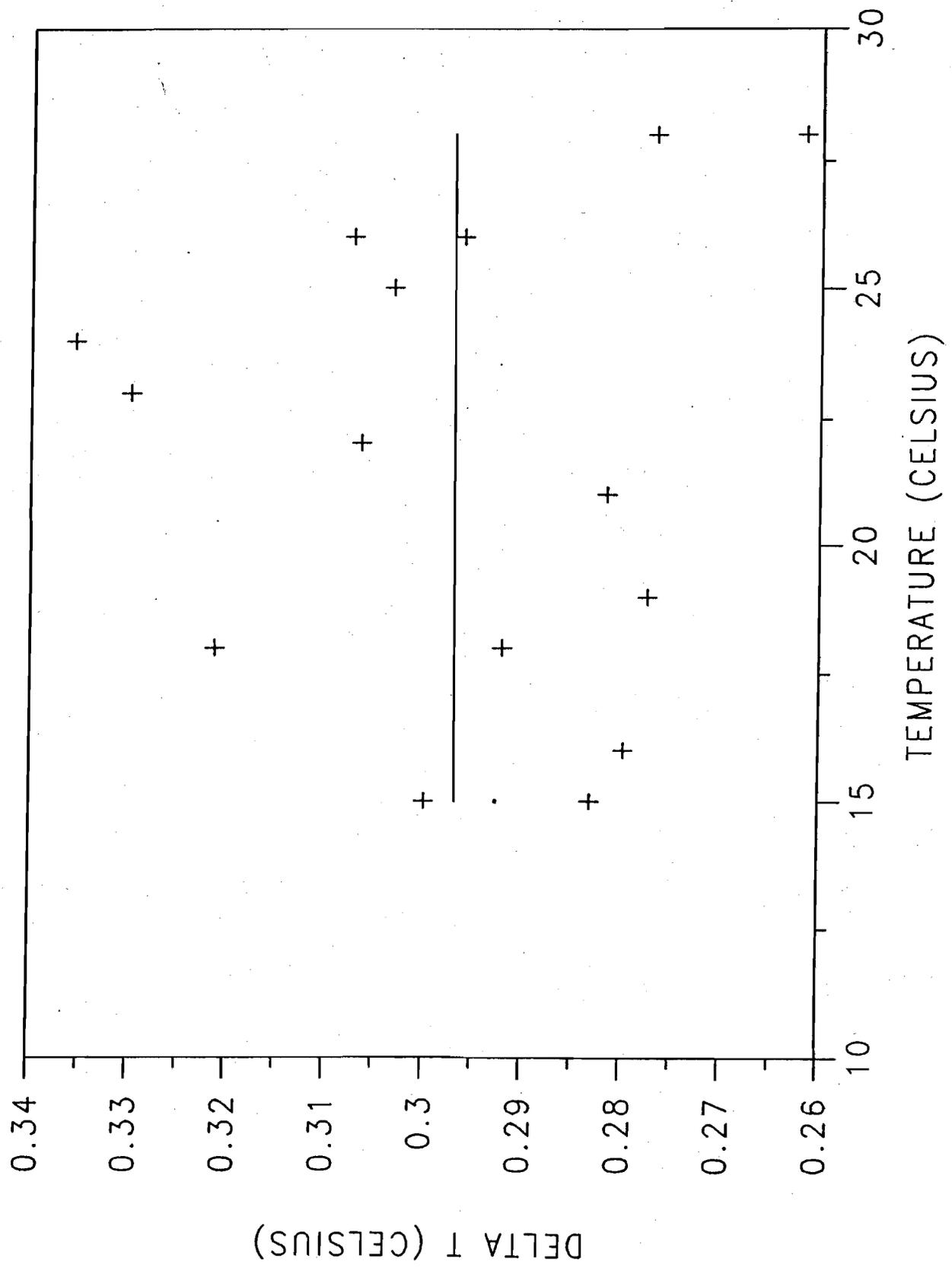


Figure 6. Delta T as a function of Sea Surface Temperature for Monsoon Expedition, 26 February to 15 March 1961.

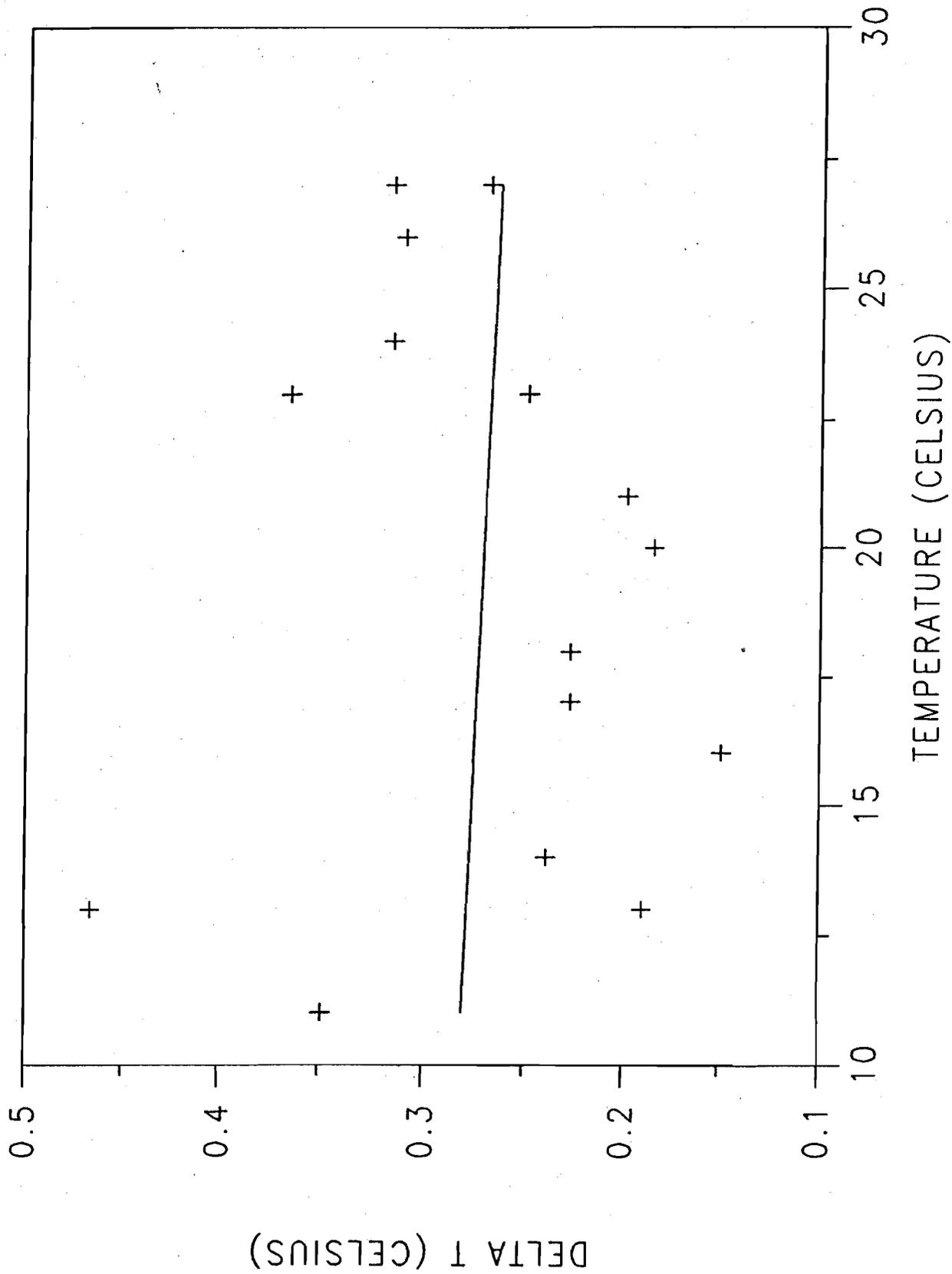


Figure 7. Delta T as a function of Sea Surface Temperature for Monsoon Expedition, 23 March to 17 April 1961.

LUSIAD EXPEDITION

As was the practice on the Downwind Expedition, preliminary data reduction was carried out at sea by the watchstanders. The equilibrator was operated virtually all the time the ship was underway except for the time during the Indian Ocean current studies. During these periods, the automatic sequencing was switched to air across reference gas and operated in this mode for several hours each afternoon while all three watchstanders worked together on data reduction.

For the 15-month duration of this expedition (15 May 1962 - 15 August 1963) there are 341 data sheets each representing a whole or partial day of operation.

The ship's heading, speed, and position, when available, along with hourly meteorological data are recorded on Cruise Operation Data sheets. Each data sheet covers 8 hours and there are three for each day of the expedition.

Determination of the RSF values for use in computation of hourly index differences required a more sophisticated manipulation of the shipboard calibrations than for either of the previous expeditions. Detector sensitivity declined gradually for the first 8 months, then increased sharply over the next one and one-half months. A new detector was installed in the analyzer in March 1963 and from calibrations made thereafter, the sensitivity steadily declined for the remainder of the expedition.

The original appraisal of the analyzer performance was made in November 1963 following final calibration at SIO of the various reference gases used throughout the expedition. Final RSF values were tabulated in Table 8B and plotted in Figure 1 of Keeling and Waterman (1968). The RSF data were originally divided into seven segments as the prevailing practice was to (1) average all RSF's in a segment and use a single value to represent the period or (2) to represent the changing RSF as a linear function and compute daily RSF values for the segment. Six segments were evaluated using method (1) and one segment using method (2). Segment 7, representing all calibrations made following the installation of the new detector, was evaluated with a least squares to fit a second order polynomial. The equation was solved to produce daily RSF's.

Technological advances since 1963 make it possible in 1995 to fit the data to more sophisticated curves. For this report the RSF data are organized in four time periods.

18 May - December 1962

$$\text{RSF} = 17.1282 - 3.79554 \times 10^{-2}T + 3.64181 \times 10^{-4}T^2 - 1.08484 \times 10^{-6}T^3, \quad (1)$$

where T = Julian date - 138.

1 January - 9 February 1963

$$\text{RSF} = 14.7173 + 8.90539 \times 10^{-2}T; T = \text{Julian Date} \quad (2)$$

10 February - 24 March 1963

$$\text{RSF} = 17.88 \quad (3)$$

25 March - 13 August 1963

$$\text{RSF} = 18.2225 - 4.32162 \times 10^{-2}T + 1.01305 \times 10^{-4}T^2; T = \text{Julian Date} - 84. \quad (4)$$

In the original data processing, three RSF values were excluded because they deviated markedly from the RSF trend, and six values were excluded because of unacceptable calibrations. The same data are excluded in this reevaluation.

The procedures to obtain "X" values from the atmospheric air and pCO₂ scale division differences obtained on the Lusiad Expedition were similar to those used for the earlier expeditions.

Barometric pressure normalization was carried out as follows:

$$\text{Adjusted Scale Difference} = \frac{\text{Scale Difference} \times 30.00}{\text{Observed Barometric Pressure}} \quad (5)$$

where Scale Differences are hourly averages (air, pCO₂) from the column labeled "L Ave." of the Daily Data Sheets (1 through 341). These data were reduced from stripchart records during the expedition. The observed barometric pressures are obtained from the Cruise Operation Data Sheets.

Computed index differences are calculated as follows:

$$\text{Computed Index Difference} = \frac{\text{Adjusted Scale Difference} \times 18.00}{\text{Daily RSF from equations (1, 2, 3, or 4)}} \quad (6)$$

The hourly index values for atmospheric air and pCO₂ are computed:

(7) Index Value = Computed Index Difference + Working reference gas index value. The working reference gas index value are obtained from Keeling and Waterman, 1968b, Table 11, data card columns 44-49.

The (I) to (J) to (X) transformations are carried out as described for the Downwind data set.

The original temperature correction for the Lusiad Expedition pCO₂ data was ~ 3%/C° (Keeling and Waterman, 1968b). As was the case for the Monsoon Expedition, readings for the equilibrator were made at 10-minute intervals and an average hourly value was computed. Seachest temperatures were obtained hourly and the surface sea temperature was computed by taking the mean of the two readings which bracketed the hour being considered. The correction factors were determined by subtracting the mean sea surface temperatures from the average hourly equilibrator values. These differences (ΔT), the correction factors, are recorded in

columns 12-14 of the "data card" sections of Table 11, pages 100-132, which is explained on page 39 (Keeling and Waterman, 1968b). Temperature corrected pCO₂ values, X', were obtained using the 4.3%/C° factor (Smethie, Takahashi et al., 1985) and accepting the data from columns 12-14 of Table 11, discussed above, for ΔT.

$$X' = X - X(0.043)\Delta T \quad (7)$$

A diurnal cycle was detected in over half of the atmospheric air measurements obtained on Lusiad Expedition. The maximum occurs between 0800 and 2000 local time (Keeling and Waterman, 1968b). For the original report, these data were eliminated by preparing a plot of all atmospheric air data and selecting only those portions of the record having steady concentrations, i.e. ±0.5 ppm departures from average for four or more hours. Data from these steady periods were used to compute interval averages (see Keeling and Waterman, 1968a).

For this report a new method was used to select uncontaminated air. Only night-time hours were used, 2100 - 0700 local time. The mean and standard deviation (SD) were calculated. Any hourly air values having a mean deviation greater than 2 SD are rejected and a new mean and SD are computed. Once again hourly values with greater than 2 SD are rejected. Accepted air data are identified in the database by a "1" in the F (Flag) column. Since these data are reported in GMT, most of the accepted periods do not correspond to 2100 - 0700 GMT in this tabulation.

Originally the diurnal cycle which produced contaminated atmospheric air measurements during daytime hours was believed to be caused by outgassing of sea salt which collected in the airline intakes or in brass couplings (Swagelok brand) used to join lengths of polyethylene tubing (Keeling and Waterman, 1968b).

From a perspective of more than 30 years it now seems likely the daytime contamination of the atmospheric air measurements came from solar exposure of the polyethylene tubing which was strung unprotected on the outside of the vessel, principally along the weather deck railings and up the side of the foremast. Two factors responsible for outgassing of the tubing are porosity of the plastic and photochemical breakdown by UV light which reduces the material to brittleness.

Metal and plastic intakes of the design used on these three expeditions have continued to be used, both with and without glass wool inserts, on subsequent cruises to the present.

For Lusiad Expedition, only one Swagelok brass union was used to join lengths of the plastic tubing for individual air lines outside the ship. The tubing was supplied in 100 ft. lengths individually packaged in sealed plastic bags. The ends of each roll of tubing were plugged. None of the air line runs on the R/V Argo required more than two lengths of tubing. The air lines, without regard for condition, were routinely renewed at major ports-of-call. The volume of the cavity in the Swagelok fitting, between the ends of the two tubes being joined, is less than one cubic centimeter. As a repository of degassing sea salt these fittings are minuscule when the whole air line is considered. Any sea salt buildup would increase gradually during the use of the air lines, and the diurnal effect would have to increase gradually also. This was not observed, however.

More convincing evidence of polyethylene tubing degassing occurred five years after the Lusiad Expedition and using the same apparatus almost identically configured. The matter of diurnal contamination had to once again be addressed in 1967 on the Eastropac and Nova Expeditions (unpublished data).

For Eastropac (February - March 1967) cursory data reduction during the expedition revealed a cyclic variation which correlated with solar exposure of the plastic tubing. When the tubing was tightly wrapped with strips of aluminum foil which reflected the sunlight, the diurnal effect disappeared.

For Nova Expedition (April - September 1967) the polyethylene tubing was placed inside a vinyl garden hose and ambient air was continuously pumped through the hose with a neoprene-diaphragm-pump operating at full capacity. No diurnal cycle was observed in these atmospheric air data.

Since the same type of polyethylene tubing used on Lusiad Expedition was also used on Downwind and Monsoon Expeditions, why were no contaminated air measurements identified?

In the case of Downwind Expedition it is unlikely more than 100 ft. of tubing was used for the primary air line to the foremast. At least half the period of monitoring was spent in high southern latitudes where total overcast prevailed for most days thus keeping the lines in the shade and least prone to photo decomposition. Another reason for not observing cyclic variation is a poor signal to noise ratio brought about by a less than optimal mounting for the infrared analyzer which was very susceptible to ship's engine vibrations.

The installation of the apparatus in the forward cargo hold on the R/V Argo for Monsoon Expedition kept the plastic air lines outside the vessel to about one-third the length necessary for runs on the Lusiad Expedition. Virtually all sampling was carried out from the forward intake which required only a line from the top of the foremast to the fo'c's'le deck, then through a bulkhead union to inside the vessel. Laying against the mast the tubing was often in the shade. Long Southern Ocean runs provided more shade from lots of overcast weather. While the analyzer mounting was improved for the Monsoon Expedition, the noise in the stripchart record was at least a factor of two greater than seen on the Lusiad Expedition when the analyzer was fully gimbaled. Had there been a cyclic variation it would probably have gone undetected.

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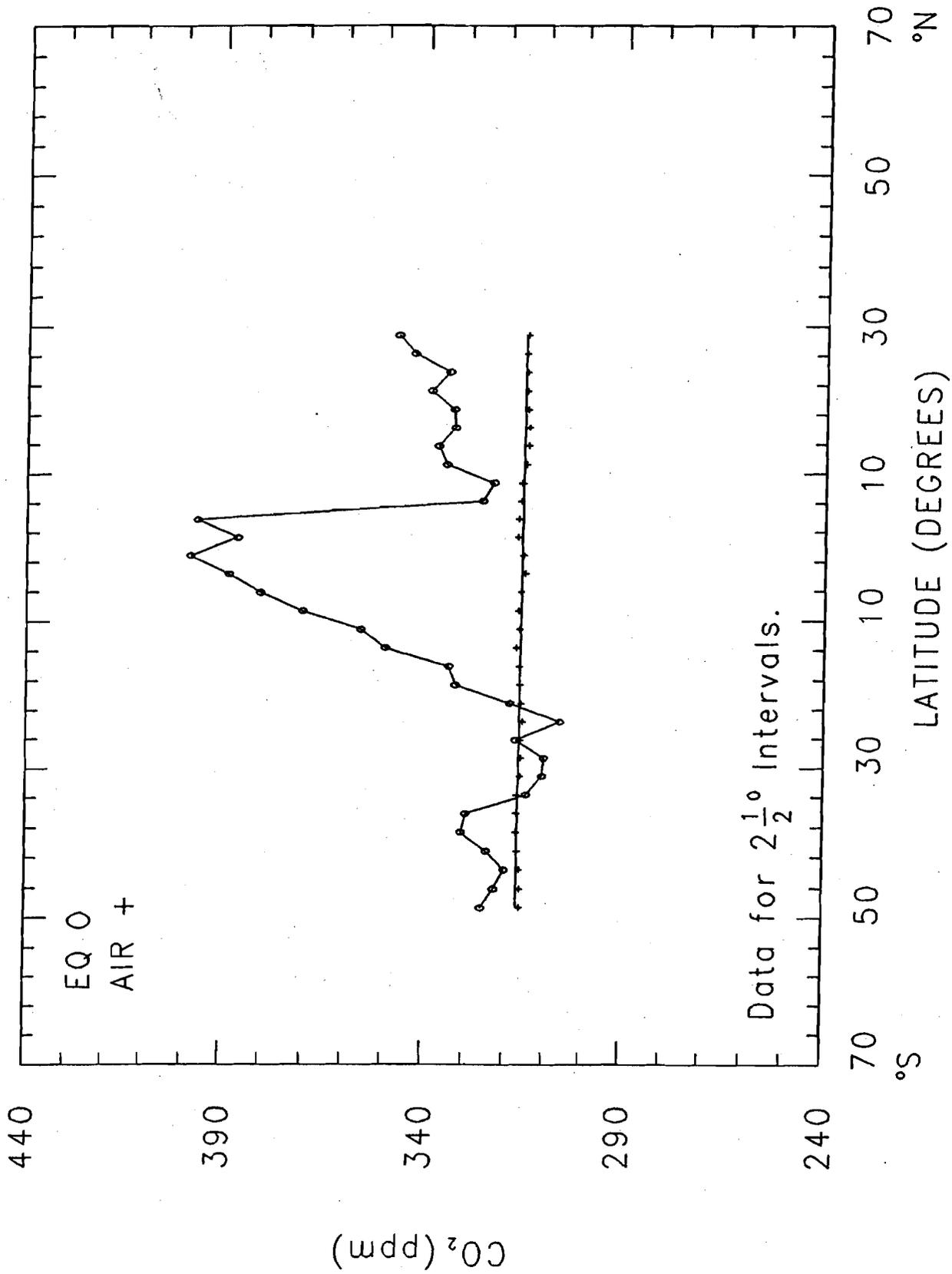


Figure 8. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the Pacific Ocean, SIO Downwind Expedition (RV Horizon), 22 October to 23 December 1957.

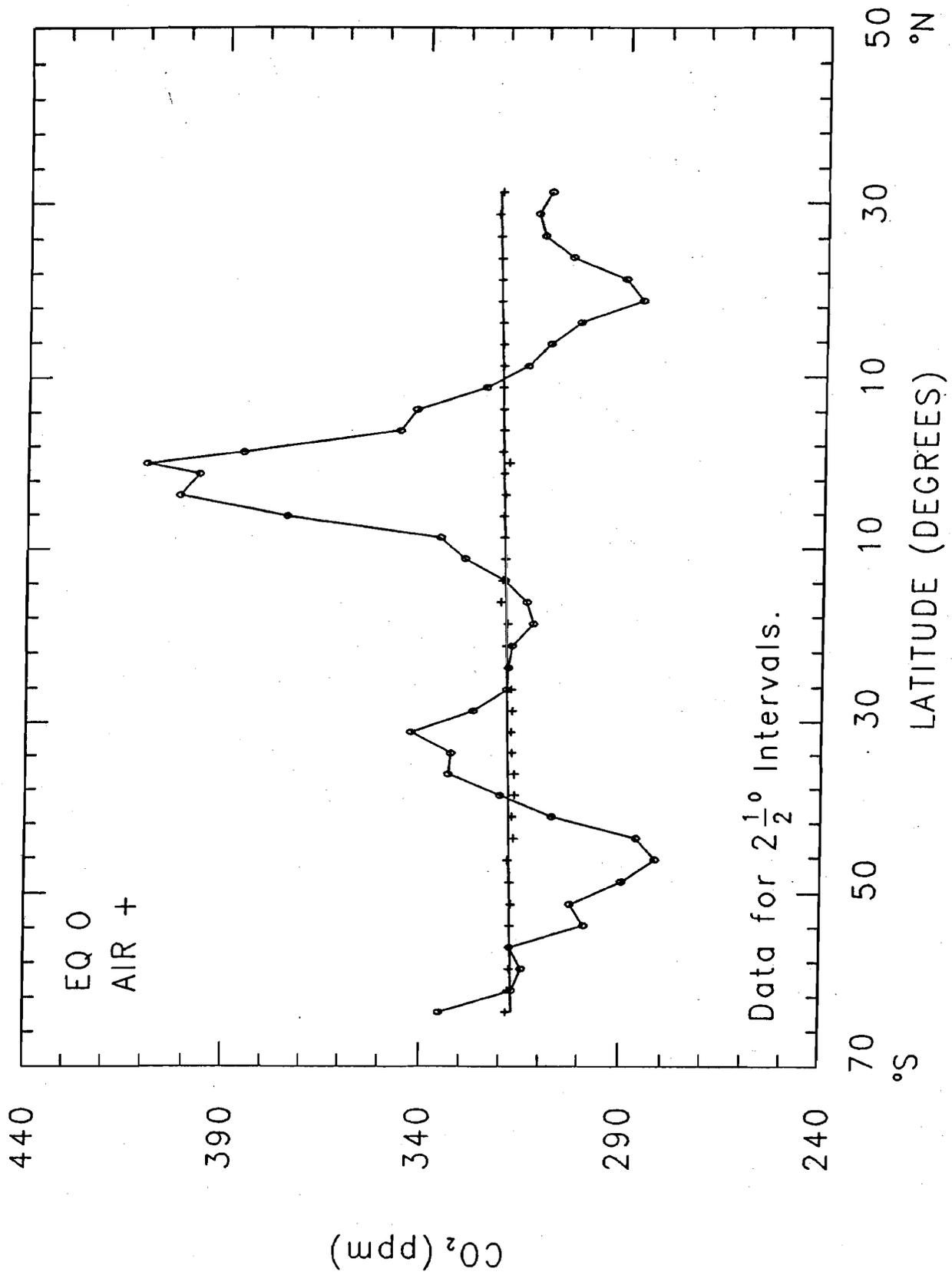


Figure 9. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the Pacific Ocean, SIO Monsoon Expedition (R/V *Argo*), 31 January to 18 April 1961.

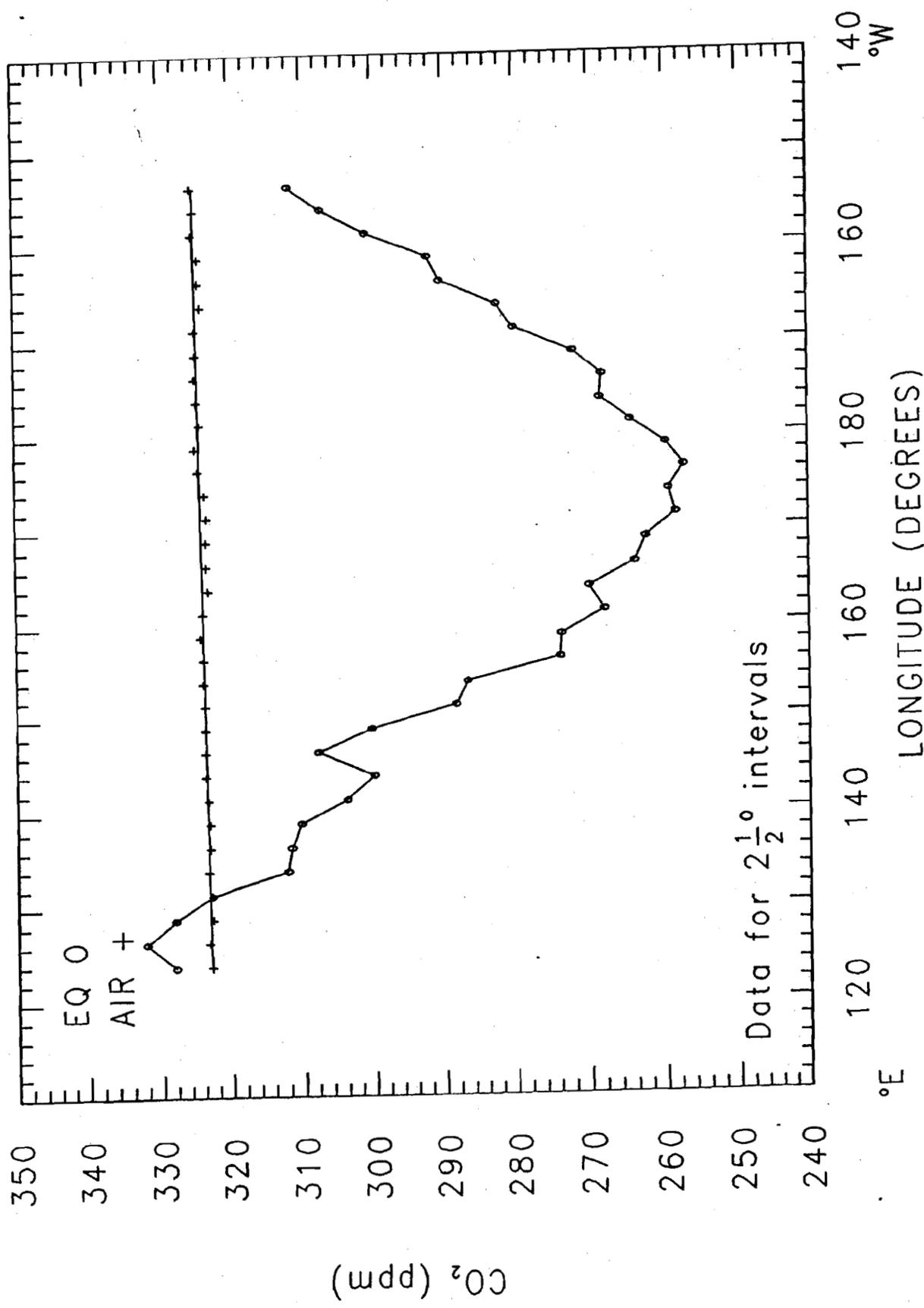


Figure 10. Near surface measurements of atmospheric CO_2 and pCO_2 in ocean surface waters as a function of longitude in the Pacific Ocean, SIO Lusiad Expedition (R/V *Argo*), 19 May to 9 June 1962.

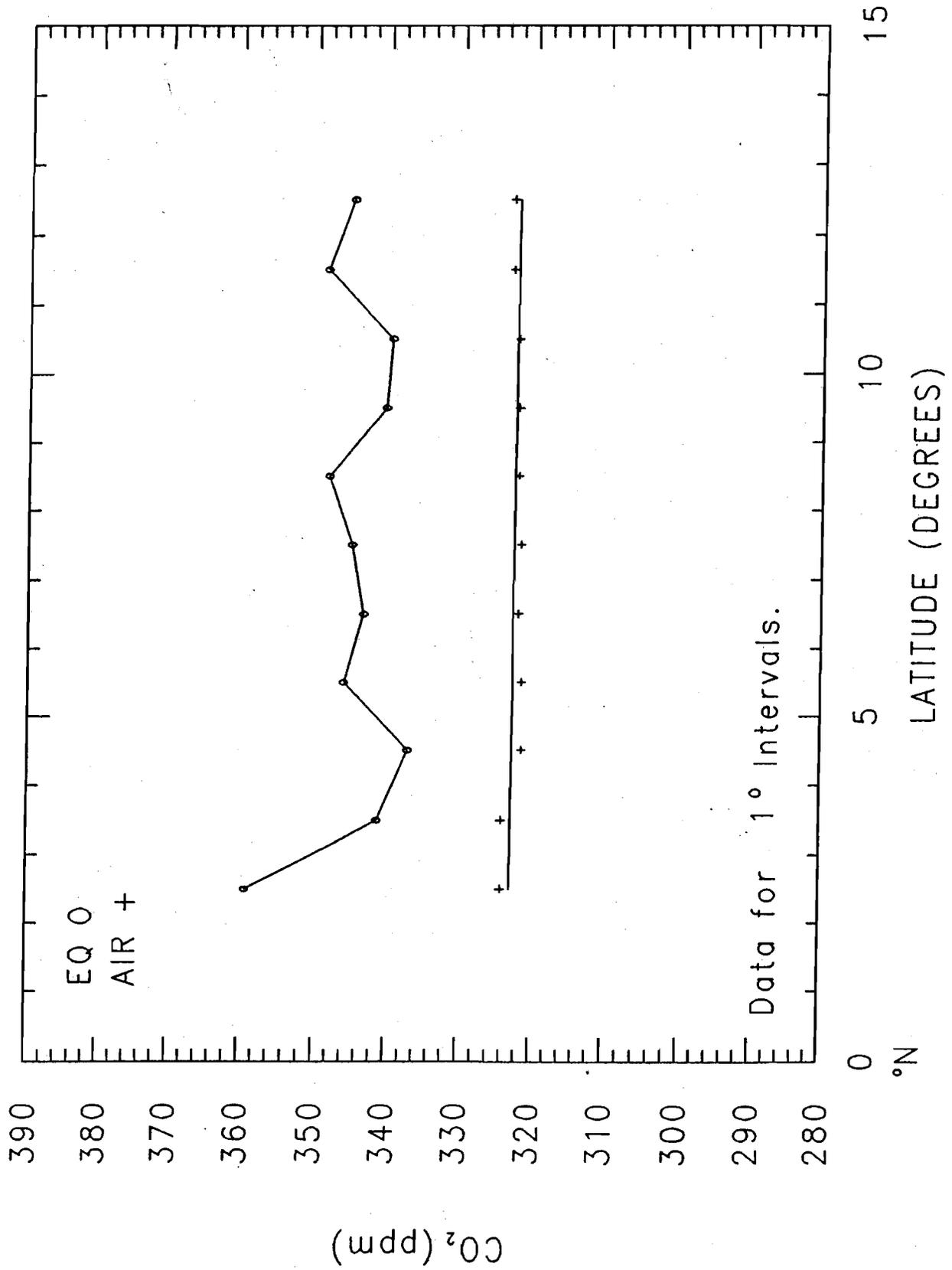


Figure 11. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the South China Sea, SIO Lusiad Expedition (R/V *Argo*). 14 to 23 June 1962.

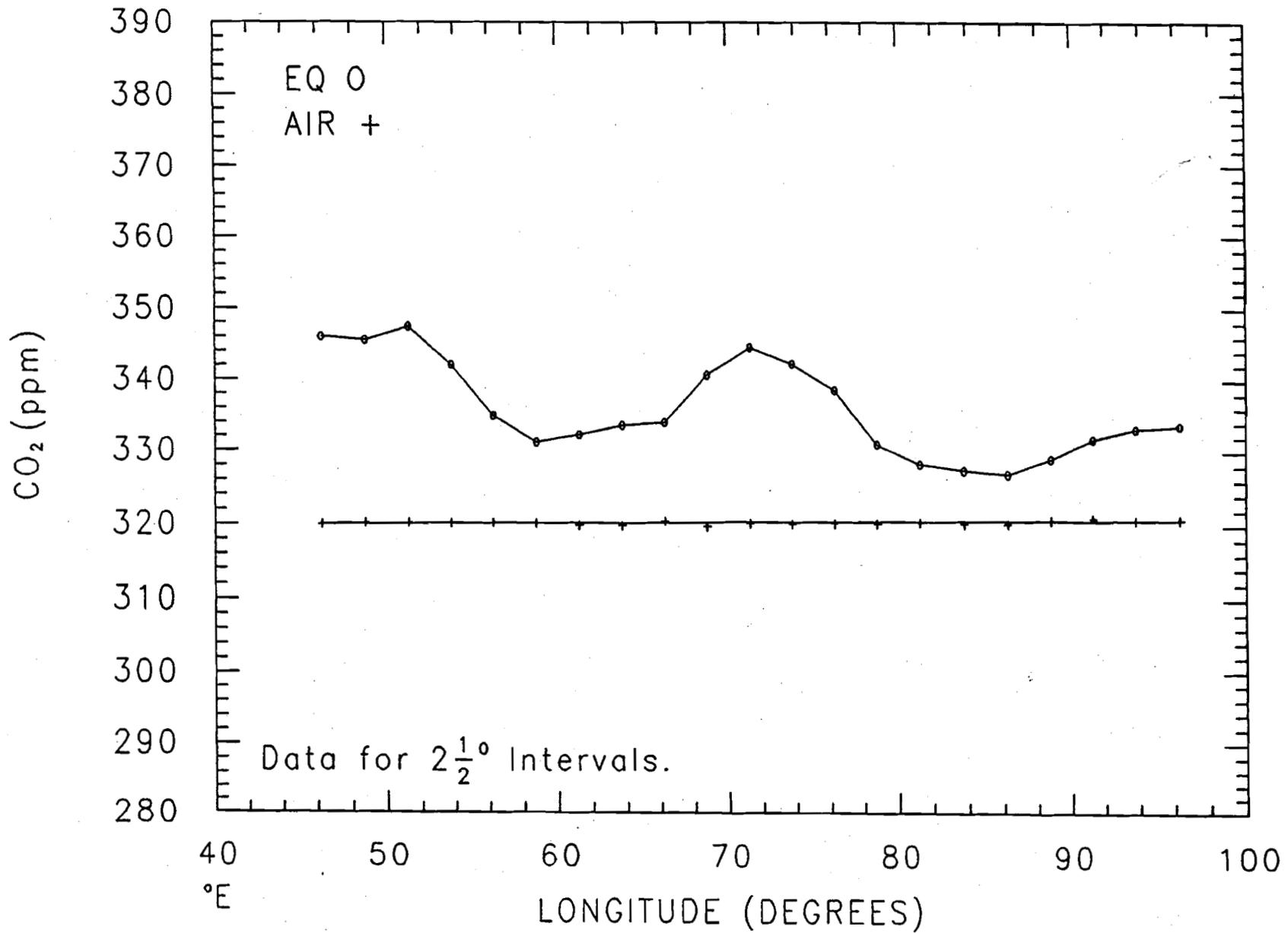


Figure 12. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of longitude along the equator in the Indian Ocean, SIO Lusiad Expedition (R/V *Argo*), 1 to 22 July 1962.

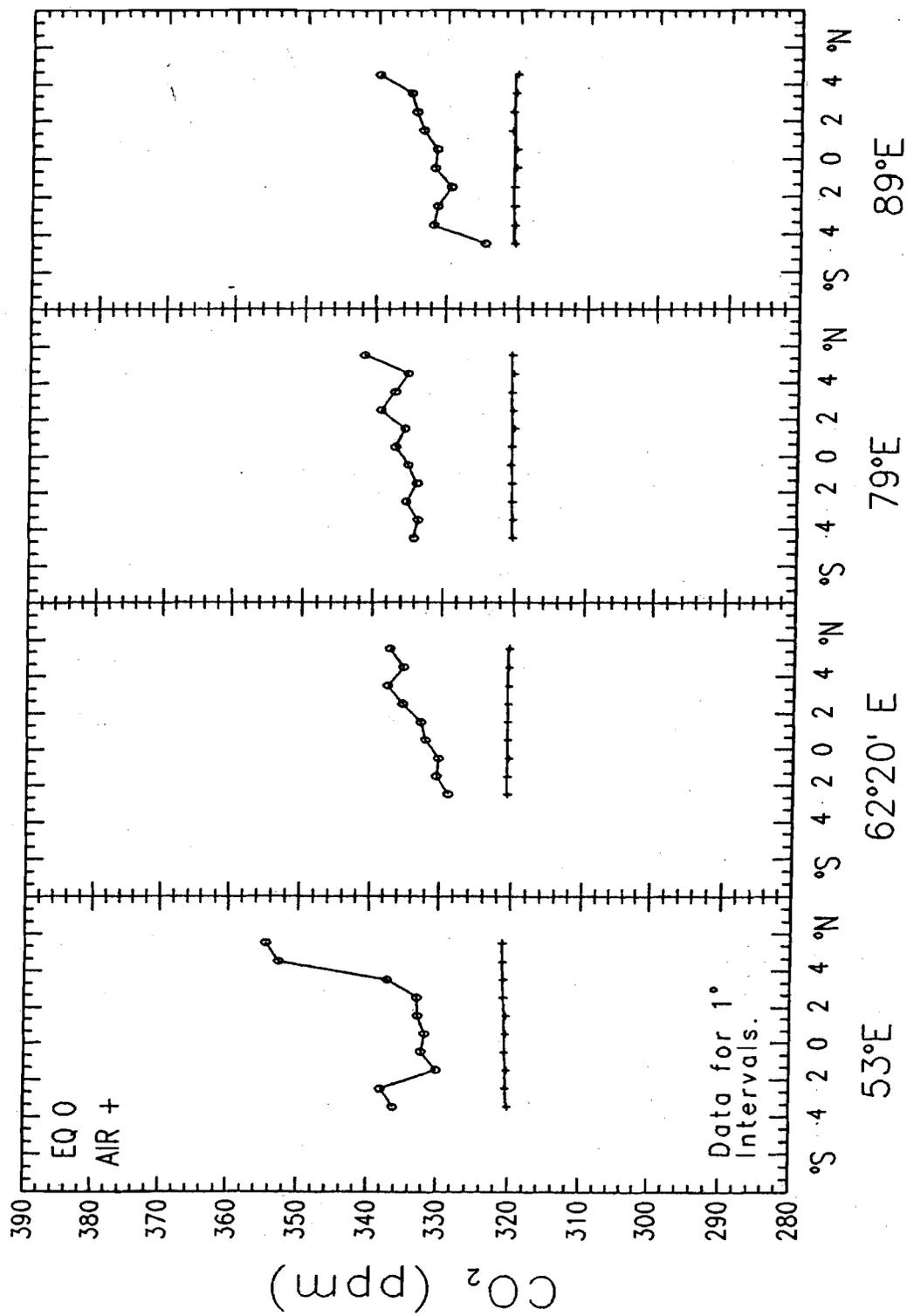


Figure 13. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude at four equatorial transects in the Indian Ocean, SIO Lusiad Expedition (R/V *Argo*), 53EE (31 July to 11 August 1962), 62E20NE (15 to 22 August 1962), 79EE (28 August to 9 September), 89EE (11 to 21 September 1962).

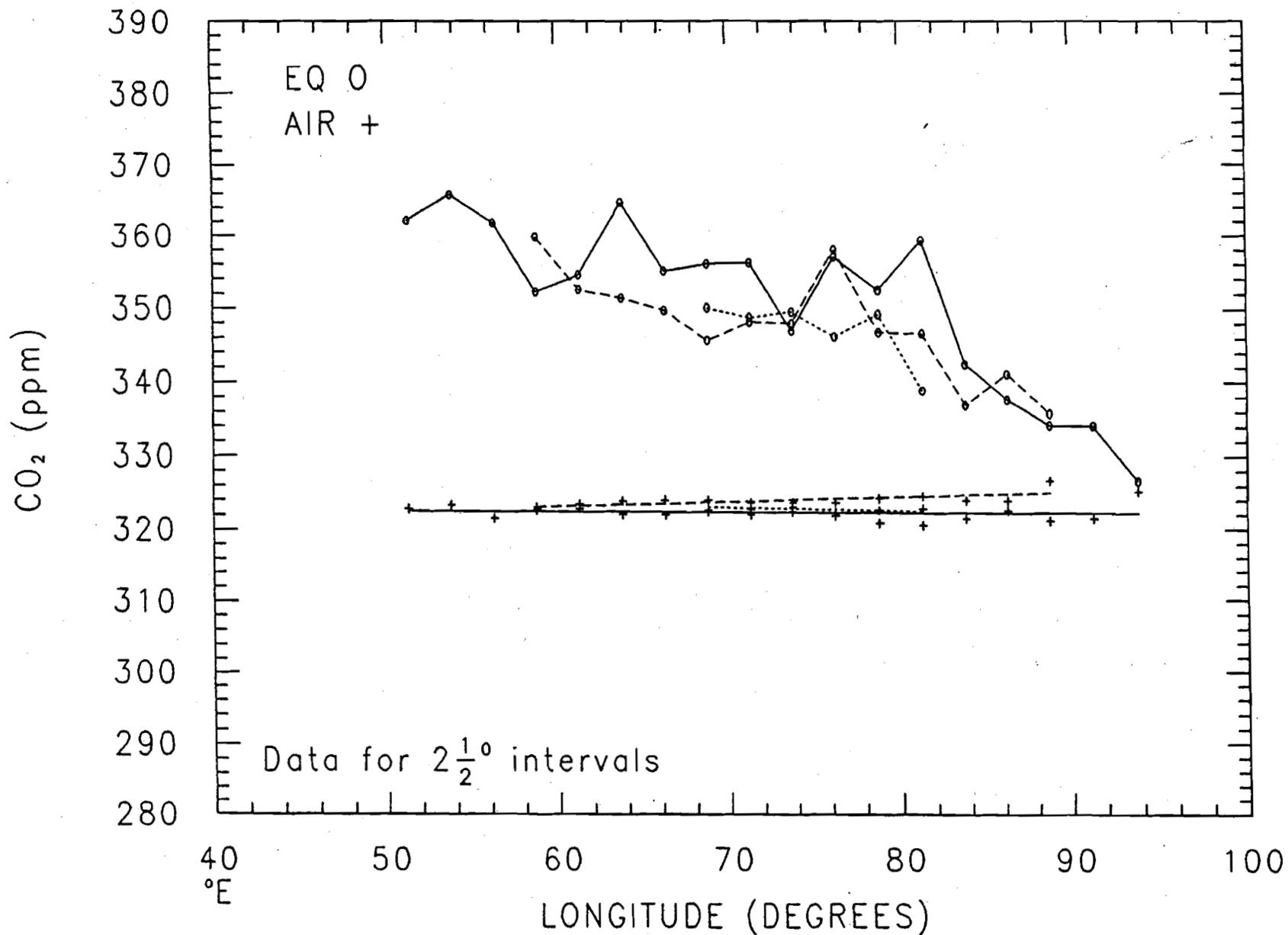


Figure 15. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of longitude along three equatorial traverses in the Indian Ocean, SIO Lusiad Expedition (R/V *Argo*) 27 February to 4 March 1963 (.....), 25 March to 10 April 1963 (), 26 April to 3 May 1962 (-----).

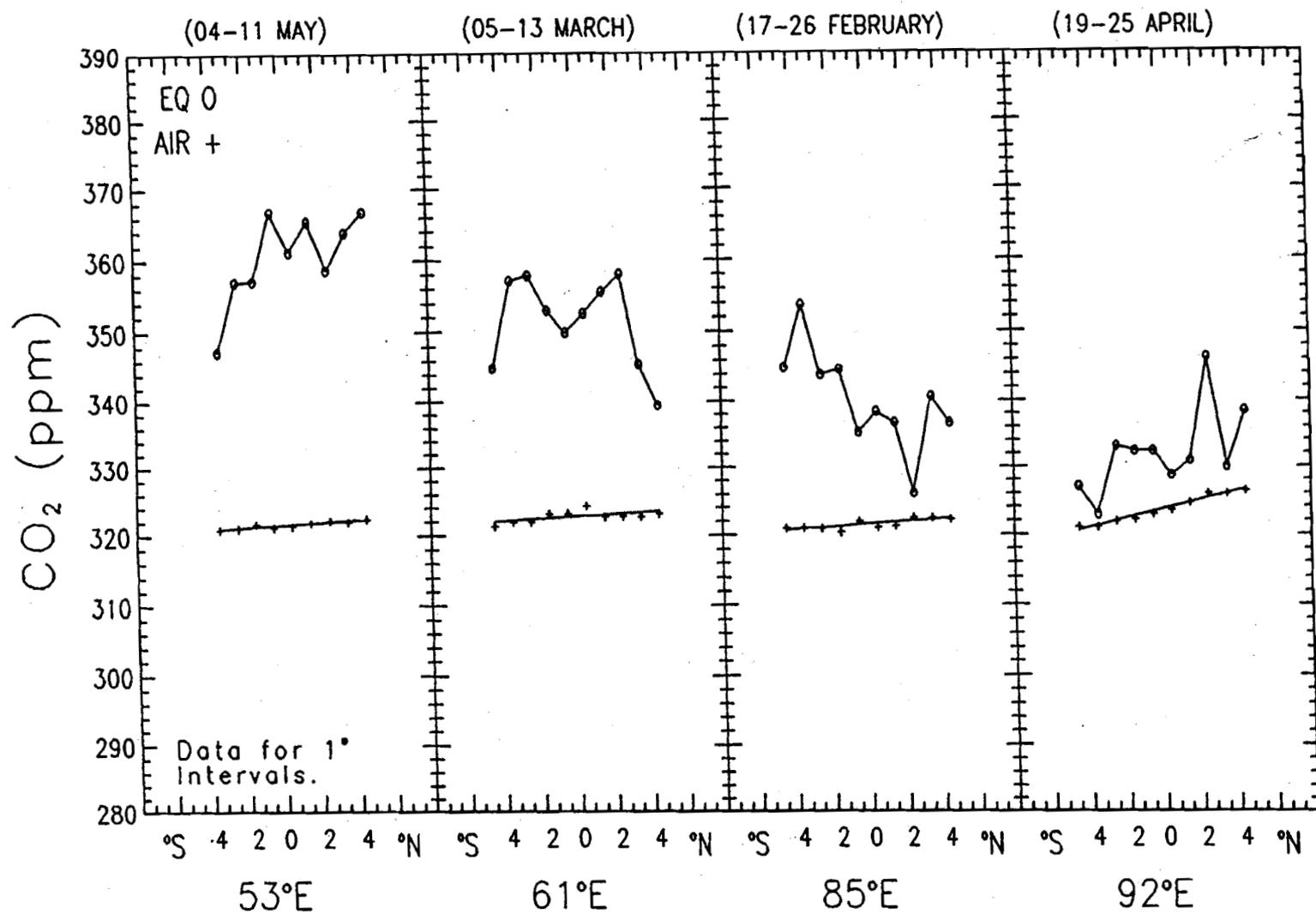


Figure 16. Near surface measurements of atmospheric CO_2 and pCO_2 in ocean surface waters as a function of latitude at 4 equatorial transects in the Indian Ocean, SIO Lusiad Expedition (R/V *Argo*), 53EE (4 to 11 May 1963), 61EE (5 to 13 March 1963), 85EE (17 to 26 February 1963), 92EE (19 to 25 April 1963).

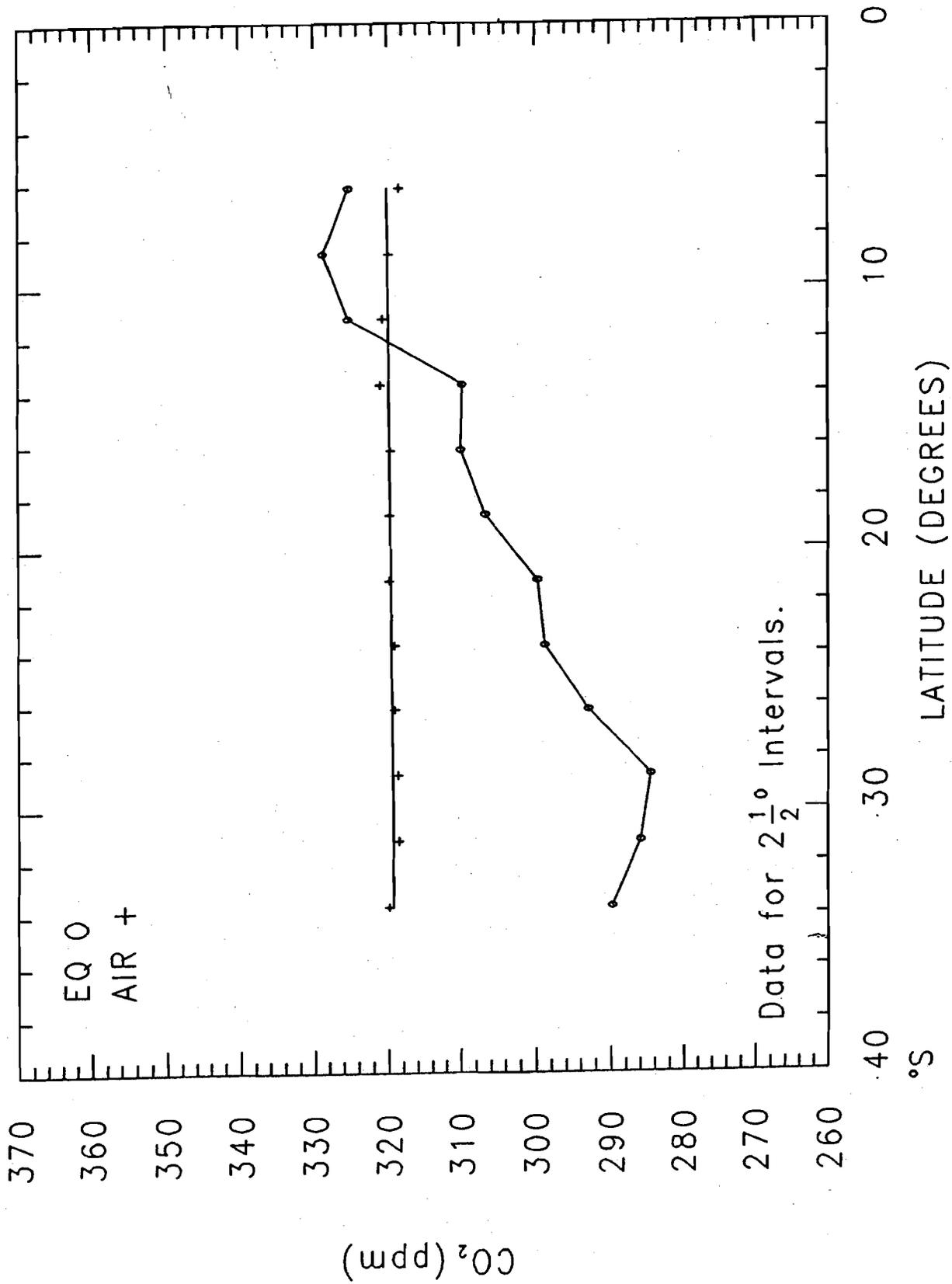


Figure 17. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the Mozambique Channel, Indian Ocean, SIO Lusiad Expedition (R/V *Argo*), 18 to 29 May 1963.

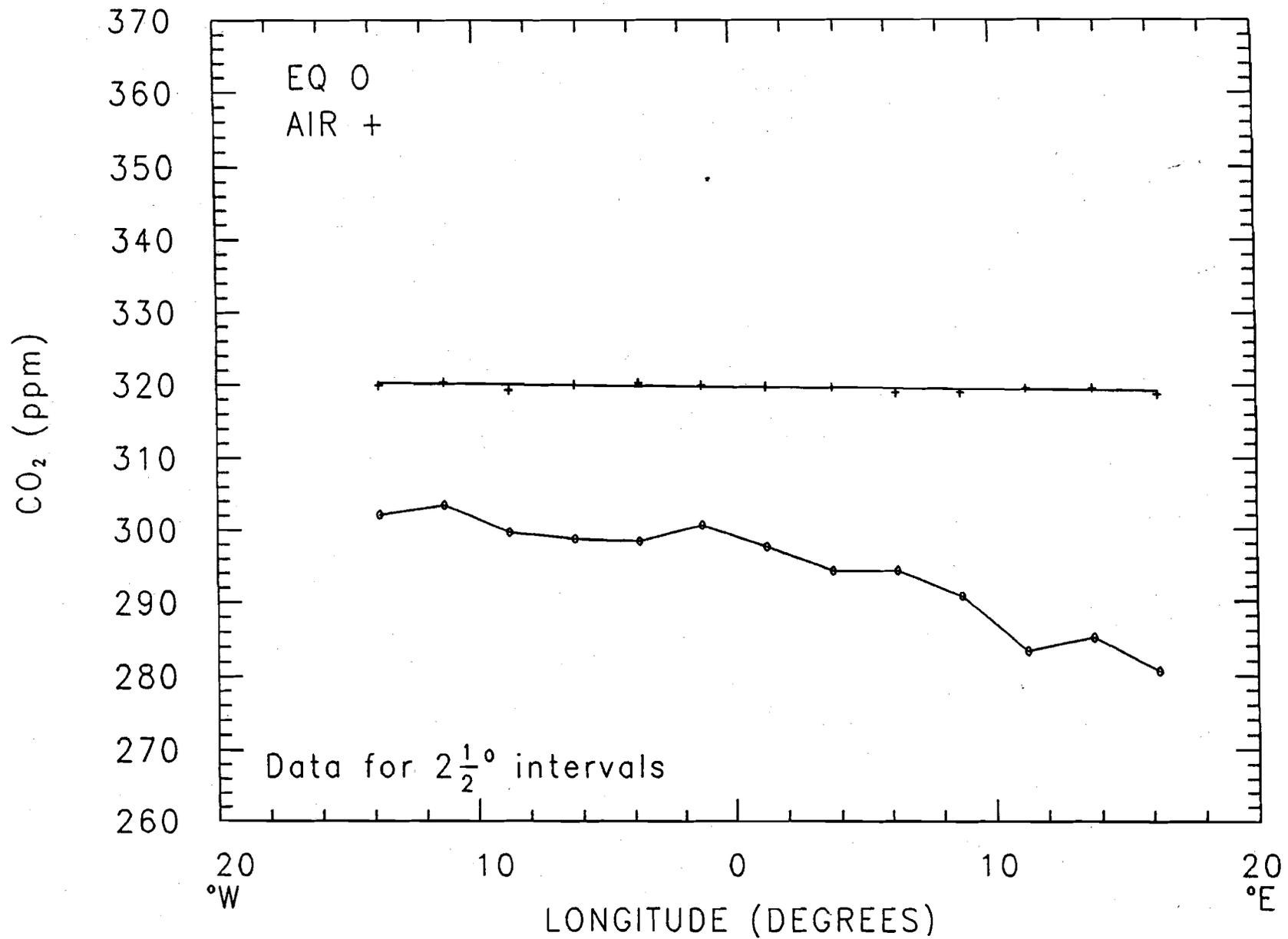


Figure 18. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of longitude in the South Atlantic Ocean, SIO Lusiad Expedition (R/V *Argo*), 4 to 15 June 1963.

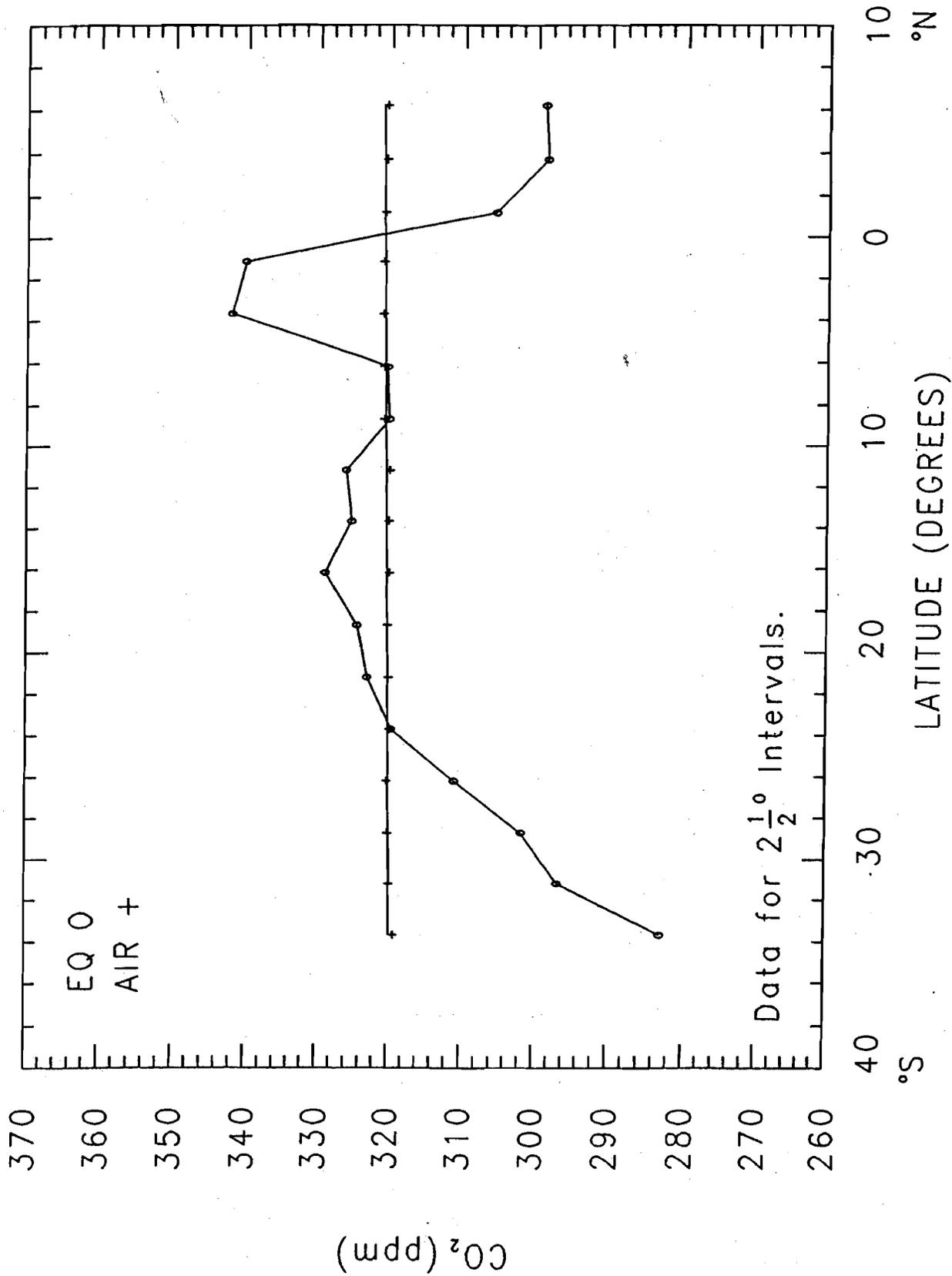


Figure 19. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the South Atlantic Ocean, SIO Lusiad Expedition (R/V *Argo*), 4 June to 8 July 1963.

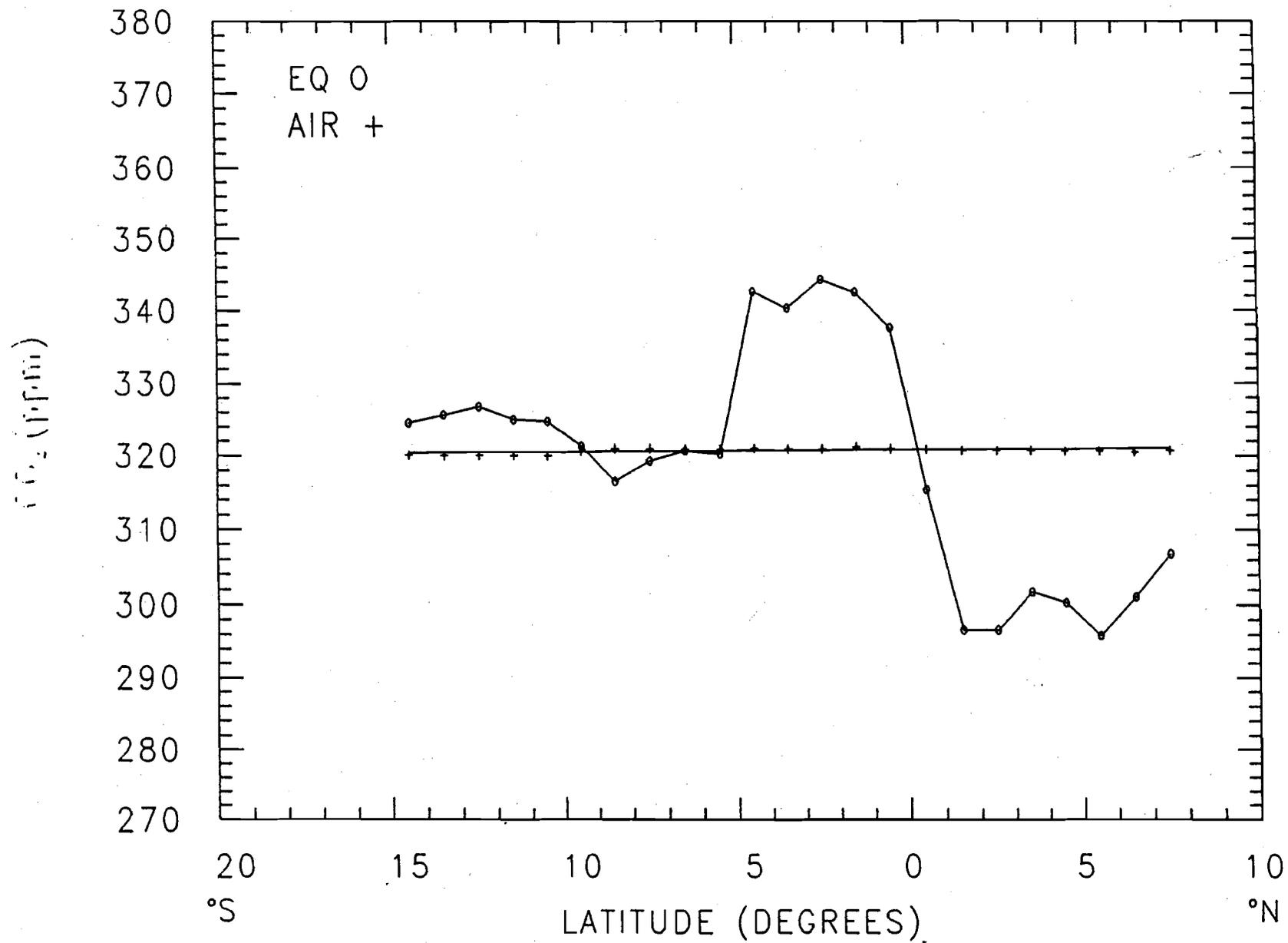


Figure 20. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the equatorial Atlantic Ocean, SIO Lusiad Expedition (R/V *Argo*), 18 June to 8 July 1963.

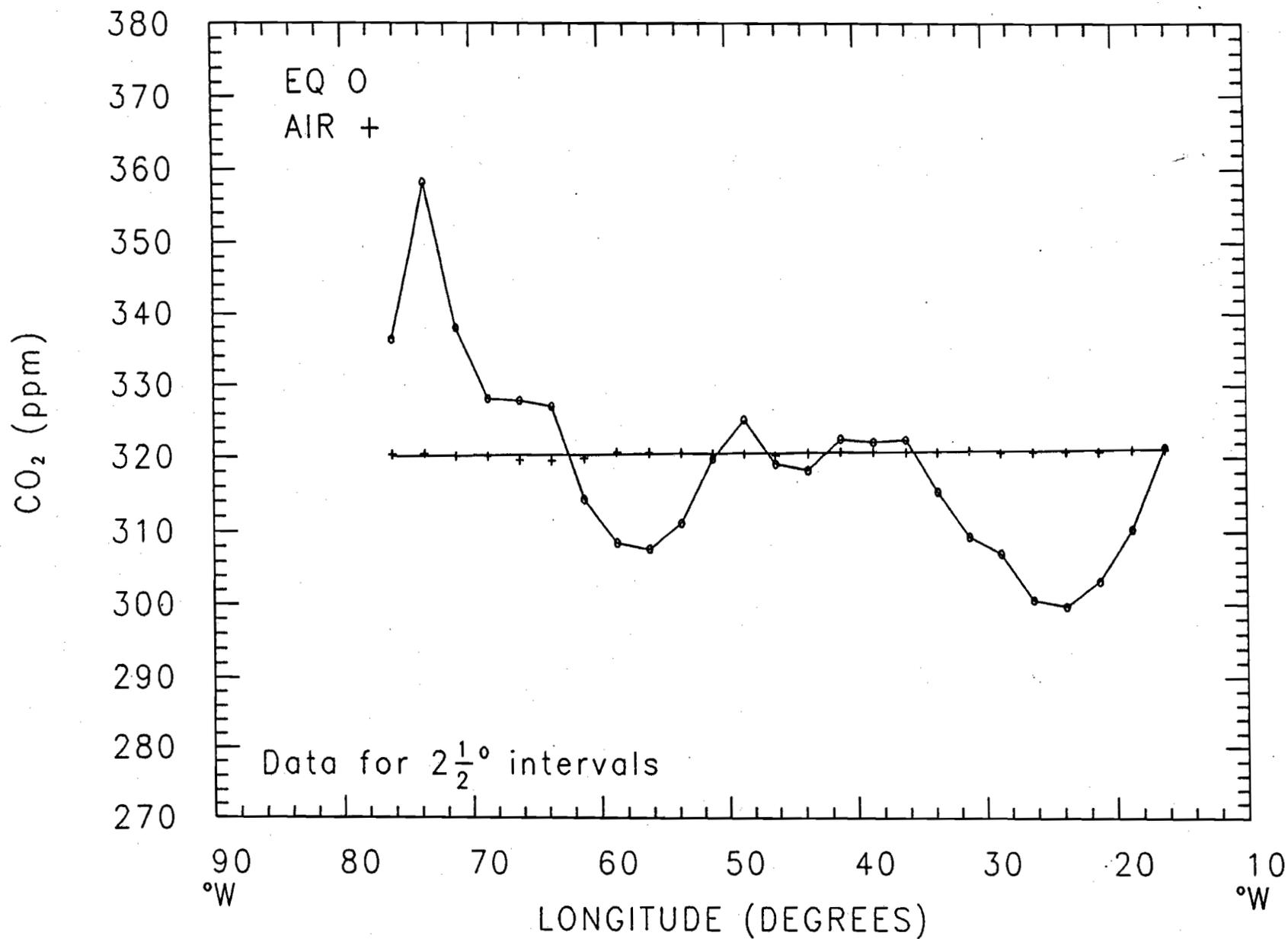


Figure 21. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of longitude in the equatorial Atlantic Ocean and the Caribbean Sea (west of 60E lat.), SIO Lusiad Expedition (R/V *Argo*), 12 to 29 July 1963.

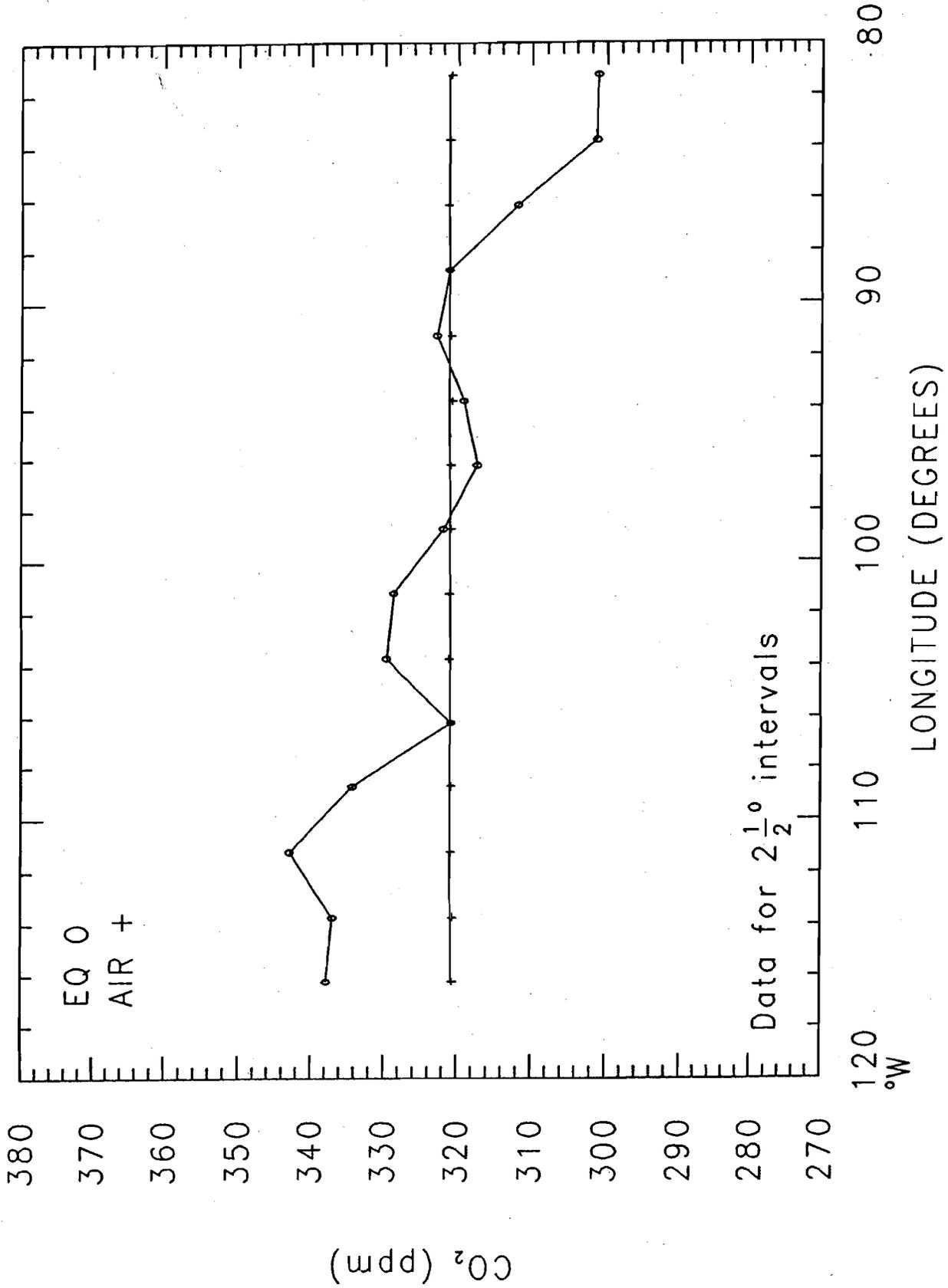


Figure 22. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of longitude in the equatorial Pacific Ocean west of the Panama Canal, SIO Lusiad Expedition (R/V *Argo*) 2 to 10 August 1963.

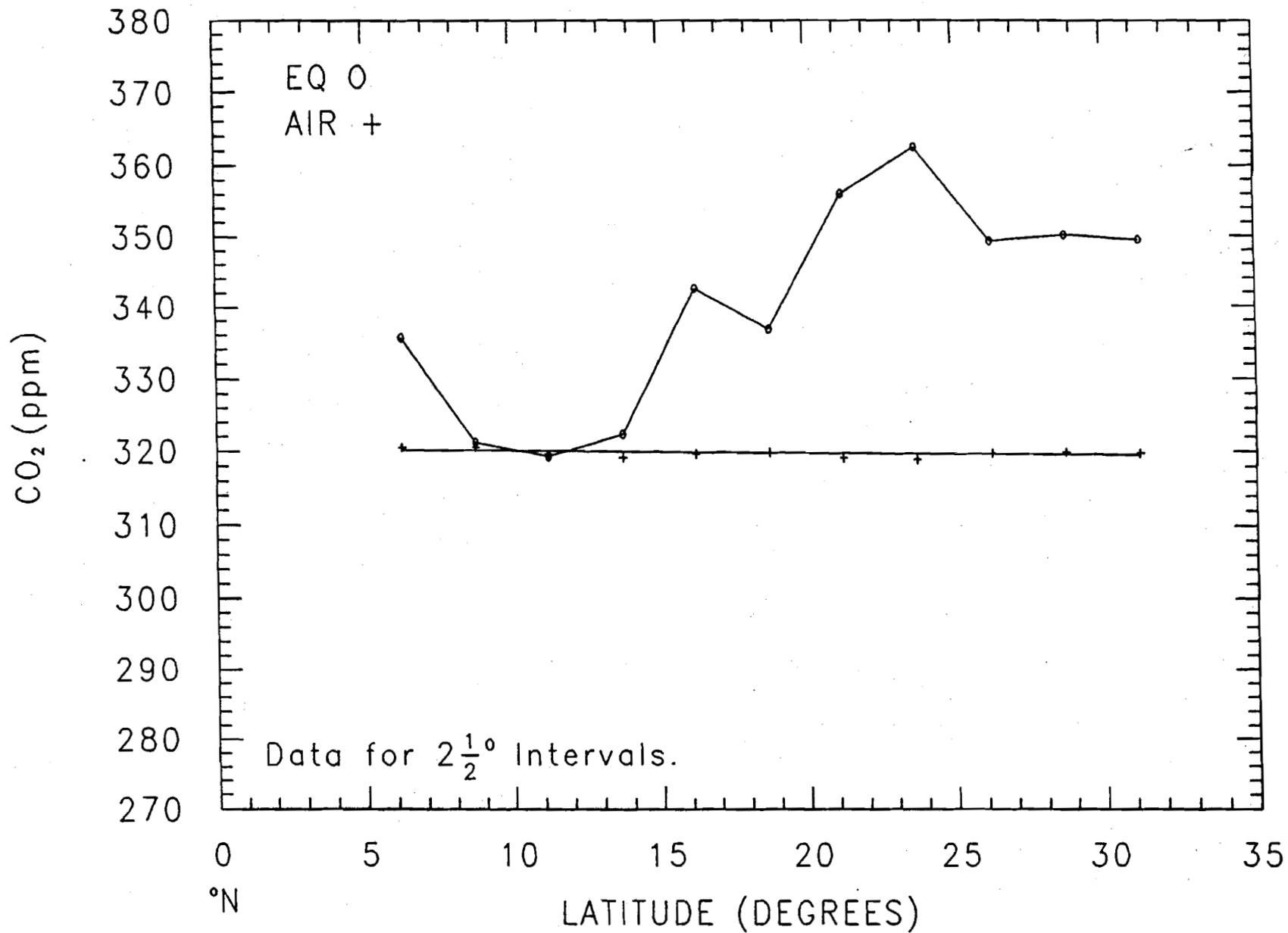


Figure 23. Near surface measurements of atmospheric CO₂ and pCO₂ in ocean surface waters as a function of latitude in the Pacific Ocean at 117°E, SIO Lusiad Expedition (R/V *Argo*) 10 to 15 August 1963.