FINAL TECHNICAL REPORT

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INVESTIGATION OF THE ATMOSPHERIC AND SURFACE OCEAN pCO_2 IN THE INDIAN OCEAN

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ABSTRACT

This report summarizes the results of measurements for the concentration of CO_2 in the marine air and the partial pressure of CO_2 (pCO_2) in the surface ocean water obtained during the Geosecs Expedition in the north and south Indian Oceans, Dec. 1977 through April, 1978. The area studied covers 13°N to 64°S in latitudes and 55°E to 115°E in longitudes. It has been found that the atmospheric CO_2 concentration in the southern hemisphere south of 15°S is remarkably constant at 334±1 ppm (expressed as mole fraction of CO_2 in dry air) throughout the period of this investigation. The CO_2 concentration in the northern hemisphere from the equator to 13°N exceeds that in the southern hemisphere by up to 5 ppm. The Inter-Tropical Convergence Zone (ITCZ) appears to represent a transition zone for the atmospheric CO_2 distribution.

The surface water pCO_2 values in the Indian Ocean range from 300 microatm. to 360 microatm. The highest values were observed in the Arabian Sea, and appear to be due to the low alkalinity water flowing out of the Red Sea. The Indian equatorial water has a maximum pCO_2 value of about 335 microatm., which is about 10 microatm. (or 3%) greater than that in the atmosphere. Thus, the equatorial water in the Indian Ocean does

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not appear to be as strong a CO_2 source as the equatorial Pacific water, in which pCO_2 values as high as 420 microatm. (about 100 microatm. above the atmospheric value) have been observed. Whether this is a year around phenomenon or varies with seasons is not known. The cooler waters of the mid-southern latitudes appear to be undersaturated with respect to the atmospheric CO_2 by about 15 microatm. (or 4%).

The Indian Ocean data have been combined with those previously obtained in the Pacific and Atlantic Oceans to yield a global mean pCO_2 value for the surface ocean water. It is found that the global mean pCO_2 for the world oceans is 10 ± 8 microatm. lower than the mean atmospheric pCO_2 value. This indicates that the net transfer rate of CO_2 from the atmosphere to the oceans corresponds to 50 ($\pm$40)% of the industrial CO_2 production rate.

INTRODUCTION

The increase in the atmospheric CO_2 concentration due to fossil fuel combustion and other industrial activities has recently become one of the major scientific and policy making concerns because of its possible adverse effects on the earth's climate. As a part of the scientific efforts for investigating the distribution of CO_2 in the atmosphere and it's sinks and sources in the natural cycle, we have investigated the concentration of CO_2 in marine air over the Indian Ocean and the partial pressure of CO_2 (pCO_2) exerted by the surface ocean water in the Indian Ocean during the IDOE/NSF sponsored Geosecs expeditions in December,1978 through April,1979. This report summarizes the results obtained during the expeditions.

THE METHOD OF MEASUREMENTS

Atmospheric CO_2 Concentrations:

The CO_2 concentration in air was determined by means of a non-dispersive infrared gas analyzer,UNOR-2,installed on board R/V Melville. The marine air was sampled continuously using a sample line (aluminum lined Dekabon tubing), whose intake was located at the top of the bow flag pole about 5 m above the sea surface. A stainless steel bellow pump was used to pull in air through the sampling line at a rate of about 10 liters/min. A portion of this air (about 500 ml/min.)was diverted into two cold water traps (made of stainless steel) held at a temperature of about -50°C in a deep freezer, and was passed through the infrared analyzer for the determination of the CO_2 concentration in air. The analyses were made for 15 minutes at a regular time intervals. The analyzer was calibrated by passing through three standard gases (N_2-CO_2 mixtures) once every two hours, and also by passing a standard gas (whose CO_2 concentration is close to that in the air) once every hour. The standard gas mixtures were calibrated before and after the expeditions against the gravimetric standards of Na_2CO_3 crystals, which were prepared by heating the CP grade Na_2CO_3 (supplied by Fisher Scientific Co.) at 180°C in air according to the procedures described by Wong (1970).

The precision for the standard gas mixtures has been estimated to be about ± 0.1% of the concentration, and the accuracy has been estimated to be about ± 0.5% or better. Since the standard gas mixtures used for this study consist of nitrogen and CO_2 gases, the CO_2 concentrations in air reported in this report have been corrected for the oxygen matrix effect by multiplying the N_2-CO_2 based values with 0.9925 (Takahashi et al, 1976). The atmospheric CO_2 concentrations reported here are thus expressed in the CO_2 mole fraction in dry air.

Our calibrated gas mixtures have been compared with those of C.D.Keeling, Scripps Institution of Oceanography, and the results are shown in Table 1. It appears that our calibration yields about 0.2% and 1.1% greater values at 340 ppm and 400 ppm respectively than the Keeling's 1976 manometric scale.

Partial Pressure of CO_2 in Surface Water:

The partial pressure of CO_2 exerted by the surface water was determined using an equilibrator-infrared analyzer system, which is schematically shown in Fig.1. Seawater is pumped continuously into the equilibration chamber by a water pump located at the ship's bow at a rate of about 22 liters/min. In the equilibration chamber (19 liters), seawater is dispersed by a shower head (made of PVC plastic) to create a large surface area for gas exchange. It is continuously discharged from the equilibrator through a drain, which is designed to maintain a constant water level in the equilibrator. The equilibrated air was dried by a cold water trap (-50°C), and the concentration of CO_2 in it was determined by the infrared gas analyzer. It has been experimentally demonstrated that the air passing through the equilibrator is equilibrated with the seawater to better than 98% during its mean residence time of 38 minutes in the equilibrator.

The partial pressure of CO_2 (pCO_2) exerted by the water sample has been computed by using the following relationship:

$pCO_2 = V_{CO_2} \cdot (Pt - pH_2O)$, where

Table 1 Comparison between the CO_2 analyses obtained by C.D. Keeling of the Scripps Institution of Oceanography with those obtained by us at LDGO. The CO_2 concentrations in air are expressed in the CO_2 mole fraction in dry air, and are corrected for the oxygen matrix effect. The numbers in the parentheses indicate the number of measurements, and the uncertainties are expressed by one standard deviation. The SIO measurements are based on the 1974 manometric scale.

	CO_2 conc.(ppm) in dry air		Difference (%)
	SIO	LDGO	
Scripps Pier air samples collected in April,1976	338.3	339.5±0.3 (3)	+0.4
Standard Gas Mixtures			
GX-26-72	306.3±0.1 (20)	307.6±0.2(10)	+0.4
GX-65-73	339.4±0.1 (20)	340.2±0.2(10)	+0.2
GX-38-72	396.4±0.2 (20)	400.8±0.1(10)	+1.1

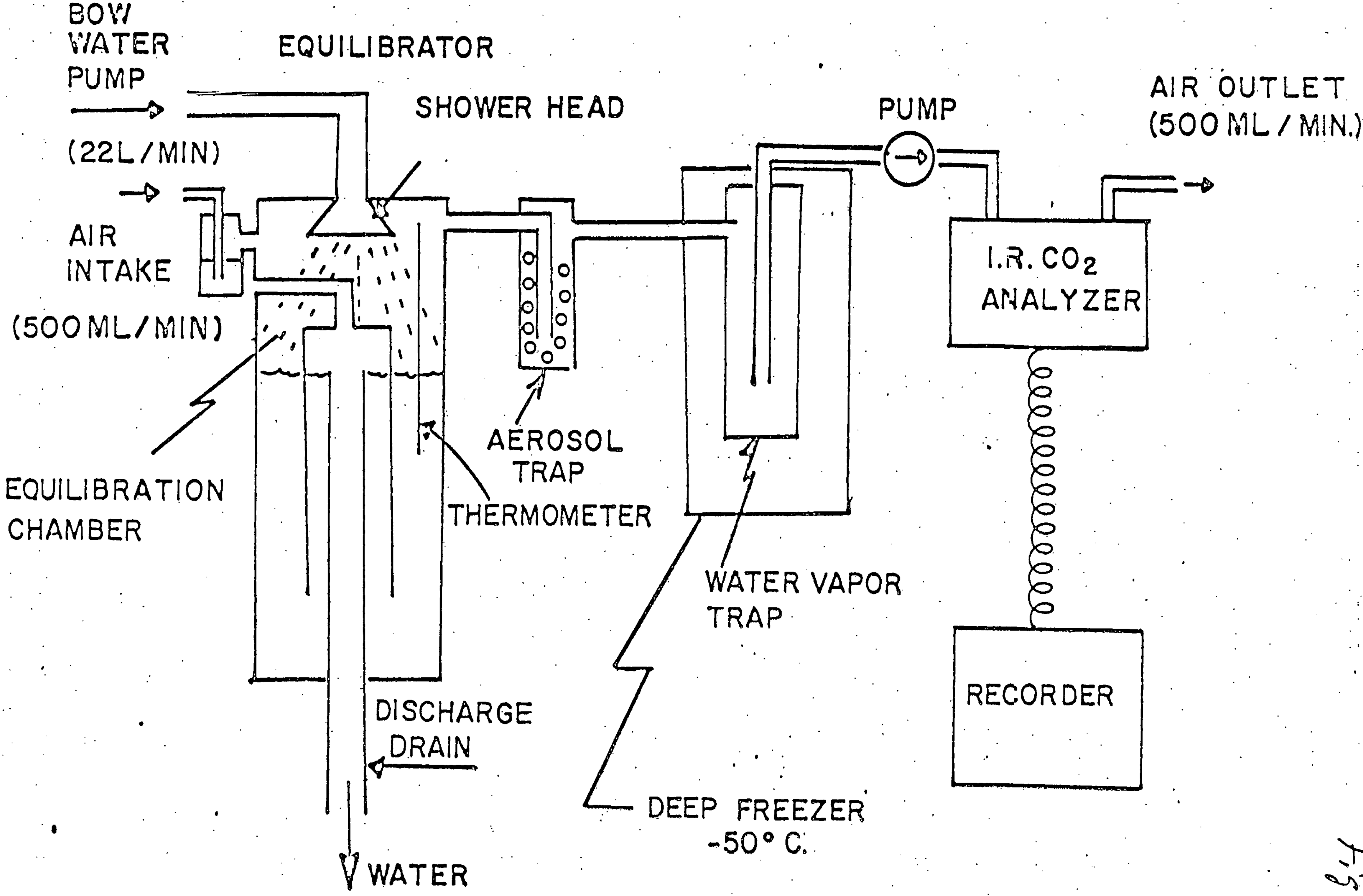

BOW WATER PUMP
(22L/MIN)
EQUILIBRATOR
SHOWER HEAD
AIR INTAKE
(500 ML/MIN)
EQUILIBRATION CHAMBER
THERMOMETER
AEROSOL TRAP
DISCHARGE DRAIN
WATER
WATER VAPOR TRAP
DEEP FREEZER -50° C.
PUMP
AIR OUTLET (500 ML / MIN.)
I.R. CO_2 ANALYZER
RECORDER

Fig. 1

V_{CO_2} is the concentration of CO_2 in the dried equilibrated air expressed in mole fraction, Pt the total gas pressure in the equilibrator, and pH_2O the saturation water vapor pressure at the temperature of equilibration.

THE RESULTS

The Atmospheric CO_2 Concentrations:

The ship's tracks for the Geosecs Expeditions in the Indian Ocean,Dec.,1977 through April,1978, are shown in Fig.2, and the leg numbers (legs 4 through 7) are identified in the figure.

Figs.3,4 and 5 respectively show the CO_2 concentrations (ppm in dry air) observed during Legs 4 and 5(west of 90°E), Legs 5(east of 90°E) and 6, and Leg 7 as a function of the latitude. The atmospheric CO_2 concnetration observed in the southern hemisphere south of 10°S is uniformly 334 ± 1 ppm. To the north across the equatorial zone, a sharp increase was observed : a 1.3 ppm increase at 7°S in Jan.,1978 (Leg 4), a 3.5 ppm increase at 10°S in March,1978 (Leg 6), and a 0.6 ppm increase at 7°S in April,1978 (Leg 7) as shown in these figures. These increases appear to be associated with the Inter-Tropical Convergence Zone (ITCZ), which separates the northern from the southern hemisphere air masses. During the time when these observations were made, the ship was sufficiently far away from the land masses as seen from the ship's tracks in Fig.2. Thus, the observed step-like increase can not be due to the local sources on the lands. On the other hand, the second step-like increase observed further to the north (the equator to 10°N) (see Figures 3,4 and 5) may well be due to the continental sources of CO_2. The observed large scatter of the data north of 10°N appears to support this explanation.

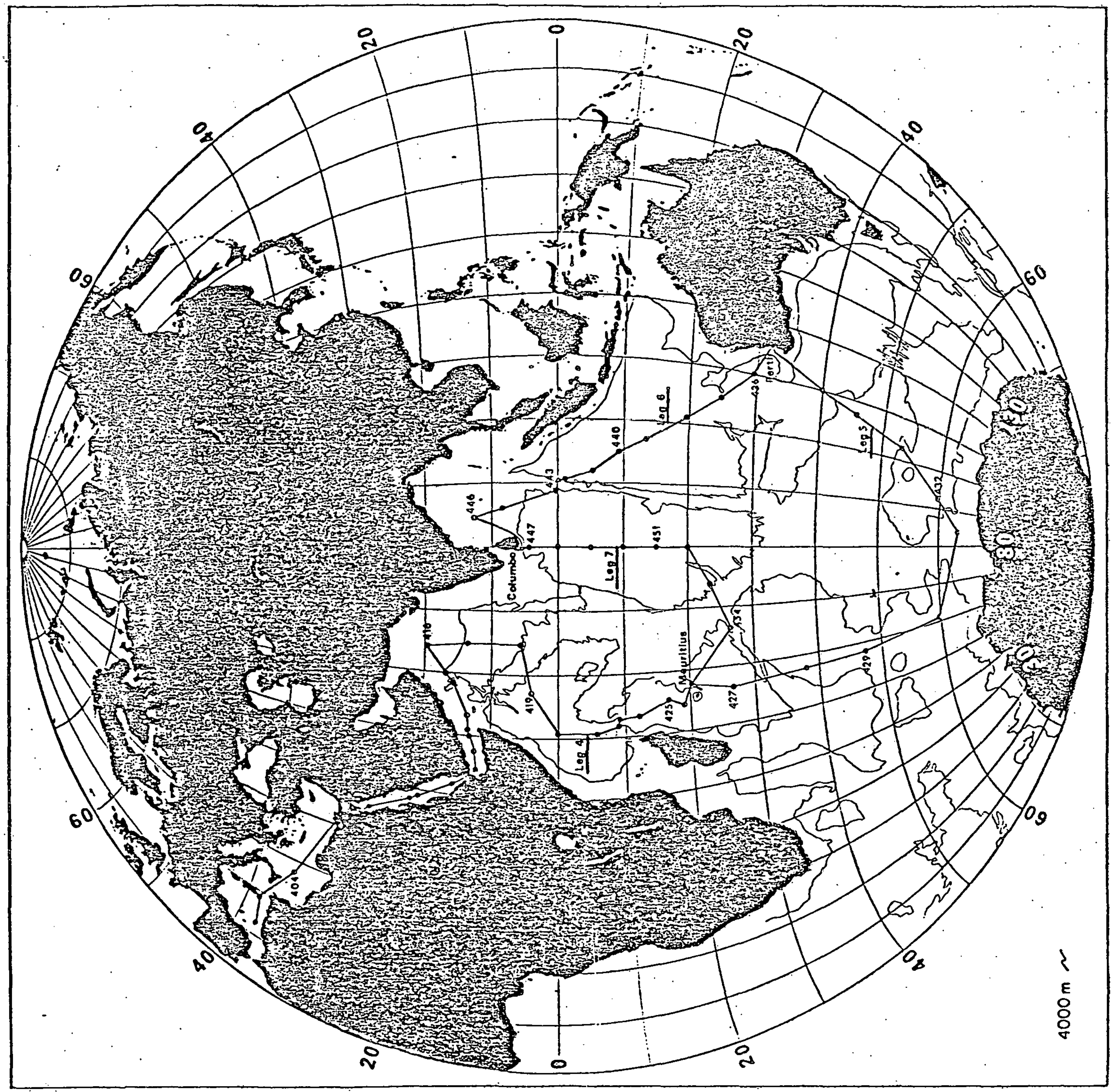


Fig.2 The ship's tracks and the leg numbers of the Geosecs Indian Ocean Expedition, Dec.1977 through April,1978.

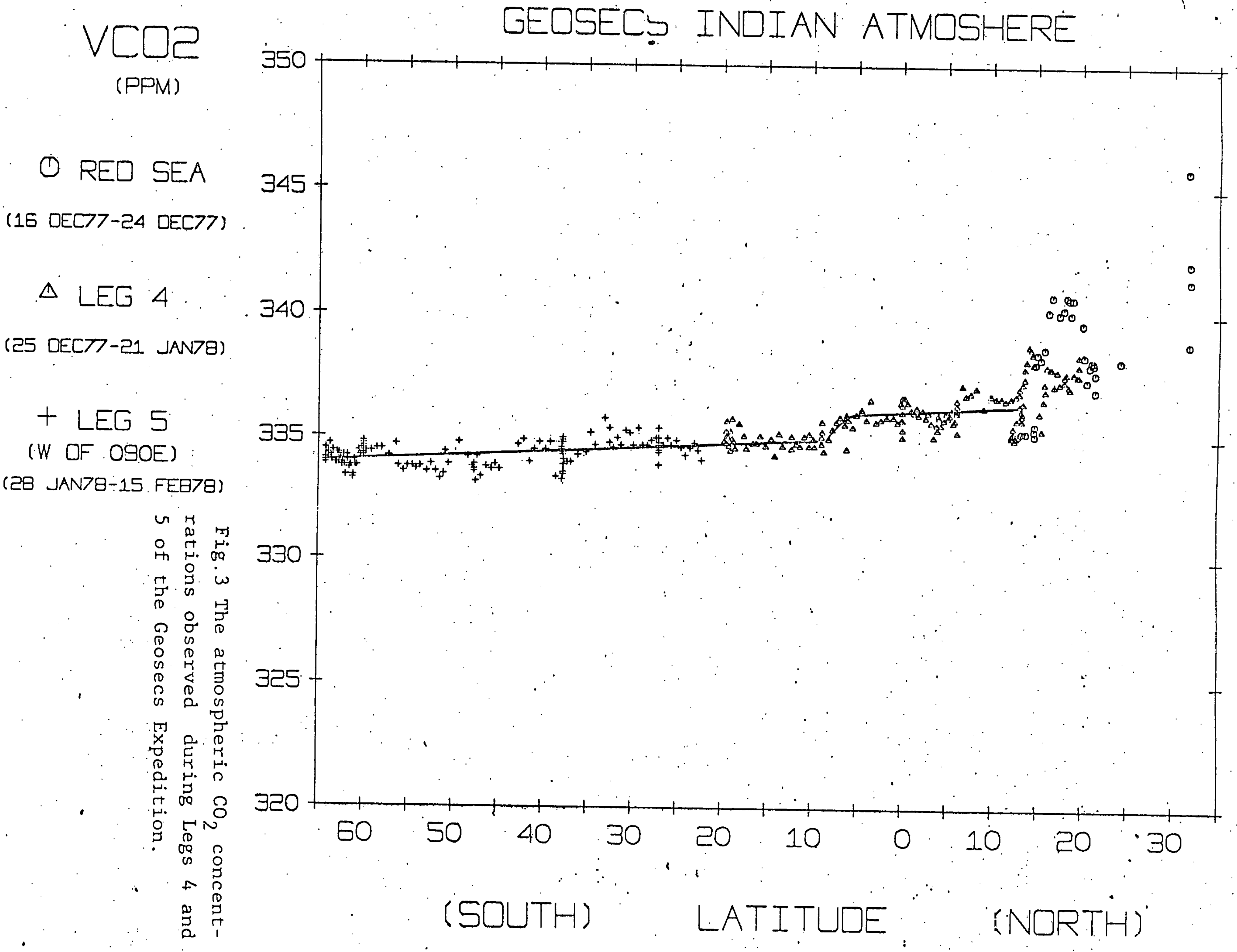


Fig.3 The atmospheric CO_2 concentrations observed during Legs 4 and 5 of the Geosecs Expedition.

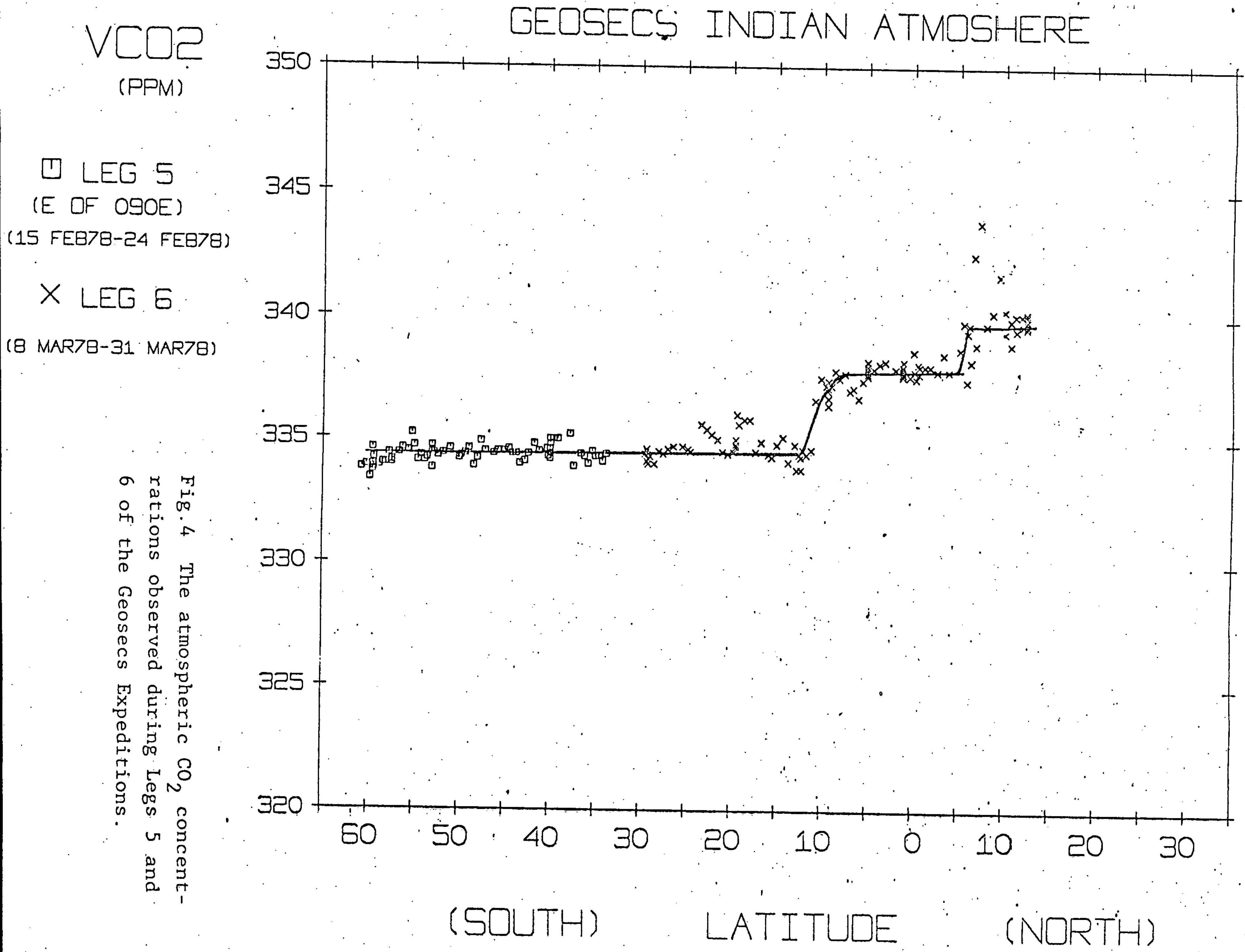


Fig.4 The atmospheric CO_2 concentrations observed during Legs 5 and 6 of the Geosecs Expeditions.

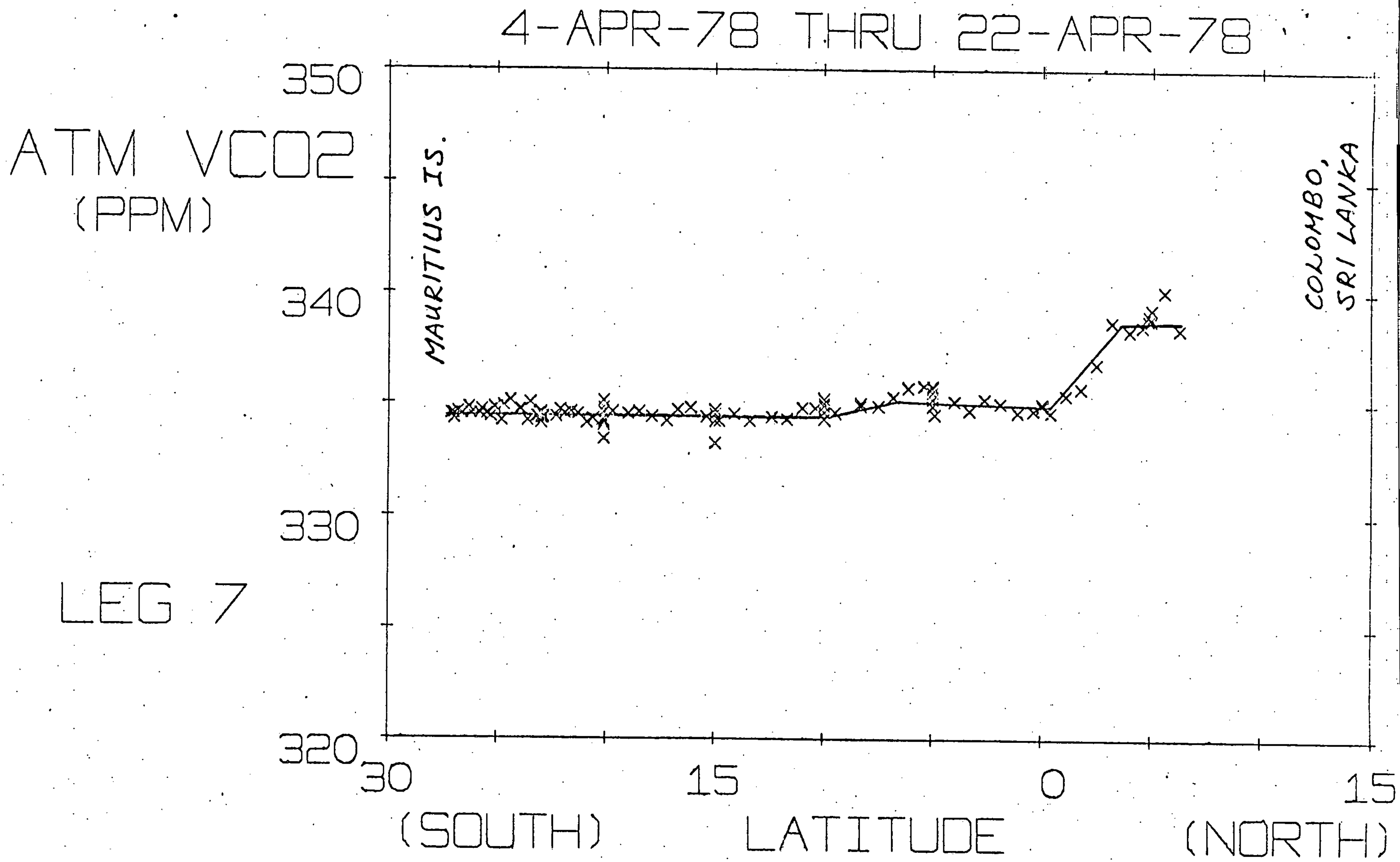


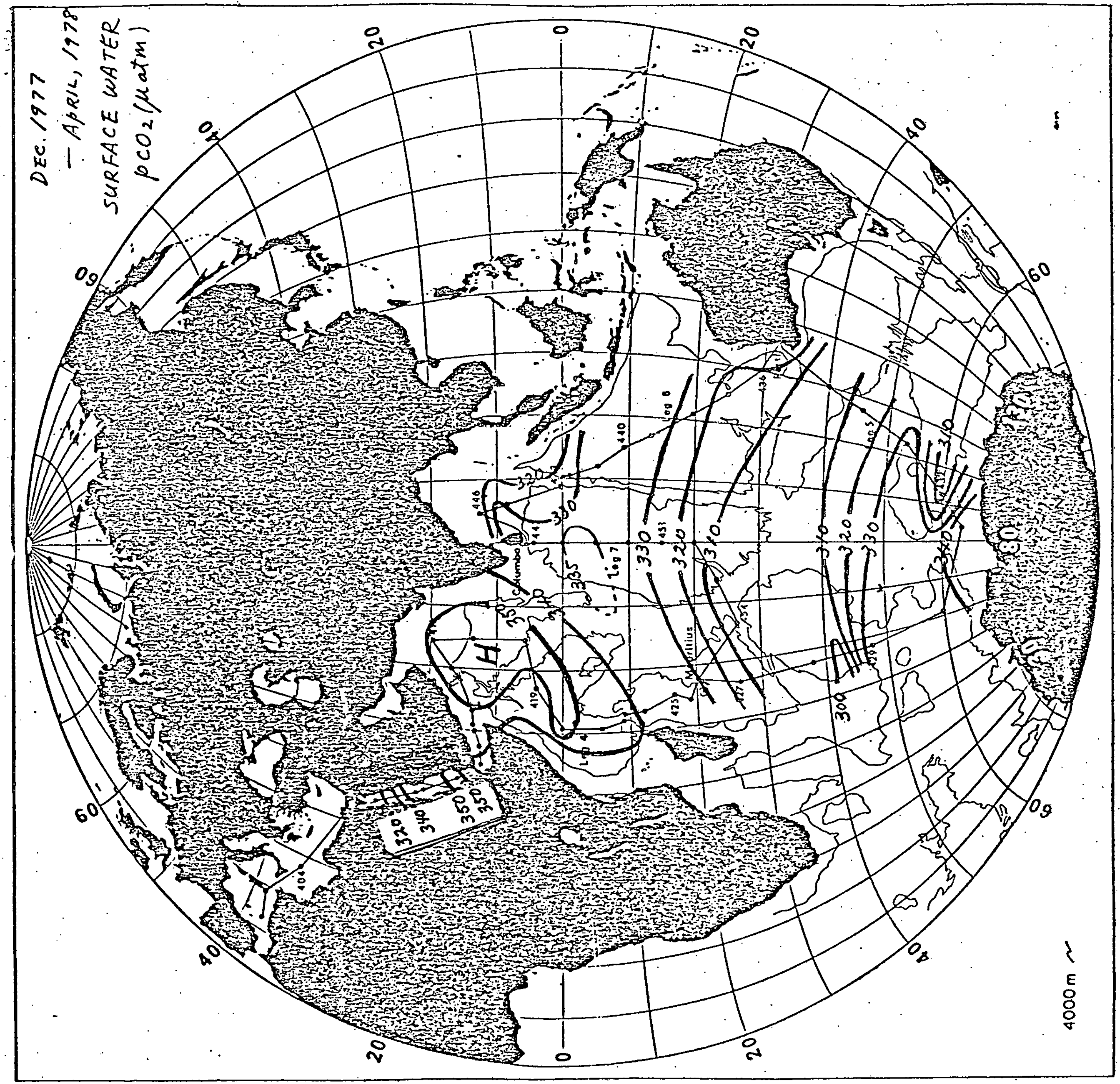
Fig.5 The distribution of the atmospheric CO_2 concentration (by volume in dry air) observed during the Colombo, Sri Lanka - Mauritius Is. leg (Leg.7) in April,1978. Note a sudden change in the atmospheric CO_2 concentration between 0 and 5°N.

pCO_2 in the Surface Ocean Water:

The results of pCO_2 measurements in the surface ocean water of the Indian Ocean are summarized in Fig.6 in the form of an iso-pCO_2 map . It is seen that the northwestern Indian Ocean ,i.e. the Arabian Sea area, exhibits the highest pCO_2 values observed during this investigqtion. This appears to be attributed to the low alkalinity water flowing out of the Red Sea, and to the high temperatures of the water in the region. The equatorial high pCO_2 belt was not clearly developed as observed in the Pacific by Keeling(1968), Miyake et al (1970) and Broecker et al (1979). The highest pCO_2 value observed in the Indian Ocean equatorial belt is about 350 microatm. in the extreme western sector (i.e. toward the African Continent), and it decreases to about 320 microatm. (nearly in equilibrium with the atmospheric CO_2) to the eastern sector (i.e toward Sumatra). Thus, the Indian Ocean equatorial belt does not appear to be a strong CO_2 source as the Pacific equatorial belt, where pCO_2 values as high as 420 microatm.(about 100 microatm. above the atmospheric value)were observed. However, the circulation pattern of the Indian Ocean during the Southwest Monsoon season (April through October) is known to change drastically from that during the Northeastern Monsoon season. (November through March). Consequently, the distribution of pCO_2 in the surface water observed mainly during the Northeast Monsoon season may be altered accordingly. Thus, without further observations, it is not possible to assess the intensity and significance of the Indian Ocean equatorial belt as a strong CO_2 source.

A broad oceanic area between 25°S and 45°S appears to be undersaturated with respect to the atmospheric CO_2 by about 20 microatm. Further south toward the Antarctica Continent, the surface water pCO_2 gradually increases to about 340 microatm. (about 15 microatm. greater than that in the air) indicating

Fig.6 The distribution of pCO_2 in the surface water of the Indian Ocean,Dec.1977-April,1978. The numbers indicate the partial pressure of CO_2 in microatmospheres.



that the cold Antarctic water is supersaturated with respect to the atmospheric CO_2. This may be caused by a rapid vertical mixing of the CO_2 rich deep water with the surface water.

The mean surface water pCO_2 value in the Indian Ocean has been computed to be 325.7 microatm.(an area weighted average) for the period January-April,1978. The mean atmospheric pCO_2 during this period has been estimated to be 329 microatm. based on the relationship: $pCO_2 = V_{CO_2} \cdot (Pt - pH_2O)$. The mean atmospheric CO_2 cocnetration of 337 ppm in dry air, the mean barometric pressure of 1014 mb (or 761 mmHg, 1.001 atm.), the mean surface water temperature of 21.9°C and the water vapor pressure of 19.7 mmHg (at 21.9°C) were used. Thus, it appears that the Indian Ocean as a whole appears to be undersaturated with respect to the atmospheric CO_2 by about 3 microatm. during the period of the present investigation, and hence a net CO_2 sink.

THE IMPLICATION OF THE PRESENT RESULTS TO THE GLOBAL CO_2 BUDGET

Since the begining of the Geosecs program in 1972, the distribution of the CO_2 partial pressure in the surface ocean waters of the three major world oceans has been investigated using the same technique described in this report: the Atlantic in 1972-1973, the Pacific in 1973-1974 and the Indian in 1977-1978 (this work). Based upon these data, the annual mean difference between the atmospheric and surface ocean pCO_2 values has been computed to be 10 microatm. for the world oceans. It has been assumed that the seasonal variation of the surface water pCO_2 is due entirely to the seasonal variation in the temperature of surface water. A change of 1.7% in pCO_2 per degree change in water temperature, which was observed in the Saragasso Sea in 1973 has been used throughout. Although it is difficult to estimate the uncertainty for the computed value, it has been estimated to be about ±8 microatm. on the basis of the following considerations. The error arising from the uncertainty in the seasonal effect is about 7 microatm. assuming ±30% error in the seasonal temperature effect of 1.7%/°C; the error due to the limited coverage of the geographical area is about 2 microatm.; and the error caused by the uncertainty of ± 0.3°C in the mean water tempeature (seasonal average) is 3 microatm. (thus totaling to $(7^2 + 2^2 + 3^2)^{\frac{1}{2}} = 8$).

The air-sea pCO_2 difference of 10 ± 8 microatm. represents the chemical driving force for the net removal of CO_2 from the atmosphere into the sea, and the net CO_2 flux across the air-sea interface may be estimated by:

$$F = E\cdot(pCO_2(\text{air}) - pCO_2(\text{seawater}))/pCO_2(\text{air}),$$

where E is the CO_2 exchange coefficient and has been estimated on the basis of natural C-14, bomb C-14 and Rn-222. If a Radon-222 based value of 16 Moles CO_2/m^2 yr. (Peng et al,1979) is used, a net CO_2 flux from the air to the sea is estimated to be 0.5 (±0.4) Mole CO_2/m^2 yr for the world oceans. On the other hand, the present rate of the industrial CO_2 production is about 1 Mole CO_2/m^2 yr. (or 5 x 10^9 metric tons of carbon). This means that 50 (±40)% of the industrial CO_2 is being absorbed into the oceans. Thus, the present surface water pCO_2 data are consistent with Keeling's observation of the atmospheric CO_2 increase rate.

The major source for the large uncertainty in the current estimate for the air-sea pCO_2 difference is the lack of our knowledge on the seasonal variation (its causes and magnitude of variations) in the oceanic pCO_2. A study being conducted across the equatorial Pacific as a part of the FGGE/NORPAX program may shed a light on this problem.

Respectfully submitted,

February 12,1980

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