

Measurements of atmospheric and oceanic CO₂ in the tropical Atlantic: 10 years after the 1982-1984 FOCAL cruises

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ABSTRACT

Measurements of CO₂ parameters in and over the tropical Atlantic ocean have been made during the CITHER 1 cruise (January to March 1993). These observations are compared to the results obtained a decade earlier in the same area during the FOCAL experiment (1982-1984). The increase of atmospheric CO₂ (1.3 to 1.5 ppm yr⁻¹) is in agreement with the secular trend. The variation of CO₂ fugacity, *f*CO₂, in surface seawater is analysed and compared with variations of hydrographic conditions. The apparent increase of ocean surface *f*CO₂ is somewhat higher than the atmospheric increase: during the 9-year period, the apparent increase of oceanic *f*CO₂ is found to range from 22.5 to 24.9 μatm. A new estimate of air-sea CO₂ flux in the Atlantic equatorial belt indicates that the oceanic source is enhanced in 1993 compared to 1984. An interannual change in total inorganic carbon, TCO₂, through the accumulation of CO₂ in the mixed layer is assessed and analysed in comparison with the *f*CO₂ increase. The agreement between the evolutions of the two parameters of the oceanic CO₂ system is acceptable by taking into account the uncertainties to estimate these evolutions.

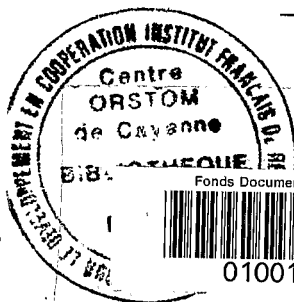
1. Introduction

Studies of temporal variations of CO₂ both in the atmosphere and in the sea surface layer are indispensable for predicting the future level of atmospheric CO₂. The CO₂ fluxes between the atmosphere and the ocean are regulated by, among other things, the gradient of CO₂ partial pressure across the air-sea interface. This gradient depends on the CO₂ concentrations both in the atmosphere and in the ocean surface layer. Long-term changes in these concentrations show the evolution of the ocean-atmosphere CO₂ system. The long-term (decadal) changes of atmospheric CO₂ are well-known since the measurements of Keeling et al. (1976) at Mauna Loa Observatory, Hawaiï and those of the stations network of GMCC (Geophysical Monitoring for Climatic Change) programme of the NOAA (Komhyr

et al., 1985). The interannual changes of oceanic CO₂ are less often noted (Takahashi et al., 1983; Roos and Gravenhorst, 1984; Keeling et al., 1987; Inoue and Sugimura, 1988; Metzl et al., 1991).

The recent CO₂ measurements in the tropical Atlantic 10 years after the 1982-1984 FOCAL cruises (Andrié et al., 1986; Oudot et al., 1987) give us an opportunity to document the long-term variation of CO₂ in surface seawater. The CITHER 1 cruise, French component of the WHP (Woce Hydrographic Programme), performed from 2 January to 19 March 1993, allowed us to revisit two cross-equatorial sections from 5°N to 5°S along the 4°W and 35°W meridians. In this paper, we compare the variations of atmospheric CO₂ concentration and those of ocean surface CO₂ fugacity between the FOCAL 6 cruise (11 January to 15 February 1984) and the CITHER 1 cruise, with the secular trends of atmospheric CO₂ and oceanic CO₂ fugacity. Besides a new estimate of the net CO₂ flux between the ocean and the air

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in the equatorial belt, we discuss the change of total inorganic carbon $T\text{CO}_2$ in the surface layer as compared to the change of CO_2 fugacity.

2. Data sources and methods

CO_2 data were collected in 1993 during the CITHER 1 cruise (January–March 1993) carried out aboard the R/V PATALANTE (France) in the equatorial Atlantic ocean (Fig. 1a). The CITHER 1 cruise starts the French contribution to the WOCE Hydrographic Programme in the South Atlantic ocean. These CO_2 data are compared with the last data collected at the same period (boreal winter) in the FOCAL programme (1982–1984). The FOCAL programme was an observational and theoretical study of the low

frequency response of the Atlantic ocean to the seasonally varying surface winds and was joint with the US SEQUAL programme. The location of observations during the FOCAL 6 cruise is given in Fig. 1b. The CO_2 data of FOCAL cruises has been described in several manuscripts (Oudot and Andrié, 1986; Andrié et al., 1986; Oudot et al., 1987).

2.1. Atmospheric CO_2

The measurement of atmospheric CO_2 concentration (ppm) was made twice a day by pumping an air stream taken at a mast at the bow of the vessel (about 20 m above the sea surface). An aliquot of air ($500 \text{ cm}^3 \text{ min}^{-1}$) was introduced for about 30 min into the Infrared Analyzer (SIEMENS Ultramat 5F) after dehumidification

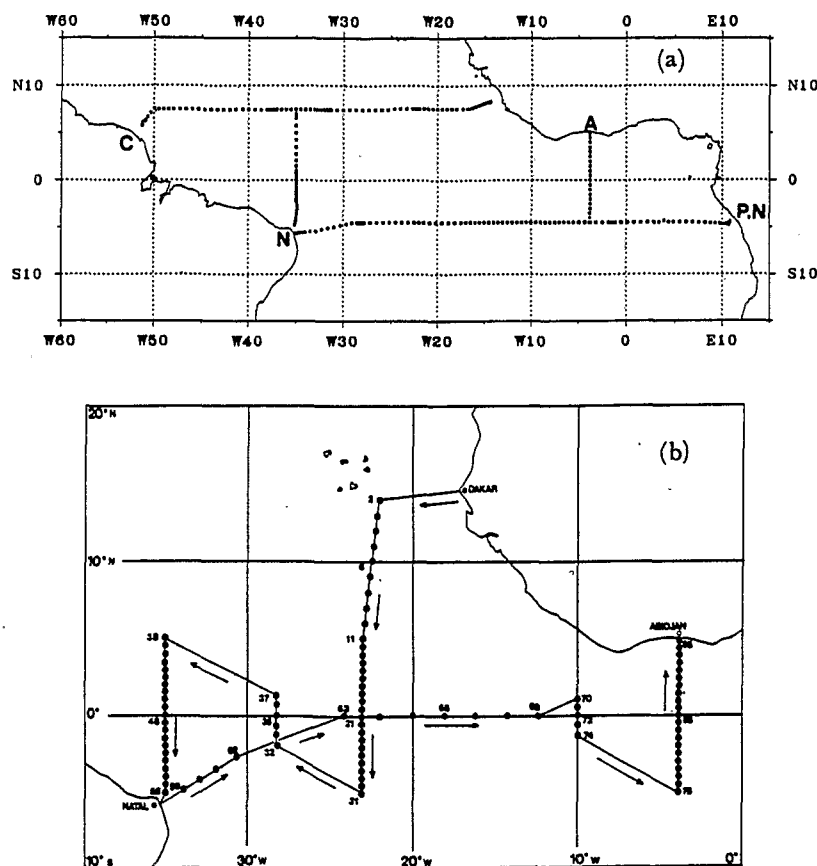


Fig. 1. CITHER 1 cruise track (R/V PATALANTE) (a) where CO_2 measurements were made during the period from 2 January to 19 March 1993. FOCAL 6 cruise track (R/V CAPRICORNE) (b) where CO_2 measurements were made during the period from 11 January to 15 February 1984 (according to Oudot et al. (1987)).

successively on a cold trap (-30°C) and on a P_4O_{10} column. The CO_2 concentration in dry air was determined after calibration of the IR Analyzer with two standard gases of 349.7 and 407.7 ppm in artificial air, supplied by Air Liquide (France). The CO_2 concentrations (with a precision of ± 0.25 ppm) produced by the French manufacturer agree within 0.25 ppm with the scale of the SiO standards (Gaudry et al., 1987). The CO_2 fugacity in the atmosphere (μatm) was then computed taking the water vapor pressure and the barometric pressure into account. The uncertainty for the atmospheric CO_2 concentration is estimated at ± 0.3 ppm.

2.2. CO_2 fugacity in surface seawater

The measurement of CO_2 fugacity in seawater was carried out as previously (Oudot and Andrié, 1986) by equilibrating an air stream with the seawater sample (550 cm^3) in the sampling flask itself, after removing a small volume of water in order to allow a gas dispersion tube to be introduced. The air driven by a bellows pump was spread in tiny bubbles in the thermostated sample (25.0°C) and flowed in a closed circuit through a sampling loop (25 cm^3). The equilibrated air inside the loop was injected with a valve into the air flow penetrating into the IR Analyzer (SIEMENS Ultramat 5F) after passing through a P_4O_{10} column. The measured signal was compared with those produced by 3 standard gases (486, 415 and 291 ppm) injected in the same way as the equilibrated air. Based on the CO_2 concentration of the dried equilibrated air, the CO_2 fugacity in the seawater sample at 25.0°C , $f\text{CO}_2$, was calculated following the Weiss (1974) equation:

$$f\text{CO}_2 = x\text{CO}_2(P - p\text{H}_2\text{O}) \times \exp[P(B + 2\delta)/RT], \quad (1)$$

where $x\text{CO}_2$ is the CO_2 concentration of the dried equilibrated air, P is the total barometric pressure at the liquid-gas interface, $p\text{H}_2\text{O}$ is the vapor pressure of water, $(B + 2\delta)$ is the CO_2 nonideality correction term, R is the gas constant and T is the absolute temperature. The vapor pressure of water is given by the following polynomial (Weiss and Price, 1980):

$$\ln(p\text{H}_2\text{O}) = 24.4543 - 67.4509(100/T) - 4.8489 \ln(T/100) - 0.000544S, \quad (2)$$

where $p\text{H}_2\text{O}$ is in atm and S is the salinity. The term $(B + 2\delta)/RT$ is calculated from Weiss (1974):

$$(B + 2\delta)/RT = 0.14386 - 3.99675 \times 10^{-4}T + 3.85746 \times 10^{-7}T^2 - 18.5404/T. \quad (3)$$

Then, the CO_2 fugacity was corrected for in situ temperature according to the temperature dependence equation described by Copin-Montegut (1989). During CITHER 1 cruise, duplicates for oceanic $f\text{CO}_2$ measurements were taken from the surface bottle of the rosette. The reproducibility of measurements tested as the mean difference for 47 pairs of duplicates is $2.4\ \mu\text{atm}$, or 0.6%, with a standard deviation of $2.1\ \mu\text{atm}$, or 0.5%.

2.3. Total inorganic carbon TCO_2

Measurements of total inorganic carbon, TCO_2 , were made by gas chromatography according to the method described by Oudot and Wauthy (1978). Since the FOCAL cruises, modifications were introduced: reduction of the sample volume (1 ml instead of 2 ml), replacement of Cheminert valves by Valco valves, use of a new integrator (DataJet) with a Spectra-Physics WINNER chromatography workstation. During CITHER 1 cruise, duplicates were taken from pairs of bottles fired at the same depth, the level being different for each hydrographic station. The reproducibility of measurements tested as the mean difference for 30 pairs of duplicates is $5\ \mu\text{mol kg}^{-1}$, or 0.25%, with a standard deviation of $3\ \mu\text{mol kg}^{-1}$, or 0.2%.

2.4. Total alkalinity TA

The total alkalinity of sea water, TA, is determined from TCO_2 and pH measurements using the equation describing the terms of component alkalinity contributions (Unesco, 1987):

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+]. \quad (4)$$

TCO_2 was determined as described in Subsection 2.3. During the CITHER 1 cruise, the pH measurements were based on the total hydrogen ion concentration scale (pH_{SWS} scale) and the electrode (Ross combination electrode, model ORION 81-02) was calibrated in 0.04M Tris buffer

prepared according to Dickson (1993). The polynomial equations used for determination of the dissociation constants relative to pH_{SWS} scale were obtained from Dickson and Millero (1987) for carbonic acid, from Dickson (1990) for boric acid and from Millero (1979) for ionization of water. During FOCAL 6 cruise, the pH measurements were made on the NBS buffer scale and the thermodynamic constants relative to NBS pH scale were obtained from Millero (1979). The reproducibility of TA results from CITHER 1 cruise, tested as the mean difference for 28 pairs of duplicates, is $5 \mu\text{eq kg}^{-1}$, or 0.2%, with a standard deviation of $4 \mu\text{eq kg}^{-1}$, or 0.2%.

3. Variation of atmospheric CO₂

The distribution of atmospheric CO₂ along the two cross-equatorial sections (35°W and 4°W) during CITHER 1 cruise (1993) is studied in comparison with that observed during FOCAL 6 cruise (1984) carried out in the same season (boreal winter) (Fig. 2). The increase of atmospheric CO₂ between 1984 and 1993 is evident. On an average, the CO₂ concentration above the Atlantic equatorial belt increases from 344.1 ± 2.0 ppm to 357.9 ± 1.3 ppm at 35°W and from 345.6 ± 1.8 ppm to 357.0 ± 1.3 ppm at 4°W (Table 1). The apparent increase is 13.8 ± 2.4 ppm in the western part and 11.4 ± 2.2 ppm in the eastern part, the difference between both values

being not statistically significant. This apparent increase in the Atlantic equatorial region, over a period of nine years, agrees with the secular trend of atmospheric CO₂. The last results (4th International CO₂ Conference, Carqueiranne, France, 13–17 September 1993, Aoki, pers. comm., Hirota, pers. comm., Peterson, pers. comm.) indicate a growth rate for atmospheric CO₂ ranged between 1.3 and 1.7 ppm per year, while our apparent increase is 1.5 ± 0.3 ppm yr⁻¹ in the western part and 1.3 ± 0.2 ppm yr⁻¹ in the eastern part of the equatorial belt.

The CITHER 1 data confirm the north-south decrease of atmospheric CO₂ from 5°N to 5°S noted during winter FOCAL cruises (Oudot et al., 1987). The decrease of atmospheric CO₂ between the northern and southern boundaries of the equatorial belt reflects the interhemispheric gradient of CO₂ (Tans et al., 1989). A regression line fitted to the CITHER 1 data (Fig. 2) shows a north-south gradient of 0.32 ± 0.10 ppm and 0.31 ± 0.09 ppm per degree of latitude at 35°W and 4°W, respectively, in good agreement with the results collected along the zonal transects of the CITHER 1 cruise. Along the 7°30'N parallel, from the American coast to the African coast (Fig. 1a), the average CO₂ concentration is 359.8 ± 1.1 ppm ($n = 28$); along the 4°30'S parallel it is 356.2 ± 1.0 ppm ($n = 30$). The difference of 3.6 ppm over 12 degrees of latitude is close to the average gradient along the 35°W and 4°W meridians. Such results on the meridional gradient of atmospheric CO₂ in the equatorial area have been

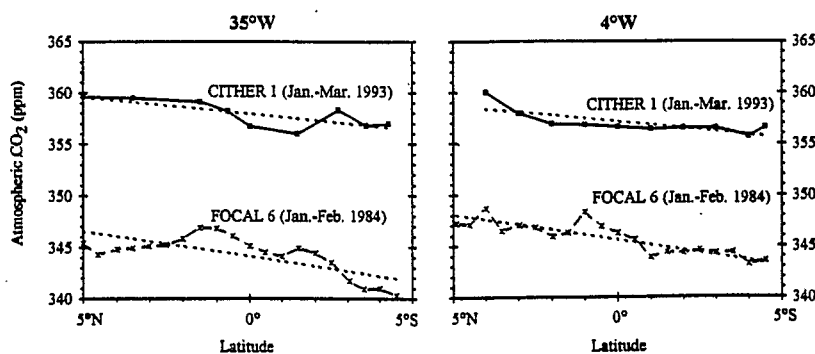


Fig. 2. Atmospheric CO₂ (ppm) along the 35°W and 4°W sections in the equatorial Atlantic during January–March 1993 (CITHER 1) and January–February 1984 (FOCAL 6). The dotted lines show the north–south trend fitted to the data (see text).

Table 1. Concentrations of atmospheric CO₂ (ppm) along the 35°W and 4°W sections in the equatorial Atlantic in 1993 (CITHER 1) and in 1984 (FOCAL 6). The mean values between 5°N and 5°S are given with 1σ

CITHER 1 (January–March 1993)			
35°W		4°W	
Latitude	CO ₂ (ppm)	Latitude	CO ₂ (ppm)
5°00N	359.6	4°00N	360.0
3°30N	359.5	3°00N	357.9
1°30N	359.1	2°00N	356.9
0°39N	358.2	1°00N	356.8
0°02S	356.7	0°00	356.6
1°28S	356.0	1°00S	356.4
2°43S	358.3	2°00S	356.5
3°35S	356.8	3°00S	356.5
4°16S	357.0	4°00S	355.7
		4°30S	356.6
mean value (5°N–5°S)	357.9 ± 1.3		357.0 ± 1.3
FOCAL 6 (January–February 1984)			
35°W		4°W	
Latitude	CO ₂ (ppm)	Latitude	CO ₂ (ppm)
5°00N	345.4	4°54N	347.2
4°33N	344.3	4°30N	347.1
4°00N	344.8	4°00N	348.7
3°31N	344.9	3°30N	346.5
3°01N	345.1	2°59N	347.0
2°30N	345.2	2°30N	346.8
2°00N	345.8	1°59N	345.9
1°30N	346.9	1°30N	346.3
1°00N	346.8	1°00N	348.3
0°30N	346.1	0°30N	346.9
0°00S	345.1	0°00	346.3
0°29S	344.5	0°31S	345.6
1°00S	344.1	1°00S	343.9
1°30S	344.9	1°30S	344.4
2°00S	344.4	2°00S	344.3
2°30S	343.5	2°30S	344.6
3°03S	341.7	3°00S	344.3
3°30S	340.9	3°30S	344.4
4°00S	341.0	4°00S	343.2
4°30S	340.3	4°30S	343.6
5°00S	340.8	5°00S	342.1
mean value (5°N–5°S)	344.1 ± 2.0		345.6 ± 1.8

already pointed out during the 1982–1984 period (Oudot et al., 1987).

4. Variation of ocean surface CO₂ fugacity

In ocean surface, the evolution of the CO₂ fugacity is not so clear (Fig. 3). Along the 35°W section (on the left) $f\text{CO}_2$ in 1993 is always higher than $f\text{CO}_2$ in 1984, but this is not the case along 4°W (on the right). We observed like Oudot et al. (1987) that $f\text{CO}_2$ is higher south of the equator than north of it, along 4°W as well as along 35°W. To compare the distribution of $f\text{CO}_2$ in 1993 with that in 1984, we have to take into account the seasonal or interannual effects of temperature and salinity on the CO₂ fugacity in seawater. These effects are due to the modification of the solubility of CO₂ and of the dissociation of carbonic acid in seawater by temperature and salinity (Weiss et al., 1982). Though CITHER 1 was conducted during the same season as FOCAL 6, we can note some differences in the distributions of temperature and salinity (Fig. 4). The difference of temperature between the two periods is more important along 35°W whereas that of salinity is more noticeable along 4°W. Therefore we corrected the $f\text{CO}_2$ data of CITHER 1 to hydrographic conditions of FOCAL 6. For the tropical region, the temperature dependence of $f\text{CO}_2$ is assumed to be 1.3% (°C)⁻¹ (Takahashi et al., 1983; Roos and Gravenhorst, 1984; Oudot et al., 1987). For the salinity dependence of $f\text{CO}_2$ we chose the empirical relationship fitting the fugacity of CO₂ to the salinity through the FOCAL data (Fig. 5) rather than the thermodynamical relationship of Weiss et al. (1982). This salinity dependence of $f\text{CO}_2$ found in the equatorial Atlantic (44 μatm per unit of salinity) is comparable with that reported by Fushimi (1987) in the western Pacific (40 μatm per unit of salinity). Corrections of the $f\text{CO}_2$ based on these temperature and salinity dependences are shown in Table 2. The last column of Table 2 indicates, for each latitude, the increase (positive change) of ocean surface $f\text{CO}_2$ between 1984 and 1993. These corrections, even if approximate, allow us to estimate an apparent increase of ocean surface $f\text{CO}_2$, that can be compared with the secular trend of the atmospheric CO₂. Some negative values, that mean a decrease of $f\text{CO}_2$ during this period, are found north of the equator

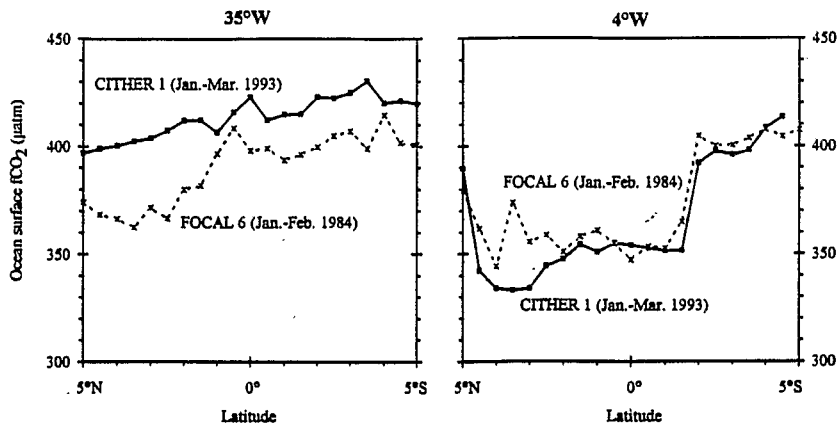


Fig. 3. CO₂ fugacity (μatm) in surface seawater along the 35°W and 4°W sections in the equatorial Atlantic during January–March 1993 (CITHER 1) and January–February 1984 (FOCAL 6).

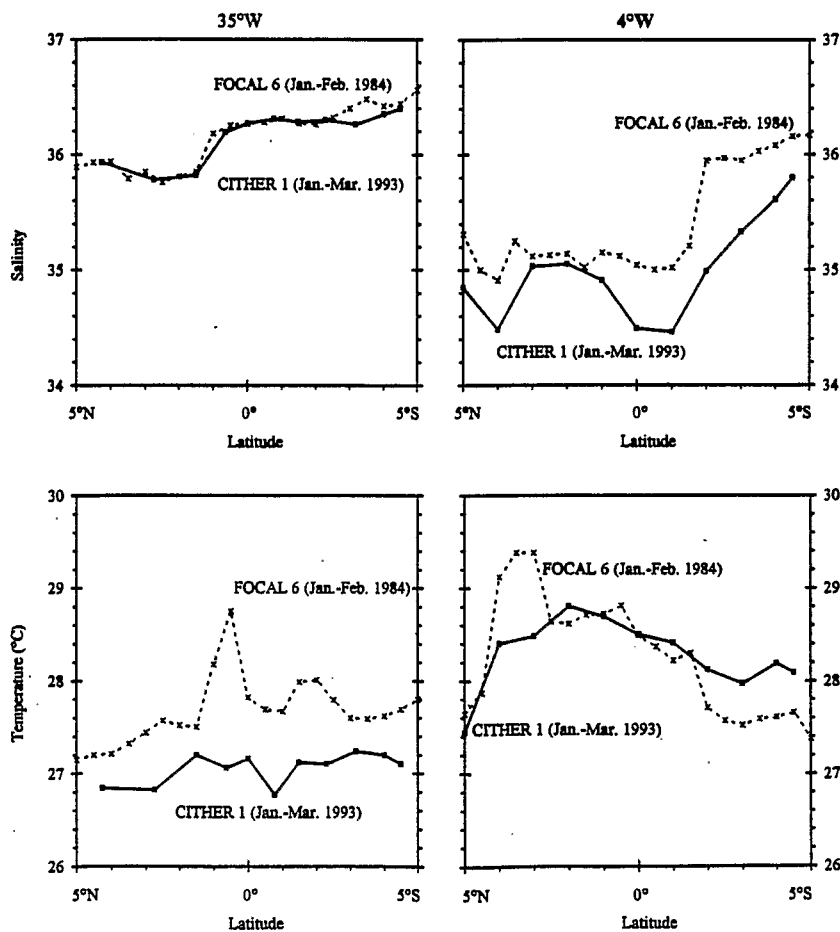


Fig. 4. Distributions of temperature (below) and salinity (above) in surface seawater along the 35°W and 4°W sections in the equatorial Atlantic during January–March 1993 (CITHER 1) and January–February 1984 (FOCAL 6).

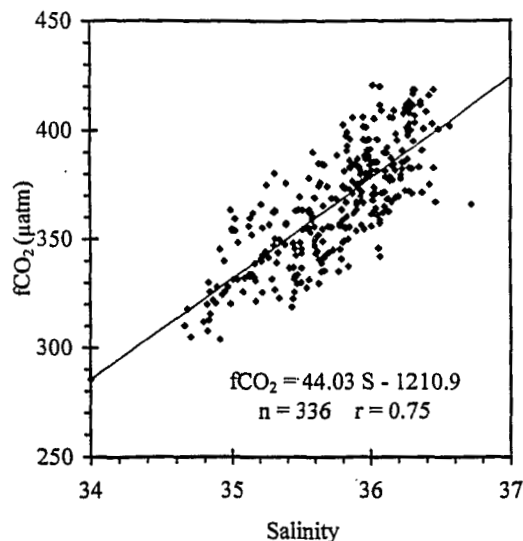


Fig. 5. Relationship between CO_2 fugacity and salinity in surface seawater in the equatorial Atlantic through five FOCAL cruises (July 1982 to August 1984) (derived from Oudot et al. (1987)).

along the 4°W section (Fig. 6). They are due to high values of ocean surface $f\text{CO}_2$ during FOCAL 6 that correspond to abnormally high values of salinity for this area (Hisard et al., 1986; Oudot et al., 1987). For this reason, we only consider the data south of the equator to estimate the evolution of $f\text{CO}_2$ between 1984 and 1993. During this period of 9 years, the apparent increase of surface seawater $f\text{CO}_2$ south of the equator ranges from 11.1 to 42.3 μatm , with a mean value of 24.9 μatm ($1\sigma = 7.6 \mu\text{atm}$) along the 35°W section, and from

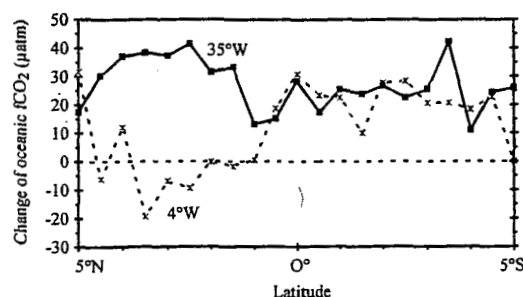


Fig. 6. Interannual change of ocean surface CO_2 fugacity between January–February 1984 (FOCAL 6) and January–March 1993 (CITHER 1). The positive values mean an increase of oceanic $f\text{CO}_2$ between 1984 and 1993.

10.0 to 30.9 μatm with a mean value of 22.5 μatm ($1\sigma = 5.9 \mu\text{atm}$) along the 4°W transect (Table 2, last column).

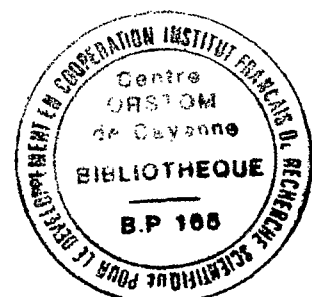
A few preceding studies include estimates of an increase of the partial pressure or fugacity of CO_2 in surface seawater. Takahashi et al. (1983) compared the 1981 TTO/NA data with those of 1972 GEOSECS and 1957 IGY in Sargasso Sea. They showed that the surface water $p\text{CO}_2$ has increased at a mean rate of $1.5 \pm 0.5 \mu\text{atm yr}^{-1}$, what corresponds to a range of 9.0 to 18.0 μatm for a 9-year period. Roos and Gravenhorst (1984) with older data in the North Atlantic came to the same estimate with an ocean surface $f\text{CO}_2$ increase ranging between 0.4 and 1.9 $\mu\text{atm yr}^{-1}$, or between 3.6 and 17.1 μatm for 9 years. In the western North Pacific and in the Southern Ocean Inoue and Sugimura (1988) found apparent increases of $20.0 \pm 10.6 \mu\text{atm}$ and $24.4 \pm 8.3 \mu\text{atm}$ respectively for the period 1969–1984. More recently, during a period similar to ours (January 1986 to January 1992), the increase in CO_2 fugacity was about 14 μatm in the western North Pacific (4th International CO_2 Conference, Carqueiranne, France, 13–17 September 1993, Inoue, pers. comm.). The results of 18 cruises, between 1984 and 1988 in the northeast and southwest subtropical Pacific (4th International CO_2 Conference, Carqueiranne, France, 13–17 September 1993, Wong, pers. comm.), lead to a weaker secular increase in surface $f\text{CO}_2$: 1.1 to 1.5 $\mu\text{atm yr}^{-1}$.

Our estimate of an apparent increase of ocean surface $f\text{CO}_2$ (22.5 to 24.9 μatm over a 9-year period) is about twice the increase of 11.4 and 13.8 ppm measured in the atmosphere during the same time period. This could be due to different reasons. First, our corrections related to the temperature and salinity effects on $f\text{CO}_2$ are approximate; the uncertainties in $f\text{CO}_2$ linked to the temperature and salinity corrections are difficult to quantify, but they should be within the standard deviations of the mean values of the $f\text{CO}_2$ change (Table 2: 7.6 and 5.9 μatm). Also, the alkalinity could have changed over the considered period. A decrease in surface seawater alkalinity could explain a too large increase in oceanic $f\text{CO}_2$. This possibility will be discussed later in the text, when we will consider a possible increase in the total inorganic carbon in the surface layer over the same period.

Table 2. Ocean surface $f\text{CO}_2$ (μatm) in January–March 1993 (CITHER 1 cruise) and in January–February 1984 (FOCAL 6 cruise); the mean values (± 1 standard deviation σ) of the $f\text{CO}_2$ change, $\Delta(f\text{CO}_2)$, are given for the area south of the equator (0° – 5°S)

Longitude 35°W				
Latitude	$f\text{CO}_2$ (μatm) CITHER 1 (1993)	$f\text{CO}_2^*$ (μatm) CITHER 1 (1993)	$f\text{CO}_2$ (μatm) FOCAL 6 (1984)	$f\text{CO}_2$ change (μatm) 1993/1984
5°00N	397.0	391.5	374.1	17.4
4°30N	399.0	398.7	368.4	30.3
4°00N	400.5	403.5	366.4	37.1
3°30N	402.5	400.9	362.5	38.4
3°00N	404.0	409.0	371.6	37.4
2°30N	407.5	408.2	366.7	41.5
2°00N	412.3	411.6	380.1	31.5
1°30N	412.5	415.4	382.0	33.4
1°00N	406.7	410.1	397.0	13.1
0°30N	416.0	423.9	408.7	15.2
0°00	423.0	426.6	398.1	28.5
0°30S	412.5	416.6	399.3	17.3
1°00S	415.0	419.2	393.7	25.5
1°30S	415.1	420.2	396.4	23.8
2°00S	423.0	426.5	399.8	26.7
2°30S	422.5	427.5	405.0	22.5
3°00S	425.0	432.8	407.2	25.6
3°30S	430.5	441.4	399.1	42.3
4°00S	420.1	425.6	414.5	11.1
4°30S	421.2	426.2	401.7	24.5
5°00S	419.6	426.9	400.8	26.1
mean value (0°–5°S)				24.9 \pm 7.6
Longitude 4°W				
Latitude	$f\text{CO}_2$ (μatm) CITHER 1 (1993)	$f\text{CO}_2^*$ (μatm) CITHER 1 (1993)	$f\text{CO}_2$ (μatm) FOCAL 6 (1984)	$f\text{CO}_2$ change (μatm) 1993/1984
5°00N	389.5	410.8	379.1	31.7
4°30N	342.2	355.4	361.6	–6.2
4°00N	334.1	356.2	344.2	12.0
3°30N	333.0	354.2	373.6	–20.5
3°00N	334.0	348.6	355.5	–6.9
2°30N	344.2	349.1	358.5	–9.4
2°00N	347.5	350.6	350.7	–0.1
1°30N	354.2	356.3	358.0	–1.7
1°00N	350.7	361.4	360.8	0.6
0°30N	354.9	373.5	354.7	18.8
0°00	353.8	378.1	347.2	30.9
0°30S	352.5	376.6	353.3	23.3
1°00S	351.3	375.1	352.6	22.5
1°30S	351.5	374.8	364.8	10.0
2°00S	392.1	432.4	404.6	27.8
2°30S	397.7	428.5	400.0	28.5
3°00S	395.8	420.9	400.4	20.5
3°30S	398.1	424.5	403.8	20.7
4°00S	408.5	426.2	407.8	18.4
4°30S	413.5	427.1	404.4	22.7
5°00S	—	—	407.6	—
mean value (0°–5°S)				22.5 \pm 5.9

$f\text{CO}_2^*$: CO₂ fugacity data of CITHER 1 corrected to temperature and salinity conditions observed during FOCAL 6 cruise.



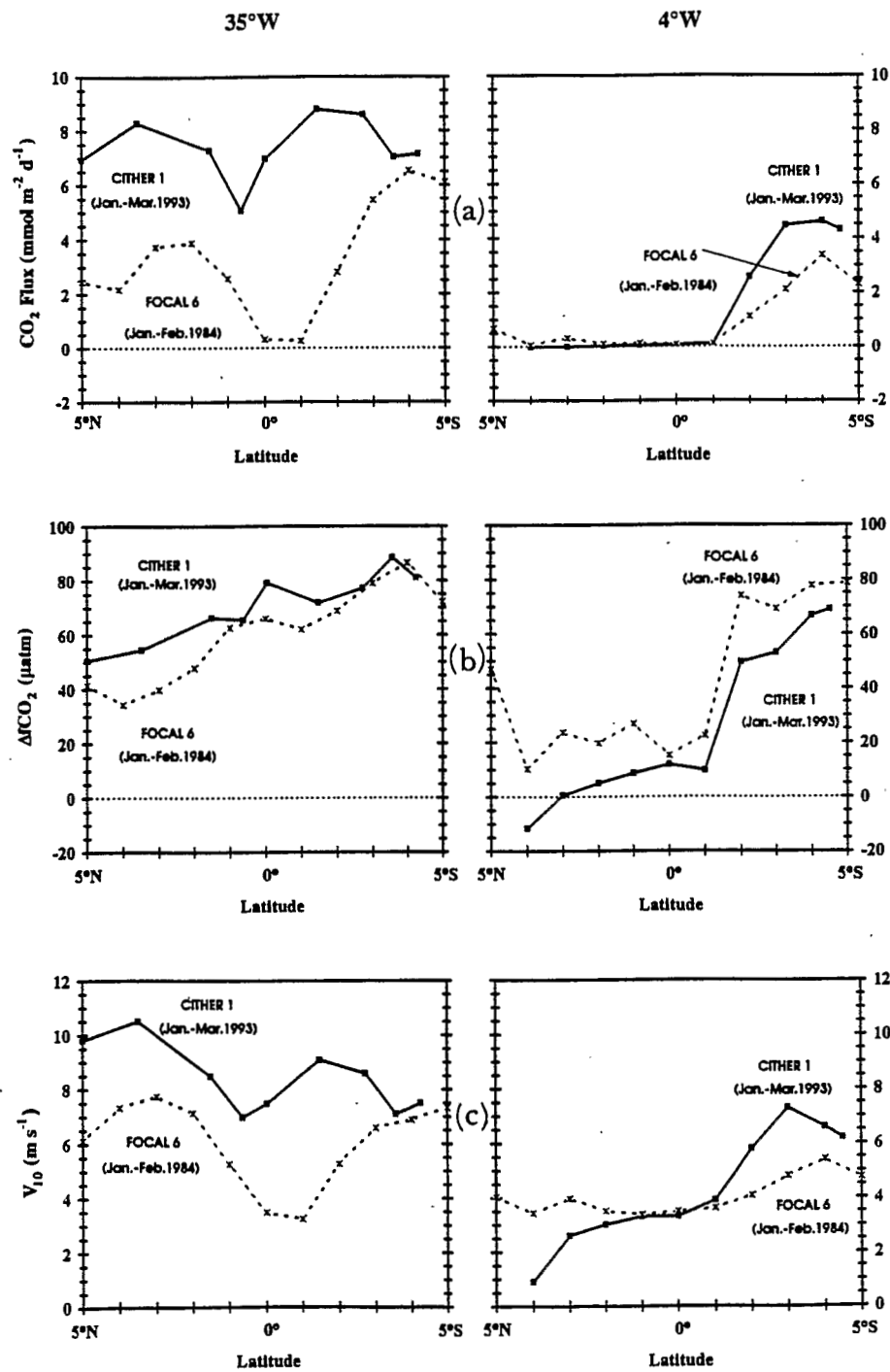


Fig. 7. Distributions of CO₂ flux (a), gradient of CO₂ fugacity, $\Delta f\text{CO}_2$, at the air-sea interface (b) and 24-h mean shipboard wind speed at 10 m above the sea level (c) along the 35°W and 4°W sections in the equatorial Atlantic, during January–March 1993 (CITHER 1) and January–February 1984 (FOCAL 6).

Table 3. CO₂ flux calculations (mmol m⁻² d⁻¹). The mean values between 5°N and 5°S are given with 1σ

CITHER 1 (January–March 1993)							
35°W				4°W			
Latitude	V ₁₀ (m s ⁻¹)	ΔfCO ₂ (μatm)	CO ₂ flux (mmol m ⁻² d ⁻¹)	Latitude	V ₁₀ (m s ⁻¹)	ΔfCO ₂ (μatm)	CO ₂ flux (mmol m ⁻² d ⁻¹)
5°00N	9.8	50.5	6.94	4°00N	0.9	-11.7	-0.01
3°30N	10.5	54.5	8.31	3°00N	2.6	0.4	0.01
1°30N	8.5	66.3	7.28	2°00N	3.0	4.9	0.02
0°39N	7.0	65.5	5.07	1°00N	3.3	8.6	0.04
0°02S	7.5	79.3	6.99	0°00	3.3	11.8	0.05
1°28S	9.1	71.9	8.80	1°00S	3.9	9.6	0.11
2°43S	8.6	77.2	8.61	2°00S	5.8	49.5	2.58
3°35S	7.1	88.5	7.04	3°00S	7.3	53.0	4.47
4°16S	7.5	81.1	7.15	4°00S	6.6	66.7	4.62
				4°30S	6.2	69.1	4.30
mean value (5°N–5°S)			7.35 ± 1.13				1.62 ± 2.12
FOCAL 6 (January–February 1984)							
35°W				4°W			
Latitude	V ₁₀ (m s ⁻¹)	ΔfCO ₂ (μatm)	CO ₂ flux (mmol m ⁻² d ⁻¹)	Latitude	V ₁₀ (m s ⁻¹)	ΔfCO ₂ (μatm)	CO ₂ flux (mmol m ⁻² d ⁻¹)
5°00N	6.13	41.5	2.45	5°00N	4.03	47.1	0.69
4°00N	7.34	34.4	2.16	4°00N	3.43	10.3	0.05
3°00N	7.76	39.8	3.73	3°00N	3.97	23.6	0.32
2°00N	7.15	47.9	3.88	2°00N	3.49	19.7	0.10
1°00N	5.29	62.7	2.56	1°00N	3.37	26.8	0.13
0°00	3.49	66.0	0.31	0°00	3.49	15.2	0.07
1°00S	3.25	62.0	0.27	1°00S	3.61	22.5	0.11
2°00S	5.29	68.9	2.81	2°00S	4.09	74.0	1.12
3°00S	6.61	79.1	5.46	3°00S	4.81	69.2	2.11
4°00S	6.91	86.6	6.53	4°00S	5.41	77.8	3.38
5°00S	7.33	72.3	6.10	5°00S	4.75	78.8	2.30
mean value (5°N–5°S)			3.30 ± 2.11				0.97 ± 1.21

5. The net CO₂ flux in the equatorial Atlantic in 1993

The net CO₂ flux between the ocean and the atmosphere is computed from

$$F = k_t \alpha \Delta f \text{CO}_2, \quad (5)$$

where k_t is the CO₂ transfer velocity (Liss and Merlivat, 1986), α is CO₂ solubility in seawater

(Weiss, 1974) and $\Delta f \text{CO}_2$ is the difference between the CO₂ fugacity in the ocean and that in the atmosphere. The CO₂ flux is positive when CO₂ escapes from the ocean into the atmosphere and negative otherwise.

The transfer velocity, k_t , is a function of the wind speed and of the temperature through the Schmidt number Sc dependency (Liss and Merlivat, 1986). The dependence of CO₂ exchange at 20°C on wind speed at 10 m above the sea surface is given for different wind regimes:

$$k_{20} = 0.17V_{10}$$

for $0 < V_{10} < 3.6 \text{ m s}^{-1}$, (6)

$$k_{20} = 2.85V_{10} - 9.65$$

for $3.6 < V_{10} < 13 \text{ m s}^{-1}$. (7)

Aboard the R/V l'ATALANTE, the wind speed was measured at 27 m above the sea level and the wind speed at 10 m height was estimated by assuming a drag coefficient of 1.5×10^{-3} . Thus $V_{10} = 0.912V_{27}$. As did Smethie et al. (1985) and Oudot et al. (1987), we used the 24-h mean shipboard wind speed to compute the transfer velocity.

Finally the dependence of the exchange coefficient on the temperature is evaluated as follows:

$$k_t = 70.74k_{20}(Sc_t)^{-2/3},$$

for $0 < V_{10} < 3.6 \text{ m s}^{-1}$, (8)

$$k_t = 24.39k_{20}(Sc_t)^{-1/2},$$

for $3.6 < V_{10} < 13 \text{ m s}^{-1}$, (9)

where Sc_t , the Schmidt number for CO_2 at $t^\circ\text{C}$, is

determined with the polynomial relationship of Wanninkhof (1992):

$$Sc_t = 2073.1 - 125.62t + 3.6276t^2 - 0.043219t^3. \quad (10)$$

The results of the net CO_2 flux throughout the CITHER 1 period are displayed and compared with those of the FOCAL 6 period, in Fig. 7.

The computed mean value of the net CO_2 flux between 5°N and 5°S is higher during CITHER 1 than during FOCAL 6 in the western part (35°W : 7.35 ± 1.13 and $3.30 \pm 2.12 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively), as well as in the eastern part (4°W : 1.62 ± 2.12 and $0.97 \pm 1.21 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively) (Table 3). The difference between the fluxes during FOCAL 6 and CITHER 1 is about 120% along 35°W and 60% along 4°W , and it is mainly due to the different wind speed fields (Fig. 7, below). In particular on the 4°W meridian, south of the equator, the net CO_2 flux is higher in 1993 than in 1984 in spite of a lower gradient of $f\text{CO}_2$ at the air-sea interface, $\Delta f\text{CO}_2$. The wind speed is

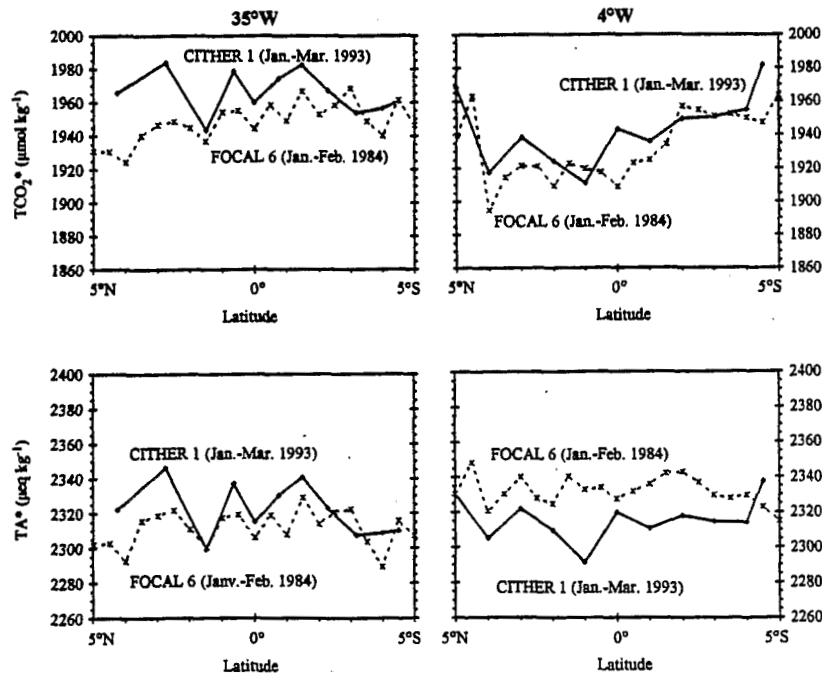


Fig. 8. Distributions of total inorganic carbon TCO_2^* (normalized to $S=35$) and total alkalinity TA^* (normalized to $S=35$) in surface seawater along the 35°W and 4°W in the equatorial Atlantic during January–March 1993 (CITHER 1) and January–February 1984 (FOCAL 6).

really seen as the dominant factor that modulates the variation of the CO₂ flux in the equatorial region. The larger increase in ocean surface *f*CO₂ than in atmospheric CO₂ causes the rise of the CO₂ gradient, Δ*f*CO₂, along the 35°W meridian (Fig. 7, in the middle) between 1984 and 1993. Along the 4°W meridian, Δ*f*CO₂ decreased between 1984 and 1993 because of the abnormally high values of oceanic *f*CO₂ in 1984.

6. Interannual variation in total inorganic carbon TCO₂

If, as it was shown on several occasions, the ocean surface *f*CO₂ increases as a result of the transfer of fossil fuel CO₂ to the ocean, it should be possible to display an accumulation of CO₂ in the mixed layer. Some studies to estimate a growth rate of TCO₂ in surface seawater were already attempted (Broecker et al., 1979; Keeling et al., 1987).

To highlight a possible interannual change in TCO₂, we plotted TCO₂ data normalized to *S*=35 (noted as TCO₂^{*}) versus latitude along the two transects 35°W and 4°W (Fig. 8). TCO₂ clearly increased along the 35°W section, between 1984 and 1993 (Fig. 8). The increase is not so obvious along 4°W. Along 35°W, TCO₂^{*} is not very different north and south of the equator. In turn, along 4°W, TCO₂^{*} is higher south than north of it, following the salinity (Fig. 4). So we consider the change of TCO₂^{*} only in the area south of the equator, as we did for the oceanic CO₂ fugacity. Between January–February 1984 and January–March 1993, south of the equator, TCO₂^{*} increases from 1954 ± 9 μmol kg⁻¹ to 1965 ± 10 μmol kg⁻¹ at 35°W and from 1942 ± 17 μmol kg⁻¹ to 1953 ± 16 μmol kg⁻¹ at 4°W (Table 4). Thus the apparent increase of TCO₂ is 11 ± 13 μmol kg⁻¹ at 35°W and 11 ± 16 μmol kg⁻¹ at 4°W, in the area south of the equator.

This TCO₂ increase (1.2 μmol kg⁻¹ yr⁻¹) is within the range of results reported in the literature. Broecker et al. (1979) estimated the mean global rate of TCO₂ increase at 0.7 μmol kg⁻¹ yr⁻¹. Keeling et al. (1987) found an interannual TCO₂ increase of about 1.7 μmol kg⁻¹ yr⁻¹ but he admitted that it was too large in a constant alkalinity environment.

We checked whether our observations of TCO₂^{*} increase are consistent with the measured change of CO₂ fugacity, via the buffer factor or Revelle factor β

$$\beta = (\Delta f\text{CO}_2 / f\text{CO}_2) (\Delta T\text{CO}_2 / T\text{CO}_2)^{-1} \quad (11)$$

The amount of CO₂ accumulated in the mixed layer can be roughly estimated from the increase of the *f*CO₂ in surface seawater, as long as alkalinity in seawater remains constant. According to the sea surface temperature range of 27 to 29°C (Fig. 4), we chose a buffer factor of 8.5 (Sundquist et al., 1979). The TCO₂ augmentations expected from the *f*CO₂ increases (22.5 μatm at 4°W and 24.9 μatm at 35°W) are about 13 μmol kg⁻¹ at 4°W and 14 μmol kg⁻¹ at 35°W. These results are not too far from the observed TCO₂ increase, 11 μmol kg⁻¹ at both longitudes.

The uncertainties of the TCO₂ determinations (reproducibility of measurements during CITHER 1 cruise = 5 μmol kg⁻¹) and of the estimations of TCO₂ and *f*CO₂ increases (standard deviations attached to the mean values) could explain the small difference between the observed apparent TCO₂ increase and TCO₂ expected from the apparent *f*CO₂ change. Furthermore, the alkalinity could have changed during the 1984 to 1993 period. Considering the increase in alkalinity (1.0 μeq kg⁻¹ yr⁻¹), Keeling et al. (1987) explain their observed TCO₂ increase of 1.7 μmol kg⁻¹ yr⁻¹ as the possible result of uptake related to raising atmospheric CO₂ and concurrent reaction of some of that CO₂ with carbonate ions. We also examined the change of alkalinity normalized to *S*=35 (noted as TA^{*}) over this period (Fig. 8, Table 4). No clear trend appears for TA^{*} between 1984 and 1993. The TA^{*} mean value, for the 0°–5°S area, increases from 2312 ± 11 to 2319 ± 13 μeq kg⁻¹ at 35°W and decreases from 2331 ± 8 to 2319 ± 10 μeq kg⁻¹ at 4°W. We cannot conclude that alkalinity changed between 1984 and 1993.

7. Conclusions

The atmospheric CO₂ in the tropical Atlantic has been increased between 1984 and 1993. The average increase of CO₂ in air is 1.3 ppm yr⁻¹ in the eastern part and 1.5 ppm yr⁻¹ in the

Table 4. Variations of temperature, salinity, total CO₂, TCO₂, and total alkalinity, TA, at the sea surface in January–March 1993 (CITHER 1 cruise) and January–February 1984 (FOCAL 6 cruise); the mean values (± 1 standard deviation, σ) of TCO₂ and TA normalized to S = 35 (noted TCO₂* and TA*) are given for the area south of the equator (0°–5°S)

CITHER 1 (January–March 1993)													
35°W							4°W						
Latitude	T (°C)	S	TCO ₂ (μmol kg ⁻¹)	TCO ₂ * (μmol kg ⁻¹)	TA (μeq kg ⁻¹)	TA* (μeq kg ⁻¹)	Latitude	T (°C)	S	TCO ₂ (μmol kg ⁻¹)	TCO ₂ * (μmol kg ⁻¹)	TA (μeq kg ⁻¹)	TA* (μeq kg ⁻¹)
4°15N	26.84	35.93	2018	1966	2389	2322	4°55N	27.44	34.85	1960	1968	2320	2331
2°45N	26.82	35.78	2028	1984	2399	2346	4°00N	28.40	34.48	1889	1917	2271	2305
1°30N	27.20	35.82	1989	1943	2353	2300	3°00N	28.48	35.03	1940	1938	2323	2322
0°38N	27.06	36.19	2046	1979	2417	2337	2°00N	28.80	35.05	1927	1924	2312	2310
0°02S	27.16	36.27	2031	1960	2399	2315	1°00N	28.69	34.91	1906	1911	2285	2291
0°46S	26.77	36.31	2048	1974	2417	2330	0°00	28.50	34.49	1915	1943	2286	2320
1°28S	27.12	36.28	2055	1982	2426	2341	1°00S	28.41	34.46	1906	1936	2275	2311
2°17S	27.10	36.30	2040	1967	2409	2323	2°00S	28.12	34.99	1949	1950	2317	2318
3°10S	27.24	36.26	2024	1954	2391	2308	3°00S	27.97	35.33	1969	1951	2337	2315
3°59S	27.20	36.35	2032	1957	2397	2308	4°00S	28.19	35.61	1989	1955	2355	2314
4°30S	27.10	36.40	2039	1961	2402	2310	4°30S	28.09	35.80	2027	1982	2391	2338
mean value (0°–5°S)				1965		2319					1953		2319
$\pm 1\sigma$				± 10		± 13					± 16		± 10

FOCAL 6 (January-February 1984)

35°W							4°W						
Latitude	<i>T</i> (°C)	<i>S</i>	<i>TCO</i> ₂ (μmol kg ⁻¹)	<i>TCO</i> ₂ [*] (μmol kg ⁻¹)	<i>TA</i> (μeq kg ⁻¹)	<i>TA</i> [*] (μeq kg ⁻¹)	Latitude	<i>T</i> (°C)	<i>S</i>	<i>TCO</i> ₂ (μmol kg ⁻¹)	<i>TCO</i> ₂ [*] (μmol kg ⁻¹)	<i>TA</i> (μeq kg ⁻¹)	<i>TA</i> [*] (μeq kg ⁻¹)
5°00N	27.15	35.89	1980	1931	2360	2302	4°54N	27.64	35.31	1957	1940	2351	2330
4°33N	27.20	35.93	1982	1931	2364	2303	4°30N	27.87	35.00	1963	1963	2348	2348
4°00N	27.21	35.94	1976	1924	2355	2293	4°00N	29.12	34.91	1890	1895	2314	2321
3°31N	27.32	35.79	2084	1940	2368	2316	3°30N	29.38	35.25	1928	1914	2347	2330
3°01N	27.44	35.85	1994	1947	2375	2319	2°59N	29.38	35.12	1928	1921	2348	2340
2°30N	27.57	35.76	1991	1949	2372	2322	2°30N	28.64	35.13	1928	1921	2336	2328
2°00N	27.52	35.81	1990	1945	2365	2311	1°59N	28.61	35.14	1917	1909	2334	2325
1°30N	27.50	35.85	1984	1937	2356	2301	1°30N	28.71	35.02	1924	1923	2342	2340
1°00N	28.18	36.18	2020	1954	2395	2317	1°00N	28.72	35.15	1928	1920	2343	2333
0°30N	28.75	36.25	2025	1955	2402	2319	0°30N	28.81	35.12	1924	1917	2342	2334
0°00	27.82	36.27	2015	1944	2390	2306	0°00	28.49	35.04	1911	1909	2330	2328
0°29S	27.69	36.28	2030	1958	2404	2319	0°31S	28.37	35.00	1923	1923	2332	2332
1°00S	27.67	36.31	2022	1949	2394	2308	1°00S	28.22	35.02	1926	1925	2337	2336
1°30S	27.99	36.27	2038	1967	2413	2329	1°30S	28.30	35.21	1946	1934	2356	2342
2°00S	28.01	36.26	2023	1953	2397	2314	2°00S	27.71	35.95	2010	1957	2406	2343
2°30S	27.79	36.32	2032	1958	2409	2321	2°30S	27.57	35.97	2009	1955	2402	2337
3°03S	27.60	36.40	2047	1968	2415	2322	3°00S	27.52	35.95	2004	1951	2393	2330
3°30S	27.59	36.48	2031	1949	2401	2304	3°30S	27.59	36.03	2010	1953	2396	2328
4°00S	27.62	36.42	2019	1940	2382	2289	4°00S	27.61	36.08	2010	1950	2401	2330
4°30S	27.69	36.44	2042	1961	2411	2316	4°30S	27.66	36.16	2012	1947	2400	2323
5°00S	27.80	36.56	2033	1946	2410	2307	5°00S	27.38	36.17	2029	1963	2392	2315
mean value (0° and 5°S)				1954		2312					1942		2331
±1σ				±9		±11					±17		±8

western part, in agreement with the secular trend. The 1993 results confirm the north-south decrease of atmospheric CO₂ from 5°N to 5°S during winter season: the interhemispheric gradient of atmospheric CO₂ above the equatorial belt is about 0.3 ppm per degree of latitude. The apparent increase of ocean surface CO₂ fugacity is somewhat higher (22.5 to 24.9 μatm) than the atmospheric CO₂ increase (11.4 to 13.8 ppm).

The air-sea CO₂ flux is enhanced in 1993 compared to 1984. This increase reflects in part the larger change of *f*CO₂ in seawater than that in air, at least in the western part (35°W), but the dominant factor which influences the CO₂ flux is the wind speed.

The apparent *T*CO₂ increase (11 μmol kg⁻¹) observed in the surface layer between the period of

the FOCAL experiment and that of the CITHER 1 cruise appears to be in rather good agreement with that (13–14 μmol kg⁻¹) expected from the apparent ocean surface *f*CO₂ increase and could be related to the accumulation of fossil fuel CO₂ to the ocean.

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REFERENCES

- Andrié, C., Oudot, C., Genthon, C. and Merlivat, L. 1986. CO₂ fluxes in the tropical Atlantic ocean during FOCAL cruises. *J. Geophys. Res.* **91**, 11741–11755.
- Broecker, W. S., Takahashi, T., Simpson, H. J. and Peng, T. H. 1979. Fate of fossil fuel carbon dioxide and the global carbon budget. *Science* **206**, 409–418.
- Copin-Montegut, C. 1989. A new formula for the effect of temperature on the partial pressure of CO₂ in seawater. *Mar. Chem.* **27**, 143–144.
- Dickson, A. G. 1990. Thermodynamics of the dissociation of boric acid in synthetic sea water from 273.15 to 298.15 K. *Deep Sea Res.* **37**, 755–766.
- Dickson, A. G. 1993. pH buffers for sea water media based on the total hydrogen ion concentration scale. *Deep Sea Res.* **40**, 107–118.
- Dickson, A. G. and Millero, F. J. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep Sea Res.* **34**, 1733–1743.
- Fushimi, K. 1987. Variation of carbon dioxide partial pressure in the western North Pacific surface water during the 1982/83 El Niño event. *Tellus* **39B**, 214–227.
- Gaudry, A., Monfray, P., Polian, G. and Lambert, G. 1987. The 1982–1983 El Niño: a 6 billion ton CO₂ release. *Tellus* **39B**, 209–213.
- Hisard, P., Henin, C., Houghton, R., Piton, B. and Rual, P. 1986. Oceanographic conditions in the tropical Atlantic Ocean during 1983 and 1984. *Nature* **322**, 243–245.
- Inoue, H. and Sugimura, Y. 1988. Distribution and variations of oceanic carbon dioxide in the western North Pacific, eastern Indian, and Southern Ocean south of Australia. *Tellus* **40B**, 308–320.
- Keeling, C. D., Bacastow, R. B., Bainbridge, A. E., Ekdahl, C. A., Guenther, P. R. and Waterman, L. S. 1976. Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus* **28**, 438–451.
- Keeling, C. D., Guenther, P. R., Lueker, T. J. and Piper, S. C. 1987. Interannual variations in the carbon chemistry of surface sea water: possible increases in inorganic carbon and alkalinity. *EOS Trans AGU* **68**, 1691.
- Komhyr, W. D., Gammon, R. H., Harris, T. B. and Waterman, L. S. 1985. Global atmospheric CO₂ distribution and variations from 1968–1982 NOAA/GMCC CO₂ flask sample data. *J. Geophys. Res.* **90**, 5567–5596.
- Liss, P. and Merlivat, L. 1986. Air-sea gas exchange rates: introduction and synthesis. In: *The rôle of air-sea exchange in geochemical cycling* (ed. P. Buat-Ménard). Hingham, Mass.: D. Reidel, 113–127.
- Metzl, N., Beauverger, C., Brunet, C., Goyet, C. and Poisson, A. 1991. Surface water carbon dioxide in the southwest Indian sector of the Southern Ocean: a highly variable CO₂ source/sink region in summer. *Mar. Chem.* **35**, 85–95.
- Millero, F. J. 1979. The thermodynamics of the carbonate system in seawater. *Geochim. Cosmochim. Acta* **43**, 1651–1661.
- Oudot, C. and Wauthy, B. 1978. Adaptation of a gas chromatograph for shipboard measurement of dissolved gases: nitrogen, oxygen and carbon dioxide (in French). *Cah. ORSTOM, sér. Océanogr.* **16**, 89–102.
- Oudot, C. and Andrié, C. 1986. Variability of oceanic and atmospheric CO₂ partial pressures in tropical Atlantic (in French). *Oceanol. Acta* **9**, 169–177.
- Oudot, C., Andrié, C. and Montel, Y. 1987. Evolution of oceanic and atmospheric CO₂ over the 1982–1984 period in tropical Atlantic (in French). *Deep Sea Res.* **34**, 1107–1137.

- Roos, M. and Gravenhorst, G. 1984. The increase in oceanic carbon dioxide and the net CO₂ flux into the north Atlantic. *J. Geophys. Res.* **89**, 8181-8193.
- Smethie, W. M. Jr., Takahashi, T., Chipman, D. W. and Ledwell, J. R. 1985. Gas exchange and CO₂ flux in the tropical Atlantic ocean determined from ²²²Rn and pCO₂ measurements. *J. Geophys. Res.* **90**, 7005-7022.
- Sundquist, E. T., Plummer, L. N. and Wigley, T. M. L. 1979. Carbon dioxide in the ocean surface: the homogeneous buffer factor. *Science* **204**, 1203-1205.
- Takahashi, T., Chipman, D. and Volk, T. 1983. Geographical, seasonal, and secular variations of the partial pressure of CO₂ in the surface waters of the North Atlantic ocean. The results of the Atlantic TTO program. In: *Carbon dioxide, science and consensus* (CONF-820970). Institute for Energy Analysis, Oak Ridge Associated Universities, Washington, DC, 123-145.
- Tans, P. P., Conway, T. J. and Nakazawa, T. 1989. Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide derived from surface observations and an atmospheric transport model. *J. Geophys. Res.* **94**, 5151-5172.
- Unesco. 1987. Thermodynamics of the carbon system in seawater. *Unesco Techn. Papers in Marine Science* **51**, 1-55.
- Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **97** (C5), 7373-7382.
- Weiss, R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* **2**, 203-215.
- Weiss, R. F. and Price, B. A. 1980. Nitrous oxide solubility in water and seawater. *Mar. Chem.* **8**, 347-359.
- Weiss, R. F., Jahnke, R. A. and Keeling, C. D. 1982. Seasonal effects of the temperature and salinity on the partial pressure of CO₂ in seawater. *Nature* **300**, 511-513.

