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Short-term changes in the partial pressure of CO_2 in eastern tropical Atlantic surface seawater and in atmospheric CO_2 mole fraction

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ABSTRACT

Continuous monitoring of oceanic and atmospheric CO_2 during periods of 8 to 12 days in two particular locations of the tropical Atlantic was carried out during June–August 1986. At the first location (convergence zone; about 5°N, 20°W), the ocean surface was generally slightly undersaturated with respect to the atmosphere, whereas at the second one (Guinea Dome; 12°N, 22°W), the ocean surface was an important source zone of CO_2 for the atmosphere. The results of PCO_2 in surface seawater, after correction of the temperature effect, show a decrease between morning and evening related to photosynthetic activity. Over a 3-day period, the CO_2 concentration in the air above the ocean may vary up to ± 0.6 ppm d^{-1} at the same location, whereas the wind direction hardly changes. The net CO_2 flux changes considerably during a short period (8 to 12 days) in the same place, as does the gas transfer coefficient across the sea surface through the variation of the wind speed: the variability is about 80–90%. The net CO_2 flux calculated from mean data is lower (about 30%) than the net CO_2 flux calculated from data taken over short time intervals. In the Guinea Dome area in summer, the net CO_2 flux can be as high (1.8 mmol m^{-2} d^{-1}) as in the equatorial area.

1. Introduction

Studies of time variations of CO_2 both in the atmosphere and in the sea surface layer have mostly been related to a seasonal or annual basis (Bolin and Keeling, 1963; Pearman et al., 1983; Takashi et al., 1983; Komhyr et al., 1985; Fushimi, 1987; Inoue et al., 1987; Peng et al., 1987). These large-scale temporal distributions have often been used to show the possible relations between changes in atmospheric CO_2 and sea surface temperature anomalies known as the El Niño phenomenon (Newell and Weare, 1977; Bacastow et al., 1980; Gammon et al., 1985; Elliot and Angel, 1987). Brewer (1986) reviewed papers dealing with the processes, physical as well as biological, that control the variability of carbon dioxide in the surface ocean; these works generally referred to a large scale in space and time. The small-scale changes (e.g., diurnal variations) are less often noted (Takahashi, 1961), except for atmospheric CO_2 over the land (Keeling et al., 1976; Beardsmore et al., 1984; Bacastow et al., 1985).

Here we present continuous CO_2 observations made at 3 long-duration oceanic stations (8 to 12 days) in the eastern tropical Atlantic. The purpose is to show the physico-chemical effects associated with temperature changes and the biological factors involved in determining the diurnal variations of oceanic CO_2 partial pressure and on the other hand the variability of the CO_2 concentration in the air over the ocean with wind direction. The studied area shows two opposite situations as regards CO_2 saturation of surface seawater; in the north equatorial convergence zone (about 5°N) the oceanic CO_2 partial pressure is lower or nearly equal to the atmospheric

CO_2 partial pressure, whereas in the Guinea Dome area (12°N), where the isothermal surface layer is extremely shallow, the former greatly exceeds the latter.

2. Data sources and procedures

The hydrological and chemical data shown in this study come from the PIRAL cruise (June–August 1986) carried out aboard the R/V *Noroit* (France) in the northeastern tropical Atlantic (Fig. 1). Three time series of observations were carried out: the first, over a 12-day period, in the north equatorial convergence zone (4°–6°N, 17°–20°W), the second (8 days) and the third (10 days) in the Guinea Dome area, at the exact center of the dome (11°50′N, 22°W) and then at a short distance away from it (12°N, 21°W) (Oudot, 1989).

The measurements of CO_2 partial pressures in air (pCO_2) and in seawater (PCO_2) were carried out by infrared absorption with two ADC 225 MK3 analyzers (Oudot and Andrié, 1986; Andrié et al., 1986; Oudot et al., 1987). Air was taken at the upper bridge of the vessel which was about 10 m above the sea surface. The seawater samples were drawn from a Niskin PVC five-liter-bottle rosette which was associated with a Neil Brown CTD probe. The surface bottle was closed at about 1–2 m below the surface. The observations of all chemical data were made twice a day at 07.30 and 18.30 h (local time).

2.1. *Calibration of pCO_2 and PCO_2*

Three primary standard gases of 311.9, 370.5 and 504.2 ppm in artificial air, supplied by Air Liquide (France), were used for the calibration of the CO_2 measurements of the samples (air and seawater) on board. In addition, an ADC GD 600 gas dilutor produced a series of secondary standard gases by dilution from the 504.2 primary standard gas: the chosen intermediate concentrations were 318.2, 345.5 and 467.9 ppm. Calibration on board was done just before each series of observations (morning and evening). At the end of the cruise, all these standard gas concentrations were checked in the land laboratory with freshly prepared standard gases (Air Liquide) of concentrations 329.0 ± 0.25, 349.6 ± 0.25 and 360.5 ± 0.25 ppm. The CO_2 concentrations produced by the French manufacturer agree within

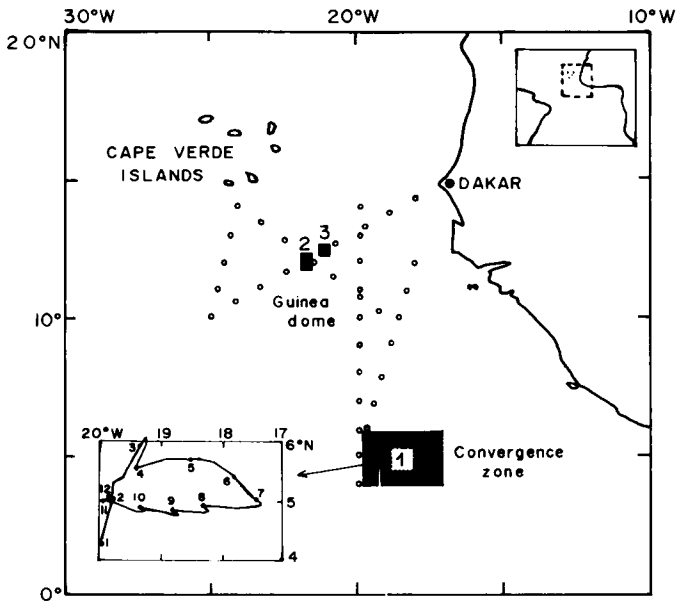

Fig. 1. Plan of the PIRAL cruise of the R/V *Noroit* (June–August 1986). The shaded parts indicate the areas of long periods of observations in the convergence zone (1) and in the Guinea Dome (2 and 3). Below on the left is shown the track of the ship during the first period of observations (12-day period).

0.25 ppm with the scale of the Scripps standards (Gaudry et al., 1987).

2.2. pCO_2 in the air

The air was pumped continuously (for about 30 min) into the laboratory on board through nylon tubing at a high flow rate. An aliquot of air (300 cm^3 min^{-1}) was introduced into the IR analyzer after dehumidification successively on a cold trap ($-30°C$) and on a P_4O_{10} column. Thus, fCO_2 (in ppm), the mole fraction of CO_2 in dry air, was measured and afterwards, pCO_2 (in μatm), the partial pressure of CO_2 in the atmosphere, was computed taking the water vapor pressure in the air into account. The uncertainty for the atmospheric fCO_2 measurement is estimated at ± 0.6 ppm (0.2%).

2.3. PCO_2 in seawater

The measurement of CO_2 partial pressure in seawater was carried out by equilibrating an air stream with the seawater sample. An air flow released by a tank was equilibrated with the seawater sample in the sampling flask (550 cm^3), after removing a small volume 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 ANALYSE cell of the infrared apparatus after passing through a P_4O_{10} column. The signal was recorded and compared with those produced by the standard gases injected in the same manner as the equilibrated air. Based on the CO_2 concentration of the dried equilibrated air, the CO_2 partial pressure in the seawater sample was calculated by correction at the 100% vapor pressure of water over the seawater at 25.0°C. In the absence of another parameter of the carbonate system required to compute the variation of PCO_2 with temperature (Skirrow, 1975), the CO_2 partial pressure was then converted at the "in situ" temperature of the sample, using an empirical relationship determined experimentally in the laboratory:

$$\log PCO_{2(s)} = \log PCO_{2(m)} + (T_s - T_m) \times (4.17 \times 10^{-2} - 3.78 \times 10^{-6} PCO_{2(m)}) \quad (1)$$

where index "m" means the measured values and index "s" means the "in situ" values. This correction of PCO_2 for the temperature rise is very similar to the temperature effect equation on PCO_2 given by Gordon and Jones (1973). The uncertainty for PCO_2 measurements on board is estimated at ± 3.0 μatm (0.8%–1.0%).

2.4. Total inorganic carbon $\sum CO_2$

Measurements of total inorganic carbon were made by gas chromatography according to the method described by Oudot and Wauthy (1978) and derived from that of Weiss and Craig (1973). The uncertainty for $\sum CO_2$ measurements is ± 4 μmol dm^{-3}, i.e., $\pm 0.2\%$.

3. Situation of the periods of observations

The first period (12 days) took place in the convergence zone between the North Equatorial Counter Current and the South Equatorial Current. In this zone, of low surface salinity (Oudot et al., 1987), the CO_2 partial pressure in surface seawater is low, on the average slightly lower than the CO_2 partial pressure in the atmosphere. During this period the surface current was strong (up to 4–5 km h^{-1}) and the vessel covered considerable distances (Fig. 1) in order to follow a surface buoy fitted to a drifting primary production line. During the first half-period the primary production line was allowed to stay in situ for 24 h per day, while from the 7th day the line was brought aboard during the night (from 18.00 h to 06.00 h, local time) and meantime the vessel was on the way back to the starting point of this experiment (Fig. 1: day 7 to day 12). At the beginning of this experiment, the surface hydrological features (temperature and salinity) varied considerably (Table 1), owing to the large meridional course of the R/V. When we move off the equator northward, the surface temperature increases whereas the salinity decreases naturally in summer, because the influence of the equatorial upwelling diminishes.

The second period (8 days) was held in the exact center of the Guinea Dome whose position was located after a preliminary phase of reconnaissance (Oudot, 1989). The Guinea Dome, first described by Mazeika (1968) then by Voituriez and Dandonneau (1974), is a thermal

Table 1. *Variations over the 12-day period (22 June–3 July 1986) of PCO_2 and related parameters in the surface seawater in the north equatorial convergence zone (4° N–6° N, 17° W–20° W)*

Station	(Day)	T (°C) 1	S 2	PCO_2 (μatm) 3	PCO_2 at $S = 35$ (μatm) 4	PCO_2 at $S = 35$ and $T = 27$°C (μatm) 5	ΔPCO_2 at $S = 35$ and $T = 27$°C (μatm) 6
13	(1)	26.29	35.36	333.2	317.4	326.4	−3.5
15		26.66	35.29	331.4	318.6	322.9	
17	(2)	26.86	35.08	328.9	325.4	327.2	−5.5
19		27.06	35.16	329.5	322.5	321.7	
21	(3)	26.96	35.17	337.0	329.5	330.0	−4.5
23		28.07	34.99	339.7	340.1	325.5	
25	(4)	27.34	34.98	329.4	329.8	325.3	−7.1
27		28.37	35.05	338.8	336.6	318.2	
29	(5)	27.75	35.05	330.8	328.6	318.7	−0.4
31		27.58	35.00	325.9	325.9	318.3	
33	(6)	27.41	35.01	327.6	327.2	321.8	−5.7
35		27.52	35.09	327.6	322.8	316.1	
37	(7)	27.31	35.12	328.3	323.0	319.0	−5.1
39		27.48	35.07	323.1	320.0	313.9	
41	(8)	27.15	35.15	329.5	322.9	321.0	(0.7)*
43		27.24	35.15	331.4	324.8	321.7	
44	(9)	27.28	35.11	327.8	323.0	319.4	(1.7)*
46		27.45	35.11	331.8	327.0	321.1	
48	(10)	27.48	35.13	329.5	323.8	317.6	−2.1
50		27.53	35.14	328.5	322.2	315.5	
52	(11)	27.26	35.27	336.0	324.1	320.7	(8.0)*
54		27.35	35.25	344.4	333.4	328.7	
56	(12)	27.26	35.23	336.9	326.8	323.4	−4.4
58		27.31	35.22	332.7	323.0	319.0	
mean		27.33	35.13	331.7	325.8	321.4	−4.3
SD		±0.42	±0.10	±4.9	±5.3	±4.2	±2.0
n		24	24	24	24	24	9

The normalization of PCO_2 ($S = 35$ and $T = 27$°C) are performed with a rate of 44 μatm/unity for salinity and 4% (°C)$^{-1}$ for temperature. The change ΔPCO_2 is counted between morning (07.30 h) and evening (18.30 h) stations (local time).

* The positive values (in parentheses) are omitted in the calculation of the arithmetic mean.

ridge, or dome, similar to that occurring in the northeastern tropical Pacific (Wyrtki, 1964; Broenkow, 1965). There PCO_2 greatly exceeds pCO_2, because the cyclonic circulation which creates the dome brings quite near the surface deep water supersaturated in CO_2. In the central area of the dome, the surface current was very weak and the vessel covered only short distances to follow the primary production line which barely drifted. The surface hydrological features were more stable, and in particular the salinity did not very much change (Tables 2, 3).

The third period (10 days), again in the Guinea Dome area, was nevertheless situated at a short distance from the exact center of the dome (about 110 km from the position of the preceding 8-day period). At that location, where the isothermal surface layer was thicker than that at the exact center of the dome, PCO_2 was lower than at the previous one.

Table 2. *Variations over the 8-day period (15–22 July 1986) of PCO_2 and related parameters in the surface seawater in the Guinea Dome (11°50′ N, 22° W)*

Station	(Day)	T (°C) 1	S 2	PCO_2 (μatm) 3	PCO_2 at $T = 27$°C (μatm) 4	ΔPCO_2 at $T = 27$°C (μatm) 5
86	(1)	26.32	36.20	398.1	408.9	(1.4)*
88		26.77	36.21	406.6	410.3	
90	(2)	26.34	36.21	395.2	405.6	(3.0)*
92		26.67	36.22	403.3	408.6	
94	(3)	26.40	36.22	396.3	405.8	−4.1
96		26.68	36.23	396.6	401.7	
98	(4)	26.40	36.23	391.3	400.7	−1.3
100		26.86	36.24	397.2	399.4	
102	(5)	26.56	36.23	395.7	402.7	−2.5
104		26.74	36.24	396.1	400.2	
106	(6)	26.53	36.24	399.4	406.9	−15.8
108		27.08	36.26	392.4	391.1	
110	(7)	26.82	36.30	394.7	397.5	−3.2
112		27.53	36.28	402.8	394.3	
114	(8)	26.87	36.30	396.6	398.7	−0.1
116		26.88	36.29	396.7	398.6	
mean		26.72	36.24	397.4	401.9	−4.5
SD		±0.31	±0.03	±4.0	±5.4	±5.7
n		16	16	16	16	6

The normalization of PCO_2 at $T = 27$°C is performed with a rate of 4% (°C)$^{-1}$. The change ΔPCO_2 is counted between morning (07.30 h) and evening (18.30 h) stations (local time).

* The positive values (in parentheses) are omitted in the calculation of the arithmetic mean.

4. Diurnal variations of PCO_2

4.1. Results

The time variations of PCO_2 at the sea surface are shown in Figs. 2, 3 and 4, for the three periods (12-day, 8-day and 10-day, respectively). For comparison, the sea surface temperature is also shown. The values of PCO_2 shown in Fig. 2 are normalized at $S = 35$ on account of the great variability of salinity (range: 34.98 to 35.36) during the period of observations in the convergence zone. The normalization is carried out using the rate of the variation of PCO_2 against salinity determined throughout the FOCAL cruises (44 μatm PCO_2 per salinity unit; Oudot et al., 1987) and similar to those reported by Kelley (1970) and Fushimi (1987). This normalization is omitted in the Guinea Dome where the salinity hardly changed (±0.02).

A certain diurnal oscillation for PCO_2, between morning and evening stations, seems to become apparent from the time series, more or less similar to that of the sea surface temperature (SST). Between 07.30 h and 18.30 h (local time), SST increases owing to diurnal solar heating and there follows of course an increase of PCO_2. The diurnal increase of SST is seen more regularly in the Guinea Dome (Figs. 3, 4) than in the convergence zone (Fig. 2) where we moved between different water masses on account of large distances covered by the R/V. But other processes than temperature can change PCO_2 at the sea surface and it is not to be wondered at that the morning–evening increase of PCO_2 does not regularly appear every day.

4.2. Discussion

On a daily scale, three factors can simultaneously alter PCO_2 in surface water: temperature, gas exchange across the air–sea interface

Table 3. *Variations over the 10-day period (29 July–7 August 1986) of PCO_2 and related parameters in the surface seawater in the Guinea Dome (12° N, 21° W)*

Station	(Day)	T (°C) 1	S 2	PCO_2 (μatm) 3	PCO_2 at $T = 27$°C (μatm) 4	ΔPCO_2 at $T = 27$°C (μatm) 5
119	(1)	27.02	36.05	369.1	368.8	(1.5)*
121		27.12	36.02	372.1	370.3	
123	(2)	26.98	36.03	379.3	379.6	−13.4
125		27.34	36.02	371.2	366.2	
127	(3)	27.21	36.01	369.6	366.5	−2.3
129		27.77	36.01	375.8	364.2	
131	(4)	27.24	36.01	375.6	372.0	−6.0
133		27.53	36.02	373.9	366.0	
135	(5)	27.31	36.01	370.7	366.1	−4.4
137		27.55	36.01	369.8	361.7	
139	(6)	27.37	36.01	372.6	367.1	−1.2
141		27.58	36.02	374.6	365.9	
143	(7)	27.35	36.01	377.5	372.2	−9.2
145		27.33	35.99	367.9	363.0	
147	(8)	27.17	35.98	367.5	365.0	−0.1
149		27.60	36.00	373.9	364.9	
151	(9)	27.32	35.99	366.4	361.7	−2.5
153		27.67	36.00	369.1	359.2	
155	(10)	27.22	35.96	369.8	366.5	(2.2)*
157		27.46	35.97	375.6	368.7	
mean		27.36	36.01	372.1	366.8	−4.9
SD		±0.21	±0.02	±3.6	±4.5	±4.5
n		20	20	20	20	8

The normalization of PCO_2 at $T = 27$°C is performed with a rate of 4% (°C)$^{-1}$. The change ΔPCO_2 is counted between morning (07.30 h) and evening (18.30 h) stations (local time).

* The positive values (in parentheses) are omitted in the calculation of the arithmetic mean.

and biological consumption of CO_2 through photosynthesis.

4.2.1. Temperature dependence of PCO_2. The variation of PCO_2 on temperature is due to the modification of equilibrium constants in the seawater carbonate system and solubility of CO_2. For a system in which salinity, alkalinity and total CO_2 remain constant, the temperature coefficient of PCO_2 is about 4% (°C)$^{-1}$ (Skirrow, 1975; MacIntyre, 1978; Broecker and Peng, 1982). To eliminate the temperature effect on PCO_2 results, we chose to reduce the latter at a constant temperature of 27°C, by applying the temperature coefficient of 4% (°C)$^{-1}$. The results are shown in Tables 1 (column 5), 2 (column 4) and 3 (column 4) for the three periods of observations. Then it appears that, without diurnal solar heating, a decrease in PCO_2 would have occurred most of the time between morning and evening.

4.2.2. Gas exchange across the air–sea interface. The net CO_2 flux across the air–sea interface is estimated from the gas exchange equation reported in Andrié et al. (1986):

$$F = k_t \alpha (PCO_2 - pCO_2) \quad (2)$$

where k_t is the CO_2 transfer coefficient (or exchange rate), α is CO_2 solubility in seawater (Weiss, 1974) and PCO_2 and pCO_2 are the CO_2 partial pressure in the water (PCO_2) and that in the air (pCO_2). The coefficient k_t is a function of

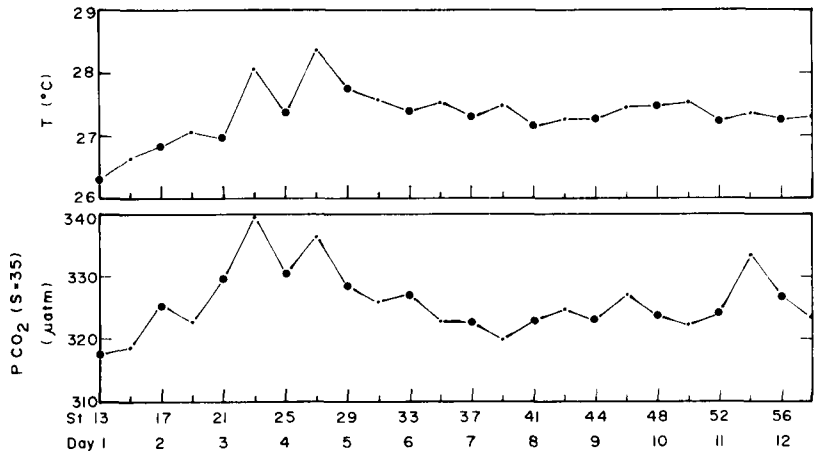

Fig. 2. Variations of CO_2 partial pressure PCO_2 normalized at $S = 35$ ($\Delta PCO_2/\Delta S = 44$ µatm) and temperature T at the sea surface over the 12-day period (4°–6°N, 20°–17°W). The station numbers and the large dots correspond to the morning station (07.30 h, local time).

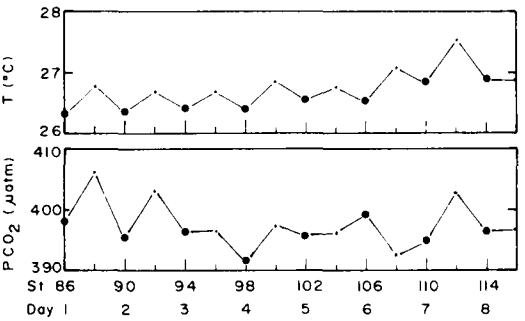

Fig. 3. Variations of CO_2 partial pressure PCO_2 and temperature T at the sea surface over the 8-day period (11°50′N, 22°W). The station numbers and the large dots correspond to the morning station (07.30 h, local time).

wind speed and of the temperature of seawater through the Schmidt number Sc dependency (Liss and Merlivat, 1986). The relationships used for the calculation of the CO_2 transfer coefficient are written as follows:

$$k_{20} = 0.17 V_{10} \quad \text{for} \quad 0 \leqslant V_{10} \leqslant 3.6 \text{ m s}^{-1} \tag{3}$$

$$k_{20} = 2.85 V_{10} - 9.65 \quad \text{for} \quad 3.6 \leqslant V_{10} \leqslant 13 \text{ m s}^{-1}, \tag{4}$$

where k_{20} is the transfer coefficient at 20°C expressed in cm h^{-1} and V_{10} is the wind speed in m s^{-1} measured at 10 m height. Finally the dependence of the transfer coefficient on the temperature is evaluated as follows:

$$k_t = 70.74 k_{20} (Sc_t)^{-2/3} \quad \text{for} \quad 0 \leqslant V_{10} \leqslant 3.6 \text{ m s}^{-1} \tag{5}$$

$$k_t = 24.39 k_{20} (Sc_t)^{-1/2} \quad \text{for} \quad 3.6 \leqslant V_{10} \leqslant 13 \text{ m s}^{-1}, \tag{6}$$

where Sc_t, the Schmidt number for CO_2 at t°C, is linearly interpolated between 20 and 30°C with the following relationship:

$$Sc_t = 1065 - 23.5t. \tag{7}$$

The results of the net CO_2 flux throughout the three periods of observations are given in Tables 4, 5 and 6. In the convergence zone (Table 4), the mean net CO_2 flux is a weak flux entering into the ocean (maximum value of 2.0 mmol m^{-2} d^{-1}), while in the Guinea Dome (Tables 5 and 6) this is a greater flux escaping from the ocean (maximum value 5.8 mmol m^{-2} d^{-1}).

Between the morning and the evening, i.e., over a 12-h period, the loss or the gain of CO_2 through the air–sea interface is at best 2.9 mmol m^{-2}. This CO_2 exchange involves a relative variation of total CO_2 ($\sum CO_2$) in the mixed layer (minimum mean thickness = 14 m) of (2.9/14)/2.000 = 0.01%. The corresponding

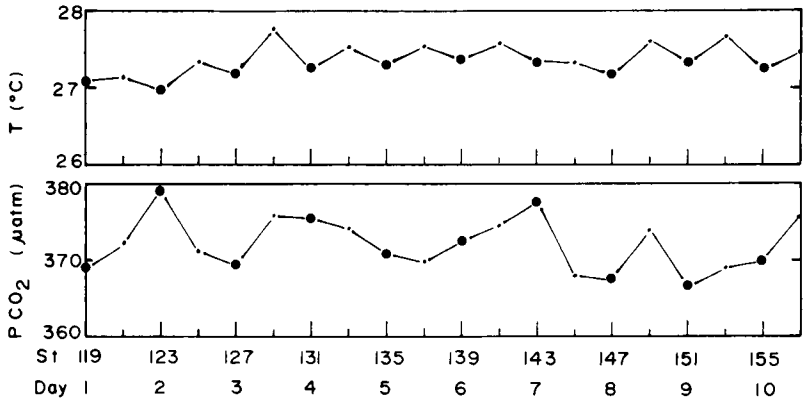

Fig. 4. Variations of CO_2 partial pressure PCO_2 and temperature T at the sea surface over the 10-day period (12°N, 21°W). The station numbers and the large dots correspond to the morning station (07.30 h, local time).

Table 4. *Variation over the 12-day period (22 June–3 July 1986) of the net CO_2 flux across the air–sea interface in the north equatorial convergence zone (4°N–6°N, 17°W–20°W)*

Station	(Day)	V_{10} (m s^{-1})	T (°C)	k_t (cm h^{-1})	$PCO_2 - pCO_2$ (μatm)	Net CO_2 flux (mmol m^{-2} d^{-1})
13	(1)	4.4	26.29	3.3	−3.0	−0.1
15		7.0	26.66	12.0	−4.3	−0.3
17	(2)	5.9	26.86	8.4	−8.5	−0.5
19		3.8	27.06	1.4	−8.9	−0.1
21	(3)	5.3	26.96	6.4	1.1	0.1
23		3.2	28.07	0.7	4.8	0.0
25	(4)	1.9	27.34	0.4	−8.7	0.0
27		1.9	28.37	0.4	2.1	0.0
29	(5)	3.1	27.75	0.7	−6.0	0.0
31		4.3	27.58	3.1	−11.0	−0.2
33	(6)	3.5	27.41	0.7	−9.3	−0.1
35		6.8	27.52	11.6	−8.7	−0.7
37	(7)	6.9	27.31	11.9	−9.5	−0.8
39		10.0	27.48	22.5	−13.7	−2.0
41	(8)	5.8	27.15	8.1	−7.0	−0.4
43		3.2	27.34	0.7	−6.2	−0.0
44	(9)	4.3	27.28	3.1	−8.3	−0.2
46		6.6	27.45	10.9	−3.5	−0.3
48	(10)	7.3	27.48	13.3	−5.2	−0.5
50		5.7	27.53	7.9	−7.7	−0.4
52	(11)	6.2	27.26	9.5	−0.3	−0.2
54		4.7	27.35	4.4	8.0	0.2
56	(12)	5.9	27.26	8.5	0.4	0.0
58		5.1	27.31	5.8	−3.2	−0.1
mean		5.1	27.33	6.5	−4.9	−0.2
SD		±1.9	±0.42	±5.5	±5.3	±0.3
CV		37%	2%	85%	108%	150%

Table 5. *Variation over the 8-day period (15–22 July 1986) of the net CO_2 flux across the air–sea interface in the Guinea Dome (11°50′ N, 22° W)*

Station	(Day)	V_{10} (m s^{-1})	T (°C)	k_t (cm h^{-1})	$PCO_2 - pCO_2$ (μatm)	Net CO_2 flux (mmol m^{-2} d^{-1})
86	(1)	4.2	26.32	2.7	61.3	1.1
88		2.5	26.77	0.5	69.6	0.2
90	(2)	4.5	26.34	3.7	58.8	1.4
92		5.7	26.67	7.7	68.4	3.5
94	(3)	5.4	26.40	6.6	60.7	2.7
96		5.4	26.68	6.7	62.3	2.8
98	(4)	5.7	26.40	7.6	56.2	2.9
100		4.8	26.86	4.7	62.9	2.0
102	(5)	4.4	26.56	3.4	61.0	1.4
104		2.5	26.74	0.5	60.1	0.2
106	(6)	5.0	26.53	5.3	63.3	2.3
108		2.9	27.08	0.6	56.5	0.2
110	(7)	1.6	26.82	0.3	58.0	0.1
112		2.6	27.53	0.6	64.3	0.2
114	(8)	4.4	26.87	3.4	58.0	1.3
116		7.8	26.88	14.7	59.1	5.8
mean		4.3	26.72	4.3	61.8	1.8
SD		±1.6	±0.31	±3.8	±3.8	±1.5
CV		37%	1%	88%	6%	83%

change in PCO_2 is given by the buffer factor (or Revelle factor) β:

$$\beta = (\Delta PCO_2/PCO_2) \times (\Delta \sum CO_2/\sum CO_2)^{-1}. \quad (8)$$

For seawater at 26–28°C, β is about 8.5 (Sundquist et al., 1979; Broecker and Peng, 1982). The maximum diurnal change of PCO_2 (between morning and evening stations) expected from the air–sea exchange is then $0.01\% \times 8.5 \times 400 = 0.3$ μatm, i.e., a negligible quantity for the daily balance of PCO_2.

4.2.3. Biological activity. In Tables 1, 2 and 3 after reducing PCO_2 measurements at a constant temperature (27°C), there generally appears a decrease of PCO_2 between morning and evening stations, which can only be the result of the photosynthetic fixation of CO_2. In the last column of Tables 1, 2 and 3, the change in PCO_2 (at constant temperature) between morning (07.30 h) and evening (18.30 h) is reported. Most of the time (9 days out 12, 6 days out 8 and 8 days out 10, respectively), this change is negative. We suppose that the positive values of ΔPCO_2, which cannot be ascribed to photosynthetic activity and which are low and within the precision of measurements (± 3.0 μatm) except once only (Table 1: 10th day), can arise from anaytical uncertainties or errors. For each period of observations we computed the mean decrease of PCO_2 by omitting the positive values of ΔPCO_2 (Tables 1, 2 and 3): the mean decreases of PCO_2 are 4.3 ± 2.0 μatm, 4.5 ± 5.7 μatm and 4.9 ± 4.5 μatm for the 12-day, 8-day and 10-day periods, respectively.

Now we have to verify if these decreases of PCO_2 are in agreement with the rate of primary production estimated by another way such as O_2 production (Oudot, 1989).

As was previously mentioned, the change in PCO_2 corresponds to a change in total CO_2 which is calculated through the Revelle factor β (relationship 8). The diurnal changes (between 07.30 h and 18.30 h) of $\sum CO_2$ and O_2 (adopting a photosynthetic ratio of -1.4; Takahashi et al., 1985) which can be expected from the changes in PCO_2 at a constant temperature are given in Table 7 for every period. The ranges of rate of O_2 production thus found (0.39 ± 0.26 μmol

Table 6. *Variation over the 10-day period (29 July–7 August 1986) of the net CO_2 flux across the air–sea interface in the Guinea Dome (12° N, 21° W)*

Station	(Day)	V_{10} (m s^{-1})	T (°C)	k_t (cm h^{-1})	$PCO_2 - pCO_2$ (μatm)	Net CO_2 flux (mmol m^{-2} d^{-1})
119	(1)	9.5	27.02	20.5	32.7	4.4
121		6.5	27.12	10.5	35.5	2.5
123	(2)	4.3	26.98	3.1	44.3	0.9
125		3.6	27.34	0.8	36.2	0.2
127	(3)	1.6	27.21	0.3	30.8	0.1
129		3.1	27.77	0.7	41.5	0.2
131	(4)	2.8	27.24	0.6	39.1	0.2
133		5.1	27.53	5.8	40.9	1.6
135	(5)	4.9	27.31	5.1	36.6	1.2
137		5.0	27.55	5.5	36.3	1.3
139	(6)	4.8	27.37	4.8	38.0	1.2
141		4.1	27.58	2.4	41.1	0.7
143	(7)	6.1	27.35	9.2	43.1	2.6
145		4.3	27.33	3.1	32.0	0.7
147	(8)	5.1	27.17	5.8	30.5	1.2
149		4.0	27.60	2.1	36.7	0.5
151	(9)	1.4	27.32	0.3	29.3	0.1
153		4.4	27.67	3.5	34.4	0.8
155	(10)	4.9	27.22	5.1	36.3	1.2
157		6.1	27.46	9.2	44.1	2.7
mean		4.6	27.36	4.9	37.0	1.2
SD		±1.8	±0.21	±4.8	±4.6	±1.1
CV		39%	1%	97%	12%	93%

Table 7. *Diurnal changes (07.30 h to 18.30 h, local time) of $\sum CO_2$ expected from the changes of PCO_2 (27°C) and O_2 production rates calcualted from $\Delta\sum CO_2$ and observed in situ*

Parameter	1st period 12 days 4°–6° N, 17°–20° W	2nd period 8 days 11°50′ N, 22° W	3rd period 10 days 12° N, 21° W
$\frac{\Delta PCO_2}{PCO_2}$	−1.34 ± 0.62%	−1.13 ± 1.43%	−1.32 ± 1.21%
$\frac{\Delta\sum CO_2}{\sum CO_2}$	−0.16 ± 0.07%	−0.13 ± 0.17%	−0.16 ± 0.14%
$\Delta\sum CO_2$ (μmol kg^{-1})	−3.0 ± 2.1	−2.6 ± 3.4	−3.0 ± 2.8
O_2 production rate calculated* (μmol kg^{-1} h^{-1})	0.39 ± 0.26	0.34 ± 0.44	0.39 ± 0.36
O_2 production rate observed† (μmol kg^{-1} h^{-1})	0.22 ± 0.11	0.07 ± 0.08	0.33 ± 0.15

* This rate of O_2 production is calculated from $\Delta\sum CO_2$ and a photosynthetic ratio of −1.4.
† This rate of O_2 production is deduced from in situ variations of O_2 concentrations (Oudot, 1989).

kg^{-1} h^{-1}, 0.34 ± 0.44 μmol kg^{-1} h^{-1} and 0.39 ± 0.36 μmol kg^{-1} h^{-1}) are in fair agreement with the rates deduced from in situ variations of O_2 concentrations: respectively 0.22 ± 0.11 μmol kg^{-1} h^{-1}, 0.07 ± 0.08 μmol kg^{-1} h^{-1} and 0.33 ± 0.15 μmol kg^{-1} h^{-1} (Oudot, 1989).

Until now, the examples of diurnal changes of CO_2 partial pressure in the surface ocean

reported in the literature have been scarce. According to Skirrow (1975), the usual observations show a daylight maximum since the physico-chemical effects associated with temperature adjustment outweigh biological factors in determining the diurnal range. From our results we may nevertheless conclude that it is possible to draw a diurnal variation of PCO_2 due to photosynthetic utilization of CO_2.

As shown by the definition of the buffer factor β (relation 8), the relative change of PCO_2 is much higher than that of $\sum CO_2$. For that reason, it becomes analytically easier to demonstrate a biological change of PCO_2: in Table 7, the results of $\Delta PCO_2/PCO_2$ are higher than the analytical precision while those of $\Delta\sum CO_2/\sum CO_2$ are lower.

5. Day-to-day trend of PCO_2

Beyond the diurnal variations, during the third period of observations a day-to-day tendency of PCO_2 ($T = 27°C$) to decrease is observed (Fig. 5). This trend is calculated by fitting a linear regression to the morning data of PCO_2 ($T = 27°C$) (Table 3). The slope of the regression line is -0.92 (± 0.48) μatm d^{-1}, which means a rate of PCO_2 change of -0.25 (± 0.13)% d^{-1}. The corresponding $\sum CO_2$ change expected from relation (8) is then -0.029 (± 0.015)% d^{-1}. The change of $\sum CO_2$ observed in situ and corrected for the total alkalinity change is -0.027 (± 0.030)% d^{-1} (Oudot, 1989). Consequently during this period of observations the trend of PCO_2 to decrease is quite consistent with the observed $\sum CO_2$ decrease which was interpreted as the result of biological activity shown by a release of oxygen in situ. In Fig. 5 the variation in dissolved oxygen is shown for comparison: the tendency of O_2 to increase from day-to-day is estimated at 0.35 μmol kg^{-1} d^{-1} (Oudot, 1989). Thus for a biological increase of 10 μmol kg^{-1} O_2 the decrease of PCO_2 should be of 26.3 μatm. We have to point out that in the coastal upwelling in front of Senegal (16°N, 17°W) we measured (March 1987) a PCO_2 decrease (at constant temperature) of 435 μatm simultaneously with an O_2 increase of 164 μmol kg^{-1} that is to say the same ratio. At this rate of decrease in PCO_2 (0.9 μatm d^{-1}) the sea surface in the Guinea Dome should return to the CO_2 equilibrium concentration with the atmosphere after about 40 days.

For the two other periods, there is no clear trend in the PCO_2 changes from day to day and the previous analysis cannot be made.

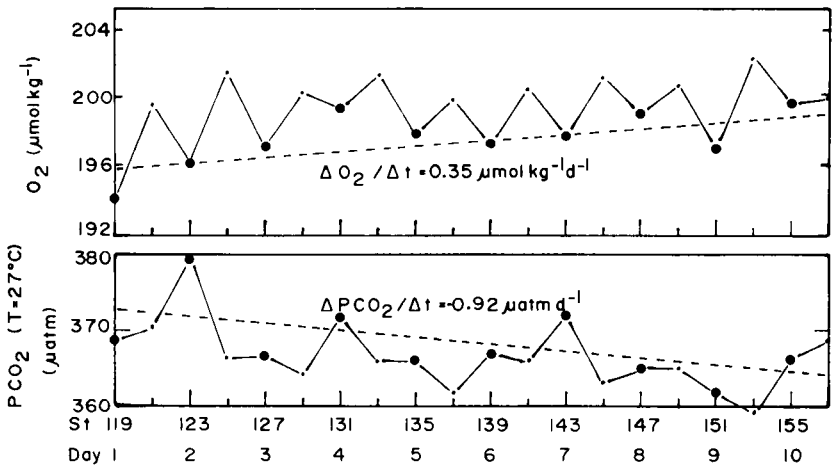

Fig. 5. Variations of CO_2 partial pressure PCO_2 normalized at $T = 27°C$ ($\Delta PCO_2/\Delta T = 4\%$ $(°C)^{-1}$) and dissolved oxygen O_2 at the sea surface over the 10-day period (12°N, 21°W). The station numbers and the large dots correspond to the morning station (07.30 h, local time). The slopes of the regression lines fitted to the morning station data (large dots) give the rate of change in each quantity over the 10-day period.

6. Time variability of atmospheric CO_2

6.1. Results

Over land areas the diurnal variations of CO_2 are a well-known phenomenon. The pattern of variations is generally related to the photosynthesis-respiration cycle of the vegetation with a minimum of the atmospheric CO_2 content during the day and a maximum during the night (Skirrow, 1975). This simple diurnal course can sometimes be disturbed by irregular events brought about by changes in wind direction (Keeling et al., 1976).

Above the ocean the data on the short-term variability of the atmospheric CO_2 content are very scarce except for seasonal variations. Figs. 6, 7 and 8 show the variations of the atmospheric CO_2 mole fraction (fCO_2) during the three periods of observations. During the first period, located between 4°N and 6°N (Fig. 6), after an increase on the first days, the CO_2 mole fraction continuously decreases from the fourth day. The rate of the fCO_2 decrease, calculated as the slope of the regression line fitted to the data (Fig. 6) is about 0.3 ppm d^{-1}. We could not help noting that the increase of fCO_2 to day 3 and the subsequent decrease in Fig. 6 is fairly similar to the trends of PCO_2 in Fig. 2. There is no doubt that this variability of fCO_2 is related to a spatial variation on account of the considerable distance covered by the R/V, in particular in a meridional direction over the first 3 days (see on Fig. 1 the track of the ship in the convergence zone area). Nevertheless the wind direction does not change very much; the wind continuously blows from the south (Fig. 6): during the first four days (Stations 13 to 29) the average of the wind direction is 172° (Standard Deviation = 13°), while during the last seven days (Station 33 to 58) the average of the wind direction is 147° (SD = 16°). At this season (northern summer), the Inter Tropical Convergence Zone (ITCZ) is located far north of the Equator, at about 9–10°N, and the 4°N–6°N latitude band is as a whole influenced by the southeast trade winds. Note that the atmospheric CO_2 content is on average 348.4 ppm (SD = 0.9 ppm).

During the second period, located in the exact center of the Guinea Dome (11°50′N, 22°W), the wind direction is not the same since the

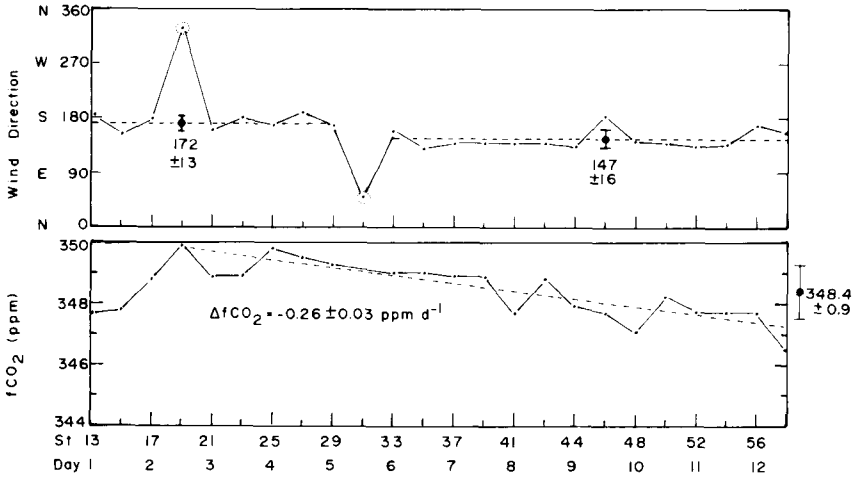

Fig. 6. Variations of atmospheric CO_2 mole fraction fCO_2 and wind direction over the 12-day period in the convergence zone (4°–6°N, 20°–17°W). A linear regression is fitted to the fCO_2 data to quantify the trend of fCO_2 to decrease over the last 10 days: $\Delta fCO_2 = -0.26 \pm 0.03$ ppm d^{-1} ($t = 7.7$, $n = 21$). On the right is shown the average of fCO_2 (with standard deviation) over the 12-day period. Upper part, the averages (and standard deviations) of the wind direction are indicated over the first 5 days and the last 6 days (the two data with circles are omitted in the calculation of the averages).

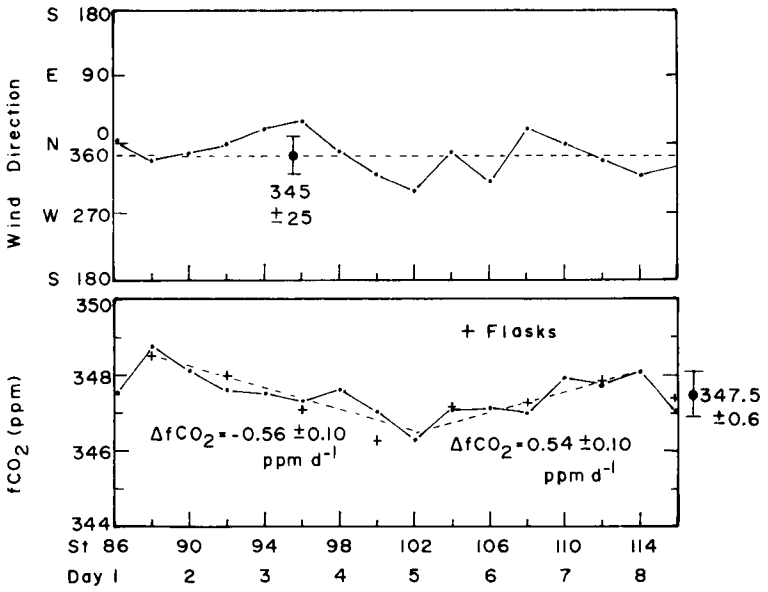

Fig. 7. Variations of atmospheric CO_2 mole fraction fCO_2 and wind direction over the 8-day period in the Guinea Dome (11°50′N, 22°W). A linear regression is fitted to the fCO_2 data to quantify the trend of fCO_2 to decrease over the first few days (St 88–102): $\Delta fCO_2 = -0.56 \pm 0.10$ ppm d^{-1} ($t = 5.63$, $n = 8$) and to increase over the last few days (St 102–114): $\Delta fCO_2 = 0.54 \pm 0.10$ ppm d^{-1} ($t = 5.31$, $n = 7$). The crosses indicate the results of measurements made later in the land laboratory (Monfray, 1987) on air samples collected in flasks simultaneously with the continuous measurements. On the right is shown the average of fCO_2 (with standard deviation) over the 8-day period. Upper part, the average (and standard deviation) of the direction over the 8-day period is also indicated.

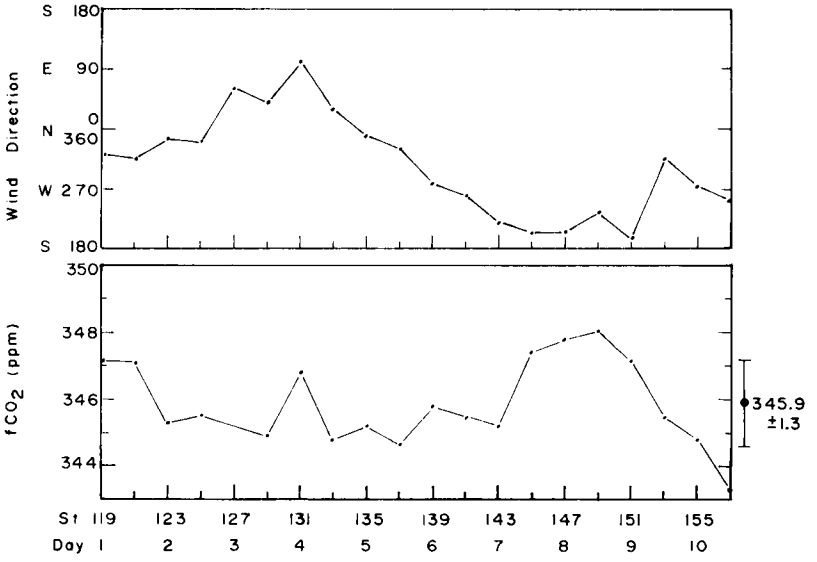

Fig. 8. Variations of atmospheric CO_2 mole fraction fCO_2 and wind direction over the 10-day period in the Guinea Dome (12°N, 21°W). On the right is shown the average of fCO_2 (with standard deviation) over the 10-day period.

obervations are made north of the ITCZ (Fig. 7). Again the variability of wind direction is weak; the wind continuously blows from the north ($345° \pm 25°$). However the CO_2 mole fraction (Fig. 7) shows a temporal variabilty even greater than previously. During the first half-period, fCO_2 decreases at a rate of 0.6 ppm d^{-1}, while during the last half-period fCO_2 increases at a rate of 0.5 ppm d^{-1}. During this period of obervations the distances covered by the R/V are not very large (a few km), and the variation of fCO_2 cannot be interpreted as a spatial variation. The range of CO_2 concentrations measured on board is confirmed by the measurements made later in the land laboratory (crosses on Fig. 7) on air samples simultaneously collected in flasks (Monfray, 1987). Note that the average of fCO_2 (347.5 ± 0.6 ppm) is significantly lower than the value during the first period of observations nearer the Equator.

During the third period of continuous observations, made in a location at a short distance north-east of the previous one, the amplitude of fCO_2 variations is the greatest (Fig. 8). The average value of fCO_2 (345.9 ± 1.3 ppm) is significantly lower than the one calculated for the previous period (347.5 ± 0.6). We remark how the wind direction changes throughout this period, and we are inclined to relate the increase of CO_2 between the 7th and the 9th days with the rotation of the wind direction to the south.

6.2. Discussion

The analysis of atmospheric CO_2 concentration data obtained during periods of ten or twelve days at the same location enables us to observe again the well-known CO_2 relation with local wind directions (Halter and Harris, 1983; Ciattaglia et al., 1987). The greater scattering of CO_2 concentrations during the last period appears to coincide well with a greater change in wind direction. Nevertheless, even if the wind blows continuously from the same direction, a certain variability can still arise. The range of variations is not negligible: 0.3 to 0.6 ppm d^{-1}. These short-term variations do not seem related to local CO_2 exchanges across the sea surface, generated by variations of temperature, PCO_2 or wind speed. This time variability of fCO_2 is important because it has an effect on the meaning of instantaneous measurements, as for every oceanographic or meteorologic parameter.

Contrary to what could be suggested from our former data of atmospheric CO_2 throughout the FOCAL cruises (Oudot et al., 1987), no diurnal variation of fCO_2 appear, in spite of the diurnal variations of sea surface temperature and PCO_2 previously discussed.

The 3 sets of CO_2 data, collected consecutively at 5°–6°N, 11°50′N and 12°N, remind us of the decrease in fCO_2 during northern summer when we are moving from the Equator towards the north, which was described in a previous paper (Oudot et al., 1987) and also reported over the Pacific Ocean (Keeling et al., 1984). This meridian gradient is due to the equatorial signal (enhancement of atmospheric CO_2 induced by the equatorial upwelling) and the depression of atmospheric CO_2 during northern summer in the northern hemisphere (Komhyr et al., 1985).

The atmospheric CO_2 data collected during the PIRAL cruise are a continuation of those collected during the years 1982 to 1984 in the same area (Oudot et al., 1987) and thus they enable us to provide some information about the secular trend of the atmospheric CO_2 increase. During the summer periods of 1982, 1983, 1984 and 1986, the mean atmospheric CO_2 content in the latitude band 10°–14°N was respectively 342.0, 342.7, 344.0 and 347.8 ppm. The linear regression analysis of these data indicates a 1.5 ± 0.2 ppm yr^{-1} increase in atmospheric CO_2 concentration from 1982 to 1986. This average rate of annual increase is in good agreement with the results reported in the literature.

7. Net CO_2 flux

The results of the net CO_2 flux throughout the three periods of observations are given in Tables 4, 5 and 6. In the convergence zone (Table 4), the mean net CO_2 flux is a weak flux entering into the ocean, while in the Guinea Dome (Tables 5 and 6) this is a greater flux escaping from the ocean. The range of the flux values during each period is wide and the variability of the flux is near 100%. The great variability of the net CO_2

flux during each period is due to the great variability of the gas transfer coefficient across the sea surface. With a coefficient of variation of wind speed of 37–39%, the coefficient of variation of k_t is from 85 to 97% (Tables 4 to 6). The air–sea CO_2 partial pressure difference ($PCO_2 - pCO_2$) during each period does not change very much; the standard deviation is about 4–5 μatm.

The precision of the calculations of the CO_2 flux mainly depends on the determination of the gas transfer coefficient, i.e., of the wind speed which is the prevailing factor. Often the wind speed used in the calculations is an average, extracted from atlases (Andrié et al., 1986) or the 24-h mean (Smethie et al., 1985). If we had calculated the mean net CO_2 flux, using the averages of wind speed, temperature and air–sea CO_2 partial pressure difference throughout the duration of each period of obervations, it would have been lower: respectively 0.2, 1.2 and 1.0 for the first, second and third periods. This follows from the fact that the gas transfer coefficient k_t is not linearly related on the one hand to wind speed (relations 3 and 4), on the other hand to temperature (relations 5 and 6), throughout the range of measurements of wind speed. It may be noted that the underestimation can reach about 30% when the flux is high (8-day period). But this error remains within the limits of the precision (83%).

Finally we wish to emphasize the high value of the net CO_2 flux in the Guinea Dome area at that period of the year. The value is similar to those calculated in the equatorial zone (Andrié et al., 1986), which is considered as an important source zone of CO_2 for the atmosphere. The reason is the presence of highly supersaturated waters ($PCO_2 - pCO_2 = 61$ μatm) in the center of the Guinea Dome, as supersaturated as in the equatorial belt of the Atlantic ocean (Smethie et al., 1985; Andrié et al., 1986) and the Pacific ocean (Feely et al., 1987). However this oceanic source of CO_2 has a limited implication in the global budget of CO_2 since the area of supersaturated waters is restricted in space and in time. In a winter situation the CO_2 supersaturation disappears since the cooling of the surface waters lowers PCO_2 below pCO_2 (Oudot and Andrié, 1986; Andrié et al., 1986).

8. Conclusions

Our results of PCO_2 in surface seawater indicate that, after correction of the temperature effect, there remains a diurnal variation due to biological activity. On a daily scale, the CO_2 exchange across the air–sea interface indeed has little influence on the CO_2 partial pressure of the surface water. Moreover there appears a day-to-day tendency of PCO_2 (corrected for temperature change) to decrease, which is not negligible (about 1 μatm d^{-1}) and is interpreted as the result of biological activity.

Above the ocean the atmospheric CO_2 concentration may change considerably in time as well as in space. Over a 3-day period, the CO_2 concentration in the air may vary up to ± 0.6 ppm d^{-1} whereas the wind direction hardly changes. Nevertheless, when the wind always blows from the same direction the atmospheric CO_2 content is more constant than when the direction is constantly changing.

The net CO_2 flux in the same place shows a great short-term variability (80–90%), due mainly to the variation of the gas transfer coefficient across the sea surface, i.e., of the wind speed. The use of mean data of wind speed to calculate the gas transfer coefficient involves an underestimation of the net CO_2 flux (up to 30%). In the Guinea Dome area, during the summer season, the net CO_2 flux can be as high (1.8 mmol m^{-2} d^{-1}) as in the equatorial belt.

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REFERENCES

Andrié, C., Oudot, C., Genthon, C. and Merlivat, L. 1986. CO_2 fluxes in the tropical Atlantic ocean during FOCAL cruises. *J. Geophys. Res. 91*, 11741–11755.

Bacastow, R. B., Adams, J. A., Keeling, C. D., Moss, D. J., Whorf, T. P. and Wong, C. S. 1980. Atmospheric carbon dioxide, the Southern Oscillation, and the weak 1975 El Niño. *Science 20*, 66–68.

Bacastow, R. B., Keeling, C. D. and Whorf, T. P. 1985. Seasonal amplitude increase in atmospheric CO_2 concentration at Mauna Loa, Hawaii, 1959–1982. *J. Geophys. Res. 90*, 10529–10540.

Beardsmore, D. J., Pearman, G. I. and O'Brien, R. C. 1984. The CSIRO (Australia) atmospheric carbon dioxide monitoring program: surface data. *CSIRO Division Atm. Res. Tech. Pap. No. 6*, 1–115.

Bolin, B. and Keeling, C. D. 1963. Large-scale mixing as deduced from the seasonal and meridional variations of carbon dioxide. *J. Geophys. Res. 68*, 3899–3920.

Brewer, P. G. 1986. What controls the variability of carbon dioxide in the surface ocean? A plea for complete information. In: *Dynamic processes in the chemsitry of the upper ocean* (eds. J. D. Burton, P. G. Brewer and R. Chesselet). New York: Plenum Publishing Corporation, 215–231.

Broecker, W. S. and Peng, T. H. 1982. *Tracers in the sea*. New York: Eldigio Press, Palisades, 690 pp.

Broenkow, W. W. 1965. The distribution of nutrients in the Costa Rica Dome in the eastern tropical Pacific ocean. *Limnol. Oceanogr. 10*, 40–52.

Ciattaglia, L., Cundari, V. and Colombo, T. 1987. Further measurements of atmospheric carbon dioxide at Mt. Cimone, Italy: 1979–1985. *Tellus 39B*, 13–20.

Elliot, W. P. and Angell, J. K. 1987. On the relation between atmospheric CO_2 and equatorial sea-surface temperature. *Tellus 39B*, 171–183.

Feely, R. A., Gammon, R. H., Taft, B. A., Pullen, P. E., Waterman, L. S., Conway, T. J., Gendron, J. F. and Wisegarver, D. P. 1987. Distribution of chemical tracers in the eastern equatorial Pacific during and after the 1982–1983 El Niño/Southern event. *J. Geophys. Res. 92*, 6545–6558.

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.

Gammon, R. H., Sundquist, E. T. and Fraser, P. J. 1985. History of carbon dioxide in the atmosphere. In: *Atmospheric carbon dioxide and the global carbon cycle* (ed. J. R. Trabalka). DOE/ER-0239. United States Department of Energy, Washington, D.C., 25–62.

Gaudry, A., Monfray, P., Polian, G. and Lambert, G. 1987. The 1982–1983 El Niño: a 6 billion ton CO_2 release. *Tellus 39B*, 209–213.

Gordon, L. I. and Jones, L. B. 1973. The effect of temperature on carbon dioxide partial pressure in sea water. *Mar. Chem. 1*, 317–322.

Halter, B. and Harris, J. M. 1983. On the variability of atmospheric carbon dioxide concentration at Barrow, Alaska during winter. *J. Geophys. Res. 88*, 6858–6864.

Inoue, H., Sugimura, Y. and Fushimi, K. 1987. pCO_2 and $\delta^{13}C$ in the air and surface seawater in the western North Pacific. *Tellus 39B*, 228–242.

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*, 538–551.

Kelley, J. J., Jr. 1970. Carbon dioxide in the surface waters of the North Atlantic Ocean and the Barents and Kara Seas. *Limnol. Oceanogr. 15*, 80–87.

Komhyr, W. D., Gammon, R. H., Harris, T. B. and Waterman, L. S. 1985. Global atmospheric CO_2 distribution and variations from 1968–1982 NOAA/GMCC CO_2 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 role of air–sea exchange in geochemical cycling* (ed. P. Buat-Ménard). Hingham, Mass.: D. Reidel, 113–127.

MacIntyre, F. 1978. On the temperature coefficient of pCO_2 in seawater. *Climatic Change 1*, 349–354.

Mazeika, P. A. 1968. Thermal domes in the eastern tropical Atlantic ocean. *Limnol. Oceanogr. 12*, 537–539.

Monfray, P. 1987. *Carbon dioxide ocean/atmosphere exchanges: variability with the sea state* (in French). Thèse Doc. Sc. Phys., Univ. Picardie, pp. 251.

Newell, R. E. and Weare, B. C. 1977. A relationship between atmospheric carbon dioxide and Pacific sea surface temperature. *Geophys. Res. Lett. 4*, 1–2.

Oudot, C. 1989. O_2 and CO_2 balances approach for estimating biological production in the mixed layer of the tropical Atlantic ocean (Guinea Dome area). *J. Mar. Res. 47(2)*, in press.

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 CO_2 partial pressions in tropical Atlantic (in French). *Oceanol. Acta 9*, 169–177.

Oudot, C., Andrié, C. and Montel, Y. 1987. Evolution of oceanic and atmospheric CO_2 over the 1982–1984 period in tropical Atlantic (in French). *Deep Sea Res. 34*, 1107–1137.

Pearman, G. I., Hyson, P. and Fraser, P. J. 1983. The global distribution of atmospheric carbon dioxide: 1. Aspects of observations and modeling. *J. Geophys. Res. 88*, 3581–3590.

Peng, T. H., Takahashi, T., Broecker, W. S. and Olafson, J. 1987. Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North

Atlantic surface water: observations and a model. *Tellus 39B*, 439–458.

Skirrow, G. 1975. The dissolved gases-carbon dioxide. In: *Chemical oceanography, vol. 2* (eds. J. P. Riley and G. Skirrow). London: Academic Press, 1–192.

Smethie, V. M., Takahashi, T., Chipman, D. W. and Ledwell, J. R. 1985. Gas exchange and CO_2 flux in the tropical Atlantic Ocean determined from ^{222}Rn and pCO_2 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. 1961. Carbon dioxide in the atmosphere and in the Atlantic ocean water. *J. Geophys. Res. 66*, 477–494.

Takahashi, T., Chipman, D. and Volk, T. 1983. Geographical, seasonal, and secular variations of the partial pressure of CO_2 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, D.C., 123–145.

Takahashi, T., Broecker, W. S. and Langer, S. 1985. Redfield ratio based on chemical data from isopycnal surfaces. *J. Geophys. Res. 90*, 6907–6924.

Voituriez, B. and Dandonneau, Y. 1974. Relations between thermal structure, primary production and nutrients regeneration in the Guinea Dome (in French). *Cah. ORSTOM, sér. Océanogr. 12*, 241–255.

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 Craig, H. 1973. Precise shipboard determination of dissolved nitrogen, argon and total inorganic carbon by gas chromatography. *Deep Sea. Res. 20*, 291–303.

Wyrtki, K. 1964. Upwelling in the Costa Rica Dome. *Fish. Bull. 63*, 355–372.