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Continuous pCO_2 measurements in surface water of the Northeastern tropical Atlantic

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ABSTRACT

The partial pressure of CO_2 in the area of the northeastern tropical Atlantic influenced by the Mauritanian upwelling is highly variable in time and space. Partial pressures between 300 and 450 μatm were observed in autumn 1991 and spring 1992. In the oceanic region off the Mauritanian coast, the range of spatial variations in pCO_2 was low (between 365 and 395 μatm, in autumn, and between 332 and 353 μatm in spring). In this area, the seasonal pCO_2 variations were mainly due to temperature effects. Even in the upwelling region, where the biomass was high, there was not a single relationship valid for the whole area between chlorophyll fluorescence and pCO_2. On the other hand, pCO_2 at a constant temperature was, on an average, decreasing with temperature. A comparison with older data shows that pCO_2 in the surface seawater of the open ocean has evolved as the atmospheric pCO_2 the last twenty years.

1. Introduction

The partial pressure of CO_2 (pCO_2) of the ocean's surface depends on the biological and physical processes that occur there. Data collected during a spring bloom of phytoplankton have demonstrated a negative covariance between chlorophyll fluorescence and pCO_2 (Watson et al., 1991), but in other conditions, the distribution of pCO_2 seems to be more correlated to physical parameters than fluorescence (Mackey et al., 1989, Copin-Montégut and Raimbault, 1994). In order to contribute to the knowledge of the distribution of pCO_2 and identify important features, continuous measurements of pCO_2, pH, chlorophyll fluorescence, salinity, and temperature were performed underway on the R/V "L'Atalante" during the Eumeli 3 and Eumeli 4 cruises of the France-JGOFS program. The sampled area was situated in the triangle bounded by the Canary Islands, Dakar, and 21° N, 31° W (Fig. 1).

Some pCO_2 measurements have been made in this region of the Atlantic (Büchen, 1971; Roos and Gravenhorst, 1984; Smethie et al., 1985). A supersaturation with respect to CO_2 has been observed near the Northwest African coast. The high pCO_2 values are explained by upwelling of deep water along the African coast. It is well known that in coastal upwellings, cool and nutrient-rich subsurface water is brought to the surface (e.g., Barber and Smith, 1981). The oxygen concentration is generally low in upwelled water, because the subsurface water has been the site of intense nutrient regeneration before being upwelled. Conversely, the carbonate concentrations and pCO_2 are high. On the other hand, this supply of nutrients to the euphotic layer is favourable to a high biological productivity in the horizontal divergent surface flow that develops in an upwelling system. The photosynthesis and the exchanges with the atmosphere decrease the carbonate concentrations in surface water. Thus, according to upwelling intensity and biological productivity, high or low pCO_2 values may be expected. The ship tracks during the Eumeli 3 and Eumeli 4 cruises permitted a detailed sampling of the upwelling region and the observation of

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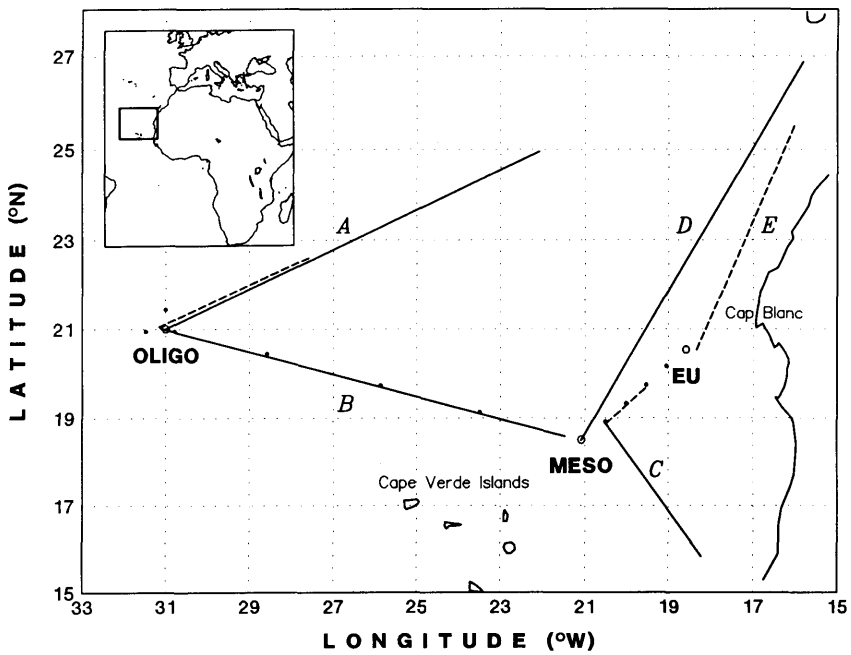

Fig. 1. Location of the CO_2 measurements during the Eumeli 3 Cruise in September–October 1991 (transects A–D), and during the Eumeli 4 Cruise in May–June 1992 (transects A, B, and E).

changes in pCO_2 between the nutrient-rich coastal area and nutrient-depleted oceanic area (Jacques, 1993).

2. Methods

The measurements were performed on water pumped at the bow to supply the shipboard thermosalinometer. The water flow was directed to a debubbler and then to the various measurement systems. The measurement and acquisition methods have been previously described in detail (Copin-Montégut and Raimbault, 1994). The chlorophyll fluorescence was measured with a Turner Design fluorometer, the pCO_2 measurements were performed according to the method of Copin-Montégut (1985), using a Maihak Infrared Analyser for CO_2, model Defor, with a barometric pressure compensation. Calibrations were made with mixtures of 350 ± 0.15 ppmv, 213 ± 0.15 ppmv, and 490 ± 0.25 ppmv of CO_2 in air manufactured by Air Liquide. The pH measurements were made with a Radiometer 84 pHmeter and a Ross combination electrode (Orion 8102). As the calibrations and the pH measurements were not performed exactly at the same temperature, a correction for the variation of the liquid junction potential of the electrode with temperature was made. The signal of the quartz temperature probe located at the ship bow was calibrated by comparison with the temperature signal of the CTD Sea Bird probe used during the cruise. The same procedure was used to correct the salinity given by the thermosalinometer. The data were logged at 1-min intervals. The precisions on the pCO_2 and pH measurements were better than 1 μatm for pCO_2 and 0.001 units for pH, but the accuracies were lower. They may be estimated to be close to 2 μatm for pCO_2 and 0.010 units for pH.

The simultaneous measurements of pCO_2 and pH permit the validation of the results. From the alkalinity measurements on discrete samples along transect D (using the method described by Copin-Montégut, 1993), a linear relationship between total alkalinity (TA) and salinity (S) was established: $TA = 42.41 \times S + 858.4 \pm 2.0$ μmole kg^{-1}, at the 95% confidence level. Then pCO_2 was calculated from pH and TA (deduced from

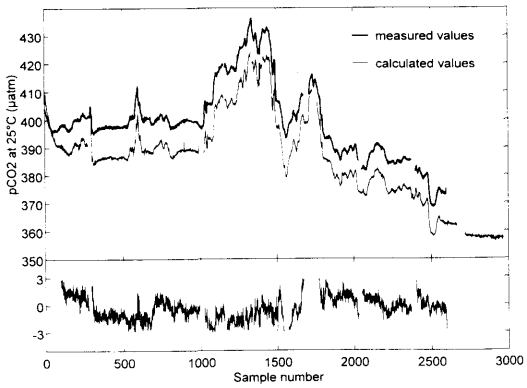

Fig. 2. Comparison between measured and calculated pCO_2 at 25°C (in μatm) along transect D. The values of pCO_2 deduced from pH and alkalinity have been shifted by -10 μatm for the figure clarity. At the bottom of the figure are presented the differences between the measured and calculated values.

salinity) using the dissociation constants of Goyet and Poisson (1989) for carbonic acid, that of Dickson (1990) for boric acid, the Weiss (1974) equation for the solubility of CO_2, and the ionic product of water determined by Dickson and Riley (1979). Fig. 2 shows the good agreement between measured and calculated pCO_2 values. The standard deviation between the measured and calculated values was 1.2 μatm for 2283 samples along transect D.

The data in electronic form are available from the authors.

3. Results

In September–October 1991, the pCO_2 values in the coastal zone (transects D and C) were situated between 360 and 410 μatm (Figs. 3, 4). Along transect D, the highest values were encountered at the latitude of the Cap Blanc where upwelling is strong (Wooster et al., 1977). The temperature of the waters with high pCO_2 values was low that confirms the presence of upwelled water in surface. On the other hand, along transect C, the high pCO_2 values were associated with high temperatures.

In June 1992, the partial pressure of CO_2 along transect E was between 300 and 450 μatm (Fig. 5), the lower values were encountered near 22° N, and the higher near 21° N, over a distance lower than

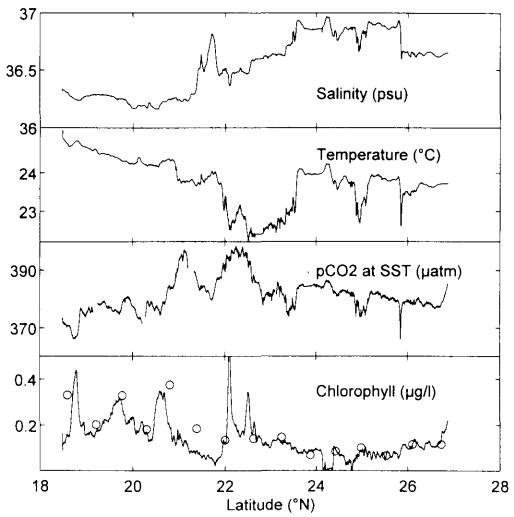

Fig. 3. Salinity, temperature, pCO_2 at sea surface temperature (SST) and chlorophyll fluorescence distributions along transect D in October 1991. The circles on the fluorescence profile correspond to the chlorophyll *a* concentrations measured on discrete samples by HPLC (results kindly communicated by H. Claustre). The fluorescence values have been converted into chlorophyll values using these discrete measurements.

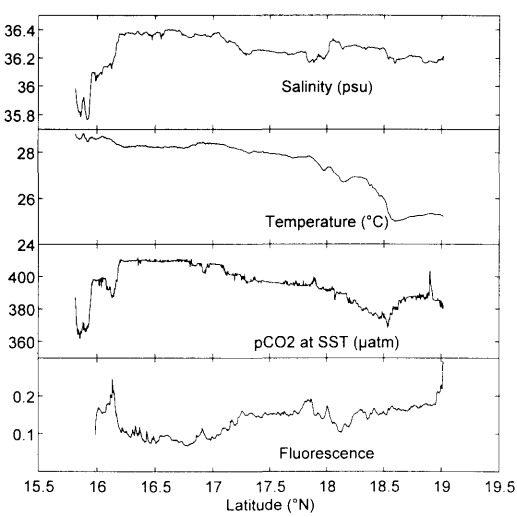

Fig. 4. Salinity, temperature, pCO_2 at SST and chlorophyll fluorescence distributions along transect C in September 1991 (the fluorescence unit is arbitrary).

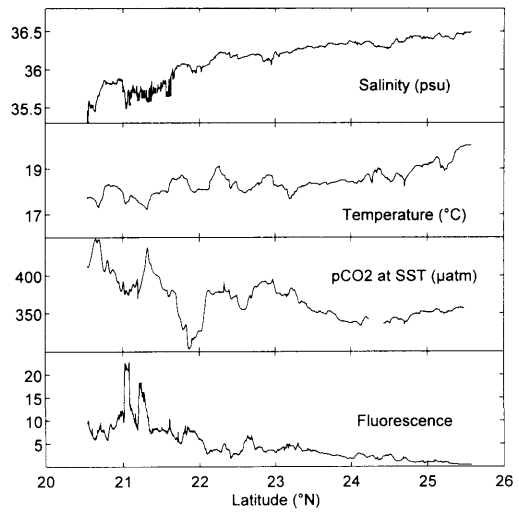

Fig. 5. Salinity, temperature, pCO_2 at SST and chlorophyll fluorescence distributions along transect E in June 1992 (the fluorescence unit is arbitrary).

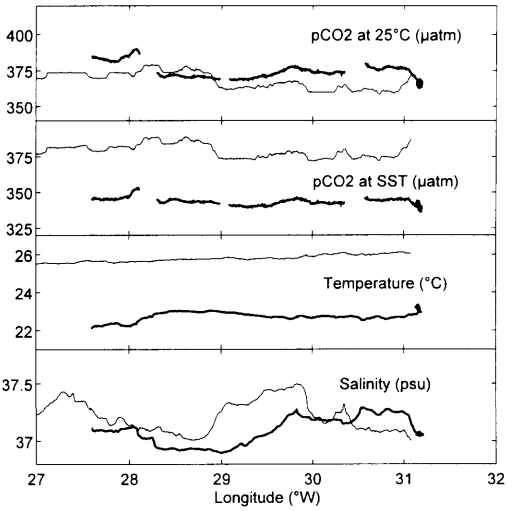

Fig. 7. Distributions of pCO_2 at 25°C, pCO_2 at SST, temperature, and salinity along transect A in September 1991 (light line), and in May 1992 (thick line).

70 km. The temporal variability was also great. At the southern boundary of transect E ("eutrophic" station), where pCO_2 measurements were performed during 44 hours, the pCO_2 fluctuations reached 80 μatm (Fig. 6). These fluctuations were probably due to the displacement of the water masses.

In the open ocean (transects A and B), the pCO_2 variations were lower (Figs. 7, 8). The partial pressure of CO_2 ranged from 365 to 390 μatm in September–October 1991 and from 330 to 360 μatm in May–June 1992. At the "mesotrophic" station which was at the boundary of the upwelling area, the pCO_2 fluctuations reached 9 μatm in 25 h

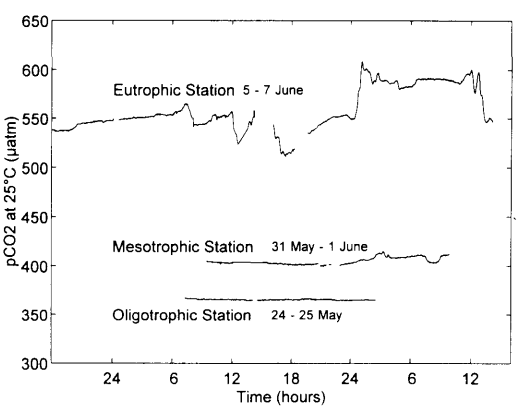

Fig. 6. Temporal variations of pCO_2 at 25°C (in μatm) at the eutrophic, mesotrophic, and oligotrophic stations in May–June 1992.

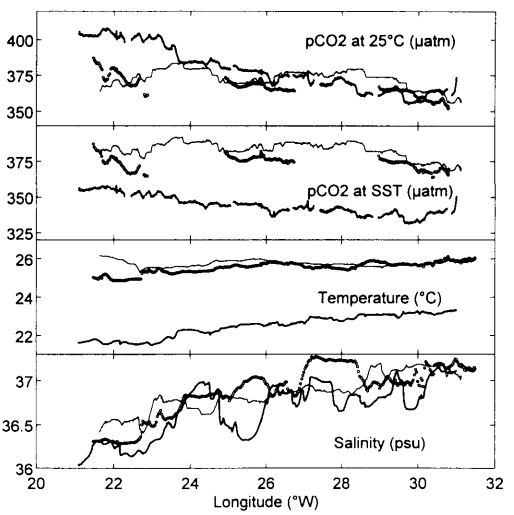

Fig. 8. Distributions of pCO_2 at 25°C, pCO_2 at SST, temperature, and salinity along transect B in September 1991 (light line), in October 1991 (circles), and in May 1992 (thick line).

in June, while at the "oligotrophic" station, the pCO_2 fluctuations amounted to 4 μatm and even to 2.5 μatm after elimination of the pCO_2 variations due to a change in temperature (Fig. 6).

4. Discussion

In order to estimate whether the surface water of the tropical Atlantic is a source or a sink of carbon dioxide for the atmosphere, it is necessary to know the partial pressure of CO_2 in the air above the surface water. The pCO_2 in air was not measured during the cruises Eumeli 3 and Eumeli 4, but we have estimated it using the measurements of CO_2 concentration in air performed at St Croix (Virgin Islands, 17°45′N, 64°45′W), in Terceira Islands (Azores, 38°45′N, 27°05′W) and at Monte Cimone (44°11′N, 10°42′E). The monthly means of CO_2 concentrations measured at these three stations are very close for the years 1979–1988 (Boden et al., 1990). The atmospheric CO_2 measurements of Oudot et al. (1987) in the eastern tropical Atlantic near 10°N are also in agreement with those of the three sampling sites. One can then suppose that the atmospheric molar fraction of CO_2 is the same over all the area delimited by the observation sites. According to the measurements performed in 1991–1992 at Monte Cimone (data communicated by the Italian Meteorological Service), the molar fraction of CO_2 was 349 ppmv in September 1991, 352 ppmv, in October 1991 and 353 ppmv in June 1992. The partial pressure of CO_2 (PCO_2) above the surface seawater depends on the atmospheric total pressure (P_t) and on the water vapour pressure (f) according to the relationship

$$pCO_2 = X(P_t - f),$$

where X is the molar fraction of CO_2 in dry air. It ranged between 338 and 345 μatm, according to the atmospheric pressures and air temperatures measured during the cruises.

The surface water was supersaturated with respect to CO_2 through all the tracks of the autumnal cruise (Fig. 9a). In June, the surface water was undersaturated near 22°N along transect E. In the open ocean, the surface waters became undersaturated westward, when the surface water temperature was higher than 22.5°C.

It is difficult to compare these results to the older ones which were obtained in other seasons. In January 1983 (Smethie et al., 1985), the difference between the surface water pCO_2 and atmosphere pCO_2 (ΔpCO_2) was 24 μatm at a station close to the "eutrophic" station where we have measured a ΔpCO_2 ranged from 45 to 120 μatm. This difference may be explained by lower production and stronger upwelling during our measurements (the surface water temperature was lower). The high variability we have observed shows anyway that a single ΔpCO_2 measurement is not representative in an upwelling area. As

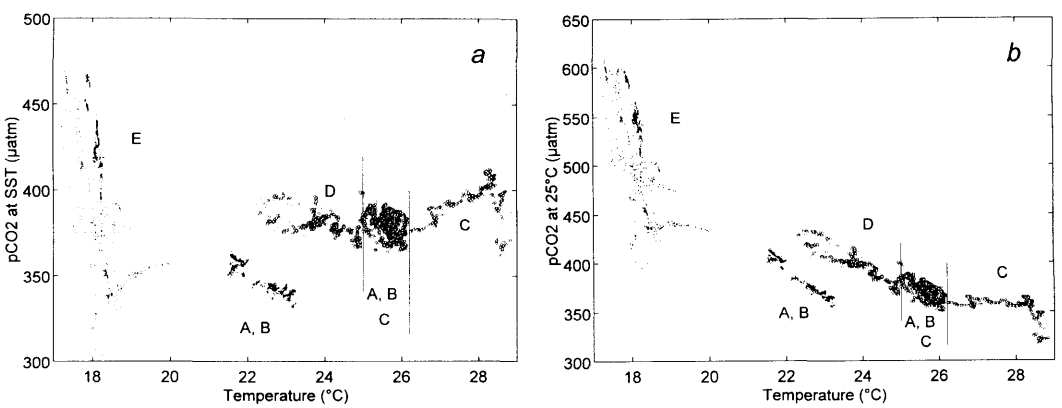

Fig. 9. (a) pCO_2 at SST (in μatm) against temperature. (b) pCO_2 at 25°C (in μatm) against temperature. The circles correspond to the measurements made in autumn and the dots to the measurements made in spring. The letters indicate the transects corresponding to the data.

the variability is lower in the oceanic region, the comparison of results is somewhat easier. The line corresponding to $\Delta pCO_2 = 0$ was situated near 29°W along 20°N in November 1973 (Roos and Gravenhorst, 1984) and near 25°W in January 1983 according to Smethie et al. (1985). It was approximately at the latter position in May 1992, but it was beyond the measurement area in September and October 1991.

It is useful to compare the pCO_2 values at the same temperature to know the origin of the observed values. This eliminates the temperature effect on carbonate equilibrium. In the open ocean, the values of pCO_2 at 25°C (pC25) were not very different in autumn and in spring (Figs. 7, 8). The temporal variability was of the same order as the spatial variability (Table 1). This indicates that the content in carbonate of the surface water was nearly the same in both seasons. Only eastward of 24°W, pC25 was higher in May than in September and October. This may be explained by the offshore extension of the coastal water from the upwelling region. The presence of nitrate and phosphate in May in the mixed layer of the "mesotrophic" station and their absence in September and October (P. Raimbault, personal communication) support this explanation.

We can compare our pC25 values in autumn 1991 with that obtained from the measurements of Roos and Gravenhorst (1984) in November 1973 at two locations, 31°N, 26°W and 26°N, 21°W near transects B and A. The pC25 values we measured near these locations were respectively 375 and 387 μatm. That calculated from the Roos and Gravenhorst measurements was 340 and 359 μatm. The difference between the old and new data (25 μatm for the first location, 28 μatm for the second) is slightly higher than the increase in atmospheric molar fraction (about 24 ppmv between 1973 and 1991). Considering the possibility of measurement errors and of variations in hydrological conditions, it appears than the surface water pCO_2 evolves as the atmospheric pCO_2 at the decennial scale. After a careful examination of old data, Roos and Gravenhorst (1984) had concluded as well that pCO_2 in the surface water of the North Atlantic had increased between the beginning of the century and their measurements in 1973.

Table 1. *Mean values of pCO_2 at 25°C (in μatm) measured along transects located in the open ocean; for transect B in June 1992, only the measurements east of 24° W are taken into account*

Transect	Mean	Standard deviation	Number of measurements
A, Sept. 91	367.4	6.4	1110
A, June 92	374.8	5.1	908
B, Sept. 91	371.7	7.1	2760
B, Oct. 91	366.7	6.7	1813
B, June 92	371.3	8.4	2354

There is a general trend toward a decrease in pC25 with temperature at a given season (Fig. 9b). The higher values of pC25 were found in the upwelling region, the lower, off Dakar. There is a linear correlation, better in spring than in autumn, between pC25 and temperature in the offshore surface waters. As the pC25 values are close in both seasons but not the temperatures, the relationships are different according to the season, but the regression slopes ($-30\ \mu atm\ °C^{-1}$) are almost equal. This linear decreasing relationship between pC25 and temperature may be explained by the mixing of the water coming from the upwelling region with warmer surface water less rich in CO_2.

The decrease in pC25 with temperature was much greater ($\sim -150\ \mu atm\ °C^{-1}$) along transect E than along all the other transects. Along transect D, the decrease was approximately the same as in the open ocean. The differences between the two transects (lower temperatures, higher and more variable pC25 values along transect E) may be explained by the difference in distance from the coast and by an intensification of the upwelling in spring (Wooster et al., 1976). The chlorophyll fluorescence was very high along transect E, then the rapid decrease in pC25 with temperature is probably due to a high primary production. The temperature of upwelled water increases during its offshore transport, and meanwhile, the high level in nutrients favours the utilization of dissolved inorganic carbon for the biological production, then pCO_2 at a constant temperature decreases.

There was no clear relationship between pCO_2 at a constant temperature and fluorescence. In the oceanic area, the chlorophyll fluorescence was low and little variable as pC25. High values of fluorescence were found in the coastal upwelling where pC25 was greatly variable. These high values of fluorescence, due to a large phytoplank-

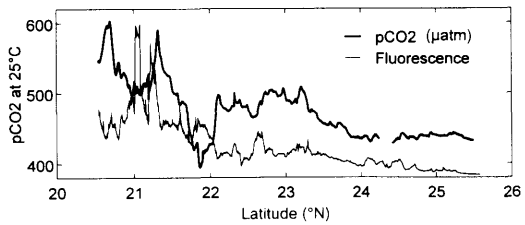

Fig. 10. pCO_2 at 25°C and chlorophyll fluorescence along transect E in June 1992.

tonic biomass, were sometimes associated with decreases in pC25, and occasionally, pC25 and fluorescence were directly related (Fig. 10). The superposition of processes with different time scales may explain this absence of general correlation. On average, in an upwelling system, the partial pressure of CO_2 decreases with the time spent by upwelled water in surface owing to the CO_2 exchanges with the atmosphere and to the biological production. The biomass is generally maximum in the waters upwelled for a few days. Then it tends to decrease when the water becomes impoverished in nutrients. According to the circumstances the relationship between pCO_2 and biomass can therefore be direct or inverse. Near the upwelling source, the relationship is a priori inverse and on the contrary, direct, far from the source. Locally, when there are favourable conditions for a high phytoplanktonic production, pCO_2 and biomass can be inversely related, as in a plankton bloom.

5. Acknowledgements

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