



Distribution of surface $f\text{CO}_2$ and air–sea fluxes in the Southwestern subtropical Atlantic and adjacent continental shelf

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Abstract

Measurements of the fugacity of CO_2 , salinity, in situ temperature, nutrients and chlorophyll-*a* were made in November 1997, January/February and June 1998, during the “Ocean Circulation in the Southwest Atlantic Region” program (COROAS). The surface water fugacity of CO_2 , $f\text{CO}_2(\text{sw})$, in the open ocean was $362.8 \mu\text{atm}$, corresponding to a fugacity difference between surface water and atmosphere ($\Delta f\text{CO}_2$) of $+3.2 \mu\text{atm}$ in November; $425.5 \mu\text{atm}$ ($\Delta f\text{CO}_2 = +75.0 \mu\text{atm}$) in January/February, and $350.6 \mu\text{atm}$ ($\Delta f\text{CO}_2 = -4.0 \mu\text{atm}$) in June, respectively, for the latitudes south of 25.3°S . These $f\text{CO}_2(\text{sw})$ values suggest that only during winter does this oceanic area absorb any atmospheric CO_2 , whereas in the remaining seasons CO_2 is released into the atmosphere. North of 25.3°S CO_2 was released into the atmosphere during all the seasons, with highest $\Delta f\text{CO}_2$ at the continental shelf. The contribution of biological and temperature effects to the seasonal $f\text{CO}_2(\text{sw})$ variations was calculated by dividing the region sampled into three subsections: the continental shelf, the continental slope and the open ocean. These calculations were compared with normalized $f\text{CO}_2(\text{sw})$ and it was concluded that the main contributions to the $f\text{CO}_2(\text{sw})$ gradients in the open ocean are the in situ temperature and the exchange of $\text{CO}_2(\text{g})$ with the atmosphere. In the slope and shelf zones the biological regenerative processes must also be considered. The estimated net sea–air CO_2 fluxes ranged between -1.1 and $0.1 \text{ mmol m}^{-2} \text{ day}^{-1}$ for the open ocean, 0.4 and $3.7 \text{ mmol m}^{-2} \text{ day}^{-1}$ for the slope and 0.3 and $9.8 \text{ mmol m}^{-2} \text{ day}^{-1}$ for the shelf zone, using the Wanninkhof 92 formula. It is reasonable to assume that the study area is a source of CO_2 for the atmosphere and the sea–air CO_2 fluxes over the continental shelf and slope could lead to refinements regarding the calculations of continental shelf pump.

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1. Introduction

The world’s oceans absorb some proportion of the anthropogenic CO_2 from the atmosphere, and a great

number of measurements of oceanic CO₂ distribution have been made over the last decade. However, the quantification of the oceanic uptake of anthropogenic CO₂ is still uncertain (Siegenthaler and Sarmiento, 1993; Houghton et al., 1995; Baliño et al., 2001; IPCC, 2001; Thomas et al., 2001; Takahashi et al., 1997 and 2002). But, reliable forecasts of climatic change depend on the understanding and quantification of sinks and sources of atmospheric CO₂, of its transport and removal to other reservoirs, the oceans among them.

Although coastal zones and continental shelves represent 7% of the total oceanic area, they host disproportional intense biological activity and/or physical mixing processes. The percentage of primary productivity of the shelf zone, compared to that of the open ocean, ranges from 20% to 40% (Walsh, 1988) and plays a significant role, therefore, in the absorption of atmospheric CO₂. The role of these ocean areas will depend on the balance between absorption and regeneration of CO₂ in these surface seawaters and their transport into the open ocean. If the CO₂ absorbed in these areas is transported to the open ocean, the current models that estimate the absorption of anthropogenic CO₂ by the oceans may be inaccurate by as much as 20–50% (Tsunogai et al., 1999; Thomas et al., 2004a).

During recent years detailed field studies have been initiated in a few areas such as the East China Sea, the Baltic and North Seas and the NW European shelf. However, on a global scale, only limited information on these CO₂ fluxes is currently available (Bakker et al., 1996; Boheme et al., 1998; Chen and Wang, 1999; Thomas et al., 1999; Thomas and Schneider, 1999; Tsunogai et al., 1999; Liu et al., 2000a,b; Frankignoulle and Borges, 2001; Borges and Frankignoulle, 2002, 2003; Friederich et al., 2002; Cai et al., 2003; Chen et al., 2003; Murata and Takizawa, 2003; Thomas et al., 2003; Thomas et al., 2004a).

Carbon cycle studies focusing on CO₂ gas exchanges in South Atlantic waters have been carried out during the last decade (e.g. Takahashi et al., 1993, 2002; Schneider and Morlang, 1995; Oudot et al., 1995; Goyet et al., 1998a; Körtzinger, 2003). However, these studies are, in general, restricted to the open ocean and are based on scanty observational data. Further studies have been carried out into carbon cycling along the western shelf of the South Atlantic

Ocean, with a focus on particulate carbon transport in mangroves margins (Ovalle et al., 1999; Jennerjahn and Ittekkot, 2002; Borges et al., 2003; Jennerjahn et al., 2003).

Within this context, the purpose of this study is the investigation of the seasonal $f\text{CO}_2(\text{sw})$ variation at the ocean surface in the western region of the South Atlantic, including the open ocean and adjacent continental shelf, as well as the examination of its impact on the calculation of the net flux of CO₂ across the air–sea interface.

2. The study area

The region sampled lies in the Southwestern subtropical Atlantic (Fig. 1).

The region section of the Brazilian coast is known as the South Brazil Bight (SBB). The continental slope in this zone begins at the 180 m isobath and the foot of the slope lies at the 2000 m isobath. The Brazil Current (BC), which flows southward as a shallow current at a depth of approximately 200 m, dominates the offshore circulation (Castro and Miranda, 1998). The meandering main axis of the BC, the location of which has been established on the basis of AVHRR/NOAA-11 satellite images (Godoi et al., 2004), is presented in Fig. 1.

The water masses in the South Brazil Bight arise from the mixing of the following water masses: the Tropical Water, TW, ($T > 20.0$ °C and $S > 36.40$) and the South Atlantic Central Water, SACW, ($T < 20.0$ °C and $S < 36.40$), both being transported southward by the BC in approximately the upper 500 m, and the Antarctic Intermediate Water, AIW. On the continental shelf the Coastal Water, CW, results primarily from the mixing of saline basin water, local runoff and the less saline water of sub-antarctic origin transported northward by the coastal branch of the Falkland Current (Emilson, 1961; Miranda, 1972, 1985).

The low concentrations of nutrients and chlorophyll-*a* in the SBB surface waters reflect the dominance of the oligotrophic BC (Aidar et al., 1993; Gaeta, 1999; Ganesella, 2000; Kampel, 2003). The SACW intrusion and upwelling on the continental shelf during summer is considered to be the main nutrient fertilization process in the euphotic zone leading to subsurface maxima of chlorophyll-*a* con-

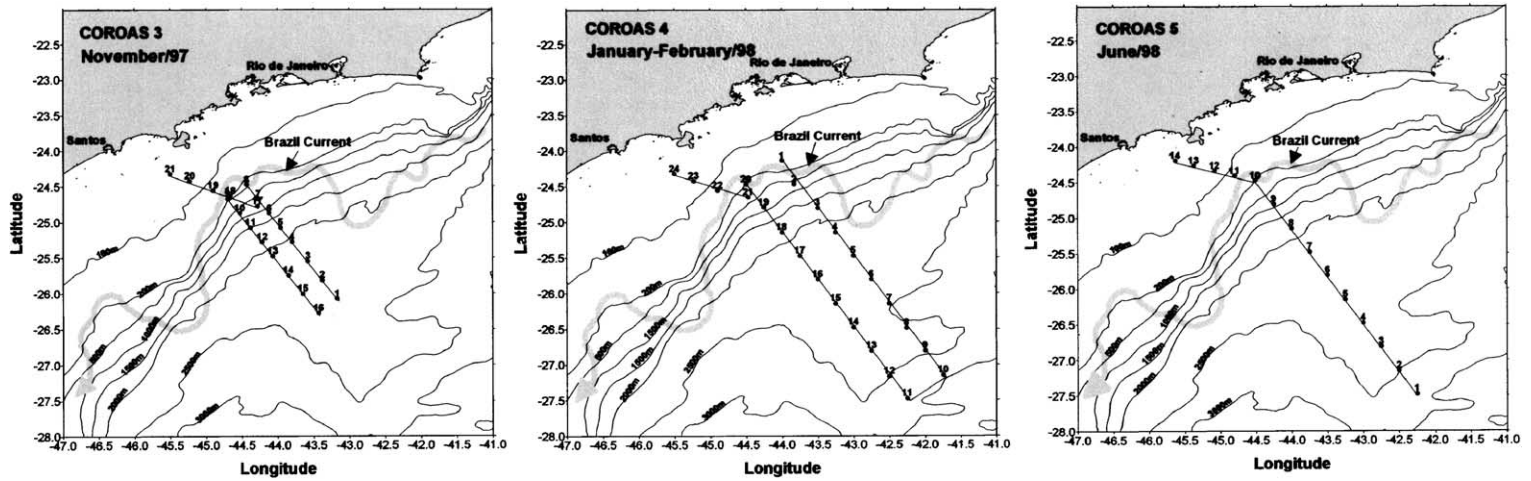


Fig. 1. Transects and stations during the COROAS cruises with R.V. “Prof. W. Besnard”. Locations of nutrients and chlorophyll-*a* sampling are indicated by numbers. The lines indicate $f\text{CO}_2(\text{sw})$, temperature and salinity measurements.

centrations (Aidar et al., 1993; Gaeta, 1999; Giansella, 2000). Higher degrees of O₂ saturation are coincident with the maxima of chlorophyll-*a*, suggesting the photo adaptation of phytoplankton in the lower layers of the euphotic zone (Aidar et al., 1993).

3. Methods

The measurements were made aboard the R.V. “Prof. W. Besnard”, from November 01 to 05, 1997; January 31 to February 06, and on June 25 and 26, 1998, during the “Ocean Circulation in the Southwest Atlantic Region” program (COROAS). The transects and the stations of the three cruises undertaken are shown in Fig. 1. Stations, depths and sampling parameters are presented in Table 1.

The November cruise was called COROAS 3, the January/February one COROAS 4, and the June one COROAS 5.

3.1. *f*CO₂ surface seawater and atmosphere measurements

The surface water was measured continuously at a depth of 3 m on the transects represented in Fig. 1. For the measurements of *f*CO₂ (air), the marine air was supplied by a pump from the top of the vessel where it was free of possible contamination from the ship itself. The *f*CO₂ (air) was measured every 6 to 12 h.

The *f*CO₂(sw) was determined by continuous equilibration of seawater with a closed loop of air and integrated non-dispersive infrared CO₂ detection (LI-COR 6262). The equilibrator was made of glass and submerged in a bath containing the overflowing seawater from which the gas phase was sampled at 1-min intervals, according to Körtzinger et al. (1996). The water temperature in the equilibrator was continuously recorded using a handmade thermo pair with a precision of ±0.01 °C. The differences between the equilibrator and the thermosalinograph temperatures did not exceed 0.6 °C.

Concentration of CO₂ in the equilibrated gas was compared every 6 h with Air Liquide standards of CO₂ in compressed air with nominal concentrations of 0.0, 240.1 and 358.0 ppmv. Its fugacity was calculated from the partial pressure corrected for the non-ideal behaviour of CO₂ using Weiss’s equation (1974).

Table 1

Parameters, depths and sampling stations during the COROAS cruises

Cruise/parameters	Depth (m)	Station number
<i>COROAS 3 (Nov/01–05/97)</i>		
<i>f</i> CO ₂ (sw)	3	underway (1 min intervals)—3 transects
<i>f</i> CO ₂ (atm)	—	each 6–12 h
Chlorophyll- <i>a</i> , phosphate, nitrate plus nitrite	3	1 to 21
Salinity	3	underway (1 min intervals)—3 transects
In situ temperature	3	underway (1 min intervals)—3 transects
<i>COROAS 4 (Jan 31–Feb 06/98)</i>		
<i>f</i> CO ₂ (sw)	3	underway (1 min intervals)—3 transects
<i>f</i> CO ₂ (atm)	—	each 6–12 h
Chlorophyll- <i>a</i> , phosphate, nitrate plus nitrite	3	1 to 24
Salinity	3	underway (1 min intervals)—3 transects
In situ temperature	3	underway (1 min intervals)—3 transects
<i>COROAS 5 (Jun/25–26/98)</i>		
<i>f</i> CO ₂ (sw)	3	underway (1 min intervals)—2 transects
<i>f</i> CO ₂ (atm)	—	each 6–12 h
Chlorophyll- <i>a</i> , phosphate, nitrate plus nitrite	3	1 to 14
Salinity	3	underway (1 min intervals)—2 transects
In situ temperature	3	underway (1 min intervals)—2 transects

The difference between the equilibrator and in situ temperatures was corrected by the Takahashi et al.’s equation (1993), where:

$$fCO_2(\text{sw}) = fCO_2(\text{equil}) \exp[0.0423(T_{is} - T_{eq})] \quad (1)$$

where T_{is} is the sea surface temperature, T_{eq} is the temperature of the seawater in the equilibrator and $fCO_2(\text{equil})$ is the CO₂ fugacity in the equilibrator.

During those periods when the vessel was at a station, measurements of $f\text{CO}_2(\text{sw})$ showed a precision of about $\pm 0.5 \mu\text{atm}$. The precision of $f\text{CO}_2$ (air) measurements was of $\pm 0.2 \mu\text{atm}$.

The accuracy of $f\text{CO}_2(\text{sw})$ is difficult to estimate. From the results of a $p\text{CO}_2$ intercomparison exercise (Körtzinger et al., 2000), the precision of the $f\text{CO}_2(\text{sw})$ measurements was estimated at $\pm 1\text{--}2 \mu\text{atm}$ and the accuracy at about $\pm 5 \mu\text{atm}$.

3.2. Hydrographic and meteorological measurements

Hydrographical and meteorological parameters—in situ temperature and salinity of surface seawater, total pressure, temperature and relative humidity—were available as 1-min averages.

The salinity and temperature of the surface seawater were monitored with a thermosalinograph, which was calibrated against a precision mercury thermometer prior to the cruises and compared with the CTD measurements during the cruises.

The precision and accuracy were $\pm 0.001 \text{ }^\circ\text{C}$ and $\pm 0.01 \text{ }^\circ\text{C}$ for in situ temperature and ± 0.001 and ± 0.005 for salinity, respectively.

3.3. Chlorophyll-*a* and nutrients

Concentrations of chlorophyll-*a* and nutrients were measured at about 20-mile intervals (Fig. 1, Table 1).

Samples for chlorophyll-*a* and nutrients (phosphate and nitrate plus nitrite) were gently filtered onto Whatman GF/F. The former was measured by spectrophotometry of acetone extracts, according to Jeffrey and Humphrey (1975), presenting precision equal to $\pm 0.01 \mu\text{g L}^{-1}$ and accuracy of better than $\pm 1\%$.

Phosphate and nitrate plus nitrite were determined according to Grasshoff et al. (1983). The precision and accuracy were $\pm 0.02 \mu\text{mol L}^{-1}$ and $\pm 15\%$ for phosphate and $\pm 0.2 \mu\text{mol L}^{-1}$ and $\pm 3.3\%$ for nitrate plus nitrite, respectively.

3.4. Calculation of sea–air flux of CO_2

The net sea–air CO_2 flux, F , can be estimated by the equation:

$$F = k k_0 (\Delta f\text{CO}_2)_{\text{sea-air}} \quad (2)$$

where k is the CO_2 gas transfer velocity, k_0 is the solubility of CO_2 in seawater (Weiss, 1974) and $(\Delta f\text{CO}_2)_{\text{sea-air}}$ is the sea–air $f\text{CO}_2$ difference.

The value for $(\Delta f\text{CO}_2)_{\text{sea-air}}$ was calculated by subtracting the $f\text{CO}_2(\text{sw})$ measured in the surface water from the average of atmospheric $f\text{CO}_2(\text{air})$ values for each cruise.

The CO_2 gas transfer velocity was estimated using the formulas of Liss and Merlivat (1986), LM86, and Wanninkhof (1992), W92.

The wind speeds used in the calculation of k were the averages of two positions for COROAS 3 (25°S – 42.5°W and 25°S – 45°W) and three for COROAS 4 and 5 (25°S – 42.5°W , 25°S – 45°W and 27.5°S – 45°W), as formulated by the European Centre for Medium-Range Weather Forecasts (ECMWF), for which the wind speeds are presented each 6 h.

The average $f\text{CO}_2(\text{sw})$, salinity and temperature data were calculated each 6 h and the average net sea–air CO_2 fluxes of the cruises were found by dividing the sampling area into continental shelf, continental slope and open ocean.

4. Results and discussion

4.1. Spatial variation

The distribution of $f\text{CO}_2$ in the surface seawater and the atmosphere and in situ temperature, for the different seasons, can be seen in Fig. 2.

The latitude trends of surface $f\text{CO}_2(\text{sw})$ showed great variation during all the sampling seasons.

During the COROAS 3 cruise (Nov/97) the $f\text{CO}_2(\text{sw})$ results suggest that the ocean was a weak source of CO_2 for the atmosphere, which had a $f\text{CO}_2(\text{air})$ average of $359.6 \pm 4.2 \mu\text{atm}$ and a $\Delta f\text{CO}_2$ of $3.2 \mu\text{atm}$. North of 25°S the $f\text{CO}_2(\text{sw})$ distribution showed great variation, presenting $\Delta f\text{CO}_2$ of up to $78.3 \mu\text{atm}$ (Fig. 2A). The water mass, which characterizes this sampling region, is of the Tropical Water (Miranda, 1985; Campos et al., 1995) (Fig. 3).

The COROAS 4 and COROAS 5 cruises presented the TW water mass in the open ocean and CW evidencing considerable influence of TW ($34 < S < 36.4$) on the continental shelf (Castro and Miranda, 1998), which results from a slight land runoff mixed with TW (Fig. 3).

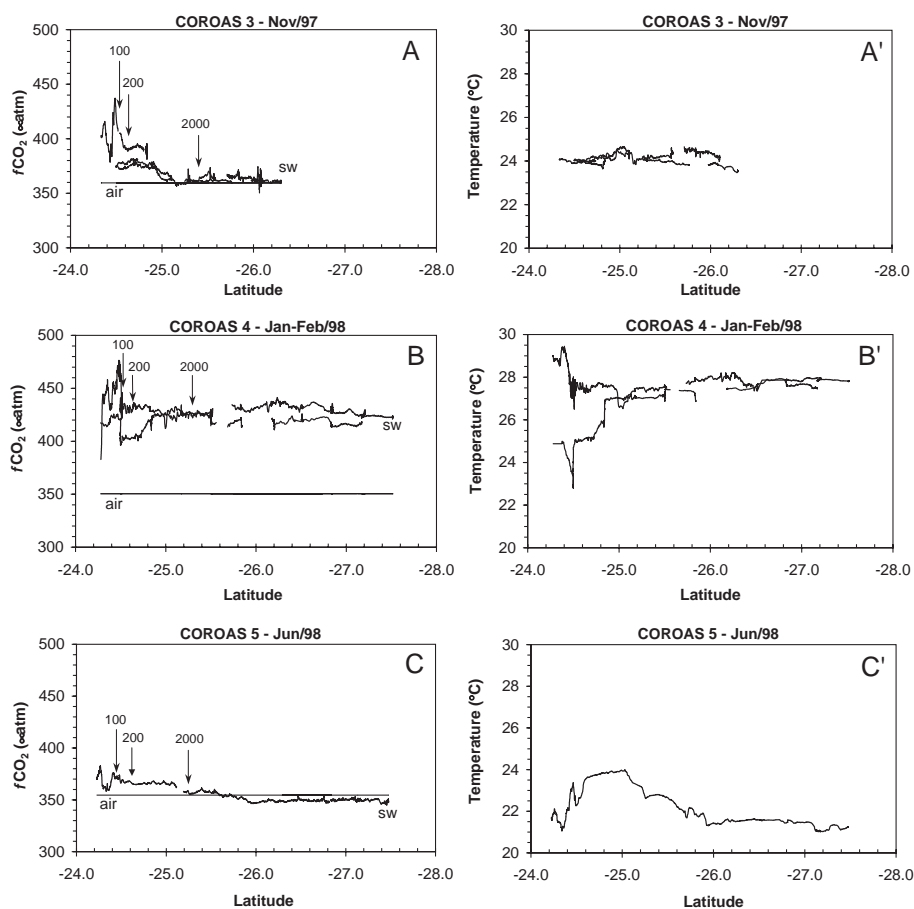


Fig. 2. Distributions of $f\text{CO}_2$ (A, B and C) and in situ temperature (A', B' and C') in surface seawater, during the COROAS 3, 4 and 5 cruises. The numbers within the graphs correspond to the 100, 200 and 2000 m isobaths.

During COROAS 4 (Jan–Feb/98) the $f\text{CO}_2(\text{sw})$ distribution indicated that there was no significant variation south of about 25°S . The $f\text{CO}_2(\text{sw})$ was greater than the $f\text{CO}_2(\text{air})$ of $350.5 \pm 0.9 \mu\text{atm}$ showing a $\Delta f\text{CO}_2$ of from 60 to $80 \mu\text{atm}$. For latitudes north of 25°S the $\Delta f\text{CO}_2$ gradients were as high as $125.8 \mu\text{atm}$. It has thus been inferred that the ocean is a source of CO_2 for the atmosphere regardless of the water masses present.

During the COROAS 5 (Jun/98) a $f\text{CO}_2(\text{air})$ of $354.6 \pm 3.0 \mu\text{atm}$ was observed and the ocean acted as a sink for atmospheric CO_2 , presenting $\Delta f\text{CO}_2$ of up to $-9.5 \mu\text{atm}$ south of 25.5°S (Fig. 2C). Between 24°S and 25.5°S the ocean is a source of CO_2 for the atmosphere with a $\Delta f\text{CO}_2$ of up to $28.3 \mu\text{atm}$.

From the rise of the continental slope, around the 2000 m isobath, up on to the continental shelf, the

$f\text{CO}_2(\text{sw})$ distribution is that of the open ocean data plus a local contribution. In that zone, the surface seawater was a source of CO_2 for the atmosphere, presenting the highest $\Delta f\text{CO}_2$ during all seasons. The highest $\Delta f\text{CO}_2$ occurred in the summer ($+125.8 \mu\text{atm}$); followed by the spring cruise ($+78.3 \mu\text{atm}$) and the winter cruise ($+28.3 \mu\text{atm}$). Besides this, during all the cruises, two maximum peaks of $f\text{CO}_2(\text{sw})$ were observed, both where the water depths were less than 100m and also above the continental shelf.

The concentrations of chlorophyll-*a*, i.e. of primary productivity, were low during all the cruises and their concentrations and distribution showed no significant effect on the $f\text{CO}_2(\text{sw})$ gradients observed (Table 2).

In general, the concentrations of phosphate (PO_4^{3-}) and nitrate plus nitrite ($\text{NO}_3^-/\text{NO}_2^-$) were low. Concentrations of up to $0.65 \mu\text{mol L}^{-1} \text{PO}_4^{3-}$ and 4.0

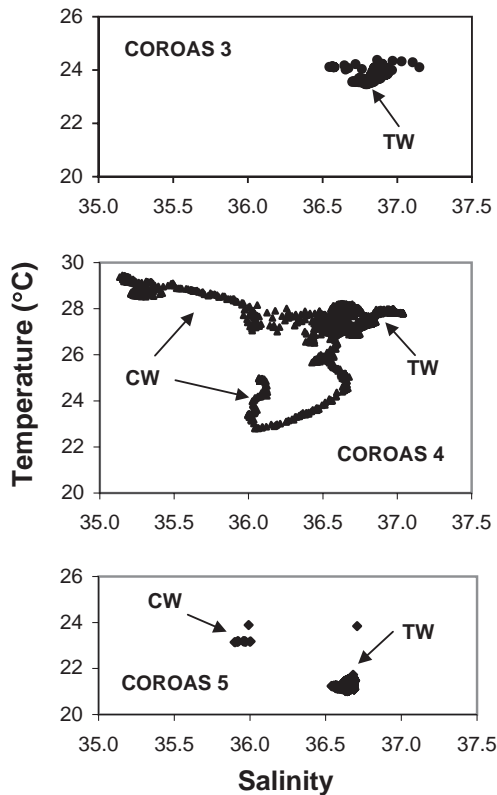


Fig. 3. T – S diagrams of surface seawater during the COROAS cruises.

$\mu\text{mol L}^{-1} \text{NO}_3^-/\text{NO}_2^-$ were found and their averages are presented in Table 2. Dissolved inorganic nitrogen ($\text{NO}_3^-/\text{NO}_2^-$) to phosphate (PO_4^{3-}) atomic ratios of about 3:1 suggest a limitation of primary production by nitrogen in this area. Low nutrient concentrations, low biomass and low productivity are the common features associated with the warm and highly salinity TW water mass (Signorini, 1978).

Despite these low concentrations, it was observed that the chlorophyll- a concentrations were relatively higher in winter than in summer and the nutrients lower in the winter. The same behaviour was observed for chlorophyll- a and primary productivity by Aidar et al. (1993) and Kampel (2003) for the coastal waters of the SSB, which was explained as being due to an intrusion of rich cold water transported from the south by a coastal current, meanders and vortices caused by the BC and coastal upwelling.

Although we observed a certain seasonal pattern in the distributions of chlorophyll- a and nutrients, no

significant correlation could be established between them and the distribution of $f\text{CO}_2(\text{sw})$.

The hydrographic conditions of the study area allow us to propose a possible explanation for the observed pattern in the $f\text{CO}_2(\text{sw})$ distribution. Studies of Castro (1996) and Castro and Miranda (1998) indicate that the T – S characteristics of the area from the continental shelf to the coastline in that region show the presence of South Atlantic Central Water (SACW, $T < 20^\circ\text{C}$ and $S < 36.40$) at about 50 km or less ($< 24.4^\circ\text{S}$) from the coast in the summer, and in the winter the SACW is detected at depths greater than 100 m. The authors report that the interactions between CW, TW and SACW in the surface seawater, which reflect mixing processes, that take place over the continental shelf mainly during the summer. Campos et al. (2000) suggested that the mechanism responsible for pumping the SACW onto the continental shelf was a meander induced continental slope upwelling in the winter, and a combination of continental slope and wind-driven upwelling in the summer. As was to be expected, the coastal upwelling of SACW takes place during the summer but in the winter this process is weaker. Due to this dynamic process, this coastal area is characterized by a higher primary productivity in the subsurface waters at the deeper layers of the euphotic zone (Aidar et al., 1993; Gaeta, 1999; Giancesella, 2000; Kampel, 2003). On the other hand, the studies of Ovalle et al. (1999) in the SBB in the latitudes between 15° and 20°S show a local variation of chemical constituents, including CO_2 . Supersaturation of CO_2 was observed to the

Table 2

Mean values, standard deviations and range of nutrients and chlorophyll- a at the stations during the COROAS cruises

	Chl- a ($\mu\text{g L}^{-1}$)	P- PO_4^{3-} ($\mu\text{mol L}^{-1}$)	N- $\text{NO}_3^- + \text{N-NO}_2^-$ ($\mu\text{mol L}^{-1}$)
COROAS 3			
Mean	0.05	0.13	0.6
S.D.	0.04	0.13	0.9
Range	0.01/0.16	0.00/0.61	0.1/3.9
COROAS 4			
Mean	0.07	0.15	0.4
S.D.	0.06	0.10	0.4
Range	0.00/0.24	0.01/0.28	0.0/1.3
COROAS 5			
Mean	0.12	0.07	0.1
S.D.	0.03	0.05	0.1
Range	0.09/0.18	0.00/0.11	0.0/0.2

south, which may be explained by the activity of the bacterioplankton that competes with phytoplankton for the nutrients in the surface waters and by the bacterial activity associated with the input of dissolved organic nutrients from the small river–mangrove systems. These observations agree with Metzler et al. (1997) who concluded that the study area is mainly of regenerative type production, where the nitrogen compounds are reduced due to plankton excretion and bacterial activity.

Thus, the observed $f\text{CO}_2(\text{sw})$ data for the shelf and slope area, as also those peaks over the continental shelf can be associated with the mechanism of coastal upwelling, with the highest values occurring in summer/spring and the lowest in the winter, and with the local metabolic activity in these waters.

4.2. Seasonal variation

On the basis of the spatial distribution of $f\text{CO}_2(\text{sw})$ and the processes associated with it, the measurements were divided into three subsections: south of latitude 25.3°S , between 24.6°S and 25.3°S , and north of 24.6°S . The former corresponds to the open ocean; the second also, through on the continental slope, and the third to the continental shelf.

For latitudes south of 25.3°S the open ocean presents different $f\text{CO}_2(\text{sw})$ for each season. It acts as a sink for or a source of atmospheric CO_2 , with mean values of $362.8 \mu\text{atm}$ ($\Delta f\text{CO}_2 = +3.2 \mu\text{atm}$) in November (Fig. 2A); $425.5 \mu\text{atm}$ ($\Delta f\text{CO}_2 = +75.0 \mu\text{atm}$) in January/February (Fig. 2B), and $350.6 \mu\text{atm}$ ($\Delta f\text{CO}_2 = -4.0 \mu\text{atm}$) in June (Fig. 2C). These $f\text{CO}_2(\text{sw})$ values suggest that this oceanic area is a slight sink for atmospheric CO_2 during wintertime only.

On the continental slope and continental shelf these gradients are higher than in the open ocean, and the ocean was a CO_2 source for the atmosphere during all seasons. The mean values of $f\text{CO}_2(\text{sw})$ in these areas are presented in Table 3.

4.2.1. Temperature and biological effects

The effects of temperature were observed during the winter cruise (COROAS 5). For the latitudes south of 24.6°S the in situ temperature presents a positive linear relationship with $f\text{CO}_2(\text{sw})$, with a correlation coefficient of 0.92 (Fig. 2C–C'). If no exchange with the atmosphere takes place during the temperature changes of surface seawater, a temperature coefficient of $1.80\%/^\circ\text{C}$ is found for the winter cruise. For COROAS 3 (south of 25°S) and COROAS 4 (south of 24.6°S) a temperature coefficient of $1.70\%/^\circ\text{C}$ is

Table 3

Average of in situ temperature, CO_2 fugacity, and the effects of seasonal temperature/biological changes on surface CO_2 fugacity during the COROAS cruises

Cruise	Temperature ($^\circ\text{C}$)	$f\text{CO}_2$ (μatm)	$(\Delta f\text{CO}_2)_{\text{bio}}$ (μatm)	$(\Delta f\text{CO}_2)_{\text{temp}}$ (μatm)	$T - B$ (μatm)	T/B
<i>COROAS 3 mean</i>						
Latitude $\geq 25.3^\circ\text{S}$	24.08	362.8				
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	24.12	376.7				
Latitude $< 24.6^\circ\text{S}$	24.01	394.9				
<i>COROAS 4 mean</i>						
Latitude $\geq 25.3^\circ\text{S}$	27.69	425.5				
Latitude $\geq 24.6^\circ$ to $\geq 25.3^\circ\text{S}$	26.97	424.6				
Latitude $< 24.6^\circ\text{S}$	27.03	431.1				
<i>COROAS 5 mean</i>						
Latitude $\geq 25.3^\circ\text{S}$	21.58	350.6				
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	23.61	364.2				
Latitude $< 24.6^\circ\text{S}$	22.04	368.7				
<i>Annual mean</i>						
Latitude $\geq 25.3^\circ\text{S}$	24.45	379.6	27.2	99.2	72.0	3.6
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	24.90	388.5	4.8	56.2	51.4	11.7
Latitude $< 24.6^\circ\text{S}$	24.36	398.2	21.7	84.8	63.2	3.9

found with positive correlations of 0.35 and 0.32, respectively. Although a direct linear relationship between temperature and $f\text{CO}_2(\text{sw})$ is not strongly supported by COROAS 3 or COROAS 4, the seasonal distribution of $f\text{CO}_2(\text{sw})$ seems to reflect the change of the in situ temperature, mainly for the open ocean waters. This behaviour is presented in Fig. 4 where all the $f\text{CO}_2(\text{sw})$ data have been normalized to the same temperature (24.57 °C) and also in Table 3 where the average of $f\text{CO}_2(\text{sw})$ and the in situ temperature for each cruise at the latitudes where the salinity was approximately constant are considered, as well as the total alkalinity and dissolved inorganic carbon.

The normalized $f\text{CO}_2(\text{sw})$ data show that COROAS 3 (spring) and 4 (summer) have a very similar distribution for the open ocean and continental slope. The COROAS 5 (winter) differs from the other cruises by about +25–30 μatm for the open ocean but is closer to them on the continental slope. In the shelf zone the summer cruise presents a somewhat different $f\text{CO}_2(\text{sw})$ distribution from those of the spring and winter cruises.

In order to understand the relative importance of the temperature and biological effects on the seasonal changes of $f\text{CO}_2(\text{sw})$ during the COROAS cruises the method of analysis proposed by Takahashi et al. (2002) is applied to the three subsections described above.

To remove the temperature effect from the $f\text{CO}_2(\text{sw})$ data, these were normalized to a constant temperature corresponding to the mean annual in situ temperature of seawater at these latitudes, in accordance with the equation:

$$f\text{CO}_2(\text{sw}) \text{ at } T_{\text{mean}} = (f\text{CO}_2)_{\text{obs}} \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})] \quad (3)$$

where T_{mean} is the mean annual in situ temperature, T_{obs} the in situ temperature values and $(f\text{CO}_2)_{\text{obs}}$ the in situ CO_2 fugacity.

The effect of temperature changes on the observed $f\text{CO}_2(\text{sw})$ is computed by using the equation:

$$f\text{CO}_2(\text{sw}) \text{ at } T_{\text{obs}} = (\text{Mean annual } f\text{CO}_2(\text{sw})) \exp[0.0423(T_{\text{obs}} - T_{\text{mean}})] \quad (4)$$

The biological effect on the $f\text{CO}_2(\text{sw})$ distribution, $\Delta f\text{CO}_2(\text{sw})_{\text{bio}}$, was calculated with the equation:

$$(\Delta f\text{CO}_2(\text{sw}))_{\text{bio}} = (f\text{CO}_2(\text{sw}) \text{ at } T_{\text{mean}})_{\text{max}} - (f\text{CO}_2(\text{sw}) \text{ at } T_{\text{mean}})_{\text{min}} \quad (5)$$

where ‘max’ and ‘min’ indicate the seasonal maximum and minimum values.

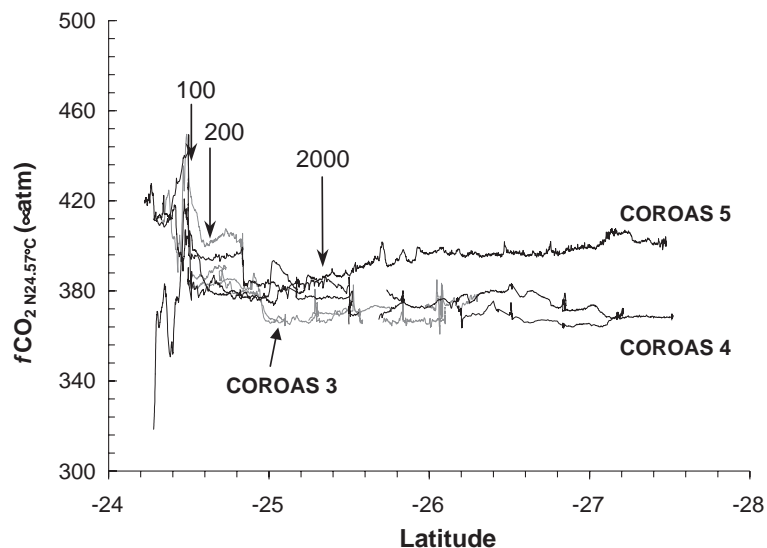


Fig. 4. Normalized $f\text{CO}_2(\text{sw})$ to the temperature of 24.57 °C during the COROAS cruises.

The temperature effect on the $f\text{CO}_2(\text{sw})$ distribution, $(\Delta f\text{CO}_2(\text{sw}))_{\text{temp}}$, was calculated by using the equation:

$$(\Delta f\text{CO}_2(\text{sw}))_{\text{temp}} = (f\text{CO}_2(\text{sw}) \text{ at } T_{\text{obs}})_{\text{max}} - (f\text{CO}_2(\text{sw}) \text{ at } T_{\text{obs}})_{\text{min}} \quad (6)$$

The relative importance of the effects presented in Eqs. (4) and (5) was calculated by the two following expressions:

$$\begin{aligned} (T - B) &= (\Delta f\text{CO}_2(\text{sw}))_{\text{temp}} \\ &\quad - (\Delta f\text{CO}_2(\text{sw}))_{\text{bio}} \text{ or } T/B \\ &= (\Delta f\text{CO}_2(\text{sw}))_{\text{temp}} / (\Delta f\text{CO}_2(\text{sw}))_{\text{bio}} \quad (7) \end{aligned}$$

where T refers to the temperature effect and B to the biological effect on the $f\text{CO}_2(\text{sw})$ distribution.

The results obtained using Eqs. (5), (6), and (7) are presented in Table 3. In all the subsections the relative importance of the temperature effect was greater than that of the biological effect. For the open ocean and shelf zone the ratios T/B were 3.9 and 3.6, respectively, which means that the temperature effect is more than three times greater than the biological

effect. On the continental slope the $f\text{CO}_2(\text{sw})$ distribution is strongly dominated by the temperature effect, and this ratio is 11.7. On the basis of the T/B ratios described and the Revelle factor equal to 8.9 (Schneider and Morlang, 1995), the seasonal biological CO_2 utilization was estimated at about $15 \mu\text{mol kg}^{-1}$ for the open ocean; about $12 \mu\text{mol kg}^{-1}$ for the continental shelf and $3 \mu\text{mol kg}^{-1}$ on the continental slope.

Data presented by Takahashi et al. (1993, 2002) for the South Atlantic ($p\text{CO}_2(\text{sw})$ versus temperature) show the same behaviour as the present data, i.e. a considerable temperature effect on the $f\text{CO}_2(\text{sw})$ data. Those authors point out that the subtropical oceans exhibit a biological effect of less than $50 \mu\text{atm}$ and a temperature effect greater than $80 \mu\text{atm}$. Although the present work is limited to three seasons, the calculated biological effect was $\leq 27.2 \mu\text{atm}$ and the temperature effect $\leq 99.2 \mu\text{atm}$ (Table 3). The normalized $f\text{CO}_2(\text{sw})$ distribution in Fig. 4 agrees with the calculations presented in Table 3 for the open ocean, where the normalized $f\text{CO}_2(\text{sw})$ on the COROAS 5 cruise differs from the others by about $+25\text{--}30 \mu\text{atm}$ and this difference can be attributed to the biological effect on these data, calculated as $27.2 \mu\text{atm}$ by

Table 4

Averages, standard deviations and range of sea–air fluxes of CO_2 in the open ocean and on the slope and shelf during the COROAS cruises, based on the LM86 and W92 formulas

Cruise	LM86 $f\text{CO}_2$ —SD ($\text{mmol m}^{-2} \text{ day}^{-1}$)	LM86 range ($\text{mmol m}^{-2} \text{ day}^{-1}$)	W92 $f\text{CO}_2$ —SD ($\text{mmol m}^{-2} \text{ day}^{-1}$)	W92 range ($\text{mmol m}^{-2} \text{ day}^{-1}$)
<i>COROAS 3 mean</i>				
Latitude $\geq 25.3^\circ\text{S}$	0.1 ± 0.1	0.0/0.2	0.1 ± 0.1	0.0/0.4
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	1.5 ± 1.1	0.5/2.7	2.3 ± 1.6	0.7/4.1
Latitude $< 24.6^\circ\text{S}$	5.8 ± 0.6	5.4/6.2	9.8 ± 1.1	8.9/8.9
<i>COROAS 4 mean</i>				
Latitude $\geq 25.3^\circ\text{S}$	2.7 ± 2.5	0.2/5.8	4.4 ± 3.3	0.4/9.3
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	2.1 ± 1.7	0.3/3.5	3.7 ± 2.2	1.2/5.5
Latitude $< 24.6^\circ\text{S}$	2.0 ± 2.8	0.5/5.2	4.2 ± 2.9	2.5/7.6
<i>COROAS 5 mean</i>				
Latitude $\geq 25.3^\circ\text{S}$	-0.6 ± 0.5	-0.1/-1.0	-1.1 ± 0.9	-0.2/-1.9
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	0.2 ± 0.0	0.2/0.2	0.4 ± 0.0	0.4/0.4
Latitude $< 24.6^\circ\text{S}$	0.1 ± 0.0	0.0/0.1	0.3 ± 0.3	0.1/0.4
<i>COROAS mean</i>				
Latitude $\geq 25.3^\circ\text{S}$	0.7 ± 1.8	-0.6/2.7	1.2 ± 2.9	-1.1/4.4
Latitude $\geq 24.6^\circ$ to $< 25.3^\circ\text{S}$	1.3 ± 1.0	0.2/2.1	2.1 ± 1.7	0.4/3.7
Latitude $< 24.6^\circ\text{S}$	2.6 ± 2.9	0.1/5.8	4.8 ± 4.8	0.3/9.8

Takahashi et al. (2002). However, it seems that over the slope and shelf zones the physical mixing processes and biological activity, other than primary productivity, must also be taken into consideration, because the normalized values still present some sharp gradients which are not to be explained by the primary productivity (chlor-*a*) effect obtained on the basis of the calculations presented in Table 3.

Taking these results into account and bearing in mind that the data show a depletion of nutrients and primary productivity (chlorophyll-*a*) during all seasons, these findings lead to the conclusion that the main contributions to the seasonal $f\text{CO}_2(\text{sw})$ patterns in this open ocean region are the CO_2 exchange with the atmosphere and in situ temperature changes. The boundary between whether the open ocean surface seawater serves as a sink or as a source of CO_2 for the atmosphere is determined by the temperature of about 23°C .

The observations on the slope and shelf zones suggest that the $f\text{CO}_2(\text{sw})$ values vary by virtue of vertical mixing processes and biological activity, as well as of the water temperature.

4.3. Net sea–air CO_2 fluxes

The averages of calculated sea–air CO_2 fluxes based on the LM86 and W92 are listed in Table 4 for the three ocean subsections: open ocean (latitude $\geq 25.3^\circ\text{S}$); slope (latitude $\geq 24.6^\circ$ to $<25.3^\circ\text{S}$) and shelf (latitude $<24.6^\circ\text{S}$). Fig. 5a, b and c present these fluxes for the study area.

In accordance with Table 4 and Fig. 5a, b and c, the CO_2 fluxes indicate that this surface ocean area is a source of CO_2 for the atmosphere except during the winter for the open ocean, where the CO_2 flux calculated was of $-1.1\text{ mmol m}^{-2}\text{ day}^{-1}$, in accordance with W92.

The COROAS 4 cruise presented only slight differences in the magnitude of the fluxes as between the open ocean and the continental shelf (around $4.0\text{ mmol m}^{-2}\text{ day}^{-1}$), whereas on COROAS 3 and 5 these fluxes became greater towards the north (Fig. 5a and c). However, the summer cruise presented greatest variation in the fluxes due to changes in wind speed (Fig. 5b).

In the continental slope waters the CO_2 fluxes ranged from $+0.4$ to $+3.7\text{ mmol m}^{-2}\text{ day}^{-1}$ and in the

shelf zone from $+0.3$ to $+9.8\text{ mmol m}^{-2}\text{ day}^{-1}$. The strongest winds during the spring favoured a greater CO_2 flux than in summer and winter over the continental shelf.

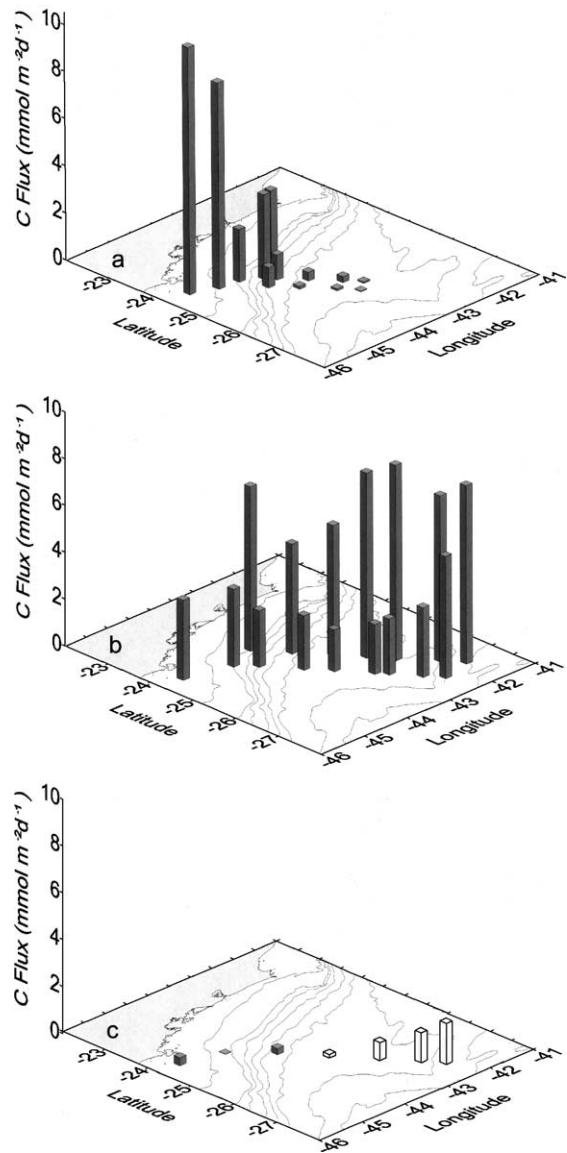


Fig. 5. Net sea–air fluxes of CO_2 ($\text{mmol m}^{-2}\text{ day}^{-1}$) during the COROAS cruises, according to Wanninkhof's formula (1992). a. COROAS 3 cruise. b. COROAS 4 cruise. c. COROAS 5 cruise. The dark grey colour bars within the graphs correspond to a CO_2 flux from the surface seawater for the atmosphere and the light grey one to a CO_2 flux from the atmosphere for the surface seawater.

The COROAS average net fluxes, in moles CO₂ m⁻² year⁻¹, for the open ocean, slope and shelf were +0.4, +0.8 and +1.6, respectively, using the W92 formula. The average flux for the open ocean is slightly higher than the mean annual net flux proposed by Takahashi et al. (2002) for the year of the reference, 1995, for which the data compiled showed a CO₂ flux of about +0.2 mol CO₂ m⁻² year⁻¹ in the corresponding area. However, this oceanic area is still a weak source of CO₂ for the atmosphere.

The sea–air CO₂ fluxes calculated for the shelf waters in various latitudes and for both hemispheres are presented in Table 5.

Most reported sea–air fluxes in Table 5, the ocean acted as a sink of atmospheric CO₂. On the other hand, annually integrated sea–air CO₂ fluxes of +2.5 mmol C m⁻² day⁻¹ (W92) in an upwelling system were reported by Goyet et al. (1998b) for the Omani coast (17–24°N). Although the same behaviour was found in the South Brazilian Bight where upwelling has been reported by several researchers (e.g. Miranda, 1985; Campos et al., 1995; Castro, 1996; Castro and Miranda, 1998, Campos et al., 2000) an upwelling event was not observed during this work and, according to those researchers, the frequency of this event is not well

Table 5
Comparison of sea–air fluxes of CO₂ in shelf waters of the Northern and Southern Hemispheres

Region	Period	$f\text{CO}_2$ (mmol m ⁻² day ⁻¹)	Calculation of transfer velocity	References
Arctic Ocean (Chukchi Sea)	Summer (3-year average)	-7.7 -12.0	LM86 ^a W92 ^b	Murata and Takizawa (2003)
Bering Sea	April/June	-1.8	B78 ^c	Codispoti et al. (1986)
Baltic Sea	Year	-2.5	W92 ^b	Thomas and Schneider (1999)
North Sea	Year	-3.78	WM99 ^d	Thomas et al. (2004a)
English Channel	Year	+0.9	N00 ^e	Borges and Frankignoulle (2003), Thomas et al. (2004a)
Arabian Sea (Omani coast)	Year	+2.5	W92 ^b	Goyet et al. (1998b)
Indian Ocean (Bay of Bengal)	March/April November/December	-4.87–11.10 -1.65–8.77	W92 ^b	Kumar et al. (1996)
East of China	Spring Summer Autumn Winter	-6.5 -4.8 -7.4 -10.8	W92 ^b	Wang et al. (2000)
Pacific Ocean (Central California)	Year (El Niño) Year (La Niña)	-0.8–1.9 +4.1+6.0	WM99 ^d	Friederich et al. (2002)
Atlantic Ocean (Gulf of Biscay)	Year	-4.79 -7.89	LM86 ^a W92 ^b	Frankignoulle and Borges (2001)
Atlantic Ocean (Galician coast)	Year	-3.5 -7.0	LM86 ^a W92 ^b	Borges and Frankignoulle (2002)
Atlantic Ocean (Middle Atlantic Bight)	Year	-3.0	W92 ^b	DeGrandpre et al. (2002)
Atlantic Ocean (South Atlantic Bight)	Year	+6.8	W92 ^b	Cai et al. (2003)
Atlantic Ocean (South Brazilian Bight)	Spring Summer Winter	+9.8 +4.2 +0.3	W92 ^b	This study

^a Liss and Merlivat (1986).

^b Wanninkhof (1992).

^c Broecker et al. (1978).

^d Wanninkhof and McGillis (1999).

^e Nightingale et al. (2000).

established to the study area. Moreover, coastal upwelling areas can act as sources or sinks of atmospheric CO₂ depending on the occurrence of these events, as has been reported by Borges and Frankignoulle (2002) and Ianson and Allen (2002) in the upwelling system off the Galician coast and to the west coast of Vancouver Island, respectively, whose areas are sinks of atmospheric CO₂ on an annual basis.

Realising the large variety in coastal and shelf systems, presently a rather coarse characterisation of these systems into CO₂ sinks and sources appears to be difficult. Our study reports a subtropical region, where the surface seawaters release CO₂ to the atmosphere. Further coastal systems of the world ocean act as CO₂ sources such as the United States South Atlantic Bight (Cai et al., 2003) or a part of the South China Sea (Zhai et al., in press). Moreover, CO₂ release to the atmosphere has, for example, been reported from the English Channel (Borges and Frankignoulle, 2003; Thomas et al., 2004a), the southern North Sea (Thomas et al., 2004a) or the southern Baltic Sea (Thomas and Schneider, 1999) or several European estuaries (Frankignoulle et al., 1998). In contrast various coastal regions absorb CO₂ from the atmosphere (Table 5). Next to the CO₂ air–sea fluxes it is relevant to understand and quantify the CO₂ export of the coastal systems to the open ocean. This export might not necessarily be predictable from the CO₂ fluxes alone, but also depends on external inputs and topographic characteristics. For example, both the South Atlantic Bight and the North Sea export carbon to the Atlantic despite their different CO₂ uptake features. On the other hand, the Baltic Sea does not act as a strong continental shelf pump, since strong sedimentation counteracts the carbon export to the North Sea (Thomas et al., 2003). Thus, CO₂ fluxes in coastal areas and carbon export to the open ocean reveal a variety of features and a classification as proposed by Cai and Dai (2004) presently appears to be unsubstantiated (Thomas et al., 2004b).

Our study in the western South Atlantic contributes to an improved understanding of the continental shelf pump as proposed by Tsunogai et al. (1999), which is essential for the understanding of the role of coastal seas in the ocean carbon cycle.

5. Conclusion

The T – S distribution in each season sampled showed that the predominant surface water mass was essentially the Tropical Water, and Coastal Water with great influence of TW on the continental shelf during the summer and winter cruises. This water mass distribution and the depletion of the nutrients and chlorophyll- a suggest, therefore, that the main contributions to the $f\text{CO}_2(\text{sw})$ gradients in the open ocean are the in situ temperature and the exchange of CO₂ with the atmosphere. This conclusion was supported by linear regression analysis of $\ln f\text{CO}_2(\text{sw})$ and in situ temperature. A temperature coefficient of 1.80%/°C was found for the summer cruise (COROAS 5). For COROAS 3 and COROAS 4 a temperature coefficient of 1.70%/°C was found. No linear relationship between temperature and $f\text{CO}_2(\text{sw})$ was discovered for the continental shelf. These conclusions were confirmed by normalizing $f\text{CO}_2(\text{sw})$ data to the temperature of 24.57 °C. The temperature and biological effects on the seasonal changes of $f\text{CO}_2(\text{sw})$ during the COROAS cruises were evaluated by the method of analysis proposed by Takahashi et al. (2002). This method was applied to the three subsections: the continental shelf, the continental slope and the open ocean. The ratios T/B or the difference $T - B$ showed that the seasonal $f\text{CO}_2(\text{sw})$ distribution is strongly dominated by the temperature effect. The comparison of these calculations with the normalized $f\text{CO}_2(\text{sw})$ data showed that the temperature effect is the main contribution as regards the open ocean, but other processes such as the physical mixing processes and local biological activity must also be taken into consideration for the continental slope and shelf.

The present $f\text{CO}_2(\text{sw})$ values vary greatly from season to season, and these differences are considerable if we take into account the $f\text{CO}_2(\text{sw})$ distribution on the continental shelf and slope. These values suggest that most of the atmospheric CO₂ is absorbed by the open oceanic area during wintertime. On the continental shelf and slope the $f\text{CO}_2(\text{sw})$ was a source of CO₂ for the atmosphere during all seasons.

The CO₂ flux calculations indicate that this open ocean area is a source of CO₂ for the atmosphere in all seasons except the winter, when the mean calculated CO₂ flux was $-1.1 \text{ mmol m}^{-2} \text{ day}^{-1}$, in accordance with W92.

In the continental slope waters the CO₂ fluxes ranged from +0.4 to +3.7 mmol m⁻² day⁻¹ and in the shelf zone from +0.3 to +9.8 mmol m⁻² day⁻¹. The strongest winds during the spring favoured a greater CO₂ flux than in summer and winter over the continental shelf.

Although the present data are restricted to three seasons, it is reasonable to assume that the study area is a source of CO₂ for the atmosphere and the CO₂ sea–air fluxes over the continental shelf and slope could lead to an improved understanding and refined assessments of continental shelf pump.

In this context, this new data set may contribute to a better understanding of the Southwest region of the subtropical Atlantic Ocean with respect to the CO₂ exchange between the surface seawater and the adjacent atmosphere.

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