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Abstract

The potential of the Bellingshausen Sea, Bransfield and Gerlache Straits as sinks for atmospheric CO₂ was investigated by studying the carbon data obtained during FRUELA 95 (December 95-January 96) and FRUELA 96 (January-February 96) cruises. Air-sea exchange of CO₂ and its relation to air-sea O₂ fluxes, surface chlorophyll concentration, physical structures and other environmental variables were also studied. The processes governing the temporal evolution of total inorganic carbon between the two FRUELA cruises were assessed by means of a carbon budget.

During FRUELA 95 the frontal region associated with the Southern Boundary of the Antarctic Circumpolar Current (SbyACC) in the Bellingshausen Sea area presented high undersaturation of surface CO₂ content (<200 µatm), whereas strong oxygen supersaturation (AOU<-48 µmol.kg⁻¹). This was accompanied by the development of a diatom bloom. Therefore, this area acted as a strong CO₂ sink and oxygen source, -6.5±6 and 25±29 (mean±STD) mmol m⁻² d⁻¹, respectively. However, no phytoplanktonic biomass accumulation was reported for this area.
in late January 96 (FRUELA 96). The mean increase of 33 µatm in surface pCO$_2$ between both surveys can be explained by seasonal warming and air-sea equilibration. On the other hand, in the Bransfield Strait area remnants of CO$_2$-rich upwelled water caused it to act as a weak source of CO$_2$ (1.3±1.1 mmol.m$^{-2}$.d$^{-1}$) in early December 95. From this period to late January 96 increasing phytoplanktonic activity reduced surface pCO$_2$ by 30 µatm, leading to a CO$_2$ uptake of −0.9 mmol.m$^{-2}$.d$^{-1}$. The Gerlache Strait presented a mean flux of CO$_2$ and O$_2$ during both FRUELA cruises of −9.6 mmol.m$^{-2}$.d$^{-1}$ and 19.9 mmol.m$^{-2}$.d$^{-1}$ respectively. The carbon budget estimated for this area indicated biological processes as the main factor controlling temporal changes between both FRUELAs. Supporting this conclusion, the estimated carbon flux from the euphotic zone in this area was confirmed from measured sediment trap data.

Significant linear correlations between air-sea CO$_2$ and O$_2$ fluxes were noted during periods of intensive phytoplanktonic activity during FRUELA 95 and in the Gerlache Strait during FRUELA 96.

Keywords: Carbon dioxide, oxygen, air-sea fluxes, carbon budget, Antarctica.
1. Introduction

High-latitude areas play an important role in the global carbon cycle due to the large oceanic area they comprise and because they are, on solubility grounds, potential sinks for dissolved gases (Jones et al., 1990; Hoppema et al., 1995).

Despite its importance to quantify the atmospheric CO$_2$ uptake by the oceans, the role of the Southern Ocean in the global carbon cycle has not yet been elucidated. The reason is its inaccessibility due to rough weather conditions, which make surveys difficult especially during autumn and winter seasons.

There are very few data sets of surface pCO$_2$ distributions in the Southern Ocean, but this situation has begun to change, as more surveys are being carried out in Antarctic waters (Metzl et al., 1991; Murphy et al., 1991 a, b; Takahashi et al., 1993; Poisson et al., 1994; Bellerby et al., 1995; Hoppema et al., 1995; Robertson et al., 1995; Bakker et al., 1997; Rubin et al., 1998). These studies showed that the different sectors of the Southern Ocean present contrasting behaviour. The Atlantic and Pacific sectors appear to be generally CO$_2$-undersaturated during austral summer, while the Indian sector presents large spatial and probably temporal variation (Bakker et al., 1997).

Modelling has been another approach used for estimating the role of the Southern Ocean in the carbon cycle. Tans et al. (1990), using an atmospheric inverse model constrained by the meridional gradient of atmospheric CO$_2$, estimated that the Southern Ocean takes 0.6 to 1.4 GtC.yr$^{-1}$, and suggested that the annually averaged CO$_2$ air-sea gradient is negative and small in this ocean as a whole. From spatio-temporal distributions of atmospheric CO$_2$, Conway et al. (1994) proposed that between 1981-1987 the Southern Ocean behaved as a sink of 0.5 GtC.year$^{-1}$, whilst on 1988-1992 period this sink increased to 1.5 GtC.yr$^{-1}$, explaining the increase in the mean inter-hemispheric gradient. The CO$_2$ uptake estimated by these authors is similar to that proposed by Ciais et al. (1995) (1.6 GtC.yr$^{-1}$) from measurements of $\delta^{13}$C in atmospheric CO$_2$.

Air-sea oxygen exchange receives scant attention, probably as a result of its global atmospheric stability (Duursma and Boisson, 1994). Additionally, few studies have undertaken the relationship between CO$_2$ and O$_2$ fluxes in Antarctic waters (Bouquegneau et al., 1992; Hoppema et al., 1995).
In this study we will present data from the FRUELA 95 and 96 cruises carried out during the summer season of 1995/96 in the western basin of the Bransfield Strait, eastern part of the Bellingshausen Sea and the Gerlache Strait, with the aims of: i) evaluating the spatio-temporal differences between both cruises; ii) estimating the CO₂ and O₂ air-sea exchange and their relationship and iii) accomplishing a carbon budget as a tool for assessing the factors controlling total inorganic carbon changes in the mixed layer.

2. Material and Methods

Two surveys on board the R/V “Hespérides” were conducted on the Gerlache and Bransfield Straits areas from December 1995 to February 1996 as part of the Spanish contribution to JGOFS in the Southern Ocean.

A detailed description of the survey strategy is given by Estrada and Anadón (this issue). Briefly, during both FRUELA 95 and 96 cruises a macroscale grid survey was conducted in the Bellingshausen Sea and western basin of the Bransfield Strait (Figure 1a). The first macroscale survey (Macro’95) was performed between 3 and 9 December 1995, and the second (Macro’96) from 21 to 27 January 1996. Additionally, a mesoscale sampling (Meso’95) was carried out in the western basin of Bransfield Strait during the FRUELA 95 cruise (Figure 1b). Moreover, during both FRUELA 95 and 96 a section along the Gerlache Strait was sampled (Figure 1c).

Continuous profiles of salinity, temperature and pressure were recorded with a EG&G CTD probe. Salinity and density were calculated using the equations of UNESCO (1984). Water samples for nutrients, dissolved oxygen, pH and alkalinity were taken at selected levels. Samples for chlorophyll a were taken from surface to 100 meters depth.

Dissolved oxygen was determined by Winkler potentiometric titration, with an estimated error of ±1μmol.kg⁻¹. Apparent Oxygen Utilisation (AOU) was calculated using oxygen saturation following the Benson and Krause equation (UNESCO, 1986). Chlorophyll a (Chl a) concentration was determined fluorometrically after extraction with 90% acetone overnight, using a 10,000 R Turner fluorometer according to Yentsch and Menzel (1963). The precision of this method is ±0.05mg.m⁻³.
A Metrohm E-654 pH-meter equipped with a Ross (Orion 81-04) combined glass electrode was used to determine pH on the NBS scale. The temperature was measured using a platinum resistance thermometer and finally pH was referred to a standard temperature of 15°C (pH₁₅) according to Pérez and Fraga (1987a). The method has a shipboard precision of ±0.002 pH₁₅ (Ríos and Rosón, 1996) and an accuracy of ±0.004 pH₁₅ using samples of Certified Reference Material (CRMs) provided by Dr. Dickson from the Scripps Institution of Oceanography (Ríos and Pérez, 1999; Ríos and Rellán, 1998).

Alkalinity was determined by automatic potentiometric titration with HCl at a final pH of 4.44 (Pérez and Fraga, 1987b). The electrodes were standardised using an NBS buffer of pH 7.413 and checked using an NBS buffer of 4.008. This method has a precision of 0.1% (Pérez and Fraga, 1987b), and an accuracy of ±1.4 μmol.kg⁻¹ (Ríos and Pérez, 1999; Ríos and Rellán, 1998). Total inorganic carbon (TIC) and partial pressure of CO₂ (pCO₂) were estimated from pH₁₅ and alkalinity data using the thermodynamic equations of the carbonate system (Dickson, 1981) and the constants determined by Mehrbach et al. (1973) and Weiss (1974) with an accuracy of ±4 μmol.kg⁻¹ and ±5 μatm, respectively (Millero, 1995, Lee et al., 1997). We used Mehrbach's constants rather than more recent constants (Roy et al., 1993) since the temperature effect on pCO₂ obtained using Mehrbach's constants is more consistent with the experimental values (Takahashi et al., 1993, Millero et al, 1994, Lee et al., 1997). This procedure was verified by Ríos and Rosón (1996).

The air-sea CO₂ exchange (mmolC.m⁻².d⁻¹) was calculated using the following equation:

\[ F_{CO_2} = 0.24 \cdot k \cdot S \cdot \rho \cdot 10^{-3} \cdot (pCO_2_{oc} - pCO_2_{at}) \]  

(1)

where k is the exchange coefficient (cm.h⁻¹), S is CO₂ seawater solubility (mol.kg⁻¹.atm⁻¹), pCO₂oc is surface ocean CO₂ partial pressure, pCO₂at is atmospheric CO₂ partial pressure (both in μatm) and 0.24 is a unit conversion factor. Seawater CO₂ solubility is calculated from Weiss (1974), ρ is seawater density in kg.m⁻³.

Seasonal and inter-annual variations in atmospheric CO₂ are small compared to pCO₂ variations in the surface ocean (Andrié et al., 1986). In addition, on the Southern hemisphere the seasonal amplitude of atmospheric CO₂ partial pressure (pCO₂at) is much smaller than in the northern hemisphere and their phases are opposite (Conway et al., 1994). We have therefore assumed a constant value of pCO₂at equal to 358.5 μatm for
FRUELA 95 and 96 cruises. This value was estimated from CO$_2$ mixing ratios taken at the Palmer station ($64^\circ 55' S$, $64^\circ 00' W$) reported by the NOAA, Climate Monitoring and Diagnostics Laboratory (CMDL), Carbon Cycle group during the sampling period.

The impact of wind speed on the exchange coefficient, $k$, was calculated using the equations given by Liss and Merlivat (1986) modified by Woolf and Thorpe (1991):

\[
\begin{align*}
    k &= 0.17 \cdot U_{10} \cdot (660/Sc)^{2/3} & \text{U}_{10} < \text{U}_1: \text{smooth water regime} \quad (2a) \\
    k &= (2.85 \cdot U_{10} - 9.65) \cdot (660/Sc)^{1/2} & \text{U}_{10} > \text{U}_1: \text{rough water regime} \quad (2b) \\
    \text{U}_1 &= 9.65 \cdot [2.85 - 0.17 \cdot (660/Sc)^{1/6}]^{-1} \quad (2c)
\end{align*}
\]

where $Sc$ is the Schmidt number defined below, and $U_{10}$ is the wind speed 10 m above the ocean surface (m.s$^{-1}$). The Schmidt number is calculated from its relation with temperature (Jähne et al., 1987; Wanninkhof, 1992):

\[
    Sc = 2073.1 - 125.62 \cdot T + 3.6276 \cdot T^2 - 0.043219 \cdot T^3
\]

where $Sc$ is the Schmidt number and $T$ is temperature (°C).

Meteorological parameters (air temperature, atmospheric moisture content, atmospheric pressure at sea level, wind speed at 10 m above sea level and wind direction) were taken from the shipboard online data-acquisition system, which produced 5 minutes averages.

One of the major uncertainties in the assessment of air-sea gas exchange is the parameterization of the dependence of the exchange coefficient on wind speed (Wanninkhof, 1992; Lundberg, 1994, Bakker, et al., 1997). The Liss-Merlivat relationship used in this study, is based on gas transfer velocities measured over 1-2 days on a small lake. If used this relationship with long-term averaged winds, low gas transfer values are obtained (Wanninkhof, 1992). Thus, ten minutes averages around the station time were used for the Woolf and Thorpe (1991) gas exchange coefficient. Considering an error of $\pm 1$m.s$^{-1}$ in the wind speed, of $\pm 4$ µatm in pCO$_2$oc and $\pm 1$ µatm in pCO$_2$at, the maximum absolute error in FCO$_2$ is $\pm 1.5$ mmolC.m$^{-2}$.d$^{-1}$, this is a relative error to its mean value of $\pm 32\%$.

Oxygen fluxes (mmolO$_2$.m$^{-2}$.d$^{-1}$) were calculated using the following equation:

\[
    \text{F O}_2 = -0.864 \cdot k_{O2} \cdot \rho \cdot 10^{-3} \cdot 10^{-3} \cdot \text{AOU}
\]

(4)
where \( k \ (10^3 \text{-cm.s}^{-1}) \) is the piston velocity for oxygen, AOU is the apparent oxygen utilisation defined previously \((\mu\text{mol.kg}^{-1})\) and 0.864 is an unit conversion factor. The relationship between \( k_{O_2} \) and wind speed has been studied by Kester (1975) and parameterized by Rosón (1992). \( \rho \) is seawater density in kg.m\(^{-3}\). The estimated relative maximum error of \( F_{O_2} \) is about ±35%.

Positive values of \( FCO_2 \) and \( FO_2 \) indicate effluxes of both gasses to the atmosphere, negative values indicate input from the atmosphere to the ocean.

3. Results

Surface distributions.

Hydrography overview.

The surveyed area is characterised by two main hydrographic features: the Southern boundary of the Antarctic Circumpolar Current (SbyACC) is a circumpolar structure, separating the Antarctic Circumpolar Current waters from an area of relatively vertical homogeneity extending on the South Shetlands continental shelf and the Bransfield current (BC) in the western basin of the Bransfield strait (Figure 1a, Figure 3a from García et al., this issue).

More detailed, hydrographic and dynamic conditions in Bransfield Strait are marked by the presence of a NE-SW thermal frontal area, the Bransfield Front (Gomis et al., this issue; García et al., this issue) (Figure 1b). This front separates Transitional Zonal Water with Bellingshausen influence (TBW) in the Northwest from Transitional Zonal Water with Weddell Sea influence (TWW) in the Southeast (García et al., this issue).

FRUELA 95

In the western basin of the Bransfield Strait, surface salinity and temperature reflected a cold (-0.6 to -0.3 °C) and relatively salty (33.95-34.13) water mass with a Weddell Sea influence (García et al., this issue). Whereas in the South-west area a warmer (-0.7 to 0.14 °C) and fresher (33.7-33.8) water mass with a Bellingshausen Sea origin contrasted to the warm water (0 to 0.5 °C) coming from the Drake passage (García et al., this issue) (Figure 2a).

Surface distributions of Chl \( a \), AOU and pCO\(_2\) (Figure 2b-d) were marked by a SW-NE frontal zone, which was related to the SbyACC. Associated with this front an
area of high photosynthetic activity on the North-eastern part of the Bellingshausen Sea (Belling.) domain (see Figure 1a for domains) can be discerned from surface distributions of these variables. The phytoplankton activity in this area was denoted not only by a strong maximum in chlorophyll (4 mg.m\(^{-3}\)) but also by minima of pCO\(_2\) (194 µatm), and AOU (-48 µmol.kg\(^{-1}\)) (station 15, figure 3b-d). Moreover, Castro et al. (this issue) described the highest rates of nutrient utilisation in this area. Surface mean characteristics in the Belling. domain during FRUELA 95 can be seen in table 1.

The Bransfield Strait (Bransf.) domain during the 1995 survey presented the lowest mean surface temperature (-0.5ºC) (see Figure 2a and table 1), Chl \(a\) concentrations ranged from 1 to 2 mg.m\(^{-3}\) and AOU values were undersaturated (12 µmol.kg\(^{-1}\)) as a mean (Figure 2b and c, table 1). But the most notable feature was the positive values of \(\Delta pCO_2\) (Figure 2d and table 1), revealing that it acted as a weak source of CO\(_2\) to the atmosphere in contrast with the Belling. domain, as we will see later on.

As suggested by the corresponding surface distributions, there existed a high correlation (model II, Sockal and Rolhf, 1995) between surface AOU and pCO\(_2\):

\[
pCO_2(\pm 25)=328(\pm 7)+2.3(\pm 0.3)\cdot AOU, \quad r^2=0.82, \quad p<0.0001
\]

This relationship shows that once oxygen is equilibrated, pCO\(_2\) is still undersaturated with respect to the atmospheric value. This fact can be related to the slower equilibration timescale for carbon dioxide (Broecker and Peng, 1982).

No significant correlation was found between pCO\(_2\) and Chl \(a\) concentration. However, two groups of stations can be discerned according to the relationship between pCO\(_2\) and chlorophyll: those with a surface pCO\(_2\) highly undersaturated (<270 µatm) corresponded to Chl \(a\) values higher than 2.5 mg.m\(^{-3}\), and those with lower chlorophyll concentrations (<2 mg.m\(^{-3}\)) associated with a wider range of surface pCO\(_2\) levels (370-270 µatm), but clearly less undersaturated than the previous group. Thus, CO\(_2\) uptake by photosynthetic organisms is supposed to control surface CO\(_2\) distribution during Macro’95.

Concerning the air-sea exchange of CO\(_2\) during Macro’ 95 (Figure 2f), only the western basin of the Bransfield Strait behaved as a weak source of carbon dioxide to the atmosphere, with a mean value of 1.2 mmolC.m\(^{-2}\).d\(^{-1}\) (Table 1). Whereas the maximum influx of CO\(_2\) was located in the Belling. domain, reaching values as low as -20
mmolC·m⁻²·d⁻¹. These maxima influxes did not coincide with the maxima pCO₂ gradient associated to the SbyACC, due to lower wind velocities recorded in this area.

The distribution of the air-sea oxygen exchange during Macro’95 (Figure 2e) resembled that of CO₂ but in opposite direction:

\[ FCO₂ (±3.6) = -2.2 (±0.9) -0.18 (±0.03)·FO₂, \quad r^2=0.69, \quad p<0.0001. \] (6)

According to this equation and supporting equation (5) there should be a residual carbon flux towards the ocean although oxygen is already equilibrated.

As commented previously, a more detailed survey was carried out in the western part of the Bransfield Strait during FRUELA 95 (Meso’95, figure 1b). Here, the Bransfield front can be discerned by hydrographic and nutrients distributions, and by surface pCO₂ (Figure 3d). In a NE-SW orientation an area with a CO₂ content around 345 μatm separated TBW in the Northwest from TWW in the Southeast with higher pCO₂ values. In contrast, neither the surface distribution of chlorophyll nor AOU presented a clear relation to hydrographic structures. However, a North-eastward increase in the cumulative photosynthetic activity can be assessed from the surface distribution of AOU (Figure 3c). Surface Chl a concentration (Figure 3b) ranged from 0.8 to 4.4 mg·m⁻³, with the highest values in the TWW area.

Neither Chl a nor AOU presented a significant correlation with pCO₂. Nevertheless in the North-eastern part of the surveyed area undersaturated values of CO₂ were associated to supersaturation of oxygen and to relatively high values of Chl a and, on the other hand, the maximum in surface pCO₂ content near Trinity I. coincided with the maximum AOU concentration (Figure 3c and d). Therefore, in this local area CO₂ effluxes were recorded and associated with maximum influxes of oxygen (Figure 3e and f).

FRUELA 96

Dynamic features remained practically the same during both Macro’95 and 96 (Gomis et al., this issue). However, hydrographic variables showed the influence of seasonal warming, the greatest rise in the mean surface temperature was recorded in the Belling. domain (1.91 °C, table 2). In general, surface pCO₂, AOU and Chl a ranges during macroscale 96 were reduced to about a half with respect to conditions during macroscale 95.
The highest concentrations of surface Chl \( a \) were reported during Macro’96 in the Bransfield Strait (Figure 4b). Although the range of surface oxygen variation was reduced from early December 95 (330-400 \( \mu \)mol.kg\(^{-1}\)) to late January 96 (326-350 \( \mu \)mol.kg\(^{-1}\)), surface AOU (Figure 4c) presented a wider range of values (from –6 to 10 \( \mu \)mol.kg\(^{-1}\)) during Macro’96 due to the greater surface temperature gradient. Warm water of the Belling. domain was slightly supersaturated as a mean (AOU=1 \( \mu \)mol.kg\(^{-1}\), table 1), while the highest undersaturations were recorded in the colder Bransfield Strait. This high undersaturation coincided with local CO\(_2\) surface values well above atmospheric levels (Figure 4d). Conversely, the lowest surface \( \text{pCO}_2 \) was recorded, as during Macro’95, in the Belling. domain.

On the other hand, no significant correlation was found between either AOU or Chl \( a \) and \( \text{pCO}_2 \) on surface waters during this period. These evidences suggest that physical factors as well as biological activity influenced surface \( \text{pCO}_2 \) distribution during Macro’96.

During late January 96, only the area near Livingston island in the Bransf. domain behaved as a source of CO\(_2\) (1.6 mmolC.m\(^{-2}\).d\(^{-1}\), figure 4f). However, considering the whole domain it was practically in atmospheric equilibrium (Table 1). The mean influx calculated for the Belling. domain was -4 mmolC.m\(^{-2}\).d\(^{-1}\), only 2 mmolC.m\(^{-2}\).d\(^{-1}\) lower than during early December 95.

Surface variability of oxygen fluxes during FRUELA 96 did not reflect that of CO\(_2\) fluxes. The oxygen flux distribution was modulated by AOU, which was in turn, mainly controlled by temperature. Fluxes of oxygen towards the atmosphere were obtained for cold surface waters in the Bransfield Strait (Figure 4e). In comparison to Macro’95 oxygen fluxes during Macro’96 were 10 fold lower.

**Gerlache Strait sections during FRUELA 95 and 96**

Temperature distribution in the upper 100m of the southwestern part of the Gerlache Strait sampled area (Figure 5a and e) was characterised by a minimum around 50m, belonging to the AASW (Antarctic Surface Water) (García *et al.*, this issue). This minimum disappeared in the stations located near the Scholaert Strait during both FRUELA cruises, resulting in a nearly homogeneous vertical profile of temperature in the Gerlache central area (Station 40 in figure 5a and 193 in figure 5e). This fact can be attributed to an intrusion of water from the Bellingshausen Sea across the Scholaert
Strait (García et al., this issue). In contrast, the upper water column in the SW and NE areas was highly stratified during FRUELA 95, the great thermal gradient, as well as a high near-surface salinity gradient (not shown) can be related to ice-melting. During early December 95, the SW and NE areas presented high surface concentrations of Chl a (>3mg.m^{-3}) (Figure 5d) especially the NE one with a maximum of 7mg.m^{-3}. These biomass accumulations were associated with shallow mixed layer depths (6-17m) and high stratification (Castro et al., this issue). A subsurface maximum of Chl a (4 mg.m^{-3}) related to a v-shaped distribution of AOU and pCO_2 was discerned in the central area of the Gerlache Strait (Figure 5b and c), in agreement with the local downwelling suggested by temperature and the deepening of the UML (35m) (Castro et al., this issue).

Surface accumulations of phytoplankton biomass on both sides of the Gerlache Strait were related to high dissolved oxygen contents (>330 µmol.kg^{-1}) (not shown), but only surface waters on the NE area presented slight oversaturations of oxygen (Figure 5c), whereas the SW area was significantly undersaturated, likely due to lower temperature values. Surface water CO_2 contents (Figure 5b) were lower than atmospheric ranging from 288 to 340 µatm, with a minimum of 270 µatm in the SW area. Below 50m pCO_2 was 457±23 µatm.

No correlation was found between surface-water pCO_2 and either AOU or Chl a.

Upper level hydrographic conditions in the Gerlache Strait during early January 96 showed the influence of seasonal warming, as water temperature increased by about 0.6 °C (Figure 5e) and salinity (not shown) decreased by about 0.3 from conditions during December 95.

The vertical distribution of Chl a concentration in January 96 (Figure 5h) presented a similar pattern to that of December 95. The highest concentrations were noted in the SW and central areas, where surface stratification was higher (Castro et al., this issue). Surface water was oxygen supersaturated (Figure 5g), in agreement with a seawater CO_2 content in the upper 30 meters strongly under atmospheric level (Figure 5f).

Although no subsurface Chl a maximum was distinguished in the central zone during FRUELA 96 (Figure 5h), Chl a reached 4 mg.m^{-3} at 40m depth, indicating once again an accumulation of phytoplankton biomass near the Scholaert Strait channel. Accordingly, pCO_2 and AOU isolines turned considerably downwards as they did
during the previous survey in the same area, showing the influence of the influx across
the Scholaert Strait.

Surface \( pCO_2 \) and AOU were significantly correlated \((\Delta pCO_2 / \Delta AOU = 1.25 \pm 0.27, r^2=0.85, p<0.0093)\). Therefore, biological activity was probably mainly controlling
the \( CO_2 \) content in the Gerlache Strait during early January 96.

Air-sea fluxes in the Gerlache Strait area are shown in figure 6. Regarding air-sea
\( CO_2 \) exchange, this area acted as a mean sink for atmospheric \( CO_2 \) \((-3.8 \text{ mmol.m}^{-2}.\text{d}^{-1},
\text{table 1}) \) during December 95, with the highest uptake of \( CO_2 \) in the central area (Figure
6a). During early January 96, the mean \( CO_2 \) influx in the Gerlache Strait changed to \(-16
\text{ mmol.m}^{-2}.\text{d}^{-1} \) (Table 1), and in contrast to the previous survey the highest fluxes were
recorded at the limits of the strait, where elevated air-sea gradients were reported.

No significant correlation was found between oxygen and \( CO_2 \) fluxes (Figure 6) in
Ger’95. Both fluxes showed the highest values in the same direction at the central area.

Oxygen fluxes in early January 96 (Figure 6b) presented an inverse pattern to
those of \( CO_2 \) following the equation:

\[
FCO_2 (\pm 5.8) = -4.6 (\pm 3.4) - 0.22 (\pm 0.05) \cdot FO_2, \quad r^2=0.85, \quad p<0.0083 \tag{7}
\]

As during Macro’95, once oxygen is equilibrated, there should be a residual flux
of \( CO_2 \) into the ocean.

**Temporal changes of \( pCO_2 \) in surface water**

Another method to assess the processes governing the variability of surface \( CO_2 \)
content is separating \( CO_2 \) temporal changes according to the formulation of Poisson *et
al.* (1993) and Bakker *et al.* (1997):

\[
\Delta f/\Delta t = [\partial f/\partial t]_T + [\partial f/\partial t]_R + [\partial f/\partial t]_R \tag{8}
\]

where \( f \) stands for \( CO_2 \) fugacity, \( \Delta f/\Delta t \) is the temporal \( fCO_2 \) variations during the period
\( \Delta t \), which are the sum of variations due to thermodynamic changes (those related to
temperature and salinity, \([\partial f/\partial t]_T \)), air-sea exchanges \(( [\partial f/\partial t]_R \)) and a residual term
\(( [\partial f/\partial t]_R) \) ascribed to the combined effects of biological activity, mixing, upwelling and
variability of water masses in the studied region. Following this formulation, we will
calculate the temporal changes (in this case daily) in surface \( pCO_2 \) from FRUELA 95 to
96 in the Bellingshausen Sea (Belling.), Bransfield (Bransf.) and Gerlache (Ger.) Strait
domains (Figure 1a, table 2).
Here we assumed an ideal-gas behaviour of CO$_2$ as the difference between fCO$_2$ and pCO$_2$ is about 0.7% (Weiss, 1974). Therefore the three first terms in equation (8) can be quantified by measurements made on board. Thus, the residual daily change of pCO$_2$ can be computed and ascribed to vertical turbulent diffusion and biological activity, neglecting water-masses mixing and upward motion (Gomis et al., this issue) (Table 2).

The estimated error for $\Delta$pCO$_2$/Δt is about ±25%. The daily thermodynamic change of surface pCO$_2$, ($[\partial$pCO$_2$/ $\partial$t]_T$), was calculated using the CO$_2$ system equations and constants referred in the “Materials and methods” section. The estimated maximum relative error for $[\partial$pCO$_2$/ $\partial$t]_T$ was about ±58%. The daily change of surface pCO$_2$ due to air-sea exchange ($[\delta$pCO$_2$/ $\delta$t]_F$), was estimated according to Bakker et al. (1997) as:

$$[\partial$pCO$_2$/ $\partial$t]_F = - F_{av} \cdot \beta \cdot pCO_{2w} \cdot TTIC^{-1}$$  (9)

where $F_{av}$ and pCO$_{2w}$ are the average air-sea exchange an surface CO$_2$ respectively, $\beta$ the buffer or Revelle factor and TTIC is the average total amount of total inorganic carbon (TIC) in the mixed layer at the beginning of the period for each domain.

The average air-sea flux $F_{av}$ was calculated as the average of fluxes for each domain. pCO$_{2w}$ is the average surface CO$_2$ content for each domain and the Revelle factor $\beta$ ($\beta=\delta\ln(pCO_2)/\delta\ln(TIC)$) was computed from surface measurements in each domain and period.

TTIC was calculated according to Bakker et al. (1997), as the product of the average TIC in the mixed layer, the mixed layer depth and the density for the beginning of each period. Mixed layer depths were estimated form CTD profiles using the criterion of Mitchel and Holm-Hansen (1991) (Castro et al., this issue). The relative error of $[\partial$pCO$_2$/ $\partial$t]_F$ was ±27%.

Taking into account the estimated errors for the total, thermodynamic and the air-sea terms the maximum relative error for the residual term was about ±33%.

In the Belling., domain surface pCO$_2$ increased at 0.65 μatm.d$^{-1}$ between FRUELA 95 and 96. This change corresponded to the combined effect of the CO$_2$ air to sea entry (0.21 μatm.d$^{-1}$) and to the raise in 1.9°C of surface temperature (as salinity effect was negligible, <1μatm in 51 days) leading to an increase in 0.35 μatm.d$^{-1}$. The residual daily changes of pCO$_2$ were small for this domain.
In the Bransfield Strait domain surface pCO$_2$ decreased at a rate of -0.59 μatm.d$^{-1}$. As air-sea CO$_2$ exchange influence was small, this change would have been almost twice as large, if the increase in 1.3°C of surface temperature had not counteracted the decrease in 0.39 μatm.d$^{-1}$. Residual daily changes in this area can be attributed to net phytoplankton uptake of dissolved CO$_2$ as suggested, by the increase in nutrients anomalies in this area between FRUELA 95 and 96 (Castro et al., this issue).

In absolute terms, the Gerlache Strait presented the highest daily variation in surface pCO$_2$ (-1.75 μatm.d$^{-1}$, table 2). The observed high reduction in surface pCO$_2$ would have been even larger if air-sea exchange of CO$_2$ had not added 1.15 μatm.d$^{-1}$, resulting in a residual daily change of –2.9 μatm.d$^{-1}$. The large decrease in surface pCO$_2$ in this area from December 95 to January 96 can be related to phytoplankton CO$_2$ uptake as suggested by the increases in surface mean Chl a between FRUELA 95 and 96 from 3.9 to 8.3 mg.m$^{-2}$ (Table 1), nutrient depletions (Castro et al., this issue) and primary productivity (Varela et al., this issue). Therefore, during this period the influence on pCO$_2$ of biological activity exceeded that due to physical processes.

**Temporal changes of total inorganic carbon in the upper mixed layer**

The total CO$_2$ content (TIC) in the upper mixed layer (UML) is controlled by the following processes: the air-sea CO$_2$ exchange, the biological CO$_2$ uptake/respiration, advective transport of water and diffusive transport of CO$_2$ (Chipman et al., 1993). In the previous section residual daily changes of pCO$_2$ in the surface layer ($[\partial pCO_2/\partial t]_R$) have been estimated and ascribed to biological activity and vertical advection. In this section, according to the formulation of Bakker et al. (1997), we will obtain net residual daily changes of TIC in the UML for each domain, which can be calculated from $[\partial pCO_2/\partial t]_R$ ($R_{pCO_2}$), or directly from TIC changes in the UML, once corrected for air-sea exchange ($R_{TIC}$) (Table 3).

As commented in section 3, residual daily changes (R) were attributed to upward diffusion (U) and biological activity. Biological activity accounts for primary production (P) minus mineralization (M), or for biomass increase (B) plus export due to sedimentation (E). Therefore:

\[
R = \text{Upward transport (U)} - \text{Primary production (P)} + \text{Mineralization (M)} \quad (10a)
\]

\[
= \text{Upward transport (U)} - \text{Biomass increase (B)} - \text{Export (E)} \quad (10b)
\]
Residual daily changes based on pCO$_2$ were calculated using the formula:

$$R_{pCO_2} = \left[ \frac{\partial pCO_2}{\partial t} \right]_R \cdot TTIC \cdot \beta^{-1} \cdot pCO_{2w}^{-1}$$  

(11)

where all these parameters have been defined in the previous section and taken from table 2 for each domain. The estimated relative error for this new variable was about ±65% from its mean value. Residual daily changes of TIC (R$_{ATIC}$) in the upper mixed layer were also obtained from changes of TIC in the UML once corrected for the air-sea exchange (R$_{TIC}$). The maximum relative error of R$_{TIC}$ was about ±31% from its mean value.

The upward flux of TIC was evaluated from:

$$U = -K_z \cdot (\delta TIC/\delta z)$$  

(12)

where K$_z$ is the eddy diffusivity coefficient, with a value of 0.5 cm$^2$.s$^{-1}$ (Gordon et al., 1984) and (δTIC/δz) is the gradient of TIC between the upper mixed layer depth and 100m, where the maximum gradient in the TIC profiles has been found (Castro et al., this issue). The lowest upward fluxes of TIC into the mixed layer were calculated for the Bransfield domain (1.8 mmol.m$^{-2}$.d$^{-1}$, table 3), whereas in the Gerlache and Bellingshausen domains greater TIC gradients leaded to upward fluxes about three fold higher.

Values of $^{14}$C primary production (P) in the UML were obtained from Varela et al. (this issue). Biomass increases were calculated solely from particulate organic carbon (POC) changes in the mixed layer (Castro et al., this issue). Changes in the dissolved organic carbon (DOC) content have been neglected assuming uniformity with time (Kähler et al., 1997, Bakker et al., 1997) due to the lack of data for the FRUELA 96 cruise.

Residual daily changes of TIC based on pCO$_2$ suggested a net TIC increase in the UML content of 2.2 mmol.m$^{-2}$.d$^{-1}$ in the Belling. Domain (Table 3). Residual daily changes based on TIC without correction for air-sea exchange (R$_{ATIC}$) (Table 3) indicated that in this domain there was a gain in the TIC content of the UML, however the large mean air-sea CO$_2$ flux in this area during both FRUELA cruises almost cancelled out this increase giving rise to a slightly net decrease (R$_{TIC}$=-0.3 mmol.m$^{-2}$.d$^{-1}$). Biomass decreased and although there was upward advection of TIC, the latter was supposed to decrease in the upper mixed layer, by export from the UML at a rate of 9 mmol.m$^{-2}$.d$^{-1}$. However, we lack of sediment trap data to confirm this conjecture.
The higher uncertainty committed when calculating residual changes of carbon based on $R_p\text{CO}_2$, led us to use $R_{\text{TIC}}$ for estimating the mineralization and export rate of carbon (Table 3). Despite the large difference, $R_p\text{CO}_2$ and $R_{\text{TIC}}$ suggest a net decrease of TIC in the UML of the Bransf. domain between FRUELA 95 and 96. Estimated values of mineralization indicate that 87% of primary productivity was recycled in the mixed layer, and about 12% exported from it (Table 3). And as in the previous area no sediment trap data were collected.

The two methods for calculating residual daily changes of TIC gave higher and more consistent values for the Gerlache domain. These results were in agreement with the elevated changes of POC (Table 3, dPOC) in the UML of this area. The high values of primary productivity and residual daily changes of TIC reported suggest low efficiency of carbon recycling. The estimated mineralization and export constituted 14% and 58% of primary production, respectively. Conversely to the other areas, we have available data from sediment traps (Anadón et al., this issue), our estimated carbon exported from the euphotic zone (23.5 mmol.m$^{-2}$.d$^{-1}$ using $R_{\text{TIC}}$ and 19.5 mmol.m$^{-2}$.d$^{-1}$ using $R_p\text{CO}_2$, table 3) is within the range obtained by these authors, 19.8-86.6 mmol.m$^{-2}$.d$^{-1}$, supporting our estimated values of $R_{\text{TIC}}$ and $R_p\text{CO}_2$.

4. Discussion

$pCO_2$ distribution and controlling factors

The results presented in this paper for different areas of the Southern Ocean (Bransfield and Gerlache Straits and Bellingshausen Sea) show that surface $pCO_2$ distribution and controlling factors during the same season vary spatially and temporally. Thus, supporting the idea of the Southern Ocean as a “mosaic” of subsystems (Tréguer and Jacques, 1992; Robins et al., 1995; Castro et al., this issue).

Bellingshausen Sea domain

Frontal regions in the Southern Ocean are highly productive zones and support high concentrations of phytoplankton (Bianchi et al., 1992; Laubscher et al., 1993; Turner and Owens, 1995; Smetacek et al., 1997). In this sense, the most important feature of the Bellingshausen Sea area is the presence of the SbyACC (García et al., this issue), which was associated with high biomass accumulation and substantial $pCO_2$ depletion during FRUELA 95. A similar situation was also reported for this region during austral spring/summer 1992 (Robertson and Watson, 1995; Bellerby et al.,
1995). These authors found a significant linear correlation between surface pCO₂ and chlorophyll suggesting that photosynthetic CO₂ uptake was responsible for the reduction of surface pCO₂. In our study, we came to the same conclusion from the significant correlation between surface pCO₂ and AOU. However, no clear relationship was observed between surface pCO₂ and Chl a. Chl a is affected by sedimentation and grazing processes, thus it is not a conservative parameter. Despite the lack of correlation between pCO₂ and Chl a, the relationship between pCO₂ and AOU points to biological activity as the main process controlling pCO₂ distribution. A similar relationship between pCO₂ and oxygen was found in other systems as a coastal embayment affected by upwelling (Álvarez et al., 1999), the Bering Sea (Codispoti et al., 1982), the Bay of Bengal (George et al., 1994) and the North Atlantic ocean (Robertson et al., 1993).

Despite physico-dynamic conditions in late January 96 remained practically the same as during December 95 no occurrence of a phytoplankton bloom was reported, probably as a result of a combination of factors as light and iron limitation, grazing pressure, etc (Estrada and Anadón, this issue). Mean surface Chl a concentration was reduced from 1.7 to 0.45 mg.m⁻³. Mean surface pCO₂ increased from 280 to 313 μatm. The low pCO₂ levels found during late January 96 in the Belling. domain may still reflect the photosynthetic CO₂ uptake 51 days before. The budget calculations suggest that the increase in pCO₂ was mainly the result of seasonal warming and air-sea exchange.

Estimated residual daily changes of surface pCO₂ were practically negligible from FRUELA 95 to 96 in this area. Hence these evidences suggest that the shift in surface pCO₂ in the Belling. domain from FRUELA 95 to 96 can be accounted for mainly by physical rather than biological factors.

**Bransfield Strait domain**

In early December 95 the Bransfield Strait region during the Macro’95 survey was characterised by high mean surface concentrations of Chl a (1.7 mg.m⁻³) and AOU (12 μmol.kg⁻¹) associated with a value of pCO₂ above the atmospheric level (372 μatm). Bellerby et al. (1995) found during spring 1992 similar values of pCO₂ related to low chlorophyll concentrations and attributed them to remnants of upwelled CO₂-rich Circumpolar Deep Water during austral winter. The above may also explain our high values of surface pCO₂ in early December 95. An alternative explanation is advection or
transport by the Bransfield current of CO$_2$-rich surface water with a Weddell Sea origin influenced by Warm Deep Water entrainment (Hoppema, et al., 1995).

About ten days after Macro’95, high concentrations of surface Chl $a$ were found south of the Bransfield front and in the Gerlache-Bransfield confluence during the intensive sampling in the western basin of the Bransfield Strait (Meso’95), supporting the idea of frontal areas as zones favourables for phytoplankton development and accumulation. Despite the lack of correlation between surface pCO$_2$ and either Chl $a$ or AOU concentrations, pCO$_2$ well below atmospheric levels were associated to elevated Chl $a$ values and low values of AOU, suggesting biological drawdown of CO$_2$. In contrast, pre-bloom conditions were found in the Antarctic shelf area (TWW domain). Here shallow mixed layer depths and high stability were accompanied by high values of AOU and nutrients and very low average Chl $a$ in the UML (Castro et al., this issue). So remnants of winter mixing and upwelling of CO$_2$-rich deep water before the cruise may explain supersaturated surface CO$_2$-content in this area.

Although mean surface Chl $a$ concentration was slightly reduced in the Bransfield Strait area from early December 95 to late January 96, mean surface pCO$_2$ decreased by 30 μatm (Table 2). Despite the lack of relationship between pCO$_2$ and AOU and between pCO$_2$ and Chl $a$ during Macro’96, this change can be ascribed to biological activity, as suggested not only by our estimates of the daily residual change of pCO$_2$ (Table 2, 3), but also by the increase in the estimated nutrient and TIC anomalies of the upper mixed layer (Castro et al., this issue).

The Bransfield Strait, without the area near Livingston I, in late January 96 had a mean pCO$_2$ of 331±11 μatm, value very similar to that reported by Karl et al. (1991) during January 1987 on the RACER study (≥325 μatm).

**Gerlache Strait domain**

This sheltered area had the highest biomass accumulations during both cruises, associated with high water column stability and shallow upper mixed layers (Castro et al., this issue). Primary production values during both surveys were notably high (Varela et al., this issue), as well as nutrients anomalies (Castro et al., this issue). These evidences corroborate the idea of CO$_2$ uptake by photosynthesis as the main factor controlling pCO$_2$ distributions, as suggested the high correlation between AOU and pCO$_2$ during Gerlache 96 and the high and negative value of residual daily changes of surface pCO$_2$ (Table 2) between the 95 and 96 surveys.
Air-sea fluxes

It is well known that the uncertainty in the transfer velocity algorithms exceeds any other source of error in the estimation of air-sea exchange (Wanninkhof, 1992; Lundgberg, 1994; Robertson and Watson, 1995; Takahashi et al., 1997). In this sense, if air-sea CO₂ fluxes for the FRUELA cruises were calculated using the Wanninkhof (1992) relationship for spot winds they would be almost a factor of two higher.

A mean flux of $-3.35 \times 10^{-3}$ MtC.d⁻¹ (thus about $-4.8 \times 10^{-14}$ MtC.m⁻².d⁻¹ for the 52 days and $7.10^{10}$ m² of the survey) was calculated for the Bellingshausen Sea and Bransfield Strait during the FRUELA cruises. Therefore the surveyed area acted as a mean sink during austral 1995-96 spring/summer season, however, the large standard deviation suggest a great variation in the magnitude of the flux, which can be accounted for by local and short-time variations in the value and direction of the fluxes. A similar conclusion was reached by Metzl et al. (1991) in the south-west Indian sector of the Southern Ocean during summer 1987. Our estimated mean flux agrees well when compared to that given by Robertson and Watson (1995) from cruise tracks in the Bellingshausen Sea (88ºW) and between 20º and 60º E (area about $9.10^{10}$ m²) during spring to late summer 1992/93 (-0.36 MtC.d⁻¹, thus about $-4.10^{-14}$ MtC.m⁻².d⁻¹). At the same time our mean daily flux (mean ± STD) (-3.4±5.1 mmol.m⁻².d⁻¹) compared to the value given by Bakker et al. (1997) (0.3 mmol.m⁻².d⁻¹) for consecutive sections between 47º and 60ºS along 6ºW in October-November 1992 is noticeably much higher.

Regarding the Gerlache Strait, its mean CO₂ flux was $-9.6\pm11.3$ mmol.m⁻².d⁻¹, the highest of the three defined domains and, once again very variable. These evidences support the idea of the Southern Ocean as a compendium of different subsystems, which may cover a small fraction of the Southern Ocean but constitute significant spring/summer sinks for atmospheric CO₂. Moreover, this emphasizes the need of not only winter surveys, but also of careful studies of subareas in order to estimate a reliable annual flux for the Southern Ocean.

Inverse linear correlations between air-sea CO₂ and O₂ fluxes were found during the Macro’95 and Ger’96 surveys. Moreover, the value of the slope of these correlations was quite similar ($\Delta F_{O_2}/\Delta F_{CO_2} \approx 6$). This situation was accompanied by high rates of primary production (Varela et al., this issue) and significant correlations between AOU
and pCO$_2$. Therefore, the development and subsistence of phytoplanktonic blooms seems to control the existence of covariation between air-sea CO$_2$ and O$_2$ fluxes.

Biologically induced air-sea fluxes of CO$_2$ are 15 times smaller than fluxes of O$_2$ (Keeling et al., 1993). However, during Macro’95 and Ger’96 we obtained a lower relationship between both fluxes, suggesting other processes influencing the air-sea fluxes.

*Temporal changes of TIC and pCO$_2*$

Residual daily changes of dissolved inorganic carbon between FRUELA 95 and 96 for the Bransfield Strait and the Bellingshausen Sea based on TIC ($R_{\text{TIC}}$) and on pCO$_2$ ($R_{\text{pCO}_2}$) differed considerably (Table 3). This fact can be attributed to the relatively high uncertainty committed in estimates of both variables (65% and 31% respectively). However, the higher residual daily changes of pCO$_2$ and TIC ($R_{\text{TIC}}$ and $R_{\text{pCO}_2}$ in table 3) corresponded rather well in the Ger. domain. In this area, the indirect estimation of the exported carbon from the euphotic zone was confirmed by direct sediment trap measurements. This is an encouraging result, as it supports an indirect reliable method for estimating the carbon flux out of the mixed layer in areas with large temporal changes.

5. Conclusions

The results support the idea of pCO$_2$ as a complex variable, whose distribution stems from the combination of physical and biological factors (Bakker et al., 1997; Brewer, 1986; Poisson et al., 1993; Takahashi et al., 1993; Watson et al., 1991). The predominance of one of these factors varies in space and time, even during the same season in a limited area of the Atlantic Sector of the Southern Ocean (Bakker et al, 1997; Hoppema et al., 1995; Robertson and Watson, 1995).

In this sense, the three hydrographic regions (Bransfield and Gerlache Straits and Bellingshausen Sea domains) differ in the processes controlling surface pCO$_2$ variability. Phytoplankton CO$_2$ uptake during an intense diatom bloom controlled CO$_2$ distribution in the frontal area of the SbyACC in early December 95. A similar situation was reported for the sheltered area of the Gerlache Strait, specially in late January 96. During periods of strong bloom development, CO$_2$ and O$_2$ fluxes presented a significant inverse correlation, implying a biological induced air-sea exchange of both variables.
On the other hand, seasonal warming dominated the increase of surface pCO$_2$ from early December 95 to late January 96 in the Bellingshausen Sea area.

Carbon export obtained from sediment trap data supported the calculated budget for total dissolved inorganic carbon in the mixed layer of the Gerlache Strait. In areas where the signal to noise ratio of the dissolved inorganic carbon residual changes are large enough, the residual changes in the upper mixed layer of TIC, based on pCO$_2$ and directly on TIC, agree.

A mean daily CO$_2$ flux of (mean ± STD) –3.4±5.1 mmol.m$^{-2}$.d$^{-1}$ was estimated for the whole period and area surveyed. Despite acting as a mean sink for atmospheric CO$_2$, the high standard deviation of this estimation confirms the different CO$_2$ flux direction and magnitude reported for each domain and period. Moreover, apart from the need of winter-time studies, points to the importance of subareas of the Southern Ocean in the estimation of an annual basin-wide CO$_2$ flux for the Southern ocean.

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Table 1
Surface mean values and standard deviation of temperature (°C), pCO$_2$ (μatm), chlorophyll $a$ (mg.m$^{-3}$) and AOU (μmol.kg$^{-1}$), wind speed (m.s$^{-1}$) and air-sea CO$_2$ and O$_2$ fluxes (both in mmol.m$^{-2}$.d$^{-1}$) for the different domains (Figure 1a). Bransf. and Ger. stand for the Bransfield and the Gerlache Strait domains respectively, and Belling, for the Bellingshausen Sea domain.

<table>
<thead>
<tr>
<th>Domain</th>
<th>Belling. 95</th>
<th>Belling. 96</th>
<th>Transf. 95</th>
<th>Transf. 96</th>
<th>Ger. 95</th>
<th>Ger. 96</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^\circ$ (°C)</td>
<td>-0.14 (±0.29)</td>
<td>1.77 (±0.35)</td>
<td>-0.51 (±0.34)</td>
<td>0.82 (±0.72)</td>
<td>0.22 (±1)</td>
<td>0.68 (±0.58)</td>
</tr>
<tr>
<td>pCO$_2$ (μatm)</td>
<td>280 (±49)</td>
<td>313 (±17)</td>
<td>372 (±10)</td>
<td>342 (±26)</td>
<td>312 (±26)</td>
<td>241 (±22)</td>
</tr>
<tr>
<td>Chl $a$ (mg.m$^{-3}$)</td>
<td>1.7 (±1.17)</td>
<td>0.45 (±0.35)</td>
<td>1.69 (±0.59)</td>
<td>1.13 (±0.46)</td>
<td>3.86 (±1.76)</td>
<td>8.25 (±2.97)</td>
</tr>
<tr>
<td>AOU (μmol.kg$^{-1}$)</td>
<td>-19 (±20)</td>
<td>1 (±4)</td>
<td>12 (±12)</td>
<td>5 (±5)</td>
<td>1 (±24)</td>
<td>-23 (±16)</td>
</tr>
<tr>
<td>Wind speed(m.s$^{-1}$)</td>
<td>7 (±3)</td>
<td>7 (±2)</td>
<td>8 (±2)</td>
<td>6 (±1)</td>
<td>6 (±4)</td>
<td>9 (±4)</td>
</tr>
<tr>
<td>F CO$_2$ (mmol.C.m$^{-2}$.d$^{-1}$)</td>
<td>-6.5 (±6.0)</td>
<td>-4.0 (±2.6)</td>
<td>1.3 (±1.1)</td>
<td>-0.9 (±1.6)</td>
<td>-3.8 (±4.2)</td>
<td>-15.9 (±13.7)</td>
</tr>
<tr>
<td>F O$_2$ (mmol.O$_2$.m$^{-2}$.d$^{-1}$)</td>
<td>25 (±29)</td>
<td>-2 (±6)</td>
<td>-18 (±21)</td>
<td>-5 (±5)</td>
<td>-12 (±32)</td>
<td>53 (±59)</td>
</tr>
</tbody>
</table>
Table 2
Changes of surface pCO₂ between FRUELA 95 and 96 in the three different domains defined. Variables used in the calculations: the time interval (Δt), mixed layer (ML) depth, changes in surface temperature (ΔT) and pCO₂ (ΔpCO₂), average surface CO₂ content in each domain (pCO₂w) and CO₂ flux (Fav), buffer factor (β) and depth integrated total dissolved inorganic carbon in the mixed layer (TTIC). Observed daily changes of pCO₂ (Δp/Δt) are the sum of daily changes due to air-sea exchange ([δp/δt]F), thermodynamical ([δp/δt]T) and residual changes ([δp/δt]R) according to equation (8). See table 1 for abbreviations of the domains.

<table>
<thead>
<tr>
<th></th>
<th>Δt (days)</th>
<th>ML depth (m)</th>
<th>ΔT (°C)</th>
<th>ΔpCO₂ (µatm)</th>
<th>pCO₂w (µatm)</th>
<th>Buffer factor β</th>
<th>TTIC (mol.m⁻²)</th>
<th>Fav (mmol.m⁻².d⁻¹)</th>
<th>Δp/Δt (µatm.d⁻¹)</th>
<th>[δp/δt]F (µatm.d⁻¹)</th>
<th>[δp/δt]T (µatm.d⁻¹)</th>
<th>[δp/δt]R (µatm.d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belling.</td>
<td>50.8</td>
<td>35-38</td>
<td>1.91</td>
<td>33</td>
<td>294.7</td>
<td>12.1</td>
<td>90.71</td>
<td>-5.42</td>
<td>0.65</td>
<td>0.21</td>
<td>0.35</td>
<td>0.09</td>
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<tr>
<td>Transf.</td>
<td>50.6</td>
<td>11-14</td>
<td>1.32</td>
<td>-30</td>
<td>355.2</td>
<td>12.3</td>
<td>41.89</td>
<td>0.06</td>
<td>-0.59</td>
<td>-0.01</td>
<td>0.39</td>
<td>-0.97</td>
</tr>
<tr>
<td>Ger.</td>
<td>40.7</td>
<td>15-17</td>
<td>0.48</td>
<td>-71</td>
<td>274.5</td>
<td>13.7</td>
<td>32.19</td>
<td>-9.88</td>
<td>-1.75</td>
<td>1.15</td>
<td>0.03</td>
<td>-2.93</td>
</tr>
</tbody>
</table>
Table 3

Estimations of terms of equations (10): \( R = U - P + M = U - B - E \) between FRUELA 95 and 96 in each domain. Residual daily changes of total inorganic carbon (R) in the upper mixed layer (UML) were evaluated from measured changes of TIC in the UML (\( R_{\text{TIC}} \)) corrected for air-sea exchange (\( R_{\text{TIC}} \)). In addition, residual daily changes of TIC were evaluated from residual daily changes of surface pCO\(_2\) (\( R_{\text{pCO}_2} \)) (Table 2) using equation (11). Upward transport U, net primary production P from \(^{14}\text{C}\) incubations (Varela et al., this issue) and biomass growth B from POC data (Castro et al., this issue) were calculated as in the text. Apparent mineralization M and carbon export E were estimated from equations (10), with R relying on \( R_{\text{TIC}} \) instead of \( R_{\text{pCO}_2} \). See table 1 for abbreviations of the domains.

<table>
<thead>
<tr>
<th></th>
<th>(^{14}\text{C}) (mgC. m(^{-2}).d(^{-1}))</th>
<th>dPOC (mmol. m(^{-3}))</th>
<th>dTIC (mmol. kg(^{-1}))</th>
<th>( R_{\text{TIC}} ) (mmol. m(^{-2}).d(^{-1}))</th>
<th>( R_{\text{pCO}_2} ) (mmol. m(^{-2}).d(^{-1}))</th>
<th>U (mmol. m(^{-2}).d(^{-1}))</th>
<th>P (mmol. m(^{-2}).d(^{-1}))</th>
<th>M (mmol. m(^{-2}).d(^{-1}))</th>
<th>B (mmol. m(^{-2}).d(^{-1}))</th>
<th>E (mmol. m(^{-2}).d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belling.</td>
<td>----</td>
<td>-4.5</td>
<td>7.0</td>
<td>5.2</td>
<td>-0.3</td>
<td>2.2</td>
<td>5.4</td>
<td>----</td>
<td>----</td>
<td>-3.3</td>
</tr>
<tr>
<td>Transf.</td>
<td>483.76</td>
<td>1.7</td>
<td>-11.3</td>
<td>-2.8</td>
<td>-2.8</td>
<td>-9.3</td>
<td>1.8</td>
<td>34.6</td>
<td>29.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1. Map of the chemical stations sampled during (a) Macro’95 and 96 (b) Meso’95 and (c) Gerlache 95 and 96 surveys. Points (●) with plain numbers stand for stations sampled during FRUELA 95 and (⊙) with underlined numbers for stations sampled during FRUELA 96. The defined domains are limited by dashed lines in figure 1a. On figure 1a are represented the Southern boundary of the Antarctic Circumpolar current (SbyACC), the Southern Polar Front (SPF) and the Bransfield Current (BC). In figure 1b are represented the Bransfield Front (BF), the area of Transitional Zonal Water with Bellingshausen influence (TBW) and Transitional Zonal Water with Weddell Sea influence (TWW).

Figure 2. Surface distribution of (a) temperature (°C), (b) chlorophyll a (mg.m$^{-3}$) concentration, (c) AOU (μmol.kg$^{-1}$), (d) CO$_2$ partial pressure (μatm) and air-sea fluxes of (e) oxygen and (f) carbon dioxide during the macroscale 95 sampling. Fluxes are in mmol.m$^{-2}$.d$^{-1}$. The emphasized isoline on figures 2e and f indicates a change in the direction of the fluxes. The emphasized isoline on figure 2d represents the mean atmospheric pCO$_2$ during the
sampling period (358 µatm). SbyACC stands for Southern boundary of the Antarctic Circumpolar current and BC for the Bransfield Current.

**Figure 3.** Surface distribution of (a) temperature (ºC), (b) chlorophyll $a$ (mg.m$^{-3}$) concentration, (c) AOU (µmol.kg$^{-1}$), (d) CO$_2$ partial pressure (µatm) and air-sea fluxes of (e) oxygen and (f) carbon dioxide during the mesoscale 95 sampling. Fluxes are in mmol.m$^{-2}$.d$^{-1}$. The emphasized isoline on figures 3e and f indicates a change in the direction of the fluxes. The emphasized isoline on figure 3d represents the mean atmospheric pCO$_2$ during the sampling period (358 µatm). BF stands for Bransfield Front, TBW for Transitional Zonal Water with Bellingshausen influence and TWW for Transitional Zonal Water with Weddell Sea influence.

**Figure 4.** Surface distribution of (a) temperature (ºC), (b) chlorophyll $a$ (mg.m$^{-3}$) concentration, (c) AOU (µmol.kg$^{-1}$), (d) CO$_2$ partial pressure (µatm) and air-sea fluxes of (e) oxygen and (f) carbon dioxide during the macroscale 96 sampling. Fluxes are in mmol.m$^{-2}$.d$^{-1}$. The emphasized isoline on figures 4e and f indicates a change in the direction of the fluxes. The emphasized isoline on figure 4d represents the mean atmospheric pCO$_2$ during the sampling period (358 µatm).

**Figure 5.** Upper 100m distributions of (a and e) temperature (ºC), (b and f) pCO$_2$ (µatm), (c and g) AOU (µmol.kg$^{-1}$) and (d and g) chlorophyll $a$ (mg.m$^{-3}$) concentrations in the Gerlache Strait during FRUELA 95 (Ger’95) and 96 (Ger’96). The emphasized isoline on figures 5b and 5f represents the mean atmospheric pCO$_2$ during the sampling period (358 µatm).

**Figure 6.** Air-sea exchange of (a) CO$_2$ and (b) oxygen in the Gerlache Strait during FRUELA 95 (Ger’95) and 96 (Ger’96). Both fluxes in mmol.m$^{-2}$.d$^{-1}$. 
REFERENCES


Figure 1

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Figure 2

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Figure 3

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Figure 6
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