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Spatio-temporal variability of air–sea fluxes of carbon dioxide and oxygen in the Bransfield and Gerlache Straits during Austral summer 1995–96

Marta Álvarez[a,*], Aida F. Ríos[a], Gabriel Rosón[b]

[a] *Instituto de Investigaciones Marinas (CSIC), C/Eduardo Cabello No. 6, 36208, Vigo, Spain*
[b] *Dpto. Fisica Aplicada, Universidad de Vigo, Campus Lagoas-Marcosende, 36200 Vigo, Spain*

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Abstract

The potential of the Bellingshausen Sea, Bransfield and Gerlache Straits as sinks for atmospheric CO_2 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 CO_2 and its relation to air–sea O_2 fluxes, surface chlorophyll concentration, physical structures, and other environmental variables were also studied. The processes governing the temporal evolution of total inorganic carbon (TIC) 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 CO_2 content ($<200\,\mu$atm), in contrast to strong oxygen supersaturation (AOU $<-48\,\mu$mol kg^{-1}). This was accompanied by the development of a diatom bloom. Therefore, this area acted as a strong CO_2 sink and oxygen source, -6.5 ± 6 and 25 ± 29 (mean $\pm$ 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 had 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.

1. Introduction

High-latitude areas play an important role in the global carbon cycle due to the large oceanic area

*Corresponding author. Fax: +34-986-292762.
E-mail address: malvarez@iim.csic.es (M. Álvarez).

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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., 1991a, b; Takahashi et al., 1993; Poisson et al., 1993; Bellerby et al., 1995; Hoppema et al., 1995; Robertson and Watson, 1995; Bakker et al., 1997; Rubin et al., 1998). These studies showed that the different sectors of the Southern Ocean present contrasting behaviours. The Atlantic and Pacific sectors appear to be generally CO_2-undersaturated during austral summer, while the Indian sector has large spatial and probably temporal variations (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 1981–87 the Southern Ocean behaved as a sink of 0.5 GtC yr^{-1}, whilst on 1988–92 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 aim of: (i) evaluating the spatio-temporal differences between both cruises; (ii) estimating the CO_2 and O_2 air–sea exchange and their relationship, and (iii) establishing a carbon budget as a tool to assess the factors controlling total inorganic carbon (TIC) 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 Anadón and Estrada (2002). 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 (Fig. 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 (Fig. 1b). Moreover, during both FRUELA 95 and 96 a section along the Gerlache Strait was sampled (Fig. 1c).

Continuous profiles of salinity, temperature and pressure were recorded with an 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 m depth.

Dissolved oxygen was determined by Winkler potentiometric titration, with an estimated error of $\pm 1\,\mu mol\,kg^{-1}$. Apparent oxygen utilisation (AOU) was calculated using oxygen saturation following the Benson and Krause equation

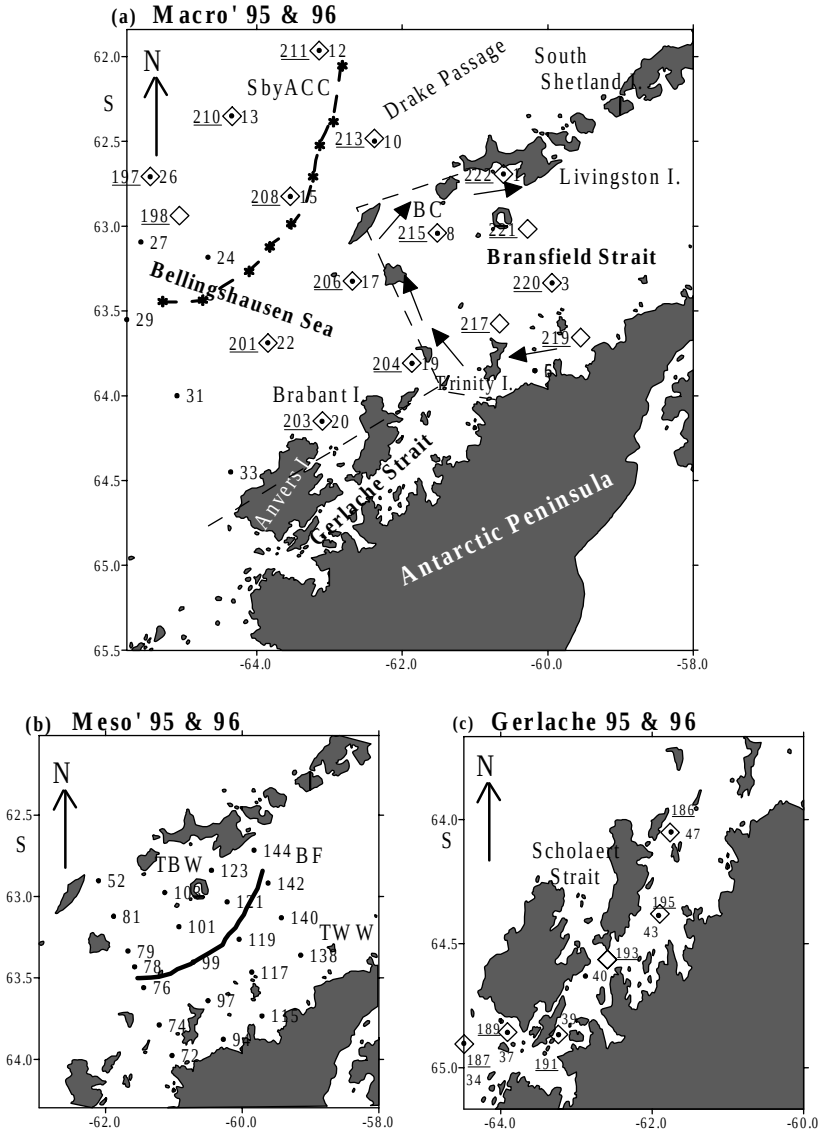

Fig. 1. Map of the chemical stations sampled during (a) Macro'95 and 96 (b) Meso'95 and (c) Gerlache 95 and 96 surveys. Points (●) with plain numbers stand for stations sampled during FRUELA 95 and (◇) with underlined numbers for stations sampled during FRUELA 96. The defined domains are limited by dashed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

(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 (1983). The precision of this method is $\pm 0.05\,\mathrm{mg\,m^{-3}}$.

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 pH was referred to a standard temperature of 15°C (pH_{15}) according to Pérez and Fraga (1987a). The method has a shipboard precision of ± 0.002 pH_{15} (Ríos and Rosón, 1996) and an accuracy of ± 0.004 pH_{15} 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 $\pm 1.4\,\mu mol\,kg^{-1}$ (Ríos and Pérez, 1999; Ríos and Rellán, 1998). TIC and partial pressure of CO_2 (pCO_2) were estimated from pH_{15} 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 $\pm 4\,\mu mol\,kg^{-1}$ and $\pm 5\,\mu atm$, 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 pCO_2 obtained using Merhbach'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 CO_2 exchange ($mmolC\,m^{-2}\,d^{-1}$) was calculated using the following equation:

$$FCO_2 = 0.24k\,S\,\rho\,10^{-3}(pCO_2oc\text{-}pCO_2\ at), \qquad (1)$$

where k is the exchange coefficient ($cm\,h^{-1}$), S is CO_2 seawater solubility ($mol\,kg^{-1}\,atm^{-1}$), pCO_2oc is surface ocean CO_2 partial pressure, pCO_2at is atmospheric CO_2 partial pressure (both in μatm), and 0.24 is a unit conversion factor. Seawater CO_2 solubility is calculated from Weiss (1974). ρ is seawater density in $kg\,m^{-3}$.

Seasonal and inter-annual variations in atmospheric CO_2 are small compared to pCO_2 variations in the surface ocean (Andrié et al., 1986). In addition, in the Southern hemisphere the seasonal amplitude of atmospheric CO_2 partial pressure (pCO_2at) 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 pCO_2at 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°55′S, 64°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):

$$k = 0.17\,U_{10}(660/Sc)^{2/3}$$
$$U_{10} < U_1:\ \text{smooth water regime}, \qquad (2a)$$

$$k = (2.85\,U_{10} - 9.65)\,(660/Sc)^{1/2}$$
$$U_{10} < U_1:\ \text{rough water regime}, \qquad (2b)$$

$$U_1 = 9.65[2.85 - 0.17\,(660/Sc)^{1/6}]^{-1}, \qquad (2c)$$

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):

$$Sc = 2073.1 - 125.62\,T + 3.6276\,T^2 - 0.043219\,T^3, \qquad (3)$$

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 min averages.

One of the major uncertainties in the assessment of air–sea gas exchange is the parameterisation 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, 10 min 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 $\pm 4\,\mu atm$ in pCO_2oc and $\pm 1\,\mu atm$ in pCO_2at, the maximum absolute error in FCO_2 is $\pm 1.5\,mmol\,C\,m^{-2}\,d^{-1}$; this is a relative error to its mean value of $\pm 32\%$.

Oxygen fluxes ($mmol\,O_2\,m^{-2}\,d^{-1}$) were calculated using the following equation:

$$FO_2 = -0.864\,k_{O_2}\,\rho\,10^{-3}\mathrm{AOU}, \quad (4)$$

where k_{O_2} ($cm\,s^{-1}$) is the piston velocity for oxygen, AOU is the apparent oxygen utilisation defined previously ($\mu mol\,kg^{-1}$), and 0.864 is an unit conversion factor. The relationship between k_{O_2} and wind speed has been studied by Kester (1975) and parameterised by Rosón (1992). ρ is seawater density in $kg\,m^{-3}$. The estimated relative maximum error of FO_2 is about $\pm 35\%$.

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

3.1. Surface distributions

3.1.1. 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 (Figs. 1a and 3a from García et al., 2002).

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., 2002; García et al., 2002) (Fig. 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., 2002).

3.1.2. FREULA 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., 2002). In the South-west area a warmer (−0.7–0.14°C) and fresher (33.7–33.8) water mass with a Bellingshausen Sea origin contrasted to the warm water (0–0.5°C) coming from the Drake passage (García et al., 2002) (Fig. 2a).

Surface distributions of Chl *a*, AOU and pCO_2 (Figs. 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 northeastern part of the Bellingshausen Sea (Belling.) domain (see Fig. 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 ($-48\,\mu mol\,kg^{-1}$) (station 15, Figs. 3b–d). Moreover, Castro et al. (2002) 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 had the lowest mean surface temperature (–0.5°C) (see Fig. 2a and Table 1); Chl *a* concentrations ranged from 1 to $2\,mg\,m^{-3}$, and AOU values were undersaturated ($12\,\mu mol\,kg^{-1}$) as a mean (Figs. 2b and c, Table 1). But the most notable feature was the positive values of ΔpCO_2 (Fig. 2d and Table 1), revealing that it acted as a weak source of CO_2 to the atmosphere in contrast with the Bellingshausen 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:

$$pCO_2(\pm 25) = 328(\pm 7) + 2.3(\pm 0.3)\,\mathrm{AOU},$$
$$r^2 = 0.82, \quad p < 0.0001. \quad (5)$$

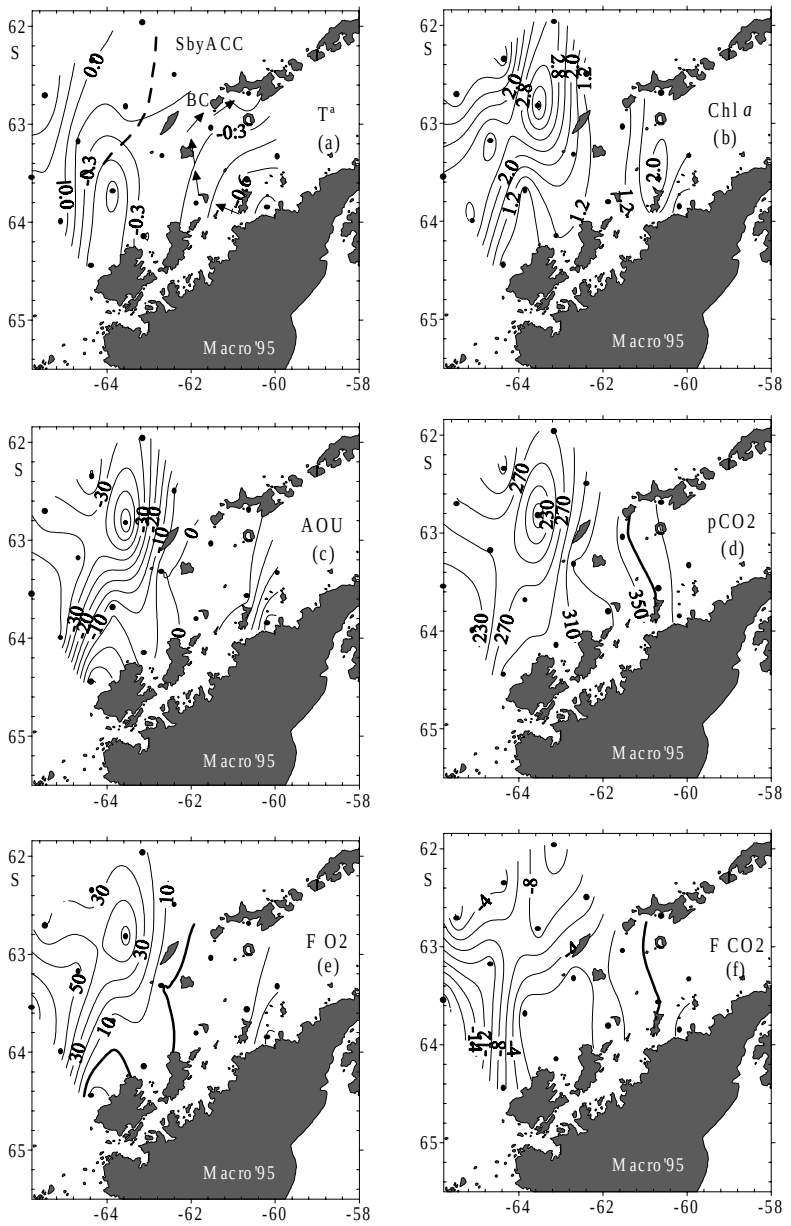

Fig. 2. Surface distribution of (a) temperature (°C), (b) Chl *a* (mg m^{-3}) concentration, (c) AOU (μmol kg^{-1}), (d) CO_2 partial pressure (μatm) and air–sea fluxes of (e) oxygen, and (f) carbon dioxide during the macroscale 95 sampling. Fluxes are in mmol m^{-2} d^{-1}. The bold isoline on Figs. 2e and f indicates a change in the direction of the fluxes. The emphasised isoline on Fig. 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.

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).

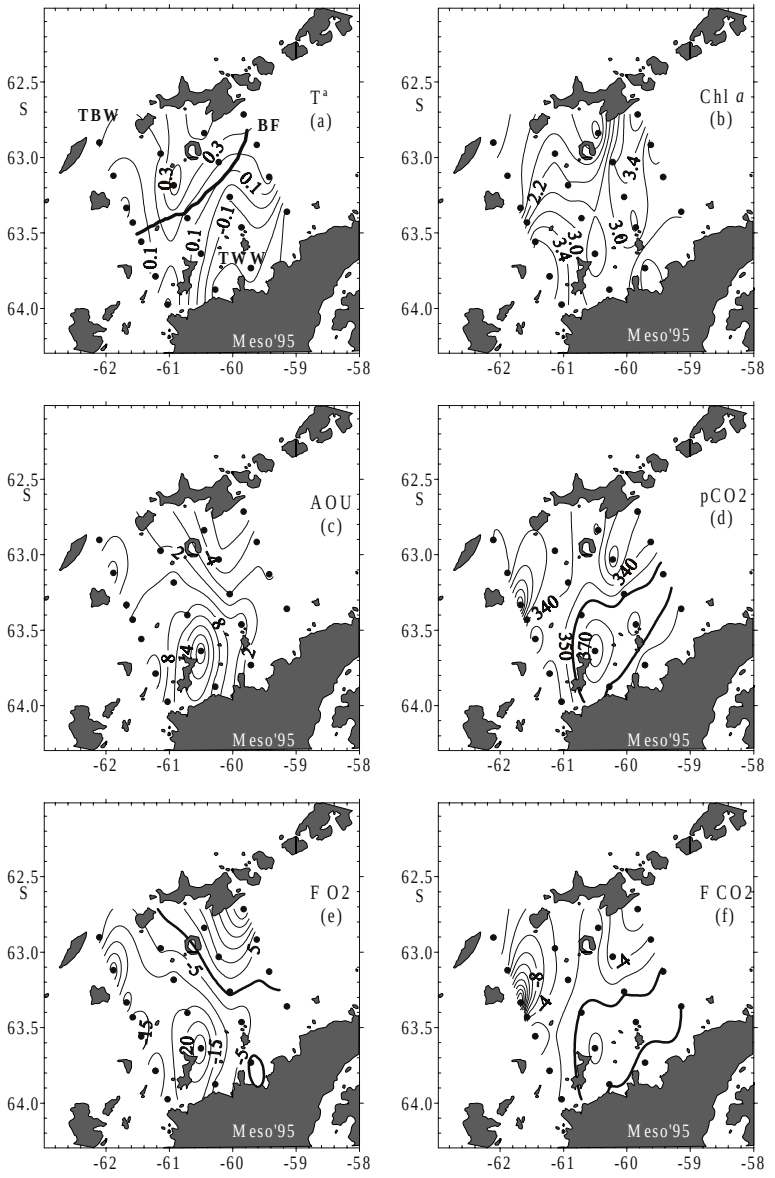

Fig. 3. Surface distribution of (a) temperature (°C), (b) Chl *a* (mg m^{-3}) concentration, (c) AOU (μmol kg^{-1}), (d) CO_2 partial pressure (μatm) and air–sea fluxes of (e) oxygen and (f) carbon dioxide during the mesoscale 95 sampling. Fluxes are in mmol m^{-2} d^{-1}. The bold isoline on Figs. 3e and f indicates a change in the direction of the fluxes. The emphasised isoline on Fig. 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.

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

Table 1
Surface mean values and standard deviation of temperature (°C), pCO_2 (μatm), Chl *a* ($mg\,m^{-3}$) and AOU ($\mu mol\,kg^{-1}$), 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 (Fig. 1a)[a]

Domain	Belling. 95	Belling. 96	Bransf. 95	Bransf. 96	Ger. 95	Ger. 96
T[a] (°C)	−0.14 (±0.29)	1.77 (±0.35)	−0.51 (±0.34)	0.82 (±0.72)	0.22 (±1)	0.68 (±0.58)
pCO_2 (μatm)	280 (±49)	313 (±17)	372 (±10)	342 (±26)	312 (±26)	241 (±22)
Chl *a* ($mg\,m^{-3}$)	1.7 (±1.17)	0.45 (±0.35)	1.69 (±0.59)	1.13 (±0.46)	3.86 (±1.76)	8.25 (±2.97)
AOU ($\mu mol\,kg^{-1}$)	−19 (±20)	1 (±4)	12 (±12)	5 (±5)	1 (±24)	−23 (±16)
Wind speed($m\,s^{-1}$)	7 (±3)	7 (±2)	8 (±2)	6 (±1)	6 (±4)	9 (±4)
FCO_2 ($mmol\,C\,m^{-2}\,d^{-1}$)	−6.5 (±6.0)	−4.0 (±2.6)	1.3 (±1.1)	−0.9 (±1.6)	−3.8 (±4.2)	−15.9 (±13.7)
FO_2 ($mmol\,O_2\,m^{-2}\,d^{-1}$)	25 (±29)	−2 (±6)	−18 (±21)	−5 (±5)	−12 (±32)	53 (±59)

[a] Bransf. Ger. and Belling, stand for the Bransfield, Gerlache Strait and Bellingshausen Sea, respectively.

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 (Fig. 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 $1.2\,mmol\,C\,m^{-2}\,d^{-1}$ (Table 1). In contrast the maximum influx of CO_2 was located in the Bellingshausen domain, reaching values as low as $-20\,mmol\,C\,m^{-2}\,d^{-1}$. These maxima influxes did not coincide with the maxima pCO_2 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 (Fig. 2e) resembled that of CO_2 but in opposite direction:

$$FCO_2(\pm 3.6) = -2.2(\pm 0.9) - 0.18(\pm 0.03)FO_2,$$
$$r^2 = 0.69, \quad p < 0.0001. \qquad (6)$$

According to this equation and supporting Eq. (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, Fig. 1b). Here, the Bransfield front can be discerned by hydrographic and nutrients distributions, and by surface pCO_2 (Fig. 3d). In a NE–SW orientation an area with a CO_2 content around 345 μatm separated TBW in the northwest from TWW in the southeast with higher pCO_2 values. In contrast, neither the surface distribution of chlorophyll nor AOU presented a clear relation to hydrographic structures. However, a northeastward increase in the cumulative photosynthetic activity can be assessed from the surface distribution of AOU (Fig. 3c). Surface Chl *a* concentration (Fig. 3b) ranged from 0.8 to $4.4\,mg\,m^{-3}$, with the highest values in the TWW area.

Neither Chl *a* nor AOU showed a significant correlation with pCO_2. Nevertheless in the northeastern part of the surveyed area undersaturated values of CO_2 were associated to supersaturation of oxygen and to relatively high values of Chl *a*, but, on the other hand, the maximum in surface pCO_2 content near Trinity Island coincided with the maximum AOU concentration (Figs. 3c and d). Therefore, in this local area CO_2 effluxes were recorded and associated with maximum influxes of oxygen (Figs. 3e and f).

3.1.3. FRUELA 96

Dynamic features remained practically the same during both Macro'95 and 96 (Gomis et al., 2002). However, hydrographic variables showed the influence of seasonal warming, the greatest rise in the mean surface temperature was recorded in the Bellingshausen domain (1.91°C, Table 2). In general, surface pCO_2, AOU and Chl *a* ranges during macroscale 96 were reduced to about a half with respect to conditions during Macroscale 95.

Table 2
Changes of surface pCO_2 between FRUELA 95 and 96 in the Bransfield, Gerlache and Bellingshausen domains[a]

	Δt (days)	ML depth (m)	ΔT (°C)	ΔpCO_2 (μatm)	pCO_{2w} (μatm)	Buffer factor β	TTIC (mol m^{-2})	F_{av} (mmol m^{-2} d^{-1})	$\Delta p/\Delta t$ (μatm d^{-1})	$[\delta p/\delta t]_F$ (μatm d^{-1})	$[\delta p/\delta t]_T$ (μatm d^{-1})	$[\delta p/\delta t]_R$ (μatm d^{-1})
Belling.	50.8	35–38	1.91	33	294.7	12.1	90.71	−5.42	0.65	0.21	0.35	0.09
Bransf.	50.6	11–14	1.32	−30	355.2	12.3	41.89	0.06	−0.59	−0.01	0.39	−0.97
Ger.	40.7	15–17	0.48	−71	274.5	13.7	32.19	−9.88	−1.75	1.15	0.03	−2.93

[a]Note: Variables used in the calculations: The time interval (Δt), mixed layer (ML) depth, changes in surface temperature (ΔT) and pCO_2 (ΔpCO_2), average surface CO_2 content in each domain (pCO_{2w}) and CO_2 flux (F_{av}), buffer factor (β), and depth-integrated total dissolved inorganic carbon in the mixed layer (TTIC). Observed daily changes of pCO_2 ($\Delta p/\Delta t$) are the sum of daily changes due to air–sea exchange ($[\delta p/\delta t]_F$), thermodynamical ($[\delta p/\delta t]_T$) and residual changes ($[\delta p/\delta t]_R$) according to Eq. (8).

The highest concentrations of surface Chl *a* were reported during Macro'96 in the Bransfield Strait (Fig. 4b). Although the range of surface oxygen variation was reduced from early December 95 (330–400 μmol kg^{-1}) to late January 96 (326–350 μmol kg^{-1}), surface AOU (Fig. 4c) showed a wider range of values (from –6 to 10 μmol kg^{-1}) during Macro'96 due to the greater surface temperature gradient. Warm water of the Bellingshausen domain was slightly supersaturated as a mean (AOU = 1 μmol 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 (Fig. 4d). Conversely, the lowest surface pCO_2 was recorded, as during Macro'95, in the Bellingshausen domain.

In contrast, no significant correlation was found between either AOU or Chl *a* and pCO_2 on surface waters during this period. These evidences suggest that physical factors as well as biological activity influenced surface pCO_2 distribution during Macro'96.

During late January 96, only the area near Livingston island in the Bransfield domain behaved as a source of CO_2 (1.6 mmol C m^{-2} d^{-1}, Fig. 4f). However, considering the whole domain it was practically in atmospheric equilibrium (Table 1). The mean influx calculated for the Bellingshausen domain was −4 mmol C m^{-2} d^{-1}, only 2 mmol C 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 (Fig. 4e). In comparison to Macro'95 oxygen fluxes during Macro'96 were 10-fold lower.

3.2. Gerlache Strait sections during FRUELA 95 and 96

Temperature distribution in the upper 100 m of the southwestern part of the Gerlache Strait sampled area (Figs. 5a and e) was characterised

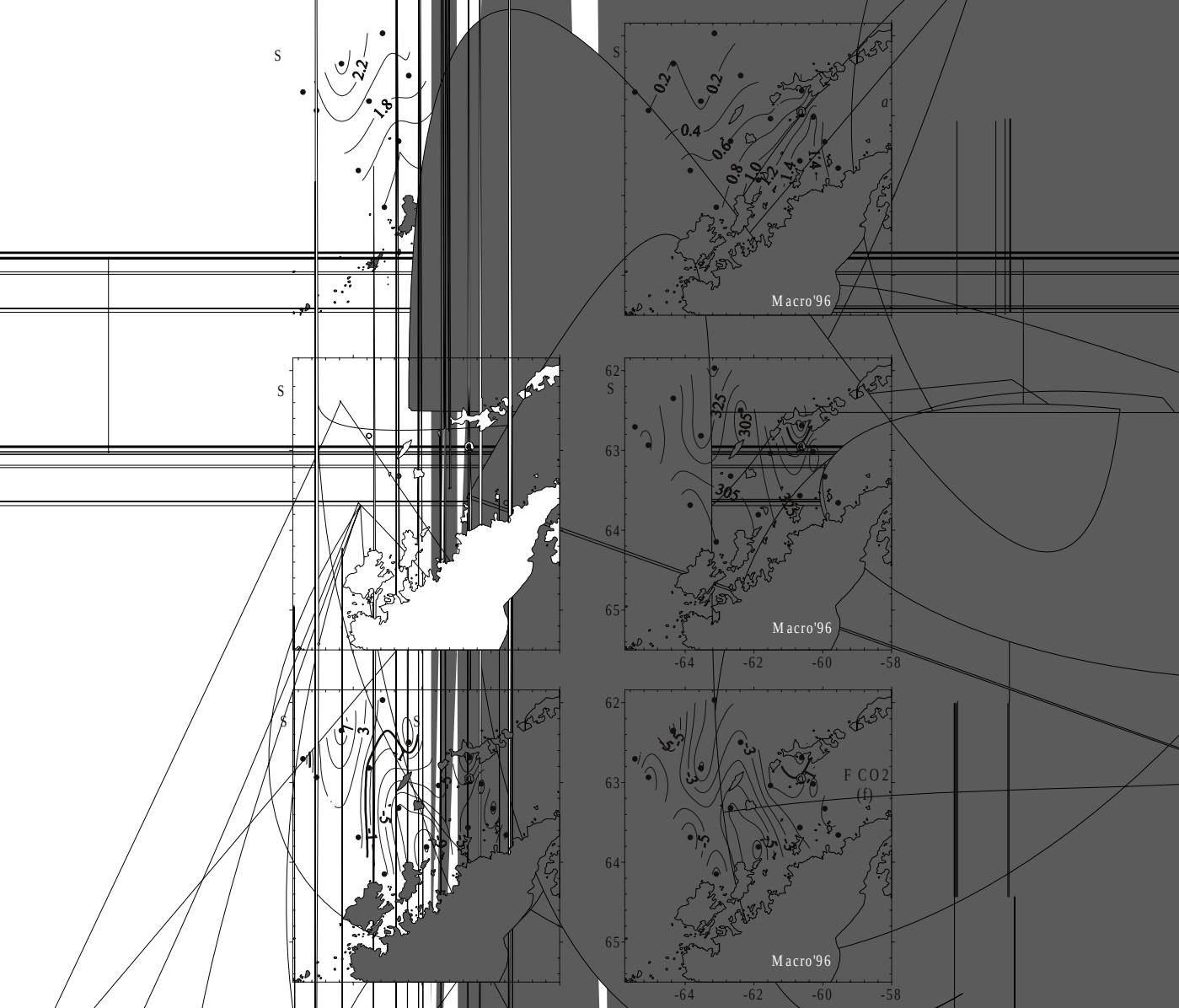

Fig. 4. Surface distribution of (a) temperature (°C), (b) Chl *a* (mg m^{-3}) concentration, (c) AOU (μmol kg^{-1}), (d) CO_2 partial pressure (μatm), and air–sea fluxes of oxygen (e) and carbon dioxide (f) during the macroscale 96 sampling. Fluxes are in mmol m^{-2} d^{-1}. The bold isoline on Figs. 4e and f indicates a change in the direction of the fluxes. The emphasised isoline on Fig. 4d represents the mean atmospheric pCO_2 during the sampling period (358 μatm).

by a minimum around 50 m, belong
AASW (Antarctic Surface Water) (Ga
2002). This minimum disappeared in t
located near the Scholaert Strait du
FRUELA cruises, resulting in a nearl

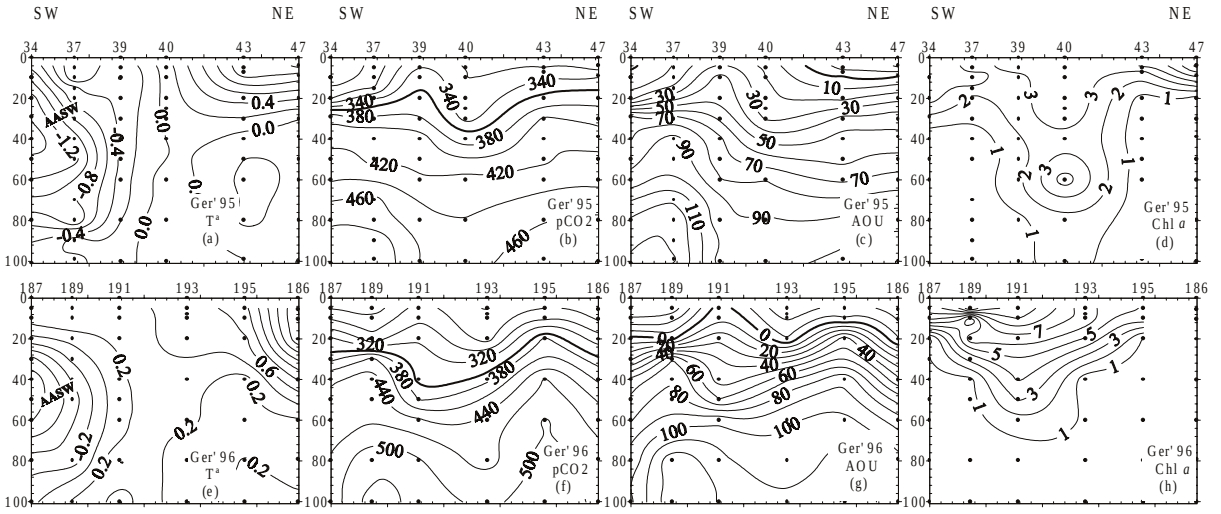

Fig. 5. Upper 100 m distributions of (a and e) temperature (°C), (b and f) pCO_2 (μatm), (c and g) AOU (μmol kg^{-1}) and (d and g) Chl *a* (mg m^{-3}) concentrations in the Gerlache Strait during FRUELA 95 (Ger'95) and 96 (Ger'96). The emphasised isoline on Figs. 5b and f represents the mean atmospheric pCO_2 during the sampling period (358 μatm).

contrast, the upper water column in the SW and NE areas was highly stratified during FRUELA 95; the thermal gradient, as well as a high near-surface salinity gradient (not shown), related to ice-melting. During early December 95, the SW and NE areas had high surface concentrations of Chl *a* (>3 mg m^{-3}) (Fig. 5d), note the maximum of 7 mg m^{-3} in the NE. These biomass accumulations were associated with shallow mixed-layer depths (6–17 m) and high stratification (Castro et al., 2002). 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 (Figs. 5b and c), in agreement with the local downwelling suggested by temperature and the deepening of the upper mixed layer (35 m) (Castro et al., 2002).

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 showed slight oversaturations of oxygen (Fig. 5c), whereas the SW area was significantly undersaturated, likely due to lower temperature values. Surface-water CO_2 contents (Fig. 5b) were lower than atmospheric, ranging from 288 to 340 μatm, with a minimum of 270 μatm in the SW area. Below 50 m 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 (Fig. 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 (Fig. 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., 2002). Surface water was oxygen supersaturated (Fig. 5g), in agreement with a seawater CO_2 content in the upper 30 m strongly under atmospheric levels (Fig. 5f).

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

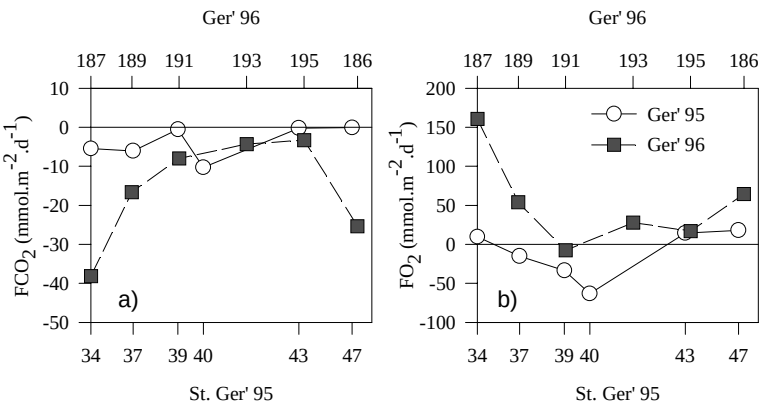

Fig. 6. Air–sea exchange of (a) CO_2 and (b) oxygen in the Gerlache Strait during FRUELA 95 (Ger'95) and 96 (Ger'96). Both fluxes in $\mathrm{mmol\,m^{-2}\,d^{-1}}$.

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 Fig. 6. Regarding air–sea CO_2 exchange, this area acted as a mean sink for atmospheric CO_2 ($-3.8\,\mathrm{mmol\,m^{-2}\,d^{-1}}$, Table 1) during December 95, with the highest uptake of CO_2 in the central area (Fig. 6a). During early January 96, the mean CO_2 influx in the Gerlache Strait changed to $-16\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ (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 (Fig. 6) in Ger'95. Both fluxes showed the highest values in the same direction at the central area.

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

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

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

3.3. Temporal changes of pCO_2 in surface water

Another method to asses 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):

$$\Delta f/\Delta t = [\partial f/\partial t]T + [\partial f/\partial t]_F + [\partial f/\partial t]_R, \tag{8}$$

where f stands for CO_2 fugacity, $\Delta f/\Delta t$ is the temporal fCO_2 variations during the period Δt, which are the sum of variations due to thermodynamic changes (those related to temperature and salinity, $[\partial f/\partial t]_T$), air–sea exchanges ($[\partial f/\partial t]_F$) 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, Bransfield and Gerlache Strait domains (Fig. 1a, Table 2).

Here we assumed an ideal-gas behaviour of CO_2 as the difference between $f\,CO_2$ and pCO_2 is about 0.7% (Weiss, 1974). Therefore the three first terms in Eq. (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., 2002) (Table 2).

The estimated error for $\Delta pCO_2/\Delta t$ is about $\pm 25\%$. 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 $\pm 58\%$. 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:

$$[\partial pCO_2/\partial t]_F = -F_{av}\beta pCO_{2w}\,TTIC^{-1}, \quad (9)$$

where F_{av} and pCO_{2w} are the average air–sea exchange and surface pCO_2, respectively, β the buffer or Revelle factor, and TTIC is the average total amount of 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 from CTD profiles using the criterion of Mitchell and Holm-Hansen (1991) (Castro et al., 2002). The relative error of $[\partial pCO_2/\partial t]_F$ was $\pm 27\%$.

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 $\pm 33\%$.

In the Bellingshausen domain surface pCO_2 increased at $0.65\,\mu atm\,d^{-1}$ between FRUELA 95 and 96. This change corresponded to the combined effect of the CO_2 air to sea entry ($0.21\,\mu atm\,d^{-1}$) and to the raise in 1.9°C of surface temperature (as salinity effect was negligible, $<1\,\mu atm$ in 51 days) leading to an increase in $0.35\,\mu atm\,d^{-1}$. 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 $-0.59\,\mu atm\,d^{-1}$. 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 $0.39\,\mu atm\,d^{-1}$. 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., 2002).

In absolute terms, the Gerlache Strait presented the highest daily variation in surface pCO_2 ($-1.75\,\mu atm\,d^{-1}$, 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 $1.15\,\mu atm\,d^{-1}$, resulting in a residual daily change of $-2.9\,\mu atm\,d^{-1}$. 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., 2002) and primary productivity (Varela et al., 2002). Therefore, during this period the influence on pCO_2 of biological activity exceeded that due to physical processes.

3.4. 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 3.3, residual daily changes (R) were attributed to upward diffusion (U) and biological activity. Biological activity accounts for primary production (P) minus mineralisation (M), or for biomass increase (B) plus export due to sedimentation (E). Therefore:

Table 3
Estimations of terms of Eqs. (10a) and (10b): $R = U - P + M = U - B - E$ between FRUELA 95 and 96 for the Bellingshausen, Bransfield and Gerlache domain[a]

	^{14}C (mg C. $M^{-2}\,d^{-1}$)	DPOC (mmol m^{-3})	dTIC (μmol kg^{-1})	$R_{\Delta TIC}$ (mmol m^{-2} d^{-1})	R_{TIC} (mmol $m^{-2}\,d^{-1}$)	R_{pCO_2} (mmol $m^{-2}\,d^{-1}$)	U (mmol $m^{-2}\,d^{-1}$)	P (mmol $m^{-2}\,d^{-1}$)	M (mmol $m^{-2}\,d^{-1}$)	B (mmol $m^{-2}\,d^{-1}$)	E (mmol $m^{-2}\,d^{-1}$)
Belling.	—	−4.5	7.0	5.2	−0.3	2.2	5.4	—	—	−3.3	9.0
Bransf.	483.76	1.7	−11.3	−2.8	−2.8	−9.3	1.8	34.6	29.9	0.4	4.2
Ger.	568.73	28.9	−47.5	−19.2	−29.1	−25.0	5.8	40.6	5.7	11.4	23.5

[a]Note: Residual daily changes of total inorganic carbon (R) in the upper mixed layer (UML) were evaluated from measured changes of TIC in the UML ($R_{\Delta TIC}$) corrected for air–sea exchange (R_{TIC}). In addition, residual daily changes of TIC were evaluated from residual daily changes of surface pCO_2 (R_{pCO_2}) (Table 2) using Eq. (11). Upward transport U, net primary production P from ^{14}C incubations (Varela et al., 2002) and biomass growth B from POC data (Castro et al., 2002) were calculated as in the text. Apparent mineralisation M and carbon export E were estimated from Eqs. (10a) and (10b), with R relying on R_{TIC} instead of R_{pCO_2}.

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

$$= \text{Upward transport } (U) - \text{Biomass increase } (B) - \text{Export } (E), \quad (10b)$$

Residual daily changes based on pCO_2 were calculated using the formula:

$$R_{pCO_2} = [\partial pCO_2/\partial t]_R \, TTIC\beta^{-1} \, pCO_{2w}^{-1}, \quad (11)$$

where all these parameters have been 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 ($R_{\Delta TIC}$) 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:

$$U = -Kz(\delta TIC/\delta z), \quad (12)$$

where Kz is the eddy diffusivity coefficient, with a value of $0.5\,cm^2\,s^{-1}$ (Gordon et al., 1984) and $(\delta TIC/\delta z)$ is the gradient of TIC between the upper mixed layer depth and 100 m, where the maximum gradient in the TIC profiles has been found (Castro et al., 2002). 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 3-fold higher.

Values of ^{14}C primary production (P) in the UML were obtained from Varela et al. (2002). Biomass increases were calculated solely from particulate organic carbon (POC) changes in the mixed layer (Castro et al., 2002). 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 Bellingshausen domain (Table 3). Residual daily changes based on TIC without correction for air–sea exchange ($R_{\Delta TIC}$) (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_{pCO_2} led us to use R_{TIC} for estimating the mineralisation and export rate of carbon (Table 3). Despite the large difference, R_{pCO_2} and R_{TIC} suggest a net decrease of TIC in the UML of the Bransfield domain between FRUELA 95 and 96. Estimated values of mineralisation 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 mineralisation and export constituted 14% and 58% of primary production, respectively. In contrast to the other areas, we have available data from sediment traps (Anadón et al., 2002); our estimated carbon exported from the euphotic zone ($23.5\,mmol\,m^{-2}\,d^{-1}$ using R_{TIC} and $19.5\,mmol\,m^{-2}\,d^{-1}$ using R_{pCO_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_{TIC} and R_{pCO_2}.

4. Discussion

4.1. 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 (Treguer and Jacques, 1992; Robins et al., 1995; Castro et al., 2002).

4.1.1. Bellingshausen Sea

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., 2002), which was associated with high biomass accumulation and substantial pCO_2 depletion during FRUELA 95. A similar situation also was 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 pCO_2 and chlorophyll, suggesting that photosynthetic CO_2 uptake was responsible for the reduction of surface pCO_2. In our study, we came to the same conclusion from the significant correlation between surface pCO_2 and AOU. However, no clear relationship was observed between surface pCO_2 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 pCO_2 and Chl *a*, the relationship between pCO_2 and AOU points to biological activity as the main process controlling pCO_2 distribution. A similar relationship between pCO_2 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).

Although 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 (Anadón and Estrada, 2002). Mean surface Chl *a* concentration

was reduced from 1.7 to 0.45 mg m^{-3}. Mean surface pCO_2 increased from 280 to 313 μatm. The low pCO_2 levels found during late January 96 in the Bellingshausen domain may still reflect the photosynthetic CO_2 uptake 51 days before. The budget calculations suggest that the increase in pCO_2 was mainly the result of seasonal warming and air–sea exchange.

Estimated residual daily changes of surface pCO_2 were practically negligible from FRUELA 95 to 96 in this area. Hence these evidences suggest that the shift in surface pCO_2 in the Bellingshausen domain from FRUELA 95 to 96 can be accounted for by mainly physical rather than biological factors.

4.1.2. Bransfield Strait

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 pCO_2 content above the atmospheric level (372 μatm). Bellerby et al. (1995) found during spring 1992 similar values of pCO_2 related to low chlorophyll concentrations and attributed them to remnants of upwelled CO_2-rich Circumpolar Deep Water during austral winter. This also may explain our high values of surface pCO_2 in early December 95. An alternative explanation is advection or transport by the BC of CO_2-rich surface water with a Weddell Sea origin influenced by Warm Deep Water entrainment (Hoppema et al., 1995).

About 10 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., 2002). So remnants of winter mixing and upwelling of CO_2-rich deep water before the cruise may explain the 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 (Tables 2 and 3), but also by the increase in the estimated nutrient and TIC anomalies of the upper mixed layer (Castro et al., 2002).

The Bransfield Strait, including the area near Livingston Island, in late January 96 had a mean pCO_2 of 331 ± 11 μatm, a value very similar to that reported by Karl et al. (1991) during January 1987 during the RACER study ($\geqslant 325$ μatm).

4.1.3. Gerlache Strait

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., 2002). Primary production values during both surveys were notably high (Varela et al., 2002), as well as nutrient anomalies (Castro et al., 2002). These data 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.

4.2. 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; Lundberg, 1994; Robertson and Watson, 1995; Takahashi et al., 1997). In this sense, if air–sea CO_2 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 -3.35×10^{-3} MtC d^{-1} (thus about -4.8×10^{-14} MtC m^{-2} d^{-1} for the 52 days and 7×10^{10} m^2 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 suggests great variation in the magnitude of the flux, which can be accounted for by local and short-term variations in the value and direction of the fluxes. A similar conclusion was reached by Metzl et al. (1991) in the southwest 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 (88°W) and between 20° and 60°E (area about 9×10^{10} m^2) 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 $\pm$ 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 47° and 60°S along 6°W in October–November 1992 is noticeably much higher. Regarding the Gerlache Strait, its mean CO_2 flux was -9.6 ± 11.3 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 constitutes significant spring/summer sinks for atmospheric CO_2. 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 CO_2 and O_2 fluxes were found during the Macro'95 and Gerlache 1996 surveys. Moreover, the value of the slope of these correlations was quite similar ($\Delta FO_2/\Delta FCO_2\approx6$). This situation was accompanied by high rates of primary production (Varela et al., 2002) 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 Gerlache 1996 we obtained a lower relationship between both fluxes, suggesting other processes influencing the air–sea fluxes.

4.3. 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_{TIC}) and on pCO_2 (R_{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_{TIC} and R_{pCO_2} in Table 3) corresponded rather well in the Gerlache domain. In this area, the indirect estimation of the exported carbon from the euphotic zone was confirmed by direct sediment trap measurements. This encouraging result 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) 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 supports 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 is 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 $\pm$ STD) $-3.4 \pm 5.1\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ was estimated for the whole area over the survey period. 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, this points to the importance of subareas of the Southern Ocean in the estimation of an annual basin-wide CO_2 flux.

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