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Summer and winter air-sea CO₂ fluxes in the Southern Ocean

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Abstract

The seasonal variability of the carbon dioxide (CO₂) system in the Southern Ocean, south of 50° S, is analysed from observations obtained in January and August 2000 during OISO cruises conducted in the Indian Antarctic sector. In the seasonal ice zone, SIZ (south of 58° S), surface ocean CO₂ concentrations are well below equilibrium during austral summer. During this season, when sea-ice is not obstructing gas exchange at the air-sea interface, the oceanic CO₂ sink ranges from -2 to $-4 \text{ mmol/m}^2/d$ in the SIZ. In the permanent open ocean zone, POOZ (50–58°S), surface oceanic fugacity fCO_2 increases from summer to winter. The seasonal fCO_2 variations (from 10 to 30 µatm) are relatively low compared to seasonal amplitudes observed in the subtropics or the subantarctic zones. However, these variations in the POOZ are large enough to cross the atmospheric level from summer to winter. Therefore, this region is neither a permanent CO₂ sink nor a permanent CO₂ source. In the POOZ, air-sea CO₂ fluxes calculated from observations are about $-1.1 \text{ mmol/m}^2/d$ in January (a small sink) and $2.5 \text{ mmol/m}^2/d$ in August (a source). These estimates obtained for only two periods of the year need to be extrapolated on a monthly scale in order to calculate an integrated air-sea CO₂ flux on an annual basis. For doing this, we use a biogeochemical model that creates annual cycles for nitrate, inorganic carbon, total alkalinity and fCO_2 . The changing pattern of ocean CO_2 summer sink and winter source is well reproduced by the model. It is controlled mainly by the balance between summer primary production and winter deep vertical mixing. In the POOZ, the annual air-sea CO₂ flux is about $-0.5 \text{ mol/m}^2/\text{yr}$, which is small compared to previous estimates based on oceanic observations but comparable to the small CO₂ sink deduced from atmospheric inverse methods. For reducing the uncertainties attached to the global ocean CO_2 sink south of the Polar Front the regional results presented here should be synthetized with historical and new observations, especially during winter, in other sectors of the Southern Ocean. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Carbon dioxide; Southern Ocean; Air-sea CO2 fluxes; Seasonality

1. Introduction

Direct estimates of the air-sea CO_2 fluxes in the Southern Ocean (south of the Polar Front, around

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 50° S) are based mostly on data obtained in austral summer. Previous studies suggest that the Southern Ocean is a summer sink around $-2 \text{ mmol/m}^2/\text{d}$ on regional average in the Pacific and Indian sectors of the Southern Ocean (Murphy et al., 1991; Metzl et al., 1995). At local scales a strong sink reaching $-20 \text{ mmol/m}^2/\text{d}$ in austral winter has been estimated at the Kerfix/JGOFS station situated near

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the Polar Front (Louanchi et al., 2001) but this result cannot be extrapolated for the whole Southern Ocean. At planetary scale, extrapolation methods based on oceanic data and climatological winds estimate a carbon dioxide (CO₂) sink around -0.4 PgC/yr south of 50°S (Takahashi et al., 2002; this value corresponds to a revision of the original calculation, available on http://www.ldeo.columbia. edu/res/pi/CO2). On average the seasonal climatological estimates correspond to about $-3 \text{ mmol/m}^2/\text{d}$ in January and $-1.2 \text{ mmol/m}^2/d$ in July. For large-scale estimates, atmospheric inverse calculations not constrained with a priori information on the ocean suggest that the Southern Ocean is a contemporary CO₂ source (e.g. Ciais et al., 1995). However, when atmospheric inversions are constrained with oceanic pCO_2 climatology, they always tend to reduce the Southern Ocean carbon sink (Gurney et al., 2002). On the other hand, global ocean carbon models generally calculate a strong CO₂ sink in the Southern Ocean on average, but at regional scale ocean models show dramatic differences of the air-sea CO2 flux distributions (Orr et al., 2001).

Seasonal CO₂ observations in the Southern Ocean are desperately needed to reduce the uncertainties on the present carbon budget, to constrain and validate numerical atmospheric and oceanic indirect estimations, and to understand why ocean models or coupled climate/carbon models are so different at high latitudes (Friedlingstein et al., 2003). In order to progress in the synthesis of the contemporary climatological distribution of air-sea CO₂ fluxes in the Southern Ocean, the need of oceanic CO₂ seasonal observations is relevant for two reasons: in summer, when primary productivity is enhanced, the spatial variability of biogeochemical properties is very high, at both large- and meso-scale (e.g. Bakker et al., 1997; Inoue and Sugimura, 1988; Ishii et al., 1998; Jabaud-Jan et al., 2004; Metzl et al., 1991, 1995, 1999; Poisson et al., 1993; Robertson and Watson, 1995; Sabine and Key, 1998; Takahashi et al., 1993). Therefore, extrapolations of local observations made in summer underestimate the pCO_2 spatial variability and consequently the air-sea CO₂ fluxes at regional and basin-scale. The second reason is that in austral winter few data are available in the Southern Ocean and therefore new observations would obviously improve the large-scale monthly pCO₂ climatology deduced from extrapolations (Takahashi et al., 2002) and reduce

uncertainties attached to indirect methods (Gurney et al., 2002). In addition to pCO_2 , the seasonal cycles of dissolved inorganic carbon (DIC) and total alkalinity (TA) are very important to observe and understand in order to validate global ocean biogeochemical models which have difficulties in simulating the carbon cycle in the Southern Ocean.

Since the 1990 cruises have been regularly conducted in the southwestern Indian Ocean to better describe and understand the pCO_2 and air-sea CO2 fluxes seasonality (Poisson et al., 1993; Metzl et al., 1995, 1999). These data have been included in the global pCO_2 data synthesis published by Takahashi et al. (2002) and suggest that the southwestern Indian Ocean represents a significant annual CO₂ sink, especially in the sub-Antarctic zone. For some periods it has been possible to start exploring interannual variability, first in the subtropical and the sub-Antarctic zones (Metzl et al., 1995) and recently at higher latitudes but for summer only (Jabaud-Jan et al., 2004). Although previous cruises represent an important contribution to the global pCO_2 synthesis (all cruises are available at CDIAC, http://cdiac.ornl. gov/oceans/pco2inv.html), no cruises were conducted during austral winter south of the Polar Front (around 50°S in the Indian sector).

In 2000 we have, for the first time, been able to obtain measurements of the oceanic CO₂ system $(pCO_2, DIC and TA)$ for the sea surface and water column at high latitudes in both summer and winter seasons. This paper extends previous analyses, by presenting new data that aids in our understanding of the seasonal CO₂ cycle and associated air-sea fluxes in high latitudes of the Southern Ocean. After a short description of the seasonal distribution at large-scale (20– 60° S) this paper is focused on the seasonal variations in the Southern Ocean, south of the Polar Front. Based on observations we evaluate the air-sea CO₂ fluxes for summer and winter. We then use a 1D semi-prognostic biogeochemical model to simulate the annual cycles of nitrate, DIC and pCO_2 in the permanent open ocean zone (POOZ), and we derive an estimate of the annual air-sea CO2 flux in this region. The observed and simulated seasonalities of pCO_2 and CO_2 flux are compared to other estimates (climatology and atmospheric inversions). Finally we attempt to extrapolate the annual flux for the circumpolar zone based on regional biogeochemical characteristics.

2. Data collection and methods

As part of the OISO program (Océan Indien Service d'Observations, INSU/IPSL), we conducted two cruises in 2000 in the southwestern Indian Ocean (20-60°S) onboard the R.S.S. Marion-Dufresne (IPEV/TAAF): one during austral summer (January 2000) and another in winter (August 2000). During these cruises, hydrological and biogeochemical properties were measured in both the surface and all through the water column from 20°S to 60°S (Fig. 1). Continuous sea-surface measurements were obtained for temperature (SST), salinity (SSS), fluorescence, CO₂ fugacity (fCO₂), total DIC and TA. Surface water was also regularly sampled to measure salinity, nutrients (nitrate + nitrite, silicate) and chlorophyll a concentrations. In addition to surface data, the water column was sampled in selected regions. For most of the stations only the first 1000 m of the water column were sampled at each station, a strategy designed to harmonize the timing of the cruise's operations for logistics to the French Sub-Antarctic Islands. During the OISO cruises in year 2000 two stations were full depth in the POOZ: one situated south of the Polar Front (Station 10 at 50°40'S, a reoccupation of station INDIGO 16, Poisson et al., 1988, and KERFIX/JGOFS time series station, Jeandel et al., 1998), and one located north of the seasonal ice zone (SIZ) (Station 11 at $56^{\circ}30'$ S- 63° E).

The hydrographic casts were performed with a conductivity-temperature-depth (CTD Seabird 911 plus) equipped with a fluorometer (Mk III, Aquatracka). Temperature and conductivity probes were calibrated before each cruise. A 24-rosette was used for water-column sampling. Bottles were fired at standard depths to measure nutrients, chlorophyll a, DIC, TA. Continuous surface and water-column salinity records were controlled by regular conductivity measurements (Guildline Autosal 8400B). Sea-surface temperature was also checked against CTD's surface temperature. Nutrients (silicate and nitrate + nitrite) were measured with an Autoanalyzer II Technicon by standard colorimetric methods. TA and total DIC were measured onboard for both surface and water-column samples by a potentiometric method with a closed cell (Goyet et al., 1991). For continuous measurements of sea-surface TA and DIC, the system was automated for sampling seawater and transferring it into the cell. For calibration, we used the certified referenced materials (CRMs, Batch #46 and #49) provided by Pr. A. Dickson (SIO, University of California). The accuracy estimated from the CRMs values for both cruises was between 1.9 (± 0.8) and 2.2



Fig. 1. Track of the OISO-4 and OISO-5 cruises conducted in January and August 2000 in the Southern Indian Ocean. This study focuses on seasonal observations made in the Southern Ocean south of Kerguelen Island. Stations 10 and 11 around 51°S and 56°S are located (filled circles). The boundary of the polar front as deduced from sea surface temperature (Moore et al., 1999) is also indicated.

 $(\pm 0.8) \mu mol/kg$ for TA and DIC. The reproducibility estimated from replicate analysis of surface and deep samples (mean difference) was on average 2.4 $\mu mol/kg$ for TA and 1.4 $\mu mol/kg$ for DIC.

The fCO_2 measurement technique has been previously described for cruises conducted during years 1990-1998 (Poisson et al., 1993; Metzl et al., 1995, 1998, 1999; Jabaud-Jan et al., 2004). This instrumentation was also used by our group during the international at-sea intercomparison of fCO_2 systems (Koertzinger et al., 2000). In short, seasurface water was continuously equilibrated with a "thin film" type equilibrator thermostated with surface seawater. The CO₂ in the dried gas was measured with a non-dispersive infrared analyser (NDIR, Siemens Ultramat 5F). Standard gases for calibration (270, 350, 480 ppm) and atmospheric CO_2 were measured every 7 h. To correct measurements to in situ data, we used polynomials given by Weiss and Price (1980) for vapour pressure and by Copin-Montégut (1988, 1989) for temperature (temperature in the equilibrium cell was about 0.2–0.8 °C warmer than SST). The oceanic fCO_2 data are accurate to about $\pm 0.7 \,\mu$ atm.

Atmospheric CO₂ concentrations measured regularly during the cruises are presented in Fig. 2. South of 30°S, the average concentrations were 366.2 ppm (\pm 0.5) in January 2000 and 367.6 ppm (\pm 0.4) in August 2000. The temporal increase of 1.4 ppm from January to August is associated with both remote anthropogenic emissions and natural but low seasonal variations of atmospheric CO₂ in this region. The average values are close to CO₂



Fig. 2. The meridional distribution of atmospheric CO₂ concentrations measured on-board for January 2000 (open triangles) and August 2000 (filled circles). The average concentrations of atmospheric CO₂ of 366.3 ppm (± 0.6) in January and 367.6 ppm (± 0.4) in August compared well with those obtained on a daily basis at the Amsterdam monitoring station located at 38°S in the South Indian ocean.

measurements made at monitoring station Amsterdam (Fig. 1) located at 38°S in the South Indian Ocean, where monthly CO_2 concentrations were 366.3 ppm (± 0.1) for January 2000 and 367.2 (+0.2) for August 2000 (M. Ramonet, LSCE/IPSL, pers. comm.). It should be noted that some noise and variabilities of atmospheric CO₂ concentrations have been identified in the northern part (maybe related to continental air masses as we observed this signal only in the western region) and in the frontal region or near sub-Antarctic islands Crozet and Kerguelen around 47-50°S in summer. We will see in the next section that the frontal zone is dominated by a large oceanic fCO_2 variability in summer. It is also interesting to note that during summer the atmospheric CO₂ concentration decreases southward (not considering one sample measured near Kerguelen Island at 49°S). During austral winter, this is the opposite, CO₂ concentrations being lower at 30-45°S compared to measurements made at 45-55°S (Fig. 2). The meridional CO₂ gradient between the subtropical and polar regions was about 0.5 ppm, representing 10% of the signal observed between the Equator and South Pole (GLOBALVIEW-CO2, 2003). Considering that the terrestrial carbon sources and sinks are almost non-existent south of 40°S (e.g. Bousquet et al., 2000), the changing distribution of atmospheric CO₂ concentrations observed in January and August during our cruises could reflect relatively large changes in oceanic CO₂ sources and sinks in both sub-Antarctic zone and Southern Ocean.

3. Seasonal observations of the CO₂ system in the Southern Indian Ocean

3.1. Large-scale oceanic fCO₂ seasonal variability

The summer and winter fCO_2 measurements made in year 2000 in the Southern Indian Ocean show large seasonal variations in all regions, from the subtropics to high latitudes along both the western and eastern tracks (Figs. 3A and B). In the subtropical region (20–35°S), the seasonal amplitude varies between 50 and 70 µatm, with undersaturation in winter when the surface ocean is colder. This is a well-known seasonal signal observed in all subtropical regions of the northern and southern hemispheres (Bates et al., 1996; Metzl et al., 1998; Poisson et al., 1993; Weiss et al., 1982; Winn et al., 1998).



Fig. 3. Meridional distribution of oceanic and atmospheric fCO_2 measured in January 2000 (open triangles) and August 2000 (filled circles) in the southwestern Indian Ocean along the western track (A) and the eastern track (B). Thin lines indicate the atmospheric fCO_2 . SIZ is specified with a grey triangle.

In the frontal zone $(35-50^{\circ}S)$, which includes the subtropical, the Agulhas, the Sub-Antarctic and the Polar Fronts (Belkin and Gordon, 1996), the changing distribution from summer to winter is complex. During summer fCO_2 variations at mesoscale are governed mostly by primary production, whereas in winter the fCO_2 distribution appears more homogeneous. On average, the oceanic CO_2 sink in the frontal zone is stronger in summer than in winter (Metzl et al., 1999). At local scale, however, this could be the reverse as shown by the measurements at 41-42°S (Fig. 3A). There, oceanic fCO_2 was near equilibrium in summer but undersaturated in winter. The low oceanic fCO_2 $(<320 \,\mu atm)$ observed in winter at 41–42°S was associated with a very strong eastward jet (up to 200 cm/s measured by ADCP onboard) and to a sharp increase of sea-surface fluorescence. This rather high biological signal for winter conditions, which is observed each year since 1998 (as deduced from an inspection of the SeaWIFS Chlorophyll a monthly data set) probably originates from the Agulhas Return Current (ARC) or is controlled by the merging of the ARC and the sub-Antarctic Front, as we did not observe such a biological event (and low fCO_2) further east during the winter cruise (Fig. 3B).

South of 50°S, in the Southern Ocean, although the SST is obviously higher in January than in August, the oceanic fCO_2 is lower during austral summer. In the Southern Ocean, seasonal variations of fCO_2 are not as large as in the subtropics or in the frontal zone but are large enough to create a changing pattern of summer CO₂ sink and winter CO₂ source. This variability is detailed in the following sections.

3.2. The seasonal distribution of the CO_2 system in the Southern Ocean

Continuous sea-surface observations of the CO₂ system south of 50°S are presented in Fig. 4. Other properties (nutrients and chlorophyll) measured from discrete sampling are shown in Fig. 5. In winter, no observations were obtained in the SIZ south of 59°S. The seasonal variations of inorganic carbon properties, nutrients and chlorophyll are clearly revealed in the POOZ (50-56°S); for this region we have calculated seasonal averages for each property (Table 1). TA is almost the same during both seasons (the seasonal difference of normalized alkalinity is less than 1 µmol/kg). Therefore, the seasonal variation of oceanic fCO_2 is controlled mainly by changes in DIC and temperature. During summer, the decreases of DIC and nutrient concentrations are due to consumption by photosynthesis. In winter, the chlorophyll concentrations are low and homogeneous (Fig. 5, Table 1), information never captured by satellite because of cloud cover. During this season, when deep mixing occurs and primary production is low because of light limitation, surface DIC and nutrient concentrations are high. The continuous measurements indicate that the seasonal change of DIC is about the same over the entire region from 50°S to 59°S (Fig. 4). On average, the increase of DIC is about $+15 \mu mol/kg$ from January to August (Table 1). This is observed both in surface waters (Fig. 4) and in the mixed layer (Fig. 6).

The seasonal variation of DIC in the Indian POOZ is significant but lower compared to other oceanic regions. For example, in the subtropics DIC varies from 20 to 40 μ mol/kg (Keeling, 1993; Bates et al., 1996; Metzl et al., 1998). In the Sub-Polar North Atlantic and Sub-Antarctic regions the observed seasonal DIC variations are about



Fig. 4. Seasonal distribution of SST, fCO_2 (ocean and air, as in Fig. 3A), DIC and TA observed during OISO cruises along a repeated track in the Southern Ocean (Indian sector, 63–68°E): for January 2000 (grey line and open triangles) and August 2000 (black line and filled circles). SIZ during austral winter is indicated by a grey triangle.

 $50 \,\mu\text{mol/kg}$ (Takahashi et al., 1993; Metzl et al., 1999). In the subarctic region of the Pacific Ocean the seasonal change of DIC could reach $100 \,\mu\text{mol/kg}$ (Takahashi et al., 1993). The seasonal variations of DIC observed during OISO cruises in the Indian Antarctic waters (Fig. 4) are also lower than those

observed in the Pacific Antarctic waters (Rubin et al., 1998): by comparing observations made in summer 1992 and summer/winter 1994, Rubin et al. (1998) indicate that DIC concentrations increase from austral summer to winter by $30-50 \,\mu\text{mol/kg}$ at different locations. On the other hand, our results



Fig. 5. Seasonal distribution of chlorophyll (top), silicate (middle) and nitrate (bottom) observed during OISO cruises along a repeated track in the Southern Ocean (Indian sector, 63–68°E): for January 2000 (grey line and open triangles) and August 2000 (black line and filled circles). SIZ during austral winter is indicated by a grey triangle.

show slightly higher seasonal changes compared to what has been observed in the Weddell Sea (around $10-15 \mu mol/kg$, Hoppema et al., 1995). Although seasonal observations of DIC in the Southern Ocean are sparse, the comparison of the Indian, Atlantic and Pacific sectors indicates that DIC is always higher during austral winter over the entire Southern Ocean.

The same conclusion can be reached when the seasonal variations of nutrients are analysed. In the Indian POOZ, average seasonal changes (winter minus summer) for year 2000 were $10.8 \,\mu$ mol/kg for silicate and $2.7 \,\mu$ mol/kg for nitrate (Table 1). In the

South Pacific POOZ, Rubin et al. (1998) reported seasonal variations that vary between 0 and $20 \mu mol/kg$ for silicate and between 3 and $7 \mu mol/kg$ for nitrate, depending on the location. Interestingly, although the seasonal amplitudes of both DIC and nutrients are not the same in the two regions (Indian and Pacific POOZ), we found about the same relative variations: attributing the seasonal changes for DIC and nutrients to biological activity only, the average measurements in the Indian POOZ lead to a C/N ratio of 5.44, which is close to the value of 62/11 (5.6) reported by Copin-Montégut and Copin-Montégut (1978) in the South Numbers in italics indicate SST (RS, Reynolds and Smith, 1994) and Chlorophyll (Chl) (monthly Chl from SeaWIFS) as well as simulated values (*f*CO₂, DIC,TA, nitrate) obtained using the 1D biogeochemical model applied in the Indian POOZ.

Indian and lower than the C/N ratio of 6.9 (\pm 0.6) reported by Rubin et al. (1998) in the South Pacific or 6.2 as deduced by Ishii et al. (1998) in the marginal ice zone (MIZ) south of Australia at 140°E. For silicate, our seasonal observations lead to a Si/C ratio of 0.72, which is also higher than the ratio of 0.66 (\pm 0.02) deduced in the South Pacific (Rubin et al., 1998) but the same (0.72) as for the MIZ (Ishii et al., 2002). These ratio are relatively close to Redfield values, indicating that biological processes are responsible for a significant part of the seasonal variations of the carbon system, including oceanic DIC and fCO_2 , and consequently the seasonal air–sea CO₂ fluxes.

4. Seasonal and annual air–sea CO₂ fluxes in the Southern Ocean

4.1. Observed fluxes in January and August 2000

The air-sea CO_2 flux, *F*, may be calculated from in situ observations following the equation

$$F = kwK'_0\Delta f \operatorname{CO}_2,\tag{1}$$

where kw is the CO₂ gas transfer coefficient, which depends on wind speed (Wanninkhof, 1992), K'_0 is the solubility of CO₂ in seawater, which is a function of temperature and salinity (Weiss, 1974), and Δf CO₂ is the sea-air fCO₂ difference (Δf CO₂ = fCO₂ocean - fCO₂atm).

In January, the sea-surface fCO_2 is always below or near the atmospheric level south of 50°S (Fig. 4). In the SIZ, undersaturation ($\Delta f CO_2$) varies from -15 to $-30 \,\mu$ atm, whereas in the POOZ, $\Delta f CO_2$ is only about -7μ atm on average. During winter fCO_2 is above the atmospheric level in the POOZ $(\Delta f CO_2 = 10 \,\mu atm)$. To obtain an estimate of the seasonal CO₂ fluxes in the SIZ and POOZ, we have calculated the fluxes using Eq. (1) with observed oceanic and atmospheric fCO2 and using two formulations for the gas transfer coefficient (Wanninkhof, 1992 or Wanninkhof and McGillis, 1999; hereinafter W92 and WM99). We also use both climatological winds (Hellerman and Rosenstein, 1983) and winds observed during the cruise. The results are summarized in Table 2.

In January, the flux ranges from -2.1 to $-4.0 \text{ mmol/m}^2/\text{d}$ in the SIZ and from -1.1 to $-1.7 \text{ mmol/m}^2/\text{d}$ in the POOZ, depending the winds and gas transfer formulation. On average, the summer sink estimated in January 2000 in the Indian sector is close to previous values reported for austral summer in the Southern Ocean (Murphy et al., 1991; Poisson et al., 1994; Metzl et al., 1995). During winter, south of 59°S (in the SIZ), the air–sea exchange is probably limited by sea-ice cover. In August, the POOZ is always a CO₂ source, with values ranging from 2.5 to 11.6 mmol/m²/d.

The large oceanic CO_2 source in the POOZ calculated for austral winter 2000 is opposite to previous results suggesting that the CO₂ sink in the POOZ is maximal (up to $-20 \text{ mmol/m}^2/d$) during the windy season (Louanchi et al., 1999, 2001). These differences are explained mostly by differences in the oceanic seasonal fCO_2 cycle, as diagnostic and semi-prognostic methods, both based on the original KERFIX/JGOFS data set for year 1993, calculated ocean CO₂ undersaturation during all seasons (fCO2 around 305-340 µatm; Louanchi et al., 2001). To understand the opposite source/sinks seasonal scenario discussed above we have analysed the original KERFIX data set (www.obs-vlfr.fr/cd rom dmtt/kfx main.htm) and found that significant corrections for DIC and TA need to be applied. Indeed, a cross-check comparison between deep samples (depth > 700 m,

Seasonal observed and modelled biogeochemical properties in surface water and air-sea CO_2 fluxes averaged in the POOZ (50–56°S) of the Indian sector of the Southern Ocean (based on OISO cruises, in January and August 2000)

Table 1

	Jan-2000	Aug-2000
SST (°C)	3.50 ± 0.52	1.94 ± 0.41
SST (RS)	3.09	1.69
fCO_2 (µatm)	356.0 ± 5.3	375.5 ± 3.9
mod. fCO_2	349.9	378.6
DIC (µmol/kg)	2130.1±6.9	2146.5 ± 6.0
mod. DIC	2134.3	2156.6
NDIC (µmol/kg)	2199.5 ± 5.3	2214.4±4.4
TA (μmol/kg)	2282.6 ± 3.3	2285.6 ± 2.8
mod. TA	2281.2	2282.7
NTA (µmol/kg)	2357.0 ± 1.6	2357.8 ± 1.4
Nitrate (µmol/kg)	25.0 ± 1.4	27.7 ± 0.9
mod. Nitrate	25.0	28.0
Silicate (µmol/kg)	13.0 ± 6.9	23.8 ± 6.6
Chl in situ (µg/l) Chl Seawifs (µg/l)	$\begin{array}{c} 0.58 \pm 0.32 \\ 0.39 \pm 0.07 \end{array}$	0.15±0.02 No data



Fig. 6. Seasonal depth profiles of potential temperature (top) and DIC (bottom) at two stations in the POOZ in the Southern Ocean: on left station OISO-11 ($56^{\circ}30'S-63^{\circ}E$), on right station OISO-10 ($50^{\circ}40'S-68^{\circ}25'E$). Seasonal data were obtained in January 2000 (open triangles) and August 2000 (filled diamonds).

salinity > 34.55) measured at the KERFIX location (DIC and TA for year 1993) and during OISO cruises suggests a correction to the original KER-FIX data by $-35 \mu mol/kg$ for DIC and $-49 \mu mol/kg$ for TA. Interestingly when these corrections were taken into account, we calculated lower fCO_2 during austral summer (345 µatm for year 1993) than during winter (360 µatm). Therefore, and after corrections, the seasonality of the air–sea CO₂ fluxes during the KERFIX/JGOFS time series (1993) appeared to be coherent with our observations made during summer and winter 2000. It is likely that during the decade 1990–2000 the POOZ in the south-western Indian Ocean was a CO_2 sink during austral summer and a source during winter.

The high CO₂ source we calculated for winter is also controlled by the winds, which were very high during the OISO-5 winter cruise (13 m/s on average). These high wind-speed values observed onboard during a few days were also detected by the ERS2 satellite sensor, from which we derived an average wind speed of 11.8 (\pm 0.7) m/s for the same period and the same region. This indicates that the oceanic CO₂ source was probably prolonged for Table 2 Air-sea CO₂ fluxes averaged in the SIZ (58–60°S) and the POOZ (50–56°S) of the Indian sector of the Southern Ocean (based on OISO

cruises, in January and August 2000)	cruises,	in	January	and	August	2000)	
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	SIZ Jan-2000	POOZ Jan-2000	POOZ Aug-2000
	Air-sea CO ₂ fl	ux (mmol/m ² /d)	
Climatological winds			
W92	-3.8	-1.1	2.5
WM99	-4.0	-1.5	4.6
Observed winds			
W92	-2.1	-1.2	4.5
WM99	-2.2	-1.7	11.6

The air–sea CO_2 fluxes are calculated using observed oceanic and atmospheric fCO_2 during the cruises, climatological or observed winds, and gas transfer formulations from Wanninkhof (1992) or Wanninkhof and McGillis (1999), noted W92 and WM99.

several weeks, may be several months, during winter 2000. This would be true if the oceanic fCO_2 is above equilibrium during the same period.

After the results here presented, given the changing pattern of summer sink and winter source in the POOZ, the quantification of an annual flux cannot be achieved with simple interpolation of the seasonal observations. One needs first to create a complete annual cycle of oceanic fCO_2 , from which the annual flux can be more realistically derived.

4.2. Annual fluxes in the POOZ estimated from a model

In order to compute an integrated annual air-sea CO₂ flux, we simulate a complete annual ocean fCO_2 cycle using a 1D biogeochemical model for the POOZ region $(50-56^{\circ}S/60-68^{\circ}E)$. The original model developed by Louanchi et al. (1996) has been applied and adapted at different locations, the Arabian Sea (Goyet et al., 1998), the subtropical Indian Ocean (Metzl et al., 1998) and the Southern Ocean (Louanchi et al., 1999; Louanchi and Hoppema, 2000; Jabaud-Jan et al., 2004). In short, this model calculates independently five processes that control the variations of oceanic fCO_2 in surface waters: the air-sea exchange, the thermodynamics, the biological activity, the vertical mixing between surface and subsurface waters, and the variations of alkalinity. The model is constrained by monthly 2000 SST (Reynolds and Smith, 1994), climatological winds (Hellerman and Rosenstein, 1983), mixed-layer depth (MLD) and Chlorophyll a (Fig. 7). The monthly variations of the MLD are adapted from both climatology and the seasonal profiles obtained at stations OISO-10 and 11 in the



Fig. 7. Annual course of forcing terms used in the 1D biogeochemical model. Top: chlorophyll concentrations (open circles) and MLD (black triangles). Bottom: SST (open diamond) and wind speed (black squares).

POOZ ($50^{\circ}40'S$ and $56^{\circ}30'S$, Fig. 6). The MLD is about 50 m in summer and 150–200 m during winter. Initial conditions for DIC and nitrates for surface and subsurface (below the winter mixed layer) are also based on observations made in summer and winter (Fig. 6). For chlorophyll, we use the monthly 2000 level-3 SeaWIFS data (NASA) averaged over the POOZ region investigated in this study ($50-56^{\circ}S/60-68^{\circ}E$). Because satellite observations are almost non-existent during June–August because of cloud cover, we create a complete annual chlorophyll cycle for year 2000 by introducing in situ observations we obtained in austral winter; during this season, the meridional distribution of sea-surface chlorophyll in the POOZ was homogeneous, with concentrations between 0.12 and $0.17 \,\mathrm{mg}\,\mathrm{m}^{-3}$ (Fig. 5). In addition to monthly values of SST, MLD, wind and chlorophyll, we need to define the atmospheric CO₂ concentration to run the model. The seasonal variations of CO₂ in the air are very low compared to oceanic fCO_2 variations in this region (Fig. 3). We thus fix an annual average value of 366 ppm for the atmospheric CO₂ concentration to calculate the air-sea CO₂ fluxes. In this study, we are interested in estimating the annual air-sea CO₂ flux, which depends on both the annual oceanic fCO_2 cycle and wind speed. In a region where winds are very high (the highest winds over the world ocean are regularly observed in this region) the process of gas exchange could control significant temporal variations for DIC and fCO_2 . We will test the sensitivity of this process by employing two different formulations for the gas exchange coefficient, the quadratic and the cubic relations previously described (W92 and WM99).

Compared to the observations, the model simulates well the nitrate and DIC concentrations for January and August 2000 (simulated concentrations are listed in Table 1). The model is also able to reproduce the oceanic fCO_2 observed during these months (Fig. 8). In addition, the model creates a significant decrease of nitrates and DIC during summer, until March. For nutrients, this is con-



Fig. 8. Annual cycle of sea surface fCO_2 simulated in the south Indian POOZ. The results are presented using different gas transfer formulations: black line, Mod-W92 (Wanninkhof, 1992) or dashed line, Mod-WM99 (Wanninkhof and McGillis, 1999). The thin line represents the atmospheric fCO_2 . Black circles represent average and standard deviation of fCO_2 observations obtained in the region. The climatological monthly fCO_2 values (Takahashi et al., 2002) averaged in the same region are also shown (open triangles).

sistent with earlier observations and biogeochemical models applied at the JGOFS/KERFIX time-series station conducted in the same region in 1992-1994 (Jeandel et al., 1998; Pondaven et al., 1998; Louanchi et al., 2001). At the end of summer, the simulated fCO_2 in March–April is slightly lower but not dramatically different compared to values observed in March 1993 (330 µatm) or April 1991 (335–345 µatm) in the Indian POOZ (Poisson et al., 1993; Robertson and Watson, 1995). However, the fCO_2 minimum simulated during summer is much lower compared to the climatological products (Takahashi et al., 2002), whereas in winter our fCO_2 observations and simulation are higher (Fig. 8); this indicates that the seasonal amplitude of fCO_2 could be much larger than in the climatology, and the same is true for air-sea CO₂ fluxes.

The model suggests that primary production is large enough in the POOZ and over a relatively long period (December-March, as in Moore and Abbott, 2000) to cause a continuous diminution of DIC and fCO_2 until late summer. When biological activity dominates the vertical mixing and warming in summer, oceanic fCO_2 decreases significantly to values well below atmospheric equilibrium (Fig. 8). In winter, this is the opposite: all properties (nitrate, DIC, fCO_2) increase when vertical mixing dominates. Although the SST decreases during winter (Fig. 7), the fCO_2 increases continuously during April-August, and its value is above atmospheric concentration over a relatively long period, from May to September. This implies significant reduction of the summer sink when the fluxes are integrated over the year. Lastly, the model shows that the choice of gas transfer coefficient formulation does not dramatically change our view of the annual fCO_2 cycle we attempt to reproduce. The largest differences are obtained during March-April when the ocean CO₂ sink is strong and affects shallow waters: during this period, DIC is $+3 \mu mol/$ kg higher and fCO_2 is $+6 \mu$ atm higher (Fig. 8) when WM99 is used instead of W92.

The annual course of the air-sea CO_2 flux is shown in Fig. 9 for both runs (W92 and WM99). Because the winds are always high in the Indian POOZ and do not vary dramatically from month to month, the air-sea CO_2 flux follows the oceanic fCO_2 cycle, slightly modulated by the value of the gas transfer coefficient. The simulated values for January (-1.4 mmol/m²/d with W92 or -2 mmol/ m²/d with WM99) and August (3.5 or 6 mmol/m²/d) compare well with estimations deduced from the



Fig. 9. Monthly air–sea CO_2 fluxes (mmol/m²/d) simulated in the Indian POOZ (50–56°S) for year 2000. Two simulations are presented with different gas transfer coefficients (W92 = black line or WM99 dashed line). These regional results are compared with the averaged monthly global fluxes (Pg C/month, right axis) estimated for the Southern Ocean (>50°S) by an AIM(average for years 1990–1997) applied at global scale by Bousquet et al. (2000).

OISO data and climatological winds (described in previous section, Table 2). The simulated flux is also consistent with previous calculations based on average observations made in austral summer in the Antarctic sectors of the Indian Ocean (Metzl et al., 1995) and of the Pacific Ocean (Murphy et al., 1991). With the model, we also learn that the summer CO₂ sink occurs over a 6-month period, December-May, and the winter source occurs from June to October. The oceanic CO₂ sink is at maximum in March, when oceanic fCO₂ is low $(<320 \,\mu atm)$. At that period the sink could be as large as $-15 \text{ mmol/m}^2/\text{d}$ when the WM99 gas exchange formulation is used. The oceanic CO_2 source is at maximum in August, with maximum value of $6 \text{ mmol/m}^2/d$. As expected the oceanic summer sink and winter source are larger when the cubic wind-speed formulation for the gas transfer coefficient is used (WM99 versus W92). However, the yearly integration of the monthly air-sea fluxes presented in Fig. 9 leads to almost the same annual flux of $-0.50 \text{ mol/m}^2/\text{yr}$ with the quadratic W92 relation against $-0.49 \text{ mol/m}^2/\text{yr}$ with the cubic WM99 relation. It is important to notice that if, in reality, the low oceanic fCO_2 in late summer is not as low as in our simulation, the integrated annual sink would be even smaller than $-0.5 \text{ mol/m}^2/\text{yr}$. As an extreme case, if the fCO_2 diminution during January-March is not as dramatic as suggested by our model, the Indian POOZ could represent an annual oceanic CO₂ source.

4.3. Regional and large-scale air-sea CO_2 fluxes in the Southern Ocean

Most of previous data-based air-sea CO₂ flux calculations in the Southern Ocean have been reported for austral summer. Few studies reported annual fluxes. In the POOZ the value derived from our model, a sink of about $-0.5 \text{ mol/m}^2/\text{yr}$, is much lower than earlier calculations for the same region (Louanchi et al., 1999, 2001); for the period 1990–1994, these authors reported a CO₂ sink that varies between -0.8 and $-5.0 \text{ mol/m}^2/\text{yr}$ at the JGOFS/KERFIX time-series station. This is two to ten times larger than in our analysis, and we believe that a strong sink in the Indian POOZ (up to $-5 \text{ mol/m}^2/\text{yr}$) was an unrealistic estimate.

At regional scale, our results could also be compared with the climatology composed by Takahashi et al. (2002). Interestingly, the average climatological value in the region $56^{\circ}S/60-70^{\circ}E$ is a sink of $-0.44 \text{ mol/m}^2/\text{yr}$, very close to our calculations. However, if the annual fluxes (the sum of the monthly values) are converging, it is important to recall that the seasonality is very different (Fig. 8). Our actual perception, based on seasonal observations and simple modelling approach is that the POOZ in the western Indian antarctic sector represents a modest annual carbon sink, because the relatively strong summer sink compensates the large winter source. Climatologies, global ocean models or atmospheric inversions should first resolve this seasonality before concluding on annual fluxes.

Atmospheric inverse methods (hereinafter, AIMs) also estimate a large-scale relatively small carbon sink in the Southern Ocean. Compared to the seasonal CO₂ source/sink balance deduced from our observations and biogeochemical model, it is interesting to note that results derived from AIMs (e.g. Bousquet et al., 2000) do suggest that the oceanic CO₂ sink is at maximum during austral summer and reduced during winter (Fig. 9). Such seasonality was also recently derived with different atmospheric transport models (TransCom project, Gurney et al., 2004): on average, the AIMs estimate a maximum carbon sink in Januray-February in the Southern Ocean and minimum carbon sink (almost at equilibrium) in September. Although this comparison is a regional ocean view (regional observations) versus a global atmospheric view, this is an encouraging result for both methods, allowing the extrapolations of our calculations. The annual fluxes deduced from AIMs vary between -0.2 and -0.5 PgC/yr (Bousquet et al., 2000; Gurney et al., 2003, 2004; Roy et al., 2003), corresponding to an average CO₂ sink of -0.4 and $-1.0 \text{ mol/m}^2/\text{yr}$ south of 50°S. Although these values are not far from our estimate of $-0.5 \text{ mol/m}^2/\text{yr}$, the comparison has to be taken with caution because in atmospheric inversion, the Southern Ocean is represented as a single big box south of 50°S. At present the regional puzzle in AIMs does not separate the POOZ and the SIZ in any of the different Southern Ocean sectors. The contrasting observations presented in this paper suggest that regionalization of the large Southern Ocean should be taken into account in future AIMs applications.

In order to compare our results with large-scale estimates one needs to extrapolate the regional value obtained in the southwestern Indian sector to the entire Southern Ocean, which is not an easy task. First, we have learned from past observations that large variability of oceanic fCO_2 exist during summer in all sectors of the Southern Ocean, mostly due to biological activity (e.g. Ishii et al., 2002; Metzl et al., 1991, 1995; Robertson and Watson, 1995). Extrapolations based on fCO₂/SST relationships have been proposed and work well for the subtropical and sub-Antarctic zones, but it has been shown clearly that such a simple diagnostic approach is not adapted for the Southern Ocean (Metzl et al., 1995). Second, there are too few observations during winter to be certain that the

data described in this paper could be extrapolated to the entire Southern Ocean. Finally, it is worth mentioning that large inter-annual variabilities of the annual mean CO₂ sources and sinks have been reported in the southern hemisphere. South of 30°S, a surface that is largely covered by oceans, Conway et al. (1994) estimated large and relatively rapid drops of the carbon sink (e.g. -0.50 PgC/yr in 1988 against -1.55 PgC/yr in 1989). For the region south of 50°S, Bousquet et al. (2000) reported that the ocean carbon sink could vary as much as 0.4 PgC/ yr, and we notice that such an event is not marginal as variations of about $\pm 0.25 \text{ PgC/yr}$ occurred at least 6 times during 15 years (1983-1997). Few repeated data exist to document the interannual variability as was conducted in the equatorial Pacific Ocean (Feely et al., 2002). Recently Jabaud-Jan et al. (2004) compared austral summer data only (January 1998 and 2000) and showed that the oceanic fCO_2 variations could be large enough to change the ocean CO_2 sink by a factor of two in the POOZ. In the SIZ they reported a different scenario as this region was a CO₂ source in January 1998 and a sink in January 2000. In this context, the association of different cruises at different periods may create unrealistic patterns of highs and lows in pCO_2 . However, as was done for the tropical Pacific, where measurements conducted during ENSO events were filtered (Takahashi et al., 2002), we have no clear indications for periods that should be eliminated for constructing pCO_2 climatology in the Southern Ocean. At present, and certainly also because the data are sparse, all available observations are used for high-latitude climatological maps.

With all these precautions in mind we could compose only a crude extrapolation for the year 2000 based on our regional results, as explained below, not for the whole Southern Ocean. Here we assume that the regional seasonal cycle observed in the POOZ and SIZ are representative of the entire surface of these two regions only. The oceanic surfaces considered in our extrapolation are neither zonal nor fully circumpolar (e.g. an integration over the entire 50-60°S band) but are referred to regions defined by hydrological and biogeochemical criteria (Moore and Abbott, 2000). Therefore, circumpolar sectors where the POOZ was not identified are not included in our extrapolation. This concerns the southwestern Pacific, the southeastern Pacific and the Drake Passage (see Plate 4 in Moore and Abbott, 2000), where the seasonal pCO_2 distributions should be representative of the sub-Antarctic and Polar Front zones at latitude 55–63°S. Also, we are not extrapolating our results to the Weddell and Ross Seas, which represents different ecological domains (Moore and Abbott, 2000) and where distribution of oceanic pCO_2 could be significantly different than what we observed in the Indian Antarctic sector. We also consider that the gas exchange at the air-sea interface occurs only during 4 months in the SIZ. The integration of the regional CO₂ flux over the SIZ and POOZ areas are respectively, 21.2 and 9 million km² (Moore and Abbott, 2000) and leads to a carbon sink of -0.12PgC/yr for the SIZ and -0.05 PgC/yr for the POOZ. Recall that south of 50°S (the northern boundary of the Southern Ocean in all AIMs approaches) our calculation excludes the Weddell and Ross Seas as well as a relatively large area in the southern Pacific. Assuming each of these regions acts as large or moderate CO_2 sink, which is certainly the case for the southern sub-Antarctic zone in the Pacific and high latitudes in the Atlantic (Miyake et al., 1974; Murphy et al., 1991; Sabine and Key, 1998; Takahashi et al., 2002), then the total air-sea flux of -0.17 PgC/vr we estimate in the entire POOZ and SIZ represents a lower limit for the annual ocean sink south of 50°S. This is also in the low range of the values deduced from AIMs approaches, between -0.2 and -0.5 PgC/yr south of 50°S (Bousquet et al., 2000; Gurney et al., 2003, 2004; Roy et al., 2003).

5. Concluding remarks

The new observations obtained during austral summer and winter in year 2000 in the Indian sector of the Southern Ocean indicate that this region is a not a permanent CO₂ sink or source. During austral summer our observations in the SIZ and the POOZ show about the same sea-surface fCO_2 distribution and air-sea CO₂ fluxes as observed during other years and in other Antarctic sectors (e.g. Murphy et al., 1991; Metzl et al., 1995). Although not as large as observed in the subtropical and sub-Antarctic zones, the seasonal variations of oceanic fCO_2 are large enough in the POOZ to move from undersaturation conditions in summer to oversaturation in winter. In this region, both biogeochemical data (nutrient, DIC, TA) and a simple modelling analysis show that the CO₂ source/sink seasonality is controlled mostly by variations of primary production and vertical mixing. Enhanced

biological processes dominate the warming during December–March; strong vertical mixing dominates the cooling in winter.

Based on reconstructed annual fCO_2 cycle for the POOZ, we estimate an annual air–sea CO₂ flux of $-0.5 \text{ mol/m}^2/\text{yr}$ whatever the gas transfer coefficient used. Compared to the Sub-Antarctic Zone (SAZ, around 40–50°S), the fCO_2 and DIC cycles in the POOZ are about the same (lower concentrations in summer), but the average fCO_2 values in the POOZ are higher by about 30–40 µatm than in the SAZ. Therefore, the annual air–sea CO₂ flux of $-0.5 \text{ mol/m}^2/\text{yr}$ in the POOZ is small compared to the $-3 \text{ mol/m}^2/\text{yr}$ estimated for the SAZ in the Indian Ocean sector (Metzl et al., 1999).

The carbon sink in the POOZ estimated in this study is much smaller than previous estimates based on oceanic observations in the same region, probably because we observed oversaturated ocean CO_2 during the windy austral winter. On the other hand, our estimate, about -0.2 PgC/yr south of 50°S, approaches the Southern Ocean sinks deduced from AIMs (Bousquet et al., 2000; Gurney et al., 2002; Roy et al., 2003). In addition and maybe more interestingly, the seasonal course of the oceanic sink/source derived from our observations and modelling confirms the seasonality deduced from atmospheric data (Bousquet et al., 2000). This is a very encouraging result in the perspective of understanding the interannual variability of the global carbon budget. Among such analyses, there is an obvious need for conducting new observations during austral winter in other regions and to verify if the POOZ always acts as an ocean CO₂ source during winter. If this is true, it could explain why all atmospheric inverse models (Gurney et al., 2003, 2004; Roy et al., 2003) always estimate a Southern Ocean CO_2 sink about half the a priori sink before inversion based on reconstructed climatology (Takahashi et al., 2002).

The estimation and understanding of the air-sea CO_2 flux variability is part of the research field that needs to be developed in the high latitudes to reduce the uncertainties attached to the Southern Ocean CO_2 sink. But this is not the only one. Progress is also needed in our understanding of climate/ocean coupling, especially in the Southern Ocean, a region recognized to be very sensitive to climate change in the context of future anthropogenic forcings (Sarmiento et al., 1998; Friedlingstein et al., 2003). The data (including DIC and TA) and seasonal processes described in this paper could serve to test

and validate various models from complex 1D ecosystem models to biogeochemical ocean global circulations models (BOGCM). Such validation represents an important step if we want to use BOGCM for predicting, in the past and future, the coupling between climate change and the ocean carbon cycle.

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References

- Bakker, D.C.E., de Baar, H.J.W., Bathmann, U.V., 1997. Changes of carbon dioxide in surface waters during spring in the Southern Ocean. Deep-Sea Research II 44, 91–128.
- Bates, N.R., Michaels, A.F., Knap, A.H., 1996. Seasonal and interannual variability of the oceanic carbon dioxide species at the US JGOFS Bermuda Atlantic Times-series Study (BATS) site. Deep-Sea Research II 43 (2–3), 347–383.
- Belkin, I., Gordon, A., 1996. Southern Ocean fronts from the Greenwich meridian to Tasmania. Journal of Geophysical Research 101 (C2), 3675–3696.
- Bousquet, P., Peylin, P., Ciais, P., Le Quéré, C., Friedlingstein, P., et al., 2000. Regional changes in carbon dioxide fluxes of land and ocean since 1980. Science 290, 1342–1346.
- Ciais, P., Tans, P.P., White, J.W.C., Trolier, M., Francey, R., 1995. A large northern hemisphere terrestrial CO₂ sink indicated by the ¹³C/¹²C ratio of atmospheric CO₂. Science 269, 1098–1102.
- Conway, T.J., Tans, P.P., Waterman, L.S., Thoning, K.W., Kitzis, D.R., Masarie, K.A., Zhang, N., 1994. Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory global air sampling network. Journal of Geophysical Research D99, 22831–22855.
- Copin-Montégut, C., 1988. A new formula for the effect of temperature on the partial pressure of CO₂ in seawater. Marine Chemistry 25, 29–37.
- Copin-Montégut, C., 1989. A new formula for the effect of temperature on the partial pressure of CO₂ in seawater. Corrigendum. Marine Chemistry 27, 143–144.

- Copin-Montégut, C., Copin-Montégut, G., 1978. The chemistry of particulate matter from the South Indian and Antarctic Ocean. Deep-Sea Research 25, 911–931.
- Feely, R., Boutin, J., Cosca, C., Dandonneau, Y., Etcheto, J., Inoue, H., Ishii, M., Le Quéré, C., Mackey, D., McPhaden, M., Metzl, N., Poisson, A., Wanninkhov, R., 2002. Seasonal and interannual variability of CO₂ in the equatorial Pacific. Deep-Sea Research II 49 (13–14), 2443–2469.
- Friedlingstein, P., Dufresne, J.L., Cox, P., Rayner, P., 2003. How positive is the feedback between climate change and the carbon cycle ? Tellus 55B, 692–700.
- GLOBALVIEW-CO₂, 2003. Cooperative Atmospheric Data Integration Project—Carbon Dioxide. CD-ROM, NOAA CMDL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLO-BALVIEW].
- Goyet, C., Beauverger, C., Brunet, C., Poisson, A., 1991. Distribution of carbon dioxide partial pressure in surface waters of the southwest Indian ocean. Tellus 43 (B), 1–11.
- Goyet, C., Metzl, N., Millero, F., Eischeid, G., O'Sullivan, D., Poisson, A., 1998. Temporal variation of the sea surface CO₂/ carbonates properties in the Arabian Sea. Marine Chemistry 63, 69–79.
- Gurney, K.R., et al., 2002. Towards robust regional estimates of CO₂ sources and sinks using atmospheric transport models. Nature 415, 626–630.
- Gurney, K.R., et al., 2003. Tanscom 3 CO₂ inversion intercomparison: 1. Annual mean control results and sensitivity to transport and prior flux information. Tellus, Series 55B, 555–579.
- Gurney, K.R., et al., 2004. Tanscom 3 inversion intercomparison: model mean results for the estimation of seasonal carbon sources and sinks. Global Biogeochemical Cycles 18 GB1010,10.1029/2003GB002111.
- Hellerman, S., Rosenstein, M., 1983. Normal monthly wind stress over the world ocean with error estimates. Journal of Physical Oceanography 13, 1093–1104.
- Hoppema, M., Fahrbach, E., Schröder, M., Wisotzki, A., de Baar, H., 1995. Winter–summer differences of carbon dioxide and oxygen in the Weddell Sea surface layer. Marine Chemistry 51, 177–192.
- Inoue, H.Y., Sugimura, Y., 1988. Distribution and variations of oceanic carbon dioxide in the western North Pacific, eastern Indian and Southern Ocean south of Australia. Tellus 40B, 308–320.
- Ishii, M., Inoue, H.Y., Matsueda, H., Tanoue, E., 1998. Close coupling between seasonal biological production and dynamics of dissolved inorganic carbon in the Indian Ocean sector and the Western Pacific Ocean sector of the Antarctic Ocean. Deep-Sea Research I 45 (7), 1187–1209.
- Ishii, M., Inoue, H.Y., Matsueda, H., 2002. Net community production in the marginal ice zone and its importance of the variability of oceanic pCO₂ in the Southern Ocean south of Australia. Deep-Sea Research II 49, 1691–1706.
- Jabaud-Jan, A., Metzl, N., Brunet, C., Poisson, A., Schauer, B., 2004. Interannual variability of the carbon dioxide system in the southern Indian Ocean (20–60°S): the impact of a warm anomaly in austral summer 1998. Global Biogeochemical Cycles 18 (1) GB1042,10.1029/2002GB002017.
- Jeandel, C., Ruiz-Pino, D., Gjata, E., Poisson, A., Brunet, C., Charriaud, E., et al., 1998. KERFIX, a permanent time-series

station in the Southern Ocean: a presentation. Journal of Marine Systems 17, 555–569.

- Keeling, C.D., 1993. Surface ocean CO₂. In: Heimman, M., (Ed.), The Global Carbon Cycle. NATO ASI Series, vol. I (15). Springer, Berlin, Heidelberg, pp. 413–429.
- Koertzinger, A., Mintrop, L., Wallace, D.W.R., Johnson, K.M., Neill, C., et al., 2000. The international at-sea intercomparison of fCO₂ systems during the R/V *Meteor Cruise* 36/1 in the North Atlantic Ocean. Marine Chemistry 2 (2–4), 171–192.
- Louanchi, F., Hoppema, M., 2000. Interannual variations of the Antarctic Ocean CO_2 uptake from 1986 to 1994. Marine Chemistry 72, 103–114.
- Louanchi, F., Metzl, N., Poisson, A., 1996. Modelling the monthly sea surface fCO_2 fields in the Indian Ocean. Marine Chemistry 55, 265–279.
- Louanchi, F., Ruiz-Pino, D., Poisson, A., 1999. Temporal variations of mixed-layer oceanic CO₂ at JGOFS-KERFIX time-series station: physical versus biogeochemical processes. Journal of Marine Research 57, 165–187.
- Louanchi, F., Ruiz-Pino, D., Jeandel, C., Brunet, C., Schauer, B., et al., 2001. Dissolved inorganic carbon, alkalinity, nutrient and oxygen seasonal and interannual variations at the Antarctic Ocean JGOFS-KERFIX site. Deep-Sea Research I 48, 1581–1603.
- Metzl, N., Beauverger, C., Brunet, C., Goyet, C., Poisson, A., 1991. Surface water pCO_2 in the Western Indian sector of the Southern Ocean: a highly variable CO_2 source/sink region during the austral summer. Marine Chemistry 35, 85–95.
- Metzl, N., Poisson, A., Louanchi, F., Brunet, C., Schauer, B., Brès, B., 1995. Spatio-temporal distributions of air–sea fluxes of CO₂ in the Indian and Antarctic Oceans: a first step. Tellus 47B, 56–69.
- Metzl, N., Louanchi, F., Poisson, A., 1998. Seasonal and interannual variations of sea surface carbon dioxide in the subtropical Indian Ocean. Marine Chemistry 60, 131–146.
- Metzl, N., Tilbrook, B., Poisson, A., 1999. The annual *f*CO₂ cycle and the air–sea CO₂ fluxes in the sub-Antarctic Ocean. Tellus 51B (4), 849–861.
- Miyake, Y., Sugimura, Y., Saruhashi, K., 1974. The carbon dioxide content in the surface waters in the Pacific Ocean. Records of Oceanographic Works in Japan 12 (2), 45–52.
- Moore, J.K., Abbott, M.R., 2000. Phytoplankton chlorophyll distributions and primary production in the Southern Ocean. Journal of Geophysical Research 105 (C12), 28709–28772.
- Moore, J.K., Abbott, M.R., Richman, J.G., 1999. Location and dynamics of the Antarctic Polar Front from satellite sea surface temperature data. Journal of Geophysical Research 104, 3059–3073.
- Murphy, P., Feely, R.A., Gammon, R.H., Kelly, K.C., Waterman, L.S., 1991. Autumn air-sea disequilibrium of CO₂ in the South Pacific Ocean. Marine Chemistry 35, 77–84.
- Orr, J.C., Maier-Reimer, E., Mikolajewicz, U., Monfray, P., Sarmiento, J.L., et al., 2001. Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models. Global Biogeochemical Cycles 15 (1), 43–60.
- Poisson, A., Schauer, B., Brunet, C., 1988. MD43/INDIGO 1, Cruise report; Les rapports des campagnes à la mer, 85(06). Les publications de la Mission de Recherche des Terres Australes et Antarctiques Françaises, Paris, 267pp.

- Poisson, A., Metzl, N., Brunet, C., Schauer, B., Brès, B., Ruiz-Pino, D., Louanchi, F., 1993. Variability of sources and sinks of CO₂ and in the Western Indian and Southern Oceans during the year 1991. Journal of Geophysical Research 98 (C12), 22759–22778.
- Poisson, A., Metzl, N., Danet, X., Louanchi, F., Brunet, C., Schauer, B., Brès, B., Ruiz-Pino, D., 1994. Air–sea CO₂ fluxes in the Southern Ocean Between 25° and 85°E. In: Johannessen, O.M., Muench, R.D., Overland, J.E. (Eds.), The Polar Oceans and their Role in Shaping the Global Environment. AGU, Geophysical Monograph 85, pp. 273–284.
- Pondaven, P., Fravalo, C., Ruiz-Pino, D., Tréguer, P., Quéguiner, B., Jeandel, C., 1998. Modelling the silica pump in the permanently open ocean zone of the Southern Ocean. Journal of Marine Systems 17, 587–619.
- Reynolds, R.W., Smith, T.M., 1994. Improved global sea surface temperature analyses using optimum interpolation. Journal of Climate 7, 929–948.
- Robertson, J., Watson, A., 1995. A summer-time sink for atmospheric carbon dioxide in the Southern Ocean between 88°W and 80°E. Deep-Sea Research II 42 (4–5), 1081–1091.
- Roy, T., Rayner, P., Matear, R., Francey, R., 2003. Southern hemisphere ocean CO₂ uptake: reconciling atmospheric and oceanic estimates. Tellus 55B, 701–710.
- Rubin, S.I., Takahashi, T., Chipman, D.W., Goddard, J.G., 1998. Primary productivity and nutrient utilization ratio in the Pacific sector of the Southern Ocean based on seasonal changes in seawater chemistry. Deep-Sea Research I 45, 1211–1234.
- Sabine, C.L., Key, R.M., 1998. Controls on fCO₂ in the South Pacific. Marine Chemistry 60, 95–110.
- Sarmiento, J.L., Hughes, T., Stouffer, R., Manabe, S., 1998. Simulated response of the ocean carbon cycle to anthropogenic climate warming. Nature 393, 245–249.
- Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W., Sutherland, S.C., 1993. Seasonal variation of CO₂ in the highlatitude surface oceans: a comparative study. Global Biogeochemical Cycles 7 (4), 843–878.
- Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y., 2002. Global sea-air CO₂ flux based on climatological surface ocean *p*CO₂, and seasonal biological and temperature effect. Deep-Sea Research II 49 (9–10), 1601–1622.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research 97 (C5), 7373–7382.
- Wanninkhof, R., McGillis, W., 1999. A cubic relationship between air-sea CO₂ exchange and wind speed. Geophysical Research Letters 26 (13), 1889–1892.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry 2, 203–215.
- Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Marine Chemistry 8, 347–359.
- Weiss, R.F., Jankhe, R.A., Keeling, C.D., 1982. Seasonal effects of temperature and salinity on the partial pressure of CO₂ in seawater. Nature 300, 511–513.
- Winn, C.D., Li, Y.-H., Mackenzie, F.T., Karl, D.M., 1998. Rising surface ocean dissolved inorganic carbon at the Hawaii Ocean time-series site. Marine Chemistry 60 (1/2), 33–47.