

# Interannual properties of the CO<sub>2</sub> system in the Southern Ocean south of Australia

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**Abstract:** In order to quantify the temporal variations of ocean properties, the MINERVE programme was designed to perform time-series measurements in the Southern Indian Ocean south of Australia. In the sub-Antarctic region (SAR,  $48.5 \pm 6.0^\circ\text{S}$ ), the mean CO<sub>2</sub> flux increased from spring to summer from  $-6.8 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in October 2005 to  $-9.9 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in February 2006. In the Permanent Open Ocean Zone (POOZ,  $57.5 \pm 3.0^\circ\text{S}$ ), we observed lower pCO<sub>2</sub> in summer than in spring (340 and 398  $\mu\text{atm}$ , respectively). The mean CO<sub>2</sub> flux showed large temporal variations from  $-0.2 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in October 2005 to  $-8.2 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in February 2006. The large temporal variation was associated with increased phytoplankton biomass. In the Continental Antarctic Zone ( $66.0 \pm 1.0^\circ\text{S}$ ), the mean CO<sub>2</sub> flux decreased from  $+14.9 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in October 2005 to  $-8.4 \text{ mmol.m}^{-2}.\text{d}^{-1}$  in February 2006. In winter and spring, deep water mixing and seasonal sea-ice strongly increase pCO<sub>2</sub><sup>sea</sup> above atmospheric level. In contrast, during summer, the effect of biological CO<sub>2</sub> uptake decreased pCO<sub>2</sub><sup>sea</sup>. Furthermore, these data allowed us to parameterize A<sub>T</sub> and C<sub>T</sub> as a function of temperature and salinity.

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**Key words:** air-sea CO<sub>2</sub> flux, partial pressure of CO<sub>2</sub>, total alkalinity, total dissolved inorganic carbon

## Introduction

The greenhouse gas CO<sub>2</sub> plays a key role in controlling Earth's climate (Matear & Hirst 1999, Plattner *et al.* 2001, Feely *et al.* 2001). Recognizing the role of anthropogenic CO<sub>2</sub> emissions in climate change, there are many studies designed to investigate, understand and quantify the global carbon cycle (Takahashi *et al.* 1993, Houghton *et al.* 2001, Thomas *et al.* 2005, Solomon *et al.* 2007). Quantifying the air-sea CO<sub>2</sub> flux over the global ocean is an important part of this effort (Goyet *et al.* 1993, Conway *et al.* 1994, Sabine *et al.* 2004). Thus, large international projects such as WOCE (the World Ocean Circulation Experiment), or JGOFS (Joint Global Ocean Flux Study), as well as French national projects such as MINERVE (Mesure à l'Interface Eau-air de la Variabilité des Echanges de CO<sub>2</sub>), or OISO (Océan Indien Service d'Observation) were designed to understand and assess the ocean's role in the global carbon cycle.

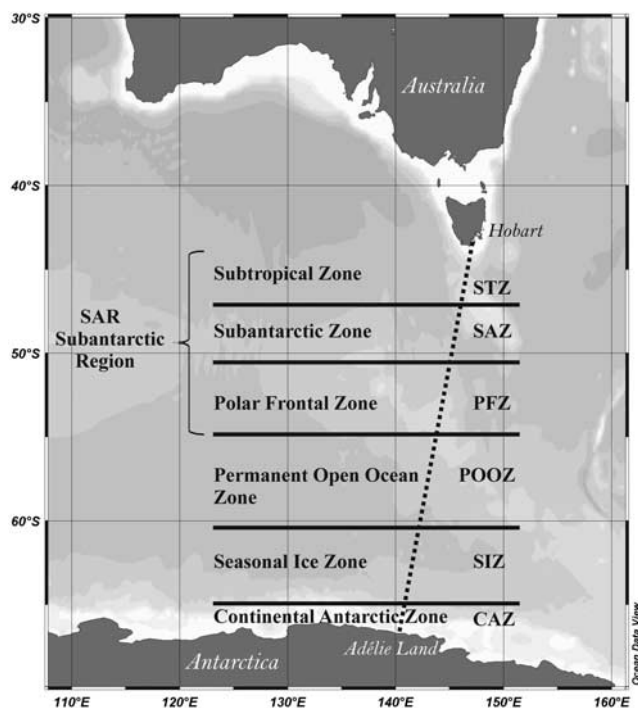
The Southern Ocean presents large sea-surface pCO<sub>2</sub> (pCO<sub>2</sub><sup>sea</sup>) variations. It is alternatively a CO<sub>2</sub> source and a CO<sub>2</sub> sink area for the atmosphere. The specific strength, location, and temporal evolution of these CO<sub>2</sub> source/sink areas are still debated (Brévière *et al.* 2006, Borges *et al.* 2007). In order to quantify and understand the spatial and temporal variations of pCO<sub>2</sub>, repeat cruises in the same ocean area over several years are necessary (Poisson *et al.* 1993, Takahashi *et al.* 1993, Metzl *et al.* 1995, 1999,

Bakker *et al.* 1997, Jabaud-Jan *et al.* 2004, Brévière *et al.* 2006). In the Antarctic Ocean, harsh weather and winter ice cover strongly limit all *in situ* observations. As a result, the dataset in this ocean area remains relatively sparse.

In this paper, we investigate the spatial and temporal variability of air-sea CO<sub>2</sub> exchanges in the Southern Indian Ocean from October 2005 (spring) to March 2006 (late summer). The analysis is performed along transects between Hobart (Tasmania, Australia;  $43.0^\circ\text{S}$ ) and Dumont D'Urville (Adélie Land, Antarctica;  $67.0^\circ\text{S}$ ) (Fig. 1), for which we continually measured pCO<sub>2</sub><sup>sea</sup>, pCO<sub>2</sub><sup>air</sup>, A<sub>T</sub>, and C<sub>T</sub> along with SSS and SST. In spring, the ship broke the ice and we sampled the seawater along the ship's track for continual measurements of pCO<sub>2</sub><sup>sea</sup>, A<sub>T</sub>, and C<sub>T</sub>, providing us data for seawater from under the ice. In this study, we quantify the temporal variations of pCO<sub>2</sub><sup>sea</sup>, as well as those of the air-sea CO<sub>2</sub> fluxes, of A<sub>T</sub> and C<sub>T</sub>. In particular, we show how they respond to changes in sea surface temperature (SST) and salinity (SSS). The work follows the study of Brévière *et al.* (2006) who used data from cruises in 2002/2003.

## Materials and methods

The three MINERVE cruises on board RV *Astrolabe* were made between Hobart ( $43.0^\circ\text{S}$ ) and Dumont D'Urville



**Fig. 1.** Map showing the study area during MINERVE cruises in October 2005/March 2006. Transect 1: from Hobart (Tasmania, Australia) to Dumont D'Urville (Adélie Land, Antarctica). Transect 2: from Dumont D'Urville to Hobart. The six different hydrographic zones are indicated.

(67.0°S) in 2005–2006 (Fig. 1). The first cruise started in spring from 18 October–8 November 2005, the second cruise in summer from 30 December 2005–26 January 2006, and the third cruise in late summer from 17 February–2 March 2006. Along each cruise track, a pump brought surface seawater (from about 5 m depth) on board for continual measurements of  $p\text{CO}_2^{\text{sea}}$ ,  $A_T$ ,  $C_T$ , temperature and salinity. In this ocean area (south of 43°S), seawater from 5 m depth can reasonably be assumed to be “surface seawater” since there is continual turbulence from wind/wave action. In addition, we regularly collected discrete 500 ml samples of surface seawater (six per day), for further  $A_T$  and  $C_T$  measurement on shore. These discrete samples were immediately poisoned with saturated mercuric chloride solution ( $\text{HgCl}_2$ ) and stored to be later analysed in the Laboratoire d’Océanographie et du Climat: Expérimentations et Approches Numérique (LOCEN/IPSL), Université Pierre et Marie Curie, Paris, France.

#### *Measurements of partial pressure of $\text{CO}_2$ in surface seawater ( $p\text{CO}_2^{\text{sea}}$ ) and in the atmosphere ( $p\text{CO}_2^{\text{air}}$ )*

The sea surface  $p\text{CO}_2$  measurement technique has been previously described (Poisson *et al.* 1993, Metzl *et al.* 1995, 1999, Jabaud-Jan *et al.* 2004, Brévière *et al.* 2006).

Surface seawater is continuously equilibrated using a “thin film” type equilibrator thermostated with surface seawater. The  $\text{CO}_2$  gas from the equilibrated dried gas is measured every six minutes with a non-dispersive infrared analyser (Li-COR 6262) with an accuracy of  $\pm 2 \mu\text{atm}$ . The continual measurement system was periodically calibrated (every six hours) with standard gases with  $\text{CO}_2$  partial pressure of  $275.5 \pm 1.0 \mu\text{atm}$ ,  $380.8 \pm 1.0 \mu\text{atm}$  and  $498.5 \pm 1.0 \mu\text{atm}$ . The entire measurement system was automated using a computer. The atmospheric  $p\text{CO}_2$  was automatically measured every six hours in air samples collected from the top of the bridge at approximately 10–12 m above the sea surface.

Temperature and salinity were measured with a Sea-Bird thermosalinograph positioned at the intake of the seawater flow. The temperature in the equilibrium cell was  $0.7 \pm 0.2^\circ\text{C}$  warmer than *in situ* temperature due to warming along the line from the intake to the equilibrium cell. We use the Copin-Montégut polynomials (1988, 1989) to correct sea surface  $p\text{CO}_2$  measurements to the *in situ* temperature.

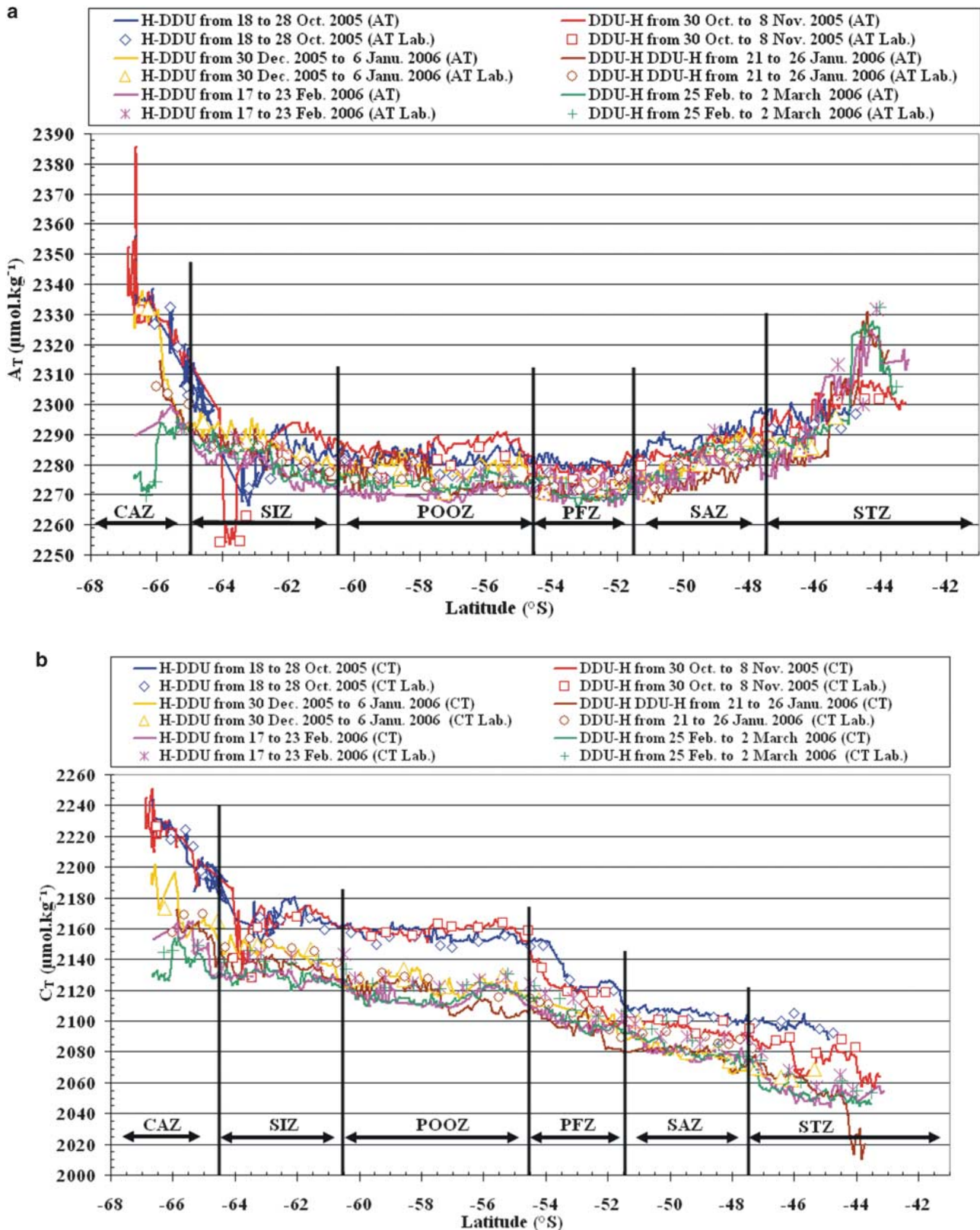
In order to quantify the net air-sea  $\text{CO}_2$  flux ( $F$ ) ( $\text{mmol.m}^{-2}.\text{d}^{-1}$ ), we used the well known relationship:

$$F = K \cdot \alpha \cdot \Delta p\text{CO}_2$$

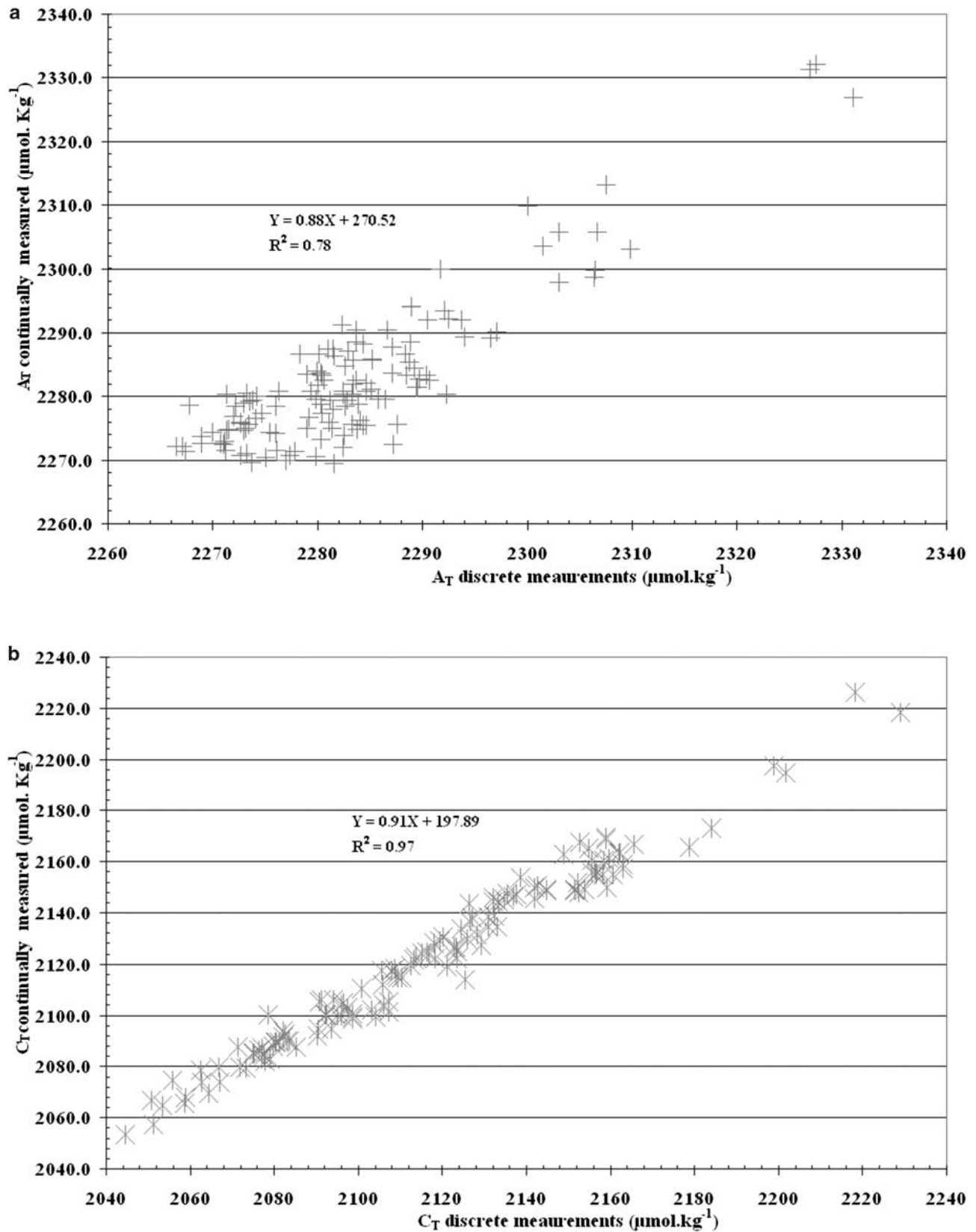
Where  $K$ , is the gas transfer velocity, calculated using the cubic wind speed relationship of Wanninkhof & McGillis (1999). Wind speeds were recorded on board once a minute. The  $\text{CO}_2$  solubility coefficient ( $\alpha$ ) is calculated as a function of SSS and SST (Weiss 1974); and  $\Delta p\text{CO}_2$  ( $p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}}$ ) is the difference of  $p\text{CO}_2$  in surface seawater ( $p\text{CO}_2^{\text{sea}}$ ) and in the atmosphere ( $p\text{CO}_2^{\text{air}}$ ). The  $\Delta p\text{CO}_2$  sets the direction of  $\text{CO}_2$  gas exchange and is controlled by complex physical (mainly temperature and salinity), chemical (mainly total alkalinity and total inorganic carbon) and biological (mainly plankton) interactions. In order to compare our results with the previous ones (Brévière *et al.* 2006), we used the cubic relationship of Wanninkhof & McGillis (1999) to calculate the gas transfer velocities.

#### *Measurements of sea surface total alkalinity ( $A_T$ ) and total dissolved inorganic carbon ( $C_T$ )*

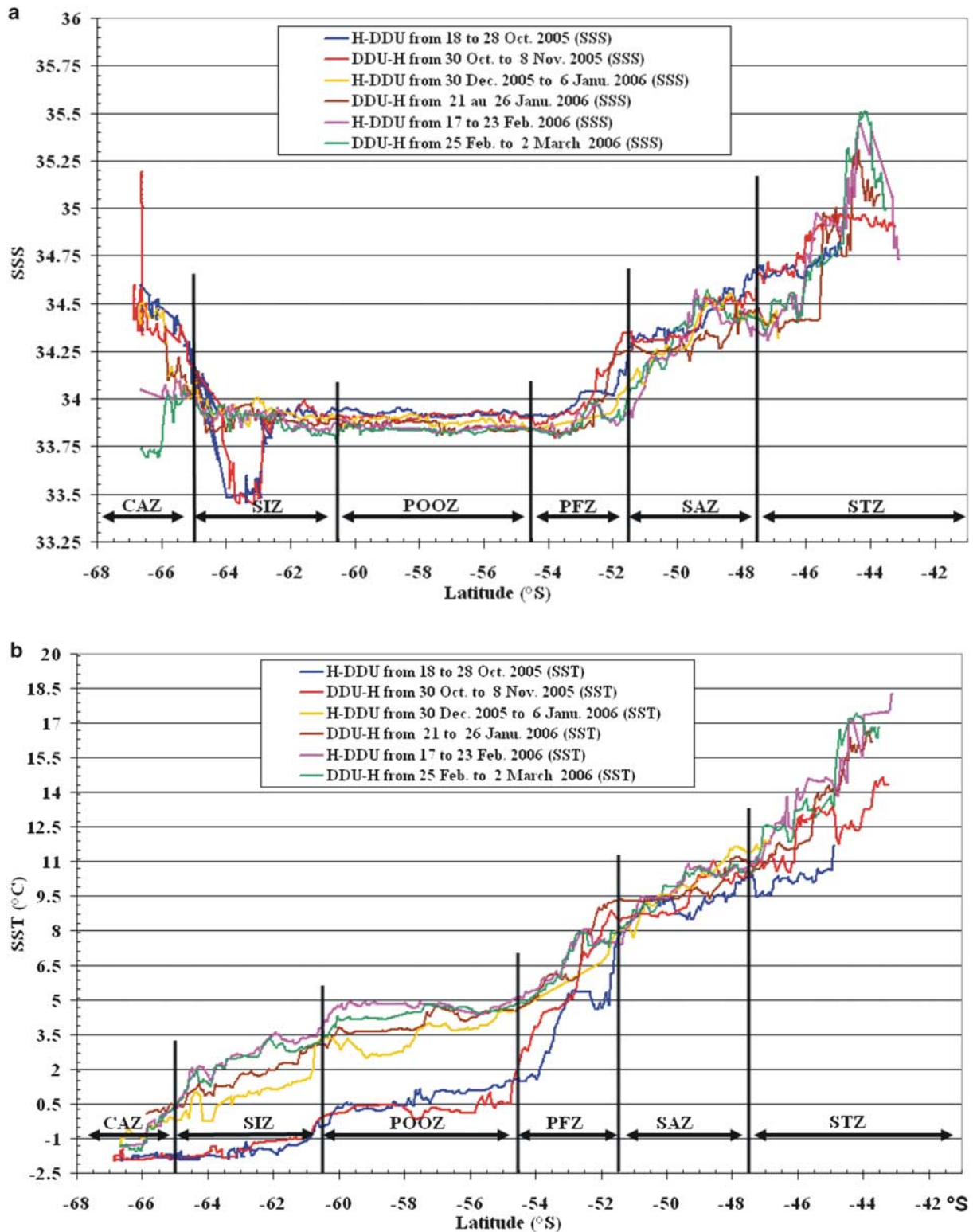
$A_T$  and  $C_T$  measurements were performed in closed cell Goyet *et al.* (1991) using a potentiometric method (Edmond 1970). A fully automated system was maintained at constant temperature ( $18.0 \pm 0.1^\circ\text{C}$ ) by a thermostated water bath, and an automatic burette, allowed us to perform continual measurements of sea surface  $A_T$  and  $C_T$  about every 25 min along the transect. The ionic strength of the hydrochloric acid solution (0.1 N) used for the titration was adjusted with NaCl in order to be similar to that of the seawater samples. The computer recorded the seawater sample temperature and salinity, transferred the seawater into the cell, and controlled the titration. Then  $A_T$  and  $C_T$  were computed



**Fig. 2. a.** Temporal variations of total alkalinity in surface seawater measured: 1 = on board (lines,  $A_T$ ), 2 = in the laboratory (symbols,  $A_T$  Lab.), along transects between Hobart (H) and Dumont D'Urville (DDU). **b.** Temporal variations of total dissolved inorganic carbon in surface seawater measured: 1 = on board (lines,  $C_T$ ), 2 = in the laboratory (symbols,  $C_T$  Lab.), along transects between Hobart (H) and Dumont D'Urville (DDU).



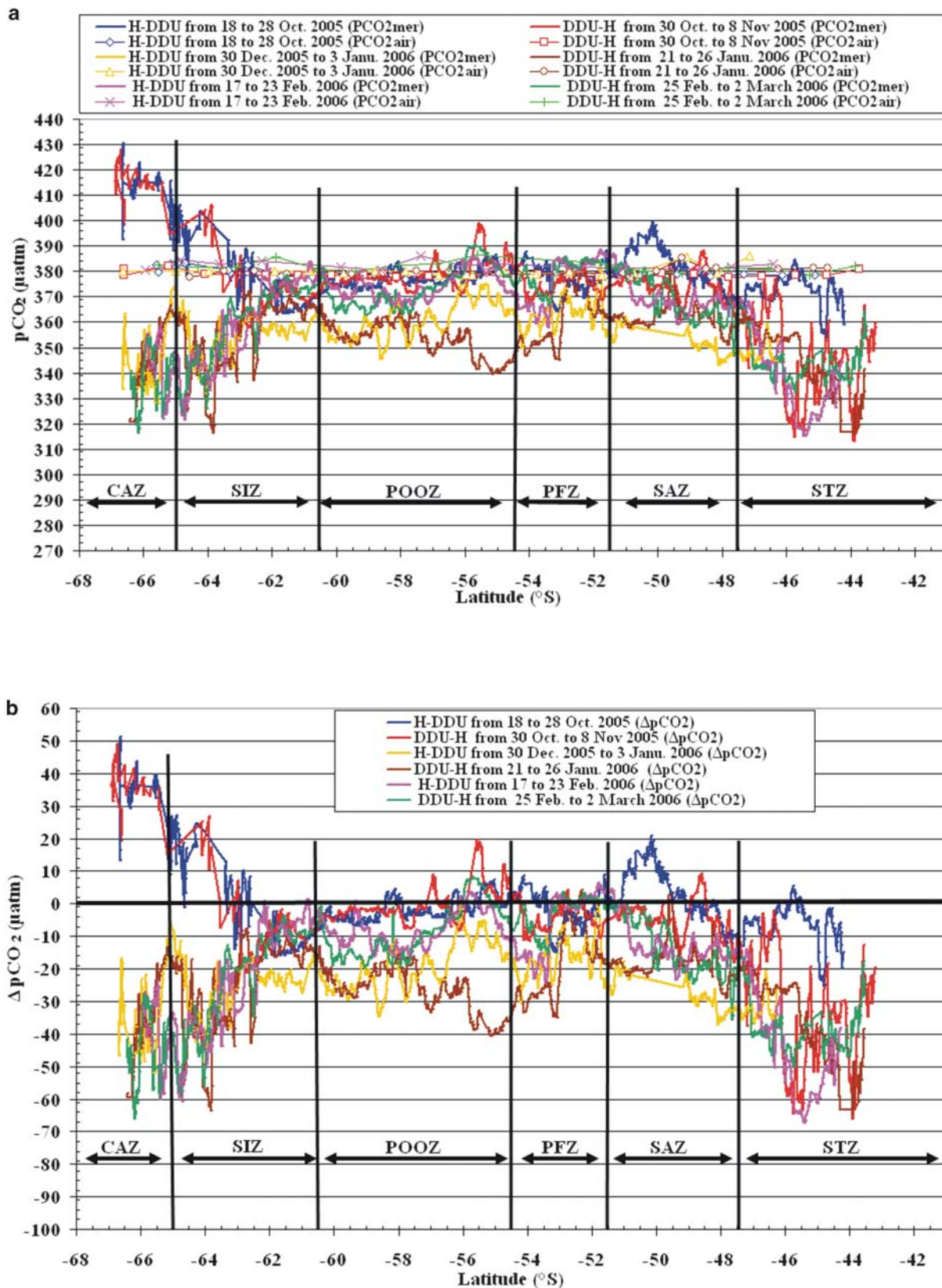
**Fig. 3. a.** Correlation between the A<sub>T</sub> measured on board and on shore for both seasons (spring and summer) along transects H–DDU and DDU–H. **b.** Correlation between the C<sub>T</sub> measured on board and on shore for both seasons (spring and summer) along transects H–DDU and DDU–H.



**Fig. 4. a.** Distribution of the sea surface salinity (SSS) between Hobart and Dumont D'Urville from October 2005 to March 2006.  
**b.** Distribution of the sea surface temperature (SST) along transects (H-DDU and DDU-H) from October 2005 to March 2006.

using a nonlinear regression method (Dickson & Goyet 1994). These  $A_T$  and  $C_T$  measurements were referenced to those of CRMs bought from Dr A.G. Dickson (SCRIPPS,

USA) measured regularly on board and on shore. The precision of  $A_T$  and  $C_T$  measurements were estimated at  $3.5 \mu\text{mol.kg}^{-1}$  and  $2.7 \mu\text{mol.kg}^{-1}$ , respectively on board, and



**Fig. 5. a.** Seasonal variability of CO<sub>2</sub> partial pressure in surface seawater ( $p\text{CO}_2^{\text{sea}}$ ) and in atmosphere ( $p\text{CO}_2^{\text{air}}$ ) along the cruise tracks. **b.** Distributions of  $\Delta p\text{CO}_2 = (p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}})$  in surface seawater of southern Ocean south of Australia along the cruise tracks.

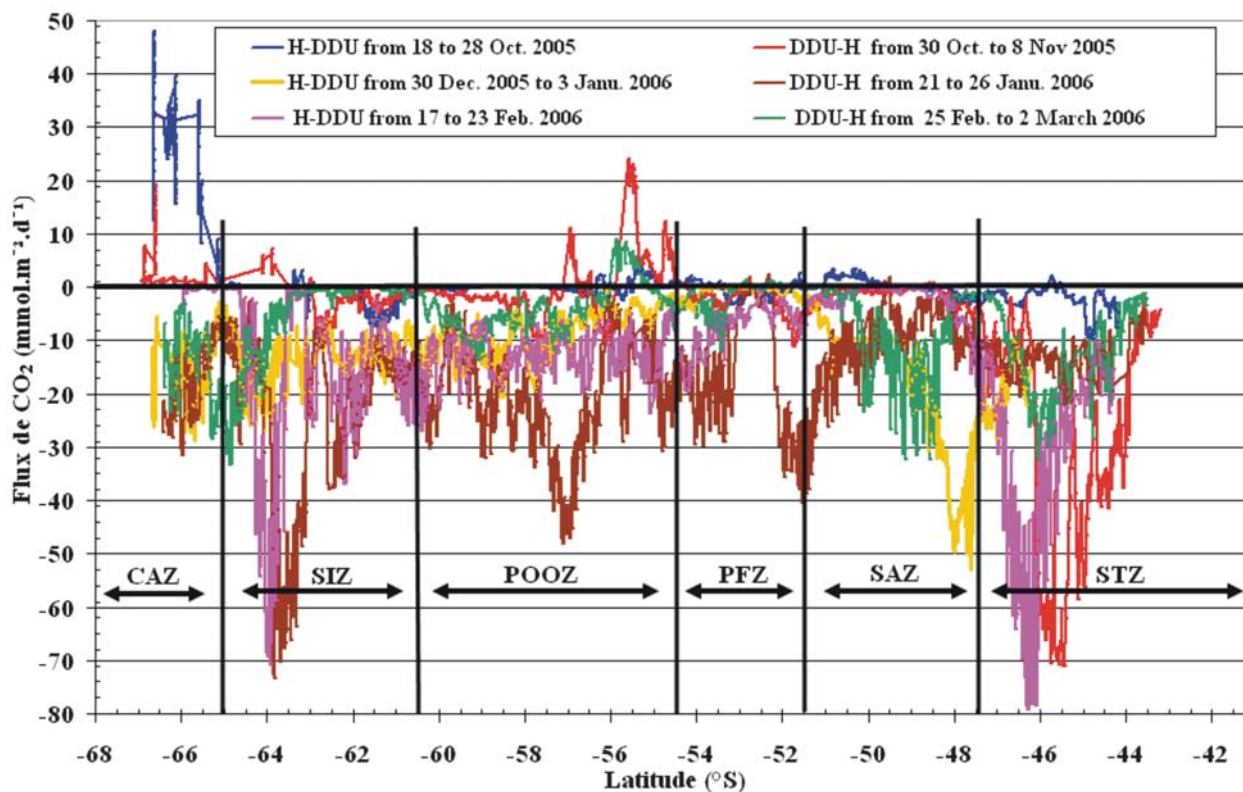


Fig. 6. Temporal variabilities of the CO<sub>2</sub> air-sea fluxes in Southern Ocean south of Australia over the six zones from October 2005 to March 2006.

of  $2.9 \mu\text{mol.kg}^{-1}$  and  $3.0 \mu\text{mol.kg}^{-1}$ , respectively on shore. The reproducibility estimated from replicate analyses of sea surface samples is  $2.9 \mu\text{mol.kg}^{-1}$  and  $2.2 \mu\text{mol.kg}^{-1}$  for  $A_T$  and  $C_T$ , respectively.

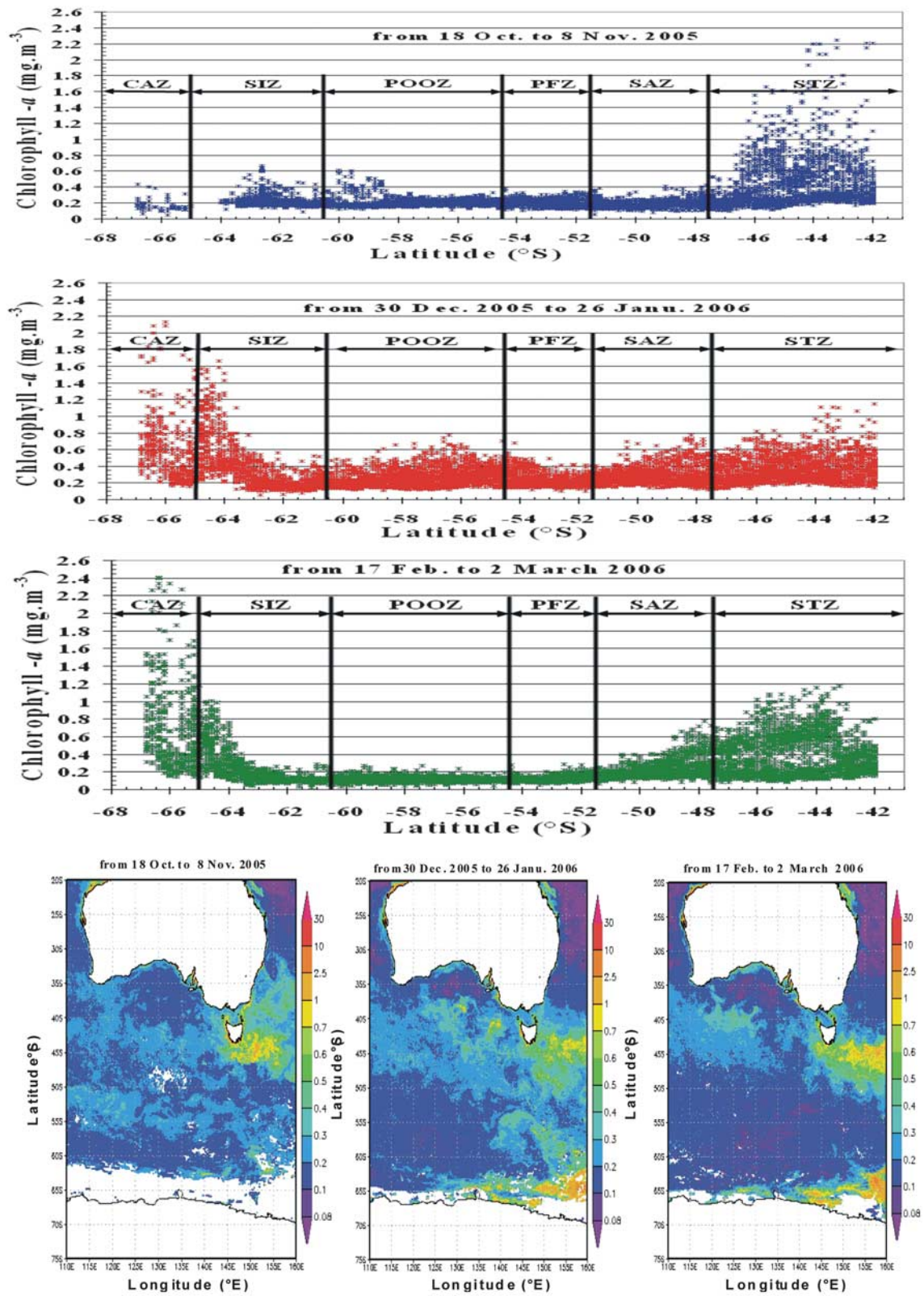
#### *Comparison between measurements performed on board and on shore and internal consistency between $A_T$ , $C_T$ and $p\text{CO}_2$*

The concentrations of  $A_T$  and  $C_T$  continually measured on board were checked against the discrete measurements performed on shore (LOCEN/IPSL). As expected,  $A_T$  and  $C_T$  displayed the same tendency along the cruises for both measurements (Fig. 2a & b). Sometimes small differences were observed. The  $\Delta A_T$  ( $-1.3 \mu\text{mol.kg}^{-1}$ ) and  $\Delta C_T$  ( $5.5 \mu\text{mol.kg}^{-1}$ ) are the mean differences between measurements on shore (discrete measurements) and on board (continually measured). These differences may be due to changes in the samples during shipping and/or storage. These on shore measurements confirmed the good quality of the on board measurements. The correlation between  $A_T$  and  $C_T$  measurements on board and on shore for both seasons (spring and summer) are better for  $C_T$  than for  $A_T$  (0.97 and 0.78 respectively) (Fig. 3a & b).

The internal consistency between  $A_T$ ,  $C_T$  and  $p\text{CO}_2$  was calculated using the programme CO2SYS of Lewis & Wallace (1998). The programme calculates  $p\text{CO}_2$  based on user-selected dissociation constants for carbonic acid K1 and K2 (Mehrbach *et al.* 1973, Goyet & Poisson 1989, Roy *et al.* 1993) and  $C_T$  and  $A_T$  measurements. The mean differences of  $\Delta p\text{CO}_2$  ( $p\text{CO}_2$  measured -  $p\text{CO}_2$  calculated) are  $11.7 \pm 11.0 \mu\text{atm}$ ,  $10.3 \pm 16.4 \mu\text{atm}$  and  $10.2 \pm 17.0 \mu\text{atm}$  respectively. Consequently, in this ocean area, the constants of Goyet & Poisson (1989) seem to provide the best results for accuracy and precision. The  $p\text{CO}_2$  calculated as a function of  $A_T$ ,  $C_T$ , temperature and salinity can be used to estimate the spatio-temporal variations in the Southern Ocean south of Australia (43–67°S).

#### *Sea surface temperature (SST) and salinity (SSS)*

A Sea-Bird thermosalinograph (SBE 21), calibrated at CSIRO (Commonwealth Scientific and Industrial Research Organisation, Australia), continuously measured sea surface temperature (SST) and salinity (SSS) at the seawater intake. The accuracies of these measurements are  $\pm 0.01^\circ\text{C}$  and  $\pm 0.002$  respectively.



**Fig. 7.** SeaWiFS (<http://seawifs.gsfc.nasa.gov/SEAWIFS.html>) distribution of monthly mean chl *a* concentrations ( $\text{mg}\cdot\text{m}^{-3}$ ) along transects between Hobart and Dumont D'Urville.



## Results and discussion

### Major oceanic zones

The Southern Ocean is divided into four main zones, with well-known fronts as boundaries (Rintoul *et al.* 1997, Chaigneau & Morrow 2002, Sokolov & Rintoul 2002, Kostianoy *et al.* 2004). The cruise tracks crossed five hydrological fronts. We used criteria based on sea surface salinity and temperature to characterize the following four different zones:

1. The Sub-Antarctic Region, SAR, located at  $48.5 \pm 6.0^\circ\text{S}$ . Within this large area, there are three zones:
  - a. The Sub-Tropical Zone, STZ, located at  $45.5 \pm 2.0^\circ\text{S}$  (salinity drops from 35.51 at  $44.11^\circ\text{S}$  to 34.31 at  $47.19^\circ\text{S}$  and temperature decreases from  $18.21^\circ\text{C}$  at  $43.15^\circ\text{S}$  to  $9.46^\circ\text{C}$  at  $47.27^\circ\text{S}$ ).
  - b. The Sub-Antarctic Zone, SAZ, located at  $49.5 \pm 2.0^\circ\text{S}$  (salinity drops from 34.68 at  $47.65^\circ\text{S}$  to 33.90 at  $51.42^\circ\text{S}$ ; temperature falls from  $11.57^\circ\text{C}$  at  $47.78^\circ\text{S}$  to  $7.43^\circ\text{C}$  at  $51.47^\circ\text{S}$ ).
  - c. The Polar Frontal Zone, PFZ, located at  $53.0 \pm 1.5^\circ\text{S}$  (salinity drops from 34.35 at  $51.70^\circ\text{S}$  to 33.81 at  $54.43^\circ\text{S}$  and temperature decreases from  $9.27^\circ\text{C}$  at  $51.61^\circ\text{S}$  to  $1.48^\circ\text{C}$  at  $54.45^\circ\text{S}$ ).
2. The Permanent Open Ocean Zone, POOZ, located at  $57.5 \pm 3.0^\circ\text{S}$  (salinity shows a slight increase from 33.81 at  $54.56^\circ\text{S}$  to 33.95 at  $60.46^\circ\text{S}$  and a sharp drop in temperature from  $4.99^\circ\text{C}$  at  $54.55^\circ\text{S}$  to  $-0.45^\circ\text{C}$  at  $60.49^\circ\text{S}$ ).
3. The Seasonal Ice Zone, SIZ, located at  $63.0 \pm 2.0^\circ\text{S}$  (salinity shows an increase from 33.94 at  $60.58^\circ\text{S}$  to 34.14 at  $64.86^\circ\text{S}$ ; temperature falls from  $3.77^\circ\text{C}$  at  $60.61^\circ\text{S}$  to  $1.81^\circ\text{C}$  at  $64.88^\circ\text{S}$ ).
4. The Continental Antarctic Zone, CAZ, located at  $66.0 \pm 1.0^\circ\text{S}$  (salinity drops sharply from 34.25 at  $65.06^\circ\text{S}$  to 35.17 at  $66.62^\circ\text{S}$ ; temperature shows a decrease from  $0.49^\circ\text{C}$  at  $65.13^\circ\text{S}$  to  $-1.92^\circ\text{C}$  at  $66.79^\circ\text{S}$ ).

Along the cruise tracks we observed an atmospheric CO<sub>2</sub> partial pressure ( $p\text{CO}_2^{\text{air}}$ ) of  $380 \pm 2 \mu\text{atm}$ . Below we analyse within each zone, the temporal variability of  $p\text{CO}_2^{\text{sea}}$ , air-sea CO<sub>2</sub> fluxes,  $A_T$ ,  $C_T$ , SSS and SST.

### Sub-Tropical Zone (STZ; $45.5 \pm 2.0^\circ\text{S}$ )

In the STZ the concentrations of  $A_T$  decreased southward, from  $2331.4 \mu\text{mol.kg}^{-1}$  to  $2275.3 \mu\text{mol.kg}^{-1}$ ; Fig. 2a. These variations are mainly associated with those of salinity and temperature (Fig. 4a & b). Both parameters (SSS and SST) also decreased southward from 35.47 to 34.34 and from  $18.0^\circ\text{C}$  to  $9.0^\circ\text{C}$  respectively.

In contrast, we observe (Fig. 2b), that  $C_T$  concentrations increased southward, with high concentrations in spring

( $2056.4\text{--}2101.8 \mu\text{mol.kg}^{-1}$ ) and low concentrations in summer ( $2010.7\text{--}2077.8 \mu\text{mol.kg}^{-1}$ ). The data showed large temporal variations for both parameters ( $A_T$  and  $C_T$ ) with low  $C_T$  concentrations and high  $A_T$  concentrations in October 2005 and March 2006 as earlier observed in the southwest Indian Ocean (Goyet *et al.* 1991).

The STZ is considered as a strong sink for atmospheric CO<sub>2</sub> (Siegenthaler & Sarmiento 1993, Metzl *et al.* 1995, Caldeira & Duffy 2000, Brévière *et al.* 2006, Borges *et al.* 2007). In this area,  $p\text{CO}_2^{\text{sea}}$  decreases from spring to summer ( $384.4\text{--}313.6 \mu\text{atm}$ ; Fig. 5a). The  $\Delta p\text{CO}_2$  is slightly positive in spring (up to  $+5.3 \mu\text{atm}$ ) and strongly negative in summer (down to  $-67.1 \mu\text{atm}$ ; Fig. 5b). As a result, CO<sub>2</sub> fluxes (Fig. 6) displayed significant spatio-temporal (spring–summer) variations. In the spring of 2005 the CO<sub>2</sub> flux minimum ( $1.2 \text{mmol.m}^{-2}.\text{d}^{-1}$ ) was centred at  $45.79^\circ\text{S}$  and its maximum ( $-71.1 \text{mmol.m}^{-2}.\text{d}^{-1}$ ) was observed at  $45.44^\circ\text{S}$ . Whereas in summer 2006, we observed the CO<sub>2</sub> flux minimum ( $-2.2 \text{mmol.m}^{-2}.\text{d}^{-1}$ ) at  $43.56^\circ\text{S}$  and its maximum ( $-77.0 \text{mmol.m}^{-2}.\text{d}^{-1}$ ) was detected at  $46.33^\circ\text{S}$ . The air to sea CO<sub>2</sub> flux exhibits a pattern already noticed south of Tasmania (Inoue *et al.* 1999, Metzl *et al.* 1999, Ishii *et al.* 2002, Inoue & Ishii 2005). The seasonal variations of  $p\text{CO}_2^{\text{sea}}$  usually follow those of sea surface temperature (Weiss *et al.* 1982, Poisson *et al.* 1993, Takahashi *et al.* 1993, Inoue *et al.* 1995, Metzl *et al.* 1995, Wong *et al.* 1995). However,  $p\text{CO}_2^{\text{sea}}$  is also affected by local biological activity characterized by chlorophyll *a* (chl *a*) concentrations. SeaWiFs data show decreased chl *a* concentrations southward, with high concentrations in spring ( $0.11\text{--}2.21 \text{mg m}^{-3}$ ) and low concentrations in summer ( $0.10\text{--}1.15 \text{mg m}^{-3}$ ; Fig. 7).

In the STZ the temporal variations of  $C_T$  and  $p\text{CO}_2^{\text{sea}}$  are mainly influenced by those of SST (Lee *et al.* 1998), especially during the summer when the mixed layer depth is relatively shallow due to reduced vertical mixing. Thus, the sea surface temperature rose from  $12.0 \pm 3.0^\circ\text{C}$  in spring to  $14.0 \pm 4.0^\circ\text{C}$  in summer (Fig. 4b). In the STZ both temperature and biological activity affect significantly  $p\text{CO}_2^{\text{sea}}$  and  $C_T$ .

### Sub-Antarctic Zone (SAZ; $49.5 \pm 2.0^\circ\text{S}$ )

Between  $48\text{--}51^\circ\text{S}$   $A_T$  concentrations (Fig. 2a) are high in spring ( $2281.3\text{--}2298.7 \mu\text{mol.kg}^{-1}$ ), and low in summer ( $2268.3\text{--}2292.0 \mu\text{mol.kg}^{-1}$ ). The variations of  $A_T$  in surface seawater are linearly linked with those of salinity (Fig. 4a). Within this area, the sea surface temperature decreased southward from  $11.6^\circ\text{C}$  to  $7.4^\circ\text{C}$  (Fig. 4b).

The  $C_T$  concentrations in surface seawater increased slightly southward and display significant temporal variations (Fig. 2b). The data indicate high concentrations in spring ( $2088.5\text{--}2110.1 \mu\text{mol.kg}^{-1}$ ) and low concentrations in summer ( $2067.6\text{--}2096.6 \mu\text{mol.kg}^{-1}$ ). The temporal variations of  $C_T$  are inversely associated with those of sea

surface chl *a* concentrations, which increased from spring (0.06–0.42 mg m<sup>-3</sup>) to summer (0.07–0.77 mg m<sup>-3</sup>; Fig. 7).

In the SAZ, pCO<sub>2</sub><sup>sea</sup> increases southward from 343.1 to 399.8 μatm; Fig. 5a. ΔpCO<sub>2</sub> (pCO<sub>2</sub><sup>sea</sup> - pCO<sub>2</sub><sup>air</sup>) was positive in spring up to +20.67 μatm (around 50°S) and negative in summer down to -37.03 μatm (around 48°S); Fig. 5b. Thus, during summer the SAZ is a CO<sub>2</sub> sink with southward variations of the air to sea CO<sub>2</sub> flux (-53.0 to -0.9 mmol.m<sup>-2</sup>.d<sup>-1</sup>, Fig. 6). In this area too, the seasonal variations of both sea surface temperature and biological activity controlled the air-sea CO<sub>2</sub> fluxes.

#### *Polar Frontal Zone (PFZ; 53.0 ± 1.5°S)*

The temporal variations of A<sub>T</sub> concentrations were relatively small. They decreased slightly from spring (2280 ± 4 μmol.kg<sup>-1</sup>) to summer (2270 ± 4 μmol.kg<sup>-1</sup>; Fig. 2a). Simultaneously, the C<sub>T</sub> concentrations decreased from spring (2124.9 ± 26.9 μmol.kg<sup>-1</sup>) to summer (2097.2 ± 17.5 μmol.kg<sup>-1</sup>; Fig. 2b). Sea surface salinity decreased southward, from a mean of 34.09 ± 0.26 in spring to 34.16 ± 0.17 in summer (Fig. 4a). Mean temperature increased from 5.25 ± 2.24°C in spring to 6.95 ± 1.25°C in summer (Fig. 4b).

Within the PFZ, pCO<sub>2</sub><sup>sea</sup> was close to equilibrium with pCO<sub>2</sub><sup>air</sup> (Fig. 5a). As observed earlier (Jabaud-Jan *et al.* 2004), the spatial distribution of pCO<sub>2</sub><sup>sea</sup> creates a mosaic with high, low, and near-equilibrium values compared to that of pCO<sub>2</sub><sup>air</sup>. Globally, mean pCO<sub>2</sub><sup>sea</sup> decreased from 375.8 ± 18.9 μatm in spring to 369.9 ± 11.5 μatm in summer. The high variations of ΔpCO<sub>2</sub> observed within the PFZ ranged from -34.93 to +8.87 μatm (Fig. 5b). Consequently, the estimated air-sea CO<sub>2</sub> flux varied from -40.6 to +2.3 mmol.m<sup>-2</sup>.d<sup>-1</sup> in summer, and from -10.5 to +2.5 mmol.m<sup>-2</sup>.d<sup>-1</sup> in spring (Fig. 6).

In the PFZ the pCO<sub>2</sub><sup>sea</sup> and C<sub>T</sub> are higher during spring than during summer. This is probably linked to the deepening of the mixed-layer in winter (i.e. mixing of surface water with CO<sub>2</sub> enriched subsurface waters). In summer, the increase of temperature induces a relatively shallow mixed layer and reduces upwelling. The mean primary production in surface waters is relatively low especially during summer (0.18 ± 0.08 mg m<sup>-3</sup>; Fig. 7) where nutrients are low. We conclude that sea surface temporal pCO<sub>2</sub> variations are mostly controlled by seasonal changes of vertical dynamics.

#### *Permanent Open Ocean Zone (POOZ; 57.5 ± 3.0°S)*

In POOZ the A<sub>T</sub> concentrations (2271 ± 7 μmol.kg<sup>-1</sup>; Fig. 2a) display no significant spatio-temporal variations. In contrast, C<sub>T</sub> concentrations show significant temporal variations with high concentrations in spring (2157.2 ± 5 μmol.kg<sup>-1</sup>) and low concentrations in summer (2117.4 ± 14.8 μmol.kg<sup>-1</sup>; Fig. 2b). Salinity (33.86 ± 0.10;

Fig. 4a) does not vary enough to create significant temporal variation in A<sub>T</sub>. As observed earlier (Volk & Hoffert 1985) the temporal variations of C<sub>T</sub> are inversely correlated with those of SST (0.58 ± 0.47°C in spring and 4.19 ± 0.61°C in summer; Fig. 4b).

The pCO<sub>2</sub><sup>sea</sup> varies from 397.1 μatm in spring to 346.7 μatm in summer (Fig. 5a). The mixed layer depth is relatively shallow, about 40–60 m in summer (Chaigneau *et al.* 2004), and reduced vertical mixing contributes to an increase of SST (Fig. 4b). Primary production is much higher (0.11–0.78 mg m<sup>-3</sup>) in summer than in spring (0.13–0.61 mg m<sup>-3</sup>; Fig. 7). Therefore, the sea surface spatio-temporal variations are mainly controlled by biological activity. As a result, the POOZ was a CO<sub>2</sub> sink in summer (on average of ΔpCO<sub>2</sub> = -15.6 ± 10.3 μatm; Fig. 5b) with an associated average CO<sub>2</sub> flux of -11.5 ± 8.9 mmol.m<sup>-2</sup>.d<sup>-1</sup> (Fig. 6).

#### *Seasonal Ice Zone (SIZ; 63.0 ± 2.0°S)*

The SIZ is a contrasting area with a transition from the permanent free ice seawater to the seasonal ice covered area. From 60.5°S to 63.0°S, within the free seawater area, we observe small variations of pCO<sub>2</sub><sup>sea</sup> and A<sub>T</sub>, in contrast to large temporal variations of C<sub>T</sub>.

The general trend of A<sub>T</sub> indicates stable concentrations around 2284.75 ± 7.15 μmol.kg<sup>-1</sup> (Fig. 2a), associated with stable salinity around 33.88 ± 0.10 (Fig. 4a). The A<sub>T</sub> concentrations in surface seawater are linearly linked with those of salinity as observed by others over the sea surface ocean (Poisson & Chen 1987, Takahashi *et al.* 1993, Millero *et al.* 1998). C<sub>T</sub> concentrations increase southward slightly with large temporal variations (Fig. 2b). Concentrations are higher in spring (2166.69 ± 5.97 μmol.kg<sup>-1</sup>) than in summer (2132.35 ± 10.55 μmol.kg<sup>-1</sup>). As shown earlier (Weiss 1974, Goyet & Brewer 1993, Takahashi *et al.* 2002, Ishii *et al.* 2002) the temporal variations of C<sub>T</sub> were negatively correlated with SST (-1.22 ± 0.37°C in spring and 2.54 ± 0.77°C in summer; Fig. 4b).

The measurements show low pCO<sub>2</sub><sup>sea</sup> around 367.13 ± 7.01 μatm (Fig. 5a) with negative ΔpCO<sub>2</sub> down to -12.98 ± 6.76 μatm (Fig. 5b). The CO<sub>2</sub> flux from the atmosphere to the ocean increases from spring (-2.86 ± 2.41 mmol.m<sup>-2</sup>.d<sup>-1</sup>) to summer (-12.92 ± 8.40 mmol.m<sup>-2</sup>.d<sup>-1</sup>; Fig. 6). The free-ice seawater area displays relatively small air-sea CO<sub>2</sub> flux variations associated with small variation of mean chl *a* concentrations (0.22 ± 0.07 mg m<sup>-3</sup> in spring and 0.21 ± 0.16 mg m<sup>-3</sup> in summer; Fig. 7).

From 63°S to 65°S in the seasonal ice covered area, growth of ice in winter and the melting of ice in summer induce strong seasonal variations. In spring, A<sub>T</sub> concentrations decrease in the area between 62.61°S and 63.79°S (from 2289.4 to 2253.4 μmol.kg<sup>-1</sup>; Fig. 2a) associated with a salinity decrease (from 33.88 to 33.45; Fig. 4a). C<sub>T</sub> concentrations show large temporal variations (Fig. 2b). In spring, C<sub>T</sub> increases strongly

**Table I.** Regional effects of temperature and biology on distribution of pCO<sub>2</sub><sup>sea</sup> along transects between Hobart and Dumont D'Urville from October 2005 to March 2006.

Zone	Latitude (°S)	spring		summer	
		biology effect (μatm)	temperature effect (μatm)	biology effect (μatm)	temperature effect (μatm)
STZ	45.5 ± 2.0	92.3	115.2	98.9	148.3
SAZ	49.5 ± 20	55.9	62.1	89.2	78.1
PFZ	53.0 ± 1.5	133.2	115.4	77.5	81.1
POOZ	57.5 ± 3.0	28.4	20.6	60.5	55.1
SIZ	63.0 ± 2.0	106.6	36.2	102.6	75
CAZ	66.0 ± 1.0	61.5	5.5	102.2	48.4

southward from 2155.6 μmol.kg<sup>-1</sup> to 2201.3 μmol.kg<sup>-1</sup> corresponding to low SST (-1.71 ± 0.16°C; Fig. 4b). The lowest C<sub>T</sub> concentrations are observed in summer (2125.4 to 2159.4 μmol.kg<sup>-1</sup>) associated with high SST (1.35 ± 0.74°C).

In the southern part of the SIZ, pCO<sub>2</sub> concentrations are high in spring (364.2–406.2 μatm) and strongly decrease in summer (361.9–322.9 μatm; Fig. 5a). Thus ΔpCO<sub>2</sub> is positive in spring (+10.55 ± 8.97 μatm) and negative (-34.74 ± 11.56 μatm) in summer (Fig. 5b). The CO<sub>2</sub> fluxes from the atmosphere to the ocean increase from spring (+1.61 ± 2.09 mmol.m<sup>-2</sup>.d<sup>-1</sup>) to summer (-18.59 ± 17.75 mmol.m<sup>-2</sup>.d<sup>-1</sup>; Fig. 6).

In spring, in the presence of ice, CO<sub>2</sub> (C<sub>T</sub>) accumulates in seawater under the ice (Ishii *et al.* 2002). In summer, after the ice has melted, the SIZ is a strong CO<sub>2</sub> sink. The phytoplankton biomass is important in summer (Ishii *et al.* 2002). The intense CO<sub>2</sub> flux in summer corresponds with increased CO<sub>2</sub> uptake and a significant increase in mean sea surface chl *a* concentrations from spring (0.21 ± 0.05 mg m<sup>-3</sup>) to summer (0.59 ± 0.32 mg m<sup>-3</sup>; Fig. 7).

#### Continental Antarctic Zone (CAZ; 66.0 ± 1°S)

The CAZ is covered by seasonal ice in spring and free of ice in summer. A<sub>T</sub> concentrations (Fig. 2a) increase southward in this zone. The highest concentrations are observed in spring (2305.9–2385.4 μmol.kg<sup>-1</sup>) around Antarctica. During seasonal cooling, the intensive vertical mixing brings deep waters rich in CaCO<sub>3</sub> to the surface and thus increases surface A<sub>T</sub> (Volk & Hoffert 1985). In summer, the A<sub>T</sub> concentrations are variable (2304.25 ± 33.35 μmol.kg<sup>-1</sup>) due to variable activity of marine biota which generally occurs with an increase in SST. C<sub>T</sub> concentrations are higher in spring (2184.0–2250.6 μmol.kg<sup>-1</sup>) than in summer (2127.3–2198.5 μmol.kg<sup>-1</sup>; Fig. 2b). During spring, C<sub>T</sub> concentrations are inversely correlated with SST (Fig. 4b), which limits in turn phytoplankton production (Lee *et al.* 1998, Jabaud-Jan *et al.* 2004). In summer, relatively high SST (-1.5 ≤ SST ≤ 0.5°C), high solar radiation, and melting of ice favour growth of phytoplankton (Fig. 7).

The CAZ is characterized by strong pCO<sub>2</sub><sup>sea</sup> temporal variations (Fig. 5a). In spring 2005, the pCO<sub>2</sub><sup>sea</sup> minimum (388.0 μatm) was centred at 65.07°S and the maximum (429.5 μatm) was detected near the DDU station (67°S).

In summer 2006, pCO<sub>2</sub><sup>sea</sup> concentrations decreased from 370.0 μatm to 316.1 μatm. The increase of mean water temperature from spring to summer (about 3°C) had a direct impact of increased phytoplankton growth in sea surface water and could explain the seasonal pCO<sub>2</sub><sup>sea</sup> variations.

The CAZ is an important area for springtime CO<sub>2</sub> accumulation below ice. The retreat of the ice edge would cause considerable outgassing of CO<sub>2</sub> to the atmosphere associated with high wind speed enhancing air-sea exchange with a mean ΔpCO<sub>2</sub> of +32.91 ± 7.78 μatm. In contrast, during summer this area is a strong CO<sub>2</sub> sink with a mean ΔpCO<sub>2</sub> of -37.41 ± 12.72 μatm (Fig. 5b). Thus, we observed large temporal variations of CO<sub>2</sub> fluxes (Fig. 6). The CO<sub>2</sub> fluxes decreased from spring (average of +14.9 ± 13.8 mmol.m<sup>-2</sup>.d<sup>-1</sup>) to summer (average of -12.3 ± 8.45 mmol.m<sup>-2</sup>.d<sup>-1</sup>; Fig. 6). The intense air to sea CO<sub>2</sub> flux is associated with greater CO<sub>2</sub> uptake by phytoplankton biomass correlated with increased of mean sea surface chl *a* concentrations from spring (0.17 ± 0.07 mg m<sup>-3</sup>) to summer (0.68 ± 0.43 mg m<sup>-3</sup>).

#### Relative importance of the temperature and biology effects

In order to assess the relative importance of the temperature and biological effects on the temporal variability of pCO<sub>2</sub><sup>sea</sup>, we used the approach earlier published by Takahashi *et al.* (2002).

In order to remove the temperature effect from the observed pCO<sub>2</sub><sup>sea</sup>, the observed pCO<sub>2</sub> values are normalized to a constant temperature, the mean annual temperature:

$$(pCO_2 \text{ at } T_{\text{mean}}) = (pCO_2)_{\text{obs}} \times \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})] \quad (1)$$

where T is the temperature in °C, and the subscripts “mean” and “obs” indicate the annual average and observed values, respectively.

The “net biology” effect on pCO<sub>2</sub><sup>sea</sup> has been computed using the equation:

$$(\Delta pCO_2)_{\text{bio}} = (pCO_2 \text{ at } T_{\text{mean}})_{\text{max}} - (pCO_2 \text{ at } T_{\text{mean}})_{\text{min}} \quad (2)$$

**Table II.** Averaged air-sea CO<sub>2</sub> fluxes, temperature and salinity in the four different regions of the Southern Ocean in October 1996 and February 1997, October 2002 and February 2003 (Brévière *et al.* 2006), as well as our measurements in October 2005 and February 2006 along transects between Hobart and Dumont D'Urville.

	SAR			POOZ			SIZ			CAZ		
	flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	SST °C	chl <i>a</i> mg m <sup>-3</sup>	flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	SST °C	chl <i>a</i> mg m <sup>-3</sup>	flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	SST °C	chl <i>a</i> mg m <sup>-3</sup>	flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	SST °C	chl <i>a</i> mg m <sup>-3</sup>
Oct 1996	-9.0	7.90	0.12	-3.3	0.90	0.09	-4.8	-0.30	0.40	-	-	-
Feb 1997	-12.3	11.00	0.35	-0.3	4.70	0.06	-1.6	2.90	0.26	-3.1	0.00	33.70
Oct 2002	-5.0	9.50	0.43	1.4	2.20	0.15	-5.0	-0.7	0.52	-	-	-
Feb 2003	-13.6	11.10	0.52	-20.6	5.20	0.52	2.6	2.27	0.07	-4.7	0.32	33.95
Oct 2005	-6.8	8.95	0.29	-0.2	0.58	0.20	-1.4	-1.45	0.22	14.9	-1.77	34.44
Feb 2006	-9.9	10.33	0.27	-8.2	4.45	0.12	-10.9	2.45	0.21	-8.4	-0.73	33.91

Where the subscripts “max” and “min” indicate the seasonal maximum and minimum values of pCO<sub>2</sub><sup>sea</sup> at T<sub>mean</sub>.

The effect of temperature changes on pCO<sub>2</sub><sup>sea</sup> has been computed by perturbing the mean annual pCO<sub>2</sub> with the difference between the mean and observed temperature Eq.(3):

$$(pCO_2 \text{ at } T_{obs}) = (\text{Mean annual } pCO_2) \times \exp[0.0423(T_{obs} - T_{mean})] \quad (3)$$

The “net temperature” effect on pCO<sub>2</sub><sup>sea</sup> has been computed:

$$(\Delta pCO_2)_{temp} = (pCO_2 \text{ at } T_{obs})_{max} - (pCO_2 \text{ at } T_{obs})_{min} \quad (4)$$

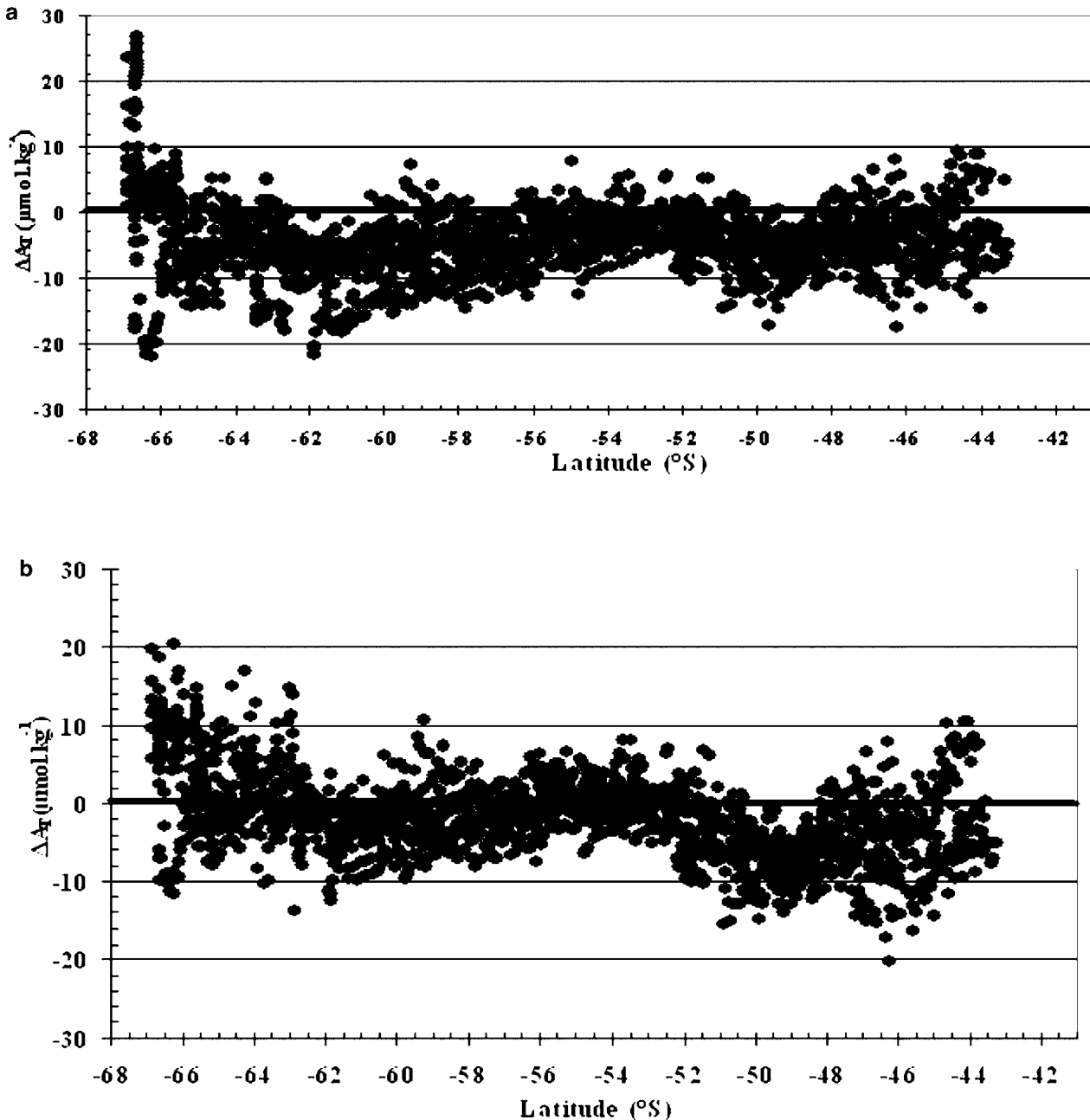
Where the subscripts “max” and “min” indicate the seasonal maximum and minimum values of pCO<sub>2</sub><sup>sea</sup> at T<sub>obs</sub>.

The relative importance of biological and temperature effects on pCO<sub>2</sub> varies according to location (Table I). In general, the temperature effect dominates the biological effect in subtropical zone (STZ) increasing from 115.2 μatm in spring to 148.3 μatm in summer when the mean temperature rises from 11.45 ± 1.46°C to 13.70 ± 2.12°C, respectively. The biology effect intensifies southward, especially in the areas south of the Polar Frontal Zone (PFZ) from POOZ to the shelf areas of Antarctica (SIZ and CAZ). This confirms that the photosynthetic drawdown of CO<sub>2</sub> in the Southern Ocean waters, as well as the shelf waters around Antarctica, plays an important role for the transport of atmospheric CO<sub>2</sub> into the deep ocean (Takahashi *et al.* 2002). In mid-latitude areas, the dominant effect alternates between spring (temperature in SAZ and biology in PFZ) and summer (biology in SAZ and temperature in PFZ).

### Comparison with previous observations

Interannual variations of CO<sub>2</sub> fluxes were determined in the Southern Indian Ocean using data from MINERVE cruises in October 1996 and February 1997, October 2002 and February 2003 (Brévière *et al.* 2006). Here we show results from the same area from October 2005 to February 2006. The mean of air-sea CO<sub>2</sub> fluxes, sea surface temperature, sea surface salinity and chl *a* concentrations in the four different regions of the Southern Ocean along transects between Hobart and Dumont D'Urville are summarized in Table II.

In the sub-Antarctic region (SAR = STZ + SAZ + PFZ), the CO<sub>2</sub> flux is always higher in summer than in spring. The mean CO<sub>2</sub> flux increased slightly from February 1997 to 2003 (-12.3 mmol.m<sup>-2</sup>.d<sup>-1</sup> to -13.6 mmol.m<sup>-2</sup>.d<sup>-1</sup>, respectively) and then decreased in February 2006 (-9.9 mmol.m<sup>-2</sup>.d<sup>-1</sup>). The mean temperature, salinity and chl *a* concentrations increased from February 1997 to 2003 (11.00°C to 11.10°C, 34.46 to 34.73 and 0.35 mg m<sup>-3</sup> to 0.52 mg m<sup>-3</sup> respectively)



**Fig. 8.** **a.** Representation of  $\Delta A_T$  ( $A_T$  measured -  $A_T$  calculated from Eq.(5)) for both seasons (spring 2005 and summer 2006) along transects H-DDU and DDU-H. **b.** Representation of  $\Delta A_T$  ( $A_T$  measured -  $A_T$  calculated from the new equation; Eq.(6)) for both seasons (spring and summer) along transects from H-DDU and DDU-H.

and then decreased in February 2006 (10.33°C, 34.36 and 0.27 mg m<sup>-3</sup>).

The CO<sub>2</sub> flux in the POOZ displays contrasting interannual changes in February. The CO<sub>2</sub> flux increases from -0.3 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 1997 to -20.6 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 2003 and decreases to -8.2 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 2006. The mean of sea surface temperature and chl *a* concentrations increased from February 1997 to February 2003 (4.70°C to 5.20°C and 0.06 to 0.52 mg m<sup>-3</sup> respectively) and decreased in February 2006 (4.45°C and 0.12 mg m<sup>-3</sup>

respectively). The mean salinity increased from February 1997 to February 2003 (33.64 to 33.73) and to February 2006 (33.84).

On average in the SIZ surface waters, the CO<sub>2</sub> sink increases with time. The CO<sub>2</sub> flux varies from -1.6 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 1997 to +2.6 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 2003 and to -10.9 mmol.m<sup>-2</sup>.d<sup>-1</sup> in February 2006. The mean of temperature and chl *a* concentrations decreased from February 1997 to February 2003 (2.90°C to 2.27°C and 0.26 mg m<sup>-3</sup> to 0.07 mg m<sup>-3</sup>, respectively) and

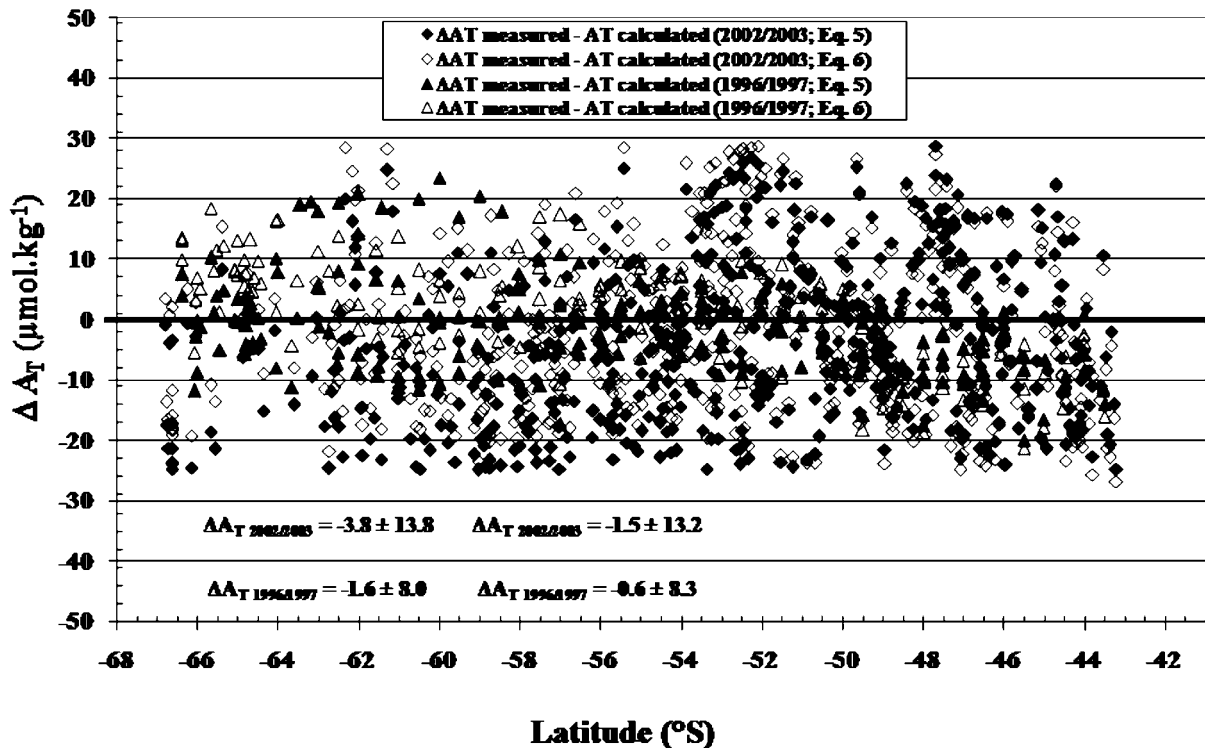


Fig. 9. Representation of  $\Delta A_T$  ( $A_T$  measured -  $A_T$  calculated from Eq.(5) and Eq.(6) for both seasons (spring and summer) along transects H-DDU and DDU-H in 1996/1997 and 2002/2003.

increased to February 2006 (2.45°C and 0.21 mg m<sup>-3</sup>). The mean salinity increased from February 1997 to February 2003 (33.53 to 33.75) and to February 2006 (33.89).

In POOZ and SIZ, the interannual variations of CO<sub>2</sub> flux are only associated with those of temperature and chl *a* concentrations.

In the CAZ, in October 2005 the mean CO<sub>2</sub> flux is positive +14.9 mmol.m<sup>-2</sup>.d<sup>-1</sup> and is associated with negative mean temperature (-1.77°C), low mean chl *a* concentrations (0.17 mg m<sup>-3</sup>) and high mean salinity (34.44). In contrast, the mean air to sea CO<sub>2</sub> flux increases from February 1997 and 2003 (-3.1 mmol.m<sup>-2</sup>.d<sup>-1</sup> and -4.7 mmol.m<sup>-2</sup>.d<sup>-1</sup>, respectively) to February 2006 (-8.4 mmol.m<sup>-2</sup>.d<sup>-1</sup>). The mean of temperature and salinity increased from February 1997 to 2003 (0.00°C to 0.32°C and 33.70 to 33.95 respectively) and decreased to February 2006 (-0.73°C and 33.91 respectively). The mean chl *a* concentrations increased from February 1997 and 2003 (0.31 mg m<sup>-3</sup> and 0.44 mg m<sup>-3</sup>) to 2006 (0.68 mg m<sup>-3</sup>). Then in this zone, the interannual variations of CO<sub>2</sub> flux are only associated with those of chl *a* concentrations.

Considerable seasonal and interannual variability is observed. The few data available do not allow us to determine a clear trend in the interannual evolution of the CO<sub>2</sub> fluxes in these ocean areas. It is thus important to continue such time series measurements to quantify the temporal variations over a few decades.

#### Relationship of total alkalinity with salinity and temperature

A few years ago, Lee *et al.* (2006) indicated that in the Southern Ocean, in surface waters  $A_T$  can be estimated by the following relationship as a function of temperature (SST) and salinity (SSS):

$$A_T = 2305 + 52.48(\text{SSS} - 35) + 2.85(\text{SSS} - 35)^2 - 0.49(\text{SST} - 20) + 0.086(\text{SST} - 20)^2 \quad (5)$$

Their study indicates that this general relationship can be applied at all longitudes over the large latitudinal range 30°S–70°S, for SST < 20°C and 33 < SSS < 36.

The mean difference  $\Delta A_T$  (measured - calculated with Eq.(5)) is  $-4.3 \pm 5.5 \mu\text{mol.kg}^{-1}$  for both seasons (spring: from 18 October–8 November 2005 and summer: from 30 December 2005–26 January 2006 and from 17 February–2 March 2006; Fig. 8a). In high latitudes regions (63–67°S), we observed large variabilities ( $0.4 \pm 9.2 \mu\text{mol.kg}^{-1}$  in spring and  $-5.2 \pm 5.9 \mu\text{mol.kg}^{-1}$  in summer). These variations are mainly due to salinity changes by freshwater inputs through the melting of ice and are in part due to the increase in the convective mixing of deep waters rich in  $A_T$  during seasonal cooling. Therefore, the increase of surface  $A_T$  concentrations are correlated with input of CaCO<sub>3</sub> rich deep waters to the upper layers.

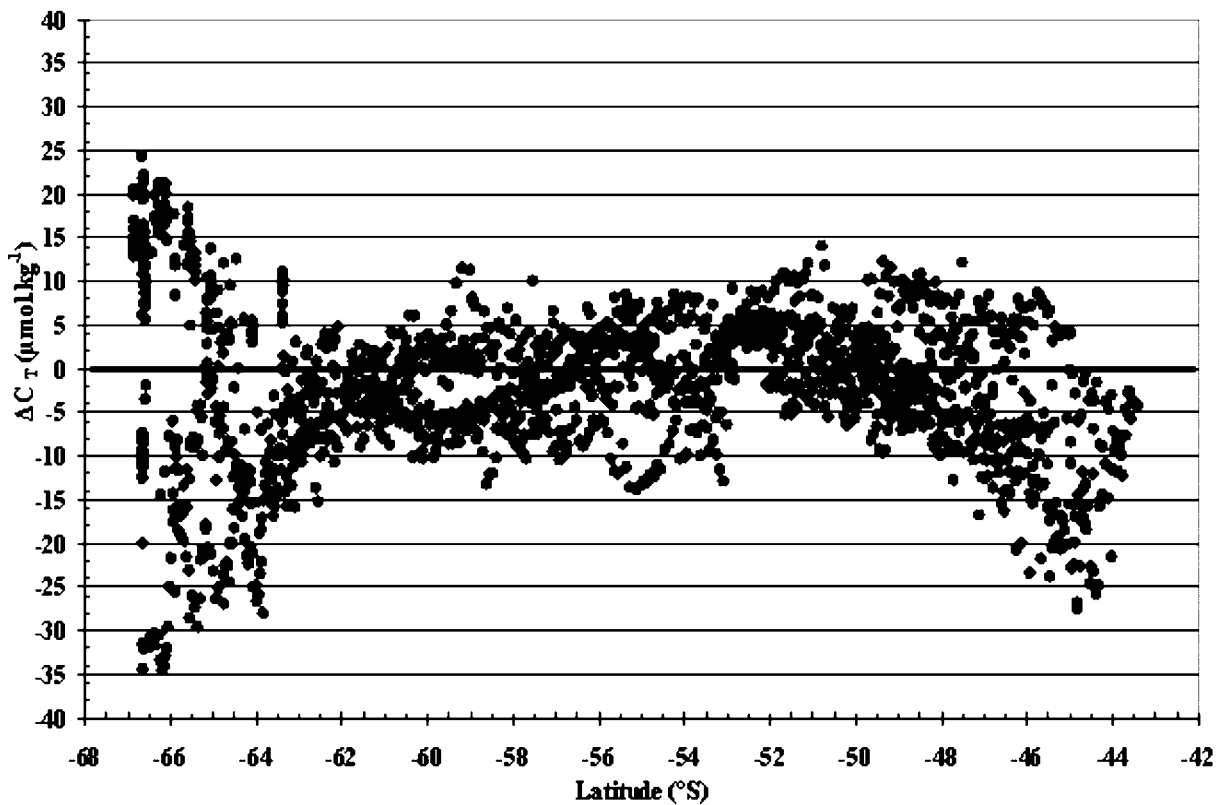


Fig. 10. Representation of  $\Delta C_T$  ( $C_T$  measured -  $C_T$  calculated from Eq.(7)) for both seasons (spring and summer) along transects H-DDU and DDU-H in 2005/2006.

In order to describe more specifically the MINERVE datasets we developed a new simple  $A_T$  relationship for both seasons (spring and summer). Using the software package TABLE CURVE™, these 2005–2006 data are best fitted with the following function involving the two properties SSS and SST:

$$A_T = 434.711 - 2.599(SST) + 54.671(SSS) \quad (6)$$

This equation is valid only in the limited ocean area between Hobart (~43°S ~147°E) and Dumont D’Urville (~67°S ~140°E) with SST < 20°C, and 33 < SSS < 36.

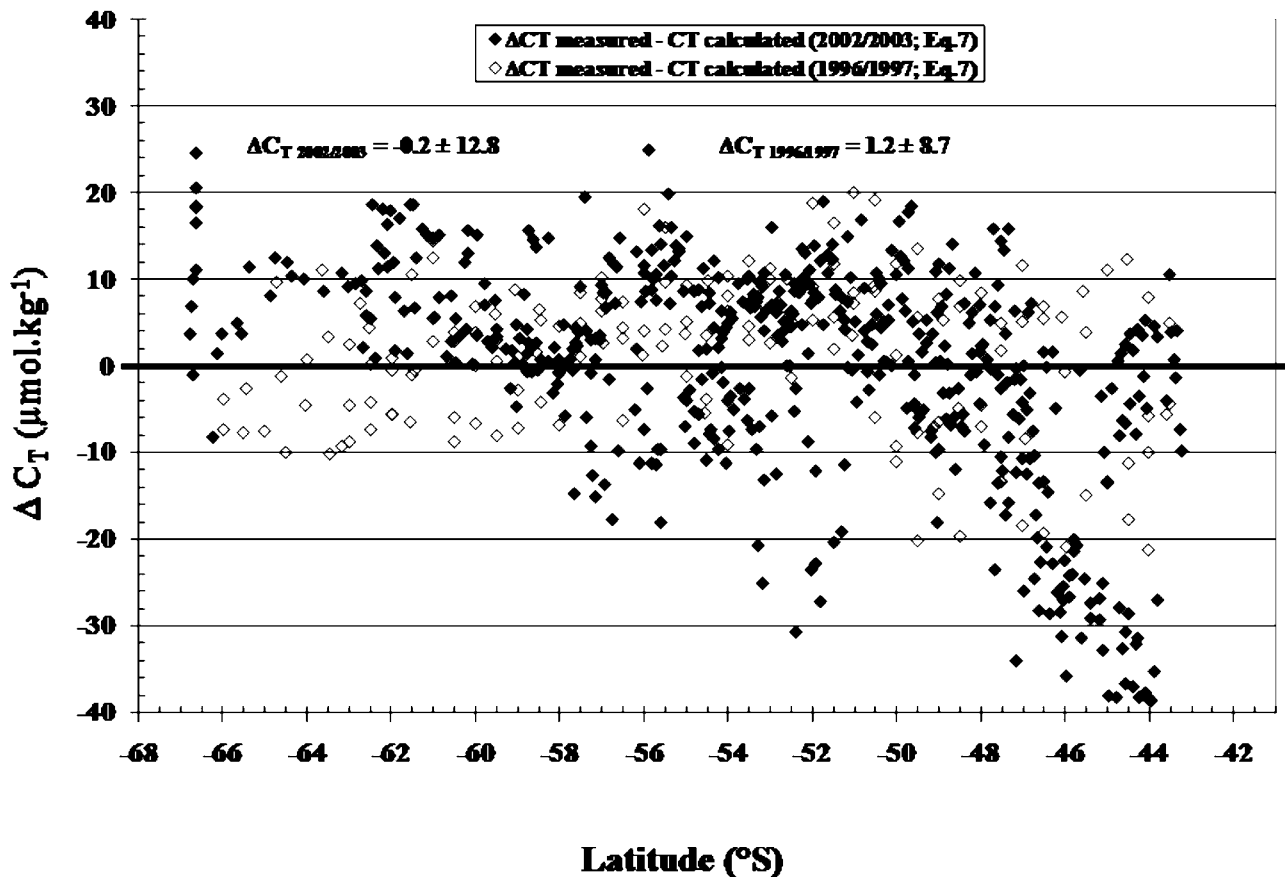
The mean difference  $\Delta A_T$  (measured - calculated with Eq.(6)) is  $-1.7 \pm 5.4 \mu\text{mol.kg}^{-1}$  (Fig. 8b). The two main

differences between the model of Lee *et al.* (2006, Eq.(5)) and this new model (Eq.(6)) are: 1) the formulation of the function with second and first degrees, respectively, 2) Eq.(5) is general for the whole Southern Ocean and Eq.(6) is specific to the limited ocean area between Hobart and Dumont D’Urville.

In order to further validate Eq.(6), we used the earlier 1996/1997 and 2002/2003 datasets from the same ocean area. Results indicate that the mean difference  $\Delta A_{T1996/1997}$  (measured - calculated with Eq.(5)) is  $-1.6 \pm 8.0 \mu\text{mol.kg}^{-1}$  (Fig. 9) and  $\Delta A_{T1996/1997}$  (measured - calculated with Eq.(6))  $0.6 \pm 8.3 \mu\text{mol.kg}^{-1}$ . In 2002/2003, the  $\Delta A_T$  (measured - calculated with Eq.(5)) is  $-3.8 \pm 13.4 \mu\text{mol.kg}^{-1}$  and  $\Delta A_T$

Table III. Regional and temporal representations of surface total dissolved inorganic carbon ( $C_T$ ) calculated in the Southern Ocean south of Australia between Hobart and Dumont D’Urville (43–67°S).

Periods	Region	$C_T$	$\Delta C_T$ (mean $\pm$ $\sigma$ )
Spring: 18 Oct–8 Nov 2005	43–67°S	$429.707 - 7.445 \times \text{SST} + 0.757 \times A_T$	$-1.8 \pm 8.9$
Summer: 30 Dec 2005–26 Jan 2006			
Spring: 17 Feb–2 March 2006	43–47.5°S	$35.714 - 10.895 \times \text{SST} + 0.946 \times A_T$	$-0.4 \pm 3.3$
Summer: 30 Dec 2005–26 Jan 2006			
Spring: 17 Feb–2 March 2006	63–67°S	$1391.076 - 6.423 \times \text{SST} + 0.327 \times A_T$	$0.7 \pm 4.6$
Summer: 30 Dec 2005–26 Jan 2006			
Spring: 18 Oct–8 Nov 2005	63–67°S	$-181.746 - 4.775 \times \text{SST} + 1.027 \times A_T$	$0.9 \pm 4.4$
Summer: 30 Dec 2005–26 Jan 2006			
Spring: 17 Feb–2 March 2006	63–67°S	$-394.924 - 3.259 \times \text{SST} + 1.109 \times A_T$	$0.6 \pm 6.0$
Summer: 30 Dec 2005–26 Jan 2006			



**Fig. 11.** Representation of  $\Delta C_T$  ( $C_T$  measured -  $C_T$  calculated from the equation Eq.(7)) for both seasons (spring and summer) along transects H-DDU and DDU-H in 1996/1997 and 2002/2003.

(measured - calculated with Eq.(6)) is  $-1.5 \pm 13.2 \mu\text{mol.kg}^{-1}$  (Fig. 9). These results show greater variability in 2002/2003 than in 1996/1997. Nevertheless, these two earlier datasets confirm the validity of Eq.(6) for the limited ocean area between Hobart and Dumont D'Urville.

#### Relationship of total inorganic carbon with total alkalinity and temperature

In order to estimate  $C_T$  variabilities in the Southern Ocean between Hobart and Dumont D'Urville, we also used the 2005/2006 dataset with the software package TABLE CURVE™ to develop a simple relationship to estimate  $C_T$  as a function of  $A_T$  and SST:

$$C_T = 429.707 - 7.445 \times (\text{SST}) + 0.757 \times (A_T) \quad (7)$$

The mean difference of  $\Delta C_T$  (measured - calculated with Eq.7) is  $-1.8 \pm 8.9 \mu\text{mol.kg}^{-1}$  for all data from October 2005–February 2006 (Fig. 10). We observed some variability at latitudes ranging from 43–47.5°S, with a mean  $\Delta C_T$  of  $-6.9 \pm 8.6 \mu\text{mol.kg}^{-1}$  correlated with temporal variations of  $0.8 \pm 5.6 \mu\text{mol.kg}^{-1}$  in spring and  $-11.8 \pm 6.3 \mu\text{mol.kg}^{-1}$  in

summer. In addition, at high latitudes from 63–67°S, the highest variabilities ( $-2.6 \pm 14.9 \mu\text{mol.kg}^{-1}$ ) are associated with highest temporal variations ( $10.1 \pm 7.9 \mu\text{mol.kg}^{-1}$  in spring and  $-15.1 \pm 8.0 \mu\text{mol.kg}^{-1}$  in summer). In order to improve the model accuracy, it could be best to formulate two equations for  $C_T$  calculations: a specific equation for spring and another for summer for each of these two regions (43–47.5°S and 63–67°S, Table III).

In order to validate this relationship (Eq.(7)), we used the 1996/1997 and 2002/2003 datasets. Similarly to  $\Delta A_T$ , the mean difference of  $\Delta C_T$  (measured - calculated with Eq.7) shows greater variability in 2002/2003 ( $-0.2 \pm 12.8 \mu\text{mol.kg}^{-1}$ ) than in 1996/1997 ( $1.2 \pm 8.7 \mu\text{mol.kg}^{-1}$ ; Fig. 11). Nevertheless, these results confirm the validity of Eq.(7) for the ocean area between Hobart and Dumont D'Urville.

#### Concluding remarks

In this paper, we studied the temporal variability of air-sea  $\text{CO}_2$  fluxes in four main oceanic regions in the Southern Indian Ocean from 43.0–67.0°S between October 2005 and March 2006. The distributions of  $\text{pCO}_2^{\text{sea}}$  and  $C_T$  were mainly associated with variations in SST and chl *a*



concentrations. The variations of  $A_T$  were directly associated with SSS and SST changes.

Temporal  $p\text{CO}_2^{\text{sea}}$  (spring–summer) measurements south of Tasmania indicate that the surface seawaters of the STZ and POOZ are stronger CO<sub>2</sub> sinks in summer than in spring. The spring–summer cycle of CO<sub>2</sub> fluxes in these zones (STZ and POOZ) exhibits a pattern noticed earlier south of Tasmania (Inoue & Ishii 2005, Brévière *et al.* 2006).

During both spring and summer, large variability in CO<sub>2</sub> flux was observed in the SIZ and CAZ. Particularly, the presence of seasonal ice had a direct impact on  $p\text{CO}_2^{\text{sea}}$  with high  $C_T$  concentrations below the ice in spring. The effect of biological CO<sub>2</sub> uptake in summer had a larger effect than rising temperature after the retreat of the sea ice. Low  $p\text{CO}_2$  waters are formed by the juxtaposition of the cooling of warm waters with the biological drawdown of  $p\text{CO}_2$  in the nutrient rich subpolar waters. High wind speeds over these low  $p\text{CO}_2$  waters increase the ocean CO<sub>2</sub> uptake rate.

The partial pressure  $p\text{CO}_2$  is calculated from the measured  $A_T$  and  $C_T$  using the software developed by Lewis & Wallace (1998) with the equilibrium constants for the dissociation of carbonic acid proposed by Mehrbach *et al.* (1973), Goyet & Poisson (1989) and Roy *et al.* (1993). In this ocean area, the calculated surface water  $p\text{CO}_2$  using the Goyet & Poisson (1989) constants provide the most accurate and precise results.

$p\text{CO}_2$  calculated as a function of  $A_T$  and  $C_T$  can be used to estimate the spatio-temporal variations in the Southern Ocean south of Australia (43–67°S) where  $A_T$  and  $C_T$  are known.

Using the approach of Takahashi *et al.* (2002) we assess the seasonal biology and temperature effects on  $p\text{CO}_2^{\text{sea}}$  in the different hydrographic regions along our transect between Hobart and Adélie Land. The effect of temperature is dominant in STZ, in contrast with POOZ, SIZ and CAZ where the seasonal variation of  $p\text{CO}_2^{\text{sea}}$  is entirely attributed to the biological utilization of CO<sub>2</sub>. In SAZ and PFZ, the seasonal amplitude of surface-water  $p\text{CO}_2$  at a given location is regulated by the biological utilization of CO<sub>2</sub> and temperature.

The mean of air-sea CO<sub>2</sub> fluxes, sea surface temperature, sea surface salinity and chl *a* concentrations in the four different regions of the Southern Ocean were compared with data from MINERVE cruises in October (1996, 2002 and 2005) and February (1997, 2003 and 2006). In the sub-Antarctic region (SAR = STZ + SAZ + PFZ), the interannual variations of the CO<sub>2</sub> flux are associated with those of temperature, salinity and chl *a* concentrations. The interannual variations of CO<sub>2</sub> flux in POOZ and SIZ are only associated with those of temperature and chl *a* concentrations. In the CAZ, the interannual variations of CO<sub>2</sub> flux are only associated with those of chl *a* concentrations.

Furthermore, this work presents new equations suitable for studying the spatio-temporal variations of  $A_T$  and  $C_T$

using SST and SSS measurements in the surface waters of the Southern Ocean south of Australia. These new  $A_T$  and  $C_T$  equations are simple and accurate. They have been validated using all data available from 1996 to 2006.

These results clearly indicate that it is very important to continue such time series measurements in order to quantify the temporal variations over several decades and the impact on the Earth's climate.

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