

Interannual controls on Weddell Sea surface water $f\text{CO}_2$ during the autumn–winter transition phase

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Abstract

The fugacity of carbon dioxide ($f\text{CO}_2$) of the surface waters of the Weddell Sea along the prime meridian has been described for the austral autumn in 1996 and 1998. For individual years, $f\text{CO}_2$ has a strong linear relationship with sea surface temperature, although the relationships cannot be reconciled to provide an interannually consistent algorithm for remotely sensed assessment of $f\text{CO}_2$. However, from the assumption that Weddell Sea surface water has a single end member (upwelled Warm Deep Water) we have determined the relative contributions of heating, ice-melt, and biological activity on $f\text{CO}_2$. A breakdown of the controls shows that the measured annual $f\text{CO}_2$ distributions can be recreated for both transects by adjusting solely for thermodynamic forcing, and model adjustments for salinity are small except in regions of significant upwelling during 1998. The incorporation of nitrate utilisation into the model results in a general and significant underestimation of $f\text{CO}_2$. This runs contrary to the earlier findings of Sabine and Key (Mar. Chem. 60 (1998) 95) in the Southern Ocean although it is consistent with models in the area (Louanchi et al., Deep-Sea Res. I 48 (2001) 1581). A major caveat to these findings is the significant departure of the thermodynamic model and a tightening of the nitrate-adjusted model in 1998 in areas with deeper mixing in the southern Weddell Sea. We propose that there are two reasons for the discrepancies in our model: the source waters are not as homogenous as the model assumes; and there are geographical and seasonal variations of CO_2 exchange with the atmosphere and the input of inorganic carbon and nitrate from below the mixed layer resulting in imbalances in the mixed layer concentration ratios.

Author Keywords: Southern Ocean; Weddell Sea; Carbon dioxide; Carbon cycle; Autumn; Interannual variability; Component analysis model

1. Introduction

Storing 93% of the non-geologically compartmentalized global carbon inventory, there is no doubt that the ocean is a major player in the global carbon budget and is important in regulating

the concentration of atmospheric carbon dioxide (CO_2). The most direct method to estimate the uptake of atmospheric carbon dioxide by the oceans is by determining the air–sea flux from measurements of the partial pressure of CO_2 ($p\text{CO}_2$), or the CO_2 fugacity ($f\text{CO}_2$), in the sea surface and the overlying atmosphere. The largest global database with oceanic $p\text{CO}_2$ data yields an estimate of CO_2 uptake by the oceans of 2.2 Pg C yr^{-1} in 1995 (Takahashi et al., 2002). A similar flux was determined for the early 1990s from carbon isotope data (Ciais et al., 1995). Keeling et al. (1996) arrived at 1.7 Pg C yr^{-1} for the same period from changes in atmospheric O_2 concentrations. Also several different modelling studies come to similar results (Sarmiento et al., 1992; Caldeira and Duffy, 2000; Le Quéré et al., 2000; Orr et al., 2001). Hence, almost all studies addressing the uptake of CO_2 by the oceans appear to converge to a value of about 2 Pg C yr^{-1} .

This convergence suggests more certainty to the issue of CO_2 uptake by the oceans than actually exists. Two aspects are to be considered here. Firstly, many models come to an estimate of about 2 Pg C yr^{-1} , but the details of the uptake are highly variable. Within the Ocean Carbon Model Intercomparison Project (OCMIP), 12 large ocean–atmosphere models all point to the Southern Ocean (south of $\sim 30^\circ\text{S}$) as the major sink region, but huge differences exist for the uptake in this region between these models. Orr et al. (2001) report that the differences are as large as 70%. Obviously, the regional processes for uptake are poorly understood. Secondly, interannual variation in the oceanic CO_2 uptake occurs (e.g. Winguth et al., 1994; Le Quéré et al., 2000). Studies based on atmospheric CO_2 data tend to estimate the interannual variability of oceanic CO_2 uptake as much higher (Conway et al., 1994; Francey et al., 1995) than those based on oceanic $p\text{CO}_2$ (Lee et al., 1998). Whilst monitoring studies have concentrated on the equatorial Pacific and highlighted this area as a significant player in promoting large interannual differences in carbon fluxes (Feely et al., 1999), the conclusion from models that the Southern Ocean is responsible for 30% of the variation (Le Quéré et al., 2000) is supported by little empirical data.

The Southern Ocean is a significant sink for atmospheric CO_2 . From $p\text{CO}_2$ data, Takahashi et al. (2002) come to an estimate of $0.47 \text{ Pg C yr}^{-1}$ for 1995, which is 21% of the global uptake for a surface area of only 10% (south of 50°S). For the year 1990 the estimate is only $0.31 \text{ Pg C yr}^{-1}$, but they impute the difference to differences in the observational database. This clearly shows that the Southern Ocean CO_2 uptake is subject to a large uncertainty. All other full Southern Ocean estimates derive from modelling studies. There appears to be an agreement between observational and modelling estimations. For the area south of 50°S , Sarmiento et al. (1992) come to $0.42 \text{ Pg C yr}^{-1}$ using an ocean circulation model, while Louanchi and Hoppema (2000) give $0.53 \text{ Pg C yr}^{-1}$ with a one-dimensional approach. Orr et al. (2001) report about four carbon cycle models that all have similar CO_2 uptake by the Southern Ocean as above (because different surface areas were considered, the figures are not exactly comparable). Also, in the Southern Ocean interannual variation is thought to be large. Conway et al. (1994) compute, using an inverse atmospheric model, an increase of CO_2 uptake from 0.5 to 1.5 Pg C yr^{-1} by the southern hemisphere for the early 1990s. Louanchi and Hoppema (2000) report interannual variability around the mean CO_2 uptake of about 25%. One of the causes of variability in the Southern Ocean is the Antarctic Circumpolar Wave (White and Peterson, 1996) in sea surface temperature, wind speed and sea-ice extent. Le Quéré et al. (2000) in a modelling study demonstrated that this feature has influence on the CO_2 uptake via the depth of the mixed layer and the extent of ice coverage. One of the few studies with in situ CO_2 time series data from the Southern Ocean reports large interannual variations in $f\text{CO}_2$ and CO_2 uptake (Louanchi et al (1999a) and Louanchi et al (2001)).

There is a lack of ground-truthing of CO_2 uptake of the Southern Ocean which stems from the seasonality of measurements. Moreover, measurements are also geographically constrained by

limited research campaigns. The data that are available appear to comply with the general picture of a large CO₂ sink in the Southern Ocean, because most show undersaturation of *p*CO₂ indicating CO₂ uptake, both in spring and summer due to biological drawdown (Poisson et al., 1993; Bellerby et al., 1995; Schneider and Morlang, 1995; Bakker et al., 1997; Bates et al., 1998) and even in winter (Takahashi et al., 1993; Hoppema et al., 1995; Stoll et al., 1999; Gibson and Trull, 1999; Louanchi et al., 2001). It should also be mentioned that occasionally CO₂ supersaturation has been reported in (early) summer (Inoue and Sugimura, 1988). Data that are based on time-series monitoring, seasonal cycles of CO₂ or budget studies, i.e. generally those studies that yield realistic annual air–sea fluxes, all find a net uptake of CO₂, for different regions of the Southern Ocean (Gibson and Trull, 1999; Metzl et al., 1999; Hoppema et al., 1999; Louanchi et al., 2001).

The *p*CO₂ in surface seawater depends on temperature, salinity, total CO₂ concentration and alkalinity; processes effectuating these determinants are warming/cooling, freshwater changes, biological activity/air–sea exchange and solid-carbonate chemistry, respectively, of which warming/cooling and biological activity are the most important (e.g. Takahashi et al., 1993). Whereas in the subtropical gyres *p*CO₂ (or *f*CO₂) can be entirely described by temperature and (minor) salinity changes (Weiss et al., 1982), this is not the case in the Southern Ocean where biological drawdown of CO₂ causes a strong seasonal signal (Karl et al., 1991; Takahashi et al., 1993; Bates et al., 1998; Louanchi et al., 1999a). Indeed neither Poisson et al. (1993) nor Metzl et al. (1999) found a large-scale correlation of *f*CO₂ and SST in the austral summer. Gibson and Trull (1999) could explain the *f*CO₂ dynamics in a coastal area in summer almost entirely through accounting for nitrate changes. In autumn and winter, remineralisation and mixing processes were dominant for the *f*CO₂ levels. Louanchi et al. (1999b) and Louanchi and Hoppema (2000) calculated a breakdown of the different processes that have impact on *f*CO₂ and showed that there are great seasonal and interannual variations of the percentile contributions of the different processes. They fail to accurately model the autumnal *f*CO₂ characteristics in the Weddell Gyre as successfully as in other regions of the Southern Ocean. Parameterisations based solely on SST and nitrate are unlikely to hold on an annual basis. Therefore, in order to obtain a greater understanding of the carbon fluxes we have determined the dominant mechanisms that control the surface *f*CO₂ characteristics in the Weddell Sea during the austral autumn when a breakdown of the seasonal pycnocline occurs. This has been performed by dissecting the *f*CO₂ signal into its component parts after Sabine and Key (1998). We assume that surface waters of the Weddell Sea originate from a common water mass below the thermocline with constant carbonate system, nutrient and hydrographic characteristics. Thus any deviations in the CO₂ system from this reference water must be due to modifications of the freshwater content, temperature and nutrient properties. Such component analysis can be used to validate models of carbon exchange in the Southern Ocean. Moreover, we use two datasets from the same transect for different years to explore the influence of interannual variability on carbon flux and its determinants.

2. Methods

The data used in this paper were collected during two expeditions aboard *FS Polarstern* to the Weddell Sea, in 1996 (Fahrback and Gerdes, 1997) and 1998 (Fahrback, 1999). Cruise ANT XIII/4 started from Capetown on 17th March 1996 and ended in Punta Arenas on 20th May 1996. Cruise ANT XV/4 started from Punta Arenas on 28th March 1998 and ended in Cape Town on 23rd May 1998. A map of the cruise tracks is given in Fig. 1. Distributions of *f*CO₂ data of cruise ANT XIII/4 have previously been described by Stoll et al. (1999) and Hoppema et al. (2000), in which also details about the measurements can be found. During both cruises the same equipment was used for measuring *f*CO₂.

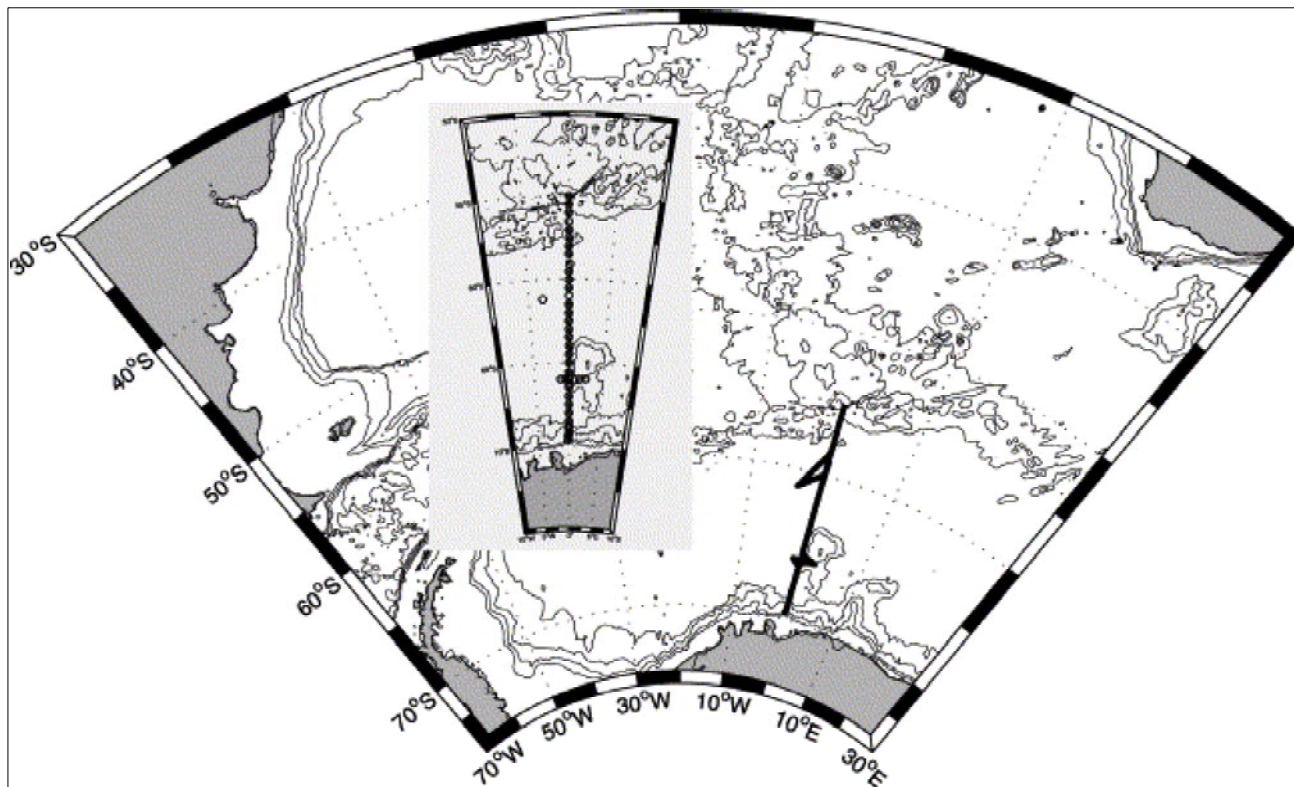


Fig. 1. The study area showing the Southern Ocean between South Africa and the Antarctic continent. The cruise tracks, relevant to this study, of expeditions ANT XIII/4 and ANT XV/4 are shown as the line in the main diagram. The inset shows the station positions where (x) represent stations sampled during ANT XIII/4 in 1996 and (o) represent ANT XV/4 in 1998.

Briefly, $f\text{CO}_2$ was measured underway in surface seawater and in the marine atmosphere with a fully automated sampling system, designed after Wanninkhof and Thoning (1993) including a Li-Cor (Model 6252) infrared analyser. Marine air was pumped continuously from the crow's nest, while seawater was drawn from the ship's continuous water supply. A continuous-flow type equilibrator was used, which is vented to marine air. Temperatures at the seawater inlet and in the equilibrator were recorded at each measurement. For the slight heating of the seawater during transport into the laboratory a correction was made according to the equations of Copin-Montegut (1988) and Copin-Montegut (1989). Obvious outliers and data points with too large a temperature difference (indicating blockage in the seawater supply) were deleted from the dataset. Sample air was dried before being measured in the infrared cell. During cruise ANT XIII/4 in 1996 the underway $f\text{CO}_2$ precision was estimated to be $1.2 \mu\text{atm}$ ($n=326$), which is considered an upper bound.

On board three reference gases were used for calibration (concentrations about 260, 340–360, 440 $\mu\text{mol mol}^{-1}$ CO_2 in air; different gases for the two cruises), which were measured approximately every hour during a duty cycle. These secondary reference gases were recalibrated in the home laboratory against three National Oceanic and Atmospheric Administration (NOAA) certified standard gas mixtures (accurate to $\pm 0.01 \mu\text{mol mol}^{-1}$).

Underway sea surface temperature (SST) and salinity were measured by the ship's thermosalinograph, which is mounted 8 m below the sea surface. On both cruises, water samples for the determination of a suite of properties were collected from the General Oceanics rosette sampler that was coupled to a conductivity temperature depth (CTD) instrument. Total CO_2 (TCO_2), i.e. the sum of all carbonate species, was determined with the coulometric method after Johnson et al. (1987) as slightly modified by Robinson and Williams (1992) and Stoll (1994), with the same equipment on both cruises. The precision during cruise ANT XIII/4 (1996) was $1.4 \pm 0.9 \mu\text{mol kg}^{-1}$ (the average plus standard deviation of 68 duplicate pairs sampled through the expedition). For cruise ANT XV/4 the precision was $1.5 \mu\text{mol kg}^{-1}$

(0.065%), which was obtained from 21 duplicate pairs, all samples being taken at one depth. Accuracy on both cruises was set by certified reference material (DOE, 1994). Standards were measured for each cell prepared for the coulometer and the cells were changed about once a day.

Nitrate concentrations were analysed by the standard photometric method on a Technicon TRAACS 800 rapid flow autoanalyser. Stock standards diluted in low-nutrient seawater were used for setting the accuracy. These primary stocks were prepared in the home laboratory by weighing. A reference standard, containing a mixture of nitrate, phosphate and silicate, was also measured at every run and used for statistical purposes and data correction. For cruise ANT XIII/4 (1996) the precision is estimated to be $0.21 \mu\text{mol kg}^{-1}$. For cruise ANT XV/4 (1998) the precision is $0.07 \mu\text{mol kg}^{-1}$ (0.19%) for nitrate+nitrite, as obtained from 21 duplicate pairs, all rosette bottles being fired at one depth. For further details, refer to Bakker (1999).

All model calculations were performed with the CO2SYS program (Lewis and Wallace, 1998) on the total hydrogen ion scale. Dissociation constants for the carbonic, phosphoric and silicic acids, bi-sulphate ion, hydrogen fluoride and water and the stoichiometric species concentration relationships used in the program were the same as those adopted in a similar study of the Pacific sector of the Southern Ocean by Sabine and Key (1998).

3. Results

Presentation and analysis of the cruise data are in two parts: a descriptive comparison of the years 1996 and 1998; and a predictive study of surface $f\text{CO}_2$ using property–property relationships and a more detailed breakdown of the relative contributions of the physical and biological pumps, including allowances for freshwater input from melt water. The transect in 1996 has previously been discussed by Hoppema et al. (2000); however, for completeness the two cruises will be discussed and compared.

3.1. Description of hydrography and $f\text{CO}_2$ in 1996 and 1998

Figs. 2a–c show the SST, salinity and $f\text{CO}_2$ for both 1996 and 1998. Across the Weddell Front (WF), marking the boundary between the Antarctic Circumpolar Current (ACC) and the Weddell Gyre, situated between 55°S and 56°S in both years, $f\text{CO}_2$ rises quickly from 345 to $365 \mu\text{atm}$, the area south of the WF becoming a source of CO_2 to the atmosphere. This feature is associated with a southward increase in salinity from 33.7 to 34.0. This must be a highly persistent feature because the distributions of $f\text{CO}_2$ and salinity are identical in both years. To the south of the WF, there is a decrease in SST until approximately 60.5°S ; the rate of cooling is similar in both years, although the surface waters are ca. 0.5°C warmer in 1996. In this region, the salinity is within 34.0–34.1 for both 1996 and 1998. There is nominal covariance between the SST and $f\text{CO}_2$ variations in 1996 as the latter falls from 365 to $350 \mu\text{atm}$ through this region. In 1998 the decrease is greater with values reaching $345 \mu\text{atm}$. Between 60.5°S and 64°S , SST is approximately constant at -0.5°C in 1996, whereas in 1998, it falls from -0.8°C to -1.3°C . Salinity remains constant at around 34.05 except in 1998, where there is a drop to 33.95 between 60.5°S and 61.5°S , with which there is no associated change in $f\text{CO}_2$. In fact, the 1998 $f\text{CO}_2$ lies between 340 and $350 \mu\text{atm}$ throughout this part of the section. In comparison, $f\text{CO}_2$ in 1996 is very erratic whilst falling from 350 to $330 \mu\text{atm}$. South of 64°S to the edge of the Antarctic Slope Front (ASF), SST in 1996 falls to -1.1°C , the coldest of the meridional transect. In 1998, SST falls to -1.7°C at 67.5°S and then rises to -1.3°C near the front. There is a lot of variation in $f\text{CO}_2$ throughout this region during both years, which may be associated with the vicinity of the topographic high Maud Rise. Similarly, the salinity during both years is very changeable. In 1996, surface salinities modulate strongly with a peak of 34.2

at 66.3°S (above the crest of Maud Rise) and a strong increase from 33.96 to 34.21 between 67.2°S and the southern end of the transect. Surface salinity changes are more prominent in 1998 in this area. At 65°S there is a salinity maximum of 34.34 and a decline to 34.2 at 66.5°S. As in 1996, there is a strong increase in salinity towards the ASF with salinity increasing to 34.32 between 66.5°S and the front. For both years, there are common features between the salinity and $f\text{CO}_2$ patterns with higher salinities being coupled with high $f\text{CO}_2$ levels. In 1996, $f\text{CO}_2$ is generally between 330 and 345 μatm . There is a low of 324 μatm associated with a salinity minimum at 67.3°S. In 1998, $f\text{CO}_2$ is oversaturated with respect to the atmosphere throughout this region. From the peak of 390 μatm at 65°S, levels fall to 360 μatm at 66.5°S before rising again to 379 μatm at the ASF.

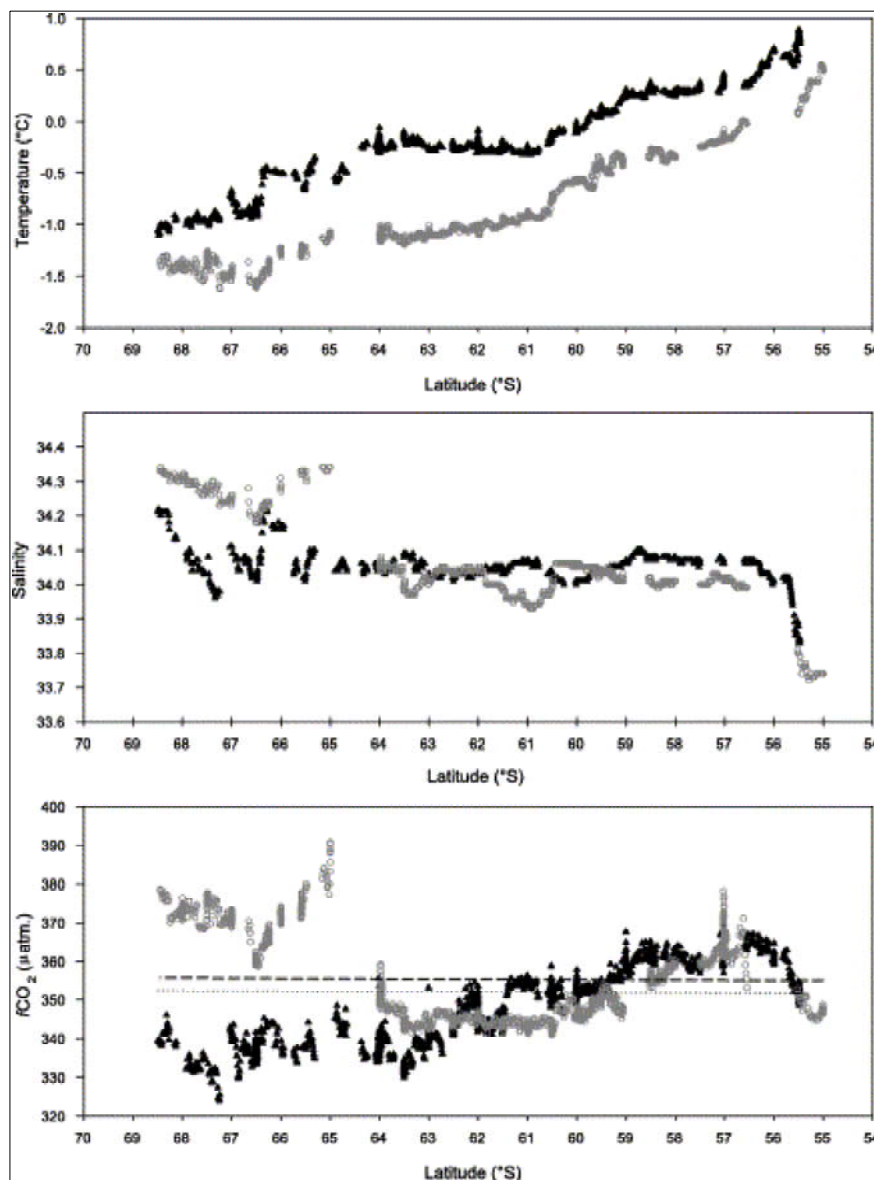


Fig. 2. Surface plots of temperature, salinity and $f\text{CO}_2$ along the prime meridian for 1996 (closed triangles) and 1998 (open circles).

3.2. To what extent can we model and predict the along-transect variability?

Surface water carbon chemistry is strongly controlled by temperature whether directly through the solubility pump or by influencing biological production and gas exchange rates. Relationships between SST and $f\text{CO}_2$ have been determined for many oceanic regimes and used to extrapolate on ocean basin scales ascribing seasonal and annual air–sea carbon fluxes to areas where no, or limited, CO_2 measurements have been acquired. Another approach has

been to assume that the surface waters of a limited region are modifications of a single source water type and that the $f\text{CO}_2$ of the surface waters can be estimated from the deviations in temperature, salt and nutrient properties from the source waters. In this study we have adapted both methods to assess the controlling mechanisms of surface $f\text{CO}_2$.

3.2.1. $f\text{CO}_2$ /SST relationships

The waters south of 64°S have earlier been described as having unusual $f\text{CO}_2$ properties for the region which are partly due to localised topographical upwelling. In this part of the study, where we aim to determine general, basin-wide characteristics, it is preferable to ignore the data from this region when we try and parameterise $f\text{CO}_2$ in relationship to SST. Likewise, we have chosen to ignore waters north of the southern extent of the WF delineated as 56°S in this study because of potential differences in specific alkalinities resulting from productivity of calcifying organisms.

In contrast to work in the tropical Pacific (Boutin et al., 1999) and in the North Atlantic (Olsen et al., 2003), the normalisation of $f\text{CO}_2$ to a constant temperature, or its relationship with temperature anomalies, gave very poor regressions with SST and so were not pursued. Instead $f\text{CO}_2$ was assessed in relationship to in situ temperature throughout the study. The $f\text{CO}_2$ /SST relationships for the two years are shown in Fig. 3.

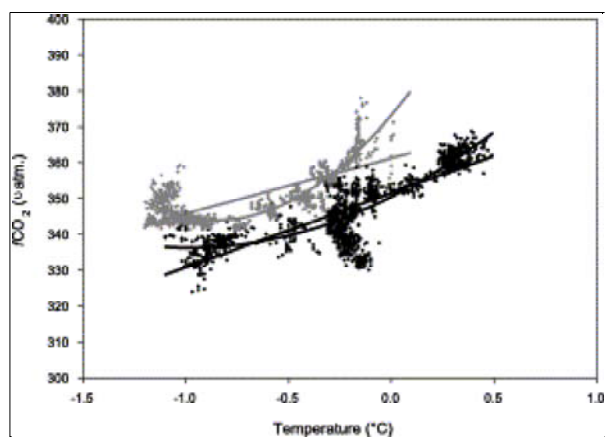


Fig. 3. Relationships between SST and $f\text{CO}_2$ for 1996 (.) and 1998 (□). $f\text{CO}_2$ is normalised to one atmosphere. The data sets are limited for both years to regions south of 56°S and for 1998 to the region north of 64°S . The regression lines are for 1996: linear, $f\text{CO}_2=362.29+18.246.SST$, $r^2=0.68$; quadratic, $f\text{CO}_2=374.64+71.918.SST+41.018.SST^2$, $r^2=0.88$; and for 1998: linear, $f\text{CO}_2=351.44+20.528.SST$, $r^2=0.64$; quadratic, $f\text{CO}_2=350.4+26.184.SST+11.313.SST^2$, $r^2=0.88$.

There is at present no regional Southern Ocean $f\text{CO}_2$ /SST modelling tool because of a scarcity of measurements on a seasonal and interannual basis. Whilst the two independent slopes for 1996 and 1998 are very similar they cannot be used individually to predict $f\text{CO}_2$ on an interannual basis because of an offset in the intercepts. Allowances for interannual temperature differences only increase the departure between the two intercepts as temperatures along the 1996 transect were always higher at any given latitude compared to 1998. The fits to the data are improved with quadratic relationships as has been shown by Olsen et al. (2003) to also apply in the North Atlantic. However, in that case it is not possible to relate the annual relationships using the temperature offsets and thus the use of the individual annual regressions is restricted to only seasonal extrapolation and not interannual interpretations.

Fig. 4 shows measured $f\text{CO}_2$ compared with $f\text{CO}_2$ calculated from SST and fits to the data from Fig. 3. Not surprisingly, with such high correlation coefficients, there is generally very good semblance between the intra-annual comparisons. There is no significant improvement to

the fit of the predicted to measured $f\text{CO}_2$ distributions when the quadratic relationships are used for both years and the offsets seen south of 64°S confirm that the relationships are not applicable for this region in 1998.

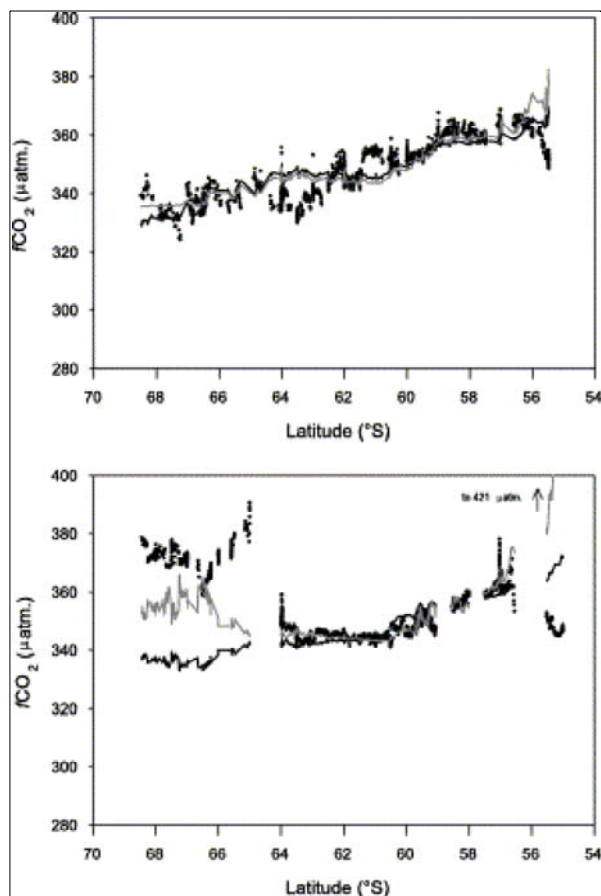


Fig. 4. Comparison of measured and modelled $f\text{CO}_2$ for 1996 (top) and 1998 (bottom) according to the fits from the relationships reported in Fig. 3. Measured $f\text{CO}_2$ is shown as \blacklozenge , and computed is shown for the linear (—) and quadratic (---) relationships.

3.2.2. Single end member approximation

As proposed by Sabine and Key (1998), assuming that an area of water is considered to be of a common water type with a common source end member, then variations in the relative strengths of the biological and physical carbon pumps throughout a region may be determined from deviations in T - S properties, and nutrient and CO_2 system chemistry from measurements at any one station within that region. For the Weddell Gyre we may well, as a first approximation, assume that such conditions apply because of the doming of isopycnals and the resultant upward transport of the Warm Deep Water (WDW).

The processes that control the CO_2 system in seawater are heat flux, water flux, organic production, carbonate production, and gas exchange. In the Weddell Gyre, calcification is minimal just as in the remaining Antarctic Ocean (Honjo, 1991), which is also evidenced by the conservativeness of alkalinity (Poisson and Chen, 1987; Anderson et al., 1991). Differences in $f\text{CO}_2$ between two areas within the Weddell Gyre should therefore be accounted for by variations in the temperature, salinity and nutrient characteristics only. The unknowns would be the gas exchange with the atmosphere and the advection of waters from the Antarctic Circumpolar Current and the Coastal Current.

For each year, a reference surface water sample from a CTD rosette was selected to be

representative of Weddell surface water. These stations were chosen because of their very similar CO₂ system properties; they are assumed to represent all surface waters within the Weddell Gyre. Importantly, these stations contained the highest nitrate concentrations and thus were assumed to be most representative of recent upwelled Weddell Sea source waters. Table 1 shows the CO₂ system, nutrient and hydrographic values for the chosen standard stations for each year. We shall model the *f*CO₂ values of the surface transect waters after successive adjustments of the reference waters for along transect variations in temperature, salinity and nitrate. We use underway SST and salinity, and the values of nitrate, TCO₂ and total alkalinity are interpolations between along-transect stations.

Table 1. Initial conditions of baseline stations used in the model study

Year	1996	1998
Station #	40	112
Latitude (°S)	58.003	58.005
Longitude (°E)	0.003	0.003
Salinity (S°)	34.05	34.03
Temperature (°C)	0.14	-0.48
TCO ₂ µ	2183.3	2183.2
<i>f</i> CO ₂ µ	360.0	359.0
TA°	2313.3	2308.1
SiO ₄ µ	66.8	58.6
NO ₃ µ	27.2	25.9
PO ₄ µ	1.8	1.7

To compensate for differences in temperature between the underway measurements and the temperature of the reference station, a heat flux correction was applied to each sample according to the relationship such that

$$fCO_{2(T)} = f(T, S_o, TA_o, TCO_{2o}), \quad (1)$$

where *T* is the underway temperature, *S* the salinity, TA the total alkalinity and the suffix ‘o’ represents the reference station value. The latter parts of the model use the measured station nutrient values.

Modifications in the water budget, through balances between ice melt and formation, and precipitation and evaporation, were made with a water flux correction according to the salinity difference

$$fCO_{2(T,S)} = f(T, S, TA_s, TCO_{2s}), \quad (2)$$

where $TA_s = TA_o \times (S/S_o)$ and $TCO_{2s} = TCO_{2o} \times (S/S_o)$.

Changes in the nitrate fields were assumed to be representative of the biological modifications with respect to the reference waters and thus an organic flux correction was applied

$$fCO_{2(T,S,N)} = f(T, S, TA_{s,n}, TCO_{2s,n}), \quad (3)$$

where $TA_{s,n} = TA_s + (N_o - N)$ and $TCO_{2s,n} = TCO_{2s} - R(N_o - N)$, and *N* is the nitrate concentration. The carbon/nitrogen nutrient ratio (*R*) was chosen to be 106:16, i.e. Redfieldian, as this appears to prevail in the surface waters of the Weddell Sea (Hoppema and Goeyens, 1999).

The measured and modelled *f*CO₂ values are shown for 1996 and 1998 in Fig. 5. In 1996 it can be seen that the *f*CO_{2(T)} models the measured *f*CO₂ very closely with the largest difference found at about 63.5°S corresponding to an approximate maximal overestimation of 20 µatm. The mean difference between the two parameters is 0±6 µatm. Water flux corrections do not

significantly improve the fit although it should be noted that generally $f\text{CO}_2(T,S)$ is lower than $f\text{CO}_2(T)$ for the majority of the transect. In contrast, significant differences are found between the measured $f\text{CO}_2$ and that predicted by $f\text{CO}_2(T,S,N)$. There is compliance between 57°S and 59°S, around the reference station, but the difference increases rapidly to either side with underestimations of up to 40 μatm to the north and 60 μatm to the south.

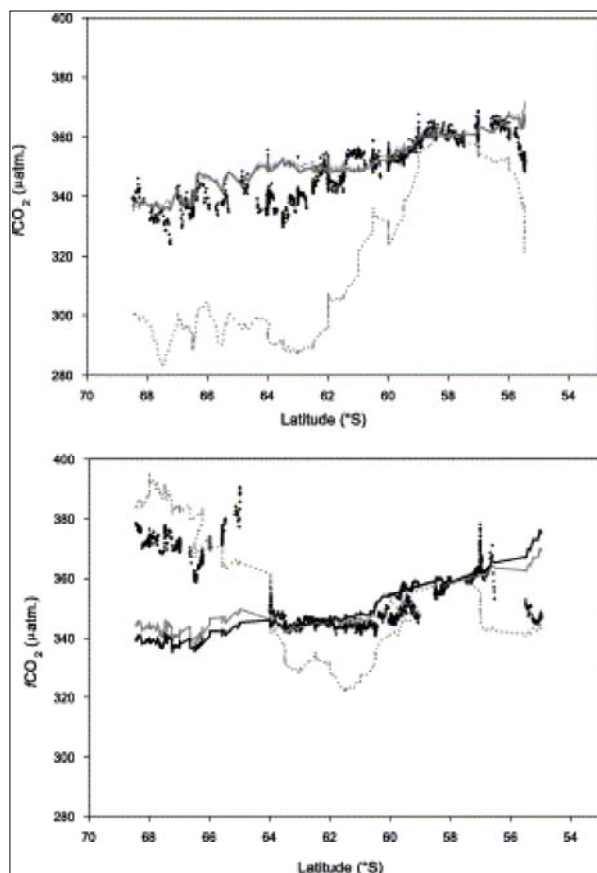


Fig. 5. Comparison of measured and modelled $f\text{CO}_2$ for 1996 (top) and 1998 (bottom). The model assumes that the surface water along the transect is a modification of water upwelled at 58°S and the three lines represent modifications due to: (1) thermal exchange (—); (2) thermal and water exchange (---); and (3) thermal and water exchange with biological uptake or regeneration (·····). The underway measurements are shown by (◆).

In 1998, again the model of $f\text{CO}_2(T)$ reproduces measured $f\text{CO}_2$ between 57.5°S and 64°S and there is a nominal correction with $f\text{CO}_2(T,S)$. Large underestimations of $f\text{CO}_2$ are shown for the region south of 64°S. The incorporation of nitrate into the model produces a smaller offset than for the 1996 run and, although overestimating $f\text{CO}_2$, improves the fit of the model south of 64°S.

3.2.3. Is the Weddell Sea less homogeneous than we believed?

It is apparent, particularly in the region south of 66°S in 1998, that there are some structural similarities between the measured $f\text{CO}_2$ and $f\text{CO}_2(T,S,N)$. This suggests that there may be a biological imprint, or more likely a localised effect of mixed layer deepening, on the measured $f\text{CO}_2$ and that the use of a single, basin-wide end member does not hold for the region. It should also be realised that the eastward (in the north) and westward (in the south) gyre water flow which crosses the transect could have different surface water properties, including $f\text{CO}_2$ and nutrients. It may be that the surface waters of the Weddell Sea can be more closely predicted if more localised properties are used as end members for a tighter, regionally based

study. Therefore, from the temperature plots in Fig. 2, we have identified three regions separated by temperature features or fronts: 56–60.5°S; 60.5–64°S; and south of 64°S. The procedure outlined in Section 3.2.2. was repeated with CO₂ system, hydrographic and nitrate properties pertaining to the surface water at the centre of these regions. There are no significant improvements in the prediction of $f\text{CO}_2$ from temperature alone or from temperature and salinity (Fig. 6). However, the offset seen in Fig. 5 with the inclusion of the biological effect on $f\text{CO}_2$ is removed and the fit of $f\text{CO}_2(T,S,N)$ is excellent and even applies to the upwelling region identified south of 64°S.

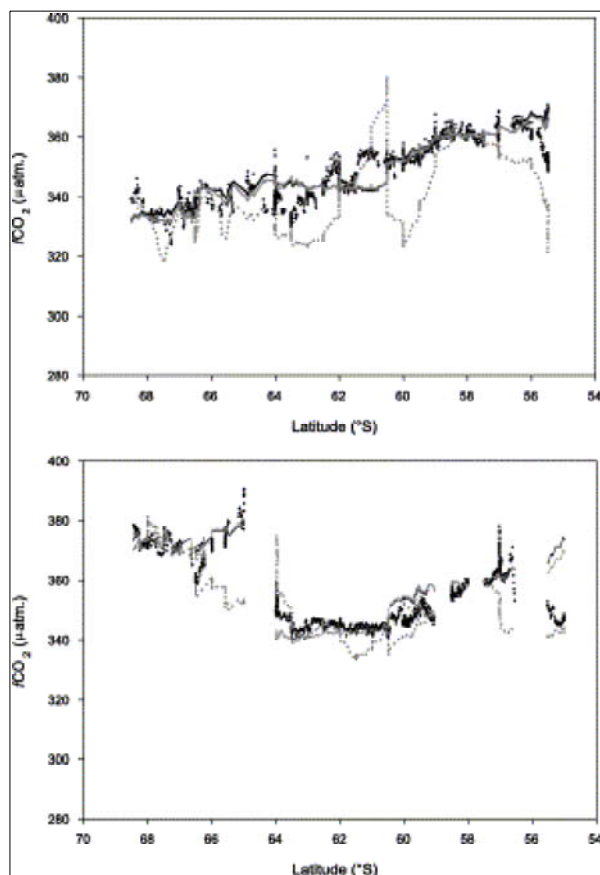


Fig. 6. Comparison of measured and modelled $f\text{CO}_2$ for 1996 (top) and 1998 (bottom). The transect has been divided into three sections; their boundaries approximated from temperature fronts identified in Fig. 1: 55–60.5°S; 60.5–64°S; and 64°S to the southern extent of the transect. The model assumes that the surface waters within the individual sections are modifications of water upwelled at 56°S, 62°S and 66°S and the three lines represent

modifications due to: (1) thermal exchange (—); (2) thermal and water exchange (---); and (3)

thermal and water exchange with biological uptake or regeneration (· · ·). The underway measurements are shown by (◆).

4. Discussion

This study has extended the data-set of surface $f\text{CO}_2$ measurements in the Southern Ocean with the addition of measurements made during the austral autumn of 1998. North of 64°S there is structural concordance between the two yearly $f\text{CO}_2$ distributions with the northern rim of the Weddell Gyre a source of carbon to the atmosphere whilst the centre is a sink. The large oversaturation of $f\text{CO}_2$ in 1998, south of 64°S, is the first documentation of significant ocean to atmosphere carbon flux in the southern Weddell Gyre. All other studies have shown the region to be a sink (Hoppema et al., 2000) even during times of ice formation and associated convective mixing (Stoll et al., 1999) due to the intense cooling in the region.

This study has shown that along the prime meridian there is a good correlation between water temperature and $f\text{CO}_2$. The linear $f\text{CO}_2$ –SST relationships have a slope equivalent to $1.7\%^\circ\text{C}^{-1}$ in 1996 and $1.4\%^\circ\text{C}^{-1}$ in 1998 which is very different from the $-0.7\%^\circ\text{C}^{-1}$ and $-2\%^\circ\text{C}^{-1}$ reported by Lee et al. (1998) for the periods January–April and May–August in the Southern Ocean. However, their analysis was averaged to water at 52°S (which is within the ACC) and the difference could be due to regional variations in source data and the subjective nature by which monthly $f\text{CO}_2$ –SST values were ascribed to the periods under investigation. Appraisal of the $f\text{CO}_2$ –SST relationship for March–May in the Southern Ocean in Fig. 2 of Lee et al. (1998) suggests that the $f\text{CO}_2$ –SST slope would be positive. Poisson et al. (1993) found no distinguishable relationship between $f\text{CO}_2$ and SST in the Indian sector of the Southern Ocean, whereas Murphy et al. (1991) documented variable correlations between $p\text{CO}_2$ and SST in the South Pacific north of 60°S . At 110°W they found a good correlation, albeit with a lower slope than this study, but at 170°W the relationship was weaker. They ascribed the latter to biological activity.

In the component analysis model, except for regions to the south in 1998, the Weddell Sea surface $f\text{CO}_2$ has been shown to be very closely modelled by temperature forcing on the CO_2 system, with a nominal contribution from salinity, from measurements of the inorganic carbon system at standard stations along the prime meridian. The fit of the model shows that it could have been run using any station along the transect and $f\text{CO}_2$ would have been predicted correctly to within $10\ \mu\text{atm}$ south of the WF and north of 64°S during 1998.

The breakdown of mechanistic controls on the surface $f\text{CO}_2$ has shown that almost all the variation can be accounted for by temperature and salinity. In contrast to the findings of Sabine and Key (1998), the component model does not fit the empirical data if nutrient consumption is included and the underestimation is greater in 1996 than 1998. Sabine and Key (1998) studied waters during the summer when biological uptake may have been optimum and nitrate concentrations would have been indicative of recent or ongoing productivity. Louanchi et al. (1999b) compared the results of their model to the 1996 data resulting in an underestimation of the data by an average of $37.5\ \mu\text{atm}$, which is comparable to the difference between measured $f\text{CO}_2$ and $f\text{CO}_2(T,S,N)$ in this study.

Both surveys in this study were performed in late summer/autumn and the surface waters still carry the signature of biological uptake of nitrate. The 1998 study was one to four weeks later in the year (depending on latitude), with correspondingly higher nitrate concentrations due to increased nutrient regeneration and mixing from below (Figs. 7c and f). Such low nitrate concentrations in the Weddell Gyre suggests that the implication by Hoppema et al. (2000) that the Weddell Gyre may be supersaturated prior to the onset of autumn cooling, because of biological regeneration of TCO_2 may have to be revised and that undersaturation may continue through from the productive summer season.

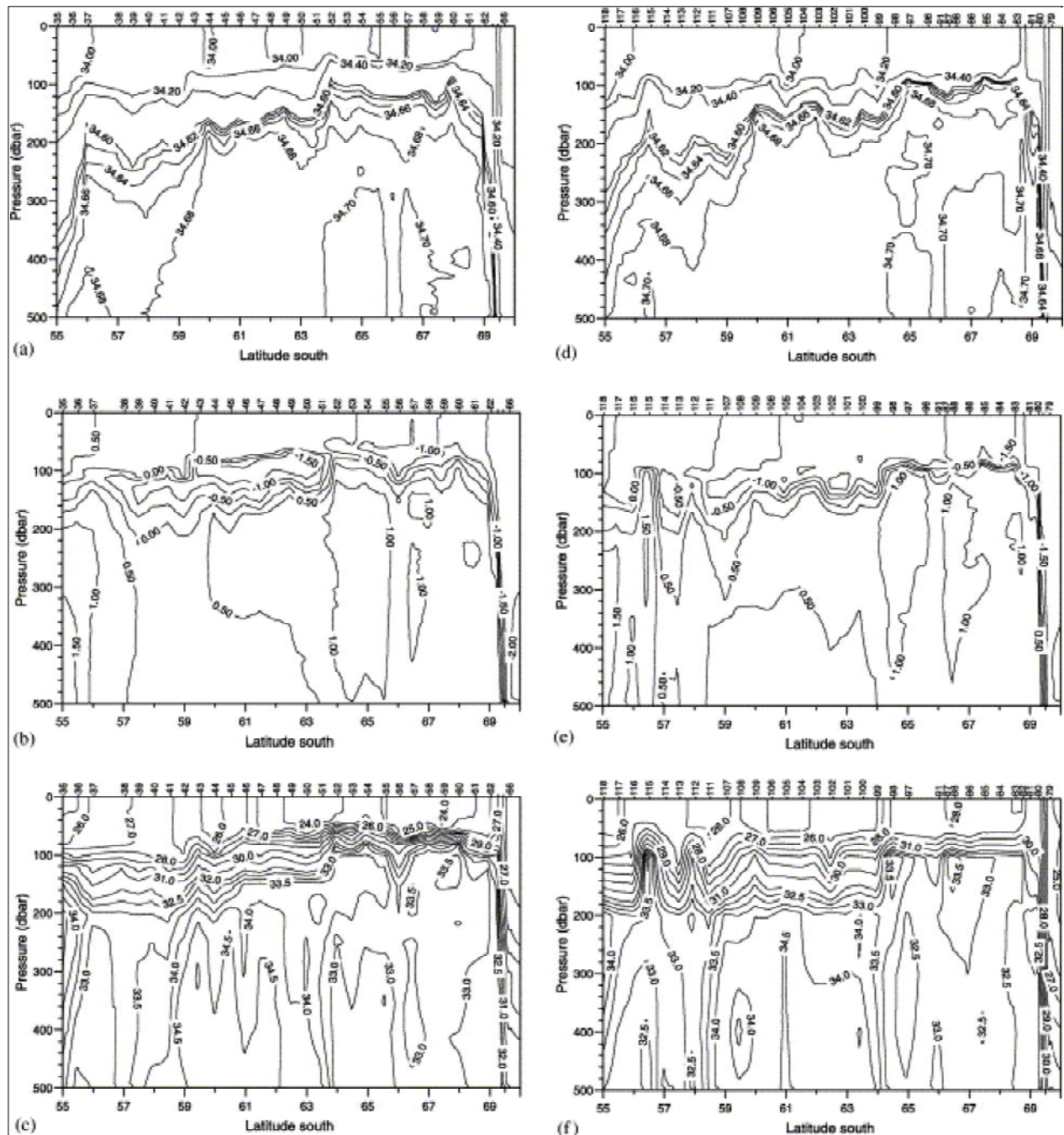


Fig. 7. Vertical profiles of salinity (top), potential temperature in $^{\circ}\text{C}$ (middle) and nitrate in $\mu\text{mol kg}^{-1}$ (bottom) for 1996 (a–c) and 1998 (d–f). The station numbers are indicated on the upper x-axis.

One explanation for the difference between measured $f\text{CO}_2$ (and $f\text{CO}_2(T)$) and $f\text{CO}_2(T,S,N)$ is that the whole region has undergone gas exchange as dictated by (i.e. its upper limit is bounded by the constraints of) the solubility pump. Sabine and Key (1998) have shown that the wind speeds in the Southern Ocean, with corresponding mixed layer depths, are sufficient to reconcile differences between $f\text{CO}_2$ and $f\text{CO}_2(T,S,N)$.

The alternative component analysis (Section 3.2.3) has shown that the surface waters of the Weddell Sea are not as homogeneous as our initial assumption suggests, at least in autumn. Whilst upwelled waters have a relatively homogeneous source water composition, waters to the north are supplied from the Central Intermediate Water (Hoppema et al., 2002) with high TCO_2 and nitrate, whilst to the south the source is the Warm Deep Water with lower concentrations. Many processes act on the water during its circulation around the Weddell Sea. There is mixing and entrainment of waters from the surface Antarctic Circumpolar Current and

from the Coastal Current (Whitworth and Nowlin, 1987; Fahrbach et al., 1992). Whilst the Redfield ratio may hold for basin-wide relationships it may have local variations due to the dominance of certain phytoplankton species (e.g. de Baar et al., 1997; Semeneh et al., 1998; Arrigo et al., 1999). Thus, the better fit of the model to the data in Fig. 6 may support the need for more detailed regional characterisation of the mechanistic controls on the carbonate system in the Weddell Sea. This is certainly true south of 64°S, where Maud Rise is thought to play an important role in modifying the surface water composition. This modification can be localised to the southern Weddell Gyre or have a wider effect following major polynya events such as witnessed in the years 1974–1976 (Holland, 2002). As documented by Poisson et al. (1993) in the Indian Ocean sector of the Southern Ocean, topographical forcing has a significant impact on surface CO₂ signature.

As can be deduced from the vertical sections (Fig. 7), the extent of upwelling/entrainment of deep water plays an important role in the observed regional and interannual differences of surface layer $f\text{CO}_2$. Near the northern rim the mixed-layer depths and subsurface vertical gradients are similar in both years (Fig. 7). Note that at the reference stations at 58°S, the property values are quite similar indeed (Table 1). The mixed layers are relatively deep, indicating that water from the temperature-minimum layer has been incorporated. To the south, there are remarkable differences between the years. In 1998, the mixed layer is significantly deeper than in 1996. Moreover, the subsurface vertical gradients are much steeper in 1998 than in 1996. This implies that in 1998 the contact between the surface layer and the deep water has been more intense. Because of this, the 1998 surface layer has a much higher salinity and $f\text{CO}_2$ (Fig. 2). In contrast, in 1996 the surface layer has properties which are not (yet) greatly influenced by the deep water. It should be added that the vertical gradients are generally steeper in the south than in the north (Fig. 7). This results in a different impact of the deep waters on these subregions of the Weddell Gyre.

5. Conclusions

The surface waters of the Weddell Sea have complex CO₂-system characteristics with regional and interannual variability. In the austral autumn the Weddell Sea is generally a sink for CO₂ from the atmosphere. However, this study has also shown significant oversaturation of CO₂ in the southern Weddell Sea, which is caused by the breaching of isopycnals at the surface bringing more saline waters with high $f\text{CO}_2$ to the surface.

The annual surface $f\text{CO}_2$ signatures can be estimated satisfactorily from empirical $f\text{CO}_2$ relationships with SST. However, it is not possible to develop interannually consistent relationships. This study has highlighted that the paucity of data from the region is still too great to adopt broad reaching parameter–parameter relationships regarding $f\text{CO}_2$. The relationships from this study contrast significantly from the seasonal relationships adopted for the Antarctic by Lee et al. (1998). We must conclude that the spatial scale of variation in Antarctic waters is too small for it to be included in such large-scale estimates.

The dominant controlling mechanisms on surface $f\text{CO}_2$ have been investigated in this study. The $f\text{CO}_2$ distributions are a complex interplay between the solubility pump and CO₂ exchange with the atmosphere. Biological activity, assumed from nitrate variations, is seen to have a local effect, but on the whole, $f\text{CO}_2$ can be predicted from temperature variations and an explicit understanding of the CO₂ system at any one station along the prime meridian. Indeed, when nitrate utilisation is accounted for, there is a large offset between measured and modelled $f\text{CO}_2$, as has been reported by other models of the area. The reason for the offset is a lack of understanding of the balance between gas exchange and mixed-layer deepening at this time of the year and an inappropriate use of nitrate, and its proxies, for calculations of $f\text{CO}_2$. The Weddell Gyre is horizontally less homogeneous than presumed. Spatial and temporal

variability of upwelling odd sub-surface water plays a large role in this. If the spatial scale is reduced, the component analysis model $f\text{CO}_2$ prediction improves significantly, including accounting for biological activity from nitrate variations. In order for models to reciprocate the empirical data in the Weddell Sea, more seasonally representative studies are required enabling the evolution of the mechanistic controls on surface CO_2 to be understood (i.e. Sweeney et al., 2000; Ishii et al., 2002).

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