Biological versus physical processes as drivers of large oscillations of the air–sea CO₂ flux in the Antarctic marginal ice zone during summer

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Abstract

The fugacity of CO₂ and abundance of chlorophyll a (Chl a) were determined in two long transects from the Polar Front to the Antarctic Continent in austral summer, December 1995–January 1996. Large undersaturations of CO₂ in the surface water were observed coinciding with high Chl a content. In the major hydrographic regions the mean air–sea fluxes were found to range from −3 to +7 mmol m⁻² d⁻¹ making these regions act as a sink as well as a source for CO₂. In the total 40-d period, the summation of the several strong source and sink regions revealed an overall modest net source of 0.3 mmol m⁻² d⁻¹, this based on the Wanninkhof (J. Geophys. Res. 97 (1992) 7373) quadratic relationship at in situ windspeed. A simple budget approach was used to quantify the role of phytoplankton blooms in the inorganic carbonate system of the Antarctic seas in a time frame spanning several weeks. The major controlling physical factors such as air–sea flux, Ekman pumping and upwelling are included. Net community production varies between −9 and +7 mmol m⁻² d⁻¹, because of the large oscillations in the dominance of autotrophic (CO₂ fixation) versus heterotrophic (CO₂ respiration) activity. Here the mixed layer depth is the major controlling factor. When integrated over time the gross influx and efflux of CO₂ from air to sea is large, but the net residual air/sea exchange is a modest efflux from sea to atmosphere.

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Keywords: Antarctic front; CO₂ system; Total inorganic carbon; CO₂ partial pressure

1. Introduction

The strong increase in atmospheric concentrations of carbon dioxide (Keeling and Whorf, 1994) has generated considerable interest in the global carbon cycle (Sarmiento, 1993; Tans et al., 1990; Sarmiento et al., 1992). The oceans are thought to have taken up $\sim 1.9 \pm 0.6$ Pg C a⁻¹ from
anthropogenic sources (IPCC, 2001) during the 1980s and some high latitude areas exhibit the largest uptake rates. Later work reported a slightly lower number of $\sim 1.7$ Pg Ca$^{-1}$ (see, e.g. Lee et al., 1998; Joos et al., 1999; Le Quéré et al., 2000) but is currently under debate (Thomas et al., 2001). The Southern Ocean is such a major high latitude area and plays a crucial role in the global carbon budget both for gross (natural and anthropogenic) as well as net (anthropogenic only) exchanges of CO$_2$ with the atmosphere (Hoppema et al., 1999; Caldeira and Duffy, 2000). In this area the upwelling of deep waters rich in dissolved CO$_2$ and major nutrients tends to cause overall CO$_2$ outgassing. However, the drawdown of CO$_2$ by phytoplankton blooms offsets this outgassing, and the overall Southern Ocean may well be a gross sink rather than a source of atmospheric CO$_2$ (Louanchi et al., 1999). In addition the formation of Antarctic intermediate water (AAIW) and Antarctic bottom water (AABW) transfers dissolved CO$_2$ into the deep ocean (Anderson and Jones, 1991). Similarly there is significant net uptake of anthropogenic CO$_2$ which eventually appears to be transported into other deep ocean basins (Caldeira and Duffy, 2000; Thomas and England, 2002).

A compilation of surface water partial pressure of CO$_2$ ($p_{CO_2}$) data by Takahashi et al. (1993, 1997) suggested that a temperature component is largely responsible for the observed $p_{CO_2}$ distribution. Recent work in Antarctic waters confirmed the effect of temperature, but plankton blooms were shown to be more important (Bakker et al., 1997; Hoppema et al., 1995). These blooms are probably regulated by the availability of light and iron (de Baar et al., 1995), since major nutrients are in abundant supply by the upwelling in this so-called high nutrient–low chlorophyll area (de Baar and Boyd, 2000). In this paper we demonstrate the impact of marginal ice zone (MIZ) phytoplankton blooms on the uptake of CO$_2$ from the atmosphere. High-resolution online surface water measurements of the carbonate system in four longitudinal transects are combined with distributions of Chla and hydrographic variables in our analysis. Finally, an attempt is made to quantify the roles of biology and physics with a simplified mass balance model.

2. Sampling and methods

Data are presented from cruise ANTXIII/2 aboard R.V. “Polarstern” from 4 December 1995 to 24 January 1996 (austral summer; Bathmann et al., 1997a). Meteorological and underway data were obtained from the ship’s data-acquisition system. Two long transects (Fig. 1) were made, each consisting of two legs (1A and 1B, 2A and 2B; see Table 1) between (but not crossing) the Polar Front and Antarctic Continent. During these transects continuous underway measurements were made of total carbon dioxide content (TCO$_2$), the fugacity of CO$_2$ and the major nutrients as well as temperature and salinity.

The sum of all inorganic carbonate species in seawater, collectively known as TCO$_2$, was determined by a high precision Coulometric titration (Stoll et al., 1993). Although the method is commonly used for analysis of discrete water samples (Johnson et al., 1987) underway measurements can also be performed (Robinson and Williams, 1992), and it is the latter that are reported here. Seawater was pumped from 8 m depth and fed through the automated extraction line. An accurate volume of subsample was taken once every 5 min and acidified with phosphoric acid (8.5%) and stripped with high purity nitrogen gas. The carrier gas together with the CO$_2$ gas was led through a cell containing a solution of ethanolamine and an indicator. The solution was electrochemically backtitrated to its original colour, and the total amount of Coulombs used was employed to calculate the moles of CO$_2$ titrated. Standardization was obtained by regular measurements of a certified TCO$_2$ standard (DOE, 1994; pooled STD $\pm 2.1 \mu$mol kg$^{-1}$) made available by Dr. A. Dickson (SCO, USA). The data were post-processed and screened for obvious outliers, resulting in a dataset totaling over 3200 data-points.

The fugacity of CO$_2$ in air and in seawater was measured with a home-built extraction unit/analyzer (designed after Wanninkhof and
Thoning, 1993) including a Li-Cor (LI-COR, Model 6252) infrared analyzer. Marine air was pumped from the crow’s nest into the ship laboratory through Dekabon tubing, which was flushed continuously until a subsample was taken. The same seawater supply as used for the TCO$_2$ determination was used for measurements of fCO$_2$ in seawater with a modified equilibrator after the design of Watson (see also Bakker et al., 1997; their Fig. 3). At a rate of approximately 40–60 cm$^3$ s$^{-1}$ the seawater is sprayed through a showerhead into the equilibration chamber. The system has a response time of less than 2 min. A vent connected to marine air supply maintained atmospheric pressure, thereby avoiding contamination of the headspace gas. The temperature of the seawater in the equilibrator and in the outflow was continuously logged with calibrated Pt-100 resistance thermometers and later coupled with the

**Table 1**

<table>
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<th>Leg</th>
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<th>End date</th>
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<td>15-12-1995</td>
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<tr>
<td></td>
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<td>2</td>
<td>2A</td>
<td>06-01-1996</td>
<td>11-01-1996</td>
</tr>
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</table>

Fig. 1. Map showing the study area. Approximate locations of the Polar Front and the WG circulation are shown, transect 1 (legs 1A and 1B) and transect 2 (legs 2A and 2B) by the solid lines. The three different hydrographic regions have been indicated (sACC = southern Antarctic Circumpolar Current).
Both seawater and air samples were dried with Aquasorb (Merck) before being passed through the IR analyzer. Because CO$_2$ in air is a non-ideal gas mixture (Weiss, 1974) we use the appropriate property fugacity of CO$_2$ ($f_{CO_2}$ in μatm) rather than the partial pressure of CO$_2$ ($p_{CO_2}$ in ppm), although the difference is rather trivial, being on the order of 0.7%.

The $f_{CO_2}$ system was calibrated with reference gases, which in turn had been calibrated versus National Oceanic and Atmospheric Administration (NOAA) certified standard gas mixtures (accurate to 0.01 ppm), before and after the cruise. For all reference gases the precision during the calibration was better than 0.07 ppm. No significant difference could be observed between the pre-cruise and post-cruise calibrations. A typical analysis cycle (which takes less than 1 h) consists of a calibration with three reference gases, air, seawater ($5^\circC$), air, seawater ($5^\circC$) and a calibration. For each sample 10 readings were taken and averaged during post-processing. Final data were obtained by interpolation between two consecutive calibration cycles.

Because of the transport of water from the ship inlet to the equilibrator, a slight warming occurred, in extreme cases up to 0.7 K but generally less than 0.1 K. Datapoints that were obvious outliers or had too large a temperature difference, indicating a blockage in the water supply, were deleted from the dataset. The remaining data were corrected for the temperature difference following the polynomial given by Copin-Montégut (1989). For the flux computations the shipboard meteorological data (England, 1997) and the assumption of 100% atmospheric moisture content at the sea surface were used. The flux ($F$ in mmol m$^{-2}$ d$^{-1}$) across the air–sea interface is given by the equation

$$F = k \Delta f_{CO_2}$$

in which $f_{CO_2}$ is the fugacity of CO$_2$, $k$ is the transfer coefficient (Wanninkhof, 1992), and $\Delta f_{CO_2}$ is the gradient between air and the sea surface. The transfer coefficient $k$ is parameterized as

$$k = [2.5(0.5246 + 1.6256 \times 10^{-2} T \\
+ 4.9946 \times 10^{-4} T^2) + 0.31u^2](Sc/660)^{-1/2}$$

after Wanninkhof (1992), in which $T$ is the temperature (°C), $u$ is the windspeed at 10 m above sea level (m s$^{-1}$), and $Sc$ is the Schmidt number, a dimensionless ratio of momentum transfer and mass transfer. The coefficient includes also the role of chemical enhancement of CO$_2$ gas transfer at low windspeeds (Wanninkhof, 1992).

Samples for nutrient determination were taken every half hour and measured on a Technicon Autoanalyser II system (Hartmann et al., 1997). The data were also coupled to the carbonate dataset. To facilitate all further computations, data were linearly interpolated over the shortest section length, thus resulting in an equidistant dataset. Table 1 lists the start and end dates of the four sections.

Based on the ship data for windspeed, the wind mixed layer (WML) depth was computed as a first approximation. WML was taken as being half of the computed Ekman depth (= 2.5 times the average windspeed at 10 m height; see also Veth, 1991) under the assumption of instantaneous mixing. Fluorescence data were also obtained from the ship data, and expressed as chlorophyll $a$, following the method described by Bathmann et al. (1997b).

### 3. Results

#### 3.1. Hydrography

The study area is situated in the Antarctic Circumpolar Current (ACC) and in the subpolar region, where it includes both the eastward and westward flowing limbs of the Weddell Gyre (WG) (see Fig. 1). In view of the fact that only surface measurements were made, the hydrography is simplified to having only Polar Front Surface Water (PFSW) and Antarctic Surface Water (ASW). A number of fronts exist in this region and have been described in detail (e.g. Orsi et al., 1995; Belkin and Gordon, 1996; Veth et al., 1997).
Based on literature and the real-time data, a distinction could be made between three different regions for our study area (which is between 50°S and 70°S). The WG area stretches from 56°S to 70°S and the ACC from 50°S to 56°S. Around 56°S latitude, also known as the ACC–WG boundary, a more detailed division of the ACC is made into two regions; the southern Polar Front (sPF) and the southern Antarctic Circumpolar Current (sACC; see Table 2; Veth et al., 1997).

Distributions of temperature and salinity in the transects are given in Fig. 2. Over the whole of Transect 1 (Figs. 2a) salinity ranged from 33.8 to 34.35. For both legs 1A and 1B, the values in the north are lower than in the south near the continent. Temperature ranged from 4.2°C in the

<table>
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<th>Hydrographic region</th>
<th>Abbreviation</th>
<th>Latitude (°S)</th>
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<td>Southern ACC</td>
<td>sACC</td>
<td>50 ≤ ACC &lt; 52.5</td>
</tr>
<tr>
<td>Southern Polar Front</td>
<td>sPF</td>
<td>52.5 ≤ sPF &lt; 56</td>
</tr>
<tr>
<td>Antarctic Circumpolar Current</td>
<td>ACC</td>
<td>50 ≤ ACC &lt; 56</td>
</tr>
<tr>
<td>Weddell Gyre</td>
<td>WG</td>
<td>56 ≤ WG ≤ 70</td>
</tr>
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</table>

Fig. 2. Plots of temperature/salinity sections of the surface waters of both transects. (a) Legs 1A and 1B of transect 1, (b) legs 2A and 2B of transect 2. Thinner lines are the legs southward and the bold lines northward. In the upper two figures the different hydrographic regions are shown by lines. ACC = Antarctic Circumpolar Current divided into the sACC (= southern Antarctic Circumpolar Current) and the sPF (= southern Polar Front); (WG = Weddell Gyre).
north to $-1.8^\circ$C (freezing point) in the south. A gradual decrease is seen southward to nearly constant values ($\sim -1^\circ$C to $-1.5^\circ$C) except for somewhat higher values near the coastline. The return leg 1B showed a local increase near 50°S of $\sim 1^\circ$C that occurred in 9d. On Transect 2 the salinity ranged from 33.25 to 34.25, in the north approximately 33.65 (Figs. 2b). The same pattern is observed for both legs 2A and 2B, where salinity minima are observed at 65°S and near the coastline, probably due to the influence of meltwater. Except for near the coastline and near the Polar Front, temperature increased slightly ($\sim 0.5^\circ$C) in the timespan of 15d between legs 2A and 2B. The nearshore areas actually showed a slight decrease in temperature. Both the transects exhibit a sharp change in temperature in the area of 52–53°S.

### 3.2. fCO$_2$

The fugacity of CO$_2$ in the atmosphere undulates (Figs. 3a and b and Figs. 4a and b), being directly correlated with variations in atmospheric pressure. Some gaps exist in the data, either due to absent auxiliary data (e.g. temperature or salinity) or due to erroneous $f$CO$_2$ data, which have been deleted. Leg 1A is characterized mostly by supersaturation in $f$CO$_2$ in the surface water, relative to the atmosphere (Fig. 3a). In the south supersaturations of $\sim 10–15$ µatm are observed, with near equilibrium values near 60°S. Further north values are seen to increase again, with a slight undersaturation present at 54°S. No clear correlation can be seen between Chla levels and the $f$CO$_2$ in the water. The return leg 1B displays pronounced undersaturation, especially north of 62°S (Fig. 3b), although a clear correlation with Chla could not be detected. Only near 50°S is a slight increase in Chla seen with a coinciding undersaturation in $f$CO$_2$.

Transect 2 (leg 2A) shows undersaturation in $f$CO$_2$ near 50°S, which increases rapidly southward to a large supersaturation (Fig. 4a) of up to 75 µatm. Further south the supersaturation changes to undersaturation ranging from −60 µatm in the continental region to −90 µatm at 63°S. The observed undersaturations are matched by elevated Chla levels in the range of 2–3 µg l$^{-1}$, comparable with findings of Schneider and Morlant (1995). The return leg 2B (Fig. 4b) shows, surprisingly, a less pronounced undersaturation in $f$CO$_2$ at the southern end of the transect but very high Chla content (up to 8.6 µg l$^{-1}$ near the continent). The $f$CO$_2$ undersaturation at 64°S diminished in a few days to a value of $\sim 40$ µatm because of the increase in WML (Figueiras et al., 1994) even though the Chla remained approximately the same. Near the Polar Front the large supersaturation decreased in a timespan of 15d to near equilibrium values with a slightly increased Chla content. Silicate increased in the time period between legs 2A and 2B in this region.

### 3.3. Chlorophyll a, plankton and nutrients

Comparing the major nutrients silicate and nitrate for both legs 1A and 1B (Figs. 3c and d) one can observe only near the Polar Front a decrease in both nutrients. Silicate decreased by $\sim 5$ µmol kg$^{-1}$ and nitrate by about 2 µmol kg$^{-1}$ over the 9-d period between the two legs. For both the legs both nitrate and silicate appear to be relatively constant from the continent to approximately 55°S. From here a rapid decrease with decreasing latitude is seen. This gradient did not change over time. In the region between 60°S and 70°S the largest undersaturations in $f$CO$_2$ were observed, thus justifying a closer look. Transect 1 (with its relatively low Chla levels) shows for both legs a nearly constant Si/NO$_3$ ratio of $\sim 2.4$, which increases near the continent to about 2.8, coinciding with an increase in Chla. These observed increases of the ratio indicate the growth of non-diatom species (e.g. *Phaeocystis*). Very close to the continent the ratio drops sharply to a value of $\sim 2.2$. The return leg depicts a similar pattern, but very near the continent the ratio has increased from 2.2 to 2.4 in a few days.

The more eastern transect 2 (Figs. 4c and d) had much higher Chla levels (Figs. 4a and b). The Si/NO$_3$ ratios start at 0.4 near the Polar Front and increase rapidly to $\sim 2.4$ near the southern Polar Front. They decreased to $\sim 2.0$ at 62°S during leg
Fig. 3. Plots for legs 1A and 1B of: (a,b) the fugacity of CO$_2$ in air (red) and water (blue) (both in μatm) and Chl$\alpha$ (in μg/l), (c,d) silicate (red) and NO$_3$ (× 3; blue) (in μmol kg$^{-1}$) and the Si/NO$_3$ ratio (green), (e,f) normalized TCO$_2$ (NTCO$_2$ versus a salinity of 35 in μmol kg$^{-1}$) and the WML (m).
2A. From here high ratios are observed coincident with high Chl a levels consistent with blooms of *Phaeocystis* (Bathmann et al., 1997a,b) rather than diatoms. Further south the ratio decreases again to about 2.4 and is at the maximum near the continent. The low ratios next to the continent are
again indicative of preceding or active diatom blooms. The return leg 2B shows a similar pattern although, the ratios have increased, as have the Chl$\alpha$ levels. The very low ratio of 2.0 at 62°S present on leg 2A has now increased to a value of 2.4.

3.4. TCO$_2$

TCO$_2$ data were normalized (NTCO$_2$) to a salinity of 35 to exclude freshwater influence and are shown in Figs. 3e and f and Figs. 4e and f. Legs 1A and 1B have values ranging from as low as 2159 µmol kg$^{-1}$ near the Polar Front (Figs. 3e and f) up to $\sim 2290$ µmol kg$^{-1}$. Especially near the Polar Front a clear decrease (up to $\sim 50$ µmol kg$^{-1}$) in NTCO$_2$ is observed, which is probably caused by a different watermass rather than by biological uptake, given the only slight increase in Chl$\alpha$ content. Only temperature increased, by $\sim 1^\circ$C; the salinity stayed constant (Fig. 2a). Figs. 3c and d, however, show a change in silicate and nitrate supporting the option of a different watermass. Such a large decrease in NTCO$_2$ cannot be explained otherwise. The southward bound leg of Transect 2 (leg 2A) shows NTCO$_2$ values ranging from 2185 to 2250 µmol kg$^{-1}$. Low values are seen near the Polar Front and near the continent showing some, albeit small, correlation with the Chl$\alpha$ signal. The return leg (leg 2B) depicts a similar pattern (values ranging from 2175 to 2255 µmol kg$^{-1}$) with a large dip seen at $\sim 64^\circ$S, which indeed matches the higher Chl$\alpha$ content. No correlation between NTCO$_2$ and temperature (Figs. 2c and d) could be found.

3.5. Air–sea CO$_2$ exchange

Fluxes of CO$_2$ across the air–sea interface were calculated from in situ values of the meteorological parameters, notably wind velocity (Wanninkhof et al., 1992; Bakker et al., 1997).

Leg 1A shows negative fluxes (Fig. 5a) (i.e., outgassing to the atmosphere and thus a decrease of surface water TCO$_2$) along the whole transect, except for a very slight positive flux (i.e., uptake) at $\sim 58^\circ$S. Such general outgassing is consistent with either continuous upwelling of older CO$_2$-rich deep waters, or seasonal warming of surface waters, or the combination of both processes. The return leg, 1B, shows outgassing in the WG area (Fig. 5b) and a very high flux to the atmosphere near 67°S, due to a very high wind-speed at this position. The flux changes sign at approximately 62°S, and continuing northward CO$_2$ is taken up by the surface waters. The ACC region has changed in this time period from a source to a sink for CO$_2$. In this season, when water temperatures are still increasing, such ocean uptake can be ascribed only to biological fixation of CO$_2$, more than offsetting the outgassing force due to upwelling or seasonal warming.

Leg 2A shows a positive flux from the continent to $\sim 61^\circ$S (Fig. 5c). This part of WG is, in contrast to what was observed on the more western transect 1 (legs 1A & 1B), a sink instead of a source. The sACC area, with the observed strong supersaturation during leg 2A (Fig. 4a), releases CO$_2$ to the atmosphere. On the return leg 2B, the air–sea gradient has decreased with an undersaturation here and there (Fig. 4b). Because of the increase in WML depth (Figs. 4e and f), the flux has increased though (Fig. 5b). The WG shows a parallel behaviour, from strong undersaturation (leg 2A) to a lesser undersaturation (leg 2B; Figs. 4a and b). The flux has increased, also because of the increase in WML depth, and the area, which is a sink, has extended to $\sim 58^\circ$S in approximately 6d (Fig. 5d). From this latitude northward the flux is generally negative, i.e., CO$_2$ is released to the atmosphere.

Fig. 5e shows the mean flux for the three different regions during legs 1A and 1B of transect 1. The WG area is a source during both legs, but the mean flux is halved (from $\sim 4$ to $\sim 2$ mmol m$^{-2}$ d$^{-1}$) in a time period of $\sim 6$d. Both the sPF and the sACC regions changed from source to a sink in a period of 9d. The sPF has nearly the same magnitude, whereas the sACC region has an almost two-fold higher value. Transect 2 (Fig. 5f) shows the WG region to be a slight sink on the order of $\sim 1$ mmol m$^{-2}$ d$^{-1}$. In 6d this value nearly tripled to $\sim 2.5$ mmol m$^{-2}$ d$^{-1}$. This change can be attributed to an increased wind velocity rather than to
an increased CO₂ gradient. The sPF region has increased the mean source value from 4 to about 5 mmol m⁻² d⁻¹. The sACC region has on leg 2A a strong mean source value of ~7.5 mmol m⁻² d⁻¹ and on leg 2B (9 d later) a value of about 4 mmol m⁻² d⁻¹. The lower value is the result of occasional undersaturation (negative flux), thus diminishing the mean value for overall outgassing.

Fig. 5. Realtime CO₂ flux (in mmol m⁻² d⁻¹) for all four legs: (a) leg 1A, (b) leg 1B, (c) leg 2A and (d) leg 2B. In the lowest two plots the mean flux per hydrographic region (e) transect 1 and (f) transect 2. Positive fluxes are into the sea, negative fluxes out of the sea.
4. Discussion

4.1. Phytoplankton growth and undersaturation of $fCO_2$

Physical processes that affect $fCO_2$ are horizontal and vertical advection, dispersion and initial state of the watermasses, the depth of the WML, and air–sea gas and heat exchange. As evident from Figs. 3e–f and Figs. 4e–f, the depth of the WML near the Polar Front is variable but on average around 30–40 m deep. Near the continent the WML tends to be rather shallow (about 10–15 m) for leg 1B and both legs of transect 2 (leg 2A & 2B). Part of the shallow WML during leg 1B may be attributed to the larger ice coverage (van den Brink and van Franeker, 1997, their Fig. 2.2), but observations showed no complete coverage and only a few places where coverage was more than 80%. Although the ice coverage was even stronger on leg 1A, a clear correlation between the depth of the WML and ice coverage cannot be found. Transect 2 showed negligible ice cover.

The observed increase in temperature ($\sim 1$ K) near the Polar Front corresponds to a potential increase in $fCO_2$ of about 14 $\mu$atm (Bakker et al., 1997). The $fCO_2$ did not increase though, but decreased in combination with a slight increase in Chl$\alpha$. The undersaturation near the Polar Front is thus probably due to the combined effect of phytoplankton growth and the advection of water with a lower TCO$_2$ content. We assume alkalinity to be conservative in the Antarctic Ocean (Anderson et al., 1991; Stoll et al., 1999) as the nitrate effect of photosynthesis on alkalinity is deemed to be of minor importance. Thus a lower TCO$_2$ would result in a lower $fCO_2$. For transect 2 the temperature increased by $\sim 0.4$ K in time between the two legs. The observed change in temperature increases the $fCO_2$ by about 5 $\mu$atm, thus lowering the observed undersaturation gradient by about 5%. The remainder is then due to phytoplankton growth, and the relation with $fCO_2$ undersaturation is still clearly visible. It is interesting to note that high Chl$\alpha$ abundance does not mean the largest undersaturation. The flux across the air–sea interface is rather small because of low windspeed and thus not able to compensate completely for large undersaturations. It is more likely that the onset of phytoplankton growth with their strong uptake of CO$_2$ results in the observed gradient of $fCO_2$. The resultant biomass increase is then seen on the return leg 2B, in which the system shows less undersaturation. The latter effect is ascribed to an influx of CO$_2$ from the atmosphere and less productive (smaller growth rate = smaller CO$_2$-uptake) phytoplankton.

In order to deduce which group of phytoplankton is responsible for the observed phenomena we plotted the silicate–nitrate ratios (Figs. 3c and d and Figs. 4c and d). During growth, uptake of nitrate and, in the case of diatoms, also silicate takes place. Transect 1 does not show a clear ratio change except near the continent on leg 1A (Figs. 3c and d). There the ambient decrease in the Si/NO$_3$ ratio suggests an increase in the diatom population. On transect 2 (Figs. 4c and d) the Si/NO$_3$ ratio increases by $\sim 40$–60% thus indicating that not diatoms but other algae are the dominant group of phytoplankton. This is also supported by data from Bracher et al. (1999), which indicate that at some stations sampled at the transects some 20–40% of the phytoplankton are diatoms, the remainder being a combination of non-silicon-containing dinoflagellates, pycnemosiophytes and chrysophytes.

Our approach to calculate the mean fluxes per region has the drawback that it is based on a latitudinal section. In order to assess the effects of different processes (seasonal warming, upwelling, biological fixation, respiration) one ideally needs a time series (Bakker et al., 1997). In this way one would have the initial state and the evolution in time, enabling quantification of the above-mentioned processes. Our four individual latitudinal sections merely are snapshots in time. However, the combination of both legs of one transect can give us an initial state and a later stage. Thus, we were able to develop a simple budget model to identify the cause of the observed changes in the carbonate system.

4.2. A simple budget model

The observed changes in TCO$_2$ and $fCO_2$ in the water, an upwelling term (Ekman pumping), an
eddy-diffusive flux and net community respiration ($\Delta B$) (Hansell and Carlson, 1998) are incorporated in the simple model described below (see Fig. 6). Other terms are mixing of water masses and the initial state of these water masses, of which the latter is ignored in this work. Our purpose is to quantify the role of biology in the carbon transfer in the system in combination with physical processes. Time series of one water mass is ideal for this kind of work. Here the online surface water measurements between two consecutive legs of one transect (1A versus 1B; 2A versus 2B) are taken as an approximation. Both transects (1 and 2) started at the Polar Front (legs 1A & 2A), and their return legs (legs 1B & 2B) end at the Polar Front; thus the time passed between two samplings at a given latitude must be taken into account to deconvolute the processes. Data were corrected for this time difference by dividing the observed change in the appropriate property by the number of days passed. The mixing of water masses can be accounted for by normalizing the initial property, TCO$_2$, to a salinity of 35. Thus the mass balance of a box of surface water (Fig. 6) (integrated over the WML depth for an area of 1 m$^2$) is described by

$$\Delta C = (\Delta D + \Delta E) + \Delta F + \Delta B$$  \hspace{1cm}(3)$$

in which $\Delta C$ is the observed change in TCO$_2$, $\Delta D$ the eddy-diffusive flux from underlying waters, $\Delta E$ the Ekman pumping term (advective flux), $\Delta F$ the atmospheric influx of CO$_2$ from air to sea and $\Delta B$ the closing term representing the apparent influence (respiration–photosynthesis) of biology needed to balance the budget (all in mmol m$^{-2}$ d$^{-1}$). Note that positive fluxes increase the TCO$_2$ of the surface water box, whereas negative fluxes decrease it. This means, positive $\Delta B$ values could be seen as net community respiration and negative $\Delta B$ values as net community production, respectively.

The change in TCO$_2$ is described by the time-corrected change in TCO$_2$ integrated over the computed WML, in the formula

$$\Delta C = (C_1 - C_0) \times \text{WML}$$  \hspace{1cm}(4)$$

with $C_1$ and $C_0$ the concentrations (µmol dm$^{-3}$) at times 1 and 0 and WML (m) the depth of the wind mixed layer. The CO$_2$ air to sea flux $\Delta F$ is based upon the concentration differences of CO$_2$ in air and the sea surface water ($\Delta p$CO$_2$) and is computed according to Bakker et al. (1997), Stoll et al. (1999), Wanninkhof (1992) and Wanninkhof and Thoning (1993). The upward terms $\Delta D + \Delta E$ describe the eddy-diffusive flux and Ekman upwelling and are taken from de Baar et al. (1995) following

$$\Delta D + \Delta E = K_Z (\partial \text{TCO}_2 / \partial z) + V_u \Delta C$$  \hspace{1cm}(5)$$

with $K_Z$ being the turbulent eddy diffusivity (de Baar et al., 1995; set constant at $3.5 \times 10^{-3}$ m$^2$ s$^{-1}$); $\partial$TCO$_2$ (and $\Delta C$) the difference in TCO$_2$ concentration between surface water and deeper layers (on average 25 µmol kg$^{-1}$; based on field data) and $\partial z$ the thickness of the corresponding boundary layer. The upwelling velocity $V_u$ is taken as $0.15 \times 10^{-5}$ m s$^{-1}$ (taken from de Baar et al., 1995).

In view of the relatively large differences between transects 1 and 2, not only hydrographically (Fig. 2) but also topographically (Fig. 1), a budget per transect is made. If the two transects had been more closely related, one could also have
looked at time-related differences between transects 1 and 2. However, the observed temperature/salinity profiles differed too much to warrant this approach.

Fig. 7 shows the time-corrected plots for the various terms of Eq. (3) of the two transects. Sections were subtracted from one another in order to arrive at net changes per day (corrected for elapsed time between samplings). Figs. 7a–e and g show the results for transect 1. The $\Delta C$ is seen (Fig. 7a) to increase sharply from about 3 to a value of about 9 mmol m$^{-2}$ d$^{-1}$ in the WG region (68$°$S). From here northward a rapid decrease is seen to a value of about $-5$ mmol m$^{-2}$ d$^{-1}$ at 63$°$S. Further north $\Delta C$ alternates from positive to negative, ending at about 0 mmol m$^{-2}$ d$^{-1}$ in the Polar Front. The air–sea flux term $\Delta F$ is positive only between 66$°$ and 68$°$S and remains mostly negative (on average $\sim -0.5$ mmol m$^{-2}$ d$^{-1}$) further north (Fig. 7c). The sums of both the eddy diffusion term ($\Delta D$) and the Ekman upwelling term ($\Delta E$) (Fig. 7e) are continuously positive but

![Fig. 7. The different terms of the mass balance model (Eq. (3); Fig. 6) plotted versus latitude for transect 1 (a, c, e and g) and transect 2 (b, d, f and h). $\Delta C =$ observed change in TCO$_2$, $\Delta F =$ in-/efflux of CO$_2$, ($\Delta D+\Delta E$) = summation of the eddy-diffusive flux and the Ekman upwelling and the closing term net community respiration ($\Delta B$) needed to balance the budget (all in mmol m$^{-2}$ d$^{-1}$).](image)
small (<0.5 mmol m\(^{-2}\) d\(^{-1}\)), indicating a continuous supply of carbon from deeper waters. Overall, \(\Delta B\) (Fig. 7g) matches closely the observed pattern in \(\Delta C\). Near the continental margin \(\Delta B\) increases from slightly below zero to about 7 mmol m\(^{-2}\) d\(^{-1}\) indicating intense respiration. In contrast \(\Delta B\) reaches very negative values (–6 mmol m\(^{-2}\) d\(^{-1}\)) at 63–64°S consistent with photosynthesis. Further north the pattern closely matches that of \(\Delta C\), but ends at small positive values for \(\Delta B\), precisely coinciding with nearly doubled Chl\(a\) levels (~51°S). This is also reflected in much lower nitrate and silicate values (Figs. 3c and d), suggesting a phytoplankton bloom that started during the preceding 2 weeks. The largest changes are actually observed in places where phytoplankton blooms start.

The budget terms of transect 2 are shown in Figs. 7b, d, f and h. The negative \(\Delta C\) (at ~67.5°S) increases sharply to high positive values (more than 8 mmol m\(^{-2}\) d\(^{-1}\)) at 65°S and also rapidly drops again to a value of 2 mmol m\(^{-2}\) d\(^{-1}\). Further north \(\Delta C\) increases again to about 4–5 mmol m\(^{-2}\) d\(^{-1}\). Here, the observed \(\Delta F\) is mostly negative, this in accordance with the observed supersaturation along this northern part of the transect (Figs. 4a and b). The large negative \(\Delta F\) at 52°S (Fig. 7d) is caused by the large change of supersaturation during leg 2A to undersaturation at leg 2B. The sum \(\Delta D + \Delta E\) (Fig. 7f) remains positive throughout the entire transect, and is quite high near the continental region. The \(\Delta B\) shows a large positive value at 65°S (Fig. 7h). The rapid increase in \(\Delta B\) to about 6 mmol m\(^{-2}\) d\(^{-1}\) corresponds to a large increase in \(\Delta C\), followed in the northward direction by a decrease to near zero levels and ending at about 3.4 mmol m\(^{-2}\) d\(^{-1}\).

In parallel with transect 1 the computed changes on transect 2 can be explained by a combination of sustained phytoplankton blooms and physical forcing. The undersaturation (<325 \(\mu\)atm) near the continent has actually weakened in a few days to values of around 340 \(\mu\)atm. The resultant \(\Delta F\) compensates partially for the very large undersaturation (<260 \(\mu\)atm) observed during leg 2A. The return leg 2B showed much smaller undersaturation in the \(fCO_2\) of the surface water, in contrast to the high supersaturation measured on leg 2A. The levels of Chl\(a\) stayed approximately the same in this region, but unexpectedly nitrate (Fig. 4d) decreases. This phenomenon is not observed near the Polar Front.

The upward supply terms \((\Delta D + \Delta E)\) were based on an assumed upwelling velocity \((V_u)\) of \(0.15 \times 10^{-5}\) m s\(^{-1}\) and a diffusion coefficient \(K_z\) of \(3.5 \times 10^{-5}\) m\(^2\) s\(^{-1}\). These are annual mean values, which might be too high for the time of our study area. Comiso et al. (1993) showed that the ACC exhibits high upwelling velocities \((0.3–0.4 \times 10^{-5}\) m s\(^{-1}\)) during the winter and lower velocities \((\sim 0.1 \times 10^{-5}\) m s\(^{-1}\)) in December/January. The latter value is lower by 33% and would thus decrease the \(\Delta E\) term in our mass balance equation. Using a lower value in our budget model would only increase the importance of the other terms; i.e. biology would play an even more important role. The resultant term \(\Delta B\) would increase by ~10%, but this would not affect our conclusions significantly.

The computations ignore the effect of lateral advection. This is an unknown variable, which has been implicitly taken included in the \(\Delta B\) term, since no data were available to quantify lateral advection independently. However, lateral advection is deemed to be of minor importance in the timeframe observed. This assumption is supported by only low averaged eastward flows of the ACC of about 0.025 m s\(^{-1}\) (Veth et al., 1997). The elapsed time of 15 d between legs would correspond to only 32 km, for which it might be reasonable to neglect lateral transports.

Phytoplankton blooms appear to have the potential for uptake (positive values) on the order of 6–9 mmol m\(^{-2}\) d\(^{-1}\), which make them the major forcing factor in the drawdown of atmospheric carbon dioxide. Physical forcings \((\Delta F\) and \((\Delta D + \Delta E)\)) have a large potential (values of up to 2 mmol m\(^{-2}\) d\(^{-1}\) were observed), but in the time frame of our study appeared to be of relatively minor importance compared to the effects of phytoplankton blooms and respiration. Our simple mass balance model has shown that at several locations over a short time span the effects of blooms and respiration can be quantified.
4.3. Concluding discussion

Both the observed coincidences of distributions of $f/CO_2$ and Chla (Figs. 3–4) and the calculated gas exchange fluxes (Fig. 5) demonstrate the importance of biological processes for local CO$_2$ exchange with the atmosphere. This is not only for uptake of CO$_2$ due to photosynthetic fixation, but also for outgassing due to biological respiration within the upper wind mixed layer. As a result a wide range of over- and undersaturations, with concomitant out- and influxes of CO$_2$, are observed (see also Takahashi et al., 1993; Bates et al., 1996; Cooper et al., 1996; Thomas and Schneider, 1999). The supersaturations also result partially from seasonal warming affecting solubility, as well as from general upwelling of CO$_2$-enriched deep waters.

The instantaneous air–sea fluxes (Figs. 5a–d) are quite valid, but basin-wide extrapolation in space, and more notably in time over the complete summer or full year, is difficult. The spatial extrapolation for a larger part of the ACC would appear quite reasonable, because of its fairly homogenous spatial hydrography and consistent eastward flow. Similarly our findings may well be representative for a larger part of the Weddell Gyre, if it is assumed that the general patchiness of blooms in both the Weddell Gyre and the ACC would cancel out statistically over a larger region.

Thus the mean fluxes (Figs. 5e and f) for three major parts of the sections (WG, sPF and sACC) may well be representative for the austral summer (December–January) in the larger regions. Here we found values ranging from $-7$ to $+3$ mmol m$^{-2}$ d$^{-1}$ where the straightforward summation over 40 d would lead to an overall source function of $-0.3$ mmol m$^{-2}$ d$^{-1}$ for this summer period. This is opposite to an overall sink function of $0.3$ mmol m$^{-2}$ d$^{-1}$ during austral spring in the same 47–60$^\circ$S region, with extremes of $3.7$ mmol m$^{-2}$ d$^{-1}$ in the Polar Front ($\sim$47–49$^\circ$S) and $2.7$ mmol m$^{-2}$ d$^{-1}$ in the ACC–Weddell Boundary (57–59$^\circ$S), respectively (Bakker et al., 1997). For one section in late summer and early autumn (March–April 1996), the strong seasonal cooling at 60–70$^\circ$S led to undersaturations as low as 335 $\mu$atm, compensated by supersaturations in the 50–60$^\circ$S latitude band (Hoppema et al., 2000). The average flux for the latter section into the ocean is $2.5$ mmol m$^{-2}$ d$^{-1}$, i.e. an influx tenfold larger than the above mean fluxes in spring and summer. For winter we have no observations.

When summing up over the whole year one would find an overall very large influx as well as an overall very large efflux term, both driven as much by biological processes (photosynthesis and respiration, respectively) as by the physics of seasonal warming/cooling and upwelling. Integrating the different fluxes for each time span of the four seasons over the entire area of the Weddell Gyre, one obtains the seasonal exchange rates (Table 3). Both spring (influx) and summer (efflux) are relatively small numbers. This is in sharp contrast with the total air to sea flux for austral autumn, which is already half of the ‘missing sink’ of about $2.0$ PgCa$^{-1}$ (e.g. Tans et al., 1990; Francey et al., 1995), which is partially compensated for during the winter season. The estimated annual average efflux of $\sim 0.5$ PgCa$^{-1}$ from the Weddell Sea (based on the above-mentioned datasets) is of the same order as that derived by Rayner et al. (1999) ($0.1 \pm 0.5$ PgCa$^{-1}$). It is clear though that the small net annual flux, whatever its

<table>
<thead>
<tr>
<th>Season</th>
<th>Flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Reference</th>
<th>Integrated rate (PgC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>$+0.3$</td>
<td>Bakker et al. (1997)</td>
<td>$+0.14$</td>
</tr>
<tr>
<td>Summer</td>
<td>$-0.3$</td>
<td>This paper</td>
<td>$-0.14$</td>
</tr>
<tr>
<td>Autumn</td>
<td>$+2.5$</td>
<td>Hoppema et al. (2000)</td>
<td>$+1.13$</td>
</tr>
<tr>
<td>Winter</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

A time period of 90 days is taken to represent the season.
direction, is the small difference between large gross influx and efflux, both of which are strongly affected by biological processes.

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