Modelled and observed sea surface $f$CO$_2$ in the southern ocean: a comparative study

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(Manuscript received 9 December 1997; in final form 25 September 1998)

ABSTRACT

The results of an existing one-dimensional diagnostic model that calculates the fugacity of CO$_2$ ($f$CO$_2$) in the surface layer of the southern ocean were compared with in situ observations from different ocean sectors and seasons. Our model is based on the translation of monthly variations of constraints fields into surface water $f$CO$_2$ variations, and was used to assess the CO$_2$ uptake of the southern ocean. In situ observations are useful to verify the model results and were here applied to improve the estimation of the CO$_2$ uptake of the southern ocean south of 50°S. The model reproduces the $f$CO$_2$ distribution in both Pacific and Indian sectors of the southern ocean satisfactorily, the mean deviation being only 5 m atm. This discrepancy requires only a minor modification of the CO$_2$ uptake calculated by the model for that area. By contrast, the model strongly underestimates the $f$CO$_2$ levels in early spring and early winter in the Weddell gyre. This indicates that the CO$_2$ uptake by the Atlantic sector of the southern ocean as calculated by the model, amounting to 0.47 GtC yr$^{-1}$, should be reduced, possibly by about half of this value. The reason for this mismatch lies in the use of climatological physical constraints by the model that do not sufficiently well describe reality. Partly, the mismatch is also caused by a difference of seasonal stage between the model which reflects climatological conditions and the real ocean which is affected by interannual variability. Based on this study it is concluded that the CO$_2$ uptake of the southern ocean south of 50°S is likely to lie somewhere between 0.6 and 0.7 GtC yr$^{-1}$ for the 1990s, which is a high value compared to estimates from other investigations.

1. Introduction

Since the beginning of the industrial era, the CO$_2$ content of the atmosphere has grown due to the combustion of fossil fuel (Keeling et al., 1989). Because CO$_2$ is a greenhouse gas, this increase has likely had an impact on climate. Since 1958 atmospheric CO$_2$ has been monitored at several stations throughout the world in such a way that the variability is known with a reasonable space/time coverage (Keeling et al., 1995; Masarie and Tans, 1995). At the beginning of the 1990s, the release of fossil fuel CO$_2$ to the atmosphere was about 6 GtC yr$^{-1}$ (1 GtC = 1 Gton C =...
10^{15} \text{g C}, whereas the atmospheric CO$_2$ concentration was growing by only 3.4 GtC yr$^{-1}$ (Conway et al., 1994). About half of the fossil fuel input disappears every year, being absorbed by the oceans and the terrestrial biosphere. One of the challenges for the scientific community is to identify and quantify the oceanic and terrestrial CO$_2$ sinks along with the processes responsible for this. The quantification of the part absorbed by these reservoirs is difficult since carbon is the basis of all terrestrial and oceanic biogeochemical cycles, giving rise to a large natural variation of CO$_2$ in these reservoirs.

The global carbon budget is not well-balanced; actually, the magnitude of the known sources is larger than that of the known sinks of CO$_2$ which is commonly referred to as the problem of the “missing sink” (Sarmiento and Sundquist, 1992). Recently, investigators questioned the current global carbon budget using atmospheric models as a basis to deduce oceanic and terrestrial source and sink distributions (Tans et al., 1990; Ciais et al., 1995; Denning et al., 1995). They contend that the oceanic CO$_2$ sink is more than a factor two smaller than previously assumed and invoked a large CO$_2$ sink in the terrestrial biosphere of the northern hemisphere. Unfortunately, large uncertainties remain in direct quantification of the terrestrial sink (Houghton et al., 1996). Although an increasing amount of in situ observations, satellite data and models are becoming available, and new methods to add constraints to the carbon budget have been developed (Keeling et al., 1993; Tans et al., 1993), the missing sink remains a matter of debate.

Oceanic $\mu$CO$_2$ data are available only for restricted periods and areas ($\mu$CO$_2$ is the fugacity of CO$_2$, which by value is nearly equal to its partial pressure). The observed spatio-temporal variations of the sea surface $\mu$CO$_2$ are so large that integrating the derived air–sea CO$_2$ fluxes over larger areas and long periods becomes highly uncertain. The Oceanic general circulation models (OGCM) of carbon are thus useful to obtain a reliable value for the oceanic uptake of CO$_2$ on large time and space scales. The results of these models converge to about 2 (±0.8) GtC yr$^{-1}$ (Sarmiento et al., 1992; Houghton et al., 1996). However, there are still uncertainties in the ocean circulation resulting in uncertainties in the oceanic carbon uptake particularly for the southern ocean (Orr, 1996; Sarmiento and Le Quéré, 1996). The southern ocean is the least documented ocean. It appears to be an important area for absorbing anthropogenic CO$_2$ and it could play a key role in the future evolution of climate (Sarmiento and Le Quéré, 1996).

In the southern ocean the observations of surface water $\mu$CO$_2$ show a high spatio-temporal variability (Takahashi et al., 1993; Poisson et al., 1993; Robertson and Watson, 1995; Bakker et al., 1997) and only a few data are available for the winter period (Stoll et al., 1998). To determine whether this ocean is a source or a sink for atmospheric CO$_2$ requires the extrapolation of the sparse available observations over a wide area and for the whole year. In this work we perform an extrapolation of $\mu$CO$_2$ fields derived from external forcings to obtain the air–sea CO$_2$ fluxes over one year south of 50$^\circ$S. To improve the reliability of this estimate, the modelled $\mu$CO$_2$ fields are compared with observations. We use several cruises conducted in the Atlantic, Pacific and Indian sectors of the southern ocean. We will briefly describe the model used to extrapolate $\mu$CO$_2$ fields in the southern ocean and the main results of this modelling study. The impact of the uncertainties of the modelled $\mu$CO$_2$ fields on the estimate of the CO$_2$ uptake in the southern ocean will be discussed.

2. Model results

2.1. Model description

Louanchi et al. (1996) have developed a simple model able to diagnose sea surface $\mu$CO$_2$ fields on a monthly scale. The model was first validated in the Indian Ocean north of 50$^\circ$S and reproduced quite well the observed seasonal and spatial variability of the surface water $\mu$CO$_2$. A striking feature of the model is the use of variations of the mixed-layer depth and of chlorophyll as constraints, avoiding the uncertainties linked to ocean circulation and to biological prognostic (sub)models (Sarmiento and Le Quéré, 1996). The model translates the monthly variations of constraints into monthly $\mu$CO$_2$ variations in a surface ocean box. The constraints are the satellite wind speed (Boutin and Etcheto, 1997), the mixed-layer depth as derived from the temperature and salinity profiles from Levitus and Boyer (1994) and Levitus.
et al. (1994), the sea surface temperature (Reynolds and Marsico, 1993), the chlorophyll concentration (Chl-CZCS) (Coastal Zone Color Scanner satellite observations of sea color) and the sea-ice coverage (Gloersen et al., 1992). The model was applied on grids of 2° latitude by 2° longitude to simulate the monthly /CO2 fields in the southern ocean south of 50°S.

The /CO2 variations are expressed by:

\[
\delta f / \delta t = (\delta f / \delta t)_B + (\delta f / \delta t)_M + (\delta f / \delta t)_F + (\delta f / \delta t)_T,
\]

where \( \delta f / \delta t \) is the total /CO2 variation for a time step \( \delta t \). The subscripts B, M, F and T refer to biological activity, mixing, air–sea flux and thermodynamical changes, respectively. Except for the thermodynamical effect which is calculated directly with the Goyet et al. (1993) polynomials, the variation of /CO2 is calculated from temperature, salinity, dissolved inorganic carbon (DIC) and total alkalinity (TA) using the constants of Goyet and Poisson (1989). Each term of the above equation corresponds to a specific process and is parametrized as a function of the constraints fields monthly variations which induce monthly changes in DIC and TA state variables. A description of the model equations in terms of DIC and TA can be found in Section 7 (Louanchi et al., 1996; Metzl et al., 1998).

Running the model for the whole southern ocean requires an adequate circumpolar characterization of the subsurface layers which act as boundary conditions in this model. The depth of the pycnocline was determined from the observed profiles of the density and represents the top of the subsurface box.

As a first step, we keep the subsurface invariant all year round. This assumption is supported by the fact that at steady state, it is believed that the organic carbon exported from the surface is balanced by the losses of carbon by mixing in the intermediate waters of the ocean. Moreover, subsurface data of DIC, TA and nitrate (TIN) in the southern ocean are rather sparse. For extending the subsurface data to the whole southern ocean, the approach has been to calculate subsurface values through linear interpolation and extrapolation of property–temperature relationships. This procedure was performed with data from the GEOSECS (Bainbridge, 1981; Broecker et al., 1982; Weiss et al., 1983), INDIGO 3 (Poisson et al., 1990), CIVA1/GOCE and Polarstern ANT X/4, X/7, XIII/4 expeditions. Subsurface concentrations of DIC and TA as obtained by this procedure have standard deviations of 10 and 6.5 µmol/kg, respectively. For the whole circumpolar ocean the subsurface TIN was taken as 30.5 µmol/kg according to the observations. The thus preconditioned model is supposed to simulate conditions for the period after 1990. The molar fraction of CO2 in the atmosphere, being \( x_{CO2} = 351.9 \) ppm (value corresponding to 1990 at Palmer Station), is kept constant (Conway et al., 1994).

Because stability of the model is reached after three years, it is not necessary to define surface DIC, TA and TIN. The subsurface values of the properties are taken to initialize the system.

2.2. Model \( \Delta f/CO2 \) in the southern ocean

Fig. 1 shows the \( \Delta f/CO2 \) fields in the southern ocean calculated by the model for February (Fig. 1a) and August (Fig. 1b) and the seasonal variation of /CO2 (Fig. 1c).

According to these model results the surface layer is on average understaturated in CO2 during the austral summer period (Fig. 1a). The strongest sinks are found in the Ross Sea with undersaturations of more than 75 µatm. Such low CO2 values of about 200 µatm were actually also observed there during austral summer (Dunbar, personal communication) and are related to intense phytoplankton blooms occurring in this period. The Weddell Sea presents both super and undersaturations and this spatial variability reflects the competition between biological CO2 uptake and dynamical CO2 enhancement of the surface layer by mixing processes. This high spatial variability was previously observed in that area (Takahashi et al., 1993). By August, the southern ocean appears to be a sink everywhere except in some locations of the Weddell Sea and along the eastern Antarctic coast in the Pacific sector (Fig. 1b). In their recent climatology, Takahashi et al. (1997) showed that this area is a sink of CO2 for the atmosphere all year round on average, some sources being mainly located in the seasonal ice zone (extending to about 55°S in the Atlantic sector and 58–60°S in the Pacific and Indian sectors).

The /CO2 in the Weddell gyre increases by about 25–30 µatm from February to August (Fig. 1c), whereas in most of the Pacific and Indian
Fig. 1. Modelled values, represented as ranges for the $f$CO$_2$ difference between the surface water and the atmosphere ($Df$CO$_2$ in $\mu$atm) in areas of 2° latitude by 2° longitude for (a) February, (b) August and (c) seasonal variations (August minus February) in the southern ocean south of 45°S. The permanently open ocean zone is located between 50° and 58°S except in the Atlantic sector where ice may extend to 54°S. Note that the grey scale for (a) and (b) is different from that of (c).
sectors a seasonal $f\text{CO}_2$ decrease of about 10–15 $\mu$atm is found. More generally the observation can be made that $f\text{CO}_2$ increases from summer to winter in the seasonal ice zone and the polar front zone (50–52°S), whereas it decreases in the Antarctic open zone (largely covered by the Pacific and Indian sectors). The circumpolar sector has been converted into a stronger sink in winter for atmospheric $\text{CO}_2$ following a decrease in surface layer temperature (i.e. thermodynamical conditions). In the Indian sector the biological uptake and the mixing effect on the $f\text{CO}_2$ nearly cancel out on a seasonal scale, inducing “thermodynamically” mediated variations of $f\text{CO}_2$ (Louanchi et al., 1998). On the other hand, in the Weddell gyre low levels of $\text{CO}_2$ in the summer period are due to the biological uptake and the increase through the winter is due to the effect of increased mixing of subsurface water (Hoppema et al., 1995). In the Pacific sector, both situations are present. The model gives an increase of $\text{CO}_2$ in the Ross Sea and associated gyres, whereas the circumpolar current area presents the features described for the Indian sector. The model simulates the seasonal cycles of upper layer $\text{CO}_2$ according to the changes in the constraints. Results indicate that in the circumpolar current water, the biological $\text{CO}_2$ uptake is weak because Chl-CZCS is low in this area. The gradient between surface and subsurface waters in $\text{CO}_2$ is not strong enough in that case to induce significant increase of DIC during the period of mixed-layer deepening. In that situation, the solubility pump acts as the main agent of the $f\text{CO}_2$ seasonal change. On the other hand, in the seasonal ice zone, high Chl concentrations (greater than 1.5 mg m$^{-3}$) induce a strong biological pump of $\text{CO}_2$ during summer. From summer to winter the increase of the mixed-layer depth increases the amount of $\text{CO}_2$ in the surface layer. Seasonal changes in temperature are too weak in that area to compensate for the mixing effect on $\text{CO}_2$.

2.3. Model air–sea $\text{CO}_2$ fluxes

According to the model, the southern ocean is a substantial sink for atmospheric $\text{CO}_2$ of 0.9 ($\pm$0.3) GtC yr$^{-1}$. All sectors are $\text{CO}_2$ sinks on an annual basis, although certain regions within a sector may be sources for some time of the year. The Atlantic sector is the most important sink with a net uptake of 0.47 ($\pm$0.20) Gton C/yr. The Indian sector is a sink for 0.23 ($\pm$0.17) Gton C/yr while the geographically largest Pacific sector is the smallest sink with only 0.17 ($\pm$0.22) Gton C/yr. The standard deviations for these flux estimates are linked to the uncertainties in interpolation/extrapolation of the subsurface properties (see Subsection 2.1). The discrepancy between this flux estimate and previous ones which are much lower (see for example Tans et al., 1990 or Sarmiento et al., 1992 or Takahashi et al., 1997) is mainly caused by the use of satellite-derived wind speeds instead of climatological wind speeds. With a simple calculation the effect on the $\text{CO}_2$ uptake is illustrated of using climatological wind speed data as compared to satellite-derived data. Applying $\Delta p\text{CO}_2$ values compiled by Tans et al. (1990) and calculating the air–sea $\text{CO}_2$ fluxes using satellite derived wind speeds we arrive at $-0.97$ and $-0.32$ Gton C/yr for the summer and winter periods, respectively. The fluxes were calculated using the ice-free area for both periods. The mean $\text{CO}_2$ uptake for the ice-free area of the southern ocean is thus 0.65 Gton C/yr, i.e. three times the estimate of Tans et al. (1990) using climatological wind speeds.

Some earlier studies integrate air–sea $\text{CO}_2$ fluxes from oceanic $f\text{CO}_2$ measurements and observed wind speeds in selected areas and periods. Murphy et al. (1991) report that the region between 50° and 60° S in the Pacific sector is a $\text{CO}_2$ sink during the period January–April. Their fluxes, as calculated with the relationship between the transfer velocity and the wind speed according to Tans et al. (1990), are similar to the model results for this area ($-0.019$ GtonC/period and $-0.020$ Gton C/period respectively). For the Atlantic and Indian ocean sectors in austral summer, Robertson and Watson (1995) and Poisson et al. (1994), using the relationship between transfer velocity and wind speed of Wanninkhof (1992), calculated $\text{CO}_2$ fluxes which are close to the model estimates ($-0.10$ Gton C/period vs $-0.08$ Gton C/period in the Atlantic sector and same value $-0.016$ Gton C/period in the Indian sector). Thus for several areas in the spring/summer period where $\text{CO}_2$ fluxes derived from field observations were available, the calculated fluxes obtained from our model appeared to be close to reality. This result suggests that the satellite-derived wind speeds better represent real-
ity than the climatological ones for the southern ocean. The wind speed data from which the climatologies are derived are rather sparse and probably not representative of climatological features, particularly in winter period.

3. Comparison between modelled and observed $f_{\text{CO}_2}$

As the air–sea CO$_2$ fluxes depend both on the CO$_2$ exchange coefficient and on the air–sea $f_{\text{CO}_2}$ gradient ($\Delta f_{\text{CO}_2}$), correctly calculated fluxes do not automatically mean that the simulated $f_{\text{CO}_2}$ fields by the model are correct. As a means to improve the CO$_2$ flux estimate for the southern ocean, the differences between observed and modelled surface ocean $f_{\text{CO}_2}$ are analyzed. Data from several cruises in the southern ocean were used (Table 1), the tracks of which are depicted in Fig. 2. To compare the model results with the observations, the data were averaged on the model grid of 2° latitude by 2° longitude, and standardized to an atmospheric pressure of 1013 hPa (used in the model). A change of 10 hPa in atmospheric pressure induces an effect of about 4 μatm in oceanic $f_{\text{CO}_2}$.

The air–sea CO$_2$ fluxes are calculated from observations with the atmospheric CO$_2$ concentration, the atmospheric pressure and the wind-speeds used in the model. The model results are extracted for the grid points over the periods for which observational data are available.

We investigated the differences between modelled and observed $f_{\text{CO}_2}$ in several areas: the Kerguelen plateau, the boundaries of the Indian sector, the Eastern Pacific sector and the Atlantic sector with the Weddell gyre (refer to Fig. 2). On each track the model results are extracted in terms of $f_{\text{CO}_2}$ and air–sea CO$_2$ fluxes and compared to the corresponding observations. The comparison track by track is described below.

![Fig. 2. Cruise tracks from which $f_{\text{CO}_2}$ data were used in the southern ocean. Tracks 1–6 are cruises in the Indian sector, 7–9 in the Atlantic sector and 10 in the Pacific sector.](attachment:image.png)
Table 1. Summary of the averaged differences between the modelled and the actually observed fCO$_2$ in the surface layer and the air–sea CO$_2$ fluxes calculated from this for several cruises in the southern ocean; also given are the corresponding differences in temperature and salinity of the surface layer. The summary for each sector includes an estimate of the air–sea CO$_2$ fluxes difference in GtC integrated over specified area and period. Cruise numbers correspond to the numbers in Fig. 2.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Period</th>
<th>Region</th>
<th>Refs</th>
<th>δTemperature (°C)</th>
<th>δSalinity (μatm)</th>
<th>$F_{CO_2}$ “obs” (mmol m$^2$ d$^{-1}$)</th>
<th>$F_{CO_2}$ mod (mmol m$^2$ d$^{-1}$)</th>
<th>δ$F_{CO_2}$ (mmol m$^2$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jan.–Feb. 1991</td>
<td>Kerguelen plateau</td>
<td>Poisson et al. (1994)</td>
<td>$-$0.49</td>
<td>$-$0.005</td>
<td>$-$2.1</td>
<td>$-$2.52</td>
<td>$-$2.68</td>
</tr>
<tr>
<td>2</td>
<td>Feb.–March 1991</td>
<td>Kerguelen plateau</td>
<td>Poisson et al. (1994)</td>
<td>$+$0.35</td>
<td>$+$0.050</td>
<td>$+$0.6</td>
<td>$-$0.72</td>
<td>$-$0.50</td>
</tr>
<tr>
<td>3</td>
<td>April–May 1993</td>
<td>Kerguelen plateau</td>
<td>Louanchi (1995)</td>
<td>$-$0.40</td>
<td>$-$0.330</td>
<td>$-$8.4</td>
<td>$+$0.88</td>
<td>$-$2.20</td>
</tr>
<tr>
<td>4</td>
<td>Feb. 1993</td>
<td>Along 30°E</td>
<td>Poisson et al. (1994)</td>
<td>$-$0.11</td>
<td>$-$0.130</td>
<td>$-$13.5</td>
<td>$-$2.83</td>
<td>$-$5.34</td>
</tr>
<tr>
<td>5</td>
<td>Feb. 1993</td>
<td>Kerguelen–Antarctica 30°E</td>
<td>Poisson et al. (1994)</td>
<td>$+$0.24</td>
<td>$-$0.190</td>
<td>$-$8.0</td>
<td>$-$2.55</td>
<td>$-$2.78</td>
</tr>
<tr>
<td>6</td>
<td>Feb. 1997</td>
<td>Along 143°E</td>
<td>Metzl et al. (1997)</td>
<td>$-$1.20</td>
<td>$+$0.120</td>
<td>$+$3.7</td>
<td>$+$1.26</td>
<td>$+$2.01</td>
</tr>
<tr>
<td>7</td>
<td>March–May 1996</td>
<td>Weddell gyre, prime</td>
<td>Stoll et al. (1997)</td>
<td>$-$0.18</td>
<td>$-$0.040</td>
<td>$-$37.5</td>
<td>$+$1.31</td>
<td>$-$8.13</td>
</tr>
<tr>
<td>8</td>
<td>Oct.–Nov. 1992</td>
<td>Along 6°W, 47–60°S</td>
<td>Bakker et al. (1997)</td>
<td>$+$1.94</td>
<td>$+$0.220</td>
<td>$-$60.6</td>
<td>$+$4.88</td>
<td>$-$7.06</td>
</tr>
<tr>
<td>9</td>
<td>Oct. 1992</td>
<td>Along 56–58°S</td>
<td>Bakker et al. (subm.)</td>
<td>$+$0.13</td>
<td>$+$0.001</td>
<td>$-$40.0</td>
<td>$+$0.14</td>
<td>$-$16.30</td>
</tr>
<tr>
<td>10</td>
<td>March 1989</td>
<td>Along 105°W and 120–130°W</td>
<td>Murphy et al. (1991)</td>
<td>$+$0.16</td>
<td>$+$0.004</td>
<td>$+$9.7</td>
<td>$-$2.16</td>
<td>$+$0.67</td>
</tr>
</tbody>
</table>

Indian Sector (20–150°E)  $-$0.14 $-$0.064 $-$4.5 $-$1.07 $-$2.03 $-$0.9
Jan. to Apr. 10.0 $10^6$ km$^2$ (ice free) $-$0.013 GtC

Pacific Sector (150°E–70°W)  $+$0.16 $+$0.004 $+$9.7 $-$2.16 $+$0.67 $+$3.8
March 15.7 $10^6$ km$^2$ (ice free) $+$0.022 GtC

Atlantic Sector (70°W–20°E)  $+$0.34 $+$0.022 $-$43.6 $+$16 $-$10.06 $+$11.2
Apr. to Nov. 7.01 $10^6$ km$^2$ (ice free) $-$0.230 GtC
3.1. Kerguelen plateau

Fig. 3 shows the modelled and observed $f$CO$_2$ in the area of the Kerguelen plateau. This region is characterized by high spatio-temporal variability both in ocean dynamics and in biological processes. The model simulates quite well the mosaic of potential CO$_2$ sources and sinks as previously described (Poisson et al., 1994). It represents also the observed large-scale north–south features. However, in a few cases differences between modelled and observed $f$CO$_2$ of up to 20 µmol m$^{-2}$ d$^{-1}$ are found. These differences are generally observed for the area near Kerguelen Island (around 50°S) where specific coastal processes occur and are not described by the model.

In January–February 1991 (Fig. 3a) the observations show a mosaic of CO$_2$ sources and sinks. This is related to the intensive topography-circulation interactions by the Kerguelen plateau. The model underestimates both $f$CO$_2$ (Fig. 3a) and the SST (Fig. 3b). The difference in SST can explain most of the discrepancy between observed and modelled $f$CO$_2$. For SST higher than 4°C, the observed salinity is lower and the observed SST is higher than in the model (imposed by the constraints). This implies that in that area the observed hydrographic parameters indicate that less mixing of subsurface waters occurred than induced by the model constraints. In the northern part of the track the modelled and observed $f$CO$_2$ are nearly equal, indicating that the overestimated effect of mixing on the modelled $f$CO$_2$ is largely cancelled out by the lower SST. The model underestimates $f$CO$_2$ by 2.1 µmol on average, leading to an overestimation of the sink by 0.2 mmol m$^{-2}$ d$^{-1}$ (Table 1).

In February–March 1991 (Fig. 3c), the model slightly overestimates the observed $f$CO$_2$ by 0.6 µmol leading to an underestimation of the sink by 0.2 mmol m$^{-2}$ d$^{-1}$ (Table 1). The mean SST is higher by 0.35°C in the model than in the observations (Fig. 3d). This temperature difference would lead to an underestimation of $f$CO$_2$ of 5 µmol. However, the salinity appears to be higher in the
model constraints than in the observations, possibly indicating that mixing of subsurface waters may in reality be more important than in the model. The enhanced effect of mixing, tending to increase the $f\text{CO}_2$, may have compensated the observed temperature difference.

In April–May 1993 (Fig. 3e) the in situ observations revealed that the ocean was nearly in equilibrium with the atmosphere with respect to $\text{CO}_2$. The model results and the observations in this area agree well, except for the region around Kerguelen Island where the model underestimates $f\text{CO}_2$ by more than 40 $\mu$atm. Half of this discrepancy is due to the temperature used as constraints of the model (Fig. 3f), which is lower than the observed temperature by more than 1°C. The in situ observed salinity is much higher in autumn (Fig. 3f) than in summer (Fig. 3b,d). This implies that intensive mixing has occurred (which at the same time leads to a temperature decrease on a seasonal scale), tending to increase the $f\text{CO}_2$. The salinity constraints in the model still represent summer conditions. Hence the mixing effect which depends on salinity profiles (see Section 7) is underestimated by the model in this period. In conclusion, the modelled $f\text{CO}_2$ in the Kerguelen plateau region is underestimated by 8.4 $\mu$atm leading to an overestimate of the sink by 3.1 mmol m$^{-2}$ d$^{-1}$.

3.2. Eastern and western boundaries of the Indian sector

In February 1993 in the western Indian sector (Fig. 4a,c), the in situ observations show that different regimes in $f\text{CO}_2$ distribution can be distinguished: In the south the oceanic $f\text{CO}_2$ is supersaturated which is linked to the occurrence of the Antarctic Divergence (AD) where $\text{CO}_2$-enriched subsurface water is transported into the surface layer (Poisson et al., 1994). North of the AD the $f\text{CO}_2$ is undersaturated with values around 330 $\mu$atm (Fig. 4a,c). On track 5 (see Table 1), the model overestimates $f\text{CO}_2$ in the northern part of the area (between 52°S and 60°S) and underestimates $f\text{CO}_2$ south of 62°S. This is mainly due to different thermodynamical conditions in the in situ observations and climatological model constraints (Fig. 4d). As based on observed hydrological and geochemical properties during CIVA1/WOCE cruise, the AD signal is located around 64–66°S. By contrast, the model by its constraints produces an AD signal around 60°S. The mean difference in $f\text{CO}_2$ due to this inconsistency is about 10 $\mu$atm, leading to an overestimation of the sink by 2 mmol m$^{-2}$ d$^{-1}$ in this area. If the modelled $f\text{CO}_2$ from the 60–50°S region is spatially translated to the 66–56°S region (represented by the dotted lines in Fig. 4a,c), then the agreement between the observations and the model improves significantly. The constraints being climatological properties, they smooth the physical structures in the area.

In February 1997, along the 143°E meridian (Fig. 4e), the observed and modelled $f\text{CO}_2$ data are in good agreement, both showing potential sources. However, the thermodynamical properties observed and those used in the model are rather different (Fig. 4f), the mean SST being lower and the salinity higher in the model than in reality. This implies that in the model the effect of mixing is too large (also see Table 1), which would lead to an overestimation of the $f\text{CO}_2$. On the other hand, correcting the model $f\text{CO}_2$ for the temperature indicates that the modelled $f\text{CO}_2$ may be too high by 15 $\mu$atm. Obviously the overestimation through mixing is largely compensated by the too low temperature in the model. Finally, on average the model slightly overestimates $f\text{CO}_2$ by 3.7 $\mu$atm leading to an overestimation of the CO$_2$ source by 0.6 mmol m$^{-2}$ d$^{-1}$.

3.3. Pacific sector

Fig. 5 shows the modelled and observed $f\text{CO}_2$ along 2 tracks in the Pacific sector. The first track is along 125–130°W (Fig. 5a,b), and the second track is along 105°W (Fig. 5c,d). There is generally a good agreement between hydrographic parameters used in the model and the observed ones (Fig. 5b,d). As a result the differences between modelled and observed $f\text{CO}_2$ are small on both tracks except in the area of the polar front around 50°S and the Antarctic divergence area around 60°S (Fig. 5a). Along 125°W, both modelled and observed $f\text{CO}_2$ are close to the atmospheric CO$_2$ level between 52 and 58°S. Whereas along 105°W, the surface layer appears to be undersaturated by −30 $\mu$atm on the same zonal band (Fig. 5c). Along 125–130°W, the model overestimates $f\text{CO}_2$ by 12.2 $\mu$atm leading to a difference of 3.6 mmol m$^{-2}$ d$^{-1}$ in air–sea CO$_2$ flux. This discrepancy
Fig. 4. Distribution of observed (circles) and modelled (cross shadowed) $f$CO$_2$ values (a,c,e) with the corresponding surface water temperature/salinity diagrams (b,d,f) for tracks 4 (along 30°E), 5 (Kerguelen–Antarctica at 30°E) and 6 (along 143°E), respectively (Fig. 2). During CIVA 1 cruise, the Antarctic Divergence (AD) was identified around 65°S from hydrographic and geochemical parameters. Levitus 94 temperature and salinity climatologies give this signal around 60°S. The dashed line represents modelled $f$CO$_2$ distribution if no mismatch in AD position was found.

Fig. 5. Distribution of observed (circles) and modelled (cross shadowed) $f$CO$_2$ values (a,c) with the corresponding surface water temperature/salinity diagrams (b,d) for tracks 10 in the Pacific sector of the southern ocean along 120–130°W and 105°W, respectively (refer to Fig. 2). Note that the model reproduces the observed spatial variation of $f$CO$_2$ on the same zonal band.

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leads to the conversion of the area from an observed sink of 2 mmol m$^{-2}$ d$^{-1}$ into a source of 1.5 mmol m$^{-2}$ d$^{-1}$. However, this difference between model and observations is largely due to temperature differences (Table 1). Applying a temperature correction (according to the polynomial of Goyet et al., 1993), the discrepancy is decreased to 4.2 μm. The mixing conditions are similar between model and observations as indicated by similar averaged salinities (Fig. 5b).

Along 105°W, the difference between observed and modelled $f$CO$_2$ is less with a value of 5.8 μm (Fig. 5c). The model slightly overestimates $f$CO$_2$, leading to an underestimation of the CO$_2$ sink on that track by 1.5 mmol m$^{-2}$ d$^{-1}$ (−2.3 mmol m$^{-2}$ d$^{-1}$ for the observed fluxes versus −0.7 mmol m$^{-2}$ d$^{-1}$ for the modelled ones). On this track, temperature is not responsible for the discrepancy (Table 1). From salinity (Fig. 5d), it appears that the stratification was more important during the cruise than induced by the climatologies for this period. Thus, the mixing conditions in the model imply higher $f$CO$_2$, whereas the data show typical late summer conditions.

Finally, the difference between data and model on average in the cruise area is 9.2 μm for $f$CO$_2$ (6.0 μm when applying the temperature correction) leading to the conversion of the observed CO$_2$ sink of −2.2 mmol m$^{-2}$ d$^{-1}$ into a small source of 0.7 mmol m$^{-2}$ d$^{-1}$ (Table 1).

3.4. Atlantic sector with Weddell gyre

Fig. 6 shows the modelled and observed $f$CO$_2$ along the tracks in the Atlantic sector. Large underestimations appear in the model results compared to the observations for both the early spring and early winter periods.

In March–May 1996 (Fig. 6a), discrepancies of up to 100 μm are found, but in the northern part the underestimates do not exceed 30 μm. The accompanying SST/salinity diagram (Fig. 6b) shows that the constraints used in the model are in good agreement with the in situ data for SST larger than 0°C. Under the ice (SST −1.8°C) the salinities in the model are underestimated (Fig. 6b), indicating less intensive admixture of subsurface waters in the model than in reality. Different mixing conditions can only partly explain the large discrepancy between the modelled and observed $f$CO$_2$. As the low $f$CO$_2$ values produced by the model are related to a relatively high biological activity in this area at this period (calculated by means of satellite-derived chlorophyll), the effect of biological activity on the $f$CO$_2$ is probably overestimated through these model constraints. The mean underestimation of $f$CO$_2$ by the model amounts to 37.5 μm for this area, leading to an overestimation of the CO$_2$ uptake by 9.4 mmol m$^{-2}$ d$^{-1}$ (Table 1).

Along the 6°W meridian in October–November 1992 (Fig. 6c), the in situ observations show that south of 50°S the ocean was supersaturated in CO$_2$ most of the time. In austral spring the retreat of the sea ice is followed by an increase of the sea surface temperature which induces an increase of the $f$CO$_2$ and a possible supersaturation. The model does not reproduce this feature (Fig. 6c). During the cruise the biological activity was low south of the polar frontal zone (Bakker et al., 1997), and the ice limit was found around 56°S. In the model constraints, the ice limit is defined near 60°S for this period, favouring the development of blooms in the area between 54°S and 60°S because biological activity in the model also depends on the ice cover (see Section 7). In fact, the observational $f$CO$_2$ data show late winter conditions, whereas the model simulates spring conditions for that track. Note that the SST/salinity diagram shows a good agreement between model and in situ observations (Fig. 6d), which suggests that the mixing conditions were satisfactorily simulated by the model. The discrepancy between modelled and observed $f$CO$_2$ thus arises primarily from differences in biological cycle stages.

Along 56–58°S latitude in October 1992 (Fig. 6c) the zonal differences between model and observations decrease eastward. The accompanying SST/salinity diagram (Fig. 6f) discloses that the hydrographic conditions definitely do not describe the real situation. During this period, the melting of the sea ice was just starting (Bakker, 1998). By contrast, the model simulates spring conditions with a low percentage of ice coverage and the beginning of stratification favouring phytoplankton blooms. Deviations both of the physical and biological description of the sea surface layer are responsible for the low level of the $f$CO$_2$ in the model results. The mean $f$CO$_2$ difference of −60.6 μm between model and observations induces an overestimation of the sink
produced by the model by $-16.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 1). Overall, the model underestimates the $fCO_2$ in the Atlantic sector by 43 $\mu$atm on average, leading to an overestimation of the CO$_2$ sink of the Atlantic sector by 11 mmol m$^{-2}$ d$^{-1}$ for the early spring and the early winter periods. These discrepancies cannot be extrapolated to the Indian sector since the differences between model and data are decreasing eastward.

The mean differences between observed and modelled $fCO_2$ are presented in Table 1 for the entire southern ocean. For the Indian sector of the southern ocean the model underestimates the $fCO_2$ by only 4 $\mu$atm which is equal to an overestimation of the CO$_2$ uptake calculated by the model of 0.01 GtC for the January–April period (Table 1). This difference is small compared to the uptake originally calculated by the model for that sector (0.23 GtC yr$^{-1}$), indicating that the model can satisfactorily be applied to this region. This can also be concluded for the Pacific sector where the difference between modelled and observed $fCO_2$ leads to a small underestimation of CO$_2$ sink by 0.02 GtC in March. For the Atlantic sector of the southern ocean the mean difference between modelled and observed $fCO_2$ is as high as $-43.6 \mu$atm from which an overestimation of the CO$_2$ uptake by 0.23 GtC for the April to November period can be calculated. The total uptake modelled for the Atlantic sector of 0.47 GtC yr$^{-1}$ would have to be reduced by 50% to reproduce the observed fluxes.

More generally, when comparing the results of the recent climatology of Takahashi et al. (1997) to the model results in terms of air–sea CO$_2$ gradient $\Delta fCO_2$ annual average, the model gives
observed sea surface in the southern ocean

−9.5 μatm and −8.4 μatm for the Pacific and Indian sectors respectively. These values are very close to the −7.9 μatm estimated by Takahashi et al. (1997) for the whole southern ocean south of 50°S. On the contrary, the Atlantic sector sink is highly overestimated with an average value of −28.5 μatm for the annual ΔfCO₂. Such a large undersaturation may not be surprising for this area in the summer period when a relatively high primary production occurs (compared to other areas of the southern ocean), but this is certainly not the case for the winter period as demonstrated by this comparative study.

4. Sensitivity analysis

As the main uncertainty regarding the CO₂ uptake originates from the Atlantic region, a sensitivity analysis was performed to assess the impact of the physical constraints on the air–sea CO₂ exchange in this region. It should be realized that the constraints fields used in the model are derived from climatological data including early observations, which indirectly introduces a large uncertainty in air–sea CO₂ fluxes (Section 3). In addition, the amount of data for the southern ocean in such data bases is relatively small, particularly for the winter period under the ice. Only when more observational data become available can the performance of the diagnostic model of fCO₂ be improved. The only data bases available at a reasonable space and time grid are those of Levitus and Boyer (1994) and Levitus et al. (1994). Most of the modelling studies currently use these data even when for some periods and some areas statistical extrapolations were performed in these data bases.

The effects of upwelling velocity, the mixed-layer depth (MLD) and the ice coverage are now discussed. In the standard analysis, the upwelling velocity was taken to be 45 m yr⁻¹ as reported by Gordon and Huber (1990). However, in certain areas the upwelling velocity may reach much higher values (Gargett, 1991). Fig. 7a shows the monthly average of the MLD derived from Levitus (1994) as used in the model. However, the MLD cycle derived from the constraints fields does neither exactly agree with the observations nor with our knowledge of the southern ocean (long

![Fig. 7. Monthly averages of the mixed-layer depth (a) and the ice coverage (b) used as constraints in the modelling study in the Atlantic sector of the southern ocean (black line). The dotted line represents the same constraints which are derived from the observed SST and satellite-derived wind speeds fields changes and used for the sensitivity analysis. Both mixed-layer depth and ice coverage used in the standard simulation show a smooth seasonal signal.](image_url)
winter period of 9 months and short spring–summer period of 3 months for the seasonal ice zone, SIZ). Typical examples of this are that the depth of the mixed-layer does not exceed 135 m for the June–August period and the spring conditions start in September–October. In addition, differences in the ice limit and hence in the SIZ definition were noticed between the observations and the model constraints for the early winter and early spring. Fig. 7b represents the monthly average of the percentage ice coverage. In Fig. 7a,b the dotted line represents the conditions used for the sensitivity tests.

The results of five simulations are presented in Table 2 in terms of annual mean $\Delta$CO$_2$ and annual CO$_2$ uptake. The standard simulation results in a mean $\Delta$CO$_2$ of $-28.5 \mu$atm for the whole Atlantic sector inducing a CO$_2$ uptake of 0.47 GtC yr$^{-1}$. If the upwelling velocity is increased from 45 m yr$^{-1}$ (standard run) to 90 m yr$^{-1}$ for the whole area, the $\Delta$CO$_2$ is reduced by about 30% and the CO$_2$ uptake by 25%. Changing the MLD according to Fig. 7a leads to a reduction of 40% in $\Delta$CO$_2$ and of 45% for the CO$_2$ uptake. Changing the ice coverage according to Fig. 7b does not affect $\Delta$CO$_2$ but the CO$_2$ uptake is reduced by 20% because less surface is available. If all these effects are taken into account the $\Delta$CO$_2$ and the CO$_2$ uptake are reduced by more than 60%. Thus, the CO$_2$ uptake by the southern ocean is very sensitive to the changes in these dynamical properties. These changes are also sensitive to variations of climatic conditions. For example, in a colder year the SST is relatively low which affects the distribution of the fCO$_2$ but also affects the ice coverage. The impact on the air–sea fluxes can be either less uptake because of the surface area for air–sea exchange is reduced, or more uptake because the SST decreases the fCO$_2$. Moreover, in a colder year the mean wind speed is generally elevated, which promotes more air–sea exchange of CO$_2$ but also more mixing of CO$_2$–rich subsurface water. It should be added that such deliberations are particularly relevant for the southern ocean because the largest CO$_2$ exchange coefficients (deduced from satellite-derived wind speeds) are found in this region (Boutin and Etcheto, 1997).

In summary, the uncertainties in the CO$_2$ uptake of the southern ocean are mainly due to the lack of observational data and to the lack of an accurate knowledge of the seasonal variation of circulation features in that area. More measurements and a better representation of the SIZ processes in the model would help to improve the quantification of the southern ocean CO$_2$ sink.

5. Conclusions

This comparative study shows that our model reproduces well the zonal and meridional distributions and the seasonal signal in the Indian and Pacific sectors of the southern ocean. On the other hand, large discrepancies between modelled and observed fCO$_2$ are found in the Atlantic sector mostly due to the constraints used in the model, translating into a difference in the annual CO$_2$ uptake by the Atlantic sector of 0.2–0.3 GtC yr$^{-1}$. However, this difference in annual uptake was calculated, presuming that the seasonal cycle in the model and in reality are exactly identical. This implies that any difference between modelled and observed fCO$_2$ counts to the full extent. However, there may also exist a temporal shift in the seasonal cycles of the model results and the in situ observations. In this case the same levels of fCO$_2$ could be reached in the model and in reality but in a different stage of the season. This would result in a much smaller calculated difference in the annual CO$_2$ uptake than the 0.2–0.3 GtC yr$^{-1}$ calculated above. A shift, or more generally, a difference in the seasonal cycles of the model and the real ocean is not unlikely as interannual differences in carbon cycling do undoubtedly

<table>
<thead>
<tr>
<th>Simulations</th>
<th>Test no.</th>
<th>$\Delta$CO$_2$ (\mu atm)</th>
<th>$\Delta$CO$_2$ flux (Gt C yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard</td>
<td>0</td>
<td>$-28.5$</td>
<td>$-0.47$</td>
</tr>
<tr>
<td>$K_z = 90$ m yr$^{-1}$</td>
<td>1</td>
<td>$-20.4$</td>
<td>$-0.35$</td>
</tr>
<tr>
<td>change MLD</td>
<td>2</td>
<td>$-17.3$</td>
<td>$-0.29$</td>
</tr>
<tr>
<td>change ice cover</td>
<td>3</td>
<td>$-26.9$</td>
<td>$-0.37$</td>
</tr>
<tr>
<td>all together</td>
<td>4</td>
<td>$-11.9$</td>
<td>$-0.18$</td>
</tr>
</tbody>
</table>

Table 2. Results of the sensitivity tests for the model results of the Weddell gyre and its impact on the air–sea CO$_2$ flux; the change in mixed-layer depth and ice cover were done according to Fig. 7: the simulation “all together” calculates the result when all three sensitivity tests are applied at the same time; for more details, see text.
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occur. Note that in our discussion in Section 3 seasonal shifts were invoked to explain specific results. Also in our previous study with the model (unpublished results) seasonal shifts in the simulation of dissolved inorganic carbon in the Weddell gyre were discerned, where in light of the present discussion the important outcome was that the seasonal amplitude of variations was correctly simulated. As indeed the model is based on monthly variations of the constraints which are climatologies of observed fields, the seasonal signal (the seasonal amplitude) is generally well reproduced. It is the lack of information in the seasonal ice zone which means that just in this area the absolute value of $f_{CO_2}$ is underestimated. It is worth adding that the $f_{CO_2}$ tracks in the Atlantic sector, that were used to validate the model (Table 1), originate from seasons (tracks 8 and 9: early spring; track 7: beginning of the winter) in which the physical conditions in the ocean were in a state of changing. This contrasts with the tracks in the Indian or the Pacific sectors, which originate from more or less stable summer conditions (Table 1). Thus, it is not surprising that, if differences exist in the seasonal cycles of the model and the real ocean, these would become visible in the Atlantic sector. In conclusion, the large difference between the modelled and observed $f_{CO_2}$ in the Weddell gyre is admittedly alarming, but as this may be explained by a seasonal shift this makes the mismatch in fluxes much less dramatic.

Thus, the model estimate for the annual $CO_2$ uptake of the southern ocean has to be moderated for the Weddell gyre by 0.2–0.3 GtC at most, leading to an uptake of 0.2 GtC yr$^{-1}$ as a lower boundary for latter area against 0.47 GtC yr$^{-1}$ for our earlier estimate (Section 2). By contrast, in the Indian sector the model reproduces quite well the observed signal in summer, mostly because of a better representation of the mixing conditions in the constraints fields. A striking result is the good simulation of the high variability in $f_{CO_2}$ encountered in the area of the Kerguelen plateau (in the Indian sector). This puts confidence in our approach using this diagnostic model for $f_{CO_2}$, provided the physical constraints on the model are reliable. Moreover, the ability of the model to reproduce a correct $f_{CO_2}$ signal in the Pacific sector is very encouraging since the model is highly dependent on the definition of subsurface parameters, and except the GEOSECS data, we had no more cruises for defining DIC and TA in that sector (Section 2). Extrapolating monthly $f_{CO_2}$ fields over large areas by using the changes in climatological constraints may be a powerful tool to successfully estimate the global oceanic $CO_2$ uptake.

The model estimate for the total $CO_2$ uptake of the southern ocean of 0.9 GtC yr$^{-1}$ has to be corrected for the discrepancy in the Atlantic sector. A more realistic estimate is 0.6–0.7 GtC yr$^{-1}$. It is worth noting that this value approaches the one from Tans et al. (1990) as reestimated by using satellite-derived wind-speeds instead of climatological ones (Section 2). The range of the new estimate is introduced due to the seasonal incongruency of the model and the real ocean. Albeit we verified our earlier estimation, some uncertainty remains, which is mainly due to the lack of winter data particularly in the seasonal ice zone.

Interannual variations in climatic conditions and hence in the constraints of the sea surface $CO_2$ system strongly affect the oceanic $CO_2$ uptake as demonstrated in this study. Francey et al. (1995) and Keeling et al. (1995) have also shown that the interannual climate variations strongly affect the global carbon budget. Lévy (1996) demonstrated that the mesoscale variability of the dynamic structure of the ocean may lead to an underestimation of the primary production and hence to uncertainty in the mesoscale $f_{CO_2}$ distribution. These spatio-temporal variabilities may induce large uncertainties in the carbon budget. As our model uses monthly climatological constraints, it is obviously unable to reproduce such local and time-specific signals in the $f_{CO_2}$ distribution.

One way to progress is to relate the MLD changes to changes in wind speed and SST (which are available from satellite at weekly and interannual scales), or to use MLD values from realistic general circulation models. Unfortunately, there are still some uncertainties in describing the oceanic circulation in the OGCMs, particularly for the southern ocean (Orr et al., 1997), and more data are necessary to better constrain the models at global and regional scale. A better representation of the sea surface $f_{CO_2}$ spatio-temporal variability will give better constraints on atmospheric models and hence on the global carbon budget.
6. Acknowledgements

We thank Dr. Jacqueline Boutin and Dr. Jacqueline Etcheto (LODYC, Paris) for providing the satellite-derived wind-speed fields. Dr. Nicolas Metzl (LPCM, Paris) is acknowledged for the data processing of the Tasmania-Antarctic cruise in 1997. We thank the captains and crews of the RV Polarstern and Marion-Dufresne for their continuous help on board. This work was supported by the PROCOPE program of cooperation between AWI Bremerhaven and LPCM Paris, and the “JGOFS-France Modélisation” program. Dr. Raymond G. Najjar and Prof. Andrew J. Watson are acknowledged for their comments on an earlier version of the manuscript. We are grateful to two anonymous reviewers for their constructive criticisms on this study.

7. Appendix

The one-dimensional diagnostic model of sea surface $f$CO$_2$ is based on the translation of variations in monthly constraints into $f$CO$_2$ variations. The main processes controlling sea surface $f$CO$_2$ variations are estimated at each time step as a function of the variations of the constraints. These physical and biogeochemical processes are: the air–sea exchange, the mixing effect, the thermodynamics of the carbonate system and the biological uptake and release. Each process affects DIC, TA and TIN the three state variables of the model. The effects on $f$CO$_2$ changes are computed at each time step from DIC, TA, temperature and salinity.

7.1. Air–sea exchange effect

The air–sea exchange of CO$_2$ is calculated according to Wanninkhof (1992). At each time step the flux at the air–sea interface ($F_{CO_2}$) is calculated as a function of the wind speed, the temperature and the salinity and translated into a change of dissolved inorganic carbon:

$$F_{CO_2} = (1 - g)Ks_{CO_2} \Delta f/CO_2,$$

where $g$ is the ice coverage, $K$ the piston velocity, $s_{CO_2}$ is the CO$_2$ solubility and $\Delta f/CO_2$ the air–sea $f$CO$_2$ difference. The air–sea exchange affects only DIC in the mixed-layer depth and the variations of the latter according to this process is computed at each time-step as follows:

$$\delta DIC = F_{CO_2} \delta t/Z,$$

where $Z$ is the mixed-layer depth.

7.2. Mixing effect

The mixing effect is estimated as the entrainment/detrainment effect described in Peng et al. (1987) as well as through the input of subsurface properties into the surface layer by the general southern ocean upwelling. These processes affect inorganic nitrogen, alkalinity and dissolved inorganic carbon and are dependent on the mixed-layer depth and the surface–subsurface gradient of the geochemical properties. The subsurface properties are maintained constant during the whole year of simulation. Changes due to the mixing effect are calculated according to:

$$\delta G/\delta t = \delta Z/\delta t (G_b - G_s)/Z + K_z(G_b - G_s)/Z,$$

where $G$ is the geochemical property, $G_b$ and $G_s$ are the concentrations of $G$ in the subsurface and surface boxes, respectively, $Z$ is the mixed-layer depth and $K_z$ is the upwelling velocity.

7.3. Biological effect

Most of the parameterizations of the biological effect on $f$CO$_2$ are adapted from Taylor et al. (1991).

7.3.1. Net primary production. The variation of chlorophyll biomass is expressed as:

$$\delta Chl/\delta t = (U - Q)Chl,$$

$U$ is the growth of the phytoplankton and is expressed as a Michaelis–Menten function of the nutrient total inorganic nitrogen (TIN):

$$U = (1 - g)U_m(TIN/(TIN + K_m)).$$

In this expression $U_m$ is the maximal growth rate and $K_m$ the half-saturation constant of the growth on TIN. $U$ is calculated at each time-step also as a function of the ice coverage $g$. If $g = 1$, no growth of the phytoplankton can occur. $Q$ represents the total loss of organic matter. It is deduced from $U$ and Chl changes in the surface layer following the equation:

$$Q = U - \delta \ln(Chl)/\delta t.$$
Finally, the variation of TIN with time is:
\[
\delta \text{TIN}/\delta t = -(U - R_s) Q \text{Chl} / \text{Chl}
\]

In this expression, \( R_s \) represents the mineralization factor in the surface layer, N/Chl is the nitrogen to chlorophyll ratio in phytoplankton.

The maximal growth rate of the phytoplankton, \( U_m = 1 \text{ d}^{-1} \), was obtained by means of sensitivity tests as the one which best represents the seasonal variation of DIC at several locations (unpublished). If \( U_m \) is increased to 2, the DIC level is reduced by 10 \( \mu \text{mol/kg} \) and the seasonal signal will be overestimated. In contrast, a smaller value of \( U_m (0.5 \text{ d}^{-1}) \) leads to a higher value of DIC and a smoothening of the seasonal signal. The model appears to be less sensitive to the upwelling rate as \( f \text{CO}_2 \) changes with less than 3 \( \mu \text{atm} \) for a 10 m/yr change. The removal factor \( R_s \) (factor of regeneration) is taken at 0.5 for the southern ocean according to Olson (1980) and Minas and Minas (1992).

7.3.2. Export production and \( \text{CaCO}_3 \) precipitation
The exported production is expressed in carbon units as:
\[
P_{\text{exp}} = (1 - R_s) Q \text{Chl} \text{C/Chl},
\]

where C/Chl is the carbon to chlorophyll ratio in phytoplankton. We assume that 20% of the exported production consists of \( \text{CaCO}_3 \).

7.4. Estimating DIC and TA changes
Finally, the total variations of DIC and TA are:
\[
\delta \text{DIC}/\delta t = [(\delta \text{TIN}/\delta t)/(\text{C/N}) - 0.2P_{\text{exp}}]

+ [(\delta Z / \delta t)(\text{DIC}_b - \text{DIC}_e)]/Z

+ K_z(\text{DIC}_b - \text{DIC}_e)/Z

+ [F_{\text{CO}_2}]/Z,
\]
\[
\delta \text{TA}/\delta t = [-(\delta \text{TIN}/\delta t)(1/1) - 2(0.2P_{\text{exp}})]

+ [(\delta Z / \delta t)(\text{TA}_b - \text{TA}_e)]/Z

+ K_z(\text{TA}_b - \text{TA}_e)/Z,
\]

where \( \text{C/N} \) is the Redfield ratio (Redfield et al., 1963). These variations are translated into \( f \text{CO}_2 \) variations using equilibrium constants of Goyet and Poisson (1989). The first term on the equations right represents the biological effect on DIC and TA variations, the second one represents the mixing effect, and the third one (only for DIC) the impact of the air–sea \( \text{CO}_2 \) exchange.

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Francey, R. J., Tans, P. P., Allison, C. E., Enting, I. G., Goyet, C. and Poisson (1989). The first term on the equations right represents the biological effect on DIC and TA variations, the second one represents the mixing effect, and the third one (only for DIC) the impact of the air–sea \( \text{CO}_2 \) exchange.