Supporting Online Material for

Saturation of the Southern Ocean CO₂ Sink
Due to Recent Climate Change

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Supplementary online material

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This supplementary material presents additional information on the models and methods used as well as an evaluation of the results of the inversion and of the process model.

I. Atmospheric inverse model

Full details of the atmospheric inverse model are given in Rödenbeck (2005; S1). The availability of observed CO₂ data are shown in Fig. S1. The data are not filtered prior to its use by the inversion. CO₂ fluxes are estimated on ~8°x10° pixels and daily time steps. To stabilize the estimation, a-priori spatial and temporal correlations are specified in a Bayesian framework, on the ocean with scales on the order of 630 km (roughly 6° latitude x 8° longitude at 45°S) and 2 weeks, respectively. The a-priori flux, however, is constant in time, such that all interannual and seasonal variability of the result is fully attributable to the information contained in the atmospheric data (deconvolving transport variability). Compared to (S1), we removed one Southern Ocean station and extended the inversion by two years.

The main differences between (S1) and the previously published version of Rödenbeck et al. (2003, S2) include i) a larger station set, ii) the use of individual flask or hourly concentration data (rather than monthly means) weighted by data density, and allowing sub-monthly flux variations, iii) the use of a flux model formulation to specify a-priori information, allowing more detailed choices to be taken (e.g. timescale-dependent
weighting and correlation patterns), iv) the inverse problem has been solved by an iterative method, rather than a matrix method.

Compared to other published inversions (S3-S6), we analysed the longest time series (24 years), including data up to 2004. The statistical significance of the difference of trends could not yet be established from the shorter periods. We also have set up our inversion to minimize spurious variability by i) using a constant station network, ii) using the original data (not monthly means or interpolated data), iii) using interannual meteorological drivers fields from the real years, and iv) not using a-priori aggregated regions. iv) and i) have the largest impact on the inversion results and explain many of the differences to previous published inversion results (Fig. S2). Note that iv) also implies differences in regional a-priori standard deviations compared to a-priori aggregated regions.

II. Evaluation of the results of the inversion

To check the results of the inversion, we transported the inverted fluxes forward in the same atmospheric model and compared the results to the original atmospheric CO2 observations. We use Taylor diagrams to summarize the results quantitatively. All results are monthly-averaged and deseasonalized before the comparison. No further smoothing is applied.

Fig. S3 shows the correlation and normalized Standard Deviation (inversion/observations) of CO2 for each of the three stations in the Southern Ocean and
each test. This figure evaluates the ability of the transport model to reproduce the inter-hemispheric transport and the seasonality. All tests correlate with the observed signal with at least $r=0.92$. All tests reproduce also over 82% of the observed Standard Deviation. Tests Is2, Is4, It2, and It3 were the least successful.

Fig. S4 shows the same information, but we subtracted the CO$_2$ concentration averaged between the three Southern ocean stations from each time series. This figure evaluates the ability of the transport model to reproduce the regional variations. As expected, the match to the station data is less good regionally. Nevertheless, most tests correlate with the observed residual signal with at least $r=0.80$ except for Is2 and Is4. I, Is1, Is3 and Is5 reproduce at least 60% of the regional standard deviation, while Is2, Is4, and the three transport tests showed poor regional results.

Based on the capacity of the various tests to reproduce the Southern Ocean mean and regional variability in the observations, we conclude that:

1. I, Is1, Is3, and Is5 are all reasonable representations of CO$_2$ fluxes in the Southern Ocean,
2. Is2, Is4, and the three transport tests deteriorate the results compared to I,
3. Id1, Id2, and Id3 are all similar to It1 (coarse grid inversion) and show that our conclusions are robust with respect to the selection of sites.

**III. Pulse response model**
The pulse response function was calculated with the HILDA box model (S7) by increasing atmospheric CO$_2$ by 10 PgC above its 1990 concentration, and following its decay in time (S8). We calculated the oceanic CO$_2$ sink as a function of time by integrating all the pulse functions in time for every annual increase in atmospheric CO$_2$ starting in 1765. As the pulse response calculation gives results for the global ocean alone, we scaled our results by the area of the Southern over the global Ocean (0.17).

**IV. Noise model**

The significance of the trend is described in note (16) of the main text.

The significance of the correlation coefficient between the inversion results and the SAM was estimated using the deasonalised raw data by generating AR(1) models of both timeseries (these models have expectation values of lag-1-autocorrelation and variance equal to that observed). A 10000-member Monte Carlo test was performed. The test gave a P-value of <0.005, based on a two-tailed test (i.e. fewer than 50 correlation coefficients were larger in magnitude than the observed correlation coefficient in the sample of 10000). We validated the noise models by comparing the spectra of the carbon flux and SAM with those of their respective noise models, and found that they matched well. The significance of the correlation coefficient of the pre-whitened series (0.166), was then assessed by deriving a student-t statistic and assessing its statistical significance using the total number of months as the number of degrees of freedom. This method also indicated that the two series are correlated with a P-value of <0.005.
V. Contribution of the SAM

It is difficult to quantify the proportion of the trend in CO₂ sink that is attributed to the changes in the SAM because CO₂ fluxes have a long equilibration time with the atmosphere (8-12 months), thus the relationship between CO₂ fluxes and the SAM is likely different for interannual and decadal time scales. Using the observed un-filtered time series, the inferred rate of increase is +0.02 PgC/y per unit SAM (hPa) from the monthly mean regression. Using the filtered time-series, (smoothed with a Hanning filter that removes the variability < 1year), the correlation increased to r=0.51 and the regression to 0.06±0.01 PgC/y per unit SAM. We used the filtered time-series to infer the contribution of the SAM to minimize the effect of high-frequency variations. Since the SAM increased by 0.64 hPa between 1981 and 2004, the inferred rate of increase in sea-air CO₂ flux during this period is +0.015 PgC/y per decade caused by changes in the SAM alone. Thus with this analysis, the variations in the SAM can account for ~20% of the 0.08 PgC/y per decade weakening of the Southern Ocean sink of CO₂. This fraction is likely a lower bound because of the long equilibration time of CO₂.

VI. Process model

The oceanic process model is based on the OPA General Circulation Model coupled to an ecosystem model that represents two phytoplankton groups, two zooplankton, co-limitation by P, Si, Fe and light, and has no nutrient restoring (S9). The physical model is global and has a resolution of 2°x 0.5-1.5°, with 30 vertical levels. The model transports tracers along isopycnals, parameterises eddy mixing (S10), and computes vertical
diffusion throughout the water column using a turbulent kinetic energy model (S11). Thermodynamic sea ice is included (S12). This model is an updated version of the published IPSL carbon model. Previous versions of this model reproduced reasonably well the observed uptake of CFCs in the Southern Ocean (S13), the interannual variability in air-sea CO₂ flux in the equatorial Pacific (S3) and Northern sub-tropics (S14), and have been used for projections of atmospheric CO₂ (S15) and ocean acidification (S16).

The model is initialized in 1948 with observed physical and biogeochemical fields. Dissolved Inorganic Carbon (DIC; the sum of carbon in the form of CO₂, HCO₃⁻ and CO₃²⁻) is corrected to its 1948 concentration by using a model estimate of the 1994-1948 uptake of anthropogenic CO₂ (S9).

The model is forced with daily winds and water fluxes from NCEP reanalysis (S17). Heat fluxes and evaporation are computed using a bulk formulation based on the difference between surface air temperature from NCEP re-analysis, and the sea surface temperature produced by the model. We perform two simulations. In the first simulation, we used NCEP forcing for each year between 1948 and 1967, and repeated the forcing for year 1967 after that year. This simulation allowed us to estimate the contribution of atmospheric CO₂ alone (after 1967). In the second simulation, we used the NCEP forcing for each year from 1948 to 2004. The difference between the two simulations allowed us to isolate the impact of climate (winds, temperature, water fluxes) from that of atmospheric CO₂ alone. We use year 1967 because this is the first non-El Niño year after the minimum in the SAM around 1965. To test the impact of our choice of constant
forcing year, we repeated the first simulation using years 1948 or 1979. The results are similar to the simulation using the constant forcing from year 1967 (Fig. 3 in the main text).

To isolate the impact of changes in temperature from the total changes (Fig. S5), we repeated a simulation using the process model with the daily NCEP forcing corresponding to the actual year of simulation, but we used monthly mean climatological temperature to compute the solubility of CO$_2$ and equilibrium constants in seawater.

To estimate the contribution of changes in biological fluxes to DIC (Fig. S5), we calculated the vertical derivative in export production between the model simulation using daily NCEP atmospheric forcing, and the model simulation using the constant atmospheric forcing. The increased export production is sustained by the increased nutrient supply from enhanced upwelling.

To estimate the contribution of changes in overturning circulation to DIC (Fig. S5), we multiplied the change in water transport South of 60°S (5.1 Sv) by the vertical DIC gradient between the top 500 m (2251 µmol/L) and the deep ocean (2321 µmol/L). This product gives a decrease in deep ocean DIC of 0.14 PgC/y, which when sustained for decades reduces the deep ocean DIC by a few PgC (Fig. S5). The natural DIC can escape to the atmosphere when it reaches the surface.
The difference in DIC between the simulation with observed forcing and the simulation with constant forcing shows that with observed forcing, DIC accumulates in the surface waters, and decreases in intermediate and deep waters (below 700 m; Fig. S5). The contribution of changes in temperature shows a decrease in DIC in surface waters attenuated with depth. The contribution of changes in biological export production shows an increase in DIC in the sub-surface (below the mixed layer) also attenuated with depth. The contribution of physical processes is estimated from the residual. The residual includes upwelling and other transport processes as well as the contribution of air-sea CO₂ exchange. Physical processes are responsible for the decrease in DIC in intermediate and deep waters. The simulation with constant forcing has an overturning of 4.6 Sv South of 60ºS compared to 9.7 Sv in the real forcing simulation. The changes in the modeled overturning circulation can account for the totality of the decrease in intermediate and deep ocean DIC estimated from the residual.

The accumulation of DIC in the surface ocean under observed forcing accelerates the acidification of surface waters by 0.05 pH units over 30 years, with the largest effect centered around 65ºS (Fig. S3). This amount is half of the pH decrease during 1750-1994 caused by the uptake of anthropogenic CO₂ alone (S18). Because of the cold temperature and low alkalinity/DIC ratio of the Southern Ocean, a pH decrease of 0.1 is estimated to cause a shallowing of the aragonite saturation depth by 1000 m, i.e. the depth at which the CaCO₃ that forms some plankton shells becomes undersaturated (S19). Based on the projected penetration of anthropogenic CO₂, the aragonite saturation depth is projected to reach the surface by 2050 and to cause a reduction in the calcification of marine
organisms and a shift in marine ecosystem composition (S16). Our model results suggests
that the surface undersaturation is sensitive to changes in the natural carbon cycle, and
thus that the timing of the surface undersaturation will be hard to predict based on
estimates of anthropogenic carbon alone.

We ran the process model forward in time by repeating the forcing of year 1967 further in
one simulation, and by repeating the forcing of year 2004 in a second simulation. Both
simulations were run up to year 2070 (results not shown). The model results show that
once the atmospheric forcing has stabilized, it takes 25 years for the ocean CO₂ sink to
recover from the perturbation and a further 25 years for the integrated changes in the sink
to return to zero. After this time period, the CO₂ sink becomes larger in the simulation
where the 2004 forcing is used, consistent with published model estimates which show
that stratification of the ocean reduces the total uptake of anthropogenic CO₂ on a century
time-scale (S20-S21).

VII. Evaluation of the results of the process model

We evaluated the results of the PISCES-T ocean GCM with coupled biogeochemistry
model as follows: (VIIa) For the mean state, we evaluated the capacity of the model to
reproduce the sea-air CO₂ fluxes observed by different methods. We also evaluated the
contribution of biological export production; (VIIb) for the anthropogenic perturbation,
we evaluated the capacity of the model to reproduce the vertical penetration of
anthropogenic CO₂; (VIIc) for the variability, we evaluated the ability of the model to reproduce the local variations in surface ocean pCO₂ observed in the Indian ocean.

VIIa.

Comparison to air-sea CO₂ flux

The process model results fall within the range of observed estimates. It reproduces a larger CO₂ sink in the Southern Sub-tropics compared to the Southern Ocean as in most of the data-based estimates (Table S1). The atmospheric inversion of Roy et al. (2003; S26) and the ocean inversion of Mikaloff Fletcher et al. (2006; 2007; S24-S25) are particularly adequate to estimate the CO₂ sink because the former focused its analysis to minimize biases in the interpretation in the Southern Ocean, and both estimates are independent of the poorly known gas exchange coefficient. Our model is closest to these two data-based estimates. The two estimates based on pCO₂ observations (S22-S23) provide additional independent support that the CO₂ sink in the Southern Ocean is between 0.1 and 0.6 PgC/y.

For comparison, we included in Table S1 the mean CO₂ sink from the inversion results of Gurney et al (2004; S27) and those from our inversions. Our inversion results reproduce the gradient between the Southern Sub-tropics and the Southern Ocean, but slightly underestimate the sink in the Southern Ocean with respect to the estimates based on pCO₂ or ocean interior data. However, this underestimation has no effect on our estimate of the trend because the mean and the variability have essentially no a-posteriori correlations
Previous studies have shown that inversions are more suited to estimate the variability in CO₂ fluxes than the mean (S2-S3).

**Comparison to biological export**

The process model reproduces relatively well the surface chlorophyll a observed by SeaWiFS satellite (Fig. S6). The model produces a biological export at 100 m of 1.53 PgC/y in the 45°S-90°S latitude band, in very good agreement with the estimate of 1.72 PgC/y based on observations (28; Fig. S6). The model reproduces relatively well the observed regional patterns of export, including the high export in the South Atlantic basin and along most coastal regions except the coast of Chile (underestimate) and the South of Australia (overestimate). The model underestimates the export in the Pacific and Indian sectors, although the chlorophyll a concentration is well reproduced. However, the uncertainty in the regional export estimates is too high to draw firm conclusions.

**VIIb Comparison to anthropogenic carbon storage**

To estimate the degree to which the process model is able to reproduce observed trends in anthropogenic carbon, we compare the model results with the observed storage of anthropogenic carbon (S18; Fig. S7). This comparison is not strictly accurate because i) our simulation spans 1948-2004 whereas the observational-based estimate is for 1750-1994, and ii) our simulation include both changes in natural carbon as well as the uptake of anthropogenic CO₂. Nevertheless, the comparison shows that the model produces an
increase in Dissolved Inorganic Carbon (DIC) that is maximal at the surface sub-tropics as observed and that penetrates deeper at the location of intermediate water formation. The results of the model are well within the uncertainty of the observational results (29). The deep ocean decrease in the modeled DIC is caused by the ventilation of natural DIC as discussed in Section VI.

**VIIc Comparison to in-situ data**

We compared the results of the process model to observations of the partial pressure of CO$_2$ (pCO$_2$) that were repeated along ~65°E in the Indian ocean in January of 1998, 2000, 2001 and 2002 (S30-S31, Fig. S8). The data were binned on 1° boxes along the ship tracks. To calculate the anomalies, the mean of the four cruises was calculated and removed from each individual cruise. This treatment was applied separately for the western and eastern ship tracks, which are separated by up to 30° of longitude. The process model was sampled at the same day and at the model box which corresponds to the location of the measurements. The seasonal cycle was removed using the same treatment as with the data. Both data and model were smoothed in latitude using a Hanning filter of 5°.

The process model is able to reproduce some of the meridional structures of the anomalies in pCO$_2$. In 1998 the south-Indian experienced positive anomalies in the sub-tropics and negative anomalies in the south. In years 2000 and 2001 anomalies are relatively low and homogeneous. In 2002 negative anomalies are observed and modeled
in the subtropics whereas they are positive at high latitude. The cruises in 1998 and 2000 are not as well reproduced as the later cruises, but even during these years, the amplitude of the modeled variability is similar to that observed. The comparison to the in-situ data lends support to the process model results, and in particular to its ability to reproduce the dominant process controlling the interannual variability in CO₂ fluxes. However, the comparison could be made only in January for four years along two transects. It is possible that variability is larger in other regions or periods of the year.

Figure Captions

Figure S1. CO₂ concentration record used in the inversions. The right hand stars specify which station was used for the 11, 17, 24 and 40 sites inversions. The full details of the site location can be found in (1).

Figure S2. Comparison of sea-air CO₂ flux anomalies in the Southern Ocean (PgC/y) between our standard inversion on the fine and coarse transport grid, various tests where we adopted set-up choices from previously published inversions (all using the coarse grid transport model), and other published estimates.

Figure S3. Taylor diagram showing the normalized standard deviation of the growth rate produced by the inversions after they have been transported forward in the TM3 model, and the correlation with observed atmospheric CO₂ growth rate. Observations are for Palmer station (red), Amsterdam Island (blue) and South Pole (green). The various
inversions tested are shown on each panel and described in the main text. The data have not been smoothed.

**Figure S4.** Same as S4 but after the average of the three Southern Ocean stations has been removed from each time-series.

**Figure S5.** Zonal mean changes in the carbon content of the ocean (µmol/L) in 2000-2004 caused by changes in atmospheric forcing estimated with a process model. Modeled changes are computed as the difference between a simulation where the observed daily atmospheric forcing is used to force the model over the 1948-2004 period, and a simulation where the atmospheric forcing of the year 1967 is repeated from that year onwards. Negative values in the deep ocean are caused by the ventilation of natural carbon. The left panel shows the total change in TgC/m (black) and the contribution of changes in biological fluxes (green), temperature (red), and all physical processes (blue). The top panel shows the changes in surface pH between the two simulations.

**Figure S6.** Comparison of modeled (a) sea surface chlorophyll a and (b) biological export production at 100 m (mol/m²/y) with observations from (c) SeaWiFS satellite and (d) ocean inverse study (S28).

**Figure S7.** Comparison of the changes in zonal mean Dissolved Inorganic Carbon (DIC; µmol/kg) between (top) the process model for the years 2000-2004 and 1955-1959 and (bottom) the estimated storage of anthropogenic DIC between 1750 and 1994 based on
indirect observations (S18). Values less than 5 µmol/kg are below the detection limit of the observation-based estimate and are thus shaded in gray in the lower panel.

**Figure S8.** Sea-air $pCO_2$ anomaly from the OPA-PISCEST model (black) and from observations in the south-Indian ocean during the OISO cruises (red) in 1998, 2000, 2001 and 2002 (S30-S31). The treatment of the data is described in the text.

**Table S1.** Comparison of estimated CO$_2$ sinks for different latitude bands and methods (in PgC/y).

<table>
<thead>
<tr>
<th>Method</th>
<th>Southern Ocean</th>
<th>Southern Sub-tropics</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process model</td>
<td>0.2 (45ºS-90ºS)</td>
<td>1.1 (18ºS-45ºS)</td>
<td>This study (1995-2004)</td>
</tr>
<tr>
<td>Ocean $pCO_2$ observations</td>
<td>0.6 (45ºS-90ºS)</td>
<td>0.9 (18ºS-45ºS)</td>
<td>Takahashi et al., 2002¹ (22), circa 1995</td>
</tr>
<tr>
<td>Ocean $pCO_2$ observations</td>
<td>&gt; 0.17 (50ºS-90ºS)</td>
<td></td>
<td>Metzl et al, 2006 (23), circa 2000</td>
</tr>
<tr>
<td>Ocean inversion</td>
<td>0.3 (44ºS-90ºS)</td>
<td>1.1 (18ºS-44ºS)</td>
<td>Mikaloff Fletcher 2006,2007(24-25), 1995</td>
</tr>
<tr>
<td>Atmospheric inversion</td>
<td>0.1 (50ºS-90ºS)</td>
<td>1.2 (18ºS-50ºS)</td>
<td>Roy et al., 2003 (26), 1980-1997</td>
</tr>
<tr>
<td>Atmospheric inversions</td>
<td>0.6±0.4 (45ºS-90ºS)</td>
<td>-0.1±0.7 (18ºS-45ºS)</td>
<td>Gurney et al., 2004 (27), 1992-1996</td>
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<td>Atmospheric inversion</td>
<td>0.1 (45ºS-90ºS)</td>
<td>1.0 (18ºS-45ºS)</td>
<td>This study, 11 sites (1981-2004)</td>
</tr>
<tr>
<td>Atmospheric inversion</td>
<td>0.1 (45ºS-90ºS)</td>
<td>0.8 (18ºS-45ºS)</td>
<td>This study, 17 sites (1986-2004)</td>
</tr>
<tr>
<td>Atmospheric inversion</td>
<td>0.1 (45ºS-90ºS)</td>
<td>0.9 (18ºS-45ºS)</td>
<td>This study, 25 sites (1991-2004)</td>
</tr>
<tr>
<td>Atmospheric inversion</td>
<td>0.0 (45ºS-90ºS)</td>
<td>0.8 (18ºS-45ºS)</td>
<td>This study, 40 sites (1995-2004)</td>
</tr>
</tbody>
</table>

¹ Corrected for wind speed at 10 m.

² Value for the open ocean and seasonal ice zone only south of the polar front (Weddell, Ross, Marginal Ice Zone excluded).

³ Results from an average of 12 transport models where the uncertainty takes into account the sensitivity of each model and the spread across models.
References


S7. U. Siegenthaler and F. Joos, Tellus, 44B (1992)


sea–air CO₂ flux anomaly (PgC/y)

Time (y)

-4.0
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0

this study, fine grid
this study, coarse grid
this study, constant winds
this study, variable station data
this study, TransCom grid
Bousquet et al. (2000)
Patra et al. (2005)
Baker et al. (2006)
Baker (2001)