An off-line 3D model of anthropogenic CO$_2$ uptake by the oceans

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Abstract. A key unanswered question in global climate research is the extent to which the oceans absorb and redistribute anthropogenic CO$_2$ (ΔDIC$_{an}$). We apply an off-line ocean carbon cycle model, one that uses atmospheric CO$_2$ concentrations and simplified ocean ventilation estimates. We estimate ocean ventilation by introducing the full age distributions of water masses obtained from a global ocean circulation model. The two model cases we use are known to respectively underestimate and overestimate observed ventilation rates, thereby providing upper and lower bounds on CO$_2$ uptake. The error in determining ΔDIC$_{an}$ is reduced significantly by minimising the number of tunable parameters. The development of the oceanic ΔDIC$_{an}$ inventory is resolved from the beginning of industrialisation to the present time. According to the model, 177Gt anthropogenic carbon have been locked up in the oceans by 1999, corresponding to an annual uptake rate of 3.9GtC*a$^{-1}$ during 1999. Uncertainties in our estimated oceanic CO$_2$ uptake are discussed.

Introduction

Carbon dioxide (CO$_2$) released from anthropogenic sources to the atmosphere is partly taken up by the world oceans [Houghton et al., 1995], thus increasing the oceanic dissolved inorganic carbon (DIC) pool. This increase is commonly determined by sophisticated methods which separate the large background variability of DIC from its minor biological and anthropogenic components [Brewer, 1978; Gruber et al., 1996; Körszting et al., 1998]. The biological component of DIC is estimated using nutrient concentrations or apparent oxygen utilisation with reference to Redfield ratios [Redfield et al., 1963] of particulate organic matter. The variability of the background DIC is eliminated by normalisation to salinity or by fixing the alkalinity/DIC relationship [Gruber et al., 1996]. Uncertainties related to the Redfield ratios [e.g. Shaffer, 1996; Thomas et al., 1999] introduce large errors in the determination of the anthropogenic component (ΔDIC$_{an}$) [e.g. Wanninkhof et al., 1999].

Here we propose an approach to reduce potential sources of errors by avoiding most of the parameters and assumptions adopted in methods used previously, thereby improving the sensitivity in detecting ΔDIC$_{an}$. We determine ΔDIC$_{an}$ using the chemistry of the marine carbonate system and the age spectra of water masses. Our technique assumes a steady state in the global distribution of the CO$_2$ partial pressure difference between the surface waters and the atmosphere (ΔpCO$_2$) during this century; supported by observations from some oceanic regions. We find deeper penetration depths and higher concentrations in our model and, as a consequence, a higher oceanic inventory for ΔDIC$_{an}$ than previously reported.

Methodology

Previously suggested methods to quantify ΔDIC$_{an}$ – notably those applying any kind of separation concept - assume that the global ΔpCO$_2$ distribution has been in steady state this century. The ΔpCO$_2$ distribution depends on ocean circulation, which is widely believed to have been in quasi-steady state for the past few centuries. The inherent assumption is moreover, that the ΔpCO$_2$ is independent from the pCO$_2$ itself, something that is indicated by field data for different parts of the World oceans [e.g. Winn, 1999; Leiferve and Schneider, unpublished data]. Results from the Ocean Carbon Cycle Modelling Intercomparison Project (OCMIP) support the ΔpCO$_2$-in-steady-state-assumption in as much that they reveal no significant change in the ΔpCO$_2$-distribution as a consequence of increasing atmospheric pCO$_2$ [Orr, 2000]. Although hitherto there has been no indication for a change of the ΔpCO$_2$ distribution with time, such a change would affect both source and sink functions of surface waters. The uptake of ΔDIC$_{an}$ would be delayed in regions of deep water formation if the oceanic pCO$_2$ increased slower than the atmospheric pCO$_2$ (increasing undersaturation / ΔpCO$_2$). On the other hand, the net-storage of ΔDIC$_{an}$ would increase in upwelling areas if the CO$_2$ released to the atmosphere is reduced due to increasing pCO$_2$ (decreasing oversaturation / ΔpCO$_2$). Both processes may partly balance each other, but since no estimations are available for the latter effects, we adopt the ΔpCO$_2$-in-steady-state-assumption. Note that this does not mean we assume ΔpCO$_2$=0, rather, we assume only that the ΔpCO$_2$ has not changed at a given location since preindustrial
times. All surface waters of the world ocean are thus subjected to the same effective increase of the pCO₂. We therefore can refer our calculations to pCO₂, atm as a measure of the effective increase of pCO₂ which is in turn responsible for the uptake of anthropogenic CO₂.

The marine carbonate system is characterized by pCO₂, DIC, pH and alkalinity (A₂). It can be described using any two of these taking into account the equilibrium constants depending on salinity (S) and temperature (T). The DIC in surface waters can hence be described as a function of pCO₂, A₂, S and T:

\[ \text{DIC} = f(\text{pCO}_2, A_2, S, T) \]  \hspace{1cm} (1)

Thus, the recent increase of atmospheric pCO₂ (pCO₂, atm) (Fig. 1a) leads to an increase in the surface DIC via the air-sea CO₂ exchange. In regions of deep water formation, descending water masses retain the DIC fingerprint generated by the pCO₂, atm at the time of their last contact with the atmosphere.

In order to describe the response of surface DIC to pCO₂, atm we choose a set of different physicochemical background conditions by changing stepwise temperature (0-20°C) and salinity (34-37). A₂ is described as a function of S [Millero et al., 1998; A₂=520.1+51.24*S], the absolute value of A₂ however is irrelevant, since ΔDIC atm is calculated as a difference [see Eq. 2]. The preindustrial DIC (DIC, preind) is calculated with reference to the preindustrial pCO₂, atm (276.8ppm) for each of these conditions according to (1). The response of DIC to changing pCO₂, atm (DIC, preind) and subsequently ΔDIC atm is obtained by increasing stepwise pCO₂, atm up to 370ppm.

\[ \Delta \text{DIC}_{\text{atm}} = \text{DIC}_{\text{pCO}_2, \text{year}} - \text{DIC}_{\text{pCO}_2, \text{preind}} \]  \hspace{1cm} (2)

Figure 1. a) Atmospheric pCO₂ [Friedli et al., 1986, Keeling and Whorf, 1999] and ΔDIC atm calculated for T=6°C and S=35 as functions of time. b) Age spectra of sampled water masses in the deep Pacific (A) and Atlantic (O) Oceans. The mean ages are 1310years and 290years, respectively [England, 1995]. The reliability of the model calculations is indicated for different time-scales, i.e., different transient tracers, and different oceanic regimes in the Southern Ocean (c) and the North Pacific Ocean (d). Over both interannual-decadal (CFCs) and centennial time-scales (³⁷Cl) the HOR experiment overestimates ocean ventilation, whereas the GM-0.5 case underestimates it [details in England and Hirst, 1997; England and Rahmstorf, 1999].

where pCO₂, preind denotes the preindustrial atmospheric pCO₂ (276.8ppm) and pCO₂, year denotes the atmospheric pCO₂ at the time when the water mass had its last contact with the atmosphere. The multiple regression of the results obtained from this exercise describes ΔDIC atm of water masses as a function of just pCO₂, S and T:

\[ \Delta \text{DIC}_{\text{atm}} = -199.6 + 0.89 * (S) + 0.42 * (T) + 0.60 \times (\text{pCO}_2) \]  \hspace{1cm} (3)

In order to determine ΔDIC atm in a given water mass we need to know the time at which it was last exposed to the atmosphere, i.e. its ventilation age. This can be estimated using tracer data [Donnet et al., 1997], e.g. using the concentration ratios of CFC11/CFC12 or ³⁷Cl/H. However, there is yet to be global high-density data coverage of these tracers. Moreover, ventilation ages derived using such tracers are strongly biased by mixing of water masses. For example, the ventilation age of a water mass can be estimated using the concentration ratio of CFC11/CFC12. However, the ratio and therefore the derived ventilation age do not change if this water mass was mixed with a CFC-free, older water mass even though the mean age of its constituent components is older as a result of the mixing event [England, 1995; England and Holloway, 1998]. Thus, the values for ΔDIC atm derived from tracer ages would be too high. On the other hand, ΔDIC atm would be underestimated using water the mass mean age, because the time history of the pCO₂, atm is not linear (Fig. 1a). Furthermore, DIC atm would be assumed to be zero in regions where the mean age is older than approximately 150years because the associated pCO₂, atm would be taken to be preindustrial. This would overlook the contributions of younger water masses. Therefore, we instead use the full water mass age distribution or “age spectra” (Fig. 1b) to obtain ΔDIC atm. The age spectrum resolves the composition of a water mass with regard to
the ages of the constituent components. To estimate the age spectra for water masses over the global ocean we employ a World Ocean model with a regular 3.75° (E-W) by approximately 4.5° (N-S) grid with 21 vertical levels. Two model cases are analysed in estimating the global age spectra in order to provide some error estimate for our ΔDIC_{atm} uptake calculation. The two model cases are known to respectively overestimate and underestimate ocean ventilation rates as seen in radiocarbon and chlorofluorocarbon validation studies [England and Hirst, 1997; England and Rahmstorf, 1999]. The distributions of these tracers (Fig. 1c, d) expose the degree of model realism in both centennial (natural 14C) and decadal (bomb-14C and CFCs) timescales. Using an idealised tracer of interior ocean ventilation [England, 1995] we resolve the age distribution with a ten-year resolution to obtain the ΔDIC_{atm} fingerprint of each component constituting a water mass. Finally, the ΔDIC_{atm} of the water mass is calculated as the weighted sum of the contributions of each relevant age level (0-150 years, Fig. 2).

For convenience we show results as the mean of values obtained using the high and low ventilation age spectra. The two model runs then provide conservative error bars of our ΔDIC_{atm} uptake estimate. The real ocean is most likely to sit near the mean value of the two runs. The high and low ventilation ΔDIC_{atm} uptake estimates are about 10% higher and lower than the mean, respectively.

Results and discussion

Highest values of ΔDIC_{atm} - up to approx. 60μmol·kg⁻¹ - are obtained for the surface layer of the oceans (Fig. 2a) as expected from previous studies [Körtzinger et al., 1998]. Within the intermediate waters of the northern North Atlantic, the concentrations and penetration depths of ΔDIC_{atm} are significantly higher than those reported elsewhere [Gruber et al., 1996; Körtzinger et al., 1998]. The high concentrations within the young Labrador Sea Water are in agreement with its rapid spreading through the North Atlantic [Sy et al., 1997]. With increasing distance from the source region the ΔDIC_{atm} concentrations decrease due to higher ages. Regions far away from areas with deep water formation, e.g. the northern Indian or Pacific Ocean show no deeper penetration of ΔDIC_{atm}. The water column of the Weddell Sea shows deep penetration of
ΔDIC

which is in agreement notably with field observations
[Hoppema et al., 1998] and with theoretical and hydrographic
analyses [Poisson and Chen, 1978; Anderson et al., 1991; Veth
et al., 1997].

For the year 1999 the global distribution (Fig. 3) shows
relatively low ΔDIC

inventories (<30mol*m -2 ) in the
equatorial and northern Indian and Pacific, which at depth
contain the world ocean's oldest waters. High values up to
100mol*m -2 are obtained for the North Atlantic Ocean, where
young and ΔDIC

-rich deep water is formed by convection
spreading southwards. The highest inventories are observed
within the Southern Ocean up to 130mol*m -2 which appears to
be a major sink of anthropogenic CO₂. As a consequence of the
increasing pCO₂ in the last 100 years, the estimated
annual uptake rate has increased to a level of ≈3.9GtC*annum-1
in 1999, yielding a world ocean ΔDIC

inventory of 176.5GtC

at the end of 1999. For the decade 1980-1989 we estimate
increasing annual uptake rates from 2.4 to 3.1GtC* a -1 , in
comparison to previous estimates of a constant uptake of
approximately 2±0.8GtC* a -1 (Fig. 4a). The latitudinal
distribution of ΔDIC

inventories (Fig. 4b) emphasises the
relative importance of the Southern Hemisphere in storing
ΔDIC

which is largely covered by ocean. On the other hand,
it may be noted that roughly two thirds of the entire ΔDIC

are stored in the oceans north of 40°S.

Conclusions

Given the recent increase of the atmospheric CO₂ due to
anthropogenic activities we consider the pCO₂ in as a major
factor controlling the oceanic uptake of anthropogenic CO₂. Using
age spectra to describe the water mass ventilation history we propose an estimate of the oceanic ΔDIC

inventory as well as its time history. We find a global oceanic
uptake of 3.9 GtC a -1 for the year 1999. Our estimates are
both higher and suggest deeper penetration of ΔDIC

than some previous studies (e.g., IPCC, 2.0±0.8 GtC* a -1 ). This
higher oceanic inventory could partly explain the imbalance in
the global carbon budget [Houghton et al., 1995], although further
studies are required to confirm this. For example, one
note of caution for previous assessments as well as for our
current estimate is the common assumption that the ΔpCO₂
distribution has been in- steady-state. We will address these
issues in future work.

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