An off-line 3D model of anthropogenic CO_2 uptake by the oceans

Helmuth Thomas[1]

Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Hamburg, Germany

Matthew H. England

Centre for Environmental Modelling and Prediction, The University of New South Wales, Sydney, Australia

Venugopalan Ittekkot

Centre for Marine and Tropical Ecology, Bremen, Germany

Abstract. A key unanswered question in global climate research is the extent to which the oceans absorb and redistribute anthropogenic CO_2 (ΔDIC_{ant}). 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_{ant} is reduced significantly by minimising the number of tunable parameters. The development of the oceanic ΔDIC_{ant} 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; *Körtzinger 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_{ant}) [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_{ant}. We determine ΔDIC_{ant} 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_{ant} than previously reported.

Methodology

Previously suggested methods to quantify ΔDIC_{ant} – 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; *Lefevre 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_{ant} 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_{ant} would increase in upwelling areas if the CO_2 released to the atmosphere is reduced due to increasing $pCO_{2,atm}$ (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 $\Delta pCO_2=0$, rather, we assume only that the ΔpCO_2 has not changed at a given location since preindustrial

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[1]corresponding author now at: Netherlands Institute for Sea Research, Department of Marine Chemistry and Geology, PO Box 59, NL-1790 AB Den Burg, Texel, The Netherlands. (email: hthomas@nioz.nl).

times. All surface waters of the world ocean are thus subjected to the same effective increase of the pCO_2. We therefore can refer our calculations to $pCO_{2,atm}$ as a measure of the effective increase of pCO_2, which is in turn responsible for the uptake of anthropogenic CO_2.

The marine carbonate system is characterised by pCO_2, DIC, pH and alkalinity (A_T). 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 pCO_2, A_T, S and T:

$$DIC = f(pCO_2, A_T, S, T) \qquad (1)$$

Thus, the recent increase of atmospheric pCO_2 ($pCO_{2,atm}$) (Fig. 1a) leads to an increase of the surface DIC via the air-sea CO_2 exchange. In regions of deep water formation, descending water masses retain the DIC fingerprint generated by the $pCO_{2,atm}$ at the time of their last contact with the atmosphere.

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

$$\Delta DIC_{ant} = DIC_{pCO2, year} - DIC_{pCO2, preind} \qquad (2)$$
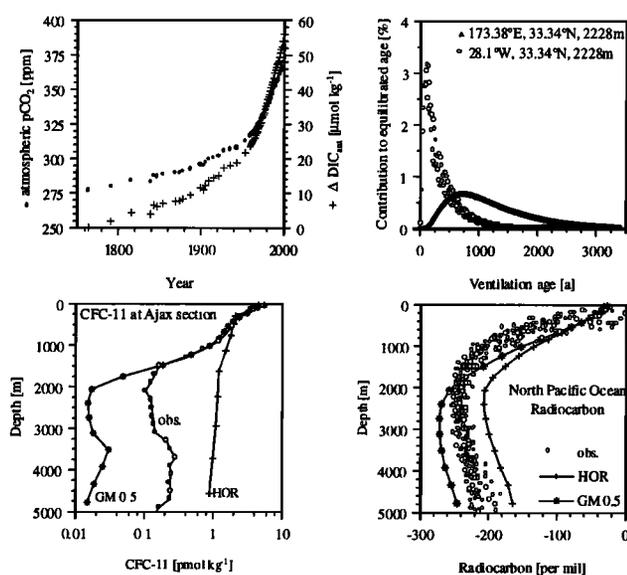
Figure 1. a) Atmospheric pCO_2 [*Friedli et al.*, 1986, *Keeling and Whorf*, 1999] and ΔDIC_{ant} calculated for T=6°C and S=35 as functions of time. b) Age spectra of sampled water masses in the deep Pacific (▲) and Atlantic (O) Oceans. The mean ages are 1310years and 290years, respectively [*England*, 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 (^{14}C) the HOR experiment overestimates ocean ventilation, whereas the GM-0.5 case underestimates it [details in *England and Hirst*, 1997; *England and Rahmstorf*, 1999].
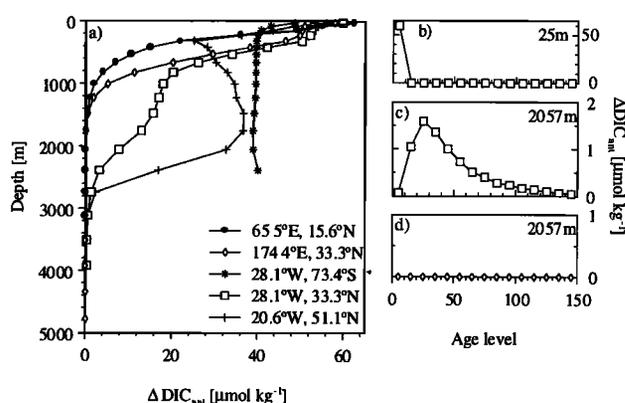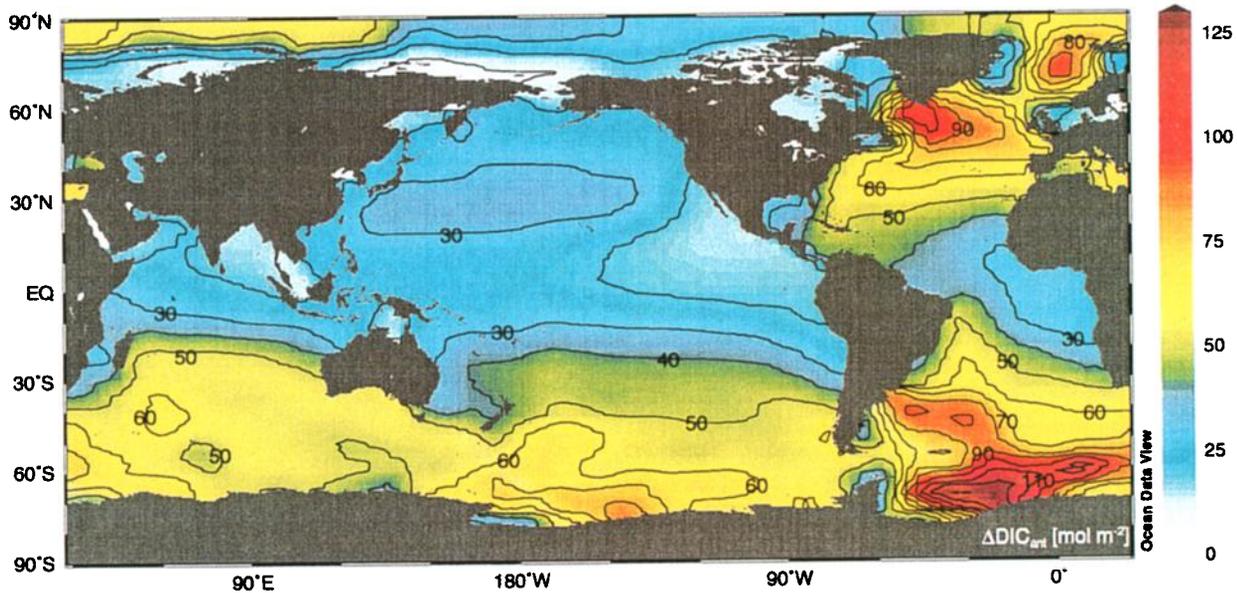

Figure 2. a) Profiles of ΔDIC_{ant} in the North Atlantic Ocean (+, □), the North Pacific Ocean (◊), the northern Indian Ocean (●) and the Weddell Sea (✳).The contributions of the individual age levels are weighted according to the age spectra (Fig. 1b) and integrated over the relevant age levels (0-150 years). The procedure is exemplified for three of the data points: In b) the surface layer of the North Atlantic Ocean is characterised only by the first age level 0-10 years. All other age levels do not contribute to ΔDIC_{ant}. In c) ΔDIC_{ant} of a water mass in the deep Atlantic Ocean (□) is composed of different age levels. Note that the mean age of this water mass is 290years, which would not allow a detection of ΔDIC_{ant} if transient ventilation was not considered (see text for discussion). In d) the very old water mass in the deep Pacific Ocean (◊) (mean age 1310years) does not show any penetration by ΔDIC_{ant} even by year 150.

where $pCO_{2, preind}$ denotes the preindustrial atmospheric pCO_2 (276.8ppm) and $pCO_{2, year}$ denotes the atmospheric pCO_2 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_{ant} of water masses as a function of just pCO_2, S and T:

$$\Delta DIC_{ant} = -199.6 + 0.89 * (S) + 0.42 * (T) + 0.60 (pCO_2) \qquad (3)$$
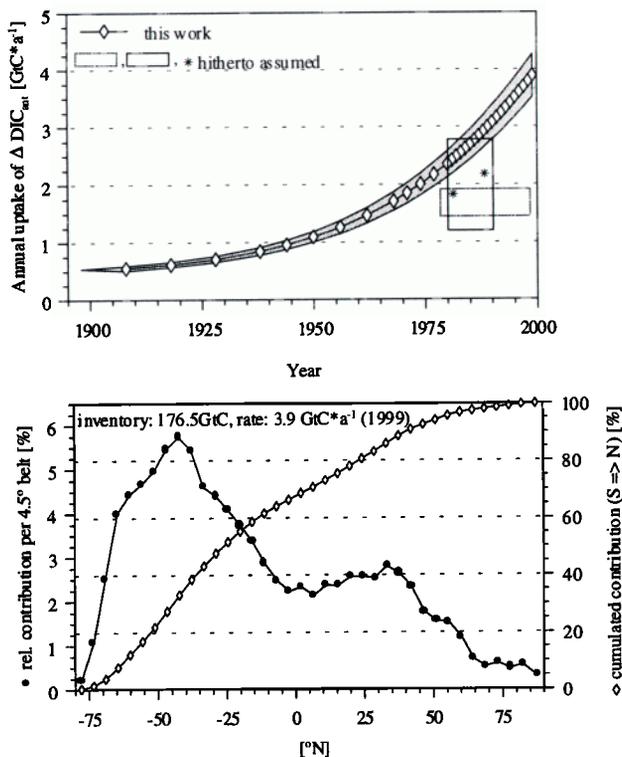$$\Delta DIC_{ant} \text{ in } [\mu mol*kg^{-1}], \text{ S, T in } [°C], pCO_2 \text{ in } [ppm]$$

In order to determine ΔDIC_{ant} 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 [*Doney et al.*, 1997], e.g. using the concentration ratios of CFC11/CFC12 or $^3He/^3H$. 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_{ant} derived from tracer ages would be too high. On the other hand, ΔDIC_{ant} would be underestimated using water the mass mean age, because the time history of the $pCO_{2,atm}$ is not linear (Fig. 1a). Furthermore, ΔDIC_{ant} would be assumed to be zero in regions where the mean age is older than approximately 150years because the associated $pCO_{2,atm}$ 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_{ant}. The age spectrum resolves the composition of a water mass with regard to

Figure 3. Estimated global distribution of ΔDIC_{ant} averaged from the two model cases with different ventilation rates.

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_{ant} 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 ^{14}C) and decadal (bomb-^{14}C 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_{ant} fingerprint of each component constituting a water mass. Finally, the ΔDIC_{ant} 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_{ant} uptake estimate. The real ocean is most likely to sit near the mean value of the two runs. The high and low ventilation ΔDIC_{ant} uptake estimates are about 10% higher and lower than the mean, respectively.

Results and discussion

Highest values of ΔDIC_{ant} - up to approx. $60 \mu mol*kg^{-1}$ - 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_{ant} 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_{ant} 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_{ant}. The water column of the Weddell Sea shows deep penetration of

Figure 4. Annual uptake of anthropogenic CO_2 by the world oceans. The shaded area depicts the range between the upper and lower bound due to over- and underestimation of the ocean ventilation rates, respectively. The surface area of the world oceans amounts to $360 \times 10^6 km^2$. The uptake rates, hitherto assumed for the 1980's, are indicated by solid box [*Houghton et al.*, 1995], by stars [*Sarmiento et al.*, 1995; *Heimann and Maier-Reimer*, 1996] and the dashed box [*Lee et al.*, 1998] (top). Relative and cumulated latitudinal contributions of 4.5° belts to the entire ΔDIC_{ant} inventory (bottom).

$ADIC_{ant}$, which is in agreement notably with field observations [*Hoppema et al.*, 1998] and with theoretical and hydrographic analyses [*Poisson and Chen*, 1987; *Anderson et al.*, 1991; *Veth et al.*, 1997].

For the year 1999 the global distribution (Fig. 3) shows relatively low $ADIC_{ant}$ 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 $ADIC_{ant}$-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 CO_2. As a consequence of the increasing $pCO_{2,atm}$ during the last 100 years, the estimated annual uptake rate has increased to a level of $\approx3.9GtC*annum^{-1}$ in 1999, yielding a world ocean $ADIC_{ant}$ 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 $2\pm0.8GtC*a^{-1}$ (Fig. 4a). The latitudinal distribution of $ADIC_{ant}$ inventories (Fig. 4b) emphasises the relative importance of the Southern Hemisphere in storing $ADIC_{ant}$, which is largely covered by ocean. On the other hand, it may be noted that roughly two thirds of the entire $ADIC_{ant}$ are stored in the oceans north of 40°S.

Conclusions

Given the recent increase of the atmospheric CO_2 due to anthropogenic activities we consider the $pCO_{2,atm}$ as a major factor controlling the oceanic uptake of anthropogenic CO_2. Using age spectra to describe the water mass ventilation history we propose an estimate of the oceanic $ADIC_{ant}$ 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 $ADIC_{ant}$ 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 ΔpCO_2-distribution has been in-steady-state. We will address these issues in future work.

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H. Thomas, Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany.

M.H. England, Centre for Environmental Modelling and Prediction (CEMAP), School of Mathematics, The University of New South Wales, Sydney, NSW 2052 Australia. (email: M.England@unsw.edu.au)

V. Ittekkot, Centre for Marine and Tropical Ecology, Fahrenheitstr. 1, D-28359 Bremen, Germany. (email: ittekkot@zmt.uni-bremen.de)