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Estimation of Anthropogenic CO₂ Inventories in the Ocean

Christopher L. Sabine¹ and Toste Tanhua²

¹Pacific Marine Environmental Laboratory/NOAA, Seattle, Washington 98115-6349;
email: chris.sabine@noaa.gov

²Leibniz-Institut für Meereswissenschaften, Marine Biogeochemie, 24105 Kiel, Germany;
email: ttanhua@ifm-geomar.de

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decadal change, ocean biogeochemistry, climate change, carbon cycle

Abstract

A significant impetus for recent ocean biogeochemical research has been to better understand the ocean's role as a sink for anthropogenic CO₂. In the 1990s the global carbon survey of the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS) inspired the development of several approaches for estimating anthropogenic carbon inventories in the ocean interior. Most approaches agree that the total global ocean inventory of C_{ant} was around 120 Pg C in the mid-1990s. Today, the ocean carbon uptake rate estimates suggest that the ocean is not keeping pace with the CO₂ emissions growth rate. Repeat occupations of the WOCE/JGOFS survey lines consistently show increases in carbon inventories over the last decade, but have not yet been synthesized enough to verify a slowdown in the carbon storage rate. There are many uncertainties in the future ocean carbon storage. Continued observations are necessary to monitor changes and understand mechanisms controlling ocean carbon uptake and storage in the future.

CFC:
chlorofluorocarbon

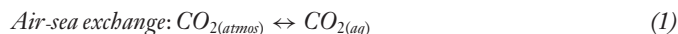
C_{ant}: anthropogenic
carbon

INTRODUCTION

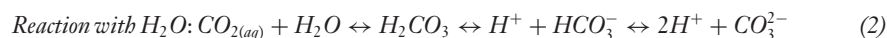
The global utilization of fossil fuels for energy is rapidly changing the trace gas composition of the Earth's atmosphere, causing a warming from excess CO₂, water vapor, chlorofluorocarbons (CFCs), methane, nitrous oxide, and other greenhouse gases. These anthropogenic gases play a critical role in controlling the Earth's climate because they increase the infrared opacity of the atmosphere, causing the planetary surface to warm. The world's oceans play an important role in the global carbon cycle as they are a vast reservoir of carbon, rapidly exchange carbon with the atmosphere, and take up a substantial portion of anthropogenically released carbon from the atmosphere.

There are only three major reservoirs with natural exchange rates fast enough to vary significantly on the timescale of decades to centuries: the atmosphere, terrestrial biosphere, and the oceans. Of this three-component system, approximately 90% of the carbon is located in the oceans. The oceans are able to hold much more carbon than the other reservoirs because most of the CO₂ that diffuses into the oceans reacts with seawater to form carbonic acid (H₂CO₃) and its dissociation products, bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions.

Seawater carbonate chemistry is governed by a series of chemical uptake, dissolution, and precipitation reactions:



The equilibration time scale for this exchange is about one year, so on a global scale surface water CO₂ generally increases at close to the same annual rate as the atmosphere (Takahashi et al. 2009). On a finer scale, local physical or biological perturbation events can make surface water CO₂ significantly deviate from atmospheric equilibrium.



These reactions are relatively rapid, and for most applications, the partitioning of inorganic carbonate species can be assumed to be in equilibrium. For typical surface ocean conditions, about 90% of the total carbon dioxide is in the form of the HCO₃⁻, ~9% as carbonate CO₃²⁻, with only ~1% remaining as undissociated CO₂ (aq) and H₂CO₃.

Although ocean biology plays an integral role in the natural distribution of carbon in the ocean, there is no conclusive evidence that the ocean uptake and storage of anthropogenic carbon, thus far, involves anything other than a chemical and physical response to rising atmospheric CO₂.

On timescales of decades, the rate at which anthropogenic carbon (C_{ant}) is moved into the ocean interior limits the rate of ocean uptake (Sarmiento et al. 1992). The physical mixing time for the ocean is two to three orders of magnitude slower than the mixing time of the atmosphere and is the primary process controlling large-scale CO₂ uptake (Stuiver et al. 1983). Currently the rate of ocean carbon storage does not seem to be keeping pace with the rate of growth in CO₂ emissions (Bindoff et al. 2007). Over hundreds to thousands of years, however, the oceans will be able to absorb 70–80% of CO₂ released to the atmosphere (e.g., Archer & Maier-Reimer 1994, Archer et al. 1997). Over these timescales ocean circulation becomes less of a limiting process and processes like potential changes in ocean biology become important. Chemical neutralization of the CO₂ through the dissolution of calcium carbonate sediments could potentially absorb another 9–15% of fossil fuel release on timescales of tens of thousands of years (Archer et al. 1997). Thus, the role of the ocean in controlling atmospheric CO₂ depends on the timescale being examined and the processes that dominate over those timescales.

To understand the oceans' role in the global carbon cycle and how it might be changing over time, one must understand the rate at which the oceans absorb anthropogenic CO₂ from the atmosphere, referred to as C_{ant} uptake, as well as how and where that CO₂ is stored in the ocean

interior, C_{amt} storage. Uptake is not necessarily the same as C_{amt} storage, because ocean transport can move carbon that is removed from the atmosphere in one place and store that carbon in another place. For example, models suggest that the equatorial Pacific is a region of significant C_{amt} uptake because the equatorial upwelling exposes older waters that have not previously seen the elevated atmospheric CO_2 values. However, relatively little C_{amt} is stored in the equatorial Pacific because the carbon is quickly transported away from the equator and stored in the subtropical gyres (Sarmiento et al. 1992).

The techniques for estimating ocean C_{amt} uptake are also different from the techniques for estimating storage. Gruber et al. (2009) recently summarized the latest C_{amt} uptake estimates from a variety of approaches including air-sea CO_2 partial pressure differences, inversion models together with measured changes in ocean interior carbon, changes in atmospheric oxygen together with concurrent measurements of atmospheric CO_2 , inversion models together with measured changes in atmospheric CO_2 , air-sea $\delta^{13}\text{C}$ disequilibrium, deconvolution of atmospheric CO_2 and $\delta^{13}\text{C}$, joint atmosphere-ocean inversions, and a suite of prognostic ocean general circulation models. The uptake estimates ranged from 1.5 ± 0.9 to 2.4 ± 0.5 Pg C year⁻¹. Gruber et al. concluded that the latest estimates from all of these techniques for the period of the 1990s and early 2000s were internally consistent within their uncertainties.

This article focuses on C_{amt} storage, not on the uptake that was recently summarized by Gruber et al. (2009). Although the spatial and temporal patterns of C_{amt} uptake may be different from the storage patterns, these two measures of the ocean carbon cycle are closely related to each other. Integrated over large enough time and space domains, the net uptake should be reconcilable with the C_{amt} storage. So far, this has only been possible in a qualitative sense or through inverse calculations using ocean Global Circulation Models (GCMs), but as techniques improve for estimating C_{amt} storage over shorter time intervals, more quantitative comparisons should be possible.

OCEAN CARBON OBSERVATIONS

A significant impetus for ocean biogeochemical research over the past several decades has been to better understand the ocean's role as a sink for anthropogenic CO_2 . Ocean uptake estimates in surface waters have the advantage that there are many opportunities to make measurements using research ships, underway measurements from ships of opportunity, autonomous measurements from moorings and drifters, and remote sensing. Air-sea exchange of CO_2 can be measured over short time intervals and with sufficient observations could provide global CO_2 uptake estimates on timescales of months to years. The disadvantage of uptake estimates from surface observations is the very large dynamic range in surface ocean CO_2 values and the uncertainties in air-sea flux parameterizations make it difficult to fully constrain the net global ocean uptake (Wanninkhof et al. 2009). For example, Takahashi et al. (2009) estimate a net CO_2 uptake for the nominal year 2000 as 1.6 ± 0.9 PgC. They attribute most of the uncertainty in the flux estimate to random errors: 13% for uncertainty in the pCO_2 estimates, 30% to the scaling factor for the gas transfer piston velocity parameterization, 20% to uncertainty in the wind speeds, and 35% for the mean rate of change in ocean water pCO_2 . The remainder of the error is for the uncertainty in their corrections for systematic biases caused by undersampling and the interpolation method used.

The advantage of using ocean interior measurements to quantify changes in C_{amt} storage is that there is much less variability in the ocean interior. The large seasonal and subseasonal variations in the ocean surface are not seen in the ocean interior, making it much easier to detect long-term secular changes due to C_{amt} accumulation. The major downsides of ocean interior measurements are that they require long oceanographic cruises to collect the necessary interior ocean data, the anthropogenic signal is small compared to the large natural inorganic carbon background in the

Pg C: petagram carbon (peta $\equiv 10^{15}$)

GCM: Global Circulation Model



GEOSECS:
Geochemical Ocean
Sections

WOCE: World
Ocean Circulation
Experiment

JGOFS: Joint Global
Ocean Flux Study

Total alkalinity (TA):
a measure of the
charge balance of
seawater (the excess of
bases over acids)

**Dissolved inorganic
carbon (DIC):** the
sum of dissolved
carbon dioxide,
carbonic acid,
bicarbonate, and
carbonate

ocean (typically less than 1%), and there are several processes that control carbon distributions in the ocean that must be understood and quantified.

The Geochemical Ocean Sections (GEOSECS) program of the 1970s provided the first global inorganic carbon data set with consistent, well-documented methods. However, shortly after GEOSECS was completed Broecker et al. (1979) commented that “. . . unless [inorganic carbon] measurements that are more accurate by an order of magnitude can be made, at least a decade will pass before direct confirmation of the model-based [C_{org} uptake] estimates will be obtained.” These words proved to be true as it has taken more than a decade and more than an order of magnitude improvement in the measurements to produce C_{org} estimates that were accepted by the carbon cycle community. In the years following GEOSECS, measurement techniques were significantly improved for regional studies like the Transient Tracers in the Ocean (TTO), and South Atlantic Ventilation Experiment (SAVE) in the Atlantic during the 1980s. The next global survey of carbon distributions in the ocean, however, did not occur until the 1990s. At that time two international research programs, the World Ocean Circulation Experiment (WOCE) Hydrographic Program and the Joint Global Ocean Flux Study (JGOFS), collaborated to complete nearly 100 cruises with inorganic carbon measurements (Wallace 2001). It was these data that created a new revolution in assessing C_{org} from direct measurements of ocean inorganic carbon and other anthropogenic tracers. Many new techniques for evaluating the observations have been developed, but the results have taken a while to make it into the scientific literature.

In the early 2000s the Intergovernmental Panel on Climate Change developed its third assessment report (IPCC 2001). This report had one chapter on observed climate variability and climate change and this chapter contained almost nothing on ocean carbon cycle observations because there were very few published results at that time. The assessment report, in general, relied almost exclusively on indirect approaches and models to estimate the ocean C_{org} uptake and storage. Also in the early 2000s, the physical and biogeochemical communities organized themselves to initiate an effort to collect full water column boundary to boundary hydrographic and geochemical data along a subset of the cruises that were initially run as part of the WOCE/JGOFS global survey in the 1990s. At least seven countries agreed to coordinate these repeat hydrographic survey cruises to monitor decadal-scale changes in the ocean. For example, the US CLIVAR/ CO_2 Repeat Hydrography Program outlined 19 cruises that it will reoccupy on a 10-year rotating basis. The program started in 2003 and is slated to complete its first decadal survey by 2012.

By the time the fourth IPCC assessment report was prepared in 2007, the number of climate observations had grown substantially resulting in three observation-based chapters, including one called Observations: Ocean Climate Change and Sea Level (IPCC 2007). The number of publications and the range of techniques that have been developed to interpret the growing number of ocean carbon observations over the last few years have greatly improved our understanding of the ocean uptake and storage of inorganic carbon.

CARBON UPTAKE AND STORAGE OVER THE LAST TWO CENTURIES

The first anthropogenic CO_2 estimates calculated from direct observations of total alkalinity (TA) and dissolved inorganic carbon (DIC) concentrations were presented about 30 years ago by Brewer (1978) and Chen & Millero (1979). Variations of this approach have been pursued by a large number of investigators in many regions of the world ocean (Chen 1982, Papaud & Poisson 1986, Poisson & Chen 1987, Goyet and Brewer 1993, Goyet et al. 1998). However, the Brewer and Chen/Millero approach (hereafter called the Chen technique) did not find general acceptance, since the uncertainties were generally regarded as too large (e.g., Shiller 1981, Broecker et al. 1985). In 1996, Gruber et al. proposed an approach for estimating anthropogenic CO_2 based on

many of the principles outlined in the Chen technique, but also addressing several of the criticisms of the original approach. This approach (hereafter referred to as the ΔC^* technique) was applied to the GEOSECS, TTO, and SAVE data in the Atlantic Ocean (Gruber et al. 1996, Gruber 1998). The ΔC^* technique was later used to estimate C_{ant} in the Indian, Pacific, and Atlantic oceans using the WOCE/JGOFS data (Sabine et al. 1999, 2002; Lee et al. 2003). Sabine et al. (2004a) combined these WOCE/JGOFS estimates into a global ocean summary of C_{ant} .

Sabine & Feely (2001) compared the Chen and ΔC^* techniques in the Indian Ocean. Application of the Chen technique to the WOCE/JGOFS Indian Ocean data set gave a total C_{ant} inventory that was essentially the same as the ΔC^* inventory, but there were substantial differences in the distributions within the water column depending on the details of how the technique was applied. In 2005, Lo Monaco et al. (2005a) adapted a version of the Chen approach to examine the C_{ant} distributions in the Southern Ocean, south of Africa. Lo Monaco et al. (2005b) compared their results with the ΔC^* estimates and found similar results north of 50°S, but they estimated larger inventories in the high-latitude Southern Ocean.

Both the ΔC^* and Chen techniques are based on the premise that the C_{ant} concentration can be isolated from measured DIC values (C_m) by subtracting the contribution of the biological pumps (ΔC_{bio}) and the physical processes involving the preindustrial end-members and the effects of the solubility pump (C_{phys}):

$$C_{ant} = C_m - \Delta C_{bio} - C_{phys} \quad (3)$$

This general approach is based on the assumption that ocean circulation and the biological pump have operated in steady state since preindustrial times. Both approaches correct for the biological term using changes in alkalinity to estimate the calcium carbonate effect and apparent oxygen utilization (AOU) together with a Redfield ratio to correct for changes due to organic matter decomposition. The main difference between the Chen and ΔC^* techniques is in how the C_{phys} term is handled. The first fundamental difference between the two techniques is that in the Chen approach changes in the properties of the subsurface waters are referenced to the mean deep-water values, whereas the ΔC^* approach divides the water column into isopycnal intervals and references the changes back to the outcrop region for each interval. The ΔC^* technique also takes a different approach to estimating the effects of the solubility pump. Rather than attempting to determine a preformed DIC concentration based on an empirical relationship between temperature and DIC as the Chen method, the C_{phys} term is divided into the DIC the waters would have in equilibrium with a preindustrial atmosphere (C_{eq}) and a term that corrects for the fact that, because CO_2 gas exchange is slow relative to the surface water biological and physical processes that can change CO_2 , surface waters are rarely in complete equilibrium with the atmosphere (C_{diseq}).

$$C_{ant} = C_m - \Delta C_{bio} - C_{eq} - C_{diseq} \quad (4)$$

The equilibrium term is by far the largest fraction of the preformed concentration and can be calculated using the equilibrium inorganic carbon constants, alkalinity, and the preindustrial atmospheric CO_2 concentration. The relatively small disequilibrium term can then be estimated on isopycnal surfaces using a time-dependent tracer such as chlorofluorocarbons (CFCs).

Shortly after the ΔC^* approach was published, Goyet et al. (1999) developed a new approach, MIX, that departs from the traditional family of reconstructions based on preformed DIC. The MIX approach uses a multiparameter mixing model (Tomczak & Large 1989) to calculate the relative contributions that a few (basin- or cruise-specific) water mass end members make to each water sample. In Goyet et al.'s application, temperature (T) and salinity (S) were used as conservative parameters and alkalinity and dissolved oxygen (O_2) were used as nonconservative parameters. The mixing model uses each sample's O_2 depletion and alkalinity enrichment relative

Biological pump: the process whereby CO_2 is removed from the surface ocean by biological production and added to the ocean interior when the organisms die and decompose while sinking into the deep ocean

Solubility pump: the process whereby CO_2 is absorbed into cold, high latitude waters that sink into the ocean interior underneath warm, lower latitude waters that cannot hold as much CO_2

to its end member composition to quantify the biological (remineralization) contribution to DIC according to

$$C_{bio} = 0.78 * \Delta O_2 + 0.5 * \Delta TA \quad (5)$$

Goyet et al. estimate a history of CO₂ changes in each end member as a function of depth from its surface source. The combination of end members' surface DIC changes and depth-penetration scales that best reproduces the present-day DIC distribution at depth is determined iteratively. The MIX approach was first applied to a zonal line in the northern Indian Ocean but was never implemented on a more extensive dataset.

Goyet later developed a different back-calculation method known as the TrOCA method (Touratier & Goyet 2004, Touratier et al. 2007) that uses a quasi-conservative tracer similar to those of NO and PO (Broecker 1974), which is based on a Redfield ratio. C_{amt} is estimated from the difference between the measured TrOCA conservative tracer and a preformed TrOCA tracer. Touratier & Goyet (2004) estimate the preformed TrOCA by regressing TrOCA against potential temperature (θ) in deep Atlantic waters with $\theta < 2.5^\circ\text{C}$. These waters are assumed to be free of C_{amt} and the relationship with θ is assumed to hold for the entire Atlantic. In Touratier et al. (2007) the implementation was expanded to regress TrOCA against θ and alkalinity using waters from the Pacific and Indian water where $\Delta^{14}\text{C}$ is less than -175 parts per mil (‰). Substantial biases in the TrOCA method has been found by comparing to observational data and model output (Yool et al. 2009).

All observationally based anthropogenic CO₂ methodologies to date rely on the assumption that C_{amt} penetrates the ocean as a passive, inert tracer responding to an evolving history in surface waters. Another approach for estimating C_{amt} is the transit time distribution (TTD) method, which fully exploits this assumption in order to relax other assumptions. The TTD method does not use DIC measurements, thus avoiding large uncertainties in back-calculation approaches related to the biological correction. This approach uses the fact that C_{amt} at any point in the ocean interior should be related to the concentration history of anthropogenic CO₂ at the surface and the spectrum of times it took the water to reach the interior ocean location. The surface history is estimated using the equilibrium inorganic carbon chemistry equations, temperature, the preformed alkalinity (estimated from salinity), and the atmospheric CO₂ record. The transit time distributions are approximated by inverse Gaussian functions based on transient tracers (often CFCs). The approach then only requires measurements of temperature, salinity, and a transient tracer if one assumes that biology is not involved, that circulation is in steady state, and that a single surface source region dominates the interior water so there is no spatial dependency in the source waters. Hall et al. (2004) used a volume-based version of the TTD method to estimate C_{amt} in the Indian Ocean, while Waugh et al. (2004) applied a pointwise version to the subpolar North Atlantic Ocean. Waugh et al. (2006) applied the method to the Global Data Analysis Project (GLODAP) data set (Key et al. 2004) to generate a global C_{amt} estimate.

An approach to scale observed carbon inventory changes between two cruises separated in time to the full anthropogenic storage over the last two centuries has been presented by Tanhua et al. (2007), taking advantage of the exponential nature of the atmospheric C_{amt} increase and exploring the transient steady state concept (Gammon et al. 1982). An exponentially changing tracer will, after a certain time, reach transient steady state, meaning that, e.g., a depth profile of C_{amt} will have constant shape over time, and the concentrations will increase proportionally to the surface layer increase. This way of calculating the C_{amt} concentration is independent from tracer data and circumvents many of the assumptions of the back-calculation methods.

A summary of the long-term C_{amt} estimate approaches is given in **Table 1**. They break down into three general categories: back-calculation, tracer based, and scaled decadal change. There

Table 1 Comparison of methods used to determine long-term C_{ant} storage

	Method	Advantages	Disadvantages
Back-calculation	Chen Technique (Brewer 1978, Chen & Millero 1979)	Based directly on observed DIC concentrations in the ocean. Relies on well-known oceanographic properties. Can be validated in deep water where C_{ant} should be zero.	Need to estimate preindustrial property fields, particularly CO_2 air-sea disequilibrium. Assumes constant stoichiometric ratios. Best done with large data set. Needs water mass age estimates.
	ΔC^* technique (Gruber et al. 1996)		
	LM05 technique (Lo Monaco et al. 2005a)		
	TrOCA (Touratier & Goyet 2004, Touratier et al. 2007)	Based on DIC. Straightforward calculation. Do not need water mass age tracer.	Assumes constant stoichiometric ratios. Preformed values crudely determined.
	MIX (Goyet et al. 1999)	Based on DIC. Does not need water mass age tracer. Can be calculated using data from a single cruise.	Cumbersome water mass analysis. Assumes C_{ant} only increases with depth. Assumes constant stoichiometric ratios.
Tracer based	TTD (Vaughn et al. 2004, Hall et al. 2004)	Less sensitive to near-surface biological processes. Will not yield negative C_{ant} values.	This technique cannot detect biological carbon changes. Sensitive to assumptions of mixing and saturation of tracers (e.g., CFCs).
Decadal change	Scaled eMLR (Tanhua et al. 2007)	Based on DIC. No assumptions of preindustrial fields necessary.	Dependent on the assumption of transient steady state. Still limited number of decadal repeat data.

are several variations of the back-calculation methods that use modern DIC measurements and other tracer data to infer the preindustrial carbon distributions and therefore the total inventory of C_{ant} . The tracer-based TTD method and the scaled decadal change approach do not have as many variations. All of these methods have their advantages and disadvantages.

Long-Term C_{ant} Storage

After completion of the WOCE/JGOFS global survey in 1998, a five-year effort was begun to compile and rigorously quality-control the US and international data sets, including a few pre-WOCE data sets in regions that were data limited. The final data set, GLODAP, with 9618 hydrographic stations collected on 95 cruises, provides the most accurate and comprehensive view of the global ocean inorganic carbon distribution available (Sabine et al. 2005). By combining these data with the ΔC^* technique, Sabine et al. (2004a) estimated that $118 \pm 19 \text{ Pg C}$ had accumulated in the ocean between 1800 and 1994. This inventory accounted for 48% of the fossil fuel and cement manufacturing CO_2 emissions to the atmosphere over that time frame.

A map of the anthropogenic CO_2 ocean column inventory (**Figure 1**) shows that the carbon is not evenly distributed in space. More than 23% of the inventory can be found in the North Atlantic, a region covering approximately 15% of the global ocean. By contrast, the region south of 50°S represents approximately the same ocean area but only has $\sim 9\%$ of the global inventory (Sabine et al. 2004a). Despite the relatively slow equilibration rate for CO_2 in seawater (approximately 1 year versus weeks for oxygen), uptake at the surface does not fully explain the spatial differences

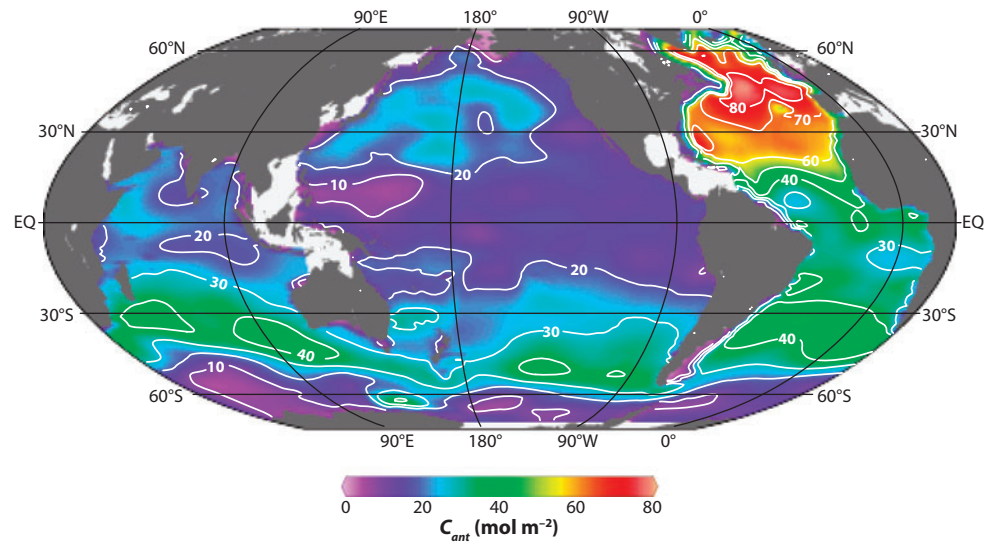


Figure 1

Global map of column C_{ant} (anthropogenic carbon) as given by Sabine et al. (2004a) based on the ΔC^* calculation method of Gruber et al. (1996). Adapted from Sabine et al. (2004a).

in storage. The primary reason for these differences is because of the slow mixing time in the ocean interior and the fact that waters only move into the deep ocean in a few locations. The highest inventories are found in the locations where mode and intermediate waters are moving anthropogenic CO_2 into the ocean interior (e.g., the northern North Atlantic or in the Southern Hemisphere associated with the Subtropical Convergence Zone at 40–50°S; **Figure 1**).

These estimates of ocean C_{ant} have been used to evaluate models (Orr et al. 2001, Matsumoto et al. 2004) and to infer air-sea fluxes of CO_2 (Gloor et al. 2003, Mikaloff-Fletcher et al. 2006). However, there are many uncertainties in the ΔC^* method. Different implementations of the method can yield different results (e.g., Wanninkhof et al. 1999, Lo Monaco et al. 2005b) and there are potential biases due to the assumptions of a single ventilation time, constant disequilibrium, and constant Redfield ratios (Hall et al. 2004, Matsumoto & Gruber 2005).

Waugh et al. (2006) also used the GLODAP data set to estimate the global C_{ant} inventory using the TTD method (**Figure 2a**). The estimated total inventory in 1994 was 134 Pg C. To evaluate uncertainties in the TTD method, Waugh et al. applied the approach to output from an ocean general circulation model (OGCM) and compared the results to the directly simulated C_{ant} . Outside of the Southern Ocean the predicted C_{ant} closely matched the directly simulated distribution, but in the Southern Ocean the TTD concentrations were biased high. This bias could be due to the TTD assumption of constant disequilibrium and also possibly due to short residence times of Southern Ocean waters, which would accentuate the different equilibration times for CO_2 (~1 year) and the CFCs (~1 week) used for the TTD estimates. The net result was a TTD overestimate of the global inventory by about 20%. Accounting for this bias and other uncertainties, an inventory range of 94–121 Pg C was given by Waugh et al. (2006). This agrees with the inventory of Sabine et al. (2004a). There were, however, differences in the spatial distributions (**Figure 2b**). The TTD estimates generally gave much higher inventories in the Southern Ocean as previously noted, but there are also differences such as higher inventories in the North Atlantic Deep Water (**Figure 2b**). The TTD estimates also generally had smaller C_{ant}

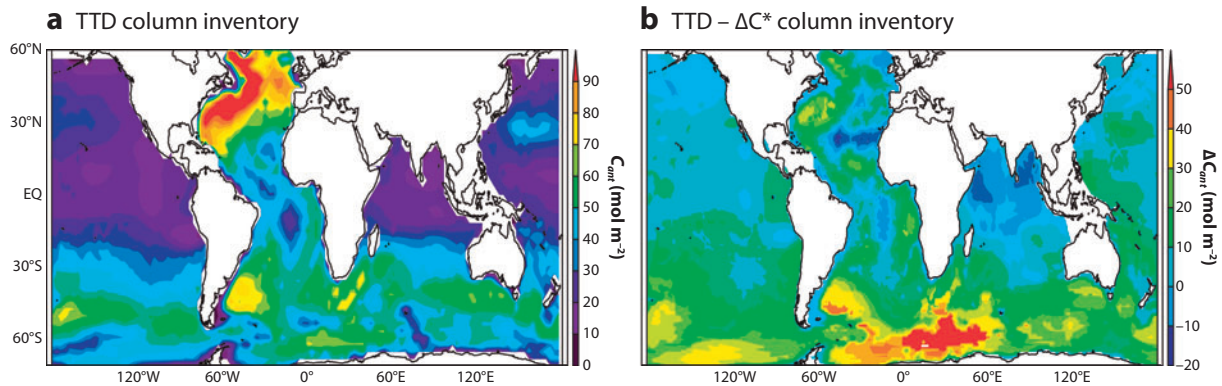


Figure 2

Global map of (a) C_{ant} column inventories from transit time distribution (TTD) calculations, and (b) difference between TTD and the ΔC^* estimates from Sabine et al. (2004a). Adapted from Waugh et al. (2006).

concentrations than ΔC^* in the upper ocean and larger at depth, consistent with biases expected in ΔC^* given its assumption of a single parcel ventilation time.

The global estimate by Sabine et al. (2004a) approximated the C_{ant} inventories in marginal Seas and the Arctic Ocean due to lack of data, whereas the estimate by Waugh et al. (2006) did not account for those areas at all. The C_{ant} inventory for the Arctic Ocean has later been estimated to 2.5–3.3 Pg C (Tanhua et al. 2009) and for the Mediterranean to 1.7 Pg C (surprisingly high anthropogenic carbon content in the Eastern Mediterranean Sea; A. Schneider, T. Tanhua, A. Körtzinger, and D.W.R. Wallace, unpublished paper) by the TTD method, showing that both of these marginal seas have higher than global average C_{ant} concentrations.

Vázquez-Rodríguez et al. (2009) compared five different approaches along a meridional line in the Atlantic. They found that all the observational methods produced reasonable C_{ant} estimates and inventories for the full length of the Atlantic Ocean. However, south of $\sim 40^\circ\text{S}$ there are significant differences between methods. The uncertainties in C_{ant} estimates due to the method applied are narrow in the subtropics but larger for polar regions. The impact of these discrepancies is most important in the Southern Ocean given its large contribution (up to 12%) to the total inventory of C_{ant} and the larger differences between methods there. A similar result is shown by Álvarez et al. (2009) for a zonal section in the southern Indian Ocean where five methods to estimate C_{ant} were compared to each other and particularly large relative differences were found for the deep waters with a southern origin.

CARBON UPTAKE AND STORAGE OVER THE LAST TWO DECADES

Some of the inherent difficulties in estimating the C_{ant} concentration in the ocean can partly be overcome by comparing repeat measurements in certain ocean regions or along oceanographic sections. At least, any systematic biases tend to cancel out when comparing two estimates using the same assumptions. Typically, comparisons are made on data separated by 10 to 25 years in time, and are measures of the increase in ocean storage in a particular density range, for a particular water mass, or over the whole water column. Since the C_{ant} signal is small in comparison to the background DIC concentration, there are technical difficulties involved in detecting any changes in DIC concentration on timescales less than about a decade. Further, natural small-scale spatial and temporal variability tend to obscure the C_{ant} signal. This type of comparison thus requires

eMLR: extended
Multiple Linear
Regressions

precise and accurate data. There have been significant advances in this respect over the last few decades, for instance by refining analytical methods and compliance to follow recommended best practices (DOE 1994, Dickson et al. 2007). For carbon measurements, the now common use of Certified Reference Materials (CRMs) has also had a significant positive impact on the consistency of the data.

The WOCE/JGOFS global survey in the 1990s offered the first possibility to detect changes compared to GEOSECS and TTO data. One difficulty in quantifying decadal uptake is that for a large number of historical data, no CRMs were available for DIC and TA measurement (a problem that still exists today for some important measurements, e.g., nutrients). This deficiency can be partly overcome by so-called secondary quality control, i.e., a process where data are objectively studied in order to quantify systematic biases, for which corrections can be made. This is mostly done by comparing measurements from different cruises in the deep ocean where steady state conditions are assumed for the relatively short time interval between cruises (e.g., Gouretski & Jancke 2001, Johnson et al. 2001, Sabine et al. 2005).

Since the time of GEOSECS it has, in principle, been possible to detect changes in ocean carbon content through direct comparisons of measured carbon concentrations in the water column in certain regions. Since several national and international projects are resampling WOCE/JGOFS oceanographic lines with high-quality carbon measurements, more decadal uptake estimates will likely be made in the future. In particular, it opens the possibility of comparing inventory changes with decadal scale changes in the uptake rate, e.g., to distinguish between pre-1990s and post-1990s storage rates.

Just as with estimates of the centennial scale C_{amt} concentrations, there are several methods to calculate decadal scale changes in DIC. One common approach is to compare measured DIC concentrations on surfaces of equal density, and to adjust for changes in dissolution of organic matter and (sometimes) calcium carbonate using oxygen, alkalinity, and/or nutrient data. Another similar method is to calculate the C_{amt} concentrations for two cruises using a back-calculating method, and then consider only the difference between the two estimates. This has the advantage that assumptions such as the preindustrial air-sea disequilibrium become irrelevant, since the two terms will cancel out in the comparison. A multiple linear regression approach (MLR) was introduced by Wallace (1995) where DIC concentration is predicted by several other parameters. This approach compensates for variability in water mass distribution and temporal variability within a water mass. The MLR method was later refined by (Friis et al. 2005) to a method known as extended MLR (eMLR).

As seen above, transient tracers can be used to determine the long term C_{amt} inventory, but they can also be used to evaluate the decadal inventory changes. Once the tracer field is established, the uptake rate can be determined for any time period with the assumption of constant circulation, i.e., that the age field remains constant (e.g., Watanabe et al. 2000). Repeat measurements of transient tracers can account for changes in circulation and specifically address the role of circulation for the storage of C_{amt} (e.g., Steinfeldt et al. 2009). However, the different input histories of C_{amt} and CFCs influences the relationship between the storage rate of the two components, so a rapid increase in CFC concentration is not necessarily associated with a rapid increase in C_{amt} (e.g., Tanhua et al. 2006), if mixing is not explicitly addressed.

Decadal Change in C_{amt} Storage

In the following we will compare some data-based estimates of decadal scale changes in concentration of dissolved inorganic carbon integrated over the whole water column and report this as annual storage change, i.e., in units of $\text{mol m}^{-2} \text{ year}^{-1}$, a measure that includes direct uptake

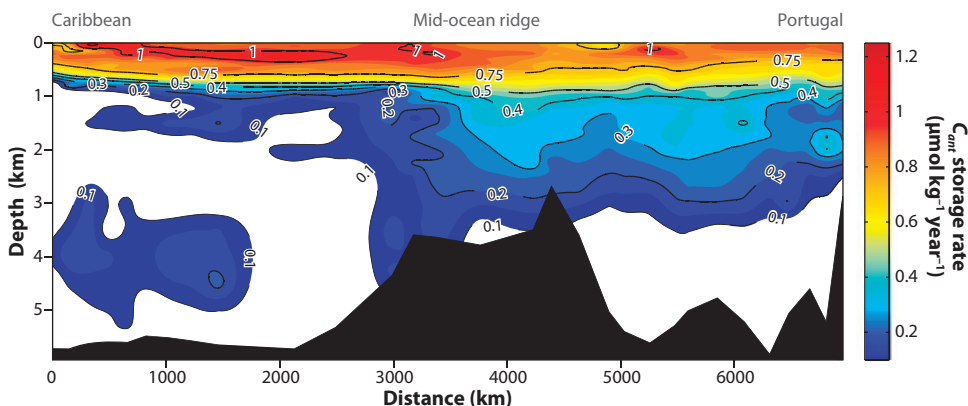


Figure 3

A section of anthropogenic carbon storage rate in the mid-latitude North Atlantic calculated as yearly means of the measured change between 1981 and 2004 with the extended Multiple Linear Regressions (eMLR) method (see cruise j in **Figure 4**; see also Tanhua et al. 2007). Storage changes $< 0.1 \mu\text{mol kg}^{-1} \text{ year}^{-1}$ are left blank.

through the air-sea interface and carbon advected or mixed into the water column from surrounding waters. We will refer to this quantity as storage rate. As an example of the vertical structure of the storage rate, we present a quasi-zonal section of the mid-latitude North Atlantic in **Figure 3**. There are high storage rates for the upper waters, particularly associated with the warm and salty waters of the southwestern part of the section where the buffer capacity is large, and a core of positive storage rates associated with the deep western boundary current in the deep western part of that section. Note that the penetration of C_{ant} is particularly deep in the North Atlantic. If the global oceanic uptake of C_{ant} ($\sim 2.2 \text{ Pg C year}^{-1}$) was evenly distributed over the world ocean, the average storage rate would be $\sim 0.55 \text{ mol m}^{-2} \text{ year}^{-1}$ (Sabine et al. 2008).

Figure 4, indices a–k, provide an overview of some published data based estimates of storage rates. (a) An early work on decadal uptake is provided by Peng et al. (1998) who calculate the C_{ant} storage rates of up to $0.65 \text{ mol m}^{-2} \text{ year}^{-1}$ in the Indian Ocean by comparison of GEOSECS data with data from WOCE (1978–1995). (b) Data from GEOSECS was also used by Tsunogai et al. (1993) to calculate storage rates in the Northwest Pacific Ocean between 1974–1991; (c) and by Peng et al. (2003) to calculate the storage rate in the Pacific Ocean between 1973–1991 with the MLR approach. The contemporary storage rate studies for the North Pacific are provided by (d) Sabine et al. (2008) and (e) Murata et al. (2009) that compared cruises from 1991–1993 with cruises in 2005/2006. The highest storage rates found by these two studies in the Northwest Pacific is $0.9 \text{ mol m}^{-2} \text{ year}^{-1}$, which is lower than both the estimates of Tsunogai et al. (1993) and Peng et al. (2003). The observed differences between early and contemporary storage rates in the North Pacific could be due to technical problems associated with systematic biases in the GEOSECS DIC data. However, it is also possible that there are real trends in storage rate, which would imply a reduction in the C_{ant} storage rate since the mid-1990s while CO_2 has continued to increase faster in the atmosphere.

(f) For the South Pacific, a study by Matear & McNeil (2003) used a MLR-based method to compare data from 1968 with data from 1991–1996 along three lines south of Australia and New Zealand. They find high storage rates in the Subantarctic Mode Water and for the Antarctic Intermediate Water (up to $\sim 0.8 \text{ mol m}^{-2} \text{ year}^{-1}$), and a large storage rate in the Antarctic Bottom Water for the westernmost section. Despite the different time interval, the storage rates found by

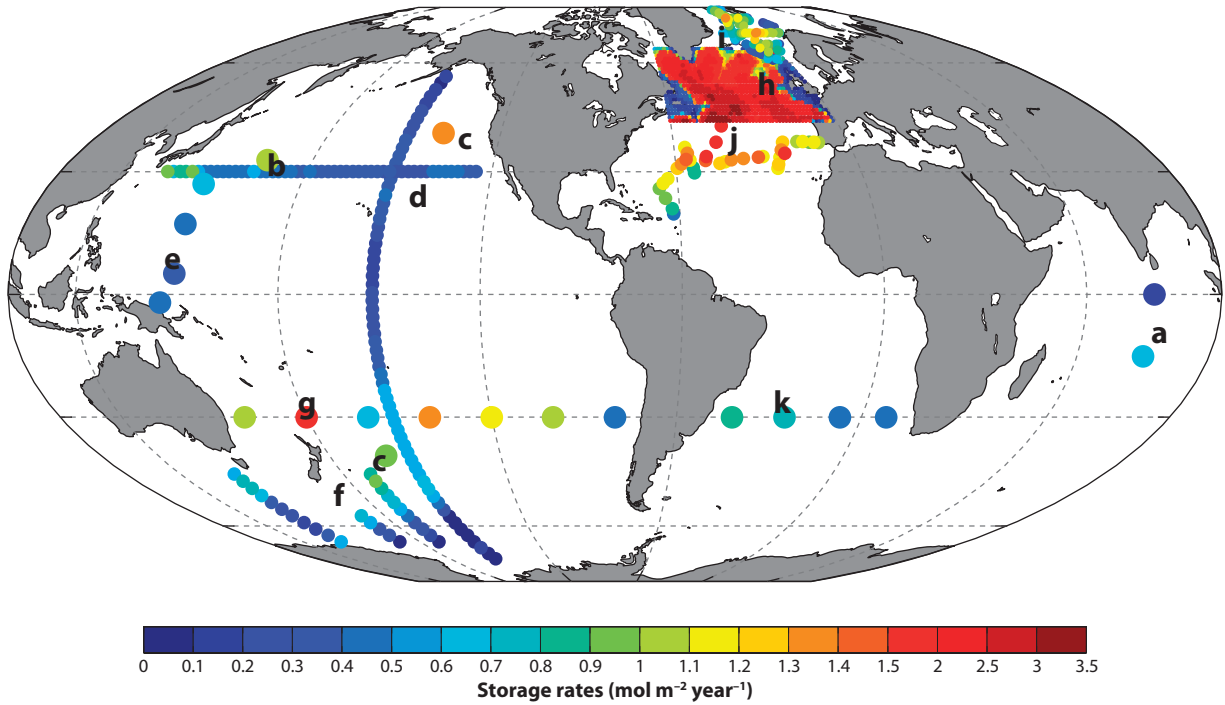


Figure 4

A world map with published data-based estimates of column inventories of anthropogenic carbon storage rates ($\text{mol m}^{-2} \text{year}^{-1}$).

Index	Data source	Time period	Method
a	(Peng et al. 1998)	1978–1995	Isopycnal, O_2 adjusted
b	(Tsunogai et al. 1993)	1974–1991	Column-integrated change in preformed carbonate
c	(Peng et al. 2003)	1973–1991	MLR
d	(Sabine et al. 2008)	1991/1992–2005/2006; 1994–2004	eMLR
e	(Murata et al. 2009)	1993–2005	Isopycnal, O_2 adjusted
f	(Matear & McNeil 2003)	1968–1991/1996	MLR
g	(Murata et al. 2007)	1992–2003	Isopycnal, O_2 adjusted
h	(Friis et al. 2005)	1981–1997/1999	eMLR
i	(Olsen et al. 2006)	1981–2002/2003	eMLR
j	(Tanhua et al. 2007)	1981–2004	eMLR
k	(Murata et al. 2008)	1992/1993–2003	Isopycnal, O_2 adjusted

Sabine et al. (2008) are similar to the easternmost values by Matear & McNeil. (g) A zonal section along 32°S by Murata et al. (2007), however, found slightly higher storage rates than Matear & McNeil using data from 2003 and 1992. Murata et al.'s high storage rates north of New Zealand were attributed to deep-water carbon storage. Even though the methods used by Sabine et al. (2008) and Murata et al. (2007) are different, the storage rates at the crossover point between the two data sets are almost identical.

It seems that only moderate adjustments need to be applied to the 1981 TTO-NAS data (Tanhua & Wallace 2005), and a number of studies have compared the TTO data with modern



data, together covering large parts of the North Atlantic and the Nordic Seas. (b) Friis et al. (2005) use data from 1997 and 1999 to calculate the storage rate in the subpolar North Atlantic and to introduce the extended Multiple Linear Regression (eMLR). The eMLR method is later used by (i) Olsen et al. (2006) and (j) Tanhua et al. (2007) to calculate the storage rate in the Nordic Seas (modern data from 2002/2003) and the mid-latitude North Atlantic (modern data from 2004), respectively. The North Atlantic clearly has the highest storage rate of the world ocean, which is to be expected since this region has the highest inventory of C_{ant} (**Figure 1**).

Figure 4 suggests that the storage rate is highest in the subpolar North Atlantic, slightly lower at lower latitudes and north of the Greenland-Scotland ridge. However, the column inventory is obviously dependent on water depth, and the Nordic Seas tends to be somewhat shallower than the North Atlantic, but the uptake rate might well be variable with time. This is shown by Perez et al. (2008) who reported on C_{ant} changes in the southern part of the Irminger Sea and found significant temporal variability in the storage rates: $0.55 \text{ mol m}^{-2} \text{ year}^{-1}$ between 1981–1991; $2.3 \text{ mol m}^{-2} \text{ year}^{-1}$ between 1991–1997; and $0.75 \text{ mol m}^{-2} \text{ year}^{-1}$ between 1997–2006. Similarly, a study comparing the CFC distributions between 1997–2003 (Steinfeldt et al. 2009) found a dramatic reduction of C_{ant} column inventories in the central Labrador Sea, i.e., storage rates smaller than $-2 \text{ mol m}^{-2} \text{ year}^{-1}$. The reason for this is related to weak formation of Labrador Sea Water (LSW) since 1997. The C_{ant} -rich LSW is advected out of the region and replaced with upper LSW and relatively C_{ant} -poor North Atlantic Deep Water. It is unclear if the decrease of Labrador Sea C_{ant} column inventory is part of a long-term trend or part of decadal variability.

(k) For the South Atlantic, Murata et al. (2008) finds average storage rates close to the global mean value of $0.55 \text{ mol m}^{-2} \text{ year}^{-1}$, but with significantly higher rates in the western basin. Murata et al. (2008) further found significant storage rates in the Antarctic Bottom Water (AABW) in the eastern part of the section (not visualized in **Figure 4k**). If the AABW is accounted for, the storage rates would increase to about $1 \text{ mol m}^{-2} \text{ year}^{-1}$ in the eastern basin. As seen before, the concentration of C_{ant} in the AABW continues to be difficult to quantify.

The results presented here clearly demonstrate that detecting decadal changes in carbon inventory is a feasible undertaking, and that these data are good indicators of integrated changes in C_{ant} storage. It is also clear that there are large spatial differences in the storage rates. There are several indications that, in some parts of the ocean, the storage rate is changing on decadal timescales, although it is unclear if this is a trend or variability. There are more cruises planned to complete the current global resurvey of the WOCE/JGOFS lines. Once these cruises are analyzed, a more comprehensive global picture of storage rates will be developed that can be used to evaluate the consistency with the independently derived ocean uptake estimates. Continued monitoring of the changing carbon inventory through repeat hydrography is important for detecting changes in the ocean carbon cycle and developing correct assessments of the anthropogenic carbon stock changes.

CARBON AND CLIMATE FEEDBACKS

We still do not fully understand the global carbon cycle or how the ocean uptake and storage of CO_2 is changing because of the strong interactions between the different parts of the system. Up to this point, the assumption has been that ocean storage of C_{ant} has been controlled by purely physical and chemical processes directly responding to rising CO_2 concentrations in the atmosphere. The average anthropogenic CO_2 fluxes for the period 2000–2005 are indicated by the red arrows in **Figure 5**. The bracketed numbers give natural (black) and anthropogenic (red) inventories. We are just now starting to appreciate that by adding approximately 135 Pg C to the ocean between 1800 and the early 2000s, the resulting changes in seawater chemistry may have

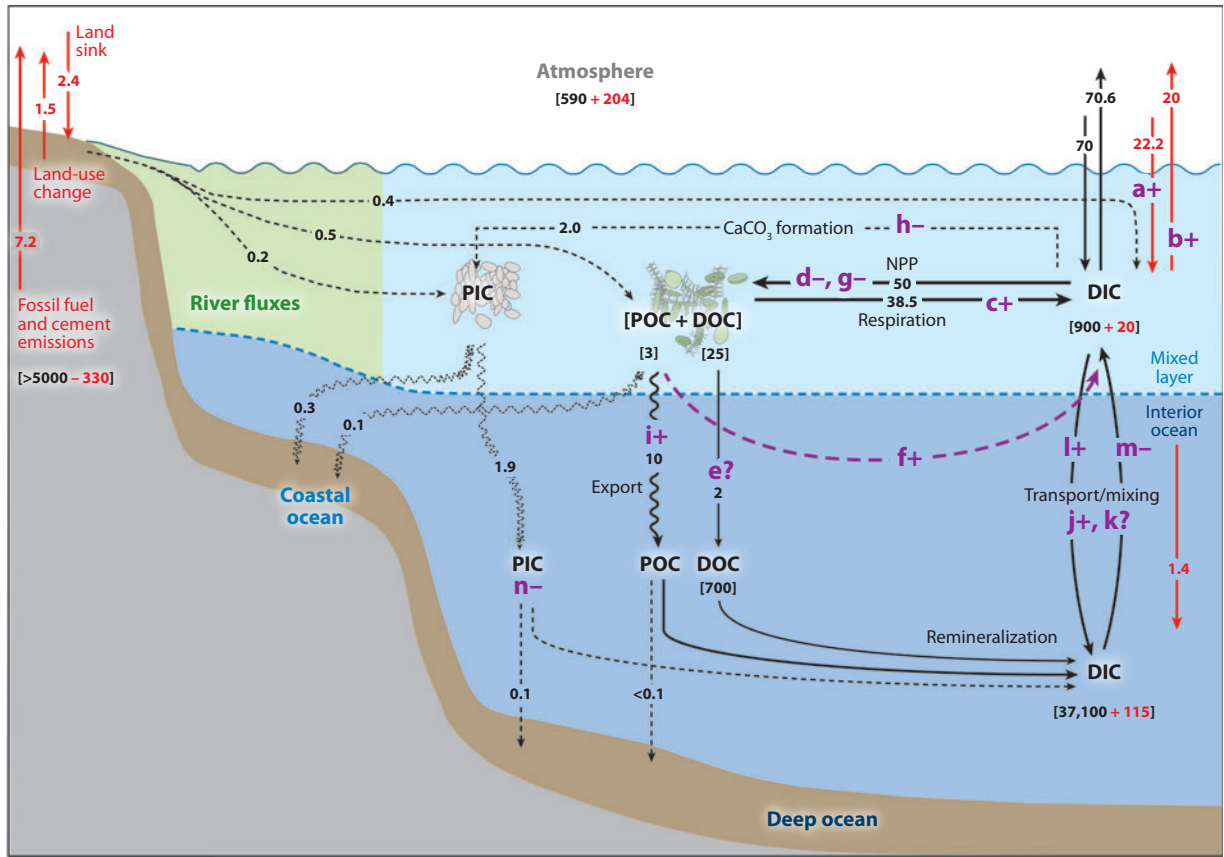


Figure 5

The Global Ocean Carbon Cycle in the early 2000s and feedback mechanisms. Bracketed values denote reservoir size (Pg C), with values in red denoting anthropogenic change. Bracketless values are fluxes (Pg C year⁻¹), with values in red denoting anthropogenic fluxes. Letters in purple denote feedback mechanisms discussed in the text, with plus and minus signs indicating positive and negative feedback loops in terms of atmospheric CO₂ concentration. Abbreviations: a+, decreased buffer capacity; b+, decreased solubility in warmer ocean; c+, enhanced recycling due to warmer ocean; d-, carbon overconsumption; e?, DOM recycling/export; f+, increased denitrification; g-, increased nitrogen fixation; h-, reduced calcification; i+, reduced particle ballast; j+, increased stratification; k?, increased Southern Ocean winds; l+, reduced deep-water formation; m-, reduced upwelling; n-, increased carbonate dissolution; PIC, particulate inorganic carbon; POC, particulate organic carbon; DOC, dissolved organic carbon; NPP, net primary production. Adapted from Sabine et al. (2004b).

a profound impact on the ocean biological and calcium carbonate cycles. A basic schematic of these cycles is shown in **Figure 5**. Changes in one part of the carbon cycle can feed back to affect another part of the carbon cycle (i.e., create a feedback loop) and it is not always clear what the net balance will be. This makes changes in the future role of the ocean in the global carbon cycle very difficult to predict.

Feedback: the process by which a system is modulated, controlled, or changed by the product, output, or response it produces

Part of the problem is that today's global carbon cycle is intimately linked with the structure of the global ecosystems. Carbon is one of the primary currencies exchanged between organisms. As we change the balance of the carbon cycle, it is not clear how these ecosystems might respond. These changes could select against or for particular classes of organisms, causing massive extinctions or population booms. As organisms (including humans) attempt to adapt to these changing conditions, the flows of carbon in and out of the primary reservoirs can be significantly altered,

throwing off the delicate balance observed over the last millennium. Here we present some evidence of feedbacks that are active in the marine carbon system, although we do not pretend to be comprehensive; we will show some of the intriguing and complex feedback systems at work. We refer to mechanisms that enhance the atmospheric CO₂ perturbation as a positive feedback mechanism (shown as plus signs in **Figure 5**), whereas mechanisms that tend to dampen the atmospheric CO₂ perturbation are referred to as negative feedbacks (shown as minus signs in **Figure 5**). The feedback loops discussed below are depicted in purple as a–n in **Figure 5**.

(a) There are relatively straightforward and well-understood feedbacks related to the chemistry of the carbonate system. Increased concentration of DIC in seawater and other factors, such as temperature, alkalinity, etc., influence the capacity of the ocean to respond to CO₂ perturbations. One way to consider this is with the Revelle factor:

$$\left(\frac{\delta pCO_2 / \delta DIC}{pCO_2 / DIC} \right) \quad (6)$$

Increasing pCO₂ increases the Revelle factor making the ocean less efficient at absorbing more CO₂, i.e., a positive feedback. The Revelle factor for surface waters has already increased by about one unit over the last 250 years (Sabine et al. 2004a).

(b) Similarly well understood is the response to increased temperatures; even though the Revelle factor decreases with increasing temperature (everything else constant), the solubility of CO₂ in seawater also decreases with increasing temperature. The latter effect is dominating so that a warmer ocean will lead to reduced CO₂ uptake, i.e., a positive feedback (Goodwin & Lenton 2009).

(c) The increased carbon concentration in the photic zone of the ocean has direct effects on biology, with more difficult to quantify feedbacks for the carbon cycle. For instance, experimental evidence indicates a shift in the balance between primary production and heterotrophic consumption of organic matter in warmer water. Enhanced recycling and respiration cause a faster replenishing of the DIC pool in the surface layers and leave less organic carbon for export, thereby potentially weakening the biological pump, i.e., a positive feedback loop induced by warmer surface waters (Wohlers et al. 2009).

(d) Similarly, experimental evidence suggests an increased carbon to nitrogen ratio in phytoplankton grown under elevated carbon concentrations (i.e., carbon overconsumption), which would lead to increased export of organic carbon from the mixed surface layer to the deeper part of the ocean (Riebesell et al. 2007), i.e., a negative feedback.

(e) Dissolved organic matter (DOM) tends to have very high carbon to nutrient ratios, particularly for the refractory fraction, and downward transport of DOM is an efficient export mechanism of carbon to the deep ocean (Hopkinson & Vallino 2005). Changes in the DOM cycle or composition can induce potentially significant feedback loops. For instance, increased remineralization depth of labile DOM will provide a negative feedback, whereas decreased near-surface stability of refractory DOM is a positive feedback.

(f) A further feedback loop on the carbon cycle is provided by increased particulate organic carbon (POC) flux to the upper water column associated with carbon overconsumption and lower sinking rates due to reduced calcium carbonate ballast (see below). Taken together, this will likely increase the extent of oceanic oxygen minimum zones (OMZ) (e.g., Hofmann & Schellnhuber 2009, Oeschlies et al. 2008), which implies increased denitrification and hence possible reduced production when this water reaches the surface ocean, creating a positive feedback.

(g) However, it is possible that the nitrate-poor water (relative to phosphate) resulting from the denitrification will stimulate nitrogen fixation in the euphotic zone (Deutsch et al. 2007), i.e., a dampening effect on the positive feedback due to increased OMZs.

pCO₂: the partial pressure of carbon dioxide, which controls the thermodynamic drive for the ocean to exchange carbon with the atmosphere

Denitrification: a process through which nitrate (NO₃⁻) is reduced to molecular nitrogen

Nitrogen fixation: a process through which molecular nitrogen is converted to bioavailable nitrate by organisms

Aragonite and calcite: two different forms of calcium carbonate used by marine organisms for shells or skeletal structures

The invasion of anthropogenic CO₂ in the oceans inevitably leads to decreasing pH, lower concentration of carbonate ion, and lowered saturation state for aragonite and calcite, i.e., ocean acidification (e.g., Doney et al. 2008). The largest effects are seen in the upper ocean where most of the anthropogenic CO₂ is stored. High-latitude cold waters are particularly sensitive to decreasing pH since the saturation state of calcite and aragonite tends to be lower than in temperate and tropical waters; i.e., a modest change in the pH might lead to calcite and/or aragonite undersaturation near poles (e.g., Orr et al. 2005). Ocean acidification will likely affect the calcification rate of some organisms. There is experimental evidence that reduced pH leads to decreasing calcification by several, but not all, marine organisms, including coccolithophorides, foraminifers, corals, and pteropods (e.g., Doney et al. 2008, Riebesell et al. 2000). However, it is not clear to what extent calcifying organisms are able to adapt to different carbonate chemistry over many generations (e.g., Langer et al. 2006) or that all calcifying organisms will respond the same way (Iglesias-Rodriguez et al. 2008, Riebesell et al. 2008). Reduced calcification will act on at least two opposing feedback systems for the carbon cycle, (h) and (i).

(h) First, the chemistry of the carbonate system prescribes release of CO₂ during calcification; i.e., less CO₂ will be released under a reduced calcification scenario and act as a negative feedback.

(i) Second, calcium carbonate particles act as ballast for POC sinking from the upper ocean, allowing organic particles to be transported to greater depths before they decompose than they would have without the extra ballast (e.g., Armstrong et al. 2002). It is possible that the particle flux of organic carbon to the deep ocean will be reduced if the calcification rate decreases, creating a positive feedback. It has been shown that even a modest increase in the remineralization depth will reduce atmospheric CO₂ substantially (Kwon et al. 2009).

(j) Changes in climate may act indirectly to affect the uptake of anthropogenic CO₂ via changes in phytoplankton community. For instance, coccolithophores, favored in oligotrophic nutrient-limiting conditions, have a positive feedback effect due to the formation of calcite shells, whereas diatoms that prefer weakly stratified, nutrient-rich environments have a negative feedback since they are responsible for large parts of the biological carbon export. A more stratified ocean in a global warming scenario would tend to reduce the nutrient supply to the photic zone, which in turn would favor the growth of coccolithophores over diatoms; a positive feedback (Cermenio et al. 2008).

(k) Changing climate, with inevitable changes in physical forcing, leads to changes in ocean circulation and properties (salinity and temperature), which will have direct or indirect implications for the carbon cycle. For instance, observations show intensification of Southern Ocean winds during the past decades, and most climate models predict this trend will continue as a response to a warmer world. Further, the Southern Ocean is an important sink for anthropogenic carbon, possibly responsible for ~40% of the total ocean C_{org} uptake (Sabine et al. 2004a). Le Quere et al. (2007) found, based on atmospheric CO₂ concentrations and an inverse method, that the Southern Ocean sink of C_{org} has weakened in the last decades compared to expectations from the atmospheric increase of CO₂. However, the study was criticized for the choice of atmospheric CO₂ data and for neglecting important processes regulating the CO₂ air-sea exchange (Law et al. 2008, Zickfeld et al. 2008b). Observational records further indicate that increased wind stress in the Southern Ocean has little effect on the transport in the Antarctic Circumpolar Current and on the meridional overturning circulation since the increased Ekman transport is compensated by an increased eddy flux. Thus, the net effect of increased wind stress on the carbon flux should be quite small (Böning et al. 2008). Non-eddy-resolving ocean models are apparently not able to correctly predict the Southern Ocean response to increased wind forcing and the feedback on the carbon cycle.

(l) Similarly, most climate models predict reduced Meridional Overturning Circulation (MOC) in a future, warmer world. This will choke the transport of surface waters, laden with anthropogenic CO₂, into the deep ocean, a positive feedback.

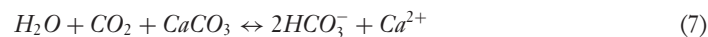
(m) At the same time, decreased MOC will also reduce upwelling of deep water with high DIC concentration, a negative feedback. The net balance between feedbacks (l) and (m) is still a matter of scientific debate (e.g., Sarmiento & Le Quéré 1996, Zickfeld et al. 2008a). Since the MOC also controls the large-scale supply of nutrients to the surface layer, there are biological ramifications for the carbon cycle in addition to the direct physical transport impacts. Reduced biological export of carbon due to changes in nutrient supplies related to reduced MOC seems to be the dominant impact over circulation changes that leads to a net positive feedback, but with large regional differences (Zickfeld et al. 2008a).

Most of the processes involved in the feedbacks described here are not understood or monitored well enough to determine whether these feedbacks are changing today as a result of climate change and increasing C_{ant} in the ocean. As stated previously, the current scientific paradigm is that anthropogenic CO_2 is entering the ocean as a passive thermodynamic response to rising atmospheric CO_2 . The current challenge for the scientific community is to determine whether these feedbacks are occurring and how they will modify the ability of the ocean to store C_{ant} over the next few decades.

LONG-TERM ACCUMULATION OF ANTHROPOGENIC CO_2

By the early 2000s, approximately 330 Pg C had been released to the environment from the burning of fossil fuels (Figure 5). There are vast amounts of fossil fuel (>5000 Pg C) remaining in geological formations that can potentially be oxidized to CO_2 by human activities, most of that in the form of coal. In addition to this, there are large deposits (5000–10,000 Pg C) of methane hydrate in permafrost and in deep-sea sediments, the latter location being the dominating source. Although it remains highly uncertain how much of these stores will end up as CO_2 in the atmosphere, we will briefly consider the ocean response to the carbon perturbation on millennial timescales. As seen above, atmospheric CO_2 will equilibrate with the global ocean on centennial timescales and a large fraction of the anthropogenic CO_2 will be stored in the ocean, independently of whether the CO_2 is released to the atmosphere or purposefully placed in the ocean (i.e., ocean sequestration). The ocean has a vast capacity to store CO_2 so it will continue to take up CO_2 as long as it is increasing in the atmosphere. The rate at which this process takes place, and the magnitude of the fraction that dissolves in the ocean, are dependent on the biogeochemical feedback loops and processes discussed in the previous section.

On millennial timescales accumulation of atmospheric CO_2 in the ocean tends to be increased by two additional feedback processes: calcium carbonate ($CaCO_3$) dissolution and silicate ($CaSiO_3$) weathering (e.g., Archer 2005, Archer et al. 1997, Montenegro et al. 2007). As discussed in the previous section, accumulation of CO_2 in the ocean lowers the pH of the ocean and makes the waters more corrosive towards $CaCO_3$ minerals (Figure 5n). Dissolution occurs both in the water column and from sediments, creating a negative feedback to the atmosphere often referred to as $CaCO_3$ compensation (Broecker & Peng 1987). The net effect of $CaCO_3$ dissolution is the restoring of oceanic pH and the increase in the fraction of C_{ant} that can be dissolved in the ocean according to the following equation:



Further, weathering of silicate-containing igneous rock restores the carbonate system on geological timescales according to the following equation:



This is a slow process; the e-folding timescale for CO₂ relaxation of silicate weathering is on the order 200 to 400 thousand years (e.g., Archer et al. 1997, Sundquist 1991). This process might be more efficient if the hydrological cycle accelerates in a warmer world, but the dynamics of this process is complicated by long timescales invoking glacial/interglacial processes and weathering changes as well as tectonic processes (Archer 2005).

The time until the atmospheric anthropogenic CO₂ burden is reduced to 25% of the total emission is calculated to be 1800 years by Montenegro et al. (2007), but only 300–450 years by Archer (2005) in a different model set-up and experiment type. However, both approaches suggest a long tail in the perturbation, with a mean lifetime of atmospheric anthropogenic CO₂ of 30–35 thousand years found by Archer (2005). Taken together, these two feedback loops tend to restore atmospheric CO₂ levels towards preindustrial levels by increasing the alkalinity and restoring the oceanic buffer capacity. However, on timescales of up to a few millennia, it can be expected that the partitioning between the ocean and atmosphere CO₂ reservoirs will be roughly maintained through restoring of the ocean buffer capacity by CaCO₃ dissolution. This leaves a fraction of ~7% of the CO₂ perturbation in the atmosphere for several hundred thousand years for silicate weathering to handle (Archer 2005). However, the magnitude of the ocean C_{ant} fraction is dependent on climate feedbacks such as the amount of ocean heating; warmer water holds less CO₂ than cold water, potentially increasing the airborne fraction up to 15% (Archer 2005). Depending on the future magnitude of the anthropogenic CO₂ emissions, release of anthropogenic CO₂ will result in higher oceanic alkalinity and DIC concentrations, up to roughly 8% increase in oceanic DIC if the majority of available fossil fuel is used.

CONCLUSIONS

The ocean's role as a sink for anthropogenic CO₂ appears to be changing over time and will likely change even more dramatically into the future. Although the uncertainties are fairly large due to necessary assumptions, most approaches agree that the global ocean inventory of C_{ant} was around 120 Pg C in the mid-1990s. This means that nearly half of the CO₂ released into the atmosphere from burning fossil fuels between 1800–1994 ended up in the ocean (Sabine et al. 2004a).

Based on ocean uptake estimates, the global ocean inventory should be increasing by about 2.2 Pg C per year, giving a total inventory of about 135 Pg C in the early 2000s (Gruber et al. 2009). Since 2000, global fossil fuel CO₂ emission has increased at an annual rate of 3.3%, giving a total cumulative emission of approximately 330 PgC by 2006 (Canadell et al. 2007). Thus, the ocean storage of carbon only accounts for ~41% of the total fossil fuel emissions since the preindustrial. This percentage has dropped since the mid 1990s because the rate of ocean carbon uptake does not seem to be keeping pace with the rate of growth in CO₂ emissions (Bindoff et al. 2007). The land use change emissions are highly uncertain, but if they are included as part of the calculation, then the oceans are only absorbing about 25% of the current total anthropogenic emissions (Canadell et al. 2007).

These estimates, however, are strongly dependent on the ocean uptake calculations. Estimates of decadal scale ocean inventory changes consistently show increases in C_{ant} in the water column, but have not been synthesized in a coordinated way to be able to confirm or deny a slowdown in the rate of carbon storage. Unfortunately, the first global estimate of decadal carbon inventory changes will not be available for a few more years, and it will be more than a decade before another survey will be able to make a global evaluation of how the rates of storage are changing based just on ocean interior observations.

Ocean interior observations, however, remain the best mechanism for verifying the changes in ocean C_{ant} inventory. It is extremely difficult to predict how the many possible carbon cycle feedbacks will affect ocean carbon storage; modeling and proxy techniques are limited by our

current understanding of the ocean carbon cycle. It is critically important that we understand how C_{ant} is accumulating in the ocean on timescales relevant to human civilization (years to decades). CO_2 emissions are growing at an ever increasing rate and the momentum of the carbon and climate system is such that decisions made today will still impact the climate for hundreds to thousands of years to come. The best way to improve our understanding is to continue using a broad suite of approaches, with both observations and models, to examine both ocean carbon uptake and ocean carbon storage over a range of timescales.

SUMMARY POINTS

1. With the synthesis of the WOCE/JGOFS data, the first robust global estimates of the total accumulation of C_{ant} were produced. Although the uncertainties are fairly large due to necessary assumptions, most approaches agree that the global ocean inventory of C_{ant} was around 120 Pg C in the mid-1990s.
2. Based on ocean uptake estimates, the global ocean inventory should be increasing by about 2.2 Pg C per year, giving a total inventory of about 135 Pg C in the early 2000s (Gruber et al. 2009). Repeat hydrographic sections are currently being run that will allow an assessment of decadal inventory changes that can be compared to these ocean uptake estimates.
3. Estimates of decadal scale ocean inventory changes consistently show increases in C_{ant} in the water column, but have not been synthesized in a coordinated way to be able to confirm or deny a slowdown in the rate of carbon storage. Ocean interior observations, however, remain the best mechanism for verifying the changes in ocean C_{ant} inventory.
4. It is extremely difficult to predict how the many possible carbon cycle feedbacks will affect ocean carbon storage; modeling and proxy techniques are limited by our current understanding of the ocean carbon cycle.
5. It is critically important that we understand how C_{ant} is accumulating in the ocean on timescales relevant to human civilization (years to decades). CO_2 emissions are growing at an ever increasing rate, and the momentum of the carbon and climate system is such that decisions made today will still impact the climate for hundreds to thousands of years to come.
6. The best way to improve our understanding is to continue using a broad suite of approaches, with both observations and models, to examine both ocean carbon uptake and ocean carbon storage over a range of timescales.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED

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