

# THE GLOBAL OCEAN CARBON CYCLE: INVENTORIES, SOURCES AND SINKS

by

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## Abstract

The ocean plays a major role in the global carbon cycle because it is a vast reservoir of carbon, its surface waters quickly exchange carbon with the atmosphere, and most importantly it absorbs and stores approximately one third of the carbon dioxide released to the atmosphere annually from human activity. Two independent approaches are used by NOAA and its national and international partners to document changes in the ocean carbon system. Long-term (decadal) changes in ocean carbon inventory are examined by repeating measurements that are made along specific cruise tracks (repeat hydrography) at intervals of 5-15 years. Within the U.S. this is accomplished with the CLIVAR/CO<sub>2</sub> Repeat Hydrography Program which has the goals of quantifying global changes in the storage and transport of heat, fresh water, carbon, chlorofluorocarbon tracers and related bio-geochemical parameters. Examinations of recent Repeat Hydrography cruises in the Atlantic and Pacific have revealed significant changes in the carbon system over the last decade. Variations in other biogeochemical parameters have shown that processes such as organic matter recycling and circulation, which were previously assumed to be in steady state, must be considered in the interpretation of the anthropogenic contribution to these water column carbon changes. Shorter-term (daily to inter-annual) changes in ocean carbon uptake are examined with sea-air CO<sub>2</sub> flux estimates from instruments deployed on ships and moorings. The growing surface CO<sub>2</sub> data set indicates that there is significant inter-annual variability in the sea-air CO<sub>2</sub> flux, but there are substantial uncertainties in the current approaches for estimating this variability.

## Background

The global utilization of fossil fuels is rapidly changing the trace gas composition of the Earth's atmosphere. These "greenhouse 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. Carbon dioxide (CO<sub>2</sub>) is the major anthropogenic greenhouse gas, contributing about 60% to the total change in radiative forcing due to human perturbations. As of the early 2000s, the release of CO<sub>2</sub> to the atmosphere from burning fossil fuels and cement manufacturing had grown to more than 7 Pg C per year (1Pg = 10<sup>15</sup>g = 1 billion metric tons) (Marland et al., 2005). Of this amount, approximately 3 Pg C of this so-called "anthropogenic CO<sub>2</sub>" accumulates in the atmosphere with distributions that are well documented through a global measurement network. The remaining 4 Pg C is sequestered by the terrestrial biosphere and global ocean. Where and how these two major sink regions (ocean and terrestrial biosphere) vary in their uptake of CO<sub>2</sub> from year to year is the subject of much scientific research (Prentice, 2001). Understanding this partitioning is critical because the ocean is believed to be a long-term sink for anthropogenic CO<sub>2</sub> while the terrestrial sink is more labile.

Several approaches have been used to estimate the ocean uptake of anthropogenic CO<sub>2</sub> for the decade of the 1990s (Table 1). There is a general consensus that the average oceanic sink for the 1980s and 1990s was about  $1.9 \pm 0.7$  Pg C yr<sup>-1</sup> (Figure 1; Sabine et al., 2004a). Most of these estimates, however, can not be used, a priori, to predict what the future ocean uptake will be or how feedbacks between the ocean carbon system and climate may alter the controls on sea-air CO<sub>2</sub> fluxes. Future policy decisions regarding possible greenhouse gas emission controls need to be based on predictive models of CO<sub>2</sub> sources and sinks and these models need to be

adequately validated against sustained ocean carbon observing system measurements. Moreover, tracking the increases in ocean carbon content, and the associated ocean acidification, will contribute to an improved understanding of the effects of elevated CO<sub>2</sub> on ocean biota (Feely et al., 2004a; Orr et al., 2005).

Two basic approaches are being used to document changes in the ocean carbon system: 1) repeated trans-basin hydrographic sections (surveys of ocean properties in the water column along a cruise track) provide information on decadal scale changes in ocean inventories and transport within the ocean interior; and 2) high frequency (in space and time) observations of surface ocean and atmospheric CO<sub>2</sub> concentrations that can be used to estimate sea-air exchanges on seasonal to inter-annual time-scales. These two approaches provide information on ocean carbon changes over a complimentary range of time and space scales. The latest findings from the ocean carbon program are presented here. These findings are placed in context with a growing body of evidence documenting the carbon cycle changes in the ocean.

## **Ocean Inventories**

In the 1990s, researchers from several countries worked together through two international programs, the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS), to conduct an extensive survey of the chemical and physical properties of the global ocean (Feely et al., 2001; Wallace, 2001). An analysis of more than 70,000 carbon measurements from this survey, found that the ocean accumulated approximately 118 Pg C between 1800 and 1994 (Sabine et al., 2004b). This accumulation accounts for 48% of the CO<sub>2</sub> released from burning fossil fuels over this same time period. Because the ocean mixes much more slowly than the atmosphere, more than half of this carbon can still be found in the upper 400 meters (Figure 2). The average penetration depth for CO<sub>2</sub> generated from human

activity is about 1000 meters, roughly one quarter of the average global ocean depth. Most of the ocean volume, therefore, has not been exposed to the higher atmospheric CO<sub>2</sub> concentrations of the industrial era so we would anticipate that the ocean would continue to take up CO<sub>2</sub> for at least the next thousand years.

Because there were no ocean carbon measurements prior to the industrial revolution, the anthropogenic CO<sub>2</sub> component of the total dissolved inorganic carbon (DIC) concentration had to be estimated using a back calculation technique based on our understanding of the physical and biological contributions to the measured DIC. As a consequence, assumptions about steady state circulation and biology over these time scales had to be made. By repeating a subset of the cruises run in the 1990s, many of the assumptions required for the back calculation technique can be avoided and the changes in ocean carbon along a cruise track run at two different times can be directly evaluated.

The U.S. CLIVAR/CO<sub>2</sub> Repeat Hydrography Program started in 2003 with three cruises in the North Atlantic (Figure 3). Analysis of these repeated lines has indicated that several biogeochemical parameters are changing with time (Feely et al., 2005a). For example, changes of -10 to 30  $\mu\text{mol kg}^{-1}$  of DIC have been observed in the upper 1000 m of the water column between the 1993 and 2003 occupations of A16N along 25°W in the North Atlantic (Figure 4a). Although the magnitude of the changes is expected, the patchiness of the changes was not anticipated. More surprisingly is the fact that there have been comparable changes in the Apparent Oxygen Utilization (AOU, a measure of the decomposition of organic matter in the ocean) of the waters indicating significant changes in the organic matter cycling over the last decade (Figure 4b). The complicated patterns of these changes clearly show that carbon is being influenced by more than simple secular changes in anthropogenic tracers. In some cases changes

in circulation and organic matter decomposition may be masking the anthropogenic changes and in other cases these changes may enhance the apparent ocean carbon uptake.

Another intriguing preliminary finding from a comparison of recent cruises in the North Pacific and North Atlantic is an indication that anthropogenic carbon inventories may be increasing in the Pacific at about twice the rate of the Atlantic over the last 10 years (Feely et al., 2005a). This is in contrast to the long-term anthropogenic CO<sub>2</sub> inventory that shows larger column inventories in the North Atlantic, thus highlighting the variability in oceanic sinks with time, and underscoring the challenge of predicting future oceanic uptake of atmospheric CO<sub>2</sub>. The explanation for these recent findings may lie in understanding the effects of climate modes like the North Atlantic Oscillation (NAO) or the Pacific Decadal Oscillation (PDO) on the decadal scale circulation. These results also point to the need for improved techniques for isolating the anthropogenic and natural components of the observed variability.

### **Ocean-Atmosphere CO<sub>2</sub> Fluxes**

The temporal and spatial variability of the partial pressure of CO<sub>2</sub> (i.e. the contribution of CO<sub>2</sub> pressure to total gas pressure, pCO<sub>2</sub>) in the surface ocean is large compared to the atmospheric pCO<sub>2</sub> variability. Atmospheric pCO<sub>2</sub> is well resolved by weekly flask sampling at ~50 stations around the world (Tans and Conway, 2005). Because of the greater variability, surface ocean pCO<sub>2</sub> distributions are only known in a climatological sense. Inferring a global CO<sub>2</sub> uptake rate is challenging because, the average pCO<sub>2</sub> of the atmosphere need only be ~7 $\mu$ atm higher than the global ocean pCO<sub>2</sub> to account for an ocean uptake of ~2 Pg of carbon each year. Taro Takahashi of Lamont-Doherty Earth Observatory and his collaborators have amassed a database of more than 1.7 million surface ocean pCO<sub>2</sub> measurements, spanning more than 30 years, and derived a pCO<sub>2</sub> climatology for the global ocean (Takahashi et al., 2002).

These data have been used to determine global and regional sea-air CO<sub>2</sub> fluxes with an average annual global open-ocean uptake of  $1.5 \pm 0.4$  Pg C/yr for a nominal year of 1995 (Takahashi et al., 2002; revised by T. Takahashi, New York, 2005, personal communication). This flux estimate represents the total net flux in 1995. This is significant because prior to human intervention the oceans were a net source of CO<sub>2</sub> to the atmosphere of approximately 0.6 Pg C yr<sup>-1</sup> (Sabine et al., 2004a). The total anthropogenic flux is the difference between the 1995 net sea-air flux and the estimated pre-industrial net sea-air flux (i.e.  $-1.5 - 0.6 = -2.1$  Pg C/yr; see Table 1).

Figure 5 shows the global distribution of total net sea-air CO<sub>2</sub> fluxes. The yellow-orange-red colors indicate oceanic areas where there is a net source of CO<sub>2</sub> to the atmosphere, and the blue-purple colors indicate regions where there is a net sink of CO<sub>2</sub>. The Equatorial Pacific is a strong source of CO<sub>2</sub> to the atmosphere throughout the year as a result of upwelling, which brings deep, high CO<sub>2</sub> waters to the surface in the central and eastern regions. This upwelling, and thus the CO<sub>2</sub> flux to the atmosphere, is heavily modulated by the El-Niño Southern Oscillation (ENSO) cycle (Feely et al., 2002, 2004b; Takahashi et al., 2003). During strong El-Niño years the equatorial Pacific CO<sub>2</sub> source can drop to zero as the upwelling is suppressed. During La Niña the upwelling, and thus the CO<sub>2</sub> source to the atmosphere, is enhanced. CO<sub>2</sub> outgassing fluxes are also observed in the tropical Atlantic and Indian oceans.

The CO<sub>2</sub> flux in the high-latitude ocean is governed primarily by deep convection in winter and biological uptake during the spring and summer months (i.e. outgassing in the winter and uptake in the spring/summer), whereas in the temperate and subtropical regions, the flux is governed primarily by water temperature (i.e., spring/summer warming causes outgassing and fall/winter cooling causes uptake). Outside of the equatorial belt and coastal upwelling regions, the  $\Delta p\text{CO}_2$  (seawater pCO<sub>2</sub> - atmospheric pCO<sub>2</sub>, which drives the air sea exchange) is highest

during winter in subpolar and polar waters, whereas it is highest during summer in the temperate regions. Thus, the seasonal variation of  $\bullet\text{pCO}_2$  and, consequently, the shift between net uptake and release of  $\text{CO}_2$  in subpolar and polar regions is about 6 months out of phase with that in the temperate regions (Takahashi et al., 2002).

Although the Takahashi  $\text{pCO}_2$  climatology has greatly improved our understanding of the sea-air flux patterns, it does not address the temporal variability in these patterns or the variability in the global net uptake. Substantial inter-annual variability in the Equatorial Pacific  $\text{CO}_2$  flux ( $\pm 0.4 \text{ Pg C/yr}$  peak-to-peak amplitude) has been well documented through sustained shipboard and moored time series measurements (e.g. Feely et al., 1995; Chavez et al., 1999; Feely et al., 2005b), but a paucity of measurements have limited similar assessments in other regions of the global ocean.

Recently, Park et al. (2005) used regional algorithms relating  $\text{pCO}_2$  to satellite derived sea surface temperature anomalies to estimate  $\text{CO}_2$  variability globally. They found the average inter-annual deviation of the global ocean  $\text{CO}_2$  flux from the Takahashi climatology to be  $\pm 0.18 \text{ Pg C yr}^{-1}$  for the period from 1982 to 2001. However, there are large uncertainties in this approach. The estimated uncertainty from the seawater  $\text{pCO}_2/\text{SST}$  relationships alone is as large as the estimated global inter-annual variability (Figure 6a).

In an effort to improve these regional algorithms, the international  $\text{CO}_2$  community is developing a surface  $\text{CO}_2$  observational network using volunteer observing ships, moorings, and drifting floats. These measurements together with modeling efforts can be used to better understand the controls on sea-air  $\text{CO}_2$  fluxes. For example, approximately 70% of the global  $\text{CO}_2$  flux variability is currently attributed to flux anomalies in the Equatorial Pacific (Figure 6b). The regional algorithm approach estimates a smaller inter-annual variability than most ocean model studies in this region. Our growing observational data base will allow us to make

improved algorithms for the Equatorial Pacific (e.g. Feely et al., 2004b). Similar efforts are going on in subtropical regions where temperature exerts a dominant control on sea surface pCO<sub>2</sub> levels (e.g. Olsen et al., 2004, Wanninkhof et al, 2005).

In the high-latitude oceans the algorithms will require additional input parameters to account for the effects of deep convection and biological uptake on surface pCO<sub>2</sub>. For example, the inclusion of mixed layer depth, obtained from the ARGO profiling floats, in the algorithms for these regions looks promising (Lueger et al., 2005). An expansion of the global observational network is needed in all parts of the global ocean to evaluate the uncertainties in the regional algorithm assessment of global inter-annual variability and to develop improved algorithms relating pCO<sub>2</sub> to satellite observations. With the proper observational program, the documentation of inter-annual CO<sub>2</sub> flux variability in the global ocean can be achieved.

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**Table 1.** Estimates of Oceanic Anthropogenic CO<sub>2</sub> Uptake in Pg C/yr.

Method	Carbon Uptake (Pg C/yr)	Reference
Measurements of sea-air pCO <sub>2</sub> Difference	2.1 ± 0.5	Takahashi et al. (2002)
Inversion of atmospheric CO <sub>2</sub> observations	1.8 ± 1.0	Gurney et al. (2002)
Inversions based on ocean transport models and observed DIC	2.0 ± 0.4	Gloor et al. (2003)
Model simulations evaluated with CFC's and pre-bomb radiocarbon	2.2 ± 0.4	Matsumoto et al. (2004)
OCMIP-2 Model simulations	2.4 ± 0.3	Orr (2004)
Based on measured atmospheric O <sub>2</sub> and CO <sub>2</sub> inventories corrected for ocean warming and stratification	2.2 ± 0.5	Keeling et al. (2005)
GCM Model of Ocean Carbon	1.93	Wetzel <i>et al.</i> (2005)
CFC ages	2.0 ± 0.4	McNeil <i>et al.</i> (2003)

Fluxes are normalized to 1990-1999 (except Keeling & Manning which is for 1993-2004)  
and corrected for pre-industrial degassing flux of ~0.6 Pg C/yr.

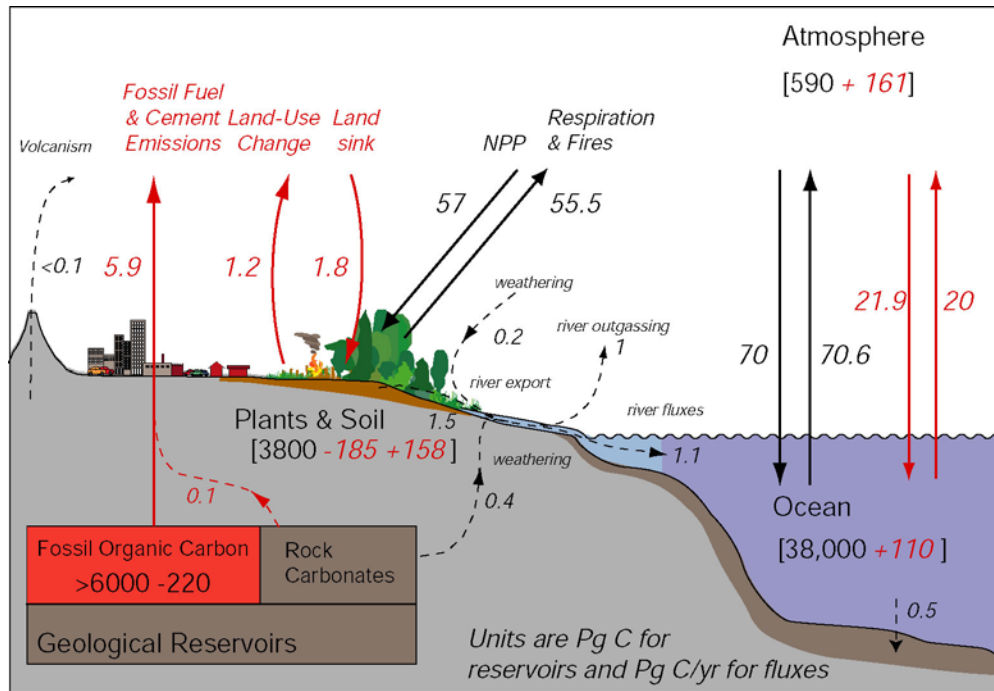


Figure 1. Schematic of global carbon cycle during the 1980s and 1990s. Black arrows represent natural fluxes and red arrows are anthropogenic fluxes (adapted from Sabine et al., 2004a).

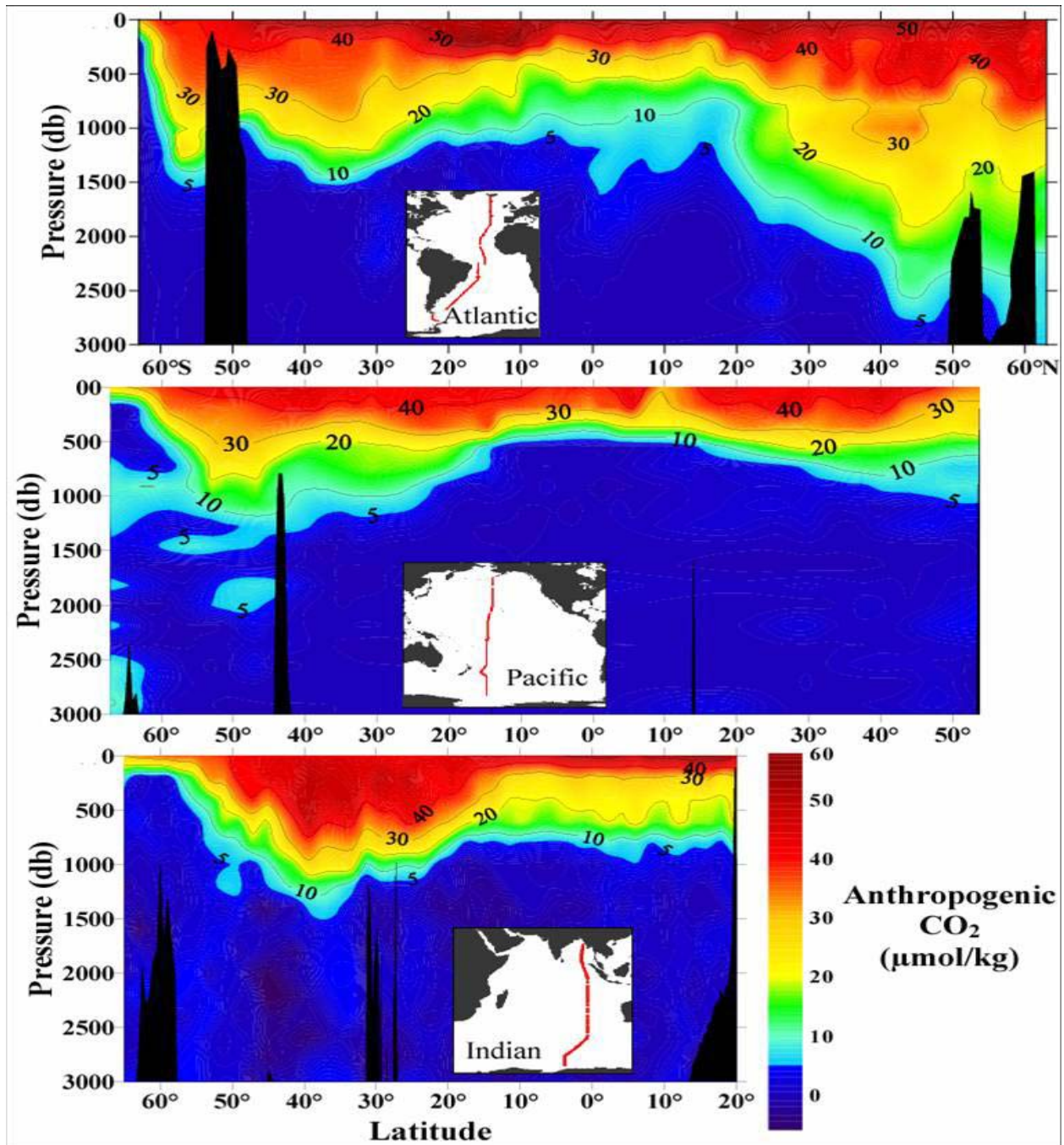


Figure 2. Example sections of anthropogenic CO<sub>2</sub> that has accumulated in the Atlantic, Pacific, and Indian oceans between 1800 and 1994 (modified from Sabine et al., 2004b).

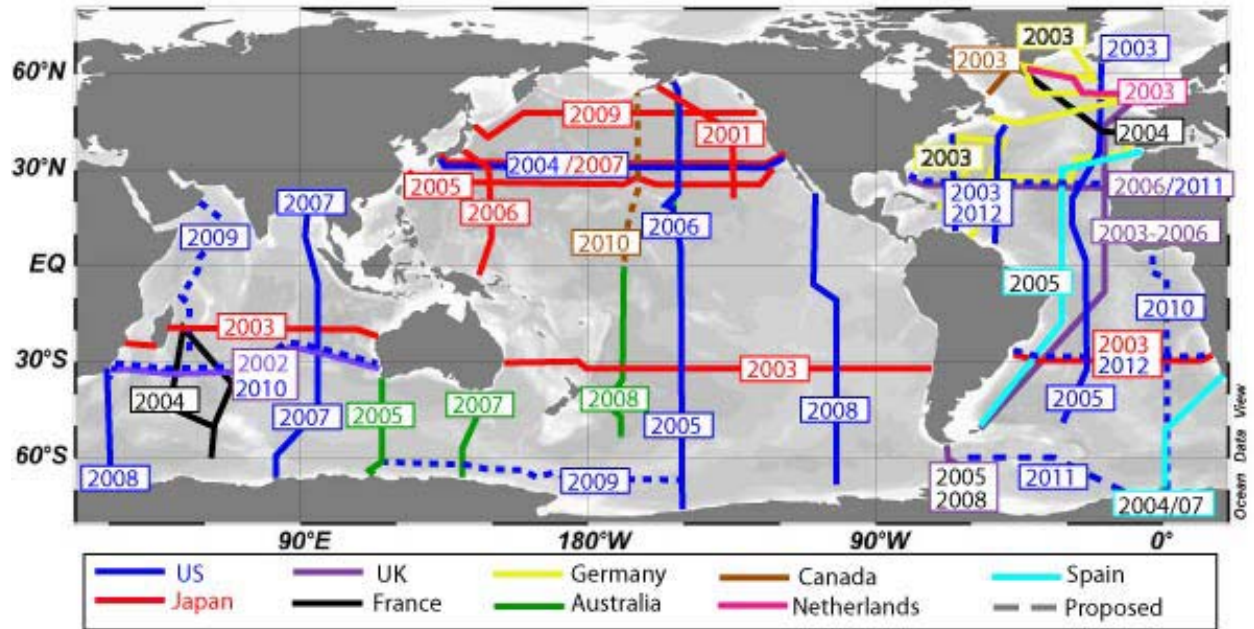


Figure 3. Map indicating recently completed and planned international repeat hydrography cruises. The U.S. CLIVAR/CO<sub>2</sub> Repeat Hydrography Program (indicated in blue) started in 2003 with three cruises in the North Atlantic.

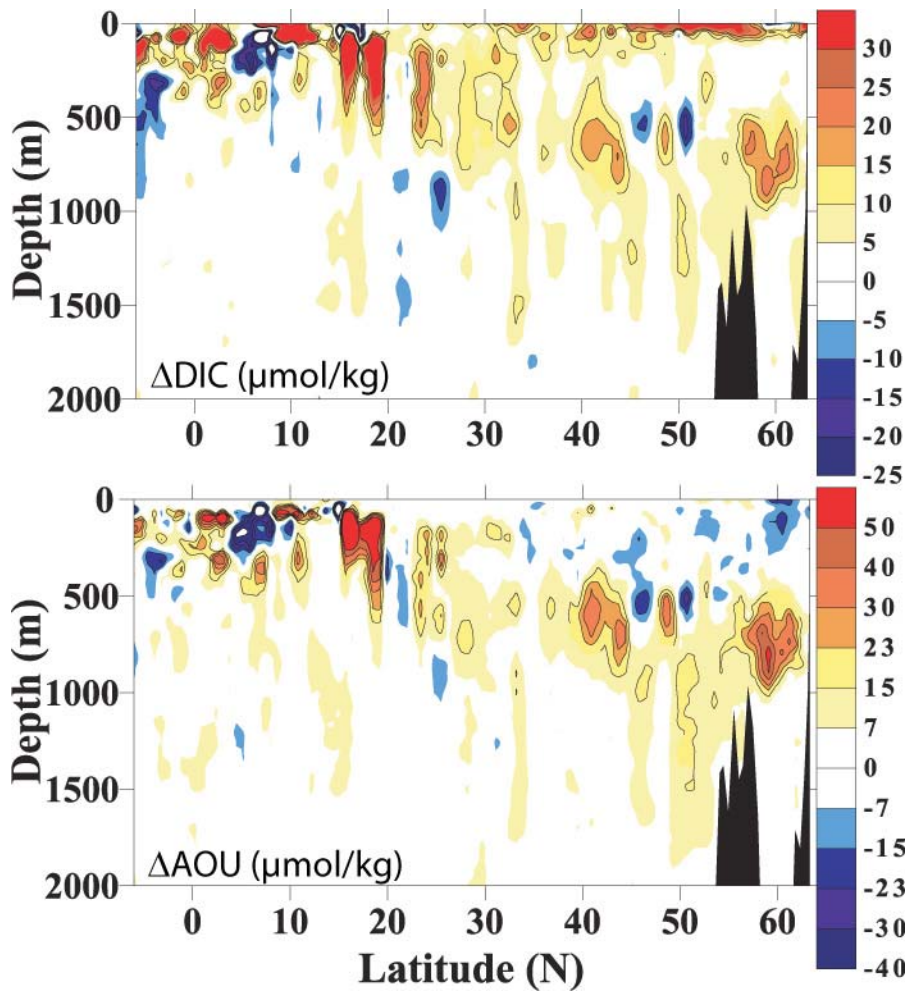


Figure 4. Changes in DIC (a) and AOU (b) between the 2003 and the 1993 occupations of A16N. Positive values represent an increase in concentrations between 1993 and 2003 (modified from Feely et al., 2005a).

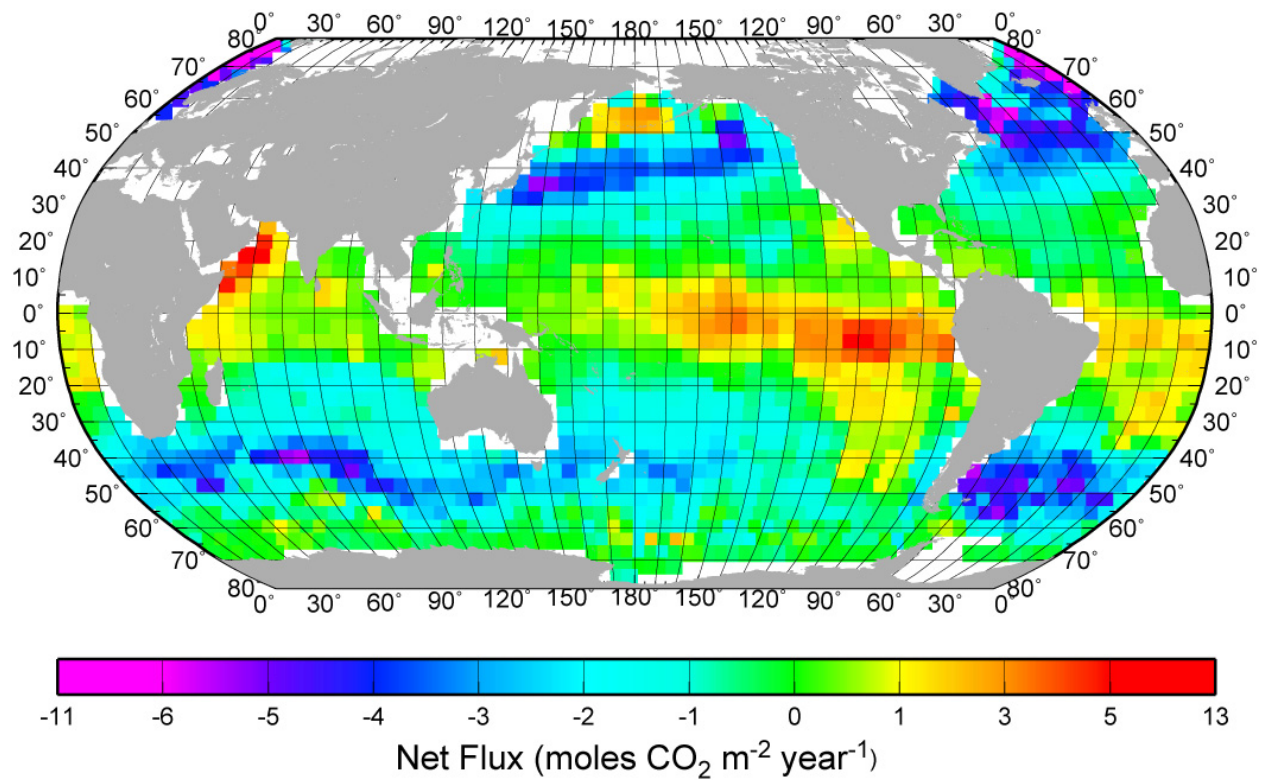


Figure 5. Annual sea-air fluxes for a nominal year of 1995. Positive values indicate a flux of CO<sub>2</sub> out of the ocean (Takahashi, 2002).



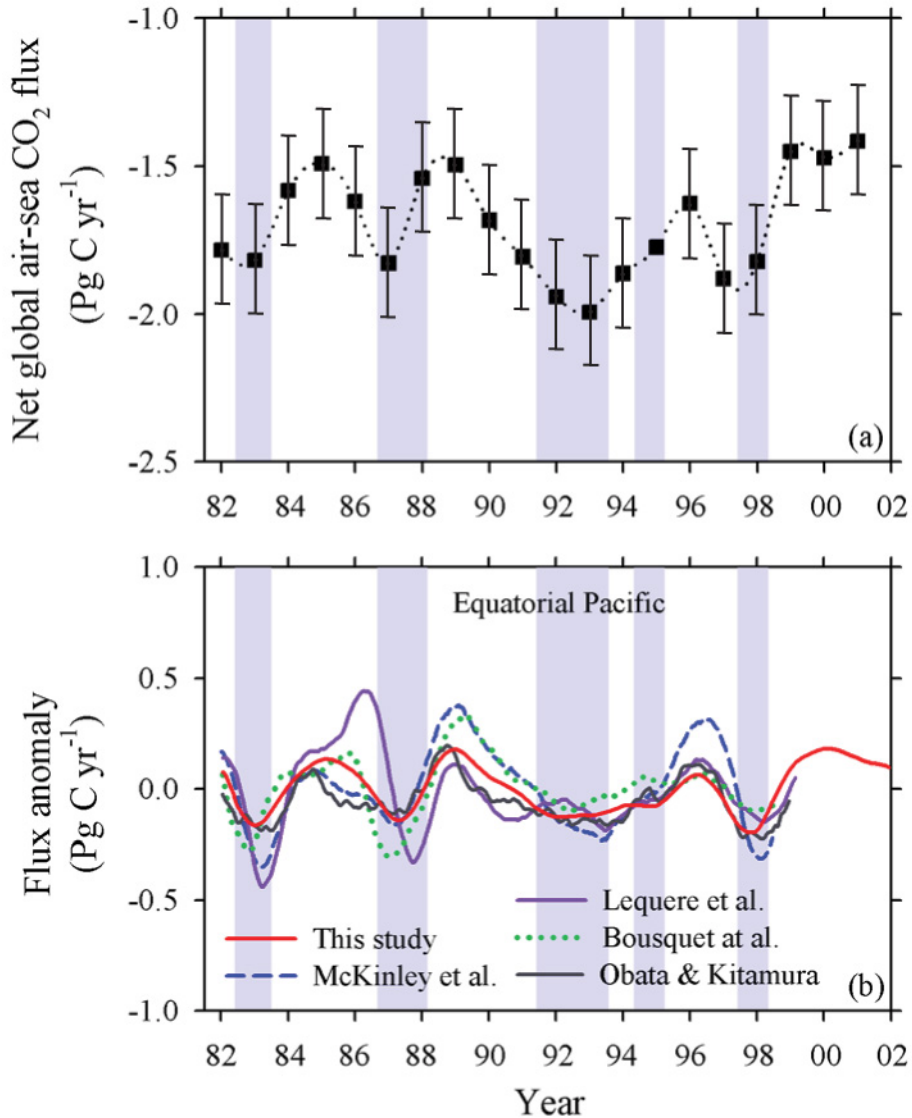


Figure 6. (a) Net global sea-air CO<sub>2</sub> fluxes in Pg C yr<sup>-1</sup> from 1982 through 2001. The dotted line is a spline fit and error bars indicate estimated uncertainty in seasonal pCO<sub>2sw</sub>/SST relationships only. Negative values correspond to net oceanic CO<sub>2</sub> uptake. Shaded bars indicate El Niño events (when SST anomaly is greater than 0.4°C in the Niño 3.4 region). (b) Comparisons of modeled CO<sub>2</sub> flux anomalies for the Equatorial Pacific (10°N–10°S, 80°W–135°E). For the period over which four independent estimates are available (1982–1997), modeled interannual variabilities obtained from Le Quéré et al. (2003), McKinley et al. (2004), Bousquet et al. (2000), Obata and Kitamura (2003), and the present study (Park et al., 2005) are ±0.18, ±0.18, ±0.14, ±0.13, and ±0.12 Pg C yr<sup>-1</sup>, respectively (modified from Park et al., 2005).