Global Carbon Sinks and Their Variability Inferred from Atmospheric $O_2$ and $\delta^{13}C$

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Recent time-series measurements of atmospheric $O_2$ show that the land biosphere and world oceans annually sequestered 1.4 ± 0.8 and 2.0 ± 0.6 gigatons of carbon, respectively, between mid-1991 and mid-1997. The rapid storage of carbon by the land biosphere from 1991 to 1997 contrasts with the 1980s, when the land biosphere was approximately neutral. Comparison with measurements of $\delta^{13}CO_2$ implies an isotopic flux of 89 ± 21 gigatons of carbon per mil per year, in agreement with model- and inventory-based estimates of this flux. Both the $\delta^{13}C$ and the $O_2$ data show significant interannual variability in carbon storage over the period of record. The general agreement of the independent estimates from $O_2$ and $\delta^{13}C$ is a robust signal of variable carbon uptake by both the land biosphere and the oceans.

Between 1991 and 1997, combustion of fossil fuels added roughly 6.2 gigatons of carbon per year (GtC/year) (1, 2) to the atmosphere in the form of CO$_2$. During this same period, the atmospheric burden of CO$_2$ increased by only 2.8 GtC/year. The balance of the CO$_2$ was taken up by the oceans and the land biosphere. Determining the ocean-land partition of carbon uptake (and the temporal variability of the partition) is essential for any mechanistic understanding of carbon storage.

We use two approaches to experimentally constrain this partition. The first approach involves measuring the rate of change of the $O_2$ concentration of air (actually, the $O_2/N_2$ ratio). Fossil fuel combustion decreases atmospheric $O_2/N_2$, and terrestrial growth releases $O_2$, attenuating the fossil fuel decrease in this ratio. Ocean uptake of CO$_2$ does not affect $O_2/N_2$. Thus, the change in atmospheric $O_2/N_2$ indicates terrestrial carbon storage (3, 4). The second approach involves measuring the change in the isotopic composition ($\delta^{13}C$) of atmospheric CO$_2$. Fossil fuels possess low $\delta^{13}C$ values. During photosynthesis, terrestrial plants assimilate carbon with a lower $\delta^{13}C$ value, thereby enriching the $\delta^{13}C$ of the CO$_2$ left behind in the atmosphere. Moreover, net uptake of CO$_2$ between the atmosphere and oceans leaves $\delta^{13}C$ essentially unchanged. Thus, the change in atmospheric $\delta^{13}C$ gives a measure of terrestrial carbon storage (5).

These approaches to determining the partition of land and ocean uptake have geochemical uncertainties that may be large. Uncertainty in the $O_2$ method arises because the ocean may be a small net source or sink of $O_2$ over the course of a year or more. Every spring, atmospheric $O_2/N_2$ rises by about 60 per meg [or 0.06 per mil (%)] (5) because of ocean biology. Net production of organic matter releases $O_2$, which supersaturates the mixed layer and escapes to the atmosphere. Every winter, $O_2/N_2$ falls by 60 per meg as the oceans take up oxygen to resaturate suboxic waters of the interior (6–8). This seasonal cycle is ~15 times larger than the annual change in atmospheric $O_2/N_2$ because of net carbon storage by the land biosphere. These natural oceanic fluxes may not be in exact balance over the course of 1 year (or even several). A natural imbalance in these fluxes would cause a change in the annual average $O_2/N_2$ ratio of air. We would erroneously attribute this change to carbon storage by the land biosphere (4, 7, 8). Such an imbalance is unlikely to persist for more than a few years. Thus, carbon fluxes based on $O_2$ are most robust when averaged over many years.

Uncertainty in the $\delta^{13}C$ method comes from uncertainties in isofluxes (also called “gross” or “disequilibrium” fluxes). Every year, large quantities of carbon pass through the land biosphere. Any net storage or release is an imbalance between two large fluxes: ~50 GtC of carbon fixed by photosynthesis and ~50 GtC released through respiration. The $\delta^{13}C$ of assimilated CO$_2$ reflects the modern atmospheric $\delta^{13}C$, whereas the $\delta^{13}C$ of respired CO$_2$ reflects the $\delta^{13}C$ of the atmosphere of years past, when the plant assimilated the carbon that is now being respired. Similarly, though the oceans annually sequester roughly 2 Gt of carbon, the oceans and atmosphere exchange about 90 GtC. Consequently, the flux of CO$_2$ into the ocean carries the current signature of atmospheric $\delta^{13}C$, whereas the flux of CO$_2$ out of the ocean carries an atmospheric $\delta^{13}C$ signature that is several decades old. In both cases, the isofluxes greatly attenuate the change in atmospheric $\delta^{13}C$ that would otherwise occur. Estimates of the isofluxes reflect uncertainties in the age spectrum of decomposing organic matter, decomposition rates as a function of latitude, switches from C3 to C4 photosynthesis, and the $\delta^{13}C$ of fossil fuels, and rates of gas exchange at the air-sea interface (9, 10). Although these uncertainties are substantial, they arise from processes that, when globally averaged, are largely constant from one year to the next (with the possible exception of switches between C3 and C4 photosynthesis). Thus, interannual variability in carbon fluxes is captured by $\delta^{13}C$, even if the long-term partition is ill-constrained. Moreover, the uncertainties described here for $\delta^{13}C$ are essentially independent of those for $O_2/N_2$. Thus, information from one species can be used to reduce uncertainties in the other.

Beginning in 1991, global $O_2/N_2$ measurement programs began (4, 8), and $\delta^{13}C$ sampling networks and interlaboratory comparisons expanded dramatically (11, 12). Results from these tracers for the years 1991–94 (8, 13–15) showed that the land biosphere was an important CO$_2$ sink. Here we present updated records of both $\delta^{13}C$ and $O_2/N_2$ from a global network of stations. With nearly 7 years of data in hand for both species, we are able to assess the carbon balance through 1997 with more confidence than was previously possible, constrain the isofluxes of carbon, and examine interannual variability in carbon storage. Taken along with other recent $O_2/N_2$-based analyses, these data indicate a persistent shift in land biosphere sequestration rates as compared with those of the previous decade.

We begin by calculating oceanic and terrestrial carbon fluxes using $O_2$. The atmospheric mass balance for CO$_2$ can be written

\[
\frac{d(CO_2)}{dt} = -0.471 \times (f_{atmosphere} + f_{cement} + f_{land} + f_{ocean})
\]

where $f_{atmosphere}$, $f_{cement}$, $f_{land}$, and $f_{ocean}$ are fluxes of carbon from the atmosphere due to fossil fuel combustion, cement manufacturing, the terrestrial biosphere, and the ocean, respectively (all negative for release to the atmosphere; $f_{ocean}$ and $f_{land}$ positive for se-

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questration). The fluxes are in GtC/year, and the atmospheric inventory term \(d(CO_2)/dt\) is in parts per million (ppm) per year (2). Similarly, the mass balance for atmospheric oxygen can be written

\[
\frac{d(O_2/N_2)}{dt} = 4.8 \times 0.471 \times (1.43 f_{fuel} + 1.1 f_{land}) \tag{2}
\]

The coefficients of \(f_{fuel}\) and \(f_{land}\) arise because 1.43 mol of \(O_2\) are consumed for every mole of \(CO_2\) combusted for today’s mix of fuels (16), and 1.1 mol of \(O_2\) are produced for every mol of \(CO_2\) sequestered by the land biosphere (17). 0.471 converts GtC to ppm \(CO_2\), and 4.8 converts ppm to per meg (5).

These equations can be solved to give \(f_{land}\) and \(f_{ocean}\) in terms of measured quantities

\[
f_{land} = -\frac{1.43}{1.1} f_{fuel} + \frac{1}{2.49} \frac{d(O_2/N_2)}{dt} \tag{3}
\]

\[
f_{ocean} = \frac{d}{dt} \left( \frac{CO_2}{0.471} + \frac{O_2/N_2}{2.49} \right) - \frac{1.1 - 1.43}{1.1} f_{fuel} - f_{cement} \tag{4}
\]

Figure 1 shows measurements of \(O_2/N_2\) and \(CO_2\) from our laboratories (18) as well as previously published data of R. Keeling (15). We use the fuel and cement production records of Marland et al. (1). We assume that fossil carbon emissions increase in 1996 and 1997 at the same rate as in 1995. We assume that atmospheric nitrogen is constant (16) and that over the period of study, oceanic \(O_2\) fluxes are balanced.

Averaging the records from the Barrow/Alert and Cape Grim stations, we calculate a global ocean uptake of \(2.0 \pm 0.6 \text{ GtC/year}\) for the years 1991.5–1997.5 (see Table 1 for errors) (19). As a check, we treat the records at Samoa (1993.5–1997.5) and Syowa (1994.0–1997.0) as globally representative. From these, we calculate ocean uptake of 2.2 and 1.4 GtC/year. Unfortunately, these latter records are too short for robust fits and error estimates.

Based on the Cape Grim and Barrow data, we calculate a global average terrestrial carbon sink (\(f_{land}\)) of \(1.4 \pm 0.8 \text{ GtC/year}\). The Samoa and Syowa records imply sinks of 0.9 and 1.4 GtC/year, respectively. These results are shown in Fig. 3.

Having calculated carbon fluxes using \(O_2/N_2\), we use this information, along with measurements of \(\delta^{13}C\), to constrain the isofluxes. Following the presentation of Tans et al. (20), we can express the change in the atmospheric abundance of the \(^{13}C\) isotope as

\[
\frac{d}{dt} \left( \frac{\delta^{13}C_{\text{atm}}}{\delta^{13}C_{\text{air}}} \right) = -f_{\text{fuel}} (\delta^{13}C_{\text{fuel}} - \delta^{13}C_{\text{air-land}}) - f_{\text{cement}} (\delta^{13}C_{\text{cement}} - \delta^{13}C_{\text{air-land}}) - f_{\text{ocean}} (\delta^{13}C_{\text{air-sea}} - \delta^{13}C_{\text{air-land}}) + G \tag{5}
\]

\(\epsilon_{\text{air-land}}\) is the kinetic fractionation that occurs during \(CO_2\) invasion into the ocean. \(\epsilon_{\text{air-land}}\) represents the fractionation during photosynthesis by the land biosphere, \(f_{\text{fuel}}, f_{\text{cement}}, f_{\text{ocean}}, f_{\text{fuel}}\), and \(f_{\text{land}}\) all represent net (one-way) fluxes. \(CO_2\) is the total atmospheric inventory in GtC. \(G\) captures the isoflux from gross (two-way) exchanges between the atmosphere and the land and ocean reservoirs. Values of \(\epsilon\) and \(\delta\) are in per mil. \(G\) has units of GtC \%/year. Having determined \(f_{\text{ocean}}\) and \(f_{\text{land}}\) with the \(O_2/N_2\) and \(CO_2\) measurements, we can now solve for \(G\).

Values used in this calculation are shown in Table 1. The \(\delta^{13}C\) data (Fig. 2) are from the National Oceanic and Atmospheric Administration–Climate Monitoring and Diagnostics Laboratory/Colorado University/Institute for Arctic and Alpine Research (NOAA-CMDL/CU-INSTAAAR) measurement program (11). The \(CO_2\) data are from the NOAA-CMDL cooperative flask sampling network (21). We find that \(G\) is \(89 \pm 21 \text{ GtC \%/year}\). The error corresponds to an uncertainty in the land-ocean partition of \(\pm 1.3 \text{ GtC/year}\). This result is in good agreement with the value of \(83 \text{ GtC \%/year}\) derived using the method of Ciais et al. (9) [updated with the observed (atmospheric) and estimated (oceanic) evolution of \(\delta^{13}C\)].

In addition to the new results from this study, Fig. 3 shows the land-ocean partition derived from archived air samples by Langenfelds et al. (22), from the firn-air study of Battle...
et al. (23), and from previously published work of Keeling et al. (15). Taken as a composite time series, the data show a substantial shift in the global carbon cycle. From 1977 to 1990, the land biosphere was neither a source nor a sink of carbon. In contrast, the first 7 years of this decade show a significant terrestrial sink of carbon. This broad temporal feature agrees with the synthesis-inversion result of Rayner et al. (24), in part because many of our data were common to that study. The oceanic sink is in good agreement with tracer-calibrated ocean circulation models (1.7 to 2.8 GtC/year) (25).

As a step toward understanding the causes of this shift, we examine interannual variations in carbon fluxes. As discussed above, we expect most of the uncertainties in \( \delta^{13}C \)-based fluxes to be constant over a 7-year record. In the case of O\(_2\), however, we have little reason a priori to expect the oceanic production-ventilation processes driving O\(_2\) fluxes to be in balance over a year or two. Thus, we would expect \( \delta^{13}C \)-based results to reflect interannual variability in fluxes more faithfully than O\(_2\)-based results. This simple picture is potentially complicated by shifts in terrestrial photosynthesis from C\(_3\) to C\(_4\) pathways. Are these conclusions justified?

Figure 4 shows the 2-year averaged trends (26) in the land and ocean carbon sinks inferred from \( \delta^{13}C \) and O\(_2\)/N\(_2\) measurements. Based on the \( \delta^{13}C \) records in Fig. 4, it appears that the terrestrial carbon sink was strongest in 1992–93 and 1996–97 and weaker in 1994–95. The ocean appears to have been a vigorous sink before 1995, with declining intensity in 1995–96. Terrestrial carbon storage seems more variable than oceanic storage. Furthermore, the similar phasing of the \( \delta^{13}C \)- and O\(_2\)-derived swings in uptake implies that the oceanic O\(_2\) cycle is roughly balanced over a 2-year period and that the \( \delta^{13}C \) record is not solely reflecting switches from C\(_3\) to C\(_4\) pathways. Are these conclusions justified?

First we consider analytic errors. Measurement errors in \( \delta^{13}C \) lead directly to errors in the land-ocean partition (13). Based on measurements of the same samples from 1992–98 and on measurements of common calibration standards in 1994, 1995, and 1997, discrepancies between the Commonwealth Scientific and Industrial Research Organization (CSIRO) and INSTAAR \( \delta^{13}C \) measurement programs have been observed (11, 12, 27). In particular, a calibration difference of 0.03 to 0.04 ‰ (corresponding to a 1-year flux of 1.2 to 1.6 GtC) developed in mid-1994. We provisionally adopt the CSIRO calibration here and use it to correct for this discrepancy. The remaining standard deviation of annual mean differences between the labs is then 0.014 ‰, corresponding to an uncertainty of \( \pm 0.5 \) GtC/ year in the land-ocean partition. The largest difference occurs for 1995, for which the uncertainty is twice as large. Furthermore, there is no discernible trend in the intercalibration between INSTAAR and CSIRO (beyond the offset in 1994).

Errors in O\(_2\)/N\(_2\) also translate directly into the land-ocean partition. All the stations shown in Fig. 4 exhibit consistent trends, which suggest minimal collection bias. Frequent sampling leads to small statistical fitting errors (the statistical error on \( f_{ocean} \) is \( \pm 0.4 \) GtC/year for a 12-month period at Cape Grim or Barrow). Nonetheless, transient calibration artifacts prob-

![Fig. 2. The global average \( \delta^{13}C \) record, measured by the NOAA-CMDL/GU-INSTAAR network with calibration as described in the text.](image-url)

![Fig. 3. Time-averaged land and ocean carbon storage from this and other studies. This study (\( \delta^{13}C \)) shows global average values calculated using the current data and the method of Ciais et al. (9) with G = 83.6 GtC/yr/year. No errors are shown for \( \delta^{13}C \) because G is determined using O\(_2\)/N\(_2\) (see text). This study (O\(_2\)) shows the average of the Barrow/Alert and Cape Grim records. The values for Samoa and Syowa are presented without error estimates because the records are too short for meaningful statistical analysis. The Langenfelds result (22) shown here has been adjusted to reflect a different averaging period (36).](image-url)

| Table 1. Values of the quantities used in this study. Uncertainties in \( d(O_2/N_2)/dt \) are due to standard drift and choice of fit (19), respectively. The latter is given for an average of data from two sites. The “values” of the measured trends in O\(_2\) and CO\(_2\) are illustrative only, because our results are calculated from related quantities [see (19)]. |
| --- | --- | --- |
| Quantity | Value | Source |
| \( f_{ocean} \) | \(-6.21 \pm 0.37 \) GtC/year | (1) |
| \( f_{current} \) | \(-0.184 \pm 0.011 \) GtC/year | (1) |
| Combustion stoichiometry | 1.43 \pm 0.02 | (16) |
| Photosynthetic stoichiometry | 1.1 \pm 0.06 | (17) |
| \( d(O_2/N_2)/dt \) | \(-16 \pm 0.8 \) per meg/year | This study |
| \( d(CO_2)/dt \) | \(-1.24 \pm 0.05 \) ppm/year | This study |
| CO\(_2\) (in 1995) | \(-770 \pm 1 \) GtC | This study |
| \( d/dt \delta^{13}C \) (in 1995) | \(-0.013 \pm 0.008 \) ‰/year | This study |
| \( \delta^{13}C \) (in 1995) | \(-29.4 \pm 1.8 \) ‰ | (32) |
| \( \delta^{13}C \) atm (in 1995) | \(-7.86 \pm 0.015 \) ‰ | This study |
| \( \epsilon_{air-land} \) | \(-18 \pm 1 \) ‰ | This study |
| \( \epsilon_{air-sea} \) | \(-2 \pm 1 \) ‰ | (33, 34) |
ably do exist and contribute at some level to the fluctuations shown in Fig. 4.

The agreement of the \( \delta^{13}C \) and \( O_2/N_2 \) records is far from perfect. The \( O_2 \)-based variability in \( f_{ocean} \) and particularly in \( f_{atm} \) is greater than that found in the \( \delta^{13}C \)-based records. Some damping of the \( \delta^{13}C \)-based signal is to be expected. Damping will occur because the \( O_2 \) calculation simply treats the atmosphere as one large box, whereas \( \delta^{13}C \) calculations use a model of atmospheric transport to estimate the effects of vertical mixing (9). Alternatively, the smaller \( \delta^{13}C \)-based swings may reflect covarying changes in carbon storage and terrestrial isotopic discrimination. Apparent discrepancies at the ends of the records probably reflect the fitting algorithm (28) and infrequent sampling of \( O_2/N_2 \) in 1991.

As the smoothing period is decreased below the 2-year value shown here, we see implausibly large variations develop in the \( O_2 \)-based records. These higher frequency variations are not due to fluctuations in our standards, because these variations at different sites are not coherent. The most likely explanation is that the \( O_2 \) data contain a significant regional component and that interannual variations in ocean production and ventilation have a significant impact on atmospheric \( O_2 \) on time scales of roughly 1 year.

With these reservations in mind, it appears that, as expected (29), the land biosphere is a highly variable reservoir. Variability must be driven by climate, but the response to forcing is complex. Although El Niño has often been posited as a control of terrestrial carbon storage (30), the multivariate El Niño index was high during our entire period of study, except for a very weak La Niña episode from August 1995 to early 1997. Thus, other factors must be at least partly responsible for the variability we observe in our 6-year record.

References and Notes


2. One \( \text{GtC} = 10^{15} \) g; the addition of 1 Gt of carbon to the atmosphere increases the amount of \( O_2 \) by 0.47 ppm.


6. Following Keeling and Shertz (4), we express changes in atmospheric \( O_2/N_2 \) in ppm as:

\[
\delta O_2/N_2 = \frac{O_2/N_2 - 0.82}{0.82} \times 10^4
\]

A change of 4.8 ppm is equivalent to 1 ppm per year, because \( O_2 \) makes up 20.9% of air.


18. \( O_2/N_2 \) was measured at the University of Rhode Island (URI) by mass spectrometry (31). \( CO_2 \) was measured by NOAA/CMDL (21). Smooth curves fit the data according to the algorithm of Thoning et al. (26). The \( CO_2 \) data points are analyses of the same flasks analyzed for \( O_2/N_2 \). The \( CO_2 \) fits shown here are made to a separate set of analyses taken as part of the NOAA/CMDL cooperative flask sampling network (27). The individual points show the values used in determining \( f_{atm} \) and \( f_{ocean} \) (see text). Each point is the average of two flasks collected simultaneously. Flask pairs are discarded if they differ by more than 16 per meg. Because the Keeling \( O_2/N_2 \) data are relative to a different standard, we adjust those data by 66.7 per meg. The mean difference between the URI and Scripps Institution of Oceanography (SIO) records at Cape Grim during the 5-year period of overlap. The adjusted SIO data that predate URI measurements are appended to the beginning of the URI record, and fits are made to the composite record.

19. To reduce errors in our calculation of \( f_{ocean} \) we combine measurements of \( O_2 \) and \( CO_2 \) for each flask (Eq. 4) and then calculate the time-rate-of-change of this quantity. In so doing, high-frequency excursions in \( O_2 \) due to local events (inversions, pollution, etc.) will be largely removed because of the inverse excursions in \( CO_2 \). To determine time-averaged ocean carbon storage at Barrow/Alert and Cape Grim, we calculate \( f_{ocean} \) and fit a straight line to (i) the 1-year trend (26) and (ii) the actual data values at the time of year when \( O_2/N_2 \) reaches a minimum at each station (an 10-week interval starting on 16 February and 21 August at Barrow and Cape Grim, respectively). Results shown are the average of these two methods. We consider criterion (ii) in order to select times when the deep mixed layer makes it most likely that the ocean will be in equilibrium with the atmosphere and the effect of ventilation imbalances will be minimized.


28. For fitting purposes, the first year of each record is taken as representative of the previous 2 years of (nonexistent) data. Similarly for the last year of data. Thus, short-term fluctuations at the beginnings and ends of the records can greatly distort the fit.


32. R. J. Andres, personal communication.


35. Samples were collected from the following stations: Alert (82°28′N, 62°30′W), Barrow (79°19′N, 156°36′W), American Samoa (14°15′S, 170°34′W), Cape Grim (40°41′S, 144°14′E), Baring Head (41°20′S, 174°50′E), and Syowa (69°00′S, 39°35′E).

36. The result of Langenfelds et al. applied to the years 1978–1997. Using the results from this work for the period 1992–1997, we infer the values for the period 1978–1991.5. This is the quantity shown in Fig. 3. Errors for the Langenfelds et al. result and our work are highly correlated because of common data and methods.

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