Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle

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Measurements of changes in atmospheric molecular oxygen using a new interferometric technique show that the O$_2$ content of air varies seasonally in both the Northern and Southern Hemispheres and is decreasing from year to year. The seasonal variations provide a new basis for estimating global rates of biological organic carbon production in the ocean, and the interannual decrease constrains estimates of the rate of anthropogenic CO$_2$ uptake by the oceans.

The dominant processes influencing the abundance of atmospheric O$_2$ on timescales less than many thousands of years are chemical reactions involving the creation and destruction of organic matter: that is, photosynthesis, respiration and combustion. These reactions cause atmospheric O$_2$ to vary inversely with atmospheric CO$_2$ with an O$_2$ : CO$_2$ exchange ratio that depends on the composition of the organic matter. Additional chemical reactions, however, influence the abundance of atmospheric CO$_2$. The difference in the geochemistry of O$_2$ and CO$_2$ arises because, whereas dissolved O$_2$ is chemically neutral, dissolved CO$_2$ reacts with water to form carbonic acid, which in turn reacts with basic compounds such as carbonates. As a result of the differing acid-base properties of O$_2$ and CO$_2$, measurements of changes in atmospheric O$_2$ can constrain aspects of the global carbon cycle that are not constrained by measurements of atmospheric CO$_2$ alone.

Consider, for example, the processes controlling the increase in atmospheric O$_2$ over the past century. The dominant sources of CO$_2$ are fossil-fuel burning and carbon releases associated with land-use changes while the dominant sinks may involve a combination of oceanic uptake and uptake by terrestrial ecosystems. With one exception, these sources and sinks of CO$_2$ are stoichiometrically linked to sources and sinks of O$_2$. The exception is the uptake of CO$_2$ by the oceans which essentially proceeds through the reaction of dissolved CO$_2$ with carbonate ions and therefore does not involve O$_2$ (ref. 3). Thus, in principle, the difference between the decrease in atmospheric O$_2$, corrected for reaction stoichiometry, and the increase in atmospheric CO$_2$ can determine the uptake of CO$_2$ by physical dissolution in the oceans.

The acid-base chemistry of CO$_2$ also leads to qualitative differences in the fluxes of O$_2$ and CO$_2$ across the air-sea interface that are driven by marine biological processes. Marine photosynthesis and respiration produce comparable changes in mol m$^{-2}$ in dissolved O$_2$ and total dissolved inorganic carbon in sea water. Changes in dissolved CO$_2$ gas are $\sim$15 times smaller, however, as determined by the chemical equilibrium between dissolved CO$_2$ gas and the other (dominant) forms of dissolved inorganic carbon, especially bicarbonate and carbonate ions. Because air-sea gas fluxes tend to be driven in proportion to the saturation anomalies in dissolved gas concentrations, biologically induced air-sea fluxes of CO$_2$ are $\sim$15 times smaller than fluxes of O$_2$ (ref. 5). Other important qualitative differences in the behaviour of CO$_2$ and O$_2$ arise because the equilibration timescale for dissolved CO$_2$ is $\sim$15 times longer (2 days) than that of dissolved O$_2$ (a few weeks).

Observed variations in atmospheric oxygen

Previous attempts to measure changes in the percentage of atmospheric O$_2$ in background air were thwarted by the high O$_2$ content of air$^{6,7}$. Here we report measurements using a new interferometric technique$^{8,9}$ which overcomes that limitation.

We detect oxygen changes through changes in the O$_2$/N$_2$ ratio of air samples. Because atmospheric N$_2$ is believed to be much less variable than O$_2$, changes in the O$_2$/N$_2$ ratio should primarily reflect changes in O$_2$ (ref. 6). Changes in O$_2$/N$_2$ are reported as relative deviations from a reference

$$\delta(O_2/N_2) = \frac{[(O_2/N_2)_{\text{sample}} - 1]}{(O_2/N_2)_{\text{ref.}}}$$

We propose the convention of multiplying $\delta(O_2/N_2)$ by 10$^3$ and expressing the result in units of 'per meg'. In these units 1/0.2095 = 4.8 per meg is equivalent to 1 p.p.m. by volume (p.p.m.v) because O$_2$ comprises 20.95% by volume.

Our reference for the O$_2$/N$_2$ determinations is based on the average composition of the air derived from a suite of six high-pressure cylinders. The O$_2$/N$_2$ ratios of flask samples are determined first relative to a working gas. We compare the working gas frequently with a pair of secondary reference gases which, in turn, are compared at roughly six-month intervals with the six primary reference gases. These primary reference gases have shown detectable changes relative to each other but no systematic trends over a period of four years.

External precision, based on analysis of replicate flasks, is roughly $\pm 4$ per meg. Additional uncertainty must be allowed, however, for day-to-day variations in O$_2$/N$_2$ ratio of the air delivered from the reference gas cylinders. Allowing for this variability, we estimate the overall precision of the average concentration of the replicate flasks to be $\pm 6$ per meg relative to the long-term mean composition of the air delivered from the primary reference cylinders.

Results from samples collected at three sea-level sites, Alert, Ellesmere Island (83.5°N, 62.3°W), La Jolla, California (32.9°N, 117.3°W) and Cape Grim, Tasmania (40.7°S, 114.7°E) are shown in Fig. 1. Significant seasonal variations in $\delta(O_2/N_2)$ occur at all three sites. An interannual decrease in O$_2$/N$_2$ is clearly evident in the La Jolla data. As discussed below, the decrease rate is consistent with the global rate of O$_2$ consumption from the burning of fossil fuels. Oxygen depletion from burning fossil fuels is not a serious environmental concern because the changes are minuscule compared with the total O$_2$ abundance in air$^{10}$.

Interpretation of seasonal variations

At the two Northern Hemisphere sites, the seasonal variations in O$_2$/N$_2$ are strongly anticorrelated with variations in CO$_2$. The amplitude of the O$_2$/N$_2$ cycle is larger than would be expected from the CO$_2$ variations. The CO$_2$ cycle is known to

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be caused primarily by seasonal uptake and release of CO₂ by land plants and soils. Taking an average O₂:CO₂ exchange ratio for the formation and destruction of terrestrial organic matter of −0.05:1 (ref. 8), we estimate that Δ(O₂/N₂) should increase by 5 per meg for each 1 p.p.m. decrease in CO₂ over the seasonal cycle. Instead, the observed ratio at the Northern Hemisphere sites is closer to 10 per meg per p.p.m. At Cape Grim in the Southern Hemisphere, the O₂/N₂ cycle is even more remarkable with a −96 per meg seasonal variation in Δ(O₂/N₂) occurring in the presence of a very small (−1 p.p.m.) variation in CO₂.

In addition to exchanges with terrestrial ecosystems, there are two processes that can contribute significantly to seasonal variations in O₂/N₂. First, the amount of O₂ that is dissolved in the upper ocean varies seasonally as the water warms and cools. Because O₂ in the upper ocean equilibrates rapidly with the atmosphere, we can estimate the air-sea flux of O₂ associated with seasonal temperature changes from the relation

\[ F_{O_2} = -\frac{dC_{O_2}}{dT} Q \frac{C_p}{X} \] (2)

where \( F_{O_2} \) is the net O₂ flux (positive into the air) in mol m\(^{-2} \) s\(^{-1} \), \( dC_{O_2}/dT \) is the temperature derivative of the O₂ solubility (mol m\(^{-3} \) K\(^{-1} \)), \( Q \) is the rate of change of heat storage in the upper ocean (J m\(^{-2} \) s\(^{-1} \)) and \( C_p \) is the heat capacity of sea water (J m\(^{-2} \) K\(^{-1} \)). The effect of these fluxes on the atmospheric O₂/N₂ ratio is reduced by about 44% due to the thermally driven flux of N₂ (ref. 5) which we can estimate by applying equation (2) to N₂.

Second, there is net production of O₂ in the euphotic zone (roughly the upper 100 m of the ocean), where, on average, gross photosynthesis exceeds gross respiration, and there is a net consumption of O₂ below the euphotic zone by respiration. Both the net O₂ production rate in the euphotic zone and the rate of vertical mixing between the euphotic zone and deeper waters undergo large seasonal variations. At midlatitude and high latitudes the highest production rates tend to occur in the spring and summer when the waters above 100 m are well stratified. A considerable fraction of the O₂ produced at this time escapes into the atmosphere. Comparable amounts of O₂ are removed from the atmosphere in the autumn and winter when stratification breaks down and oxygen-depleted waters from below 100 m depth are brought back into contact with the surface. The air-sea O₂ fluxes associated with this seasonal cycle are linked to the rate at which organic material is produced and exported from the euphotic zone.

![Graph showing measurements of Δ(O₂/N₂) and CO₂ mole fraction at Alert, La Jolla, and Cape Grim.](image)

**FIG. 1.** Measurements of Δ(O₂/N₂) and CO₂ mole fraction at (a) Alert, (b) La Jolla and (c) Cape Grim. The axes are scaled (5 per meg = 1 p.p.m.) so that changes in Δ(O₂/N₂) and CO₂ are directly comparable on a mol O₂ to mol CO₂ basis. Averages of flasks taken on a given day: daily averages for background conditions using the continuous in situ measurement method. Supplementary CO₂ data from programmes at the NOAA Climate Monitoring and Diagnostics Laboratory and the Scripps Institution of Oceanography. The curves are least-squares fits to the function \( X = a + bt + c \sin(2\pi t) + d \cos(2\pi t) + e \sin(4\pi t) + f \cos(4\pi t) \), where \( t \) is in years. For the Cape Grim and Alert O₂/N₂ data, the trend coefficient \( b \) is forced to have the same value as for the La Jolla data; all other curves are six-parameter fits. Samples are collected in 5-litre glass flasks equipped with a pair of glass-bore stopcocks sealed with Viton O-rings. Flasks are generally collected in triplicate. Sampling times are chosen so that the air is at or near background composition as indicated by other tracers (such as CO₂ or radon). The flasks are exposed at the sampling sites by flushing them with cryogenically (−50 °C) dried air at ambient pressure. Air samples are further dried with two cold traps (−80 °C) before analysis. Samples are analysed for CO₂ concentration using an infrared analyser (Siemens Ultramat 3) which is calibrated against CO₂ standards prepared at the Scripps Institution of Oceanography. The O₂/N₂ measurements are corrected for the small interfering effect of CO₂ on the refractivity ratio. Interferences of other trace gases may contribute to an offset of several per meg to the O₂/N₂ determinations, although the variability in this offset is believed to be smaller than the precision of the measurements.
Marine photosynthesis and respiration as well as changes in surface water temperature also produce variations in the CO₂ partial pressure of surface waters. The air-sea CO₂ exchange driven biologically is heavily suppressed, however, by the inorganic chemistry of CO₂ in seawater, as mentioned above. The thermal effects on pCO₂ are comparable in magnitude and generally opposite to the biological effects, thus leading to even smaller seasonal air-sea CO₂ fluxes than would be expected from either marine biology processes or thermal processes alone. In contrast, the thermal effects and biological effects on O₂ tend to reinforce each other as both lead to higher O₂ supersaturations in the warmer months.

In the Northern Hemisphere, we can use the seasonal variations in CO₂, which largely reflect terrestrial exchange, to correct for the effects of terrestrial exchange on the O₂/N₂ variations, thus deriving the residual O₂/N₂ variations attributable to the oceanic exchanges alone (Fig. 2). In the Southern Hemisphere, the lack of a large seasonal variation in CO₂ indicates that the O₂/N₂ variations are almost entirely of marine origin.

The amplitude of the oceanic component of the O₂/N₂ variations within each hemisphere is closely related to the total seasonal net outgassing (SNO) of O₂ in that hemisphere. Here SNO is defined as the areally and temporally integrated flux of O₂ from the ocean into the atmosphere where the time integration extends over the seasonal period when the areally integrated flux is directed into the atmosphere. The close relationship between SNO and the seasonal O₂/N₂ variations follows because the timescale for seasonal variations (\(\tau_{\text{season}} = \text{1 year} \div 2 \times 66\) days) is short relative to the timescale for atmospheric inter-hemispheric exchange (\(\tau_{\text{atm}} = 1.1 \text{ years}\)) but longer than the timescale for tropospheric mixing within each hemisphere (\(\tau_{\text{hem}} = 30 \text{ to 60 days}\)). Here we construct preliminary estimates of SNO for the Northern and Southern Hemispheres (Table 1) by assuming that the seasonal amplitudes in O₂/N₂ at the surface are equivalent to what would be achieved if the surface O₂ fluxes were homogeneously diluted into an air mass equal to 50% of the air mass in each hemisphere. This level of atmospheric mixing is consistent with mixing rates for atmospheric CO₂ in the Northern Hemisphere based on recent two- and three-dimensional transport models calibrated with other tracers.

The estimate of SNO derived in this way includes both biological and thermal components. The thermal component, however, includes only the excess O₂ flux not compensated for by the thermal N₂ flux because only the uncompensated O₂ flux can change the observed O₂/N₂ ratio. The uncompensated thermal component can be estimated independently by applying equation (2) to O₂ and N₂, and thus the biological component can be derived by subtraction. The results (Table 1) indicate that uncompensated thermal degassing accounts for only ~15% of the oceanic component of the O₂/N₂ variations; the remaining 85% is evidently of marine biological origin.

What do these oxygen fluxes tell us about the rates of biological productivity in the ocean? To answer this question it is useful to introduce the concept of net euphotic zone production (NEZP), defined as the net community production (gross production of autotrophs less the gross respiration of autotrophs and heterotrophs) integrated over the depth of the euphotic zone. NEZP may be defined with respect to either organic carbon or O₂. If we accept that net community production of carbon or O₂ requires inputs of "new" nutrients, then NEZP may be roughly equated with the concept of "new" production as given in ref. 15. We prefer to express our results in terms of NEZP because the concept of "new" production of organic matter or O₂ becomes ambiguous whenever organic matter is formed with varying C : N or O₂ : N ratios, or whenever significant nitrification occurs in the euphotic zone.

Areally and annually integrated NEZP of O₂ can be related

<table>
<thead>
<tr>
<th>TABLE 1 Components of seasonal variations in oxygen</th>
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<tr>
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<tr>
<td><strong>Total seasonal amplitude</strong></td>
</tr>
<tr>
<td><strong>Northern</strong></td>
</tr>
<tr>
<td><strong>Southern</strong></td>
</tr>
<tr>
<td>Amplitude</td>
</tr>
<tr>
<td>Oceanic component of seasonal amplitude</td>
</tr>
<tr>
<td>Total SNO</td>
</tr>
<tr>
<td>Excess thermal component of SNO†</td>
</tr>
<tr>
<td>Biological component of SNO‡</td>
</tr>
</tbody>
</table>

* Estimated from the average of the peak-to-peak amplitudes for the fitted curves for the La Jolla and Alert data shown in Fig. 1.
† Estimated from the peak-to-peak amplitude of the fitted curve for the Cape Grim data in Fig. 1.
‡ Estimated from the peak-to-peak amplitude of the fitted curve for the La Jolla and Alert data shown in Fig. 2.
§ Assumes that the terrestrial exchanges can account for 10 per cent of the seasonal variations at Cape Grim, on the basis of a modelling study for CO₂ at 42°S, 175°E by Heimann et al.
¶ Calculated assuming that the surface fluxes are effectively diluted into a volume containing 4.4 \(\times 10^{13}\) mol of dry air (50% of the dry air mass in the hemisphere).
** Estimated from equation (2) using ocean heat storage potential data of Samuels and Cox and solubility data of Weiss (see ref. 5). The reported O₂ flux has been reduced by 40% to account for the compensating flux of N₂. In other words, the reported flux accounts only for the excess O₂ flux not compensated by N₂.
× Calculated by subtracting the uncompensated thermal component of SNO from total SNO. The biological and thermal components of the SNO should be largely in phase with each other.
to biological SNO as follows

$$\text{SNO} = g \text{ NEZP}$$

(3)

where $g$ is a dimensionless number between 0 and 1.0. $g$ is less than unity because only a fraction of the net O$_2$ produced throughout the year is reflected in the spring-summer pulse of O$_2$ injected into the atmosphere: some O$_2$ is produced in autumn and winter when the net flux is directed into the ocean, and some of the summertime O$_2$ production is exported into the oxygen-depleted water below the euphotic zone rather than into the atmosphere. In general, we expect middle and high latitudes to dominate the hemispheric SNO, whereas low, middle, and high latitudes should all contribute significantly to hemispheric NEZP. We expect that upwelling regions, where O$_2$ fluxes are generally into the ocean throughout the year but where productivity is high, will reduce hemispheric SNO but make positive contributions to hemispheric NEZP. At present, the uncertainty in $g$ makes it difficult to relate our oxygen signals directly to NEZP. For preliminary estimates, we will adopt $g = 0.5$ for the hemispherically averaged fluxes. This value seems plausible considering that the hemispheric average must include low-latitude waters, where seasonal outgassing is minimal, as well as middle- and high-latitude waters where a significant fraction, probably greater than 50%, of the annual net O$_2$ production is reflected in the seasonal outgassing.

Taking $g = 0.5$, the above estimates for SNO lead to estimates of $9.2 \times 10^{14}$ and $12.6 \times 10^{14}$ mol O$_2$ yr$^{-1}$ for NEZP for the Northern and Southern Hemispheres, respectively, or $22.8 \times 10^{14}$ mol O$_2$ for the world as a whole. Taking an O$_2$:C ratio of $1.4:1$ (ref. 17) for marine organic matter, we obtain an estimate of $16 \times 10^{14}$ mol C yr$^{-1}$ (19 gigatonne C yr$^{-1}$) for global NEZP of organic carbon, or 4 mol C m$^{-2}$ yr$^{-1}$ for the global average. This result is higher than recent estimates of global new production ($4-17$ Gt C yr$^{-1}$) but generally agrees with low estimates derived from observations of O$_2$ in the upper ocean.

The preliminary nature of this analysis must be emphasized: uncertainties in estimated productivities are probably a factor of two or more. Measurements from additional stations are needed to characterize more accurately the large-scale variability in O$_2$/N$_2$. More accurate account of atmospheric transport and of the relation between oxygen fluxes and marine productivity is also needed (see also ref. 5). Nevertheless, these results illustrate the contribution that atmospheric O$_2$ measurements can make to studies of biological activity in the ocean. Measure-ments made at various locations in O$_2$/N$_2$ extending over many years could provide an index of interannual variations in marine productivity on large spatial scales. Such data would be valuable for monitoring the sensitivity of marine productivity to climate change, decreasing stratospheric ozone, eutrophication or other perturbations.

**Interpretation of interannual decrease**

Schematically, we can represent the global budget for atmospheric CO$_2$ according to

$$\Delta \text{CO}_2 = F + C - O + B$$

(4)

where $\Delta \text{CO}_2$ is the annual averaged change in atmospheric CO$_2$, $F$ is the source of CO$_2$ from burning fossil fuels, $C$ is the CO$_2$ source from cement manufacturing, $O$ is the oceanic CO$_2$ sink, and $B$ is the net source or sink of CO$_2$ from terrestrial ecosystems (B can be positive or negative), all in units of mol yr$^{-1}$. Likewise, we can represent the budget for atmospheric oxygen according to

$$\Delta \text{O}_2 = -F - H - \alpha_B$$

(5)

where $\Delta \text{O}_2$ is the change in atmospheric oxygen, $H$ is the O$_2$ sink owing to the oxidation of elements other than carbon (predominantly hydrogen) in fossil fuels and $\alpha_B$ represents the O$_2$/$C$ exchange ratio for terrestrial biomass. The oceans do not significantly buffer the decrease in atmospheric O$_2$ because of the low solubility of O$_2$ in sea water.

**TABLE 2 Terms in global O$_2$ and CO$_2$ budgets**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value around 1990 ($10^{14}$ mol yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \text{O}_2$</td>
<td>Measured O$_2$ depletion rate*</td>
<td>6.7 ± 1.7</td>
</tr>
<tr>
<td>$\Delta \text{CO}_2$</td>
<td>Measured CO$_2$ increase†</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>$F$</td>
<td>Fossil-fuel CO$_2$ source‡</td>
<td>4.85 ± 0.32</td>
</tr>
<tr>
<td>$H$</td>
<td>Fossil-fuel O$_2$ sink from elements</td>
<td>2.01 ± 0.17</td>
</tr>
<tr>
<td>$C$</td>
<td>Fossil-fuel O$_2$ sink§</td>
<td>6.86 ± 0.41</td>
</tr>
<tr>
<td>$O$</td>
<td>Total fossil-fuel O$_2$ sink‖</td>
<td>0.12 ± 0.01</td>
</tr>
</tbody>
</table>

* Derived by multiplying the total number of moles of O$_2$ in the atmosphere $(3.705 \times 10^{19}$ (ref. 8)) by the coefficient $(b = -18.2$ per meg yr$^{-1}$) of the fitted curve to the La Jolla data in Fig. 1. The standard error in $b$ estimated from the formal covariance matrix of the fit is ±1.8 per meg yr$^{-1}$, but we adopt an uncertainty of ±3 per meg yr$^{-1}$ based on a subjective assessment of possible drift in the reference gases.
† Derived from the coefficient $(b = 1.250 ± 0.14$ p.p.m. yr$^{-1}$) of the curve fitted to the La Jolla CO$_2$ data in Fig. 1. The uncertainty in $b$ is estimated from the formal covariance matrix of the fit assuming that the standard error in individual data points is equal to the mean square of the residuals to the fit.
‡ Using CO$_2$ production figures for 1989 from ref. 23.
§ From ref. 8 using fossil-fuel production figures for 1989 from ref. 23.
‖ Derived using $b = -3.0 \alpha_b \Delta \text{CO}_2 + F + H$ from equation (5) using $\alpha_b = 1.05$ (ref. 8).
‖ Using equation (5).

Adding equations (4) and (5) and solving for $O$ yields

$$O = (-\Delta \text{O}_2 + H) - (\Delta \text{CO}_2 - C) - \alpha_B$$

(6)

The last term on the right-hand side of equation (6) can be evaluated by solving equation (5) for $B$, although this term is virtually negligible as $\alpha_B \approx 1$.

Once sufficiently long time series for oxygen are available, it will be possible to estimate oceanic uptake of CO$_2$ using equation (6). Although the existing records are too short to yield definitive results, we can nevertheless use these data to illustrate the method. We have estimated (Table 2) the terms in equations (4) to (6) using the data from the La Jolla to estimate global trends in $F$, $O$, and CO$_2$. The global O$_2$ depletion rate inferred from the La Jolla data agrees well with the trend expected from the burning of fossil fuels, implying that the net terrestrial carbon source is zero within the uncertainties. The data suggest that the oceans were a sink of $2.5 ± 1.7 \times 10^{14}$ mol C yr$^{-1}$ ($3.0 ± 2.0$ Gt C yr$^{-1}$) over the period from 1989 to 1991. This estimate of the oceanic sink agrees, within rather wide error margins, with estimates derived from ocean models calibrated with bomb 14C data. The largest uncertainties in the estimated oceanic uptake are contributed by the trend in O$_2$/N$_2$, and this uncertainty will decrease as longer time series are obtained.

Accurate determination of the O$_2$ depletion rate from measurement time series will require very stable standards. In this respect the present procedure, which relies on the stability of O$_2$/N$_2$ in compressed air cylinders, may not be adequate. To insure against the possibility of parallel drift in O$_2$/N$_2$ in reference cylinders, new methods of absolute standardization of O$_2$/N$_2$ mixtures are needed.

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