

THE O₂ BALANCE OF THE ATMOSPHERE: A Tool for Studying the Fate of Fossil-Fuel CO₂

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ABSTRACT

Carbon dioxide is a radiatively active gas whose atmospheric concentration increase is likely to affect Earth's climate. CO₂ is added to the atmosphere by biomass burning and the combustion of fossil fuels. Some added CO₂ remains in the atmosphere. However, substantial amounts are taken up by the oceans and land biosphere, attenuating the atmospheric increase. Atmospheric O₂ measurements provide one constraint for partitioning uptake rates between the ocean and the land biosphere. Here we review studies of atmospheric O₂ concentration variations and discuss their implications for CO₂ uptake by the ocean and the land biosphere. We compare estimates of anthropogenic carbon fluxes from O₂ studies with estimates from other approaches and examine the contribution of natural ocean carbon fluxes to atmospheric O₂ variations.

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1. INTRODUCTION

Man is currently adding CO₂ to the atmosphere at the rate of about 6.4 Gt C/yr by combusting fossil fuels and (to a small extent) by making concrete (1). We are adding another ~1 Gt C/yr by deforestation, mostly in the tropics. If all this CO₂ remained in the atmosphere, the CO₂ concentration of air would rise by about 3.5 ppm/year, much more than the observed increase of about 1.5 ppm/year. The difference between fossil-fuel input and accumulation, today as in the past, is attributable to the CO₂ uptake by the oceans and by the growth of the land biosphere, as demonstrated by CD Keeling in a series of seminal publications (e.g. 2, 3).

Even at its attenuated rate of increase, the elevated CO₂ concentration of air is likely to have a significant impact on Earth's climate. Since 1800, the CO₂ concentration has risen from a "preindustrial" value of approximately 280 ppm to its current level of 360 ppm. Usage according to current patterns is likely to cause atmospheric CO₂ to be twice the preanthropogenic level during the coming century. Complex mathematical models that attempt to simulate the global climate suggest that average temperatures would rise by about 3°C at this point, and a range of other important global environmental changes would occur.

Because of its influence on climate, there is considerable interest in determining CO₂ uptake rates by the ocean and the land biosphere and in understanding controls on these rates. Several independent approaches exist for constraining these terms. In this paper, we discuss one of these approaches, based on monitoring the O₂ concentration (actually the O₂/N₂ ratio) of the global atmosphere. We also put this discussion in a broader context by reviewing the geochemistry of O₂ and outlining its relationship to primary production in the oceans.

How does the distribution of O₂ in air inform us about the fate of fossil-fuel CO₂? As the foregoing discussion indicates, CO₂ added to air by combustion accumulates in the atmosphere, dissolves in the ocean, or is taken up by the land biosphere. Input by combustion is well known from industrial records, and atmospheric accumulation can be computed from ongoing CO₂ measurements being made at roughly 100 monitoring stations worldwide. The difference between combustion and atmospheric increase equals CO₂ uptake by the oceans and land biosphere. O₂/N₂ ratios allow us to separate these latter two terms. Ocean uptake leaves the atmospheric O₂ concentration unchanged, whereas land biosphere uptake produces O₂ and releases it to air.

Expressed in absolute concentrations units, O₂ is more variable than any other gas in the atmosphere except H₂O. Because O₂ is so abundant, however,

fractional changes in its concentration are very small. Variations in O₂ are expressed normalized to a (nearly) conservative constituent, N₂. These changes are reported in units of per meg, defined by the following equation:

$$\delta\text{O}_2/\text{N}_2(\text{per meg}) = \left[\frac{(\text{O}_2/\text{N}_2)_{\text{sample}}}{(\text{O}_2/\text{N}_2)_{\text{reference}}} - 1 \right] \times 10^6.$$

One per meg is 0.001 ‰, and a change of 4.8 per meg in the O₂/N₂ ratio of air corresponds to a change of 1 ppm in the O₂ concentration.

Several approaches in addition to O₂ studies are used to determine anthropogenic CO₂ uptake by the land biosphere and by the ocean. One involves modeling studies that ask how fast CO₂ dissolves in the ocean, given the known rates of (a) CO₂ dissolution into undersaturated seawater and (b) ocean mixing (which brings old, undersaturated waters to the surface). Another involves following changes in the ratio of the two natural stable isotopes of C, ¹²C and ¹³C, in atmospheric CO₂. Dissolution in seawater and uptake by photosynthesis cause the ¹³C/¹²C ratio of air to change in opposite directions, giving a marker that allow us to discriminate between these two processes.

Combustion of fossil fuels and annually averaged net CO₂ uptake by the land biosphere are not the only processes influencing the O₂/N₂ ratio of air. We discuss these other processes briefly here and more extensively later, because they explain the nature of the atmospheric record and they illuminate features we need to consider in evaluating the significance of O₂/N₂ ratios for anthropogenic perturbations. First, the annual cycle of the land biosphere causes CO₂ uptake by net photosynthesis in summer and CO₂ release by net respiration in winter. This biotic cycle leads to the well-known seasonal variations in the CO₂ concentration of air, with minima in summer and maxima in winter. Seasonal variations in O₂/N₂ due to the land biosphere are inverse to those of CO₂; maxima occur in summer. The amplitude of the O₂ cycle, in molar units, is estimated to be 1.1 times larger than the CO₂ cycle, a reflection of the reduced H, N, and S content of land organic matter. Second, the annual cycle of the ocean biosphere leads to a similar pattern of seasonal variations in the O₂/N₂ ratio of air. As discussed in more detail below, in spring and summer, O₂ is produced along with organic carbon in the surface ocean, and is transferred to the atmosphere. O₂ returns to the ocean in fall and winter, the time of year when interior ocean waters, undersaturated in O₂, mix to the surface. Oceanic CO₂ exchange with the atmosphere is small on the seasonal timescale, and does not have an important impact on seasonal variations in the CO₂ content of air. Third, warming of the surface ocean in summer decreases the solubility of all gases in seawater and leads to their transfer from ocean to atmosphere. This process raises the O₂/N₂ ratio of air, because O₂ is more soluble than nitrogen. In fall and winter the flux is reversed, and the O₂/N₂ ratio falls. The seasonal amplitude is about 80 per

meg in temperate latitudes, far larger than annual fossil-fuel CO₂ consumption of 20 per meg/year and recent average land biosphere production of 4 per meg/year. One needs to account for the large seasonal changes when interpreting the longer trends. These processes, which have been recognized since the inception of O₂/N₂ studies, are discussed more extensively by RF Keeling et al (4–6), Bender et al (7), and Balkanski et al (8).

As a rough guide, ocean thermal effects account for about 5% of the seasonal variability in the northern hemisphere, with the remainder roughly split between land and ocean biology. Ocean thermal effects and land biology each account for about 10% of the variability in the southern hemisphere, with the remainder due to ocean biology.

There are three geochemically significant features in the variability of the O₂/N₂ ratio of air. The amplitude of the O₂ seasonal cycle, in excess of the CO₂ amplitude, constrains the rate of seasonal net production in the oceans. The observed rate at which the O₂/N₂ ratio of air is falling, compared with the fossil O₂ consumption rate, constrains the rate of CO₂ sequestration in the land biosphere. Finally, the meridional (latitudinal) gradient in O₂/N₂ is influenced by, and reflects, the meridional distribution of land CO₂ uptake. Corrected for other features, high O₂/N₂ in temperate and boreal regions would imply a land sink in those areas, while high O₂/N₂ in the tropics would imply a tropical sink.

2. METHODS FOR MEASURING THE O₂/N₂ RATIO OF AIR

RF Keeling (9) first developed a high-precision method for measuring the O₂/N₂ ratio of air. His technique is based on the fact that the refractive index of O₂ is greater than that of N₂ in the UV. This difference diminishes (actually reverses) in the visible. Keeling passes light of 2537 Å and 4360 Å emitted by a Hg-vapor lamp through dry air, and measures the relative refractive indices at the 2 wavelengths. The refractive index of the shorter wavelength is about 3% greater than that of the longer wavelength, allowing one to measure the difference in the O₂/N₂ ratio of air to a precision considerably better than ±1 ppm (±5 per meg). He and his collaborators have used this technique to measure atmospheric O₂/N₂ variations at various sites since 1989, establishing the longest and most comprehensive record of this property.

Bender et al (10) developed a high-precision method for measuring the O₂/N₂ ratio of air using an isotope ratio mass spectrometer. These instruments use ratioing procedures to measure variations in relative abundances of 2 isotopes to a very high precision. A sample gas is admitted to the source of a mass spectrometer, ionized, and accelerated into a magnetic field. Ion paths bend in the magnetic field, which is adjusted so that the 2 desired ions exit the field

and impinge on metal plates, producing electrical currents. These currents are amplified and their ratio measured. After about 15 seconds, the flow of sample gas is diverted and a standard gas flows into the mass spectrometer, where its isotopic ratio is measured. A single-sample analysis typically involves switching between sample and standard 25 times. The simultaneous measurement of multiple ion beams eliminates most instrumental instabilities associated with temperature, ionization efficiency, etc, while repeated comparisons with the standard allow the very precise measurement of small variations in isotopic abundance. To measure O₂/N₂ ratios by mass spectrometry, one admits dry air to the instrument and measures the ratio of O₂ ions (¹⁶O¹⁶O⁺) to N₂ ions (¹⁴N¹⁴N⁺ or ¹⁴N¹⁵N⁺). The standard error is currently about ±3 per meg for a 30-min measurement, and considerable improvement may be possible. This method has been used for atmospheric O₂/N₂ measurements by the University of Rhode Island (U.R.I.) since 1991, and by the Commonwealth Scientific and Industrial Research Organization, Aspendale, Australia, since 1995.

Of the two techniques, refractometry is faster and more precise. As the methods are currently used, mass spectrometry allows analysis of smaller samples and allows replicate analyses of air in a given sampling flask. It relies on a standard “off-the-shelf” instrument, while refractometry requires a unique instrument made to order. Most importantly, O₂/N₂ ratios are measured by two completely independent analytical approaches. Generally good agreement between the two methods confirms that each gives reliable results.

3. RESULTS OF EXPERIMENTAL STUDIES

Programs at UC San Diego, U.R.I., and CSIRO are involved in measuring the O₂/N₂ ratio of air at about 20 remote sampling sites from Alert, in the Canadian Arctic (82°N), to the South Pole.

O₂/N₂ ratios and CO₂ concentrations measured at Arctic, tropical, and temperate southern sites are shown in Figure 1. Data are from Battle et al (in preparation). CO₂ concentrations are rising with time at all sites, the result of CO₂ addition by fossil fuel burning. Annually averaged CO₂ concentrations are highest in the northern hemisphere where man is burning most fossil fuels. There is a seasonal cycle, with low values in summertime when photosynthesis exceeds respiration, and high values in wintertime when respiration dominates. The seasonal amplitude is greatest in the north, because most continental land-mass is in the northern hemisphere.

O₂/N₂ ratios vary inversely with CO₂. Concentrations are decreasing with time because of O₂ consumption during combustion. O₂/N₂ ratios are lowest in the northern hemisphere where most fossil fuel is burned. The seasonal cycle is strongly expressed in both hemispheres. O₂/N₂ is highest in summer, because

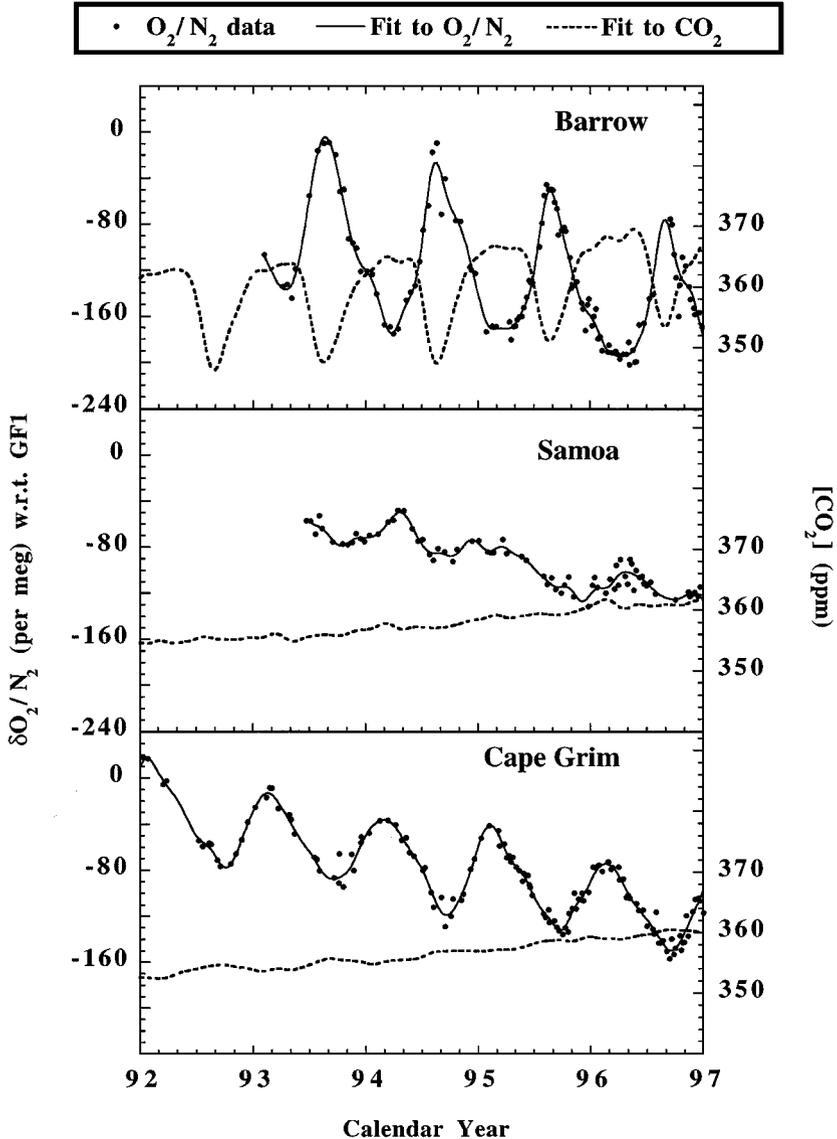


Figure 1 O_2/N_2 and CO_2 concentrations of air at Barrow, Alaska, Samoa, and Cape Grim, Australia (from 7 and Battle et al, manuscript in preparation). O_2/N_2 ratios are expressed in units of per meg relative to the University of Rhode Island standard GF-1. CO_2 concentrations are measured at the Climate Monitoring and Diagnostics Laboratory, NOAA, Boulder, CO.

of seasonal production by the land and ocean biosphere, as well as the ocean thermal effects discussed above.

4. SEASONAL CYCLES OF O₂/N₂ AND OCEAN PRIMARY PRODUCTION

In Figure 1, CO₂ concentrations and O₂/N₂ ratios are scaled such that a given displacement in CO₂ due to the land biosphere will lead to an O₂/N₂ displacement of the same distance (1 ppm CO₂ corresponds to 5.3 per meg in O₂/N₂). It is clear that seasonal O₂/N₂ variations exceed those for CO₂ (4, 7). The excess O₂ comes from the two ocean sources. Ocean warming in summer causes degassing and a small increase in the O₂/N₂ ratio (4, 11). Most of the oceanic signal comes from the interaction of biology with ocean mixing. In winter, cool surface waters form a mixed layer that is typically 100 m deep. (Below, waters become progressively colder and denser with depth, accounting for the density-stratified ocean.) The wintertime mixed layer is also rich in dissolved nutrients. However, growth of phytoplankton (single-celled marine photosynthesizers) is small in winter, a consequence of low solar irradiance, cold temperatures, and especially the deep mixed layer. The latter keeps phytoplankton from accumulating at shallow depths, where irradiance is highest and they can grow rapidly.

In spring, the surface waters warm and form a new, shallow, mixed layer that typically extends to 20–40 m depth. In this regime, phytoplankton stay closer to the surface and benefit from the warmer waters and greater solar irradiance. They also take advantage of the nutrients present at winter's end. They grow very rapidly in spring and continue to grow, albeit at a slower rate, throughout the summer. The O₂ produced supersaturates the mixed layer and drives a flux of O₂ into the atmosphere, causing the O₂/N₂ ratio of air to rise (11–14).

Marine organic matter turns over very rapidly, on timescales of hours to months, although a small fraction of material is refractory and survives much longer. Most organic matter fixed in the ocean mixed layer during spring and summer is rapidly decomposed, or respired, and will not contribute to the net production of carbon or O₂. However, some survives for months to years as dissolved organic carbon (DOC), and some sinks out as particulate organic carbon (POC). The sinking POC is remineralized back to CO₂ in water below the mixed layer, consuming O₂ and causing subsurface waters to be undersaturated. DOC mixing down into the ocean interior will undergo the same fate. Remineralization is pervasive in the ocean interior, causing almost the entire ocean to be undersaturated in O₂ at depths below about 60 meters.

In summary, the nature of the spring/summer rise in O₂/N₂ due to the ocean biosphere differs from that due to the land biosphere. The land contribution to

the seasonal O_2/N_2 increase reflects production of organic matter and its storage. In contrast, the oceanic contribution reflects organic-matter production in the surface ocean, which exchanges O_2 with the atmosphere over a timescale of weeks. This is followed quickly by organic-matter oxidation in the interior realm, which exchanges O_2 with the atmosphere over a timescale of years or decades. The ocean biomass is very small, but ocean carbon fluxes are nevertheless of the same order of magnitude as land fluxes.

In wintertime, surface waters cool and their density rises. This rise puts them in contact with deeper, interior, waters of the same density, which are thus entrained into the deepening mixed layer. The entrained waters are depleted in O_2 . As they mix to the surface, they present an oxygen demand to the atmosphere, thereby causing the O_2/N_2 ratio of air to fall toward its lower, wintertime values.

As discussed above, warming and cooling of the surface ocean contributes to seasonal variations of O_2/N_2 in excess of those linked to atmospheric CO_2 changes (i.e. those from the land biosphere) (11). One can estimate the thermal contribution starting with data summarizing seasonal changes in upper ocean temperatures. To do this, one first calculates the variations in saturation gas inventories associated with the temperature-driven solubility changes. These calculated inventory variations then equal the flux of gas between the atmosphere and ocean. Gas fluxes during the period of cooling are calculated from a similar approach. One then uses a model of atmospheric circulation to look at the variations in atmospheric O_2/N_2 ratios induced by the fluxes of gases from ocean to atmosphere. Atmospheric mixing models of various complexity indicate that the amplitude of seasonal O_2/N_2 variations due to warming and cooling of the oceans is about 12 per meg in temperate and subpolar latitudes of the Southern Hemisphere. The amplitude is smaller in the north, about 8 per meg, because of greater continental area.

The approach used to estimate ocean productivity is similar. One starts with a model of the ocean carbon cycle which specifies the net rate of organic C production (+ or -) as a function of latitude, longitude, and depth in the water column. This organic carbon is redistributed using the general ocean circulation model (OGCM). The resulting distribution leads to air-sea fluxes of O_2 , which are dispersed using a model of atmospheric circulation. Several different models of the ocean carbon cycle have been used in this context. Keeling & Shertz (4) simply chose a value for ocean carbon production that predicted the observed seasonal amplitude of atmospheric O_2/N_2 variations given the assumption that half of the net O_2 production was transferred from the ocean to the atmosphere on a seasonal basis. Keeling et al (11) used air-sea O_2 fluxes calculated from a 3-dimensional model of ocean mixing and biogeochemistry. In this model, carbon fluxes are inferred from the observed ocean distribution of PO_4^{3-} . Organisms take up PO_4^{3-} from surface water to support fixation of

organic carbon, and release it back to seawater when they are decomposed during respiration. Organisms thus continuously take up PO₄³⁻ in shallow waters, transport it downward by sinking, and release it to deep waters by remineralization. This downward flux is opposed by the return flux of PO₄³⁻ as deep waters mix toward the surface. Najjar & Keeling (15) calculated the biological fluxes of P needed to maintain the observed oceanic PO₄³⁻ gradients in the presence of mixing, which serves to dissipate these gradients. The P/C ratio of marine organic matter is roughly constant at a value of about 1/106. One thus computes net organic carbon production by multiplying P fluxes by 106. In turn, O₂ production is calculated from net carbon production. Finally, one calculates air-sea O₂ fluxes by computing the transfer rates needed to maintain surface waters at saturation with the atmosphere.

Six & Maier-Reimer (14) also used an ocean general circulation model to calculate water and nutrient fluxes. They computed net carbon production in surface waters with a simple ecosystem model, and assumed that sinking organic matter was remineralized at a rate that decreased with depth. Balkanski et al (8) calculated organic carbon and O₂ fluxes based on vertical mixing rates in each grid box. They used simple parameterizations to describe net production as a function of the nutrient concentration, solar irradiance at the sea surface, and respiration as a function of depth.

The air-sea fluxes of O₂ estimated from these models provide input to the atmospheric general circulation models to calculate the distribution of O₂ in air as a function of latitude, longitude, elevation, and time of year.

We can compare O₂/N₂ variations from models of the ocean biosphere with observations such as those in Figure 1. Before doing so, we need to take into account the fact that observed amplitudes include ocean thermal effects, land biosphere effects, and fossil-fuel contributions. We can compute the contribution of ocean thermal effects as described earlier and account for effects of the land biosphere from the seasonal variations in the CO₂ concentration at the site. This approach assumes that air-sea exchange of CO₂ does not have a substantial impact on seasonal variations in the atmospheric CO₂ concentration (a reasonable assumption, because nearly all CO₂ in seawater is associated as HCO₃⁻). Fossil fuel is emitted throughout the year at a roughly constant rate and does not contribute to seasonal variability.

The resulting estimates for seasonal variations in the O₂/N₂ ratio of air due to the ocean biosphere are in good agreement with the observations presented above. Data on the distribution of O₂ in air thus validate models describing the global ocean carbon cycle. The rate of net organic carbon production needed to give seasonal O₂/N₂ amplitudes in agreement with observations is in the range of about 10–18 Gt C/yr. These numbers are at the upper end of global ocean carbon flux estimates based on other constraints.

Associated with the cycles in atmospheric O_2 concentration are cycles in the dissolved O_2 content of the upper few hundred meters of the ocean. These oceanic cycles have recently been documented throughout the world's oceans from observations made by ships over many years (15). The average cycles observed in the Pacific between 30° and $42^\circ N$, at various depths, are shown in Figure 2 (15). The maximum degree of supersaturation of surface waters, as measured by the O_2 saturation anomaly, occurs in the late spring, when biological production and warming of surface waters is driving the largest flux of O_2 into the atmosphere. As a result, spring is the time of year atmospheric oxygen is increasing most rapidly. The maximum degree of undersaturation occurs in early winter, when surface cooling increases the capacity of the water

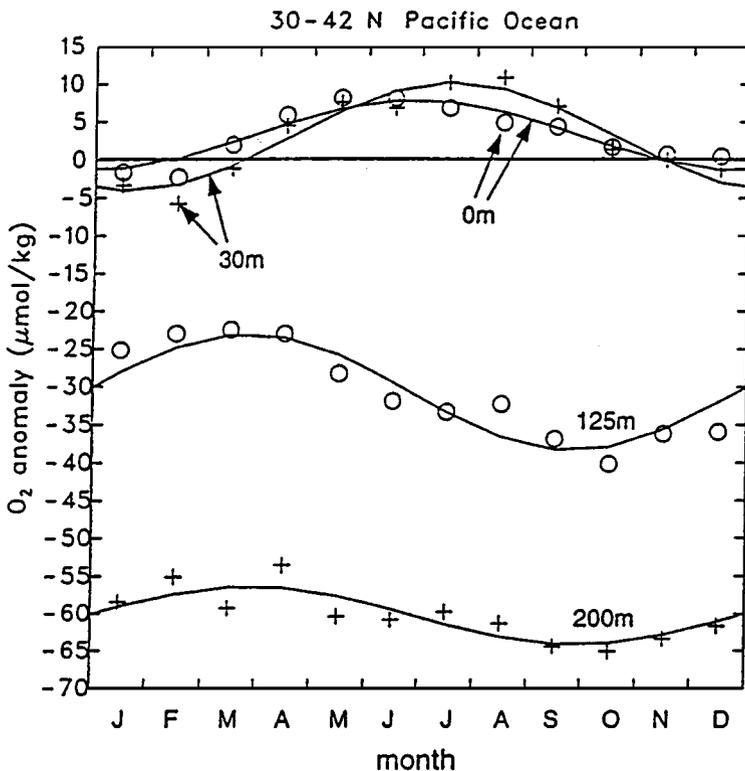


Figure 2 The average observed oxygen anomaly (circles and crosses) at 0, 30, 125, and 200 m in the Pacific Ocean between $30^\circ N$ and $42^\circ N$ (15). The lines are least-squares harmonic fits to the observations. The observations are based on data archived at the National Oceanographic Data Center.

for dissolving O₂ at the same time that deep mixing is bringing O₂ undersaturated waters up to the surface. Similar cycles are observed throughout the top few tens of meters of the ocean, where the water is stirred by wind and waves.

Below this summer wind-mixed layer, there typically exists a narrow depth zone where the water is more isolated from the surface but where diffuse sunlight still penetrates. Here O₂ produced by photosynthesis tends to build up throughout the spring and summer, leading to a cycle in the O₂ anomaly with a later maximum than the cycle observed at the surface. This buildup is eliminated in the fall, when the wind-mixed layer deepens to include this depth zone. At even greater depths, cycles with opposite phasing from the surface are observed, reflecting the seasonal inputs of organic material from sinking particles which are consumed by bacteria and other organisms in dark interior of the ocean.

Are the O₂ cycles observed in the oceans consistent with the cycles observed in the air? This question was recently explored by RF Keeling et al (13) using the observed O₂ anomalies in surface waters to compute the air-sea fluxes on a regional basis, and then simulating the effect of these cycles on the atmospheric composition using an atmospheric transport model. The simulation results, which also allow for air-sea exchanges of N₂, compare favorably with the cycles observed at nine locations around the world, as shown in Figure 3. The comparison not only demonstrates the general consistency between the ocean and atmospheric observations, but also yields information on the magnitude of the air-sea exchange velocity, which is a critical parameter relating the magnitude of the air-sea flux of a gas to the magnitude of the saturation anomaly. This comparison has also yielded global maps of the monthly O₂ fluxes which are validated against the atmospheric observations and which should prove useful for determining patterns of ocean biological productivity and vertical water mass exchanges.

5. LONG-TERM O₂ DEPLETION AND THE FATE OF FOSSIL-FUEL CO₂

As noted earlier, about 40% of the fossil-fuel CO₂ added to the atmosphere accumulates there. The rest is partitioned into the ocean and the land biosphere. Land biosphere CO₂ uptake produces O₂ and attenuates the decrease in atmospheric O₂/N₂ ratios due to combustion. Ocean CO₂ uptake has no effect on O₂/N₂. Thus measurements of the O₂/N₂ ratio of air allow us to determine CO₂ uptake rates by the oceans and by the land biosphere from the fossil combustion rate and the atmospheric increase.

Fossil-fuel burning is consuming oxygen at a rate such that, in the absence of other influences, we would expect to see the atmospheric O₂/N₂ ratio dropping at 19.7 per meg/year for the years 1992–1996. This expectation is based on the

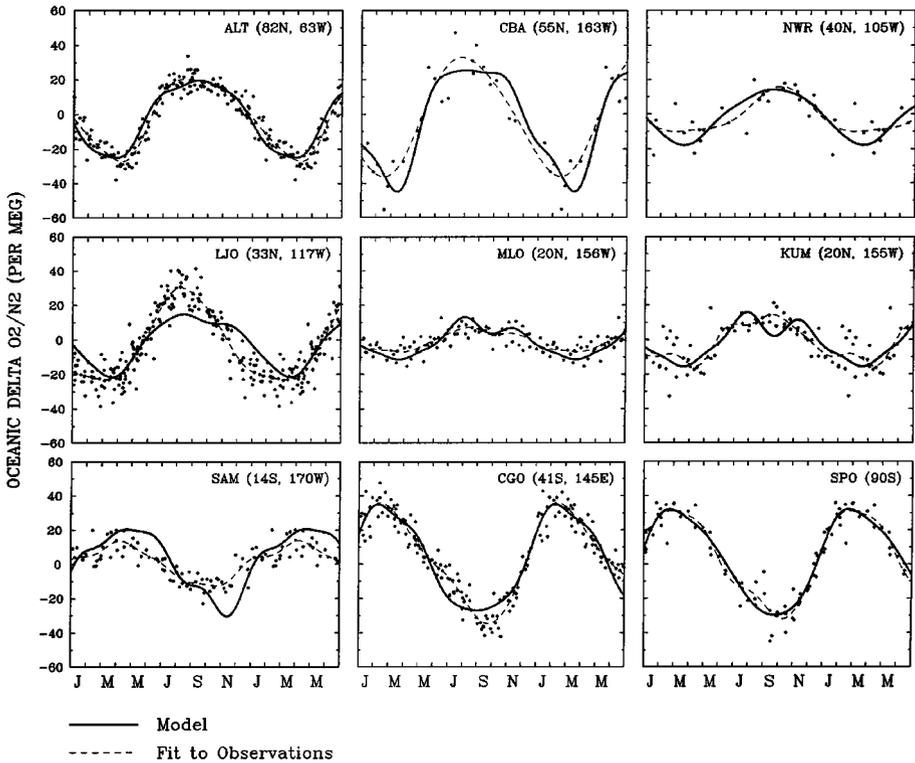


Figure 3 The oceanic component of the seasonal O_2 cycles and model simulations of these cycles at nine stations worldwide, from Keeling et al (13). The observations have been interannually detrended and plotted against a single climatological year. The land biotic contribution to the total observed cycle was subtracted using concurrent CO_2 observations. The gas exchange velocities used in the simulations are based on the Wanninkhof (20) formulation using ECMWF winds and with additional optimization factors for the regions poleward of 31° in both hemispheres (see Table 5 of Ref. 13). The observations are based on flasks collected and analyzed as a part of the atmospheric oxygen program at Scripps Institution of Oceanography. O_2/N_2 ratios determined by Keeling and collaborators are in good agreement with those determined by Bender and collaborators, but results are offset by about 65 per meg because different standard gases are in use.

combustion tallies of Marland et al (1) through the end of 1995, and a constant growth in CO_2 emissions (at the 1995 level) assumed for 1996. Direct measurements of O_2/N_2 (4, 6, 7) actually show a slower decrease. The Cape Grim data shown in Figure 1 decrease at a rate of 17.5 per meg/year. The difference must be due to a globally significant O_2 source, and the only reasonable candidate is net growth of the land biosphere. The average stoichiometry of carbon storage in terrestrial photosynthesis is such that for every mole of carbon stored, 1.1 mol

of O₂ are released (16). Thus, the 2.2-per-meg annual O₂ source corresponds to a terrestrial carbon sink of 0.9 Gt C. Since fossil-fuel burning releases 6.3 Gt C/year to the atmosphere and the atmospheric CO₂ increase (preliminary global average figures from NOAA/CMDL) corresponds to a burden of 2.8 Gt C/year, the ocean uptake must then be 2.6 Gt C/year (simply by mass balance). Naturally, each term in this calculation carries an uncertainty. The standards against which we measure O₂/N₂ may drift, the photosynthetic stoichiometry is known to roughly 5%, and fossil-fuel combustion records are good to 10%. These all combine to yield an uncertainty of roughly 0.9 Gt C/year in the inferred terrestrial carbon sink.

Any attempt to use O₂/N₂ in this way must confront the possibility, alluded to in the introduction, that atmospheric O₂ is unbalanced because of natural variations in the ocean carbon inventory. These variations could arise because the springtime and summertime flux of O₂ to air associated with net production differs from the fall-winter O₂ uptake due to ventilation. Modeling studies may eventually give some insight into the magnitude of natural variations in ocean and atmosphere O₂ inventories. At present, we cannot rule out the possibility that such variations are large enough to have a significant impact on the biosphere and ocean carbon uptake rates we estimate from the O₂ balance.

Imbalances in natural carbon fluxes could arise in two basic ways (7). The first is from interannual variability in net production. Production pumps O₂ into the atmosphere and causes O₂ to be consumed at depth as the sinking organic matter is consumed in the ocean's interior. Years of higher net production will be years when the annual average O₂/N₂ ratio of air is anomalously high, even if the excess flux to the atmosphere in summer is balanced by a higher return flux in winter. The reason is that spring/summertime production pumps O₂ into the atmosphere and elevates the O₂/N₂ ratio above its "baseline" wintertime value.

The second imbalance concerns interannual variability in ventilation rates. At shallow depths (typically 60–100 m), the temperate and subpolar ocean is ventilated vertically on an annual timescale. That is to say, sinking organic matter produced in spring and summer is partly respired between 60–100 m depth, causing O₂ undersaturation here. In wintertime, surface water cools and becomes denser, entraining subsurface waters and causing them to mix to the surface and be resaturated (ventilated). This part of the annual cycle is probably closely balanced over the course of a year. At greater depths, the ocean is ventilated largely laterally on a decadal timescale. Most mixing in the oceans occurs along isopycnal (constant density) surfaces. A given isopycnal tends to be deep in low latitudes where the surface ocean is warm, shallower at intermediate latitudes, and outcropping at the sea surface at high latitudes where surface waters are cold and therefore dense. Interior waters mix with other waters of similar density and outcrop where their density horizon rises

to the surface. Ocean O₂ uptake during fall and winter is probably due in roughly equal parts to vertical mixing of shallow subsurface waters and lateral, isopycnal mixing of deeper subsurface waters.

Interior waters have ages ranging from a few years to about a thousand years. "Age" in this context refers to the time elapsed since the water sample was last at the surface and in contact with the atmosphere. Ventilation at high latitudes replaces O₂ molecules consumed by respiration a few decades previously on average. The O₂ transfer from atmosphere to ocean in fall and winter depends on the rate of respiration in the ocean interior during recent decades, which determines how highly undersaturated the waters are, and on seasonal fields of winds, sea surface temperatures, and ocean currents, which determine the quantity of water in a given year that upwells to the surface to be ventilated. Over a long enough time period, the O₂ flux to the atmosphere from production must equal the O₂ flux to the ocean by ventilation. During any given year, or any period of a few years, however, there may be imbalances between production of ventilation. These imbalances would cause changes in the atmospheric O₂ inventory which we would erroneously interpret as reflecting land sources or sinks of CO₂.

While imbalances in ocean production and ventilation must be considered when interpreting short-term records of atmospheric O₂, the imbalances become negligible when averaged over a sufficiently long period. To date, two different approaches have been used to acquire longer records of atmospheric O₂. Battle et al (17) collected samples of air trapped in the porous layer of snow (firn) that accumulates on top of the Antarctic ice sheet. Because the firn is porous, air within the firn is in diffusive contact with the atmosphere but does not exchange freely. Consequently, firn air records the composition of the atmosphere at some time in the past, with deeper samples reflecting an older atmosphere. By looking at the covariation of O₂/N₂ and CO₂ in the firn, Battle et al found that over the years 1977–1985, the land biosphere neither stored nor released carbon (carbon release was calculated at 0.4 ± 1.1 Gt C/year).

The second approach is described by Langenfelds et al (personal communication). They studied a set of high-pressure tanks that had been filled with atmospheric air at regular intervals, beginning in 1978. In 1997, the tanks were analyzed for their O₂/N₂ content. This method has the advantage of avoiding the complexities introduced by diffusion processes in the firn, and the record spans a full 19 years. Unfortunately, a significant number of the tanks comprising this air archive have O₂/N₂ ratios that have clearly been compromised by chemical or physical processes. When these tanks are excluded from the record, they show an O₂ trend indicating an average CO₂ uptake of 0.3 ± 0.9 Gt C/year by the land biosphere. Both the firn air studies and the analysis of archived samples thus indicate that the land biosphere was roughly in balance between ~1977 and 1990.

6. COMPARISON OF CO₂ UPTAKES RATES ESTIMATED FOR THE OCEANS AND THE LAND BIOSPHERE USING DIFFERENT METHODS

The causes of CO₂ uptake by the land biosphere are poorly understood. A number of factors may contribute, including reforestation of abandoned agricultural lands, fertilization of growth by the higher CO₂ concentration of air (2) and by deposition of anthropogenic N onto nutrient-limited ecosystems (2), and increases in precipitation associated with global warming. Using global models to quantify CO₂ uptake by the land biosphere is currently beyond our abilities, because of both the heterogeneous nature of climate properties and the biosphere as well as the difficulty of quantitatively describing a diverse suite of biological processes. In contrast, controls on the rate of ocean CO₂ uptake are fairly well understood. This understanding comes largely from modeling studies that relate oceanic CO₂ uptake to the undersaturation of surface seawater with respect to the rising concentration of atmospheric CO₂. These models concur in emphasizing that saturation of surface waters is relatively rapid, whereas the mixing of CO₂-undersaturated waters to the surface is slower and, therefore, rate determining. Global ocean CO₂ uptake rates of 2 Gt C/year are estimated from these models (e.g. 18).

A second way of evaluating ocean uptake rests on the assumption that most ocean mixing occurs along isopycnal surfaces whose temperature and salinity variations combine to produce water of a constant density. As discussed above, isopycnal surfaces in the ocean generally rise to meet the sea surface as they extend from low latitudes to high latitudes. This is because surface water gets colder and thus denser as one goes poleward. The age of water on an isopycnal surface is defined as the time elapsed since the water was last at the surface, and thus in contact with the atmosphere. Water at the surface today has an O₂ concentration at saturation with the atmosphere. As one samples waters of the same density going away from the surface exposure into the ocean interior, the O₂ concentration falls. O₂ decreases because of respiration, which produces CO₂. One uses the O₂ concentration to calculate how much CO₂ has been added to a given volume of water by respiration. Subtracting this amount of CO₂, together with a correction for CaCO₃ dissolution based on alkalinity, gives the "initial" CO₂ concentration of this buried water volume at the time in the past when it was at the sea surface, in contact with the atmosphere. Plotting the initial CO₂ concentration vs water age shows that the initial concentrations along isopycnal surfaces have risen going forward (toward today) in time. This increase simply reflects the rise in atmospheric CO₂ concentration, which transfers progressively more CO₂ to seawater. The older water samples along an isopycnal surface would have little or no anthropogenic CO₂. The amount by which the initial

CO₂ concentration of other samples is elevated is equal to their anthropogenic CO₂ burden. Integrating this CO₂ excess gives a direct measure of oceanic CO₂ uptake. To date, this approach has been most extensively applied to the Atlantic Ocean (19). The basinal inventory is in good agreement with predictions of the ocean models described earlier, strengthening our confidence in their results.

The final approach to constraining global uptake rates of CO₂ by the ocean and the land biosphere is based on the rate of change of the $\delta^{13}\text{C}$ of CO₂. This term, which expresses the $^{13}\text{C}/^{12}\text{C}$ ratio, is defined as the difference in per mil between sample and reference:

$$\delta^{13}\text{C} = \left[\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{reference}}} - 1 \right] \times 10^3.$$

The $\delta^{13}\text{C}$ of atmospheric CO₂ is decreasing because of the addition of fossil fuel, which is depleted in ^{13}C . However, the observed decrease is much slower than would be expected for the addition of fossil CO₂ to a static CO₂ reservoir. The slowness has several causes. Atmospheric CO₂ exchanges with CO₂ in seawater, as described earlier. It also exchanges with carbon in the land biosphere via the processes of photosynthesis and respiration. Both of these “gross exchange” processes effectively take up modern atmospheric CO₂ depleted in ^{13}C , and replace it with older CO₂ less depleted in ^{13}C . Finally, net CO₂ uptake by the land biosphere attenuates the fossil $\delta^{13}\text{C}$ decrease by fixing ^{13}C -poor CO₂ into plants. Knowing the amount of fossil-fuel combustion and correcting for the gross exchange terms yields the signal of net biospheric uptake. Again, ocean uptake is estimated at about 2 Gt C/year⁻¹ and land uptake at about 1 Gt C/year. Each of these estimates has considerable uncertainty, but each estimate is also independent. The good agreement gives us confidence that our estimates are robust.

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