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KEYNOTE PERSPECTIVE

Carbon cycle studies based on the distribution of O_2 in air

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The distribution of O_2 in air, first studied by Keeling and Shertz (1992), is receiving increasing attention as an indicator of natural carbon fluxes and their anthropogenic perturbations. O_2 and CO_2 are (inversely) linked by photosynthesis, respiration, and combustion. However, their concentrations do not covary perfectly because they have different solubilities. Within the combined ocean–atmosphere system, about 98% of the CO_2 is in the ocean, while 99% of the O_2 is in the atmosphere. Because O_2 is partitioned almost quantitatively into air, atmospheric inventory changes accurately reflect O_2 fluxes of the carbon cycle at the hemispheric or global scale. Because air mixes rapidly, one can measure O_2 inventory changes and use them to accurately constrain large-scale carbon fluxes. In this paper, we briefly summarize the basis and status of efforts to measure the distribution of O_2 in air and its implications for the carbon cycle.

Changes in the air O_2 content are reported normalized to N_2 in units of per meg:

$$\delta(O_2/N_2) = \left[\frac{(O_2/N_2)\text{sample}}{(O_2/N_2)\text{reference}} - 1\right] \times 10^6 \quad \text{(per meg)}.$$

Normalization to N_2 eliminates variations associated with changes in humidity, CO_2 concentration, and other atmospheric changes unrelated to O_2 or CO_2 fluxes.

The O_2/N_2 ratio of air then varies for the following reasons:

(1) *Combustion.* Combustion of fossil fuels consumes O_2. The molar ratio of O_2 consumption to CO_2 production varies from about 1.1 for coal to 2 for methane, with an average weighted for modern fossil fuel utilization of about 1.38 (Keeling et al., 1996). During the 1990s, combustion of fossil fuel has been drawing down the O_2/N_2 ratio of air by about 20 per meg yr^{-1}.

(2) *Carbon sequestration by the land biosphere.* Net accumulation of organic carbon by the land biosphere links net O_2 production and its input to air. Biospheric accumulation can be positive (land biosphere is a sink of CO_2) or negative (land biosphere is a CO_2 source).

(3) *The seasonal cycle of the land biosphere.* The land biosphere grows in spring and summer, sequestering CO_2 and producing O_2. Respiration occurs throughout the year. It is more rapid in summer, when temperatures are warmest, but the biosphere is net autotrophic in summer and heterotrophic in winter. The resulting seasonal CO_2 variations are well documented by the long-term variations in the CO_2 concentration of air at Mauna Loa (Keeling et al., 1989), and other sites. The O_2/N_2 ratio of air must vary in a complementary way, with a $\Delta O_2/\Delta CO_2$ ratio of about -1.1 (Severinghaus, 1995).

(4) *The seasonal cycle of the ocean biosphere.* The annual evolution of upper ocean temperatures drives a seasonal cycle of productivity and air–sea O_2 fluxes which make a major contribution to the seasonal cycle of the O_2/N_2 ratio of air (Keeling and Shertz, 1992; Keeling et al., 1993; Bender et al., 1996). O_2/N_2 variations associated with the ocean biosphere are actually due to two independent pro-

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cesses, net production and ventilation, which are coupled, albeit imperfectly, at all time scales.

(a) *Net production.* The illuminated upper ocean, which typically extends to 100 m depth, is a site of both photosynthesis and respiration, whereas the underlying dark ocean is a site of respiration only. Photosynthesis and respiration are almost perfectly in balance in the global ocean. Therefore, the upper ocean is a site of net O_2 production, whereas the deep ocean is a site of net O_2 consumption. Net O_2 production in the upper ocean causes supersaturation of surface waters and the transfer of O_2 to the atmosphere. In the tropics, this process continues throughout the year and leads to a small meridional gradient but little seasonality in the O_2/N_2 ratio. In temperate to polar regions, net O_2 production and its transfer to the atmosphere are highly seasonal. The seasonality in biology is a response to the temperature structure of the upper ocean. In wintertime, there is a deep, cool mixed layer which typically extends to 100 m or more in depth. The concentrations of limiting nutrients (NO_3^- and PO_4^{3-}) are high but solar irradiance is low, and phytoplankton spend a large portion of their lives in the deeper part of the mixed layer. They cannot grow rapidly under these conditions. In spring, solar irradiance increases. Simultaneously, a warm water layer forms, typically extending to 30–50 m depth and floating on the colder water below. Under these conditions, phytoplankton thrive and bloom, resulting in net carbon production, mixed layer O_2 supersaturation, and a flux of O_2 to the atmosphere. Eventually, nutrients are drawn down and net production decreases, but it continues through the summer, perhaps supported by influx of nutrients from below driven by several independent mixing processes. The fate of the net carbon production is complex. Some remains as dissolved organic carbon (DOC) to be advected with the water and respired (or possibly photo-oxidized) over various timescales. Some remains as particulate organic C with the same fate. However, a large fraction of net production sinks into the dark ocean, where it is gradually oxidized as it settles through the water column. Respiration creates an O_2 deficit in the deeper ocean, but has no immediate effect on the atmospheric O_2/N_2 ratio.

(b) *Respiration and ventilation.* Respiration continuously consumes O_2 and leaves the dark ocean everywhere undersaturated with O_2. The dark ocean is reaerated by the process of ventilation. In winter, surface waters in temperate to polar regions cool. Their temperatures fall to the average values of waters in the ocean interior. These interior waters then mix to the surface. Colder (deeper) interior waters mix to the surface at higher latitudes, where wintertime surface temperatures are lowest. Atmospheric O_2 dissolves into undersaturated waters and the O_2 concentration of air falls, completing the seasonal cycle of air O_2/N_2 linked to ocean biology. Over a sufficiently long time, ocean O_2 uptake by ventilation must be almost exactly equal to the O_2 flux to the atmosphere due to net production. The reason is that all organic carbon is oxidized in the oceans except for a very small amount which is buried in sediments. Over a period of years, however, annually averaged air–sea O_2 fluxes may be unequal. The reason is that ventilation replaces O_2 consumed, on average, years to decades earlier. Net production rates and ventilation rates may vary interannually, and there is no oceanographic process linking the rate of O_2 export due to net production with O_2 uptake during the same year. Thus oceanographic processes allow the possibility of natural interannual variations in O_2/N_2 ratios. For example, net ocean production might be higher in years when strong spring winds bring a large flux of aerosol iron to the deep sea; ventilation might be more intense in years of strong winter winds. Such effects would cause imbalances in changes in the annually averaged atmospheric O_2 inventory.

(c) *Ocean thermal effects.* The solubility of gases falls as temperature rises. For this reason, there is a flux of gas to the atmosphere in summertime and a return flux in wintertime. Because O_2 is more soluble than N_2, the O_2/N_2 ratio of air rises in summer and falls in winter.

Quantitatively, the processes which influence the O_2/N_2 ratio of air produce the following component signals of the atmospheric O_2/N_2 ratio, listed below, which add to give the observed variations in the O_2/N_2 ratio of air. First, the combustion of fossil fuels causes a long-term decrease (of $\sim$20 per meg/yr in the 1990s) in the O_2/N_2 ratio of air. Second, annually averaged CO_2 uptake by the land biosphere attenuates the long-term decrease by O_2 input to air. 1 Gt C/yr CO_2 uptake attenuates the atmospheric O_2/N_2 decrease by 2.5 per meg/yr. Third, the seasonal cycle of the land biosphere causes a seasonal variation with maximum O_2/N_2 in summer. O_2 changes 1.1 times as much as CO_2 and a 1 ppm change in O_2 corresponds to a change of 4.8 per meg in $\delta(O_2/N_2)$. Consequently the amplitude of the O_2/N_2 change from the land biosphere in per meg is 5.3 times the amplitude of the CO_2 change in ppm. Fourth, the seasonal cycle of the ocean biosphere causes a sympathetic cycle in O_2/N_2. Net production of the ocean biosphere raises O_2/N_2 in spring and summer, while ventilation lowers it in fall and winter. The amplitude depends on ocean fertility, and provides a measure of this term at the hemispheric scale. The observed amplitude is about 40 and 60 per meg in temperate and higher latitudes of the northern and southern hemispheres, respectively. Fifth, seasonal warming and cooling of the upper oceans transfers O_2 to the atmosphere in summer, with a return flux in winter. The amplitude of the seasonal cycle is about 12 per meg in the southern hemisphere and 8 per meg in the north (Keeling et al., 1993). Sixth, industrial activity, CO_2 uptake by the land biosphere, ocean production and ocean transport induce meridional gradients in annually averaged O_2/N_2 ratios. Industrial activity, concentrated in the northern hemisphere, consumes O_2 there leading to an interhemispheric gradient with low O_2/N_2 in the north. Based on O_2/N_2 data, uptake of CO_2 by the land biosphere appears to be concentrated in the northern hemisphere (Keeling et al., 1996), and attenuates the meridional gradient due to combustion. In the ocean, O_2 input by net production is greater than ventilation at low latitudes, introducing a very small meridional gradient with a maximum at the equator. Of greater interest is the modest contribution to the interhemispheric gradient which results from formation of deep water in the North Atlantic and its partial ventilation in the southern ocean. This transport of O_2 must affect the interhemispheric gradient in the O_2/N_2 ratio of air (Keeling and Peng, 1995).

Data on the O_2/N_2 ratio and CO_2 concentration of air at Barrow, Alaska, and Cape Grim, Tasmania (Fig. 1) illustrate the points discussed above. The O_2/N_2 ratio has fallen throughout the period of observation. The rate of decrease is slightly less than O_2 consumption by fossil fuel combustion, and implies CO_2 uptake by the land biosphere of about 1 Gt C/yr since 1991.

The seasonal variability in the O_2/N_2 ratio comes from ocean biology fluxes, ocean thermal fluxes, and land biosphere fluxes. One can use CO_2 variations to subtract the land biosphere contribution. One can estimate and subtract the thermal contribution by using data on seasonal changes in upper ocean heat storage (and assuming upper ocean gas saturation) to calculate air–sea fluxes of O_2 and N_2. Distributing these fluxes through the atmosphere using a 3-D tracer transport model gives estimates of the seasonal thermal variations which can then be subtracted from observations to give the variability in O_2/N_2 from ocean biology.

These variations from ocean biology have in turn been used to test ocean carbon cycle models and estimate ocean carbon fluxes based on ocean and atmosphere models of varying complexity (Keeling and Shertz, 1992; Keeling et al., 1993; Bender et al., 1996; Six and Maier-Reimer, 1996). The general approach involves using an ocean general circulation/carbon cycle model to calculate air–sea O_2 fluxes in time and space. A 3-D atmospheric tracer transport model is then used to calculate the resulting atmospheric O_2/N_2 distribution, which is compared to observations. Several recent models, involving global rates of seasonal net carbon production around 12 Gt C/yr, predict O_2/N_2 variations in good agreement with observations. 12 Gt C/yr is at the high end of the range of estimates of seasonal net carbon production derived from other approaches. Estimates are evolving as oceanic and atmospheric models improve.

A number of recent efforts are extending the scope of studies of the atmospheric O_2 cycle. Battle et al. (1996) extended the record of O_2/N_2 variations back in time by studying air in the firn at South Pole. Firn is the porous layer of incompletely compacted snow which typically forms the top 70–100 m of an ice sheet. They measured the covariation of O_2/N_2 with CO_2 in firn air and used it to estimate the rate of O_2/N_2 decrease between 1977–1985. Langenfelds et al. (1997) determined the atmospheric O_2/N_2 ratio in 1978 and 1987 by analyzing samples from the Cape Grim Air Archive. Both these studies were consistent with the synthesis in the 1992 IPCC report estimating that the land biosphere was

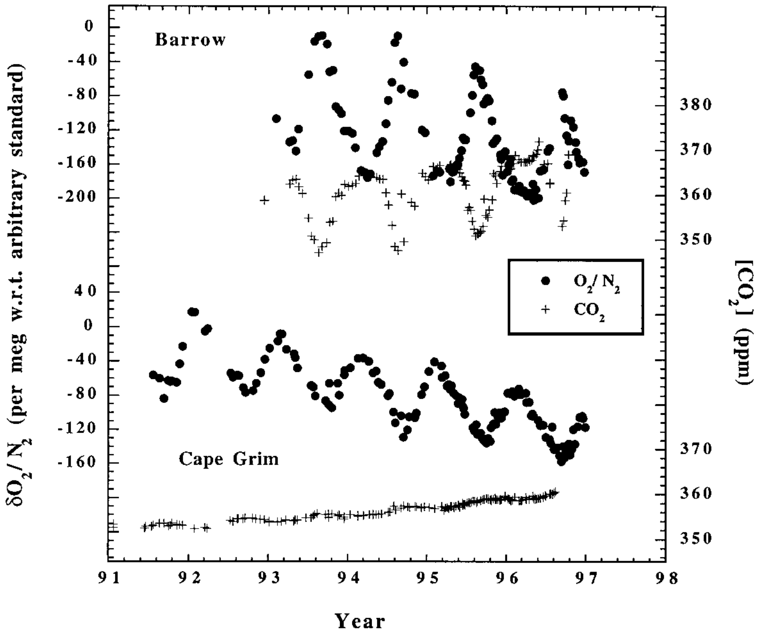

Fig. 1. O_2/N_2 and CO_2 values measured in flasks collected at Cape Grim, Tasmania and Point Barrow, Alaska. O_2/N_2 values were measured at the University of Rhode Island. CO_2 values were measured by NOAA/CMDL in Boulder, Colorado.

approximately in balance during the 1980's, with the ocean taking up about 2 Gt C/year. Keeling and collaborators at the Scripps Institution of Oceanography and our lab are routinely analyzing samples from almost 20 remote sampling sites; Langenfelds, Francey and collaborators, Division of Atmospheric Research, CSIRO Aspendale, are monitoring the O_2/N_2 of Cape Grim air; and measurement programs are in preparation at several other institutions. The CSIRO group has an aircraft measurement program underway which will give critical data on variations of O_2/N_2 ratios with elevation. Finally, analytical efforts currently underway may give new methods for measuring O_2/N_2 ratios.

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