5.5. ATMOSPHERIC OXYGEN CONCENTRATIONS AT ALERT STATION IN RELATION TO THE GLOBAL CARBON CYCLE

Ralph F. Keeling
Elizabeth M. McEvoy
Andrew C. Manning

Scripps Institution of Oceanography, La Jolla, CA 92037

With the development of the interferometric oxygen analyzer [*Keeling*, 1988a, 1988b] in the late 1980's, it became possible to measure atmospheric O_2 concentrations with sufficient precision to detect changes in the background atmosphere. At that time, a flask air-sampling program was initiated under the direction of one of us (R.K.) to sample air globally and document spatial and temporal trends in O_2 concentration. Among the primary goals was to use measurements of atmospheric O_2 in conjunction with measurements of atmospheric CO_2 to better determine the magnitude of ocean and land biotic sinks for CO_2 at the global and hemispheric scales and to improve our understanding of the rates of biological productivity in the oceans [*Keeling and Shertz*, 1992; *Keeling et al.*, 1993, *Bender et al.*, 1996].

Alert station was selected as the first remote baseline site in that program, and a cooperative program was initiated with Atmospheric Environment Service of Environment Canada to collect flask air samples at regular bi-weekly intervals and to ship the samples to the O_2 analysis laboratory (then at the National Center for Atmospheric Research, in Boulder, Colorado but which moved to Scripps in Jan., 1993) for analysis of O_2 and CO_2 concentrations. Air sampling procedures used at Alert and the laboratory analysis procedures for O_2 and CO_2 have been described previously in *Keeling* (1988a) and *Keeling et al.* (1998). The Alert collaborative program has continued up to the present, and the O_2 record from this site is now more than seven years in length. The Alert data, shown in Figure 1, reveal a pronounced seasonal cycle superimposed on an irregular interannual decrease. These features, as well as differences between Alert and other stations, have been discussed in four publications [*Keeling and Shertz*, 1992, *Keeling et al.*, 1996; *Keeling et al.*, 1998; *Stephens et al.*, 1998], as described further below.

As background, the geochemistry of atmospheric O_2 is closely tied to that of CO_2 through chemical reactions that create or destroy organic carbon, such as photosynthesis, respiration, and combustion. Typical O_2:C ratios vary between 1.0 and 1.2 for photosynthesis and respiration of land biota [*Severinghaus*, 1995], ~1.1 to 1.2 for coal combustion, 1.4 to 1.5 for liquid fuels, and 1.9 to 2.0 for natural gas combustion [*Keeling*, 1988b]. If only these processes were operating, atmospheric CO_2 increases would always be coupled with O_2 decreases and vice versa. Complicating this simple coupling are exchanges of O_2 and CO_2 with the oceans. Dissolved O_2 and CO_2 are both influenced by temperature-induced solubility changes in seawater and by marine photosynthesis and respiration, which typically occurs with an O_2:C ratio of ~1.4.

Dissolved CO_2 is additionally influenced by inorganic chemical reactions involving carbonate and bicarbonate ions and involving the precipitation and dissolution of calcium carbonate. These inorganic reactions cause the oceans to have an unusually large storage capacity and an unusually slow equilibration time with the atmosphere for CO_2 as compared with other gases such as O_2 [*Keeling and Shertz*, 1992; *Keeling et al.*, 1993].

Atmospheric O_2 measurements can improve our ability to determine the magnitude of land biotic sinks for CO_2 largely as a consequence of the very different capacities of the oceans for storing O_2 and CO_2. Globally, fossil fuel burning adds CO_2 to the atmosphere and removes O_2 from the atmosphere at relatively well known rates. Superimposed on the global atmospheric CO_2 increase are changes caused by CO_2 exchanges with land biota and the oceans. The oceans take up excess CO_2 largely by inorganic reactions in seawater, which have no influence on O_2. An estimate of the influence of land biota on atmospheric O_2 can thus be derived from the

residual year-to-year change in atmospheric O_2 not accounted for by fossil-fuel combustion. This effectively determines the net land biotic effect on CO_2 because of the close O_2:C coupling in land biotic exchanges, and also determines the net oceanic effect on CO_2 from the residual changes in atmospheric CO_2 content that are not accounted for by fossil-fuel burning or land biota. One complication with this method, however, is the possibility that O_2 may be exchanged with the oceans on interannual time scales by processes unrelated to inorganic reactions, such as changes subsurface O_2 concentrations caused by variations in ocean mixing [*Bender et al.*, 1996; *Keeling et al.*, 1993, 1996]. Interannual air-sea O_2 exchanges must be independently determined in order to use the O_2 budget to provide rigorous estimates of land and ocean carbon fluxes.

Atmospheric O_2 provides a new window for studying marine photosynthesis, respiration, and

vertical watermass exchanges largely as a result of the rapid equilibration rate of O_2 between the upper ocean and the atmosphere. The seasonal spring and summer growth of phytoplankton in surface waters produces O_2 which is largely degassed into the overlying air. Comparable amounts of O_2 are removed from the air in the fall and winter when phytoplankton growth rates are slower and when O_2-depleted deeper waters are mixed to the surface. These O_2 exchanges are closely linked to the rates at which organic carbon is produced and exported seasonally from surface waters into the ocean interior. The plankton growth/mixing cycle also produces changes in dissolved CO_2 in the water, but the buffering effect of the inorganic carbon reactions effectively suppresses the air-sea gas exchange of CO_2 on seasonal and shorter time scales [*Keeling and Shertz*, 1992; Keeling et al., 1993].
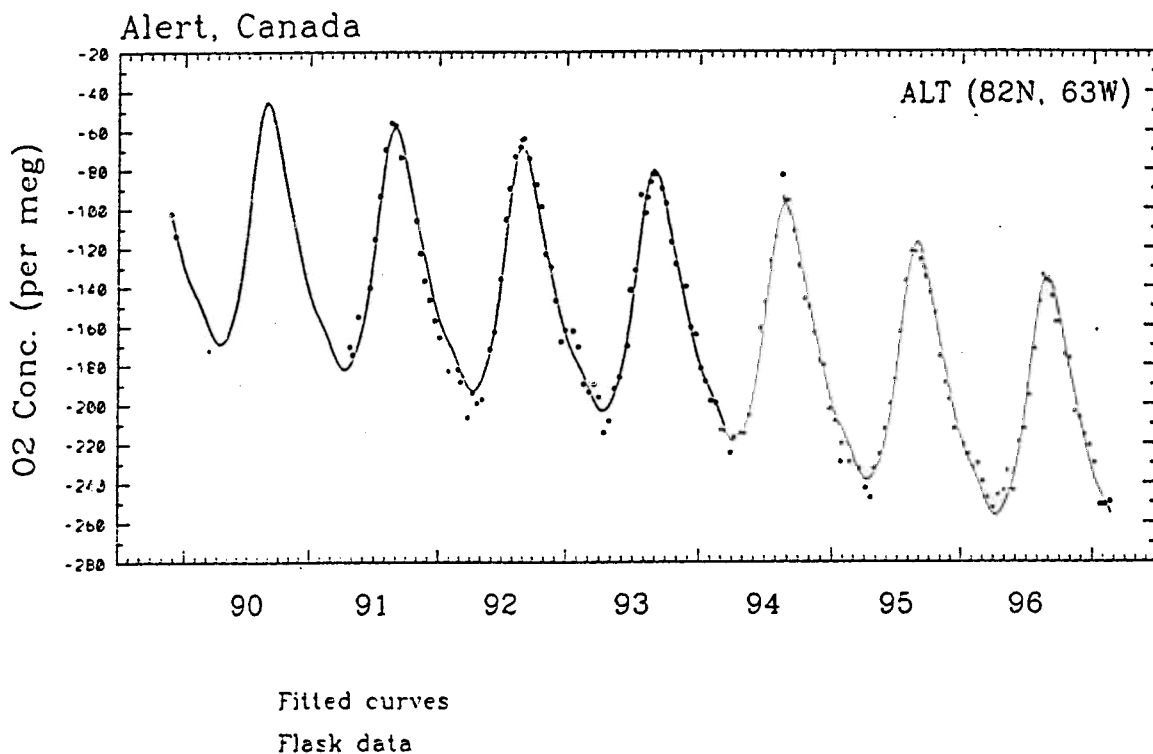

Figure 1. Time series from 1989 to 1997 of atmospheric oxygen concentration measured in flask samples collected at Alert Station. Points are averages of flask replicates collected on a given date. The curve is a least-squares fit consisting of a four-harmonic fit to the seasonal cycle plus a stiff spline fit to the interannual trend. Note that small interannual variations in the shape and amplitude of the seasonal cycle are not captured by the fit. Concentrations are expressed as changes in the O_2/N_2 ratio, such that a change of 1 per meg is defined to equal a change of 10^{-6} in the normalized ratio $(O_2/N_2)_{sample}/(O_2/N_2)_{reference}$ (see also *Keeling et al.*, 1998). In these units, adding 1 mole of O_2 to a mole of dry air would induce a change of +4.8 per meg.

The first full year of the Alert O_2 record was presented in *Keeling and Shertz* [1992], where the data were used along with data from La Jolla, California and Cape Grim, Tasmania, to derive global estimates of the rates of photosynthetic organic carbon production in surface oceans based on the amplitude of the seasonal O_2 cycles. These cycles are caused partly by exchanges with land biota, and partly by O_2 exchanges with the oceans. The land biotic contribution can be estimated from concurrent observations of the seasonal CO_2 cycle, which is predominately caused by land biotic exchanges due to the slow exchange with the oceans, and which therefore can be related to the land biotic component of the O_2 cycle based on the known O_2:C exchange ratio with land biota. At Alert, for example, about half of the O_2 cycle is caused by land biota, and the other half of the cycle is caused by oceanic exchanges. Of this oceanic component, about 15% is caused by thermal degassing and ingassing of O_2 and N_2 due to solubility changes, and the remainder is caused by the oceanic cycle of biological production and vertical mixing. Keeling and Shertz concluded that the non-thermal oceanic component to the cycle required that global organic carbon production (i.e., "new" production) in the oceans must be around 19 Pg C/yr, which was considerably higher than most earlier estimates.

Four years (1991-1994) of the concurrent O_2 and CO_2 records from Alert were presented in *Keeling et al.*, [1996] along with results from La Jolla and Cape Grim. These data were used to estimate global interannual O_2 and CO_2 trends and to resolve gradients in annually averaged O_2 and CO_2 concentrations between the northern and southern hemispheres. The interannual trends showed that, from 1991 through 1994, the oceans and land biota each removed from the air an amount of CO_2 comparable to roughly 30% of fossil-fuel emission. The gradients provided evidence that the land biotic CO_2 uptake was concentrated in the northern middle or high latitudes, as opposed to the tropics. The Alert data was critical for this analysis by defining trends in the northern hemisphere and the differences in average concentration from the Southern Hemisphere.

The interpretation of the combined O_2 and CO_2 gradients was explored in more detail in *Stephens et al.* [1998], where more than six years of Alert data were combined with records from eight additional stations. The emphasis in this study was on the average differences in concentration between stations along a north-south transect and

their relation to exchanges of O_2 and CO_2 with the oceans. The O_2 and CO_2 data were combined to derive a novel tracer, "potential oxygen", which is effectively equal to the sum of O_2 and CO_2 and which is in principle is not changed by photosynthesis and respiration of land biota. The observations show a large deficit in potential oxygen in the northern hemisphere relative to the southern hemisphere, with Alert station showing the lowest concentrations globally. The observed north-south gradients in annual-average potential oxygen were compared with model simulations incorporating O_2 and CO_2 fluxes across the air-sea interface derived from three different ocean carbon cycle models and incorporating O_2 and CO_2 fluxes from fossil fuel burning. These fluxes were imposed at the surface of an atmospheric transport model to produce simulated atmospheric concentration fields. A striking result of this study was that the model simulations failed to account for the full magnitude of the northern deficit in potential oxygen. Stephens et al argued that a likely cause for at least part of the discrepancy is difficulties in the ocean models' representation of large-scale water-mass transports, particularly as they relate to meridional heat transports. Evidently all three ocean models tested may share similar deficiencies. The inability of the simulations to account for the low potential oxygen concentrations at Alert, for example, may imply that the ocean models underestimate the transport of heat to high northern latitudes.

Finally, another application for O_2 measurements, involving placing constraints on the kinetics of air-sea gas exchange, was explored in *Keeling et al.*, [1998]. Here, the oceanic components of the seasonal cycles in O_2 were examined at nine stations, including Alert. The observed cycles were compared with model simulations using an atmospheric tracer transport model with seasonal air-sea O_2 fluxes derived from a climatology of O_2 saturation anomalies in the oceans [*Najjar and Keeling*, 1997] and N_2 fluxes computed indirectly from the net air-sea heat flux. Effectively, the only free parameter in the model is the air-sea gas exchange velocity, which relates the saturation anomaly to the air-sea flux. This parameter is tightly constrained by the ocean and atmospheric observations. The results showed that the constraint on large-scale average gas exchange velocity required by the seasonal cycles in O_2 agrees well with the constraints on gas exchange velocity derived some years ago based on mass balance of radiocarbon in the oceans [*Broecker and Peng*, 1974; *Broecker et al.*, 1985, 1986).

Such constraints are important because they suggest the appropriate transfer velocities for computing large-scale air-sea fluxes, such as uptake of anthropogenic CO_2 by the oceans or sources of other trace gases by the oceans.

In summary, the O_2 data from Alert have played an important role in improving our understanding of several aspects of the global carbon cycle, including constraining rates of uptake of CO_2 by land biota and the oceans, and constraining the natural processes affecting carbon cycling in the oceans, including rates of photosynthesis, rates of gas exchange, and rates of watermass exchange. The Alert O_2 record is the longest from a clean baseline site in the northern hemisphere, and the length of this time series makes the record pivotal for documenting long-term trends in O_2 globally. Relative to stations further south, Alert is also a key station for constraining O_2 and CO_2 exchanges throughout the northern high latitudes because of its strategic location for sampling arctic air masses free of local influences.

REFERENCES

Bender, M., J.T. Ellis, P.P. Tans, R.J. Francey and D.Lowe, 1996, Variability in the O_2/N_2 ratio of southern hemisphere air, 1991-1994: Implications for the carbon cycle, *Global Biogeochemical. Cycles,* 10, 9-21.

Broecker, W.S., T.-H. Peng, 1974, Gas exchange rates between air and sea, *Tellus*, 26, 21-25.

Broecker, W.S., T.-H. Peng, G. Ostlund and M. Stuiver, The distribution of bomb radiocarbon in the ocean, *J. Geophys. Res.*, 90, 6953-6970, 1985.

Broecker, W.S., J.R. Ledwell, T. Takahashi, R. Weiss, L. Merlivat, L. Memery, T.-H. Peng, B. Jähne and K.O. Münnich, 1986, Isotopic versus micrometeorological ocean CO_2 fluxes: A serious conflict. *J. Geophys. Res.*, 91, 10517-10527.

Keeling, R.F., 1988a, Measuring correlations between atmospheric oxygen carbon dioxide mole ractions: a preliminary study in urban air. *Journal of Atmospheric Chemistry*, 7, 153-176.

Keeling, R.F., 1988b, Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O_2 mole fraction, Ph.D. thesis, 178pp., Harvard University, Cambridge, Mass.

Keeling, R.F. & S.R. Shertz, 1992, Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, 358, 723-727.

Keeling, R.F., R.P. Najjar, M.L. Bender, P.P. Tans, 1993, What atmospheric oxygen measurements can tell us about the global carbon cycle. *Global Biogeochemical Cycles,* 7, 37-67, 1993.

Keeling, R.F., S.C. Piper, M. Heimann, 1996, Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration. *Nature* 381, 218-221.

Keeling, R.F., B.B. Stephens, R.G. Najjar, S.C. Doney, D. Archer, M. Heimann, 1998, Seasonal variations in the atmospheric O_2/N_2 ratio in relation to the kinetics of air-sea gas exchange of O_2, *Global Biogeochemical Cycles*, 12, 141-163.

Najjar, R.G., R.F. Keeling, 1997, Analysis of the mean annual cycle of the dissolved oxygen anomaly in the world ocean. *J. Marine Res.,* 55, 117-151.

Severinghaus, J.P., 1995, Studies of the terrestrial O_2 and carbon cycles in sand dune gases and in Biosphere 2, Ph.D. thesis, 148 pp., Columbia University, New York.

Stephens, B.B., R. F. Keeling, M. Heimann, K.D. Six, R. Murnane, K. Caldeira, 1998, Testing global ocean carbon cycle models using measurements of atmospheric O_2 and CO_2 concentration, *Global Biogeochemical Cycles*, 12, 213-230.