Partitioning of the global fossil CO$_2$ sink using a 19-year trend in atmospheric O$_2$

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Abstract. O$_2$/N$_2$ is measured in the Cape Grim Air Archive (CGAA), a suite of tanks filled with background air at Cape Grim, Tasmania (40.7$^\circ$S, 144.8$^\circ$E) between April 1978 and January 1997. Derived trends are compared with published O$_2$/N$_2$ records and assessed against limits on interannual variability of net terrestrial exchanges imposed by trends of $\delta^{13}$C in CO$_2$. Two old samples from 1978 and 1987 and eight from 1996/97 survive critical selection criteria and give a mean 19-year trend in $\delta$(O$_2$/N$_2$) of -16.7 $\pm$ 0.5 per meg yr$^{-1}$, implying net storage of +2.3 $\pm$ 0.7 GtC ($10^{15}$ g carbon) yr$^{-1}$ of fossil fuel CO$_2$ in the oceans and +0.2 $\pm$ 0.9 GtC yr$^{-1}$ in the terrestrial biosphere. The uptake terms are consistent for both O$_2$/N$_2$ and $\delta^{13}$C tracers if the mean $^{13}$C isotopic disequilibrium flux, combining terrestrial and oceanic contributions, is 93 $\pm$ 15 GtC % per yr$^{-1}$.

1. Introduction.

Direct, high precision monitoring of O$_2$/N$_2$ in the global atmosphere began in 1989, with the primary aim of determining the proportion of anthropogenic CO$_2$ re-absorbed by the terrestrial biosphere [Keeling et al., 1996; Bender et al., 1996]. The approach is limited by the relatively short timespan of these records and uncertainties about the oceanic contribution to O$_2$/N$_2$ changes. Battle et al. [1996] report a trend in O$_2$/N$_2$ from Antarctic firn air for the period 1977-1985, but difficulties in calibrating the different methodologies prevent a close link to the modern records. Fractionating processes, probably related to molecular geometry, that affect O$_2$/N$_2$ at lower depths of the firm, limit the length of the Battle et al. record and have also prevented recovery of any meaningful trends from air sealed in ice. The CGAA continues to provide high precision reconstructions of many atmospheric trace gas species including SF$_6$, many long-lived halocarbon species [see Langenfelds et al., 1996] and greenhouse gases and their isotopes [e.g., Frayce et al., 1999]. The CGAA provides a unique opportunity to confirm and extend knowledge of changes in atmospheric O$_2$/N$_2$, and thereby constrain the global carbon budget over the last two decades.


Measurements of O$_2$/N$_2$ were made by mass spectrometry as the ratio of mass/charge (m/e) 32 and 29, using techniques adapted from those described by Bender et al. [1994]. Data are expressed in units of per meg as $\delta$(O$_2$/N$_2$)$_{sample}$ = [(O$_2$/N$_2$)$_{sample}$ / (O$_2$/N$_2$)$_{interm}$ -1] x 10$^4$, where per meg $\equiv$ 0.001%o. O$_2$/N$_2$ studies place critical demands on the collection and storage of air samples [Keeling, 1988; Bender et al., 1994], creating the major challenge for this CGAA study. Extensive quality assessment of individual samples has examined collection procedures and compared CGAA measurements to parallel records of a range of other trace gas species [Langenfelds et al., 1999]. Unsuitable sampling procedures (e.g., pre-sampling evacuation or incomplete removal of pre-filled N$_2$) are demonstrated as the reason for most rejections. Tanks that have developed leaks show enrichment in $\delta^{15}$N of N$_2$ and $\delta^{18}$O of O$_2$ and must also be fractionated in O$_2$/N$_2$. For escape of gas from a pressurized vessel through a small orifice by molecular effusion [Moore, 1962], the rate of effusion varies inversely as the square root of the molecular weight. This theory predicts a linear relationship with slope 1.74 for $\delta^{15}$O/$\delta^{15}$N$_2$, as observed in the $\delta^{15}$N$_2$-enriched tanks, and a slope of 2.85 for $\delta^{18}$O/$\delta^{15}$N$_2$. Samples with $\delta^{15}$N$_2$ enriched by $>$70 per meg are rejected, but for smaller values (up to 37 per meg) we correct $\delta$(O$_2$/N$_2$) for effusion by 2.85 x $\delta^{15}$N$_2$. Allowance is made for uncertainty in the factor within a range 2.85-3.41, where the upper bound is determined empirically from (rejected) CGAA samples that exhibit larger $\delta^{15}$N$_2$ enrichments up to 1560 per meg. The higher empirical value, if real, suggests factors other than mass may contribute to O$_2$/N$_2$ fractionation. It cannot be explained by modification due to molecular geometry as observed in firn/ice but may reflect a chemical process. Of 65 analysed CGAA samples, 17 (contained in electropolished stainless steel tanks

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and cryogenically trapped by immersion in liquid N₂ at -195°C) survive the selection procedures described above, including 9 collected between 1978 and 1987, and 8 in 1996/97.

Two filling strategies were used for these tanks, "wet" and "dry" (using ethanol traps cooled to -80°C with dry ice or liquid N₂). No significant differences are observed between wet CGAA samples and dry samples collected in glass flasks during 1996/97. However, it is possible that corrosion in the old, wet CGAA tanks has occurred slowly on a time scale of many years with resulting loss of O₂. Although N₂ reacts with newly electropolished stainless steel in dry air, oxide layers form rapidly and prevent further corrosion. Thus significant O₂/N₂ depletion in the dry CGAA samples, filled years after electropolishing, is unlikely. In the old, wet tanks, it is also possible that corrections (up to 6 per mg) applied for fractionation by preferential dissolution of O₂ relative to N₂ into trapped water might be underestimated. Most of the water that condenses in undried samples, together with any dissolved gases, is expelled after 1-2 days by allowing it to drain into the tank valve and briefly opening the valve. Corrections are applied for volume of water trapped, estimated from humidity, tank volume and sample pressure, and assuming equilibration at 20°C. Accuracy of estimates for 1996/97 samples was confirmed by measurement of expelled water volume. For earlier, undried samples, we cannot exclude the possibility of additional water, trapped either before or during sample collection, or subsequent expulsion of water equilibrated at < 20°C, either of which would have resulted in larger fractionation. Anomalies in δ¹³C of CO₂ have also been observed in wet CGAA samples [Francey et al., 1999], consistent in sign with fractionation from dissolution but with larger than expected magnitude.

3. Results and Discussion

The relatively small number of selected tanks, and their uneven distribution over the two decades seriously limits the ability to assess the influence of interannual variability on derived trends (and associated assessment of the internal consistency of the retained data). Fortunately, we can explore constraints on interannual variability by comparison with a higher time resolution record of δ¹³C in CO₂ extracted from Cape Grim marine air [Francey et al., 1995]. The δ¹³C trend can be used to predict variations in the associated O₂/N₂ trend using a simple 1-box model [Francey et al., 1995; Keeling and Shertz, 1992]:

\[
\frac{d}{dt} \delta a = \frac{F + N_a + N_b}{N_a} \delta a
\]

(1)

\[
\frac{d}{dt} \delta N_a = F \delta N_a + N_a (\delta N_a + \epsilon_a) + N_b (\delta N_b + \epsilon_b)
\]

(2)

\[
\frac{d}{dt} \delta N_b = R_f \delta N_a + R_n \delta N_b
\]

(3)

where \( C_a \), \( O_2 \), and \( O_2 \) are the atmospheric burdens of CO₂ (GtC) and O₂ (calculated from O₂/N₂ assuming negligible change in \( N_a \) and converted to units of GtC equivalent on a mol/mol CO₂/O₂ basis so that 1 per mg \( \delta O_2/N_2 = 0.45 \) GtC equivalent); \( F \), \( N_a \) and \( N_b \) denote carbon fluxes due to fossil fuel emission, net and gross exchange respectively; subscripts \( a \), \( f \), \( s \) and \( b \) refer to atmosphere, fossil fuel emission, oceans and terrestrial biosphere respectively; \( \delta N_a \) and \( \delta N_b \) represent atmospheric δ¹³C in equilibrium with the oceans and terrestrial biosphere;

\( \epsilon_a = -1.8 \) and \( \epsilon_b = -14.8 \) represent isotopic discrimination associated with net air-sea [Keeling et al., 1989] and air-biosphere [Lloyd and Farquhar, 1994] fluxes respectively; \( R_f \) and \( R_n \) are O₂/CO₂ exchange ratios for fossil fuel combustion and cycling through terrestrial biomass. We treat \( R_n \) as a constant [Keeling et al., 1996] while \( R_f \) has a mean value of -1.38 but varies with time according to the relative proportions of fuel types combusted [Keeling, 1988; CD&A]. The major uncertainty in using δ¹³C to directly partition net oceanic and terrestrial carbon uptake has been the size of the isotopic disequilibrium flux (G) terms at the right of Equation (2). It has generally been assumed that apart from a steady increase in the global disequilibria in response to continued fossil fuel emissions, their contributions to decadal or shorter period variations in atmospheric δ¹³C are negligible. We also make this assumption, thus enabling use of δ¹³C to predict O₂/N₂ variations due to net terrestrial carbon exchange.

CGAA O₂/N₂ data are shown in Figure 1a, along with the contemporary Cape Grim flusk records of Scripps Institution of Oceanography (SIO), University of Rhode Island (URI), both commencing in 1991 and Commonwealth Scientific and Industrial Research Organisation (CSIRO), commencing in 1995. Also plotted is a "predicted" O₂/N₂ curve, constructed using disequilibria values independently estimated for the terrestrial biosphere [Enting et al., 1993] and oceans [based on Tans et al., 1993] and mean seasonality defined by the harmonic component of a fit to the combined 1991-1997 O₂/N₂ records. As plotted, the CGAA data already usefully constrain the global carbon budget, though scatter among pre-1990 points is larger than expected from analytical uncertainty alone. A more informative comparison of all records in Figure 1a is obtained by removing the seasonality and subtracting the predicted curve (Figure 1b). Mean non-zero trends of residuals in this plot are possible due to large uncertainty in the mean size of the δ¹³C disequilibria but shorter term variations are expected to be small. Thus if O₂/N₂ interannual variability is well-described by that in the δ¹³C record, the residuals would form a straight line through the 1996/97 CGAA data. A negative slope on the line would imply that the mean disequilibria terms used to generate the predicted curve are underestimated. Much of the interannual variability in the SIO and URI trends is accounted for by this procedure. The remaining variability, suggested in the SIO and URI curves of Figure 1b, might be due to oceanic influences, for example variations in upper ocean ventilation rates or marine biological cycling [Keeling et al., 1996; Bender et al., 1996]. This is the subject of ongoing studies. For present purposes, however, the O₂/N₂ curve predicted from the Cape Grim δ¹³C record provides a useful benchmark against which to assess the integrity of the remaining CGAA O₂/N₂ data.

In Figure 1b, the pre-1990, "wet" CGAA values (a) all fall below a line consistent with the dry, pre-1990 values (consistent in sign with water-related depletion of O₂/N₂), (b) exhibit structure that implies much larger interannual variability than observed in the 6-year contemporary records (for example, a net 1.8 GtC yr⁻¹ ocean source of CO₂ sustained over more than 4 years is required between 1986 and 1991 to reconcile the 1986 CGAA data with the SIO and URI records; an anomaly of this magnitude is not supported by other records of atmospheric δ¹³C over this period [Keeling et al., 1995; Nakazawa et al., 1997]), and (c) exhibit disagreement among the 1978/79 samples that indicates unaccounted modification of at least the wet sample collected 7 July 78. We have found no reason to suspect un-
explained modification of O$_2$/N$_2$ in the dry, pre-1990 or 1996/97 samples and thus place most emphasis on the results from these samples. A weighted, least-squares fit to the retained data (Figure 1c) yields a best estimate of the mean 19-year trend of -16.7 ± 0.5 per meg yr$^{-1}$. The corresponding curve constructed from 8$^{13}$C is closely consistent with both contemporary and firn slopes. Over the common period of modern records (91.56 - 96.65), SIO, URI and CGAA best-fit slopes are -16.3, -17.0 and -18.1 per meg yr$^{-1}$ respectively, as compared to -14.2 for the initial 8$^{13}$C-predicted slope in Figure 1a.

Uncertainty in our carbon budget due to oceanic influence on the atmospheric O$_2$ trend can be evaluated for the period 1991–1997 by comparing observed and predicted interannual variability within the 6-year period, assuming there are no longer-term perturbations. Variations of contemporary records about their mean trends are within ±10 per meg (Figure 1b), translating to an upper limit in budgeting uncertainty of ±0.5 GtC yr$^{-1}$. One identified mechanism capable of altering the assumed steady state of the marine organic carbon pool over longer time scales is N fertilisation resulting from flux of anthropogenic N to the ocean. Sequestration of all anthropogenic N through biological uptake at Redfield C:N ratios of 6.6 would account for uptake of 0.4 GtC yr$^{-1}$ although the actual value is likely to be smaller due to rapid remineralisation of a large fraction of the N [Galloway et al., 1995]. Following calculations by Keeling [1988], changes in the ocean’s physical capacity to store O$_2$ can be estimated from observed changes in sea level [IPCC, 1995]. Assuming sea level has risen by 1.8 mm yr$^{-1}$ with 50% of the rise caused by thermal expansion of water at a mean temperature of 8$^\circ$C, the resulting O$_2$ flux into the atmosphere leads to a small budget error of 0.1 ± 0.1 GtC yr$^{-1}$ which would be incorrectly allocated to terrestrial carbon uptake. We make this adjustment in our budget and allow for overall uncertainty due to net oceanic O$_2$ fluxes of ±0.3 GtC yr$^{-1}$.

Using the derived O$_2$/N$_2$ trend of -16.7 per meg yr$^{-1}$, the observed CO$_2$ trend and estimates of fossil fuel carbon emission (see Figure 1a caption), Equations (1) and (3) give mean net uptake of ±2.3 ± 0.7 and ±0.2 ± 0.9 GtC yr$^{-1}$ by the oceans and terrestrial biosphere, respectively. Note that the wet, pre-1990 samples, while rejected by our analysis due to likely O$_2$/N$_2$ depletion, still usefully constrain the carbon budget. A fit to all data, both wet and dry (but excluding the sample filled 7 July 78) gives a lower limit to the rate of δ(O$_2$/N$_2$) decline of -15.3 per meg yr$^{-1}$, corresponding to 0.6 GtC yr$^{-1}$ higher terrestrial uptake than implied by the best estimate of the trend. Uptake terms represent storage of carbon such that the oceanic uptake includes a contribution of 0.4-0.7 GtC yr$^{-1}$ transported by rivers [Sarmiento and Sundquist, 1992]. Uncertainties are calculated by quadratically adding components arising from the δ(O$_2$/N$_2$) trend measurement of ±0.5 per meg yr$^{-1}$ (±0.2 GtC yr$^{-1}$), ±5% (16) in fossil fuel emissions (±0.4 GtC yr$^{-1}$) [Marland and Rotty, 1984], and allowance for ±0.05 in R$_o$ and ±0.04 in R$_r$ (±0.3 GtC yr$^{-1}$). An additional ±0.3 GtC yr$^{-1}$ is allowed for possible net oceanic O$_2$ flux. The mean 19-year isotopic disequilibrium flux is calculated by Equation (2) to be 93 ± 15 GtC% yr$^{-1}$ (Table I).

This is larger than the value of 49 estimated by Tans et al. [1993] for the earlier period 1970-1990, with part of the difference being attributable to the different averaging periods.

These results provide observational evidence supporting the role of the oceans as the dominant recent net sink of anthropogenic CO$_2$. The rate of oceanic carbon sequestration is in close agreement with results from modelling of the ocean carbon cy-

Figure 1. (a) δ(O$_2$/N$_2$) observed at Cape Grim. CGAA data are denoted by solid (dry) and open (wet) symbols. Error bars (1σ) relate to measurement precision and correction for fractionation according to δ$^{15}$N$_2$. Flask records of SIO (short-dashed), URI (thin-solid) and CSIRO (thick-dotted) are shown as smoothed curves and aligned to the SIO scale based on the mean difference in monthly means during the period of overlap. The thin-dotted line shows δ(O$_2$/N$_2$) predicted from the trend in δ$^{13}$C at Cape Grim. It is anchored to the mean δ(O$_2$/N$_2$) of 1977 CGAA samples (-1.156 per meg) and is constructed using (1) δ$^{13}$C from the in-situ trapping record back to 1982 [Francey et al., 1995], linearly interpolated to 1978 linking δ$^{13}$C data from the oldest CGAA sample [Francey et al., 1999], (2) a mean CO$_2$ trend of 1.47 ppm yr$^{-1}$ (3.1 GtC yr$^{-1}$) from CSIRO in-situ analysis at Cape Grim and (3) mean emission from fossil fuel combustion and cement manufacture [Marland et al., 1984; CDIAC] of 5.63 GtC yr$^{-1}$, calculated for the earlier period 1977-1995 to allow for an interhemispheric exchange time of about 1 year. (b) Difference in δ(O$_2$/N$_2$) from the δ$^{13}$C-derived curve in Figure 1a. Symbols and lines correspond to the raw CGAA, SIO, URI and CSIRO records in a) with an additional (long-dashed) line representing a weighted, least-squares, linear fit to the two dry, pre-1990 and eight wet, 1996/97 CGAA points. Error bars are as for Figure 1a but including a component for the seasonality correction. (c) Cape Grim δ(O$_2$/N$_2$) data from Figure 1a with seasonality removed and showing only retained CGAA data. Symbols and lines are as for a). The long-dashed line is constructed from δ$^{13}$C to provide an optimal fit against varying disequilibrium flux and arbitrarily superposed above it is the slope of the firm data of Battle et al. [1996] (thick-dashed).
Table 1. Calculation of $^{13}$C Isotopic Disequilibrium Flux.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$CO$_2$ (GtC yr$^{-1}$)</th>
<th>$\Delta$δ$^{13}$C (%)</th>
<th>Product (GtC yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>-16.2 ± 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fossil Fuel</td>
<td>5.63 ± 0.3</td>
<td>-20.65 ± 0.5$^a$</td>
<td>-116.3 ± 6.8</td>
</tr>
<tr>
<td>Oceans</td>
<td>-2.3 ± 0.7</td>
<td>-1.8 ± 0.2$^a$</td>
<td>4.1 ± 1.3</td>
</tr>
<tr>
<td>Biosphere</td>
<td>-0.2 ± 0.9</td>
<td>-14.8 ± 2$^a$</td>
<td>3.0 ± 13.3</td>
</tr>
<tr>
<td>Disequilibrium Flux (= A-F-O-B)</td>
<td>93 ± 15</td>
<td></td>
<td></td>
</tr>
</tbody>
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$^a$ Calculated from the average CO$_2$ content of the atmosphere for 1978-1997 (738 GtC) and the mean δ$^{13}$C trend (-0.02 ± 0.02 δ‰ yr$^{-1}$). $^b$ Average annual difference for the period 1982-1992 between δ$^{13}$C in the atmosphere and from emissions by fossil fuel combustion and cement manufacture (CDIAC); while δ$^{13}$C declined in the atmosphere, the difference remained fairly stable due to consumption of an increasingly higher proportion of lighter carbon fuels.

Uncertainties quoted for oceanic and terrestrial δ$^{13}$C isotopic discrimination and for the difference between atmospheric and fossil δ$^{13}$C are estimated from the range of values reported in recent papers.

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