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7-1-1999

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Recommended Citation

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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°S, 144.8°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 ± 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 ± 15 GtC ‰ 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 firn, 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

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Langenfelds et al., 1996] and greenhouse gases and their isotopes [eg. Francey 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.

2. Methods.

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 $\delta(O_2/N_2) = [(O_2/N_2)_{sample} / (O_2/N_2)_{reference} -1] \times 10^6$ where 1 per meg = 0.001‰. 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 (eg. 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 $\delta^{34}O_2/\delta^{29}N_2$, as observed in the $\delta^{15}N$-enriched tanks, and a slope of 2.85 for $\delta(^{32}O_2/^{29}N_2)/\delta^{29}N_2$. Samples with $\delta^{29}N_2$ 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 $\delta^{29}N_2$. 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 $\delta^{29}N_2$ 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

and cryogenically trapped by immersion in liquid N_2 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 N_2). 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 O_2. Although O_2 reacts with newly electropolished stainless steel in dry air, oxide layers form rapidly and prevent further corrosion. Thus significant O_2/N_2 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 meg) applied for fractionation by preferential dissolution of O_2 relative to N_2 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 $\delta^{13}C$ of CO_2 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 $\delta^{13}C$ in CO_2 extracted from Cape Grim marine air [*Francey et al.*, 1995]. The $\delta^{13}C$ trend can be used to predict variations in the associated O_2/N_2 trend using a simple 1-box model [*Francey et al.*, 1995; *Keeling and Shertz*, 1992]:

$$\frac{d}{dt}(C_a) = F + N_s + N_b \qquad (1)$$

$$\frac{d}{dt}(C_a\delta_a) \approx F\delta_f + N_s(\delta_a + \varepsilon_{as}) + N_b(\delta_a + \varepsilon_{ab})$$
$$+ G_s(\delta_a^s - \delta_a) + G_b(\delta_a^b - \delta_a) \qquad (2)$$

$$\frac{d}{dt}(O_2)_a \approx R_f F + R_b N_b \qquad (3)$$

where C_a and $(O_2)_a$ are the atmospheric burdens of CO_2 (GtC) and O_2 (calculated from O_2/N_2 assuming negligible change in N_2 and converted to units of GtC equivalent on a mol/mol $CO_2:O_2$ basis so that 1 per meg $\delta(O_2/N_2)$ = 0.45 GtC equivalent); F, N and G 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; δ_a^s and δ_a^b represent atmospheric $\delta^{13}C$ in equilibrium with the oceans and terrestrial biosphere;

$\varepsilon_{as} = -1.8$ and $\varepsilon_{ab} = -14.8$ 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_b are O_2/CO_2 exchange ratios for fossil fuel combustion and cycling through terrestrial biomass. We treat $R_b = -1.1$ as 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; *CDIAC*].

The major uncertainty in using $\delta^{13}C$ to directly partition net oceanic and terrestrial carbon uptake has been the size of the isotopic disequilibrium flux (G.δ) 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 $\delta^{13}C$ are negligible. We also make this assumption, thus enabling use of $\delta^{13}C$ to predict O_2/N_2 variations due to net terrestrial carbon exchange.

CGAA O_2/N_2 data are shown in Figure 1a, along with the contemporary Cape Grim flask 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" O_2/N_2 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 O_2/N_2 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 ^{13}C disequilibria but shorter term variations are expected to be small. Thus if O_2/N_2 interannual variability is well-described by that in the $\delta^{13}C$ 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 O_2/N_2 curve predicted from the Cape Grim $\delta^{13}C$ record provides a useful benchmark against which to assess the integrity of the remaining CGAA O_2/N_2 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 O_2/N_2), (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 CO_2 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 $\delta^{13}C$ over this period [*Keeling et al.*, 1995; *Nakazawa et al.*, 1997]), and (c) exhibit disagreement among 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 $\delta^{13}C$ 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 $\delta^{13}C$-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 ±0.3 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°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 $\delta(O_2/N_2)$ 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 $\delta(O_2/N_2)$ trend measurement of ±0.5 per meg yr^{-1} (±0.2 GtC yr^{-1}), ±5% (1σ) in fossil fuel emissions (±0.4 GtC yr^{-1}) [*Marland and Rotty*, 1984], and allowance for ±0.05 in R_b and ±0.04 in R_f (±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 1). 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-
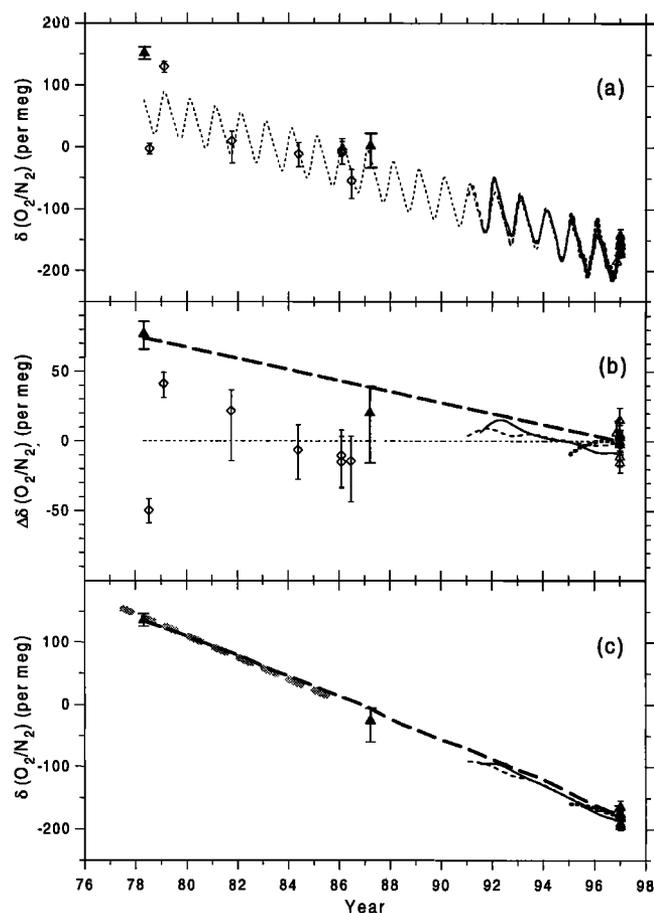
Figure 1. (a) $\delta(O_2/N_2)$ observed at Cape Grim. CGAA data are denoted by solid (dry) and open (wet) symbols. Error bars (1σ) relate to measurement precision and correction for fractionation according to $\delta^{29}N_2$. Flask records of SIO (short-dashed), URI (thin-solid) and CSIRO (thick-dotted) 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 $\delta(O_2/N_2)$ predicted from the trend in $\delta^{13}C$ at Cape Grim. It is anchored to the mean $\delta(O_2/N_2)$ of 1997 CGAA samples (-156 per meg) and is constructed using (1) $\delta^{13}C$ from the *in-situ* trapping record back to 1982 [*Francey et al.*, 1995], linearly interpolated to 1978 linking $\delta^{13}C$ 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 $\delta(O_2/N_2)$ from the ^{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 $\delta(O_2/N_2)$ 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 $\delta^{13}C$ to provide an optimal fit against varying disequilibrium flux and arbitrarily superposed above it is the slope of the firn data of *Battle et al.* [1996] (thick-dashed).

Table 1. Calculation of ^{13}C Isotopic Disequilibrium Flux.

	ΔCO_2 (GtC yr^{-1})	$\Delta\delta^{13}$C (‰)	Product (GtC ‰ yr^{-1})
Atmosphere			-16.2[a] ± 1.5
Fossil Fuel	5.63 ± 0.3	-20.65[b] ± 0.5[c]	-116.3 ± 6.8
Oceans	-2.3 ± 0.7	-1.8 ± 0.2[c]	4.1 ± 1.3
Biosphere	-0.2 ± 0.9	-14.8 ± 2[c]	3.0 ± 13.3
Disequilibrium Flux (= A-F-O-B)			93 ± 15

[a] Calculated from the average CO$_2$ content of the atmosphere for 1978-1997 (738 GtC) and the mean δ^{13}C trend (-0.022 ± 0.002 ‰ 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.
[c] Uncertainties quoted for oceanic and terrestrial ^{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.

cle (eg. 1.9 GtC yr^{-1} for 1980-1989 [*Sarmiento et al.*, 1992]) and from observation of the changing oceanic ^{13}C inventory between 1970 and 1990 (2.1 GtC yr^{-1} [*Quay et al.*, 1992]), forced by the decline in atmospheric δ^{13}CO$_2$ due to burning of fossil fuels. The terrestrial biosphere has been essentially in balance, notwithstanding an ongoing source of 1.6 ± 1.0 GtC yr^{-1} to the atmosphere through predominantly tropical deforestation [*Houghton et al.*, 1997]. Compensating growth of the biosphere is implied, attributable to reforestation, higher rates of net production in response to climatic trends, fertilisation by elevated levels of atmospheric CO$_2$ or nitrogen deposition or a combination of these factors [*Houghton et al.*, 1997].

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