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Citation

Huang, Junling, and Michael Brendon McElroy. 2012. The contemporary and historical budget of atmospheric \(CO_2\). Canadian Journal of Physics 90(8): 707-716.

Published version

https://doi.org/10.1139/p2012-033

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The contemporary and historical budget of atmospheric CO_2

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Abstract

Observations of CO_2 and O_2 are interpreted to develop an understanding of the changes in the abundance of atmospheric CO_2 that have arisen over the period 1995 to 2007. Fossil fuels accounted for an addition of 89.3 Gt C to the atmosphere over this time period, 29 % of which was transferred to the ocean, 15 % to the global biosphere, with the balance, 57 %, retained by the atmosphere. Analysis of historical data for CO_2 derived from studies of gases trapped in ice at Law Dome in Antarctica indicate that the biosphere represented a net source of atmospheric CO_2 prior to 1940, switching subsequently to a net sink.

1. Introduction

The bulk of the Earth's carbon resides in the sediments. The ocean ranks number two, followed by soils, the biosphere and the atmosphere. The concentration of CO_2 in the atmosphere has varied between about 180 ppm and 280 ppm over much of the past million years or so - low during glacial epochs, high during the relatively short duration interglacial environments that punctuated global climate conditions over this interval. The glacial/interglacial variability of atmospheric CO_2 reflects primarily a redistribution of carbon between the atmosphere on the one hand and the combined ocean/biosphere/soil reservoir on the other.

The lifetime of carbon in sediments is measured in hundreds of millions of years. Carbon is returned from sediments to the ocean/atmosphere/biosphere/soil when sediments are uplifted and weathered or when the sediments are drawn down into the mantle and cooked. Return in the latter case occurs in conjunction with hot springs and volcanoes. Changes in sediment cycling rates over time have resulted in a variety of different levels of carbon in the atmosphere and for a wide range of different climate conditions. The lifetime of carbon in the ocean/atmosphere/biosphere/soil reservoir is a few hundred thousand years. We would expect variations in CO_2 occasioned by temporary imbalances in the sediment source/sink to be manifest therefore on time scales at least this long. The challenge at the moment is that demands for the fossil fuels (coal, oil and natural gas) and cement production in our modern economy are seriously accelerating the natural rate at which carbon is returned to the atmosphere from sediments, by more than a factor of 50. It is not surprising under the circumstances that the abundance of CO_2 in the atmosphere is rising rapidly at the present time.

The increase began in the late 18^{th} century roughly coincident with the industrial revolution. It has risen in the interim from a level of about 285 ppm characteristic of typical unperturbed (natural) interglacial conditions to a contemporary value of close to 390 ppm. There can be little doubt that combustion of fossil fuel has been a major contributor to the recent rise in the abundance of atmospheric CO_2. A portion of the CO_2 added to the atmosphere over the past several hundred years has been absorbed by the ocean. At the same time there have been important changes in the quantity of carbon stored in the biosphere and soils. The early rise in CO_2 was clearly due to a net release of carbon from the biosphere and most likely also from soils.

Conversion of forested land to agriculture in the eastern region of North America in the late 18th and early 19th centuries for example resulted without question in a net transfer of carbon to the atmosphere: the observed increase in the abundance of atmospheric CO_2 in this period exceeds by a significant factor the quantity of CO_2 produced as a consequence of the early use of fossil fuels. As richer soils in the interior of the continent were opened up for development, poorer lands in the east were abandoned and forests were allowed to regrow. Plowing the carbon rich soils of the Mid West resulted almost certainly in an additional net transfer of carbon to the atmosphere. Regrowth of the forests previously depleted in the east would have resulted in a net sink for atmospheric carbon. Closer to present, it is apparent that clearance of land in the tropics and subtropics, deforestation, has contributed an important additional source of atmospheric CO_2. On the other hand, as we shall see, the biosphere/soil system on a global scale is presently responsible for a net sink.

The objective for this paper is to develop a quantitative understanding of the relative importance of ocean uptake, exchange with the biosphere/soil system and combustion of fossil fuel in determining the change in CO_2 that has taken place in the atmosphere over the past several hundred years. The late Charles David Keeling was the early pioneer in developing a high quality record of modern changes in the abundance of atmospheric CO_2. Data from the stations he established on Mauna Loa, Hawaii, and at the South Pole have provided an essentially continuous record of the changes in the abundance of CO_2 at these stations since the late 1950's. Keeling's ambition was to use precise measurements of CO_2 as a window on the carbon cycle. He extended his observations later to include measurements of the isotopic composition of atmospheric CO_2, the ratio of ^{13}C to ^{12}C. The photosynthetic process favors absorption of ^{12}C

over ^{13}C. As a consequence, reduced forms of carbon (carbon in biosphere, soil, and fossil fuel materials) are isotopically light relative to carbon in the atmosphere. Combustion of fossil fuels adds a source of isotopically light carbon to the atmosphere. Net transfer of carbon from the atmosphere to the biosphere (in what follows we use biosphere as a shorthand to indicate the combination of above ground and below ground sources of organic carbon) would result in a net increase in the abundance of ^{13}C relative to ^{12}C in the atmosphere, a net decrease if the biosphere should act as a net source of atmospheric CO_2. Isotopic fractionation associated with transfer of carbon between the atmosphere and ocean is much less than the fractionation associated with exchange between the atmosphere and biosphere.

The isotopic composition of a sample containing carbon (the abundance of ^{13}C relative to ^{12}C) is expressed in terms of a quantity $\delta^{13}C$ defined as follows

$$\delta^{13}C(‰) = [\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}] \times 10^3 \qquad (1)$$

where $\delta^{13}C$ is expressed in parts per thousand ($^0/_{00}$), and R_{sample} and R_{standard} express the molar ratios of ^{13}C relative to ^{12}C in the sample and in a standard gas respectively. Addition of carbon to the atmosphere associated with combustion of fossil fuel has resulted in a net decrease of about 0.7 $^0/_{00}$ in the value of $\delta^{13}C$ for atmospheric CO_2. A number of authors, including Charles David Keeling, have exploited observations of the abundance of CO_2 in the atmosphere in combination with measurements of $\delta^{13}C$ over the past 30 years to distinguish the relative contributions of atmosphere/biosphere and atmosphere/ocean exchange to the overall budget of atmospheric CO_2 [1-4]. An alternate approach, based on a combination of measurements for CO_2 together with data on the changing abundance of atmospheric O_2 is adopted for purposes of the present analysis.

The premise of the oxygen approach is basically simple. If you know the concentrations of atmospheric CO_2 and O_2 at time t and if you also know the concentrations at some later time t + Δt, the question is how you make the transition from the conditions appropriate for time t to those applicable at time t + Δt. Combustion of fossil fuel is responsible for a net increase in the abundance of CO_2 with an associated decrease in the abundance of O_2. Consider a two dimensional diagram in which one axis (the vertical for example) is represented by the concentration of CO_2, the other measures the concentration of O_2. If you know the composition of the fossil fuels that are consumed, and this can be determined, you can immediately draw a line indicating the trajectory in the 2-dimensional diagram representing the change attributable to the fossil fuel source. Uptake of CO_2 by the ocean will cause the trajectory to continue along an essentially horizontal path since exchange with the ocean is not expected to result in any significant change in the abundance of O_2 (oxygen is relatively insoluble in the ocean). The challenge then is to arrive at the final destination. Biospheric exchange results in a predictable change in the ratio of the change in CO_2 as compared to the change in O_2 (i.e. the slope of the final segment of the trajectory is predetermined). The procedure, subject to its assumptions, results in a unique determination of the magnitude of the ocean sink and the magnitude of either the source or sink associated with the biosphere. A schematic illustration of this procedure is plotted in Figure.1. There is a minor complication to this analysis to be discussed later. The ocean on a short time scale could contribute either a small source or sink for O_2 reflecting a temporary imbalance in rates for photosynthesis and compensatory respiration and decay. Additional release of CO_2 from the ocean to the atmosphere could arise as a result of net warming of surface ocean waters. The assumption is that by averaging data over several

(relatively short) years, the limitations imposed by these complications can be minimized. The oxygen approach was developed by another member of the Keeling family, Charles David's son Ralph. It would not strain credulity too much to assert that a large fraction of what we now know about the contemporary atmospheric CO_2 budget can be attributed to the ingenuity and persistence of a pair of talented individuals from a single family, the Keelings.

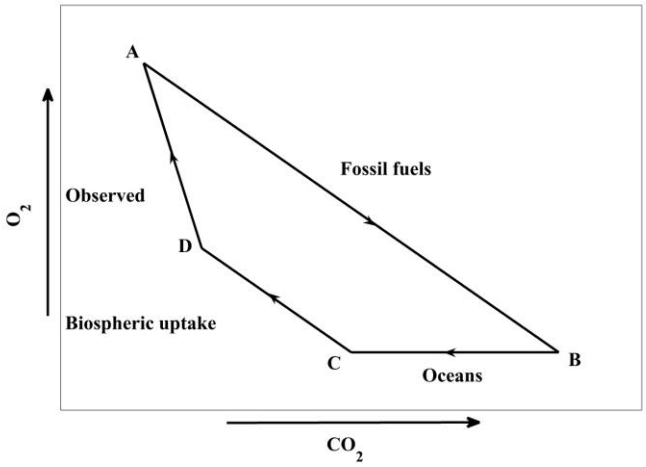


Fig.1. Schematic illustration of trends in CO_2 and O_2.

The data on CO_2 and O_2 adopted for this analysis together with information on the emissions of CO_2 from fossil fuel are described in Section 2. Results from a global balance model are presented in Section 3, which includes an account of the physical and chemical processes regulating uptake of CO_2 by the ocean. The model is applied on a hemispheric basis in Section 4. The analysis in Sections 3 and 4 is limited by the available O_2 data to the time interval 1995-2007. The time horizon is extended in Section 5 to cover the period 1840 to 2007 based in this case on consideration of what is known as the air borne fraction, the fraction of CO_2 emitted that persists in the atmosphere rather than being incorporated in the ocean. Summary concluding remarks are presented in Section 6.

2. Data sources for the study

Our objective here is to develop a record establishing the changes in the global average concentrations of CO_2 and O_2 that have arisen in the past. Observations of O_2 are available only for the period subsequent to 1995. Data from analyses of gases trapped in ice cores allow the record of CO_2 to be extended much further into the past. As indicated above, the time horizon selected for purposes of the studies described in Sections 3 and 4 is 1995-2007. The time horizon addressed in Section 5 extends back to 1840.

To calculate global and hemispheric average concentrations of CO_2 for the recent time period we selected observations from 11 stations covering a latitude domain extending from 82.3^0 N (Alert, NWT, Canada) to the South Pole. The observational CO_2 data used in the research is from Scripps Institute of Oceanography CO_2 program (http://scrippsco2.ucsd.edu/data/data.html). The choice of stations is summarized in Table 1. The stations are located in remote regions such that data from these stations are not expected to be impacted significantly by either local sources or sinks. Measurements from individual stations are assumed to be representative of conditions in the latitude zones in which the stations are located. Hemispheric and global averages were computed by weighting monthly averages of station data in proportion to the surface area of the Earth appropriate for the latitude zones to which the stations were assigned. Trends in global averages and hemispheric contrast computed in this fashion are presented in Figures 2a and 2b. Measurements of gases trapped in a series of three cores drilled at Law Dome in East Antarctica were used to extend the CO_2 record back to 1830. These data were selected in recognition of the fact that the Law Dome cores are characterized by a relatively high accumulation rates, low concentrations of impurities and regular stratigraphic layering unperturbed either by surface

winds or by ice flow at depth [5]. The ice core results, taken as representative of global average conditions, are displayed in Figure 3.

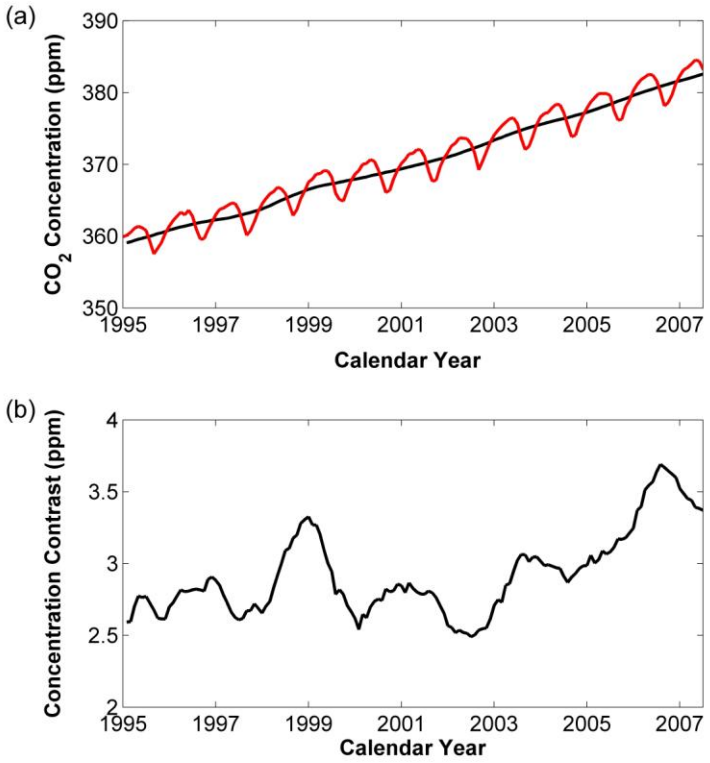


Fig.2. Panel a: Global atmospheric CO_2 concentration from 1995 to 2007, in ppm, derived by weighting monthly averages of station data in proportion to the surface area of the appropriate for the latitude zones to which the stations were assigned. The red line is with the seasonal cycle, the black line with the seasonal cycle removed. Panel b: Hemispheric CO_2 contrast (northern hemisphere CO_2 concentration minus southern hemisphere concentration) from 1995 to 2007, in ppm, reflecting the fact that fossil fuel combustion is largely concentrated in the northern hemisphere.

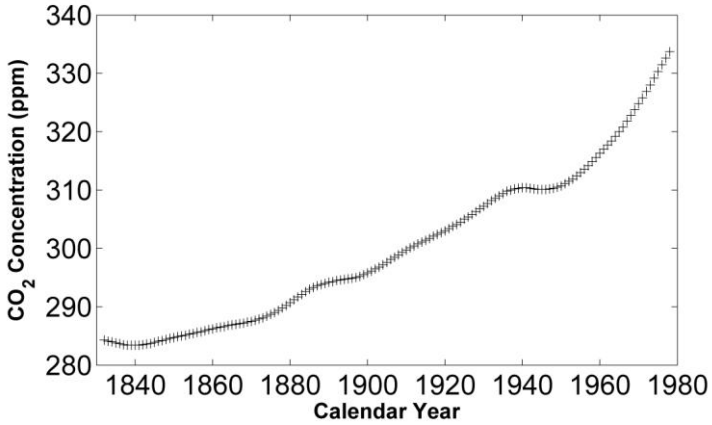


Fig.3. CO_2 mixing ratios from DE08 and DE08-2 ice cores records smoothed using a spline fit with a 20 year cutoff.

Table 1: Stations included in the global & hemispheric CO_2 averaging process

Station	Latitude (deg.)	Longitude (deg.)	Elevation (m)
Alert, NWT, Canada	82.3 ^{o}N	62.3 ^{o}W	210
Point Barrow, Alaska	71.3 ^{o}N	156.6 ^{o}W	11
La Jolla Pier, California	32.9 ^{o}N	117.3 ^{o}W	10
Baja California Sur, Mexico	23.3 ^{o}N	110.2 ^{o}W	4
Cape Kumukahi, Hawaii	19.5 ^{o}N	154.8 ^{o}W	3
Christmas Island	2.0 ^{o}N	157.3 ^{o}W	2
American Samoa	14.2 ^{o}S	170.6 ^{o}W	30
Kermadec Island	29.2 ^{o}S	177.9 ^{o}W	2
Baring Head, New Zealand	41.4 ^{o}S	174.9 ^{o}E	85
Palmer Station, Antarctica	64.9 ^{o}S	64.0 ^{o}W	10
South Pole	90.0 ^{o}S		2810

Changes in the abundance of O_2 are expressed in terms of changes in the ratio of the concentration of O_2 relative to N_2. Expressed using the δ notation, the fractional difference in the O_2 content of a sample relative to the concentration in a reference gas is given by

$$\delta\left(\frac{O_2}{N_2}\right) = \frac{\left(\frac{O_2}{N_2}\right)_{sample}}{\left(\frac{O_2}{N_2}\right)_{reference}} - 1 \qquad (2)$$

where $\delta (O_2/ N_2)$ denotes the ratio of the concentration of O_2 relative to N_2 in the sample and defines the ratio for the reference gas. Values of $\delta (O_2/ N_2)$ are quoted conventionally in units of per meg. One per meg equals 0.0001 percent. The observational CO_2 data used in this article are taken from the Scripps Institute of Oceanography O_2 program (http://scrippso2.ucsd.edu/osub2sub-data). The choice of stations is summarized in Table 2. The trend in global average $\delta (O_2/ N_2)$ was computed using the same procedure as was applied to compute the averages for CO_2 displayed in Figure 2, and is presented in Figure 4a. As indicated, the abundance of O_2 relative to N_2 decreased by approximately 250 per meg between 1995 and 2007. Over the same period, as illustrated in Figure 2a, the concentration of globally averaged CO_2 increased by 25 ppm. The contrast in O_2/ N_2 between the northern and southern hemisphere is illustrated in Figure 4b. As expected, the abundance of O_2 in the northern hemisphere is lower than that in the southern hemisphere, reflecting the fact that fossil fuel combustion is largely concentrated in the northern hemisphere.

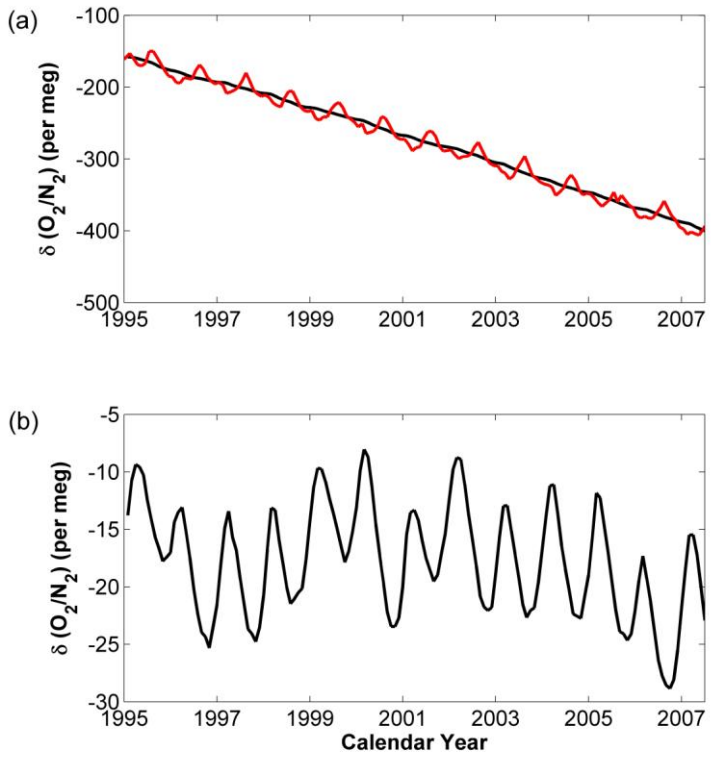


Fig.4. Panel a: Global atmospheric δ (O_2/ N_2) from 1995 to 2007, in per meg. The red line includes the seasonal cycle, the black line has the seasonal cycle removed. Panel b: Hemispheric O_2 contrast (northern hemisphere CO_2 concentration minus southern hemisphere concentration) from 1995 to 2007, in per meg, reflecting that fact that fossil fuel combustion is largely concentrated in the northern hemisphere.

Table 2: Stations included in the global & hemispheric O_2 averaging process

Station	**Latitude (deg.)**	**Longitude (deg.)**
Alert, NWT, Canada	82° N	62 °W
Cold Bay, Alaska	55° N	163 °W
Cape Kumukahi, Hawaii	20° N	155 °W
La Jolla Pier, California	33° N	117 °W
Mauna Loa Observatory, Hawaii	20° N	156 °W
American Samoa	14° S	170 °W
Cape Grim, Australia	41° N	150 °W
Palmer Station, Antarctica	65° S	64 °W
South Pole	90° S	

Trends in emissions of CO_2 associated with combustion of fossil fuels and production of cement are presented in Figure 5: for the period 1995 – 2009 in Figure 5a and for the longer record extending back to 1750 in Figure 5b. CO_2 emission data are available from *Carbon Dioxide Information Analysis Center* (CDIAC) (http://cdiac.ornl.gov/trends/emis/meth_reg.html). Data for the recent period were derived using procedures developed by Marland and Rotty (1984) [6] applied to energy statistics published by the United Nations (2010) [7] compiled on the basis of annual questionnaires distributed by the U.N. Statistical Office. Etemad et al (1991) [8] published a compilation of data on the production of coal, brown coal, peat and crude oil by nation and year back to 1751. Historical data on trade in fossil fuels were presented in a series of papers by Mitchell (1983, 1992, 1993, 1995) [9-12]. The results displayed in Figure 5b were computed using a combination of the data presented by Etemad et al (1991) [8] and Mitchell (1983, 1992, 1993, 1995) [9-12]. They indicate that approximately 350 billion tons of carbon have been released to the atmosphere from a combination of fossil fuel consumption and cement manufacture since 1751, amounting to half of the total since the mid 1970's.

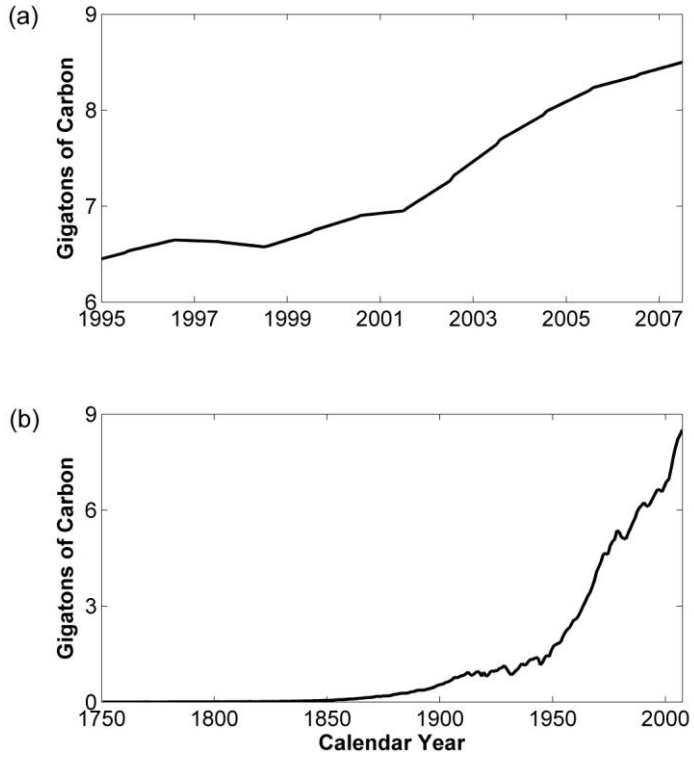


Fig.5. Carbon Dioxide Emissions from Fossil-Fuel Consumption and Cement Manufacture. One gigaton equals one billion metric tons. Panel a: period from 1995 to mid 2007. Panel b: period from 1750 to mid 2007.

3. Post-1995 global CO_2 budget

Given the mix and composition of the fossil fuels included in the contemporary global energy economy, it is estimated that 1.43 moles of O_2 are consumed for every mole of CO_2 released as a result of fuel combustion [13]. Uptake (release) of carbon by the biosphere is estimated to be responsible for a source (sink) of 1.1 mole of O_2 for every mole of CO_2 involved in the atmosphere/biosphere exchange process [14]. The larger value for the ratio of O_2 relative to CO_2 associated with fossil fuel combustion as compared to biospheric exchange reflects the influence of hydrogen rich components in the fuel mix. Combustion of CH_4 in natural gas for responsible for example for consumption of 2 moles of O_2 associated with production of every mole of CO_2.

The slopes of the fossil fuel and biospheric segments of the CO_2/O_2 trend curves discussed above are set by these considerations.

Results derived using the monthly averages of global concentrations for CO_2 and O_2 summarized in Figures 2 and 4 are presented in Figure 6. The data in Figure 6a indicate significant interannual variations in both ocean and biospheric uptake. A portion of this variability may be attributed to changes in the tropics associated for example with the ENSO phenomenon. A number of writers [15-18, 1] have pointed out that the reduction in upwelling in the tropical Pacific ocean during the warm (El Nino) phase serves to decrease what would normally be a source of CO_2 from the ocean in this region contributing therefore to a net increase in the overall global ocean sink for CO_2 (smaller source in the tropics, continuing sink at mid and higher latitudes implies a global increase in uptake). At the same time, there is evidence for a significant source of CO_2 from the biosphere in the tropics during the warm El Nino phase [19-21]. The region of intense rainfall shifts during this phase from the region near Indonesia to the middle of the Pacific. Subsequent drying out of vegetation in the previously moist region results in net release of CO_2, arising both as a consequence of natural processes but also, at least in some years, as the result of an increase in unsanctioned burning and clearance of land. A portion of the interannual variability may be attributed to the potential year-to-year changes in release and uptake of O_2 by the ocean discussed earlier [22-24]. Ralph Keeling notes that global warming may cause a decrease in the oceanic O_2 inventory with associated outgassing of O_2. The change in the oceanic inventory through the 1990s is estimated at $0.3 \pm 0.4\times10^{14}$ mol of O_2 per year [25]. The assumption of a source of O_2 from the ocean would result in an increase in the magnitude of

the sink attributed to the biosphere in the present analysis. Conversely, if the ocean represents a sink for O_2, the sink attributed to the biosphere would be reduced accordingly.

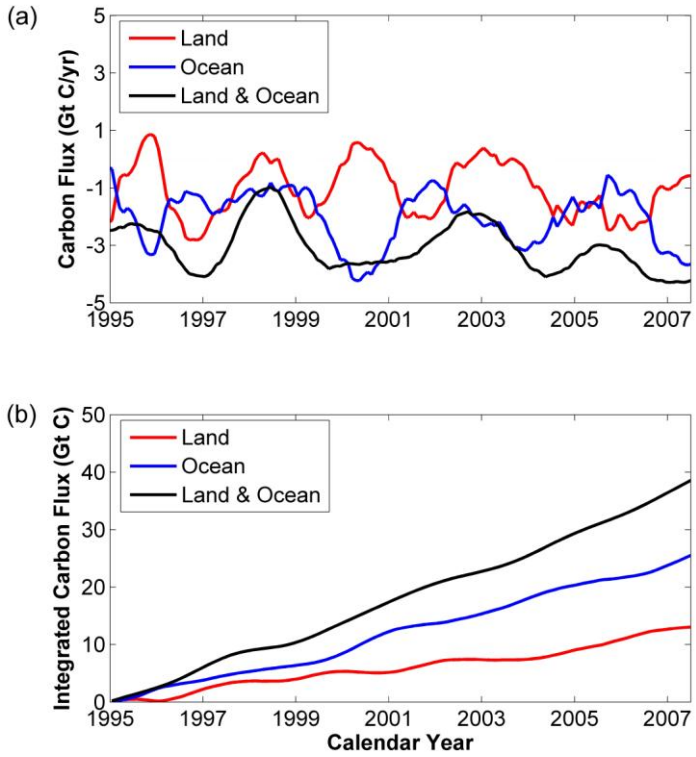


Fig.6. Terrestrial and oceanic carbon sink (or source) derived though analysis of global CO_2 concentrations and $\delta(O_2/N_2)$. Panel a: terrestrial and oceanic annual carbon flux, in GtC/yr. Negative sign means that the carbon goes into the terrestrial or ocean from the atmosphere. Panel b: integrated terrestrial and oceanic carbon flux over time since 1995, in GtC.

The ambiguities introduced by short period fluctuations in biospheric and ocean exchange can be reduced by averaging data over multiple years. Results inferred for the cumulative uptakes of CO_2 by the ocean and biosphere post 1995 are presented in Figure 6b. Net uptake of CO_2 by the ocean and biosphere between 1995 and mid 2007 amounted to 25.7 and 13.1 Gt C respectively. Over the same period, fossil fuels added 89.3 GtC to the atmosphere and the abundance in the atmosphere increased by 50.5 GtC. Defining the airborne fraction as the fraction of net carbon

added to the atmosphere that persists in the atmosphere, these results imply an airborne fraction of 56.5% . An alternate definition of the airborne fraction concept focuses exclusively on the fate of the fossil fuel source. The present results would imply that the increase in the abundance of CO_2 In the atmosphere between 1995 and 2007 was equivalent to 66.3 % of the fossil fuel source.

Uptake of CO_2 by the ocean is determined by the difference between the partial pressures of CO_2 in the air and in surface waters of the ocean. The abundance of CO_2 in the ocean is regulated by an equilibrium among the three primary forms of inorganic carbon dissolved in sea water, HCO_3^- , CO_3^{2-} and CO_2. Uptake of CO_2 may be described by the net reaction

$$CO_2 + CO_3^{2-} \overset{H_2O}{\Leftrightarrow} 2HCO_3^- \qquad (3)$$

It follows that transfer of CO_2 from the atmosphere to the ocean is limited ultimately by the supply of CO_3^{2-} to the surface waters that are exposed to the atmosphere. A comprehensive discussion of ocean chemistry is presented in Broecker and Peng (1982) [26]. Following some algebraic manipulation, that the airborne fraction may be defined in terms of the partial pressure of CO_2 $(P_{CO_2})_0$ in the atmosphere prior to disturbance (the pre-industrial reference), the value for the contemporary partial pressure of CO_2 P_{CO_2}, the initial abundance of carbonate ion $[CO_3^{2-}]_0$ in upper-level ocean waters, the total abundance of CO_2 in the atmosphere prior to disturbance M_0, and the volume of ocean water V that has been in contact with the atmosphere over the intervening interval of time:

$$f_{atms} = [1 + \frac{(P_{CO_2})_0}{P_{CO_2}} [CO_3^{2-}]_0 \frac{V}{M_0}]^{-1} \qquad (4)$$

Assuming a value of 280 ppm for the initial concentration of atmospheric CO_2 corresponding to a value of 5×10^{16} moles for M_0, with the concentration of $(CO_3^{2-})_0$ taken equal to 200×10^{-6} mol l^{-1}, it follows that if 10% of the ocean water had been exposed to the atmosphere over time since the industrial revolution (a reasonable assumption), the airborne fraction at the present time (P_{CO_2} = 390 ppm) would be equal to about 70%. The estimate quoted above for the airborne fraction appropriate for the 1995-2007 time interval, accounting both for the fossil fuel source and the biospheric sink, 66.3%, is consistent with an assumption that 12.8 % of ocean water has been exposed to the atmosphere over the modern era. The airborne fraction is predicted to increase with time as sources of CO_3^{2-} available to neutralize CO_2 are depleted, a projection supported by analyses of the contemporary CO_2 budget [27]. Using a tracer technique proposed initially by Gruber et al (1996)[28], Sabine et al (2004)[29] concluded that uptake by the ocean accounted for approximately 48% of the carbon added to the atmosphere as a result of fossil fuel combustion and cement manufacture over the period 1800 and 1994. This would imply an airborne fraction for the fossil fuel/cement source of 52% in reasonable agreement with expectation based on (4): the actual value for the airborne fraction should be adjusted to account for the cumulative contribution associated with exchange of carbon between the atmosphere and biosphere. The tracer technique suggests that the North Atlantic (representing only 15% of the total surface area of the ocean) accounts for 23% of the anthropogenic carbon incorporated in the ocean. More than 40% of the total sink is identified with regions of the ocean between 30^o S and 50^o S. Approximately 60% of the total is incorporated in oceans of the Southern Hemisphere, in rough proportion to the surface area of the oceans in this hemisphere [29].

4. Hemispheric Budgets

Exchange of air within hemispheres (north and south) proceeds significantly more rapidly than transfer between the hemispheres. This provides an important opportunity to exploit hemispheric average observations of the concentrations of CO_2 and O_2 to develop hemispheric budgets for CO_2. SF_6 is widely deployed as an electrical insulator in the modern world. The concentration of the gas in the atmosphere has increased by two orders of magnitude since 1970 [30]. Its source is largely confined to the northern hemisphere and the extended lifetime of the gas in the atmosphere, estimated at as much as 3200 years [31], establishes it as an ideal tracer for calibration of rates for interhemispheric exchange[32,33].

The rate of change of the average concentrations for SF_6 in the northern and southern hemispheres may be described by the following equations:

$$dC_{SH}(t)/dt = (C_{NH}(t) - C_{SH}(t))/\tau_{ex} \qquad (5)$$

$$dC_{NH}(t)/dt = S(t) - (C_{NH}(t) - C_{SH}(t))/\tau_{ex}$$

where $C_{SH}(t)$ and $C_{NH}(t)$ denote the abundances of the gas in the northern and southern hemispheres respectively, τ_{ex} defines the rate at which air is exchanged between the hemispheres (assumed to be proportional to the difference in hemispheric concentrations) , and S denotes the magnitude of the source (assumed to be confined to the northern hemisphere). Extensive measurements of atmospheric SF_6 are available since 1995 from the Halocarbon and other Atmospheric Trace Species (HATS) program at NOAA. Measurements from flask samples began in 1995, focusing initially on 8 stations, extended later to include sampling from 12 remote locations. Data from the flask program have been complemented more recently with in situ measurements from gas chromatographic instrumentation installed at six field stations. The gas chromatographic measurements provide an hourly record of changes in the concentrations of

SF_6 at these stations. Hemispheric average concentrations of SF_6 were computed on the basis of the NOAA measurements following the procedures described earlier to calculate hemispheric average concentrations for CO2 and O2. Data for this analysis were taken from the Earth System Research Laboratory compilation (http://www.esrl.noaa.gov/gmd/hats/combined/SF6.html). Details of the data source are described in ref.34 and 35. Using trends in $C_{NH}(t)$ and $C_{SH}(t)$ derived from the observational data, equation (5) can be employed to calculate temporal variations both in S and in τ_{ex}. Observed changes in the average north-south concentration contrasts, together with results inferred for the changes in S and τ_{ex} with time, are presented in Figure 7. Over the period from 1995 to mid 2007, the average global annual source of SF_6 is estimated at 5.81 Gg, and the average exchange time is equal to 1.2 yr.

Hemispheric budgets for CO_2 computed using results for τ_{ex} derived from the SF_6 analysis are displayed for the northern and southern hemispheres in Figures 8 and 9 respectively. Trends in biospheric and ocean uptake as a function of time are summarized in Figures 8a and 9a with results for cumulative uptake displayed in Figures 8b and 9b. The results presented here indicate significant contributions from both the biosphere and ocean to the net sink for CO_2 in the northern hemisphere. Uptake by the ocean is important in both hemispheres with the contribution from the southern hemisphere exceeding that from the northern hemisphere by about 50% (a cumulative total of 15 Gt C in the former case as compared to 9 Gt C in the latter). The inference that the sink associated with the biosphere is located primarily in the northern hemisphere is consistent with conclusions reached earlier by Keeling et al (1996) [36] and by Fan et al (1998) [37]. Fan et al (1998) [37] suggested that removal of atmospheric CO_2 by the

biosphere was concentrated mainly in mid-latitude regions of Eurasia and North America, averaging approximately 2 Gt C yr^{-1} between 1981 and 1987 with a somewhat higher rate inferred for removal between 1988 and 1992.

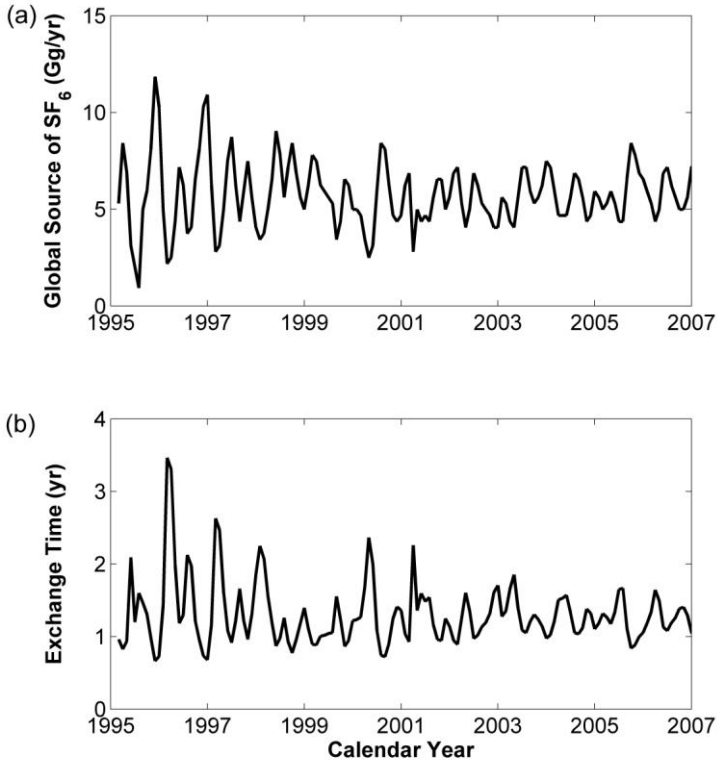


Fig.7. Panel a: Global source of SF_6 calculated using equation (5); Panel b. exchange time calculated with equation (5), assuming that SF_6 is well mixed within each hemisphere.

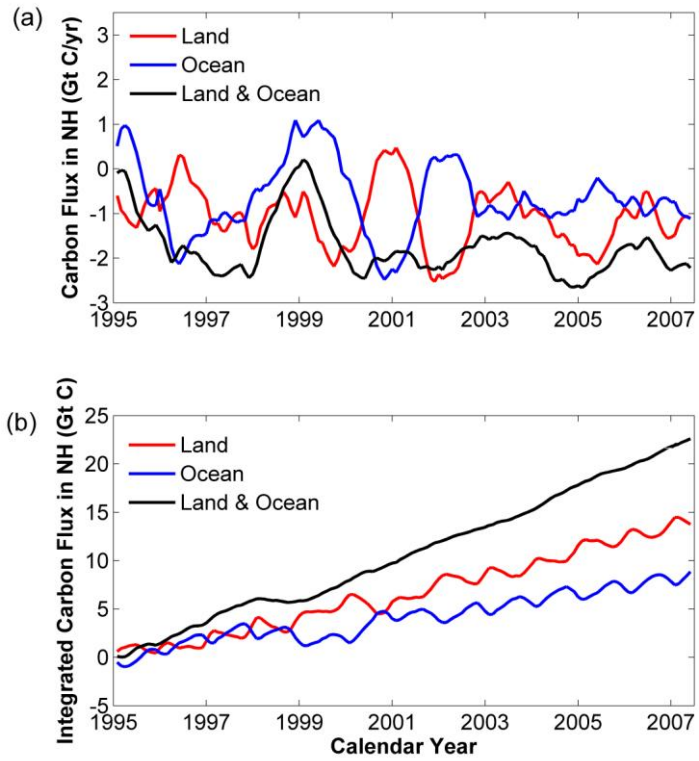


Fig.8. Same as Fig.5, but for the northern hemisphere.

The results in Figure 8b imply an average rate for removal by the northern hemispheric biosphere as a whole of about 1.3 Gt C yr^{-1}. It is possible that the composite sink inferred here could reflect the combination of a mid-latitude sink offset to some extent by a source at higher latitudes. A study of the carbon balance of a mature black spruce forest in Central Canada by Goulden et al (1998) [38] indicated a small though significant net source of CO_2 from soils in this ecosystem over the period 1994-1996. Soils at high latitude represent an important reservoir for organic carbon, estimated to include as much as 500 Gt C [39]. Release of carbon from this environment triggered by regional warming could be responsible for a significant present, and potentially even more important future, source not only of CO_2 but also of CH_4 [40,41].

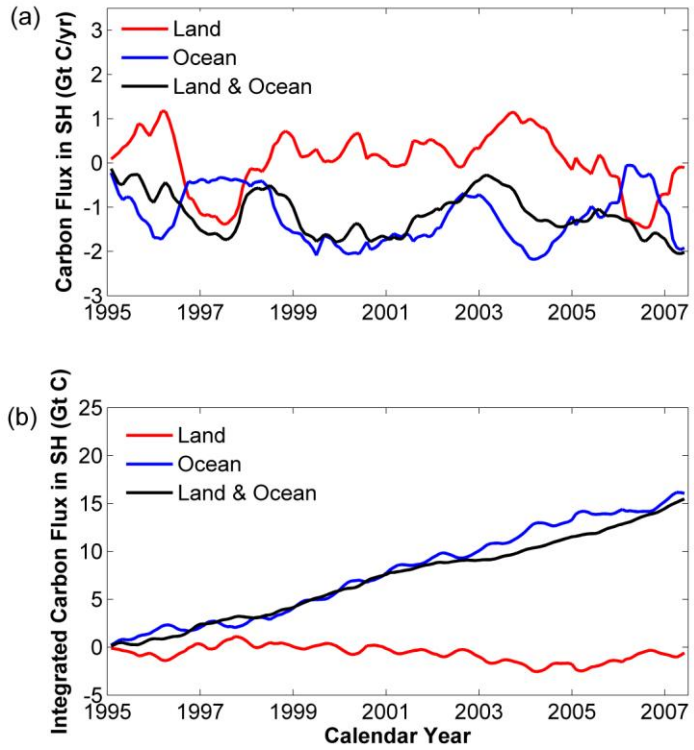


Fig.9. Same as Fig .5, but for the southern hemisphere.

5. Longer term trends

Keeling et al (1995) [42] presented an analysis of the CO_2 record from1958 to 1995 in which the data were interpreted initially in terms of a constant airborne fraction of 55.9% with an assumption that fossil fuel combustion and cement manufacture were responsible for the dominant source of CO_2. This simple procedure resulted in a remarkably accurate representation of the data record over the entire time interval. They proceeded to focus on an interpretation of the departures of the data from the reference fit, attributing these anomalies primarily to fluctuations in the rate of exchange of carbon between the atmosphere and biosphere. A similar approach is adopted here to a study of the longer-term record of CO_2 dating back to 1830.

Table 3: A summary of prior analyses of the historical CO_2 budget

	1800 to 1994	1850 to 2000
Emission from fossil fuels and cement production	244 ± 20 Gt C [a]	275 Gt C [c]
Atmospheric increase	165 ± 4 Gt C [a]	175 Gt C [d]
Oceanic uptake	118 ± 19 Gt C [a]	140 Gt C [e]
Net terrestrial source	-39 ± 28 Gt C [a]	-40 Gt C
Land-use change (source)	-174 Gt C [b]	-156 Gt C [b]
Residual terrestrial sink	135 Gt C	116 Gt C
Air-Borne Fraction	0.583	0.556

a: ref. 29
b: ref. 43
c: ref.44 and 45
d: ref.46
e: ref.47

A summary of prior analyses of the historical CO_2 budget is presented in Table 3. Separate entries in the Table refer to the time periods 1800-1994 and 1850-2000. The data for 1800-1994 imply an overall value for the average airborne fraction of 0.583, with 0.556 for the interval 1850-2000. As indicated earlier, we expect the value of the airborne fraction to decrease with time as the supply of CO_3^{2-} to surface waters is depleted. Our analysis of the budget from 1995 to 2007 indicated an airborne fraction of 0.663. Given the inevitable uncertainty in the appropriate value for the airborne fraction and the expectation that it may have varied significantly over time, we elect for present purposes to consider a range of values, from a low of 0.56 to a high of 0.66.

Following Keeling et al (1995) [42], we assume that the dominant contributions to the rise in CO_2 over the past century and a half can be attributed to the combination of fossil fuel combustion and cement manufacture. With this assumption, the historical record for CO_2 is fitted adopting a constant value for the airborne fraction, either 0.56 or 0.66. Departures from the fits

are interpreted as indications of the contributions to the observed trend attributable to exchange with the biosphere. Results are presented in Figure 10. The analysis suggests that the biosphere was responsible for a net source of CO_2 from 1840 to about 1940. This conclusion appears to be relatively independent of the choice of airborne fraction. Assuming an airborne fraction of 0.56, the biospheric source, integrated from 1840 to 1940 is estimated at about 55 Gt C corresponding to an annual source of about 0.55 Gt yr^{-1}. The rise in CO_2 is dominated by the fossil fuel – cement source only for the period subsequent to about 1900. After 1940, the biosphere switches from a net source to a net sink. The imputed biospheric source, as would be expected, is slightly less if we assume a larger value for the airborne fraction. With an airborne fraction of 0.66, the transition from biosphere dominated source to fossil fuel-cement dominated source also occurs in about 1900. The integrated biospheric source from 1840 to 1940 is estimated at 44 Gt C.

6. Concluding remarks

The contemporary increase in the concentration of CO_2 in the atmosphere is due mainly to emissions associated with combustion of fossil fuels. Since 1995, approximately 57% of the carbon released as a result of the fossil fuel source has persisted in the atmosphere, 29% has been transferred to the ocean, and the balance, 15%, has been absorbed by the biosphere. It is clearly important to define the nature of the biospheric sink and indeed its location. Evidence suggests that it is concentrated primarily at mid-latitudes of the northern hemisphere. Possible explanations include a climate induced extension of the growing season, enhanced uptake by photosynthesis prompted by the increasing level of CO_2 in the atmosphere, and, potentially, regrowth of vegetation representing return to conditions prevalent prior to the mid 20^{th} century when the biosphere is estimated to have provided a net source rather than a net sink for CO_2

(regrowth of forests depleted previously in conjunction with conversion of land for purposes of agriculture). Compounding the challenge is the likelihood that soils at high latitude may be responsible for a net source of CO_2 and that there may be additional release associated with deforestation in the tropics (in countries such as Brazil and Indonesia), the latter representing a repeat of what happened earlier in the mid-latitude regime. Natural forests are important as a source of environmental services. The sad fact is that eliminating these systems and converting them to either pasture or agriculture can provide a more immediate return to those who own or control the land. Current economic accounting fails regrettably to recognize the intrinsic value of the environmental services provided by these natural ecosystems.

If we are to avoid unacceptable future disruption to the global climate system, it will be necessary to constrain future growth in the concentration of the key greenhouse gases, not only CO_2 but also CH_4 and N_2O. Reduction in emissions of CO_2 from fossil fuels can make an important contribution to this objective but will require a major shift from the current fossil fuel dominated energy economy to one emphasizing low or zero carbon energy alternatives. It will be critical also in meeting our objective to preserve a supportive global climate system to develop an improved understanding of the complex functions of the global biosphere, its role not only in regulating the concentrations of the key greenhouse gases in the atmosphere but also the contribution it makes to maintaining an accommodating hydrological cycle. We have learned a great deal about the function of the carbon cycle over the past 50 years, due in no small measure to the contributions of Charles David and Ralph Keeling and their colleagues. The present paper is offered as a status report on where we are: it is clear though that there is more work to be done.

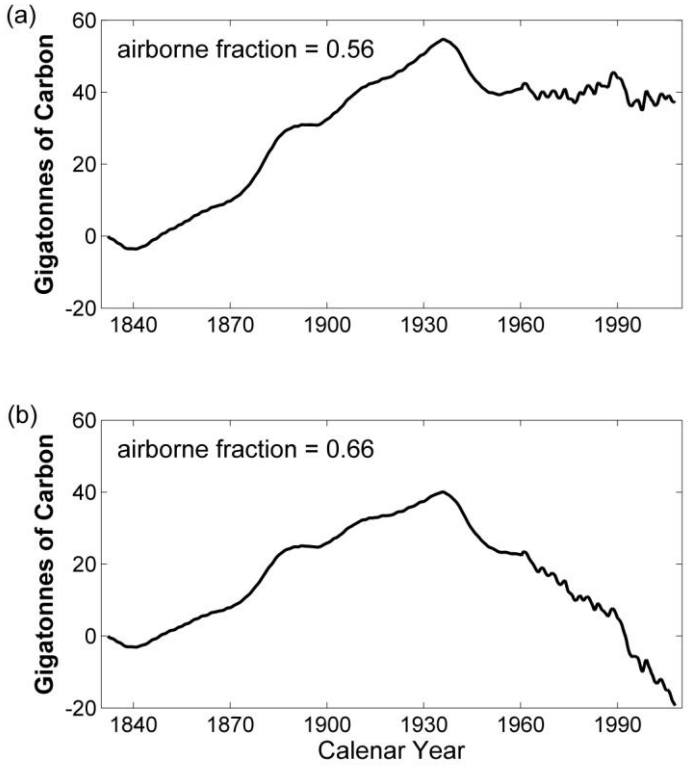


Fig.10. Cumulative terrestrial carbon fluxes: panel a. assumes an airborne fraction of 0.56; panel b. airborne fraction equal to 0.66.

Acknowledgements

As indicated at the outset, this paper is dedicated to the memory of Donald M Hunten. The work described here was supported by the National Science Foundation under grant ATM-1019134 to Harvard University.

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