Simple Equation of Multi-Decadal Atmospheric Carbon Concentration Change

Ari Halperin
defyccc.com
Texas, USA
ah@defyccc.com

ABSTRACT

Surplus CO2 is removed from the atmosphere by natural sinks at rate, proportional to the surplus CO2 concentration. In other words, it undergoes exponential decay with a single decay constant. This conclusion is rigorously proven, using first principles and relatively recent observations of oceans. Historical data for CO_2 concentrations and emissions from 1958–2013 are then used to calculate the half-life of the surplus concentration. This theoretically derived formula is found to be an excellent match to the historical CO_2 concentrations over the measurement period. Furthermore, the "initial" CO_2 concentration in the formula came out to be very close to the likely "pre-industrial" CO_2 concentration. Based on the used datasets, the half-life of the surplus concentration of CO_2 in the atmosphere is found to be approximately 40 years.

Cite as:

SUMMARY

The aim of this paper is to derive a formula describing the natural change of surplus CO_2 concentration created by CO_2 release from human activity. On the multi-decadal scale, there are two important sinks: oceans and land. The ocean sink can be divided into the marine biota sink and the ocean proper. The land carbon reservoir consists of plants and soil, which are considered together. Thus, the paper addresses three sinks, in this order of significance: deep ocean water (>50% of total), land biomass, and marine biota.

The Deep Ocean Sink

Surplus atmospheric CO_2 quickly penetrates the top ocean layer (50–100 m) through wave action, air entrapment, turbulent mixing of water, and diffusion. Vertical transfer of inorganic carbon to deeper layers happens mostly through vertical currents – downwelling. In the areas with denser surface water the surface water sinks, taking excess inorganic carbon with it. The surface water is denser mostly where it is cold (higher latitudes, especially the North Atlantic), but also where it has higher salinity (some areas of the Indian Ocean). Deep water rises at low latitudes (near the equator), bringing back inorganic carbon at concentration that was in the deep water ~500 years ago. The operation of this mechanism is well understood, and can be clearly seen in [*Sabine et al.*, 2004]. For example, Sabine's Fig. 2a (the Atlantic ocean) shows a concentration of anthropogenic CO_2 of nearly 30 µmol/kg at a depth of 2,000 m at 65°N. This is half of the concentration at the surface. At the same time, the concentration is less than 5 µmol/kg at merely 1,200 m, near the equator. The surface concentration is the same 60 µmol/kg everywhere. Graphs in Fig. 2b and 2c show similar effects for other oceans, clearly demonstrating the vertical transfer of CO_2 by downwelling, rather than by some other mechanism. (To avoid ambiguity, this is the only place this paper distinguishes between anthropogenic and non-anthropogenic CO_2).

In terms of CO_2, the top ocean layer behaves more like the atmosphere than like the rest of the ocean: a) CO_2 emissions spread vertically through the top ocean layer in a matter of months, comparable to the span when they spread horizontally in the atmosphere, and b) almost all marine photosynthesis occurs in the top ocean layer, just like land photosynthesis occurs in the atmosphere.

Thus, this paper introduces the notion of an ***extended atmosphere***, which includes the real atmosphere and the top ocean layer. The effective capacity of the top ocean layer to contain surplus carbon is

computed in the paper to be ~10% of the real atmosphere's capacity, so the results do not require accurate determination of the depth of the top ocean layer. Carbon exchange between the extended atmosphere and the deep ocean through vertical currents is described by equation (6).

The Land Biomass Sink

An increase in atmospheric CO_2 leads to an increase in the Net Primary Production (NPP) by land plants, which removes carbon from the atmosphere. Some NPP increase is offset by increased decomposition. Most of the produced biomass either dies and decomposes within one to two years (annual plants and leaves), or becomes wood and does not decompose for hundreds or even thousands of years. The ratio is different for each ecosystem, but assumed to be independent from the atmospheric CO_2 concentration. Thus, the land biomass sink is described by equation (11).

The Marine Biota Sink

The mechanisms that make marine biota a carbon sink are different from those for land biomasses, and are less well understood. Due to the Revelle factor, changes in the CO_2 concentration in the surface water are ~10 times smaller than corresponding changes in the air (e.g., a 100% increase of CO_2 concentration in the air results in a 10% CO_2 concentration increase in the water). Marine biota is also a relatively small sink. The author assumes that its individual carbon sink rate can be expressed as a differentiable function of surplus atmospheric CO_2, and applying Taylor's series theorem, describes it with a linear function in equation (12).

Solution and Results

Adding up all the sinks and separating the members that sum up to the hypothetical "pre-industrial equilibrium" yields the main result of the paper: the surplus concentration of CO_2 in the atmosphere is subject to exponential decay, in absence of additional anthropogenic CO_2 release (formula (15)). Most quantities and coefficients introduced before formula (15) are either eliminated or folded into the rate coefficient λ. The "equilibrium" and the rate coefficient λ are for the sum of all sinks. No result is obtained for individual sinks. No data for actual CO_2 release or concentration changes was used in derivation of (15). Formula (16) is a corollary of (15), taking into account anthropogenic CO_2 release.

Validation by Data

Sections 3 – 6.1 validate the derived formulas (15) and (16) against historical data for CO_2 concentrations (the Keeling curve) and anthropogenic CO_2 release, and calculate the rate coefficient λ. The calculated rate coefficient corresponds to an excess CO_2 half-life of ~40 years, and the excellent match between the theoretical results and the data fully validate the theoretical result. The paper calculates residuals and shows them in a graph, but does not attempt residuals analysis. The reason is that the emissions datasets might have error distributions that are unusual for natural sciences. Parameter D_0 can be interpreted, with caution, as a not very accurate estimate of the "pre-industrial" CO_2 concentration in atmosphere. D_0 is slightly outside of the range of concentrations, for which the formula was derived (315 – 560 ppm), and is quite sensitive to errors in the data. Nevertheless, its proximity to the proxy data provides additional satisfaction.

Table of Contents

1. Introduction [1, 2]

As this paper is intended for a broad range of readers, it is worth noting that carbon dioxide (CO_2) in the atmosphere is sometimes discussed in terms of carbon. Concentration values in ppm (mole fraction) are the same for both, but the mass of CO_2 equals the mass of carbon multiplied by 3.67. This paper uses the mass of carbon, usually expressed in GtC, and it derives and validates a formula for the sink rate of the surplus carbon concentration in the atmosphere. This should be distinguished from the CO_2 residence time in the atmosphere. Residence time is usually defined as an average time that a molecule spends in a system. The residence time of a CO_2 molecule in the atmosphere is about 5 years, but most CO_2 molecules removed from the atmosphere by ocean or land biota are replaced by other CO_2 molecules entering from those "reservoirs." The CO_2 residence time is of little interest, except as an indication of the fact that there is a dynamic exchange of carbon between the atmosphere and other "reservoirs." Human activities release CO_2 into the atmosphere, creating a surplus carbon concentration. The important subject is how the surplus carbon concentration in the atmosphere changes over time.

It was observed that the CO_2 concentration in the atmosphere were growing nearly exponentially since the beginning of measurements in 1957 through early 1980's. Further, some papers, such as [*Bacastow and Bjorkstrom*, 1981] used an exponential function to approximate the growth of an anthropogenic CO_2 release. As the integral of an exponent is an exponent, the cumulative release was proportional to the annual release in that model, and the physically meaningless concept of the airborne fraction (AF) of

---

released CO_2 became popular. Later, a very different Bern model [*UNFCCC and IPCC*, 1995] was introduced for purely political reasons; therefore, it is not discussed here.

A significant portion of published research attempts to study unrealistically large pulses of CO_2 over periods of hundreds or thousands of years using computer models. For example, [*Archer*, 2005] models a range of pulses from 300 GtC to 5,000 GtC on timescales expressed in kilo-years, while [*Archer et al.*, 2009] models pulses of 1,000 GtC and 5,000 GtC over hundreds of years. Results of such modelling, even if correct, are not applicable to the real world on timescales of a century or less. Current anthropogenic release is 10 GtC/year and we have less than 60 years of reliable measurements of atmospheric carbon content.

[*Raupach et al.*, 2014] (R2014) notes that the CO_2 sink rate and sink rate coefficient are more useful quantities than AF. Unfortunately, R2014 relies on incorrect estimates of land use change emissions (cited as Le Quéré et al. 2013 in R2014), which include historical data revision, based on dubious "methodological improvements" from 2010 Forest Resources Assessment by UN Food and Agriculture Organization. This error, aggravated by incorrect application of statistical methods (Appendix C3 in R2014), causes it to make an unfounded conclusion that the sink rate coefficient has been decreasing since 1959.

A number of works showing the exponential natural decrease in the surplus CO_2 concentration has been published recently. [*Jacobson*, 2005] includes it as a correction to another paper. [*Andrews*, 2013] makes a simple time fit, but falls to the confusion between residence time and surplus concentration time, while [*Docmartyn*, 2010] makes the same point, but less rigorously.

The following web pages provide concise (not necessarily fully accurate) background information on carbon cycle processes: [*Bralower and Bice*, 2014a], [*Bralower and Bice*, 2014b], [*Gordon*, 2004]. In addition, a historical paper [*Carbon Dioxide Assessment Commtee et al.*, 1983] remains relevant.

2. Physical Effects

In the absence of an anthropogenic impact, a number of natural processes influence the carbon content of the atmosphere. It is assumed here there is a natural multi-centennial equilibrium atmospheric CO_2 concentration, at which natural emissions and sinks compensate for each other (when averaged over a few years), this equilibrium concentration is considered constant and is denoted D_0. No assumption is made about this value. On the multi-decadal scale, the most important processes are carbon exchange with land and marine biota and carbon exchange with the oceans. The water–air interface is not an obstacle for CO_2 molecules, where the CO_2 diffusion rate in water is much lower than in air, but active mixing by waves and turbulence carries CO_2 (in all chemical forms) far away. In a well-mixed vessel, the partial pressure of CO_2 would be the same in water as in air. Most CO_2 chemically reacts with water, producing HCO_3^-, which does not participate in partial pressure. Measurements of CO_2 in the oceans are frequently performed at a depth of 5–8 meters, and this shows a partial pressure difference. This difference is usually small and tracks the air CO_2 concentration [*Calleja et al.*, 2013]; [*CDIAC, Oak Ridge National Laboratory*, 2011]; [*Takahashi et al.*, 2009]. Mixing rates gradually decrease with depth. Thus, it makes physical sense to consider an ocean surface layer a part of the "extended atmosphere," rather than a part of the ocean. The surplus partial pressure of CO_2 is quickly (within months) equalized throughout the whole extended atmosphere globally. The average depth of this surface layer should be somewhere around 50–100 meters, and it can vary between geographic locations. Almost all primary production by marine biota happens within this surface layer. This observation leads to considering three large CO_2 sinks in direct contact with the extended atmosphere— land, marine biota, and deep ocean—as shown in Fig. 1.
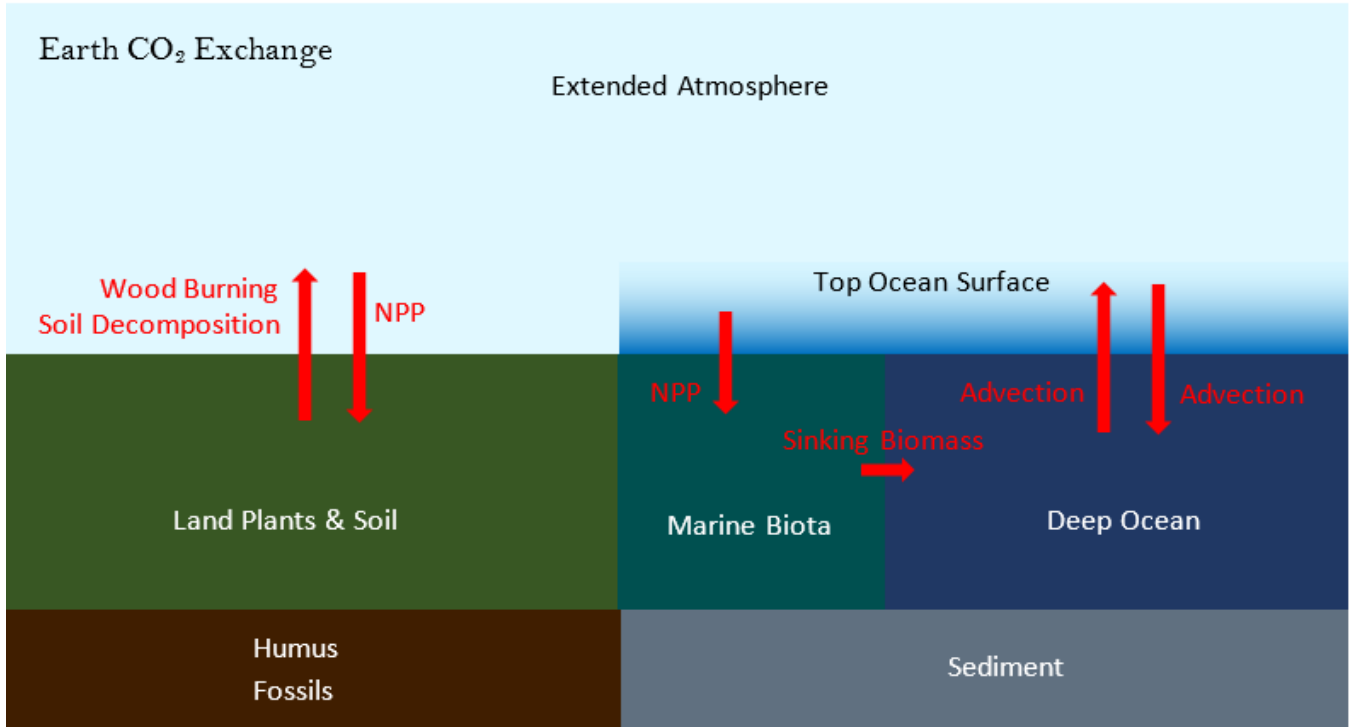
Fig. 1. Major carbon "reservoirs" and exchanges relevant on a multi-decadal timescale. The top ocean surface layer is shown as a part of the extended atmosphere.

Figure 1 shows major natural carbon exchanges. Plants and marine biota convert atmospheric CO_2 into biomass at the rate, exceeding plants respiration (Net Primary Production, or NPP). The decomposition of land biomass and soil returns CO_2 into the atmosphere. Some marine biomass sinks into the deep ocean, where upwelling moves CO_2-rich waters of the deep ocean up into the extended atmosphere, mostly in the equatorial areas, while downwelling moves CO_2-poor waters from the extended atmosphere into the deep ocean, mostly in the polar areas. The effects of diffusion and turbulent mixing with the deep ocean are neglected based on the definition of the extended atmosphere here. The conversion of land soil into humus, fossilization, and ocean sedimentation are ignored as slow processes.

The most convenient quantity for understanding CO_2 sinking processes is the surplus carbon concentration in the air C. The surplus carbon concentration in the surface layer is proportional, as $k_{wa}C$.

k_{wa} is proportional to Revelle factor, which depends strongly on water temperature, but weakly on alkalinity, for the atmospheric carbon concentration of the interest to this paper: 315 to 560 ppm. The current (July 2015) concentration is 403 ppm. More accurately, Revelle factor changes only between -8% and +14% at the extremes of the range of interest, based on [*Zeebe and Wolf-Gladrow*, 2001, p.73], so this dependency is disregarded. Consequently k_{wa} also becomes constant from C.

Total air carbon concentration D and surplus carbon concentration are related as follows:

$$D = D_0 + C \tag{1}$$

The total mass M of carbon in the extended atmosphere is comprised of carbon in the air and carbon in the surface layer. This paper is concerned only with differences in this amount, which can be described as follows:

$$\Delta M = \Delta M_{air} + \Delta M_{surface} \tag{2}$$

, which is for a given C

$$\Delta M = k_{apM}C + k_{lin}hC \tag{3}$$

where k_{apM} is a conversion coefficient from ppm to atmospheric GtC, h is the average depth of the surface layer, and k_{lin} indicates an increase in the mass of the carbon per meter of the surface layer per ppm of the surplus carbon concentration in the air (GtC/ppm/m).

$$k_{lin} = k_{H,pc}RAk_{cp}m_m$$

where $k_{H,pc}$ is simply the Henry coefficient, A is a small ocean area, R is the Revelle factor in this area, k_{cp} is the conversion coefficient from concentration to pressure, and m_m is the molar mass of carbon. Equation (3) can be re-written as follows:

$$\Delta M = k_{apM}(1 + k_{ext})C \tag{4}$$

where $k_{ext} = \frac{k_{lin}}{k_{apM}}h$ can be called the virtual atmosphere extension increment. R and $k_{H,pc}$ depend on temperature, so an average surface layer temperature of is used, yielding $k_{lin} = 0.0028 \, GtC/ppm/m$. From [O'Hara, 1990] $k_{apM} = 2.13 \, GtC/ppm$, selecting $h = 75m$ gives $k_{ext} = 0.1$.

The sink rate is defined here as the first derivative of C: $C' = D'$ and is proportional to M'. Sinking carbon amounts are negative. The movement of carbon between the atmosphere and the three sinks is:

$$M' = M'_{land} + M'_{mbe} + M'_{ocean} \tag{5}$$

where M_{mbe} is for the marine biota net exchange with the deep ocean. The rest of this section is devoted to the derivation of simple formulas (15) and (16), which eliminate most parameters in (6)–(14).

Vertical ocean advection moves carbon by the simple mechanical motion of carbon-containing waters. The displaced surface water moves laterally within the extended atmosphere. The total exchange with the deep ocean can be described as follows:

$$M'_{ocean} = L_{up} - \int_{AOD} c_x v(s)(D_{surface,0} + k_{wa}(s)C)ds \tag{6}$$

The surface integral is taken over the total ocean downwelling area (AOD). c_x is a constant conversion coefficient, $D_{surface,0}$ is the carbon concentration in the surface layer corresponding to D_0 in the air (at equilibrium), L_{up} is the amount of carbon arriving from the global upwelling area per unit of time, and $v(s)$ is the vertical advection speed in each location s. L_{up} is constant on a multi-decadal scale because the ocean water circulation takes about 500 years.

Land Net Primary Production dependence on air CO_2 concentration may be considered linearly dependent on surplus CO_2 [Kohlmaier, Siré et al. 1989]:

$$p(D) = p(D_1)\left(1 + \beta \frac{D - D_1}{D_1}\right) \tag{7}$$

Here, NPP is a mass of carbon acquired from the atmosphere. D_1 is an historical value of the carbon concentration slightly below 315 ppm, average $\beta \approx 0.29$, but differs significantly between plants and ecosystems. Lately, a hypothesis of logarithmic dependence was introduced:

$$p(D) = p(D_1)(1 + \beta_2 \ln \frac{D}{D_1}) \tag{8}$$

Even in the case of logarithmic dependence, given a narrow range of interest for D (315 – 560 ppm), it can be well approximated by a linear function. Some of this production happens in annual plants or in the leaves and toher short living parts of perennial plants. Per [*Bothwell et al.*, 2014], these parts of biomass typically die and decompose within a couple of years from production, returning carbon to the atmosphere, so their contribution can be eliminated. Only long-living woody parts of perennial trees store carbon for a long time. The growth of these parts can be assumed proportional to the growth of the whole:

$$p_{ti} = \gamma p \tag{9}$$

where the coefficient of proportionality γ can be around 0.7 for forests [*Gough*, 2011], but varies widely for different ecosystems. Nevertheless, the formula for true incremental primary production for each land area can be written as:

$$p_{ti}(D) = p_{ti}(D_0)(1 + \beta \frac{C}{D_0}) \tag{10}$$

A complementary quantity is multi-year decomposition L_{myd}. p_{ti} does not include primary production of short living biomass, L_{myd} does not include its decomposition. Trees can live for hundreds of years, then decompose for hundreds more, so an increased primary production does not cause significant increase in L_{myd} on multi-decadal scale. Integrating (10) over the whole land surface yields the following equation:

$$M'_{land} = L_{myd} - \int_{AL} p_{ti}(D_0, s)(1 + \beta(s)\frac{C}{D_0})ds \tag{11}$$

The surface integral is taken over the total land area (AL). Phytoplankton produces biomass from CO_2 by photosynthesis, just as land plants, but its parameters are very different. The lifetime of individual phytoplankton organisms is very short, reproduction speed is very high, and diversity is astonishing. It is also less researched. Marine biota remove CO_2 from the extended atmosphere through the sinking of dead biomass to large depths of the deep ocean. Opinions of how net primary production by phytoplankton depends on an increase in CO_2 concentrations in ocean water differ, with some even claiming that it does not change (see [*Schippers et al.*, 2004]). In any case, this change is currently small compared with changes in the removal rates by other sinks, so it can be approximated as linear dependence:

$$M'_{mbe} = M'_{mbe,0} - k_{mb}C \tag{12}$$

where $M'_{mbe,0}$ is the removal rate at equilibrium and k_{mb} is some unknown constant, not necessarily positive.

By substituting expressions from (6), (11), and (12) for the individual exchanges in (5) and re-arranging additive sub-expressions, we obtain:

$$M' = \left(\left(L_{myd} - \int_{AL} p_{ti}(D_0,s)ds \right) + M'_{mbe,0} + \left(L_{up} - \int_{AOD} c_x v(s)D_{surface,0}ds \right) \right) -$$

$$\left(\int_{AL} p_{ti}(D_0,s)\beta(s)\frac{C}{D_0}ds + k_{mb}C + \int_{AOD} c_x v(s)D_{surface,0}k_{wa}(s)Cds \right) \tag{13}$$

The expression in the first pair of large brackets is the sum of exchanges at equilibrium, which is zero by definition. Eliminating it and moving C out from the remaining pair of brackets, we obtain:

$$M' = -\left(\int_{AL} \frac{p_{ti}(D_0,s)\beta(s)}{D_0}ds + k_{mb} + \int_{AOD} c_x v(s)D_{surface,0}k_{wa}(s)ds \right) C \tag{14}$$

The expression within brackets is not dependent on C (i.e., a constant), M is proportional to C (with a constant coefficient), so (14) can be re-written as follows:

$$C' = -\lambda C \tag{15}$$

where λ is a constant sink rate coefficient. This is a well-known formula of exponential decay. Taking into account the anthropogenic CO_2 release from fossil fuel combustion and cement manufacturing (at rate r_{ff}), land use change (at rate r_{luc}) and unaccounted natural CO_2 release fluctuations (at rate r_{misc}) give the following formula for the surplus carbon concentration in the atmosphere:

$$C'(t) = r_{ff}(t) + r_{luc}(t) + r_{misc}(t) - \lambda C(t) \tag{16}$$

with the initial condition $C(0) = 0$ corresponding to the equilibrium, which possibly existed hundreds years ago, assuming validity of the equation for CO_2 concentration at that time. In addition, $r_{misc} = 0$ is assumed throughout this paper.

3. Data Collection and Preparation

To calculate λ and D_0, the author used the following data:

- The monthly CO_2 concentration in the atmosphere at the Mauna Loa Observatory (MLO) from 1958 to 2014, [*R. F. Keeling et al.*, 2015a]

- The monthly CO_2 concentration in the atmosphere at the South Pole from 1958 to 2014 [*R. F. Keeling et al.*, 2015b]

- Annual emissions data from fossil fuels according to the Carbon Dioxide Information Analysis Center-Fossil Fuels (CDIAC-FF) from 1958 to 2010 [*Boden et al.*, 2013]

- Annual emissions data from land use change according to the Carbon Dioxide Information Analysis Centre-Land Use Change (CDIAC-LUC) from 1958 to 2005, [*Houghton*, 2008]

- Annual emissions data from the Global Carbon Budget 2014 (referenced here as GCB15) [*Quéré et al.*, 2015] used for 2006 to 2013, as described below.

Annual CO_2 concentrations were computed as weighted averages of four months around December 31 each year and averaged between the MLO and MLO-adjusted South Pole to represent the end-of-year MLO concentrations. For fossil fuel (FF) CO_2 release data, the CDIAC-FF dataset was extended using corresponding values from GCB14 for 2011–2013, because both datasets had the same values for 1958–2010.

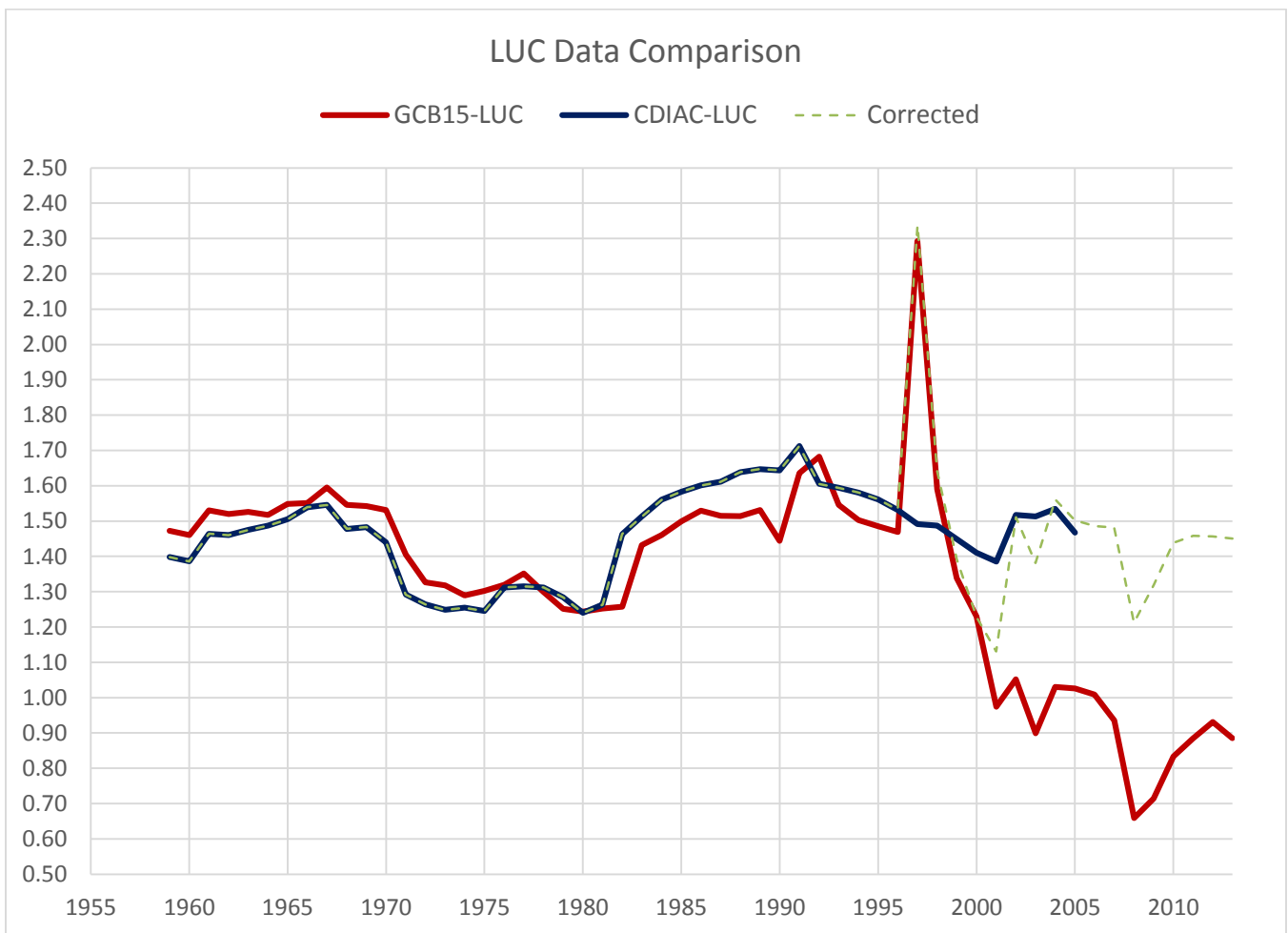Datasets for the land use data change from GCB15-LUC and CDIAC-LUC were substantially different.

Fig. 2. Comparison of the land use change datasets. Sources: [*Quéré et al.*, 2015] for GCB15, [*Houghton*, 2008] for CDIAC-LUC.

GCB15-LUC has an advantage of a more precise representation of emissions from 1997 Indonesian fires thanks to the incorporation of the GFED4 dataset. On the other hand, it shows an unrealistic drop in land use change (LUC) emissions starting with 2000, showing a 33% drop from 1995 to 2001 . LUC emissions cannot exhibit such a sharp drop because they come mostly from soil decomposition, which is a gradual process. The 2008 trough, showing an additional 34% drop from two years before and a 20% increase two years later, is simply absurd. The GCB14-LUC is based on the official UN FAO data, which relies on unverified government reports. Apparently, some governments were making inaccurate reports since at least 2006. Such political events as signing the Kyoto Protocol in 1997, the beginning of carbon credits trading in 2005 and REDD negotiations [*UNFCC*, 2006], might provide a relevant context. In light of these deficiencies, the author decided to use the CDIAC-LUC with the following corrections:

a) to extrapolate data from 2006–2013 using a simple average of the last five years minus 1%;

b) to incorporate a correction for the 1997 Indonesian fires using GFED4 data in the same way as GCB14-LUC.

The data for CO2 emissions does not take into account CO_2 production from the oxidation of human-released methane and a possible variation in volcanic and non-volcanic CO_2 outgassing.

4. Calculation of D_0 and λ

To find D_0 and λ, equation (16) was discretized in annual intervals

$$C_{n+1} - C_n = E_{ff,n+1} + E_{luc,n+1} - \lambda C_n \tag{17}$$

where C_n and C_{n+1} are end-of-year surplus carbon concentrations, and E_{ff} and E_{luc} are annual anthropogenic release amounts expressed in ppm.

D_0 and λ were calculated by minimizing the mean squared error of computed vs. apparent sink values over the period 1959–2012 using Excel Solver. The Excel file, containing the calculations and the source data, is attached as Supporting Material. The result is $\lambda = 0.0174$, corresponding to a half-life of 39.7 years for the surplus carbon concentration, and $D_0 = 258$ ppm. This estimate of equilibrium concentration is an excellent match to 265 ppm, measured in the air trapped in glacial ice around 1850 according to [*Carbon Dioxide Assessment Commtee et al.*, 1983, p.186].
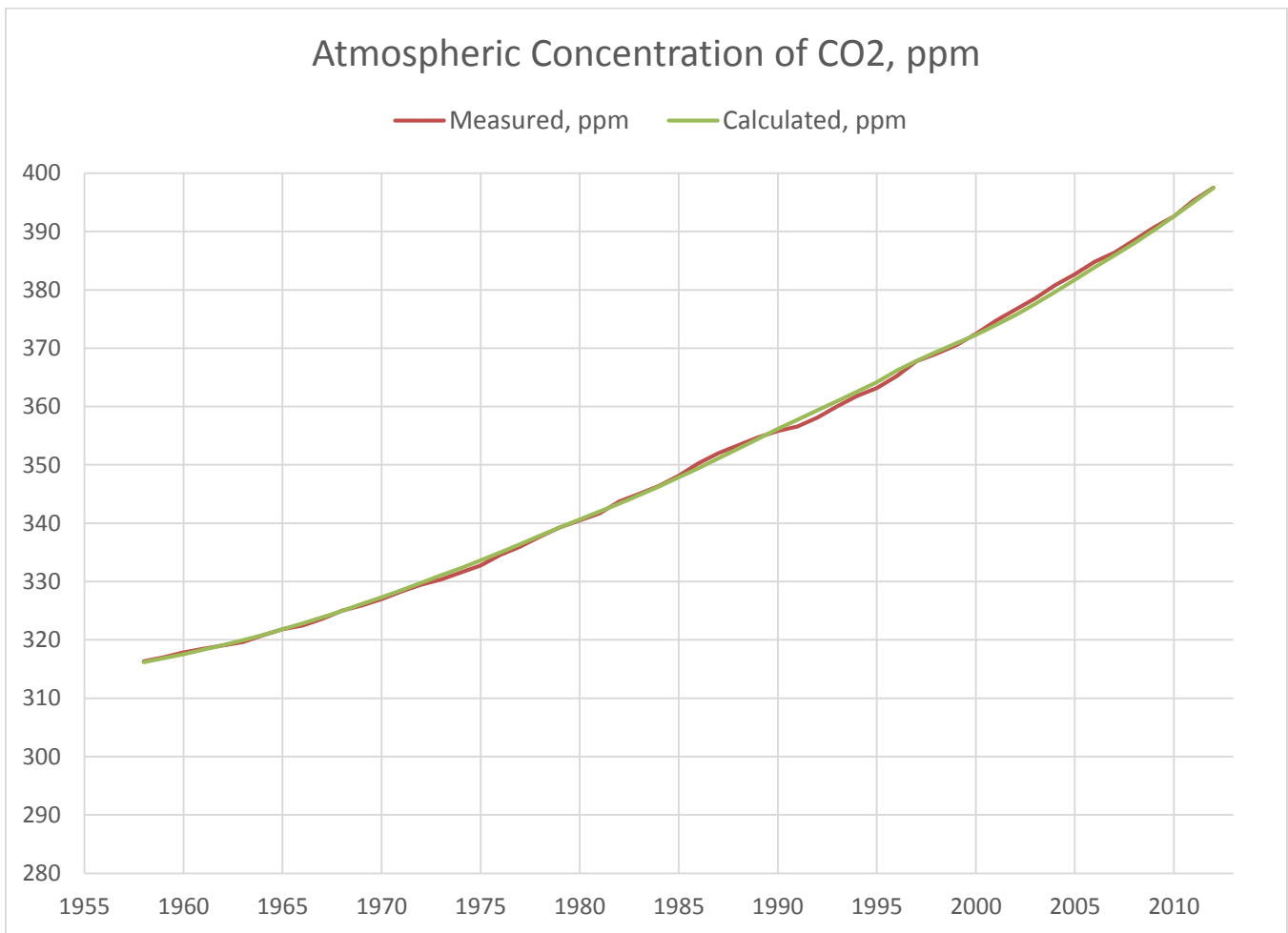

Fig. 3. Comparison of the measured concentration of CO_2 in the atmosphere (Keeling curve) and computed using formula (17). Sources for measured concentration: [*R. F. Keeling et al.*, 2015a], [*R. F. Keeling et al.*, 2015b].

The match is surprisingly good, given large error margins and uncertainties in the data.

5. Results

As a first approximation, the change in the surplus atmospheric concentration of CO_2 can be described by formula (16) on a multi-decadal scale. This can be reformulated in accordance with formula (15) as follows: the surplus carbon concentration in the atmosphere undergoes an exponential decay with an approximate half-life of 39.7 years ($\lambda = 0.0174$) in the absence of additional anthropogenic or irregular natural releases. The surplus concentration is measured from the hypothetical equilibrium concentration $D_0 = 258$ ppm. Noting that the surplus airborne carbon mass M is proportional to C, the result can be reformulated in terms of pulse response function: the instantaneously released mass of carbon at the background carbon concentration within the range of 315–560 ppm decreases according to the exponential decay formula with the aforementioned half-life (for a realistic mass and within an applicable time period).

6. Discussion

6.1. Residuals

The graph in FIG. 4 shows CO_2 sink values, calculated according to formula (17), and compared with apparent sinks, calculated from the data, where the 5-year sinks average is weighted.
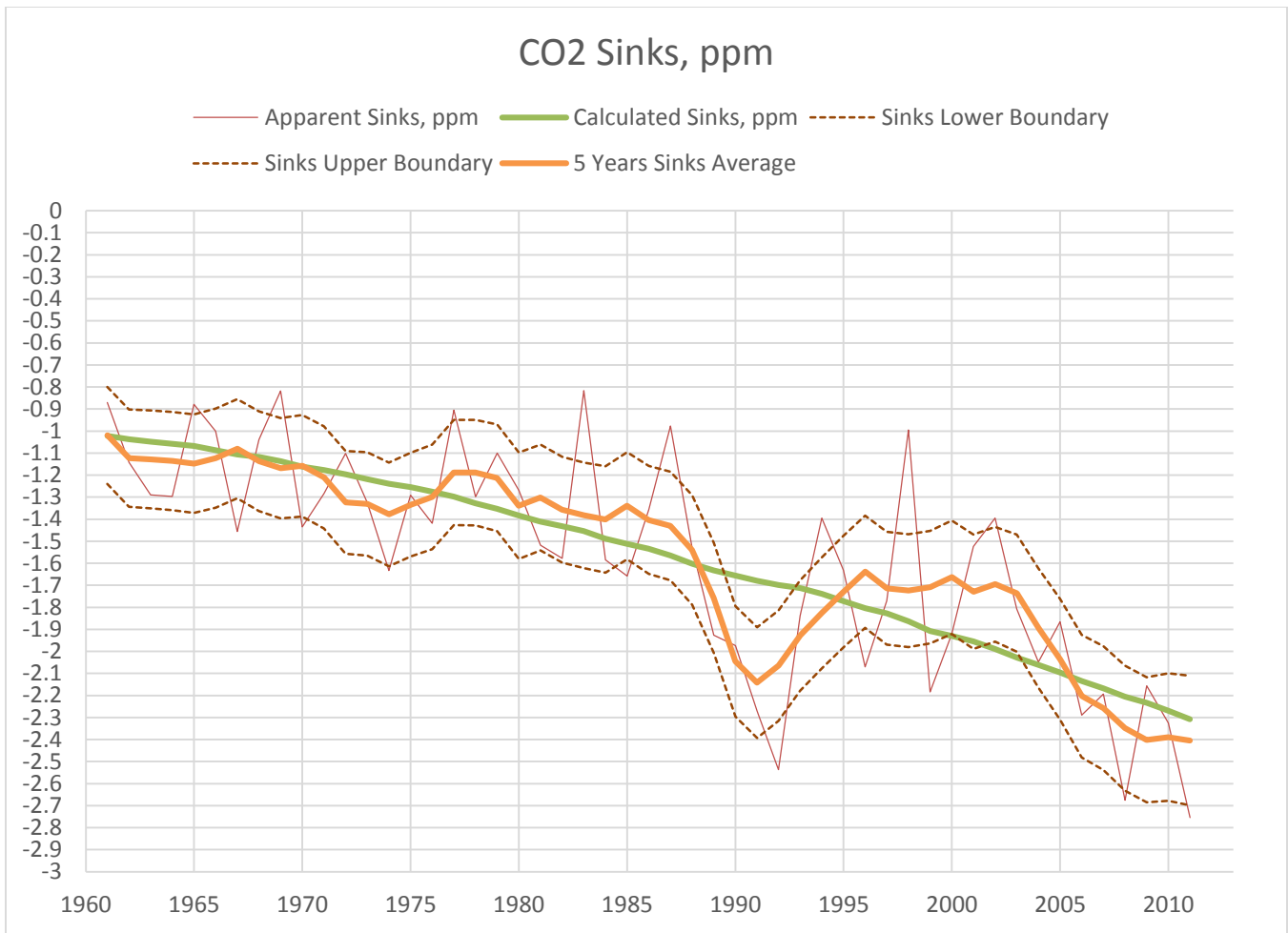
Fig. 4. Comparison of the apparent sinks from the reported data and computed ones using formula (17).

The dashed line shows sink value error boundaries based on stated "uncertainty" margins from GCB14 and an assumption that FF and LUC errors are independent. The author is convinced that the error margins are severely underestimated by the GCB14, in part because the GCB14 acknowledges their low confidence 1σ, in part because it arrives at them by comparing actual numbers with an output of an "ensemble" of mutually disagreeing computer models and in part because of the issue discussed in section 4. Nevertheless, residuals are within these extra-narrow boundaries almost everywhere. The only significant deviation is around 1991. Partially, it might be caused by the 1991 Pinatubo volcano eruption, reducing ground insolation and photosynthesis. Partially, it may be an error in the data. The FF

emissions dataset appears not to reflect the sharp drop in manufacturing in Eastern Europe and the former Soviet Union in 1989–1993, thus exaggerating the amount of carbon released at that time. Formula (15) does not capture many natural effects, including ENSO, volcanoes, variations in solar activity, and CO_2 outgassing. There are also significant and uncertain errors in the emissions data. It will be possible to further verify formula (16) around 2025, if accurate emissions data is available.

6.2. Limits of applicability

The sink rate coefficient λ, derived and calculated above, is not a physical constant. It is determined by various factors of the climate system, which can be affected by natural changes (especially solar variability) and human actions (including emitting black soot and aerosols' precursors). The sink rate coefficient is expected to change gradually with time and carbon re-distribution between the sinks. The physical description is greatly simplified compared to reality and may neglect effects causing a change in the sink rate coefficient λ. Nevertheless, existing data does not indicate that the carbon sink rate coefficient has changed significantly in the last 50 years. There is no reason to think that the sink rate coefficient will be changing rapidly in the next decades.

There is a question of the potential limits to the total sink capacity. Of course, there are limits, but they are not factors on a multi-decadal scale. For example, at equilibrium with an atmospheric CO_2 concentration of 560 ppm, 60% of ocean water can take in more than 4,000 GtC, equivalent to 400 years of today's carbon release. Only rough estimates can be done for the biosphere. [*Revelle and Munk*, 1977] determined that the "lid" is up to $7,800 - 2,800 = 5,000$ GtC. The land plant growth rate is limited by other factors besides atmospheric carbon dioxide, but this dependence is already captured by β-factor. There may be additional limiting effects, but there are also multiple counter-effects, such as the phenotypic plasticity of individual plants and the flexibility of ecosystems (i.e., plants that can better take advantage of higher concentrations of CO_2 might outgrow the rest). It should be noted that some of

the most productive modern ecosystems have evolved at a time when the CO_2 concentration was much higher than 560 ppm. For example, Amazon rainforest has evolved in Eocene ([*Morley*, 2000], [*Eocene, Wikipedia*, 2015], [*Eocene, Wikipedia*, 2015]). In any case, the data does not indicate a sink rate coefficient decrease.

Marine biota are a wild card. A surplus concentration of carbon in the ocean surface layer is about 10x lower than in the air. However, as a carbon sink, marine biota hold three key advantages over land plants. In the most productive land areas, plants cover almost all surfaces, and their growth is limited by the amount of light necessary for photosynthesis. Phytoplankton receives only a tiny part of the solar energy falling on the ocean area where it lives, so its growth is not significantly limited by it. Marine biota have a very high rate of growth and reproduction in suitable conditions (demonstrated by algae blooms). Finally, the sinking rate of dead marine biomass is determined by the coagulation of small particles, which is a second-order reaction. Consequently, the carbon removal rate by marine biomass can grow very fast. There is evidence that marine biota are much less dependent on non-carbon nutrients than thought, and not even limited by the Redfield ratio [*Riebesell*, 2004], [*Riebesell et al.*, 2007].

6.3. Equilibrium and historical CO_2 concentrations

The equilibrium carbon concentration is not necessarily the same as the "pre-industrial" carbon concentration. Further, the equilibrium concentration D_0, calculated over the period 1958–2013, may be different from the "true" multi-centennial equilibrium concentration. One important factor for both differences is a long-term variation in solar activity per [*Soon and Yaskell*, 2004] and [*Soon and Baliunas*, 2003], influencing photosynthesis rates and having disproportionally strong impact on relatively small photosynthesis – respiration difference.

7. Conclusions

Formulas (15) and (16) for atmospheric carbon concentration change on multi-decadal scale have been derived based on well known laws of physics, chemistry, oceanography and biology. The derived formulas were then validated and confirmed by available statistical data. On the multi-decadal scale, anthropogenically released CO_2 is removed from the atmosphere by the deep ocean, land biota, and marine biota according to formula (16). Without accounting for new release and natural perturbations, the surplus atmospheric concentration of CO_2 undergoes an exponential decay with a half-life estimated ~40 years.

8. Acknowledgements

9. Disclosure statement

The author declares an absence of conflicts of interests.

10. References

Andrews, R. (2013), The residence time of CO2 in the atmosphere is …. 33 years? | Energy Matters, Available from: http://euanmearns.com/the-residence-time-of-co2-in-the-atmosphere-is-33-years/ (Accessed 26 July 2015)

Archer, D. (2005), Fate of fossil fuel CO2 in geologic time, *J. Geophys. Res. Oceans*, *110*(C9), doi:10.1029/2004JC002625.

Archer, D. et al. (2009), Atmospheric Lifetime of Fossil Fuel Carbon Dioxide, , doi:10.1146/annurev.earth.031208.100206.

Bacastow, R., and A. Bjorkstrom (1981), Comparison of Ocean Models for the Carbon Cycle, in *SCOPE 16. Carbon Cycle Modelling*, edited by B. Bolin.

Boden, T., B. Andres, and G. Marland (2013), Global CO2 Emissions from Fossil-Fuel Burning, Cement Manufacture, and Gas Flaring: 1751-2010,

Bothwell, L. D., P. C. Selmants, C. P. Giardina, and C. M. Litton (2014), Leaf litter decomposition rates increase with rising mean annual temperature in Hawaiian tropical montane wet forests, *PeerJ*, *2*, e685, doi:10.7717/peerj.685.

Bralower, T., and D. Bice (2014a), The Marine Carbon Cycle | EARTH 103: Earth in the Future, Available from: http://www.webcitation.org/6aJHxCTh6 (Accessed 23 July 2015)

Bralower, T., and D. Bice (2014b), The Terrestrial Carbon Cycle | EARTH 103: Earth in the Future, Available from: archived: http://www.webcitation.org/6aJHsE6Wx (Accessed 23 July 2015)

Calleja, M. L., C. M. Duarte, M. Álvarez, R. Vaquer-Sunyer, S. Agustí, and G. J. Herndl (2013), Prevalence of strong vertical CO2 and O2 variability in the top meters of the ocean, *Glob. Biogeochem. Cycles*, *27*(3), 941–949, doi:10.1002/gbc.20081.

Carbon Dioxide Assessment Commtee, Board on Atmospheric Sciences and Climate, Commission on Physical Sciences, Mathematics, and Resources, and National Research Council (1983), *Changing Climate: Report of the Carbon Dioxide Assessment Committee*.

CDIAC, Oak Ridge National Laboratory (2011), Maps of Sea-Air pCO2 Difference, Available from: http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/delta_pco2_maps.html (Accessed 22 July 2015)

Docmartyn (2010), Comment on Lindzen: "Earth is never in equilibrium" | Watts Up With That?, Available from: http://wattsupwiththat.com/2010/04/09/lindzen-earth-is-never-in-equilibrium/#comment-364034 (Accessed 26 July 2015)

Eocene, Wikipedia (2015), Eocene, Wikipedia, Available from: http://www.webcitation.org/6aJLuvCmM (Accessed 24 July 2015)

Gordon, A. (2004), Ocean Circulation, Available from: http://www.webcitation.org/6aJUesBk2 (Accessed 26 July 2015)

Gough, C. M. (2011), Terrestrial Primary Production: Fuel for Life., *Nat. Educ. Knowl.*, *3*(10), 28.

Houghton, R. A. (2008), Carbon Flux to the Atmosphere from Land-Use Changes 1850-2005,

Jacobson, M. Z. (2005), Correction to "Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming," *J. Geophys. Res. Atmospheres*, *110*(D14), doi:10.1029/2005JD005888.

Kohlmaier, G. H., Siré, E. O., Janecek, A., Keeling, C. D., Piper, S. C., & Revelle, R. (1989), Modelling the seasonal contribution of a CO 2 fertilization effect of the terrestrial vegetation to the amplitude increase in atmospheric CO 2 at Mauna Loa Observatory., *Tellus B*, *41*(5), 487–510.

Morley, R. J. (2000), *Origin and Evolution of Tropical Rain Forests*.

O'Hara, F. (1990), Conversion Tables, Available from: http://cdiac.ornl.gov/pns/convert.html (Accessed 26 July 2015)

Quéré, C. L. et al. (2015), Global carbon budget 2014, *Earth Syst. Sci. Data*, *7*(1), 47–85, doi:10.5194/essd-7-47-2015.

Raupach, M. R., M. Gloor, J. L. Sarmiento, J. G. Canadell, T. L. Frölicher, T. Gasser, R. A. Houghton, C. Le Quéré, and C. M. Trudinger (2014), The declining uptake rate of atmospheric CO_2 by land and ocean sinks, *Biogeosciences*, *11*(13), 3453–3475, doi:10.5194/bg-11-3453-2014.

Revelle, R., and W. Munk (1977), The carbon dioxide cycle and the biosphere, *Energy Clim. Stud. Geophys.*, 140–158.

R. F. Keeling, S. C. Piper, A. F. Bollenbacher, and S. J. Walker (2015a), Atmospheric CO2 concentrations (ppm) derived from in situ air measurements at Mauna Loa, Observatory, Hawaii,

R. F. Keeling, S. C. Piper, A. F. Bollenbacher, and S. J. Walker (2015b), Monthly atmospheric CO2 concentrations (ppm) derived from flask air samples and merged in situ air measurements, South Pole,

Riebesell, U. (2004), Effects of CO2 enrichment on marine phytoplankton, *J. Oceanogr.*, *60*(4), 719–729.

Riebesell, U. et al. (2007), Enhanced biological carbon consumption in a high CO2 ocean, *Nature*, *450*(7169), 545–548, doi:10.1038/nature06267.

Sabine, C. L. et al. (2004), The Oceanic Sink for Anthropogenic CO2, *Science*, *305*(5682), 367–371, doi:10.1126/science.1097403.

Schippers, P., M. Lürling, and M. Scheffer (2004), Increase of atmospheric CO2 promotes phytoplankton productivity, *Ecol. Lett.*, *7*(6), 446–451, doi:10.1111/j.1461-0248.2004.00597.x.

Soon, W., and S. Baliunas (2003), Proxy climatic and environmental changes of the past 1000 years, *Clim. Res.*, *23*(2), 89–110.

Soon, W., and S. Yaskell (2004), *Maunder Minimum: And the Variable Sun-Earth Connection*, World Scientific Pub Co Inc, River Edge, N.J.

Takahashi, T. et al. (2009), Climatological mean and decadal change in surface ocean pCO2, and net sea-air CO2 flux over the global oceans, *Deep-Sea Res. II 568-10*, (10.1016/j.dsr2.2008.12.009), 554–577, doi:10.1016/j.dsr2.2008.12.009.

UNFCC (2006), Report of COP11, held at Montreal from 28 November to 10 December 2005,

UNFCCC, and IPCC (1995), Parameters for tuning a simple carbon cycle model, Available from: http://unfccc.int/resource/brazil/carbon.html (Accessed 21 July 2015)

Zeebe, and Wolf-Gladrow (2001), *CO2 in Seawater: Equilibrium, Kinetics, Isotopes, 1st Edition*.